STUDIES ON BIOSORPTION OF PHENOLIC COMPOUNDS FROM AQUEOUS SYSTEM USING AGRICULTURAL WASTES

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Abbreviations

EPA-Environmental Protection Agency.

WHO- World Health Organization

SCB- Sugarcane Bagasse

2-CP- 2-chlorophenol

o-CPh- ortho-chlorophenol

4-CP- 4-chlorophenol

TeCP-Tetrachlorophenol

TCP-Trichlorophenol

P-CPh- para-chlorophenol

PCP-Pentachlorophenol

2,4-DCP- 2,4-dichlorophenol

o,p-DCPh- ortho, para-dichlorophenol

UAE-United Arab Emirates

US EPA- United States Environmental Protection Agency

DNA- Deoxyribonucleic acid

NADPH- Nicotinamide Adenine Dinucleotide Phosphate.

NIOSH-National Institute for Occupational Safety and Health

SBAC-Sludge Based Activated Carbon

RfC-Reference Concentration

AOPs-Advanced Oxidation Processes

4-AAP-4-aminoantipyrine

UV- Ultra Violet

W/V- Weight/Volume

IUPAC- International Union of Pure and Applied Chemistry

CPs- Chlorophenols

2,4-D- 2,4-dichloro-phenoxiacetic acid

FOK-First order kinetic

SOK- Second order kinetic

ABSTRACT

Title: Studies on biosorption of phenolic compounds from aqueous system using agricultural wastes

The present work is studied using agricultural waste sugarcane bagasse (SCB) for biosorption of phenol and phenolic compounds from water and industrial effluent as well the synthetic solutions of phenols used to develop the biosorption technique. The biosorption efficiency of agricultural solid waste bagasse to adsorb phenolic compounds phenol, ortho-chlorophenol (o-CPh), para-chlorophenol (p-CPh), and ortho, para-dichlorophenol (o,p-DCPh) from the solution system and industrial effluents under batch equilibrium conditions was investigated. The elemental ions of the biosorbent bagasse are identified by Fourier transform infrared (FTIR) spectroscopy. The biosorption technique has been carried out using batch experiment by the experimental parameters of biosorbent dose (0.5-5 g), contact time (upto 5 hrs), initial concentration of sorbates (0.5 to 10.0 mg/L), particle size of biosorbent, pH of system solutions (3 to 12) and operational temperature (30 to 50 °C). The biosorption of phenolic compounds is raised with raising the pH from 3.0 to optimal value and then dramatically downize with raising the pH from that optimal value to avobe. The highest biosorption is achieved at pH 6.5 for phenol, ortho-chlorophenol and para-chlorophenol and at pH 6.0 for ortho, para-dichlorophenol. Biosorption equilibrium is established within 90 minutes for phenol and o-CPh and 120 minutes for p-CPh, and o,p-DCPh. The biosorption experimental data were employed to analyze in the isotherm and kinetic equations. The data found from experiments were fitted well into the pseudo first order kinetic equation, with the correlated coefficient (R^2) greater than 0.99 in all cases respectively. The maximum monolayer biosorption capacity of sugarcane bagasse for the selected phenolic compounds phenol, o-CPh, p-CPh and o, p-DCPh has found to be 0.357, 0.361, 0.282 and 0.363 mg/g respectively, as calculated by the Langmuir isotherm equation at 30°C. The biosorbed compounds could be recovered by desorption with the help of 1M alkaline solution (NaOH) in all cases. After regenerations bagasse can be used as fuel purposes. The studies showed that the agricultural waste bagasse has the promise for use as an effective adsorbent material for biosorption of phenolic compounds from water and industrial effluents.

Studies on biosorption of phenolic compounds from aqueous system using agricultural wastes

Chapter 1

Introduction

Chapter 1: Introduction

Phenolic compounds and other organic pollutants are deteriorating the water quality day to day for non stop entrance of the chemicals into water sources. This addition of the phenols into the water body is from nature, industries, households, agricultural lands, municipalities and otherpoints of sources are going to inform serious alarm to protect the lives on the earth. Being the utmost importance of water, the need for its quality improvement and preservation, is growing continuously for eliminating phenol and phenolic compounds from industrial effluents and water bodies.

1.1 Overview

This section presents a general overview on the background of water sources and the environment; related to the selected topic on phenolic compounds. The origins and the reactivities of phenols in the aqueous system, the toxicity, toxic effects on the environment along with humans are also included. Finally, searching agricultural wastes available in Bangladesh and establish the biosorption method for eliminate the phenol and phenolic compounds from industrial effluents.

All living organisms including man are the parts of the environment and they are dependent on all other components of the environment such as air, water, soil, etc. Among them, water is an important part of our lives. The total water of the earth is about 26.6 trillion tons, approximately 94.7% of this occurs in the lithosphere, bound water in the rocky belt. The surface water which includes water of rivers, lakes, and ponds together with groundwater is only 0.03%. This small fraction of water is mainly used for drinking, domestic, industrial, and agricultural purposes. The necessity of utilizing this water is increasing tremendously with increasing both the population and industrialization. Due to dispose of the domestic sewage, industrial effluents, animal excreta, chemicals for agricultural activities containing phenolic compounds make it polluted. The accumulation of these objectionable substances gradually changes the physical, chemical, and biological properties of the surface water. For this complex inter-relationship in the ecosystem phenolic compounds and other organic-inorganic matters that alter a minor part in any sector harm almost all other parts in the ecosystem. As a result, some water-borne diseases like cholera, typhoid, dysentery, yellow fever are frequently observed along with mutagenic, carcinogenic, and other effects. These phenomena are drawing attention to the point of water pollution along with the pollution of air and soil. This problem is particularly tragic for the children indirectly along with the serious effect on the industrial workers directly[1,2].

An increase in awareness of environmental pollution and the imparted impacts have prompted to take related efforts towards environmental regulations. Contamination of water bodies by the organic and inorganic matters is an environmental issue for the earth due to their toxic effects and accumulation through the food chain. The wastewater that contains the highest concentration of phenol and phenolic compounds is ordinarily generated worldwide from coke processing unit, resin plants, textiles, pharmaceuticals, refineries, agro-chemical activities, etc. Various national and international organizations like United States Environmental Protection Agency (USEPA), the World Health Organization (WHO), etc. have set a program for the safety of human health from the potential toxic effects caused by exposure to phenols. WHO is stricter on phenols regulation due to alarming pollution prevail all where at present[3]. Therefore, from the attitudes and activities of these organizations; it is recognized that phenols are listed as a toxic substance and are included in the priority list of hazardous substances as well, which demonstrates its serious health and ecological effects. Hundreds of rivers across Bangladesh, either directly or indirectly are contaminated by a huge amount of untreated industrial waste matters and effluents from various industries. Such industries are dyes, fertilizers, food processing, metal processing, petrochemical industries, petroleum refineries, pesticides, pharmaceuticals, pulp and paper, textiles and tannery, synthetic rubber, plastics, coking, paper, phenolic resin industries and so on[4,5].

Phenol and its derivatives are distinguished as priority pollutants because it is harmful to human, wild and aquatic lives. Public attention has been drawn due to the presence of phenols in groundwater, rivers, and drinking waters. Most of the country specifies maximum allowable concentration of phenol in wastewater[6] which make the necessity to flourish technological methods that allow one to detect, quantify and remove phenols from wastewater. With increasing phenolic effluents discharge to the natural environment, standard value selection marks the highest considerations and should be made for selecting a feasible treatment process. Several ongoing methods for the treatments of phenolic (wastewater) effluents are reverse osmosis, anaerobic processes, combined applications of flotation, adsorption, biosorption etc. All of the treatment processes like chemical, biological and physical have their merits and demerits. Use of some agricultural wastes matters that could help in this regard, in addition to regeneration, use of these waste materials can be an effective advantage. 'Biosorption' process for phenols containing effluent treatment can be the best as the simplicity of design, operational easiness, availability of this biowastes, and treating appropriateness[7].

The process of biosorption is that in which a sorbate, in gas or liquid phase, brings together in an insoluble solid body known as sorbent. Sorbents are porous materials with large surfaces to selectively preserve compounds on its surface. The biosorption techniques of the sorbate

molecules from the bulk aqueous state to the sorbent surface is involved in three stages as mass transfer of the sorbate molecules across the outer frontier surfaceas to the hard particle, then moves from the hard surface to the active sites by diffusion with the pore-filled water and transfer to the solid sites of the pore. Biosorption of phenols on the binding sites of the interior surfaces of the sorbent pores, once the molecule is sorbed, it may migrate on the pore surface through surface diffusion. Extension of biosorption is based on the properties of the particle surface, particularly the particle's porosity and boundary area. A larger number of sorbents that have greater surface area have been established. The porous property does not only elevate the surface area but also make sorption ease; porosity affects the kinetics of the biosorption. Large surface area and less time for biosorption equilibrium are the main characters of a good sorbent[8,9]. So, biosorption is a reputed and strong process for the treatment of effluents at the discharged point of households, municipalities, and industries. However, sorption onto activated carbon (AC) surface, the most widely used process for wastewater treatment. Sorbent surface carbons can adsorb huge unwanted compounds occurring in water and wastewater. Due to the high cost and variable performances of carbon regeneration of AC, single-use materials[9] is expected. For this reasone, research workers used to search for low-cost, more convenient, high performance, practical, and effective process. In the run of search to selected materials are bottom ash, brick-kiln ash, fly ash, peat, rice husk and straw, jute stick, wood, sawdust, bagasse, and carbonized bark used as new biosorbent for organic pollutants. Biosorption methodology has been established to be a feasible alternative for sorption phenols from effluents. The studied sorbents reveal that biosorbent sugarcane bagasse (SCB) can be an ideal one for the biosorption of phenol and phenolic compounds from aqueous system[10,11].

SCB is used for water and industrial wastewater treatments and the effectiveness of their eventual uses may be resolute by their sorption capability, renewal, and physical properties of subsequent results. Over the years, sorption has turned up as an efficient and cost-effective substitute for eliminating phenol and phenolic compounds from effluents and water bodies. As an agricultural waste SCB residues are found at a minimum cost which can be considered as waste matter. Many agricultural wastes like SCB are composed of cellulosic matters, like cellulose, hemi-cellulose and lignin etc[11]. These constituents turn the bagasse into a good component to introduce as a new biosorbent for phenolic wastewater purification techniques. In our study, the waste SCB is used without any chemical modification. This SCB was continuously explored for the sorption of phenolic compounds from aqueous system. Some biosorption affecting factors like bagasse dose, the contact time of bagasse with phenols, particle size of bagasse, the initial concentration of phenols, the pH of the system medium, and

the temperature have been investigated. Besides, experimental data are employed in the isotherms and kinetics equations for finding the sorption behavior.

Various agricultural wastes like eggshell, used tea leaves, orange peel, coconut husk, maize husk, sugarcane bagasse, banana peel, rice straw and rice husk etc are available in rural area of Bangladesh which contains various of functional groups for binding and separating the organic and inorganic pollutants without using any treatment from industrial effluents.

In this study, phenol, ortho-chlorophenol (o-CPh), para-chlorophenol (p-CPh), and ortho, para-dichlorophenol (o, p-DCPh) are considered as adverse organic pollutants. These pollutants are found in the water sources from the discharge point of industrial effluents. For the high toxicity and carcinogenic character even at low concentration has been made an important targeted issue to eliminate phenol and phenolic compounds from wastewater before discharge into water bodies.

Literature review

1.2 Literature review

The literature on phenolic pollutants includes phenols toxicity; impart effects on environment and human health and socio-economy along with its permissible limit and existing quantity in the environment, phenols sources, effects on living creatures, human health and aquatic lives which direct to take attempt for elimination the problems. The best attempt can be considered for the research work to maintain a sound environment through proper concept on agricultural wastes as sorbents for low cost, available, regenerating capable and eco-friendly. Targeted view points can be achieved being studied literature review related to the topic on phenolic compounds. Finally, the review may guide the work for the establishment of an optimal biosorption process for phenolic wastewater treatment.

1.2.1 General concept

A vast of researchers reported for the last decades clearly showed an increasing interest in establishing a research field for phenolic wastewater treatment. Contaminated soil and water related to the degradation of phenols by variety pure or mixture of microorganisms have been isolated due to its ability to degrade pollutant into non-harmful by-product to control pollution[12]. Governments have also created laws and orders for regulating the phenols level in drinking water and effluents discharged from factories as pollution prevention activities to monitor and control it. These issues are indicated that phenolic compounds can be classified as a toxic contaminant[13]. In each country, laws and acts have been created to observe the level of allowable organic or inorganic compounds present in effluents and water bodies. USEPA and

WHO have set a guideline to regulate the phenols concentration in drinking water. The WHO has set up a priority of chemical pollutions of toxic chemicals according to toxicity, persistence, mobility, and bioaccumulation ability. Phenol and phenolic compounds exist in the environment through two major processes; chemical and natural; naturally, it is formed by the part of coal tar and creosote, decomposition product of organic matter, and as secondary metabolite in plant. Phenols are either free or bound compounds; naturally prevail in foods such as red grapes, cocoa, and tomatoes. Phenols are also naturally produced during plant decomposition processes, usually in the form of intermediates such as ρ-cresol or lignin[14]. Phenol is commercially available in a colorless, needle-like crystalline substance thateasily dissolves in water and solvents like alcohol, glycerol, and petroleum. Phenol itself is transparent and can easily mix with water at room temperature. It has a sweet odor and can be volatile when heated. Chemically, phenol can be produced through the oxidation process of toluene, and the heating of monochlorobenzene together with sodium hydroxide. High phenol concentration in water (100-1000 µg/L) can cause unpleasant odor and taste, and leads to carcinogenic problem whenever it presents in water because it can react with chlorine to form chlorophenols and they are toxic to the organism that can make it persistence[15]. Phenol and phenolic compounds can also vaporize easily making them widely present in the atmosphere. Since phenols are serious toxic matters even in a small amount. So, studies on mitigation of the compounds from the effluents at the discharge points are the demand of time.

1.2.2 Permissible limit and existing quantity of phenolic compounds in the environment

In each country, laws and acts have been created to observe the level of allowable phenolic compounds present in effluents and water bodies. The existing quantity of phenolic compounds in water bodies and effluents may remark points where the mitigation is required.

Maximum permissible limit of phenolic compounds in consuming and discharging water:

According to EPA and WHO's regulation, the permissible concentration limit of phenols in drinking watersis 1.0 µg/L[16] and in the treated effluent 0.1 mg/L. According to European Council Directive (ECD) it has been limited the elements upto 0.5 µg/ L in drinking water while Japan permitted the phenol level of 5.0 mg/L in the effluent before discharge into water bodies. This limit in UAE is 0.1 mg/L, it is limited upto 2.0 µg/L in drinking water in Argentina, in India it has been permitted the phenols in industrial effluents when discharg into municipal sewers and surface water is 1.0-5.0 mg/L[17] and in Bangladesh that is also 5.0 mg/L.

Literature review on phenols doses found in environment:

The concentrations of phenol and phenolic compounds in water are different. The highest 1000.0 mg/L phenols are estimated in the effluent from coke processing plants; in resin plants

the range is 12.0-300.0 mg/L, and in natural water that is 0.01-2.0 µg/L[18]. 2.6-5.6 µg/L phenols are found in surface water in the Netherlands, 40.0 mg/L are detected in the river drainage from petrol processing plants[19]. 9.7 µg/m1 phenols prevail in the location of impregnate wood factories[20]. 5.0 µg/kg phenols are found in honey[21], in coffee from ferulic acid is found trace amount of phenol, in grilled sausage and in pork are found 7.0 and 28.6 µg/kg phenol respectively[22]. 37.0-70.0 mg/kg phenols are found in the outer layer of smoked meat. On the contrary 4.0 mg and 2.0 mg/ day/ person exposed to phenol by inhalation from dense industrialized areas, 0.3-0.4 mg of phenols are released from per cigarette when one smoked, inhabitants expose in 10.0-240.0 mg of phenol per person in dense bulk industrial area[23]. 6.0 µg/L 2, 4-dichlorophenol[24] was found inthe Vistula River, 0.1-6.0 µg/L chlorophenols was determined in water in the Gulf of Gdansk. 2.0 µg/L very toxic tetrachlorocatechol (TeCP) was found polluted Ner River (Central Poland). 0.028 to 1.22 µg/L nonylphenol was found in Odra River (Poland). 3.8 to 26.6 µg/m1 phenols were found in dense and heavy industrial and urban areas of the Upper Silesia region of Poland. 5.0-10.0 ng/L of chlorophenols (CPs) were found in oceanic waters, 2.0-2000.0 µg/L is the highest CPs in river waters, and 0.1-10.0 mg/L pentachlorophenols (PCPs) were found in industrial sewages[25]. 0.25 to 7.8 ng/m1 chlorinated phenols were found in the atmosphere; upto 1.0 µg/m1 in the atmosphere in urbanized areas of Holland. 2.0 mg of TeCP and 0.18 mg of trichlorophenol (TCP) per kg of soil were found in the farmer site of pesticide plant. 500.0 to 3500.0 µg/kg chlorophenols were identified in near preserving facilities at four different sawmills[23]. 1.0 to 45.0 µg/kg of wet weight TeCP and PCP were depicted in carrots, potatoes, and turnips, 2.0 to 3.0 µg/kg chlorophenols were detected in chicken flesh of poultry, 10.0 mg/kg chlorinated phenols are also detected in serum and adipose tissue in the body of general population. A chronic exposure of 2.48 µg/L PCP was detected in blood plasma in both children and adults in Germany. 0.64 µg/L PCP were also found by investigating in human plasma in Czukczi Penisula, Uelen locality of Arctic area of Russia. 2, 4-DCP, TeCP and of TCP were detected 3.84 µg, 1.62 µg and 0.084 µg /60-kg/person respectively in Canada; about 10.0 µg per person including PCP, and about 10.0-30.0 µg/person chlorophenol exposure per day were estimated by NRCC[18] in Canada. The literature prompts the researchers to get attempt to mitigate the unexpected quantity of phenolic compounds released to the water sources from effluents at discharging points.

1.2.3 Sources of phenolic compounds

Phenols have been used in industry since the 1860s. Its production in the United States is 1.36-billion kg/year and 2.72 billion kg/year in the world. The ranking position of phenol production in the United States is 50 in the list of chemical production/year[26]. In alkylphenols, cresols, aniline, and resins industries use phenolic compounds and generate the compounds to the water

bodies with the effluents. In the same way, phenols are also added in the aqueous environment from oil, gas, and coal industries; non-polymer additives polycarbonate plastics and epoxy resins are produced from bisphenol; nylon 6 (poly-caprolactam) and some fibers (synthetic) are manufactured using caprolactam as raw material, some pesticides and other insecticides are also the derivatives of phenols; in wood distillation, water disinfection, cooking processes and paper production use chlorophenols[17]. Phenol, chlorophenols such as phenol, o-CPh, p-CPh and o, p-DCPh, are detected in the natural water from the biodegradation of pesticides, insecticides and herbicides, etc o, p-dichlorophenoxyacetic acid, p-chloro-o-methyl-phenoxy acetic acid, o, p, m-trichlorophenoxy acetic acid, pentachlorophenol dissociated to other chlorine substituents, medicinal compounds (body lotions, ointments, mouth washes and oral sprays and anesthetic purposes or for sore throat treatment) contain phenolic compounds, it is also in the daily uses, decorating materials, babies toys, etc (soaps, toys, paints, lacquers, perfumes and varnish removers); p-cresols, p-tertbutylphenol and bisphenol, chlorophenols, p-nonylphenol, p-tertoctylphenol and phenol, etc. are detected in leachates from municipalities wastes stock sites[27]. Untreated leachates release solid fly ash, incombustible materials into the natural water and pollute the surrounding area with phenolic compounds. Phenols are also the constituents of aquatic or terrestrial plants. In plants phenols are derived from amino components in it through UVL irradiation, salicylic acid is found from willow bark plant[28]. Macromolecules of phenols are the components of green and red marine algae. Phenols are existed in metabolic products of man and animal[29]. The compounds are also detected in the gut of mammals in presence of tyrosine in their digestive tract.

1.2.4 Toxicity of phenolic compounds on living organisms

Phenols are distinguished as the main concern pollutants impart harmful and toxic effects to the environment. These compounds are considered harmful as they accumulate in living organisms. Due to the concern, the levels of phenols in drinking water and effluents are limited by the international act. The countries all over the world, many profitable and non-profitable established agencies such as EPA, and WHO etc have limited the dose before discharge into the water bodies. Phenols exposure caused by either directly or accidentally can disrupt systems activities in the microorganisms, human or animal. Phenol is considered a priority pollutant because it is harmful to human and wild and aquatic lives. The toxicity of phenol and its derivatives is always associated with their ability to disrupt the structure of membrane permeability and its barrier by causing a cascade effect which leads to the imbalance of intracellular cell environment, and the disturbance in its function can finally results in the cells' death[30]. It has been found that the action of toxicity initially due to environmental stress factors. These factors lead the changes happened in microorganisms by the transition of saturation

degree in membrane phospholipids cis-fatty acid into trans-fatty acid, and by the alteration of hydrophilic groups in lipids[31]. The toxicity of phenol depends on its aromatic ring where benzene ring itself can also undergo several chemical reactions such as halogenations, alkylation, nitrification, and polymerization. Most phenol and its derivatives are classified based on toxic activities. The toxicity of phenolic compounds will also increase according to the number of chlorines being substituted in phenol ring. Toxicity of phenol related to two major mechanisms are hydrophobic involvement and the generation of biological and free radicals. Main factors that alter the hydrophobicity are[32] pKa (the compound dissociation constant) and P_{OW} (P is the octanol-water partition coefficient of undissociated acids). Another factor is the hydroxyl group attached reactive groups that can easily dissociate and undergoes different chemical reactions such as esterification, etherification, oxidation, and substitution. The presence of hydroxyl group at the ring is causing it to become sensitive to the oxidizing agents thus undergoing other reactions. The hydrogen atoms at the ring and hydroxyl group can also be substituted or eliminated. The ability of phenol to persist in the environment depends on the properties of chemical groups attach to it and also on their position on the ring itself[33].

1.2.5 Toxic effects of phenolic compounds on animals and human health

Acute toxicity to animals including human:

Phenol involves irritation in the skin that causes nercosis, its effects on kidneys, liver, muscle and eyes are very crucial and damage the organs. Skin is damaged due to the coagulation reaction of phenol with amino acids existing in keratin of epidermis and collagen in inner skin. 1.0 g phenol is a sufficient cause to death for an adult man; receiving dose tolerance can be different for different persons. It is reported that one can survive in the administration of 30.0 g of phenol; i.e., 60.0 ml of 50% solution. If fast absorption is occurred by skin from 60%-90% even contact of hand with this phenol solution may cause death. The poisonous activities of phenol are systemized through parch and xerostomia, dark-urine and feel burn in mucous membranes. It is noted that if animals are exposed in phenolic environment for long term leads to chronic changes in about all important organs like lungs, liver, kidneys, skin, esophagus, and also urogenital tract. These are called pathological changes are mainly induced by lipid peroxidation. Workers who are exposed to phenol vapors suffer from anorexia, loss of body weight, feel weakness, headache, muscle pain, and icterus. Acute poison of chlorophenols is detected through systemized in the mouth with white necrotic lesions, burning pain, in throat feel burning pain; esophagus and stomach are also affected with white necrotic lesions results vomiting, headache, irregular pulse, decrease of body temperature, and muscle weakness, convulsions and death[34]. Hypotension, fall of body temperature, weakness and abdominal pain

are resulting from long term exposure to chlorophenols. When 16.0 µg (pentachlorophenol) is allowed to intake daily per person of 70.0 kg weight, directed affection is drastically acute toxicity. An example of air pollution in New York, USA with a mixture that contained 2-chloro-6-fluorophenol is the result of an accident near a chemical factory made the symptoms like dryness in the mouth and throat, coughs, headaches, and abdominal pain[35]. 62% pentachlorophenol and 63% tetrachlorophenol dissolved in fats and skin and sorbe them easily. So, proceedings of chlorophenols accumulation in kidneys, spleen, liver, heart, brain, and fat tissue make acute toxicity in man and animals.

Mutagenic effect of phenolic compounds on living organisms:

Phenols mutagenic activity was investigated by hamster. From this investigation, it is noted that phenol inhibits the synthesis and replication of DNA in HeLa cells. DNA preparation in diploid human fibroblasts is also inhibited by phenol. Hydroquinone (1, 4-dihydroxyphenol) induced damages of chromosomes in human lymphocytes, increasing deletion ratio is 7. Chromosome may lead to leukemia development. Morphological changes in the cells of hamster embryos are influenced by phenol, catechols, and hydroquinone. Enzymatic DNA synthesis is disturbed seriously by catechols and hydroquinone. As a result, activation and proliferation of T lympho cytes becomes to an end of the worst position. Proliferation cycles of lymphocytes in the G1 phase are also disturbed by phenol, catechols, and hydroquinone[36].

Carcinogenic effects of phenolic compounds on living organisms:

Tumours and lung cancer etc. are detected from the pathological test with exposure to chlorophenols. So, it is clear that chlorophenols or sodium salt of chlorophenols are carcinogenic matters for lives like man and animal. Carcinogenic changes are observed when the 2-chlorophenol's dose is taken 5.0 µg/kg of body weight and dose of 2, 4-dichlorophenol is 3 µg/kg of body weight daily. USEPA narrated that phenolic compounds have carcinogenic nature. Para-cresol and 2, 4-dimethylphenol are distinguished as carcinogenic matters for animals and carcinogenic influence matters for mammals respectively. Long-term exposure to 2, 4-dimethylphenol for an animal like a rat, is responsible for tumours in the rat skin; on the contrary dose of 3% dimethyl-benzanthracene is claimed for skin tumours. 18% of these tumours are turned into skin cancer. 2-quinones; particularly quinones methide is also responsible to produce elevated toxicity and poses reactive oxygen to be carcinogenic. Phenoxyherbicides increase the death of industrial workers with long term exposure. Respiratory system, lymphoma, and myocardial ischemia are claimed for death linked with cancer. Exposed in vinyl chloride production factories of 10,000 workers were suffered from liver and lung cancer. Inthe vinyl chloride production unit chlorophenols are released as main by-products[34].

Other toxic influence of phenols:

Phenols affect the function of the hormonal system. Some phenols are capable of disturbing sexual hormone function, which finally may lead to sterility in animals and humans. The examples are o, p-dichlorophenol, and pentachlorophenol. It was noted that simple phenols and in particular trichlorophenols may block ion channels in a micromolar concentrations range. Investigation concluded that phenol and hydrophobic residues alkyl chains or additional phenyl rings substituted in third, fourth, and fifth positions are responsible for the above-described kind of toxic activity. The second metabolite generates a superoxide radical that in a dismutation reaction forms hydrogen peroxide converted in the presence of Fe^{3+} to a highly reactive oxygen form hydroxyl radical. The investigations led by Bukowska, Duchnowicz, and co-workers have revealed numerous toxic effects caused by phenols on human erythrocytes. The authors observed lipid peroxidation in erythrocytes incubated with o, p-DCPh[37]. Chlorophenols decreased human membrane erythrocytes acetyl cholinesterase activity. Chlorophenol changed ATPase activity and membrane fluidity and also damaged membrane proteins. o, p-DCPh decreased the activity of catalase. The changes in the above parameters provoked hemolysis of the cells. The level of hemolysis was the highest in the presence of catechols and the lowest in the presence of phenol.

1.2.6 Literature review on agricultural wastes

Huge amounts of agricultural wastes and by-products are available in agro-industries. These are important resources of waste materials. These wastes are exclusive alternatives of available used adsorbents. Among the agricultural wastes orange peel, citrus waste, rice husks and straw, barley and wheat husks, and palm oil waste clinker sugarcane bagasse etc can be used as biosorbents. SCB is one of the most cost-effective and available agro-industrial wastes. Many of the countries of the world; specially Brazil, India, China, and Bangladesh produce a huge amount of sugarcane. Bagasse can be collected from the sugar and sugarcane related factories of these countries. Every year 1.5 lakh metric tons of sugar is produced and 8.0 lakh metrictons of SCB is also produced as a by-product[38] in different industries of Bangladesh. This bagasse can be used as a biosorbent as it can sorb a large number of organic and inorganic compounds that are responsible for environmental pollution; SCB is a fibrous waste that contains different functional groups. These groups can bind pollutant ions onto the surface carbon[39]. Over the past decade, sugarcane bagasse and its derivatives (including bagasse fly ash and bagasse-based activated carbon) have been extensively studied as potential adsorbents in both their modified forms. The sorption efficiency of sugarcane bagasse depends on the biosorbent dose, contact time, initial pollutant concentration, solution pH and temperature, and sorbent particle size. It is observed that a maximum Cd (II) removal capacity of 96% using SCB, which occurred at an

initial Cd (II) concentration of 10 ppm in an aqueous solution at pH 7.0, and required 25 minutes of contact time[40].

Literature review on agricultural waste bagasse sorbent:

SCB is available low-cost agricultural waste is obtained from sugarcane. Sugarcane is a branch-free renewable resource. Traditionally bagasse waste is turned to ash by burning in the field. It can be used as a biosorbent for sorption of varieties compounds those pollute environments.

Figure 1.1: Sugarcane tree.

Bagasse is a fibrous material that is obtained from sugarcane or sorghum stalks after extraction of its juice. The ratio between sugarcane and its bagasse is 10:3. This bagasse is a by-product in the sugarcane industry and in every county; its quantity is dependent on the production of the sugarcane. The SCB is exclusively a heterogeneous material containing about 30-40 percent pith fiber that is obtained from the core of sugarcane tree in Figures 1.1-1.2. The constituents of the bagasse are cellulosic materials are known as fibrous waste[38].

(a) **(b)**

Figure 1.2 Sugarcane (a) before extraction of juice, (b) extracting juice

Sugarcane bagasse compositions and its potential as a biosorbent:

SCB in Figure 1.3 is an agricultural waste that is cost-effective and available in agricultural countries. The contents of SCB are mainly based on cellulose, hemi-cellulose, and lignin. So, it is known as agro-industrial lignocellulosic material to the researchers. Besides cellulosic matters, a trace amount of extractives are also found in this bagasse. SCB's constituents are characterized for binding capability of various pollutant ions as its huge number of functional groups have made it feasible to bind with pollutant ions. Humic and fulvic, lignin, cellulose, hemicelluloses, and proteins which are act as macromolecules have the miscellaneous functional groups, their performances act as biosorption sites. These functional groups (-OH, -COOH, $-NH_2$, $-CONH_2$, $-OCH_3$, etc.) enable the biosorbents to bind the ions of pollutants through ion exchange process with hydrogen ion. The biosorption processes are also performed through formatting complexation providing electron pairs. The sites present in bagasse and 10.3% silica contentable bagasse to bind the contaminants prevail in water and industrial waste water is feasible for mitigating contaminants. This mitigation capability of contaminants from water and industrial effluent is not only the contribution of chemical components of the bagasse material, but also on its construction system[38].

Bagasse surface constrruction system can be identified by scanning electron micrographs. The irregular structure of bagasse is capable of biosorb of phenolic ions because varieties types of porosity are present in bagasse. On the contrary, SCB is insoluble with water molecules; physical treatment is easy, and homologous to various agro-based industrial wastes, such as tea waste, corncobs, sawdust, apple peel, and grape stalks. The probability of SCB as a biosorbent is also recognized by its desorption capability; this desorption rate is gradually decreased after three times, SCB is also proceeded in reuse for biosorption, in this case, a slight loss of initial sorption capability. These properties increase the favor of the sorption technique of phenols onto SCB at minimum cost[38].

Figure 1.3 : Bagasse, after extraction of juice.

Physical or mechanical modification of sugarcane bagasse:

Milling, auto claving, thermal drying, boiling, cutting, and grinding can be physical moderation of SCB. These processes can change the biosorbent surface and size of particles of SCB. The particle size affects the biosorption techniques; the greater number of particles as well equals mass weight effectively acts, because of elevated surface area and the ratio of carbon: silica, an example is established that a huge quantity of metal ions was sorbed by the small size of bagasse particles. Physical moderation is also elevating the surface area of SCB by particle size reduction on 0.08 m^2 g^{-1} with elevation of particle numbers, the sorption capability developed to 91% of dye-containing effluents. Since physical changing processes of SCB are defined as slower sorption than chemical one, chemical moderation cannot be having friendly or eco-friendly for the natural environment. So, physical moderation is favorable[38].

1.2.7 Mitigation of phenolic compounds from aqueous system

Mitigation of phenol contamination from industrial effluents in discharge points is an essential need for saving lives; human, wild, and aquatic creatures. Developing an effective process to mitigate toxic elements from the polluted environment can be an efficient effort. Applying proper techniques for separating phenols will not only mitigate problems of possible dangers but also the waste disposal will be easy as well as adding values with agricultural biowastes. For this, various processes can be employed to separate phenols efficiently from water and industrial effluent before discharging to water bodies. These are photocatalytic degradation, coagulation, flocculation, ozonation, adsorption/biosorption, extraction techniques, biological method, membrane-based separation method, electro-Fenton method, ion exchange processes[41] etc.

Adsorbents used for sorption phenolic compounds:

Water and wastewater are treated all over the world using sorbent activated carbons (ACs). Among various ACs charcoal is the oldest sorbent for the treatment of wastewater. In 1970 charcoal was used to mitigate bad tastes and odors from wastewater. In 1900 Raphael Von Ostrejko emerged for commercial AC. For the high cost of commercial AC and variance of carbon generations, the alternative carbon-containing materials are being searched by the environment-related research workers. So, alternatives of AC; it is required to looking for natural things that are available and cost-effective. The porosity of the natural material is an important property. With moderation, these natural biosorbents can be improved physically and mechanically. Bottom ash, brick-kiln ash, fly ash, peat, rice husk and straw, jute stick, wood, sawdust, bagasse, and carbonized bark are some new biosorbent can be used for sorption

of organic pollutants. Polymeric materials can be synthesized and it can be a sorbent as its porous properties and can sorb pollutants like phenolic compounds[41].

Biosorption of phenolic compounds by naturally occurring materials:

Naturally occurring materials such as agricultural wastes like eggshell, used tea leaves, orange peel, coconut husk, maize husk, sugarcane bagasse, banana peel, rice straw and rice husk etc are available in rural area of Bangladesh can play an important role for the biosorption of phenolic compounds. These sorbents contain many functional groups for binding and separating the organic and inorganic pollutants from industrial effluents without using any chemicals. Among these natural things, many of them are working as sorbent effectively and some do not show efficiency but whether activate them, they become effective sorbent. It has been studied on the biosorption of phenol and o-CPh from aqueous solutions onto chitosan (obtained from chitin; a natural polymer from crustacean shells e.g., prawns, crabs, shrimps etc.) calcium alginate blended beads[41].

Biosorption concepts and mechanisms:

Biological materials can be used as non-reactive biosorption of organic and inorganic compounds either is as homogeneous or inhomogeneous (insoluble) conditions from water or industrial effluents. Biosorption is different from bioaccumulation. Biosorption has high efficiency with compare to other bio-separation techniques. Removing ions become at a lower concentration in the system, if biosorption method is applied. It is said that the process separates pollutants ion salt together, using a low-cost biosorbent. The process is influenced by sorbent dose, contact time, particle size of the sorbent, initial concentration, pH value of the aqueous medium. In some cases, biosorption percentage is increased with the increase of biosorbent dose upto a certain limit; again, by increasing surface area of the sorbent can be increased active sites which bind increased number of pollutant ions. If the initial concentration of the pollutant ions is increased, indicating that active sites for binding pollutants become less. Exceeding the equilibrium time, no sorption efficiency found with increasing contact time. The pH of pollutant ions medium also controls the biosorption process for the protonation and deprotonation properties of both the sorbent and sorbate. Sorption mechanism with low-cost sorbents is effective for the sorption of phenols. chelation, complexation, ion exchange etc techniques are involved in mechanisms of phenolic sorption onto cellulosic sorbents have shown in Figure 1.4. The functional groups on the surface of the sorbent and the H_3O^+ of the system medium can activate sorption[38].

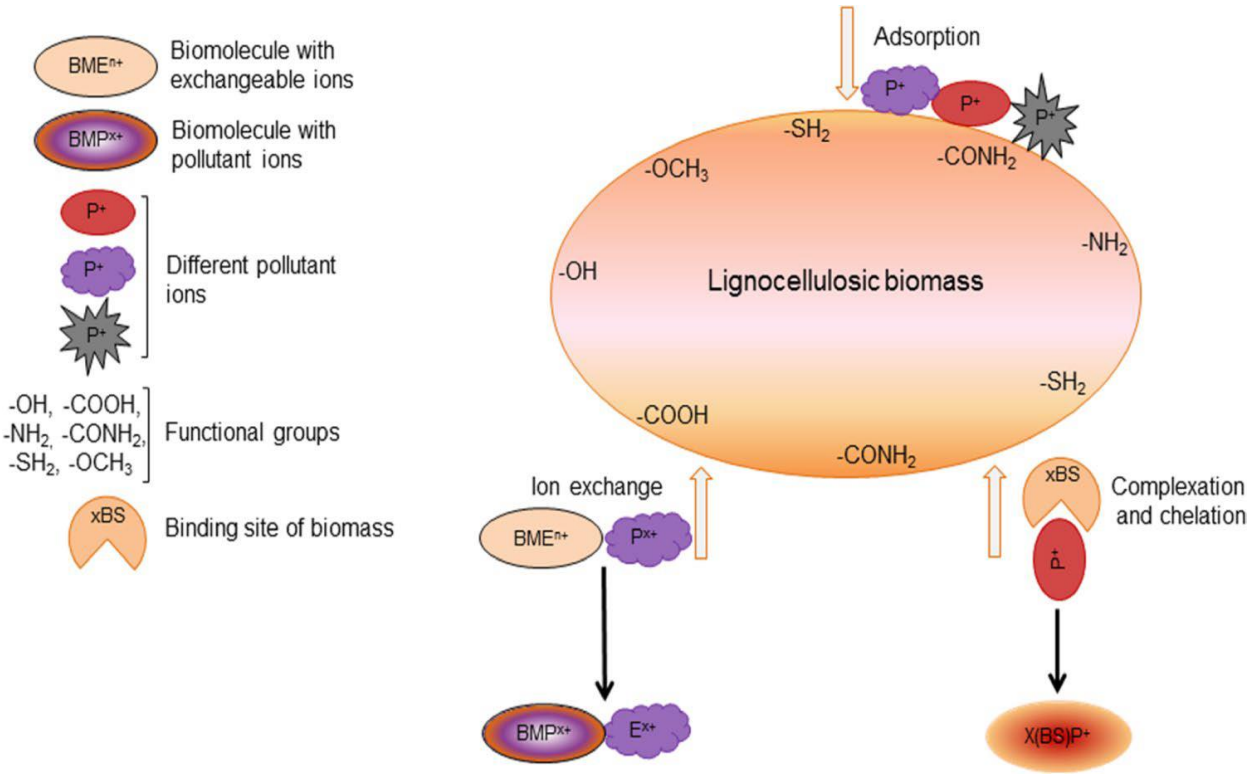

Figure 1.4: Mechanisms of biosorption using low-cost biosorbents.

1.2.8 Safety factors

If any organ is exposed to phenols, alcohol solution should be used; if at all possible, because alcohol has a greater solubility with phenolic compound. Eyes should be washed with warm water. Areas in which people handle phenol and phenolic compounds should be equipped with alcohol solution cans and safety showers. Personnel who could be exposed to phenolic compounds should wear chemical workers' goggles, face shields, rubber gloves, and suits or aprons, depending on the working circumstances.

Eyes, nose, and skinare burned with contact of phenolic fumes. It is noticed by the National Institute for Occupational Safety and Health (NIOSH), control should be made for the industrial workers as none of them exposed to phenol concentrations more than 20 mg/m^3, which is a time-weighted average concentration for upto a 10-h workday, 40-h work week.

1.3 Objectives

Water is very useful in industrial activities; various industries use water for various purposes. The effluents of the industries contain phenolic compounds and pollutes the surroundings water reservoir of the industry site. The phenolic pollutants in the natural water from industrial effluent change the physical states and chemical and microbiological constituents. So that natural water becomes unsuitable or less suitable for safe and beneficial consumption.

The study aims to explore the possibility of using waste bagasse for biosorption of selected phenols following batch experiment from pollutedwater. Carbolic acid (phenol), o-CPh, p-CPh and o, p-DCPh have been chosen for model target pollutants in the industrial wastewater because they are widely used in the industries and daily life, and have caused considerable damage in the ecosystem of water bodies and human health. Since these are potentially carcinogenic and mutagenic to mammalian as well as aquatic lives; hence, the design of a suitable process for mitigation of the selected toxic compounds from aqueous medium is an important issue for the present study.

Low capital investment in operating systems for mitigation of selective phenol and phenolic compounds and potential recovery of the sorbate and sorbent through rapid kinetics of sorption and desorption with no sludge generation are the attempts of the present study. In this study, bagasse is used as a biosorbent material for sorption of phenols. Due to the highest sorption capacity of bagasse among the selected agricultural wastes; it has the potentiality to be used as a sorbent. Besides, the fiber structure, insolubility in water, chemical stability, and high mechanical strength, desorption capacity and availability in all over the world with low cost baggase may turn to success the biosorption process in the effluent discharge point for phenolic pollutants free aqueous environment.

In the search for new and low-cost agricultural wastes as source material for wide use, bagasse by-product seems to be an inexpensive biosorbent material for waste management. However, the biosorption behavior of phenols onto bagasse, without any treatment, has not been extensively studied. The present work is performed to evaluate an exceptional sorbent that can be run the research smoothly to develop a very simple but highly efficient technique. For mitigation of phenolic compounds from water and industrial effluents using a suitable sorbent like bagasse is locally available from the agro-industries before discharge to the aqueous environment can be made a safety ditection from harmness of phenolic compounds. Desorption and regeneration can make the work eco-friendly. From the introduction and review of biosorption method for sorption of phenolic compounds using agricultural wastes might be gaining considerable importance.

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Chapter 2

Biosorption of phenol from aqueous system using agricultural waste bagasse

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2.1 Introduction

Phenol is an organic compound that is used as the raw material for the production of various industrial products, releases several by-products with industrial effluents, and pollutes water bodies as it has toxic nature. For this, treatment of the effluent containing the phenol is essential before discharge to natural water. In the present work an attempt has been taken to mitigate the typical pollutant organic compound phenol as a targeted toxic chemical from the industrial effluent. Phenol represents high toxicity and pollutes natural water with the industrial effluents. Petrochemical, pharmaceutical, plastics, pesticide chemical, textile, and resin industries release the phenol with the effluents[1]. Phenol is characterized as having extensive toxicity and a carcinogenic nature even at low concentration[2]. It has caused considerable damages the lives of water bodies and human health. In Bangladesh, the permissible limit is 5.0 mg/L[3] which can be discharged with the effluent from the phenol-based textile plant and large industrial processing units. Environmental Protection Agency (EPA) for USA has made regulation for the permissible limit of phenol content in the wastewater is less than 1.0 mg/L[4]. So, necessary steps to be taken have emerged for the treatment of industrial effluent in the discharge points of the industries. Prevailed employing phenol removal techniques from water and wastewater are advanced oxidation, membrane filtration, biological degradation, electrochemical oxidation, photocatalytic degradation, and adsorption and biosorption etc[5]. Among the methods, biosorption can be a feasible and powerful method for the treatment of the effluents released from households and industries. Activated carbon is widely used for the treatment of the effluents[6]. Though the biosorption efficiency of activated carbon is high, it is high cost and shows in variable performances in carbon regeneration, low-cost single used material is acceptable[7]. So, economically feasible, practical, and efficient sorbents are essential. Bottom ash, ash, fly ash, rice husk, wood, sawdust, bagasse, and carbonized bark are various agro-waste materials may be new sorbents, can be used for the biosorption of phenol[8].

The new and low-cost agro-wastes can be source materials for widely used biosorbents. Sugarcane bagasse (SCB) is an agro-industrial by-product which is an inexpensive biowaste material for effluent treatment. The potential ultimate use of SCB has been selected for its sorption capacity, regeneration characteristics, and physical properties of subsequent uses. Bagasse is the low cost and available agro-industrial by-product, especially in tropical regions[9]. Brazil followed by India, China, and Bangladesh produce a huge amount of sugarcane. Bagasse is produced in large quantities as a by-product of the sugar and bioethanol mills in each of these

countries. Bangladesh produces 1.5 lakh tons of sugar and generating 8.0 lakh tons of SCB as a by-product in 15 sugar mills. Recently, researchers related to the environment emerged on low cost and effective sorption process that can separate phenol from effluent. Bagasse is supposed a good biowaste is produced more than 13.0 crore tons yearly as a by-product in the world[10]. However, the biosorption behavior of phenol onto SCB, without using chemicals, has not been extensively studied. The present work has been performed to evaluate the use of waste SCB as an alternate sorbent for biosorption of phenol from aqueous system.

2.2 Materials and Methods

2.2.1 Materials

Agricultural wastes based biosorbents:

Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk are the agricultural Biowastes.

Chemicals used and their specification:

Chemicals and reagents used were of analyticalgrade. The stock solutions have been prepared in deionized water. The chemicals used and their specifications are as follows:

Buffer solution pH 10:

500.0 ml of buffer stock, pH 10.00 ± 0.05 (20°C); Merck, Germany.

Potassium Ferricyanide:

BDH Chemical Ltd. Poole England. It is bright, ruby red, crystals; soluble in about 2.5 parts of water; insoluble in alcohol.

2.2.2 Apparatus and Equipment

(i) Photometric equipment (ii) Shimadzu UV-VIS1700 Spectrophotometer, equipped with absorption cells providing light paths of 1cm. (iii) Microprocessor bench pH meter. (iv) Oven. (v) Mechanical shaker (vi) Rotary shaker. (vii) Crusher. (viii) Pipette. (ix) Micropipette. (x) Burette. (xi) Conical flask (xii) Volumetric flask.

2.2.3 Experimental procedure

Collection of biosorbents:

Biowastes eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk were collected from the local vendors. The agricultural wastes

are initially investigated to observe their biosorption efficiencies and it is revealed that bagasse is comparatively efficient than the rest of the biosorbents.

Preparation of biosorbent bagasse:

After collecting, bagasse is treated by rinsinginto water to remove impurities then left to dry at room temperature. The bagasse is kept to dry initially into hot air oven at 60°C for 24 hours and then the dried bagasse has been sieved into six size fractions of 50, 70, 100, 150, 200 and 250 μm (micrometer) and these are separated by selective standard test sieves. These sieved particles of biosorbent bagasse are stored in stopper bottles for subsequent use.

2.2.4 Preparation of solutions

Preparation of phenols solutions:

0.5 g selected phenols (phenol, ortho-chlorophenol, para-chlorophenol, ortho, para-dichloro-phenol) are dissolved in 500 ml deionized water in volumetric flasks separately. These solutionsare known as approved solutions of the phenols, (1000 ppm of each). The stock solutions are diluted into the required concentrated sample solutions.

Preparation of potassium ferricyanide (2% W/V) solution:

2.0 g of potassium ferricyanide has been diluted in deionized water up to 100 ml. This is a 2% (W/V) potassium ferricyanide solution. This solution is kept in a suitable glass bottle then used. Daily a new solution is prepared.

Preparation of buffer pH 10 solution:

This is manufactured by Merck, Germany. This solution is used to maintain the medium of the system solution.

Preparation of 4-aminoantipyrine (4-AAP) solution:

0.5 g 4-AAP is diluted in deionized water up to 100 ml. This is known as a 0.5% (W/V) 4-AAP solution. This solution has to make daily.

2.2.5 Operational procedures

The estimation of phenol is done spectrophotometrically by the modified 4-AAP method using Shimadzu UV-1700 double beam spectrophotometer. For the modification of the process detailed experiments are carried out varying all parameters as follows:

Introductory experiments:

These experiments are implemented by spectrophotometer for estimation of phenol following the modified 4-AAP method with solution at pH 10.0 and absorbance is estimated at 500 nm respectively did not give satisfactory results. Maximum absorption is at 500 nm and the required time to reach apoint of maximum color is 25 minutes. Therefore, it is decided to modify the method first and then to apply the modified method for the estimation of phenol. We took an attempt to modify the 4-AAP method for the spectrophotometric measurement of phenol; Total studies are implemented with including the investigations making the color using the absorption spectra, optimum solution media, suitable reagent concentration, adherence Beer's law etc. As a result, the modified method may be applied for the estimation of a trace amount of phenol in the solution.

General Procedure (Direct Spectrophotometry):

An appropriate aliquot of the test solution containing a definite amount a 5.0 mg/L of phenol is taken in a 25 ml volumetric flask three times separately. This is followed by the addition of 0.1 ml, 0.6 ml, 1.0 ml buffer concentrate (pH 10) solution; and then the addition of 0.9 ml 4-AAP and 0.7 ml potassium ferricyanide solutions each time. The samples are then diluted with double distilled water, up to the mark (25ml). A reagent blank is prepared under identical conditions, against which the absorbance is measured at the wavelength of maximum absorption (A max) after 15 minutes.

Color Reaction:

In the experiments, phenol offers brownish-red color with 4-AAP in presence of potassium ferricyanide in an alkaline medium instead of an acidic medium. In an alkaline medium color intensity gradually increases with the increasing amount of buffer concentrate (pH 10) solution up to 1.0 ml, beyond which decreases the color intensity. This is the reason to modify the spectrophotometric method for detection of trace amount of phenol.

2.2.6 Modification of 4-AAP method for determination of phenol

Effect of potassium ferricyanide solution on color development:

The result of the potassium ferricyanide (2% W/V) solution is shown in Table 2.1(b) which indicates that 0.7 ml of potassium ferricyanide (2% W/V) tincture is enough to develop maximum color in the arrangement of 5.0 mg/L phenol tincture. Graphically the results are represented in Figure 2.1. This indicates that the volume beyond 0.7 ml of the potassium ferricyanide (2% W/V) solution decreases the color intensity of the system. Therefore, 0.7 ml potassium ferricyanide (2% W/V) solution is used for the optimum color development of the system containing 5.0 mg/L phenol.

Table 2.1(a) Conditions on the effect of potassium ferricyanide for color intensity

Volumeof 4-AAP solution	1.0 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of phenol	5.0 mg/L
Volume of potassium ferricyanide solution (ml)	Different Volume
Color development time	20 minutes
Total volume of the solution	25 ml

Table 2.1(b) Effect on volume of potassium ferricyanidesol^{n} for color development

Volume of potassium ferricyanide (ml)	λ_{max}(nm)	Absorbance
0.2	500	0.2912
0.4		0.3965
0.5		0.4607
0.6		0.5113
0.7		**0.5267**
0.8		0.5097
0.9		0.4879
1.0		0.4672
1.2		0.4296
1.3		0.4058
1.4		0.3921

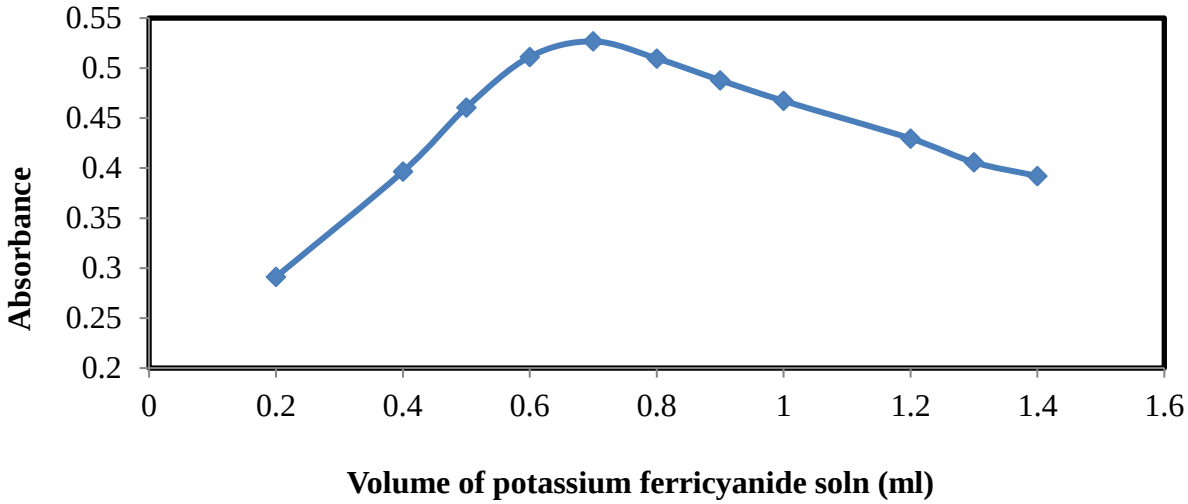

Figure 2.1 Effect on volume of potassium ferricyanide (2.0%W/V) solution for maximum color intensity; phenol: 5.0 mg/L; 4-AAP (0.5%w/v) sol^{n}: 1.0 ml; buffer (pH10) sol^{n}: 1.0 ml and time: 20 min at λ_{max}: 500 nm

Effect of 4-AAP solutionon color development:

The results of the 4-AAP (0.5% W/V) tincture are shown in Table 2.2(b) which denotes that 0.9 ml of 4-AAP tincture is enough to develop maximum color of the arrangement having 5.0 mg/L of phenol in the system. The results are graphically represented in Figure 2.2. The figure

depicts that volume beyond 0.9 ml of 4-AAP solutions decreases the color intensity of the system. Therefore, 0.9 ml of 4-AAP (0.5% W/V) solutions is used for the optimum color development of the arrangement having 5.0 mg/L of phenol.

Table 2.2(a) Conditions on effect of 4-AAP for color development

Volume of 4-AAP solution (ml)	Different volume
Volume of buffer solution (pH 10)	1.0 ml
Concentration of phenol	5.0 mg/L
Volume of potassium ferricyanide solution	0.7 ml
Color development time	20 minutes
Total volume of the solution	25 ml

Table 2.2(b) Effect on volume of 4-AAP solution for development of maximum color intensity

Volume of 4-AAP solution (ml)	λ_{max}(nm)	Absorbance
0.4	500	0.3053
0.5		0.3797
0.6		0.4432
0.7		0.4843
0.8		0.5105
0.9		**0.5301**
1.0		0.5267
1.2		0.4595
1.3		0.4214
1.4		0.4032

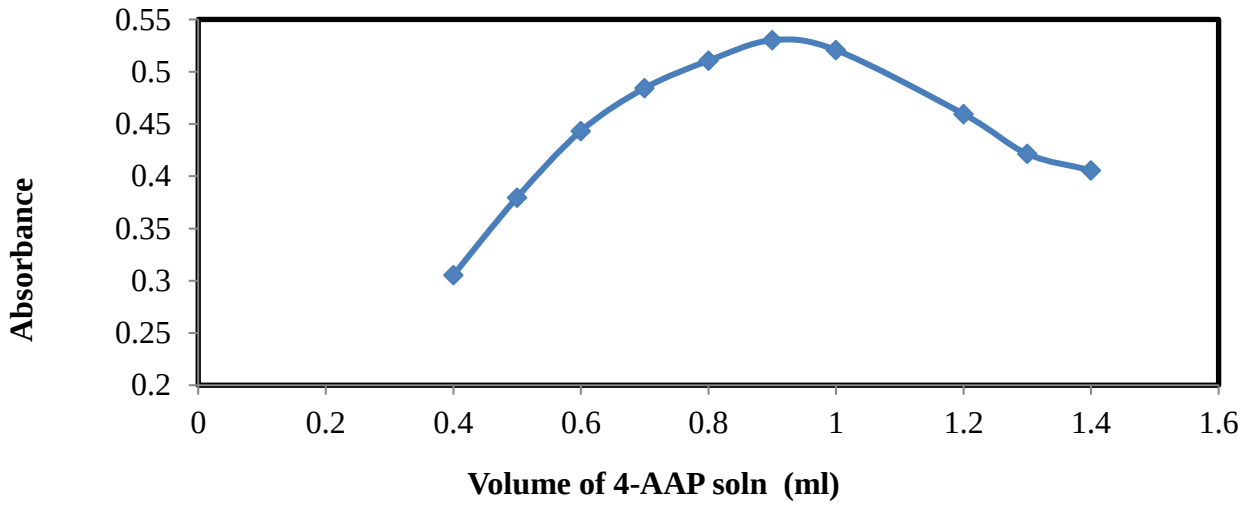

Figure 2.2 Effect on volume of 4-AAP sol^n (0.5%W/V) for maximum color intensity; phenol: 5.0 mg/L, PFC (2.0%w/v) sol^n: 0.7 ml; buffer (pH10) sol^n: 1.0 ml; λ_{max}: 500.0 nm and time: 20 min at 30°C

Effect of buffer solution (pH 10) for maximum color development:

The effect on volume of buffer solution (pH 10) is shown in Table 2.3(b) which shows that 1.0 ml of buffer stock (pH 10) is enough to develop the maximum color of the arrangement having 5.0 mg/L phenol solution. The graph of the results is represented in Figure 2.3. The figure indicates that volume beyond of 1.0 ml buffer solution (pH10) decreases the color intensity of the system containing 5.0 mg/L of phenol solution.

Table 2.3(a) condition on effect of buffer solution (pH 10) for color development

Volume of 4–AAP solution	0.9 ml
Volume of buffer solution (pH 10) (ml)	Different volume
Concentration of phenol	5.0 mg/L
Volume of potassium ferricyanide solution	0.7 ml
Color development time	20 minutes
Total volume of the solution	25 ml

Table 2.3(b) Effect on volume of buffer solution for development of maximum color intensity

Volume of buffer solution (pH 10) ml	λ_{max}(nm)	Absorbance
0.4	500	0.3636
0.5		0.4078
0.6		0.4293
0.7		0.4697
0.8		0.4998
0.9		0.5078
1.0		**0.5301**
1.2		0.5082
1.3		0.4402
1.4		0.4043
1.5		0.3283
1.7		0.2376

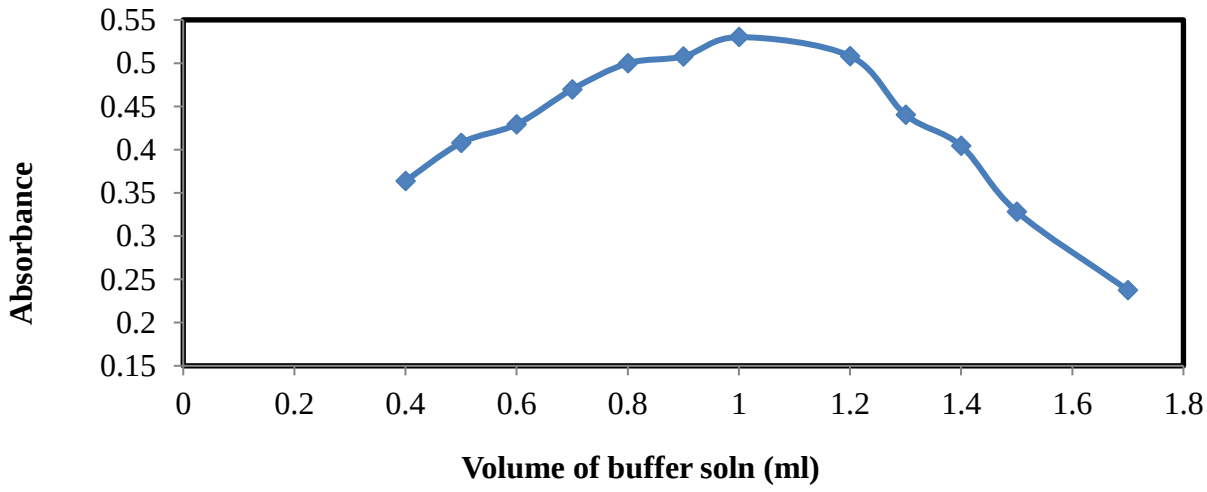

Figure 2.3 Effect of volume of buffer (pH10) solution on maximum color intensity; Phenol: 5.0 mg/L; 4-AAP (0.5%w/v) sol^n: 0.9 ml; PFC (2.0%w/v) sol^n: 0.7 ml; λ_{max}: 500 nm and time: 20 min at 30°C

Effect of time on color development reaction to reach equilibrium:

The result of the required time is shown in Table 2.4(b) which shows that 25 minutes is enough to develop maximum color intensities of the arrangement having 5.0 mg/L phenol in the system with 0.7 ml potassium ferricyanide tincture, 0.9 ml 4-AAP, and 1.0 ml buffer solution (pH 10). The graph of the results is represented in Figure 2.4. The figure shows that 25 minutes is required for the stable color intensity of the system and after 25 minutes, the color intensity of the system remains constant and falls on equilibrium for a while, and then the color becomes liberated. Therefore, reaction time is 25 minutes for the optimum color development of the arrangement having 5.0 mg/L of phenol system

Table 2.4(a) Conditions on effect of reaction time for color development

Volume of 4-AAP solution	0.9 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of phenol	5.0 mg/L
Volume of potassium ferricyanide solution	0.7 ml
Effect of time (minutes)	Different time
Total volume of the solution	25 ml

Table 2.4(b) Effect of time on maximum color intensity

Time (min)	λ_{max}(nm)	Absorbance
10	500	0.4503
15		0.4788
20		0.5301
23		0.5342
25		**0.5363**
30		0.5309
35		0.5245
40		0.5157

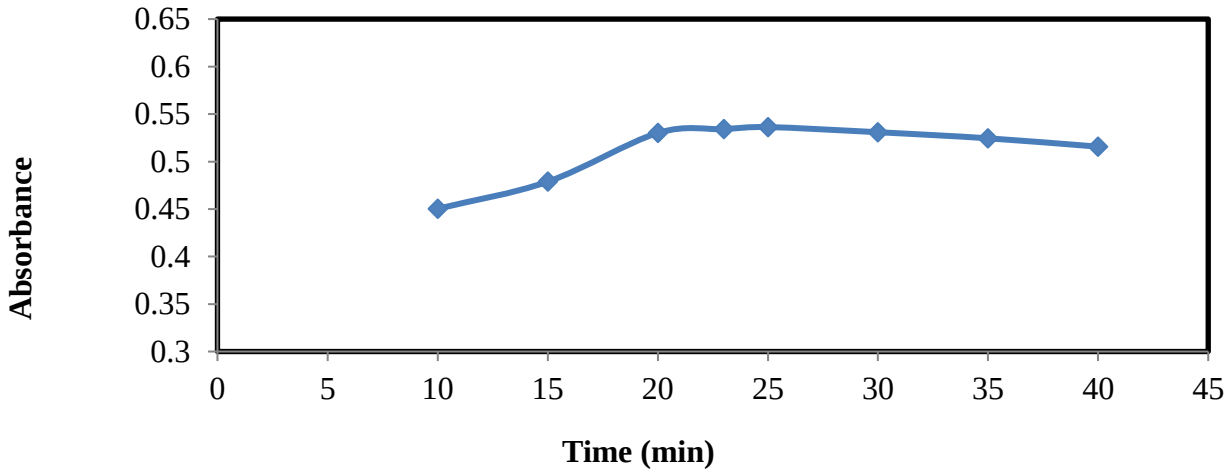

Figure2.4 Effect of reaction time for maximum color intensity; Phenol: 5.0 mg/L; 4-AAP (0.5%w/v) sol^n: 0.9 ml; PFC (2.0%w/v) sol^n: 0.7 ml; buffer (pH10) sol^n: 1.0 ml and λ_{max}:500.0 nm at 30°C

2.2.7 Preparation of standard calibration curve for determination of phenol

A standard curve is a graph relating a measured optical density to the concentration of the substance of interest in "known" samples. The standard calibration curve is drawn by plotting absorbance (on the vertical axis) versus concentration (on the horizontal axis). Results of the calibration curve are shown in Table 2.5(b). This curve is determined by the system containing 1.0-10.0 mg/L of phenol solution with 0.7 ml potassium ferricyanide solution, 0.9 ml 4-AAP, 1.0 ml buffer solution (pH 10) within 25 minutes for development of maximum color intensity is 25 min. The graph of the results is shown in Figure 2.5.

Table 2.5(a) Conditionon preparation of a standard calibration curve

Volume of 4-AAP solution	0.9 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of phenol(mg/L)	Different concentration
Volume of potassium ferricyanide solution	0.7 ml
Color development time	25 Minutes
Total volume of the solution	25 ml

Table 2.5(b) Evaluating the optimum value for standard calibration curve

Concentration of phenol (mg/L)	λ_{max}(nm)	Absorbance
1	500	0.1151
2		0.2305
3		0.3356
4		0.4293
5		0.5363
6		0.6315
7		0.7365
8		0.8289
9		0.9471
10		1.0511

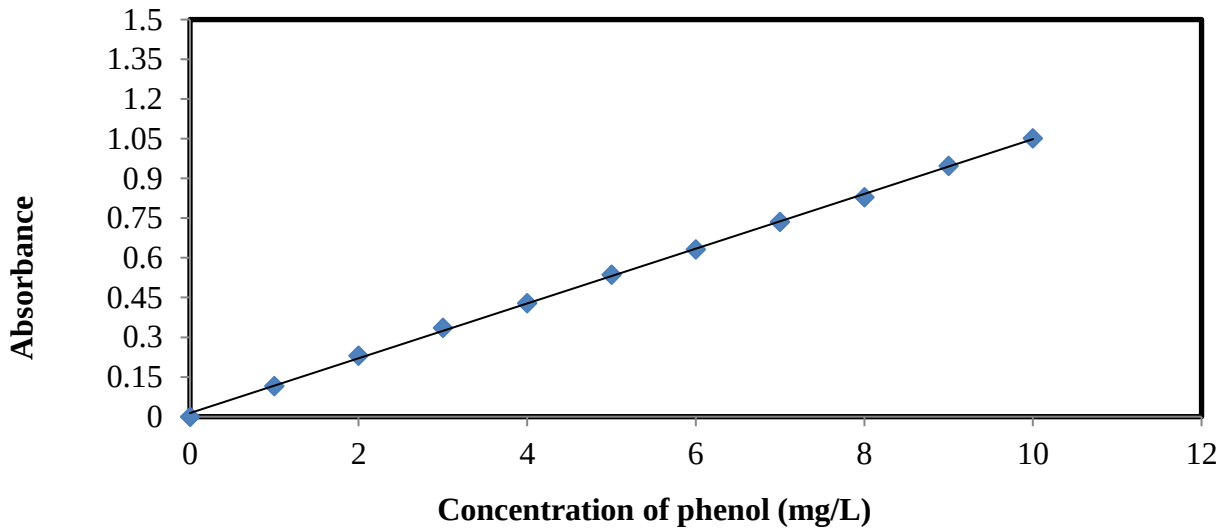

Figure 2.5 Standard calibration curve for det^n absorbance of phenol; Phenol concentration: 1.0-10.0 mg/L; 4-AAP (0.5%w/v) sol^n: 0.9 ml; PFC (2.0%w/v) sol^n: 0.7 ml; buffer (pH10) sol^n: 1.0 ml; time: 25 min and λ_{max}: 500 nm at 30° C

2.3 Results and Discussions

2.3.1 Performances of biosorbents

Preliminary evaluation of performances of nine agricultural wastes (Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk) are selected for the biosorption of phenol from system solutions. The biosorption of phenol has been performedby the conditions; phenol concentration, 5.0 mg/L; temperature (ambient temperature), 30˚C; sorbent dose, 1.0 g; contact time, 60 minutes; particle size, 150 µm and pH value 6.5. The studies indicate for sorption effectiveness of phenol with Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk are 13.3%, 12.2%, 13.1%, 28.7%, 13.9%, 31.2%, 17.3%, 28.8%, and 28.2%, respectively. Among these, eight biosorbents have lessersorption efficiencies from bagasse. So, those are not selected for use in this research work. Hence, agro-biowaste bagasse is taken as a comparatively more efficient biosorbent for the soption of phenol from water system.

2.3.2.1 Effect of bagasse dose on biosorption of phenol from aqueous system

Study on biosorbent doses is an important factor due to determine the sorptione fficiency of a sorbent for a given initial concentration of the phenol solution[11]. Biosorption of phenol onto bagasse carried out at different bagasse dose by keeping other parameters constant. In this present investigation, the biosorption system has been studied by plotting the percentage of sorption efficiency of phenol against the different doses (0.5-5.0 g) of bagasse at a constant initial concentration (5.0 mg/L) and the results have been shown in the figure 2.3.1. The figure depicts that biosorption percentage of phenol is increasing with the increase in bagasse dose up to 2.0 g/100 ml from a constant concentration (5.0 mg/L) of phenol and then the sorption remains constant. These phenomena are attributed due to a large availability of sorption sites with higher sorbent doses on the initial rate of phenol uptake up to 2.0 g then the sorption reaches the saturation situation and remains constant. Similar types of trend in the sorption of phenol on different types of low-cost sorbents were reported[12]. The effect of bagasse doses introduces to an increase in phenol sorption 59.96%, with enhance upto 2.0 g bagasse; above the range, sorption effectiveness is negligible. In case of the enhancing the sorption with increase in bagasse dose can be provided to a larger surface area with the availability of huge sorption sites[13]. If the bagasse dose is further increased after 2.0 g in the process unit, stoichiometrically, the dose is more than the equivalent amount of phenol in the solution. It can also be concluded that the rate of phenol binding with sorbent bagasse increases more rapidly in the initial stages and after some points, the sorption is marginal and becomes almost constant[14,15]. For this reason, biosorption does not increase with the increase in bagasse dose. Results show that 2.0 g sorbent bagasse of 150 µm particle size sorbed 59.96 % phenol from

the 5.0 mg/L solution within 60 minutes with pH 6.5 at 30˚C and this dose of 2.0 g bagasse is selected for subsequent experiments.

Table 2.3.1(a) Condition on effect of bagasse doses for biosorption of phenol

1	Concentrationof phenol	5.0 mg/L
2	Temperature (Room temperature)	30 ˚C
3	pH of the solution	6.5
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Contact time of phenol solution and bagasse	60 minutes
8	Parlicle size of Bagasse	150 µm
9	Bagasse dose (g)	Different doses

Table 2.3.1(b): Effect of bagasse dose on sorption of phenol in aqueous system

Bagasse dose (g)	Absorbance	Conc. of phenol (mg/L)	Biosorptionof phenol (%)
0.5	0.4540	4.230	15.50
1.0	0.3702	3.440	31.20
1.5	0.2598	2.295	54.10
2.0	0.2307	2.002	59.96
2.5	0.2307	2.002	59.96
3.0	0.2307	2.002	59.96
3.5	0.2307	2.002	59.96
4.0	0.2307	2.002	59.96
4.5	0.2307	2.002	59.96
5.0	0.2307	2.002	59.96

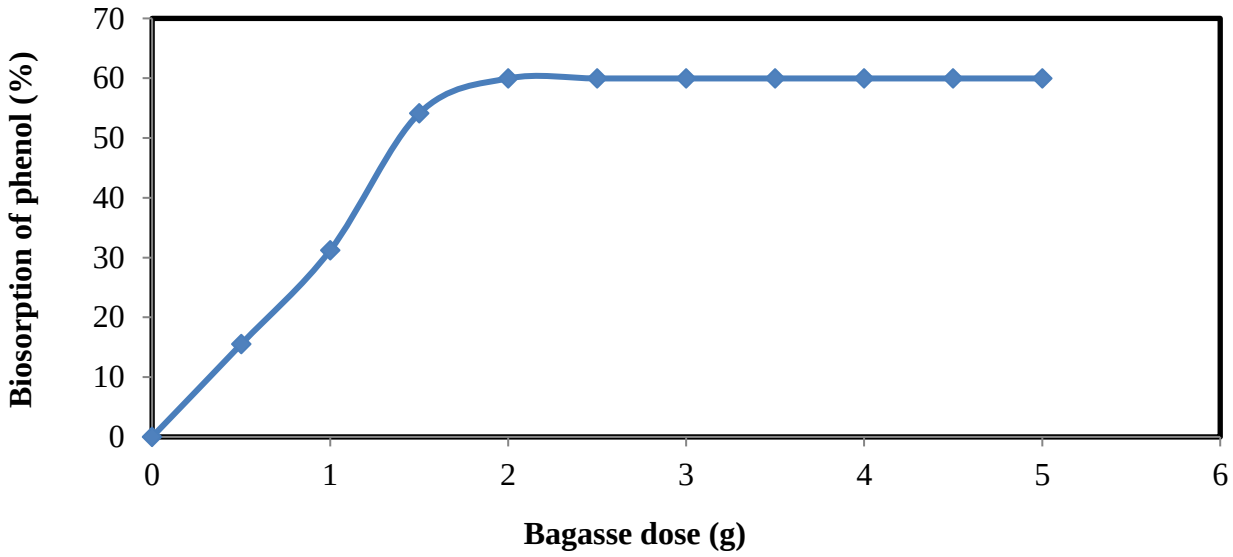

Figure 2.3.1 Graphical presentation on the effect of sorbent bagasse doses for phenol sorption from aqueous system; phenol concentration: 5.0 mg/L; bagasse particle size: 150 µm; contact time; 60 min and pH 6.5 at 30° C

2.3.2.2 Effect of Contact time on biosorption of carbolic acid onto bagasse

The effect of time on biosorption process has been estimated to reach the equilibrium level. The experiments have been implemented for the effect of contact time on the sorption of carbolic acid onto bagasse from the aqueous system, which is shown in Figure 2.3.2. From the figure, it is observed that 90 minutes is required to reach the point where the sorption and desorption rate is equal for the phenol onto bagasse. No further change has been observed in the biosorption of phenol later on 90-300 minutes[16]. In the first stage of sorption of the phenol species has been observed fast because most of the sorption occurs within the initial 60 minutes of contact period. As shown, the sorption is carried out through three stages: (1) an initial stage sorption occurs rapidly, (2) later on, sorption becomes slower, and (3) finally sorption remains constant when sorption-desorption is equal. In the first stage sorption is rapid due to vacant sorbent sites are available on the sorbent surface and rapid sorption observed by surface mass transfer, more than 80% sorption of phenol is completed in this stage in all respects. In the second stage, it is observed slower sorption as may be lessening active sites and various external parameters prevailed in the system. No significant change in the biosorption efficiency at contact times longer than 90 minutes. Such results render an efficiency of using this low-cost sorbent or so-called eco-sorbent for the treatment of aqueous solutions rich in organic pollutants in general and phenol in particular[17]. The biosorption data for the uptake of phenol versus contact time at constant (5.0 mg/L) phenol concentration with 2.0 g bagasse is carried out at pH 6.5 and the biosorption efficiency is obtained 67.40% within 90 minutes equilibrium time at 30˚C. Therefore, 90 minutes is the required equilibrium time for subsequent experiments of the bagasse-phenol aqueous system.

Table 2.3.2(a) Condition on contact time for sorption of phenol onto bagasse

1	Concentration of carbolic acid (phenol)	5.0 mg/L
2	Temperature	30^{o}C
3	pH of the solution	6.5
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of phenol solution and bagasse (minutes)	Different time
9	Particle size of bagasse	150 µm

Table 2.3.2(b) Effect of contact time on biosorption of phenol onto Bagasse

Time (min)	Absorbance	Concentration of phenol (mg/L)	Biosorptionof phenol (%)
05	0.5204	4.570	8.61
10	0.4463	4.020	19.52
15	0.4037	3.510	29.75
20	0.4814	3.070	38.52
30	0.3026	2.680	46.43
45	0.2599	2.260	54.82
60	0.2205	2.002	59.96
75	0.2103	1.831	63.39
90	0.1876	1.630	**67.40**
120	0.1876	1.630	67.40
150	0.1876	1.630	67.40
180	0.1876	1.630	67.40
210	0.1876	1.630	67.40
240	0.1876	1.630	67.40
270	0.1876	1.630	67.40
300	0.1876	1.630	67.40

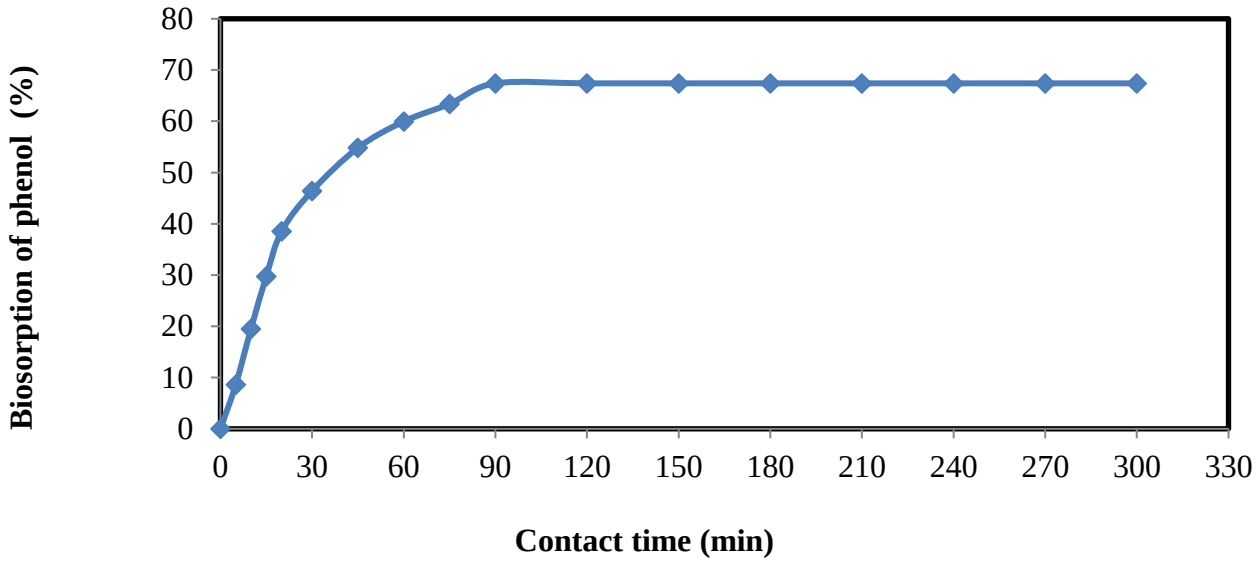

Figure2.3.2 Graphical presentation on the effect of contacttime of biosorption of phenol onto bagasse in aqueous system; phenol: 5.0 mg/L; bagasse dose: 2.0 g; p. size: 150 µm and pH: 6. 5 at 30 °C

2.3.2.3 Effect of particle size of bagasse on biosorption of phenol from aqueous system

The experiments are implemented for biosorption of carbolic acid (phenol) from the system solution using six different particle sizes (in average diameter of 50, 70, 100, 150, 200, and 250 µm). The results are shown in Figure 2.3.3. The figure depicts that with decreasing particle size from 250 to 50µm; biosorption of phenol is increased[18] from 60.0 to 76.0%. This is due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of sorption sites[19]. The same amounts of biosorbent of different particle sizes have been

introduced in different solutions of phenol of the same volume and same initial concentration[19]. We have selected the 150 µm particle size for further experiments for convenience.

Table 2.3.3(a) Condition on effect of bagasse particle sizes for sorption of phenol

1	Initial concentration of phenol	5.0 mg/L
2	Operational temperature	30 ˚C
3	pH of the solution	6.5
4	Volume of potassium ferricyanide	0.7 ml
5	Volume of 4 aminoantipyrine	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Amount of bagasse	2.0 g
8	Contact time ofphenolsolution (5.0 mg/L) and bagasse	90 minutes
9	Particle size of bagasse(µm)	Different sizes

Table 2.3.3(b) Effect of particle sizes onbiosorption of phenol from aqueous system

Particle size (µm)	Absorbance	Conc.of phenol (mg/L)	Biosorptionof phenol (%)
50	0.1309	1.18	76.41
70	0.1448	1.31	73.82
100	0.1620	1.46	70.81
150	0.1876	1.63	67.40
200	0.2049	1.79	64.13
250	0.2313	2.02	59.65

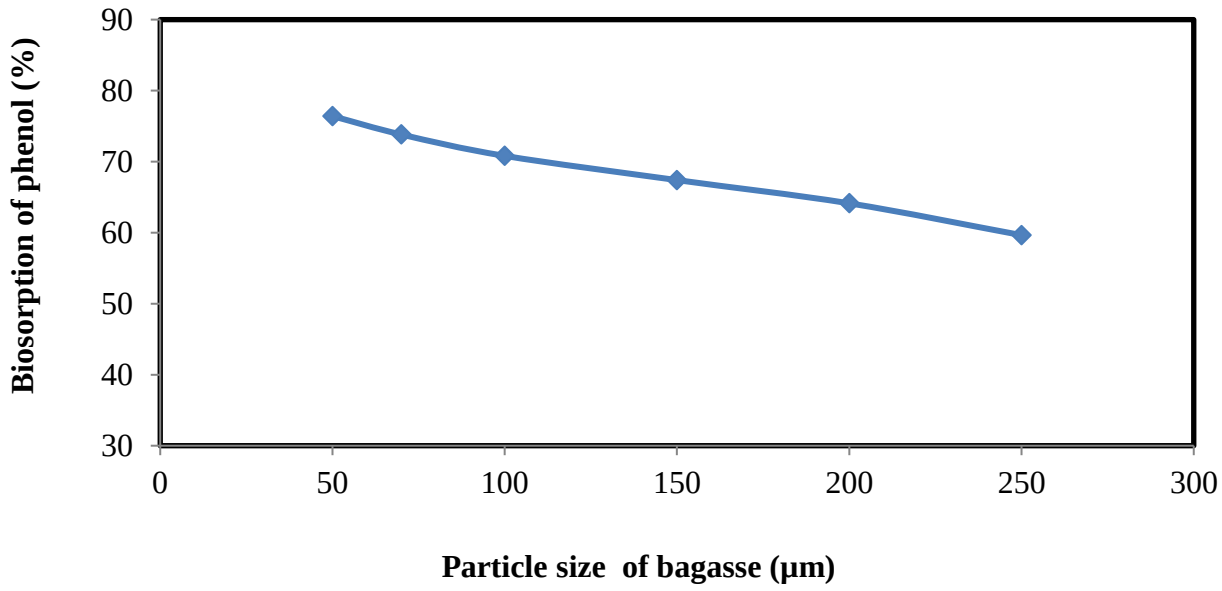

Figure 2.3.3 Graphical presentation of effect of bagasse particle size on the biosorption of phenol; phenol conc.: 5.0 mg/L; bagasse dose: 2.0 g; contact time: 90 min and pH 6.5 at 30 ºC

2.3.2.4 Effect of initial concentration of phenol on biosorption onto bagasse

Biosorption efficiency is highly dependent on the initial concentration of phenol in the sample solution. The effects of the initial phenol concentrations on the biosorption of phenol with bagasse are presented in Figure 2.3.4. As seen from the results, the biosorption efficiency of the bagasse is decreased with increase in phenol concentration. When the initial phenol concentration is increased from 0.5 to 10.0 mg/L, the biosorption percentage decreases from 75.0 to 41.0%. In case of lower initial concentration of phenol, the ratio of the initial number of moles of phenol to the available surface area of bagasse is higher and subsequently, the fractional biosorption becomes independent for initial lower concentration. It is evident that initially at the lower concentration of phenol the number of sorption sites on the bagasse surface is available and higher, the driving force for the mass transfer is greater. Therefore, the sorbate phenol reaches the biosorption site with ease[20]. With the increase of initial concentration, the number of active sites becomes less, impeding the movement of the phenol and decreases biosorption. The decrease in biosorption rate can be accounted with the increase in phenol concentration. The initial lower phenol concentration provides an important force to overcome all mass transfer resistances of the phenol between aqueous and solid phase[14]. This would result for higher biosorption of phenol at lower concentration[21]. On a relative basis, however, the biosorption percentage of phenol is decreased as the initial phenol concentration increases. The equilibrium uptake of phenol has been occurred for the bagasse, which is expected, because of the greater specific surface area and the microporous structure of the bagasse. We have selected phenol concentration 5.0 mg/L as the limit is allowable in the discharged industrial effluent to the environment[3].

Table 2.3.4(a) Condition on effect of initial concentration on the biosorption of phenol

1	Initial concentration of phenol (mg/L)	Different concentration
2	Operational temperature	30 ˚C
3	pH of the solution	6.5
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of phenol solution and bagasse	90 minutes
9	Particle size of bagasse	150 µm

Table 2.3.4(b) Effect of initial concentration of phenol on biosorption onto the bagasse

Initial conc. (mg/L)	Absorbance	Conc. of phenol (mg/L)	Biosorption of phenol (%)
0.5	0.0155	0.13	75.11
2	0.0649	0.52	73.89
3	0.0989	0.84	72.18
4	0.1372	1.19	70.23
5	0.1876	1.63	67.40
6	0.2394	2.19	63.53
8	0.3679	4.25	46.88
10	0.6012	5.87	41.28

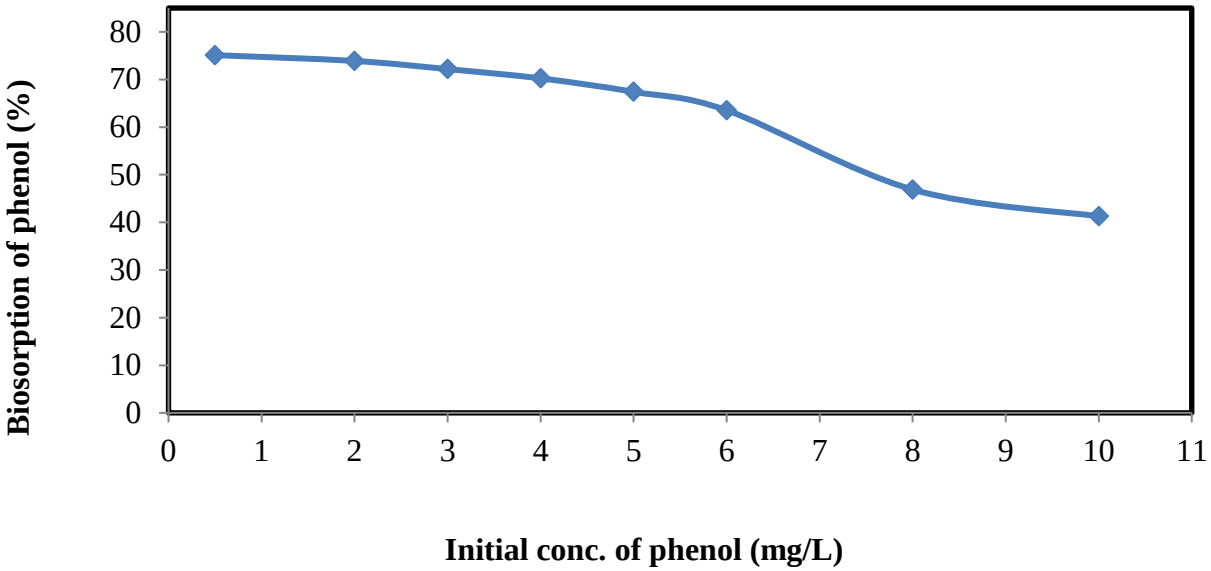

Figure 2.3.4 Graphical presentation on the effect of initial concentrationof phenol on biosorption onto bagasse; bagasse dose: 2.0 g; particle size: 150 µm; contact time: 90 min and pH: 6.5 at 30 ˚C

2.3.2.5 Effect of pH on biosorption of phenol onto bagasse from aqueous system

The biosorption of phenol from water is dependent on the pH of the aqueous system. pH affects the surface charge of the bagasse, degree of ionization, and speciation of the phenol species. The sorption of phenol onto bagasse has been studied at various pH values from 3 to 12. The biosorption percentage increases with an increase in the pH upto 6.5, then observe a dramatic decrease in phenol sorption with increase in the pH value upto 12[8,22]. The increase in biosorption has been occurred for reaching solution pH to neutral position and dramatic decreasing has been attributed depending on phenol ionization (Loss of a hydrogen cation, H^+ from the hydroxyl group of phenol), forms a corresponding negative phenolate ion or phenoxide ion, and the corresponding salts are called phenolates or phenoxide, although the term aryloxides are preferred according to the IUPAC (Gold Book.) on the pH value. Accordingly, phenol which is a weak acid has to be sorbed to a lesser extent due to the repulsive

force at higher pH value between the negative groups on the bagasse surface and phenolate ion or phenoxide ion[23]. Also, in the higher pH range phenol forms salts, which readily ionize negative charge on the phenolic group. At the same time, the presence of OH^- ions on the biosorbent prevents the uptake of phenolic ions[23]. P^H also affects the surface properties of the sorbent. Surface charge of the cells used as sorbent. At very low pH values the surface of the sorbent would also be surrounded by the hydronium ions, which enhance the phenol interaction with the binding site of the sorbent by greater attractive forces, hence phenol uptake on polar sorbent is reduced[23]. Furthermore, at very low pH, the -COO- group existing in bagasse is protonated to -COOH group. Hydrogen bonds are formed with -COOH groups and resulting in a decrease of phenol uptake. However, the study indicates that the maximum biosorption of phenol is 67.40% at pH 6.5. Both the sorbent and the sorbate have functional groups that are subjected to protonation/deprotonation depending on the solution pH. Therefore, the negative effect of increasing pH on phenol sorption is likely due to the charge properties of both sorbate and sorbent. Since the phenol is a weak acid, it is in its neutral form at pH ≤ 6.5 and the content of anionic species is negligible is shown in Figure 2.3.5. Thus, the biosorption in the neutral system has occurred phenol-bagasse interactions other than electrostatic attraction. On the other hand, electrostatic repulsion prevails when the relative content of the anionic nature of phenol is high and negative charges of the bagasse surfaces build up. As the pH is increased to the value above 6.5, the anionic form of phenol becomes predominant for its neutral counterpart. The concomitant build-up of net negative charges on the surfaces of the sorbent is led to an enhanced electrostatic repulsion between the phenol and bagasse, resulting in a dramatic decrease in phenol sorption at pH>6.5. In this study it is found that maximum sorption is 67.40% at pH 6.5. Thus, pH 6.5 is chosen as the optimum, and all the subsequent experiments are carried out at this pH.

Table 2.3.5(a) Condition on effect of pH on the biosorption of phenol onto bagasse

1	Initial concentration of phenol	5.0 mg/L
2	Operational temperature	30 ^oC
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of phenol solution and bagasse	90 minutes
9	pH value ofthe system solution	Different value

Table2.3.5 (b) Effect of pH on the biosorption of phenol onto bagasse

pH	Absorbance	Concentration (mg/L)	Biosorption of phenol (%)
3	0.2831	2.50	50.00
4	0.2662	2.31	53.80
5	0.2357	2.05	59.00
6	0.2035	1.77	64.50
6.5	0.1876	1.63	67.40
7	0.2068	1.79	64.11
8	0.2403	2.09	58.20
9	0.2782	2.44	51.20
10	0.3109	2.78	44.30
11	0.3631	3.25	35.00
12	0.4013	3.74	25.20

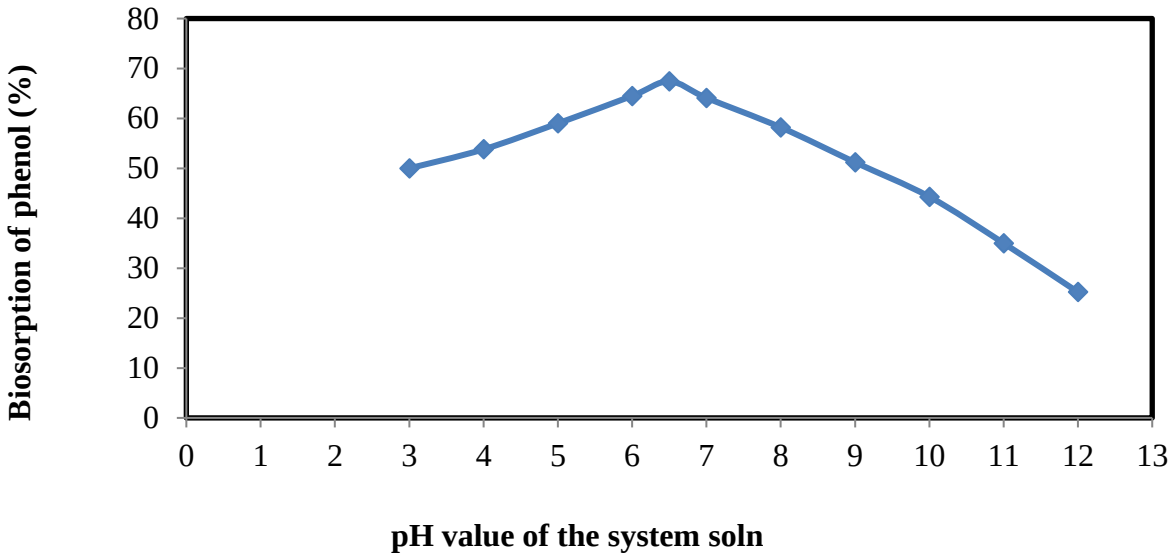

Figure 2.3.5 Graphical presentation on effect of pH of the system sol^{n} for the sorption of phenol onto bagasse; phenol conc.: 5.0 mg/L; bagasse dose: 2.0 g; p. size: 150 µm and cont. time: 90 min at 30°C

2.3.2.6 Effect of temperature on biosorption of phenol onto bagasse from aqueous system

Temperature is an important parameter for any separation process. Biosorption of phenol onto bagasse has been studied at five different temperatures; 30 (room temperature), 35, 40, 45, and 50 ˚C. The plot of biosorption capacity as a function of temperature is shown in Figure 2.3.6. The figure indicates that biosorption of phenol onto bagasse is enhanced, when temperature goes from 30 to 50˚C, suggesting that the process is endothermic. Besides this, temperature has not been raised beyond 50˚C for formation of color is observed in the test solution. Hence a higher temperature is more favorable for the biosorption of phenol. The increase in biosorption with an increase in temperature is partly due to the intraparticle diffusion rate of sorbate ions into the pores has to be intensified as temperature increases, as diffusion is the endothermic

process. So, the sorption increases with an increase in temperature[17]. Therefore, the biosorption capacity would largely depend on the interaction between functional groups on the bagasse surfaces, and the sorbate and sorption are increased with temperature rising. This might be due to higher temperature intensify the pores on the sorbent surface and reduce the thickness of the outer surface of the sorbent and increase the kinetic energy of phenol molecules. As a result, phenol molecules are easily sorbed on the biosorbent surface[24,25]. Therefore, the room temperature is preferred for convenience.

Table 2.3.6(a) Condition on effect of temperature for biosorption of phenol

1	Initial concentration of phenol	5.0 mg/L
2	pH of solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of phenol and bagasse	90 minutes
9	Temperature of the system (˚C)	Different temperature

Table 2.3.6(b) Effect of temperature on biosorption of phenol onto Bagasse

Temperature (°C)	Absorbance	Concentration (mg/L)	Biosorptionof phenol (%)
30	0.1876	1.63	67.4
35	0.1816	1.58	68.45
40	0.1740	1.54	69.29
45	0.1705	1.48	70.36
50	0.1605	1.44	71.28

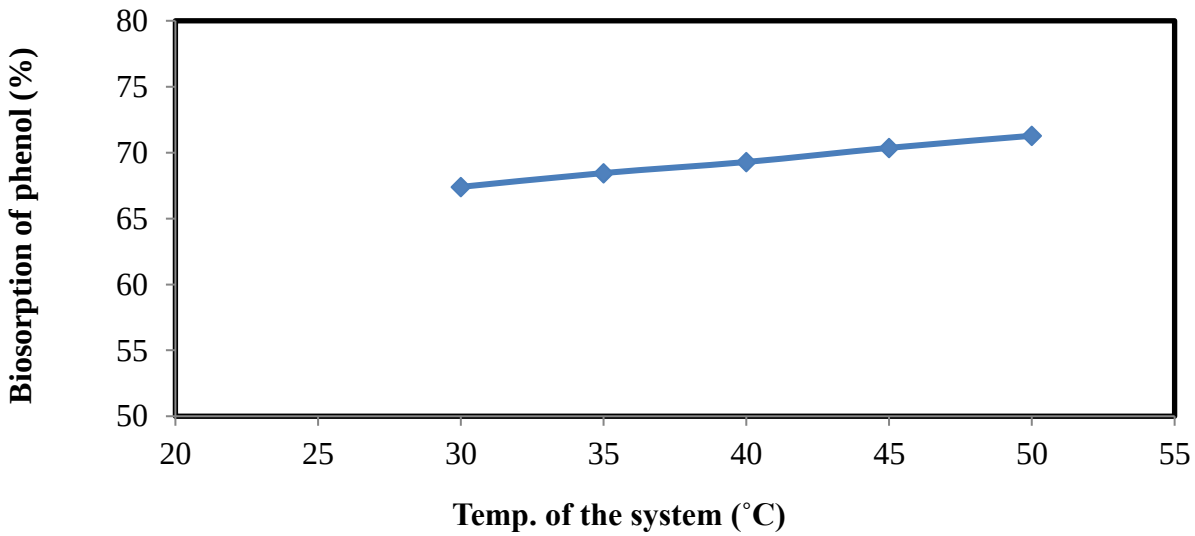

Figure 2.3.6 Graphical presentation on effect of temperature on phenol sorption onto bagasse; phenol conc.: 5.0 mg/L; bagasse dose: 2.0 g; particle size: 150 µm and contact time: 90 min at pH 6.5

2.3.3: FTIR spectroscopy studies

The infrared spectra were used to determine changes in the structure of cellulose, hemicellulose, and lignin during the sequence of treatments subjected to bagasse (native). Table 2.3.7 shows the FTIR spectrum of natural sugarcane bagasse. The band at 1162 cm^{-1} is characteristic of C-O-C asymmetrical stretching, 1335cm^{-1} is characteristic of C-O aromatic ring, 1423 cm^{-1} is characteristic of CH_2 symmetrical stretching, 1732 cm^{-1} is characteristic of C=O unconjugated stretch, 2885 cm^{-1} is characteristic of C-H symmetrical stretching, and 3300 cm^{-1} is characteristic of O-H linked shearing.

Table 2.3.7 Structural characterization of the bagasse

Wave number (cm^{-1})	Vibration
3300	O-H linked shearing
2885	C-H symmetrical stretching
1732	C=O unconjugated stretch
1423	CH_2 symmetrical stretching
1335	C-O aromatic ring
1162	C-O-C asymmetrical stretching

2.3.4.1 Langmuir isotherm model for biosorption of phenol onto bagasse

The Langmuir isotherm assumes that the surface of any sorbent material contains several active sites where the sorbate attaches itself. This attachment can either be physical or chemical. When the attachment is via Van der Waals interactions it is known as physical sorption and when via covalent bond it is known as chemisorptions. Langmuir model indicates the physical sorption that there is not much interaction between the sorbate molecules and once a saturation value has been reached no further sorption would take place[26].

The linear form of the Langmuir isotherm model is represented by the following equation[8,23].

$1/q_e = 1/q^o + 1/(bq^oC_e)$

Where q°(mg/g) and b (L/mg) are the Langmuir constants related to the maximum biosorption capacity and the energy of biosorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot of the experimental data of $1/q_e$ versus $1/C_e$ showed in figure 2.3.7(a), and Table 2.3.8(a) and Table 2.3.8(d)

The essential feature of the Langmuir isotherm can be employing by means of dimensionless separation factor (R_L) which is calculated using the following equation;

$R_L = 1/ (1+bC_o)$

Where b denotes the Langmuir constant and C_o is the initial concentration[27] of phenol in an aqueous system. At all temperatures, R_L values have been found less than unity showed in Table 2.3.8(d) indicating that the sorption process is favorable.

Table 2.3.8(a) Experimental data for study on Langmuir isotherm model

Conc. of phenol (mg/L)	Biosorpt^n of phenol (%)			30°C		40°C		50°C	
	30^0C	40^0C	50^0C	$1/C_e$	$1/q_e$	$1/C_e$	$1/q_e$	$1/C_e$	$1/q_e$
0.5	75.11	77.81	80.35	8.0354	53.2552	9.0131	51.4073	10.1781	49.7822
1	74.62	77.22	79.65	3.9401	26.8025	4.3899	25.9000	4.9140	25.1099
2	73.89	76.41	78.82	1.9150	13.5337	2.1195	13.0873	2.3607	12.6871
3	72.18	75.33	77.91	1.1982	9.2362	1.3512	8.8499	1.5090	8.5569
4	70.23	74.18	76.63	0.8398	7.1195	0.9683	6.7404	1.0698	6.5248
5	67.4	69.29	71.28	0.6135	5.9347	0.6513	5.7728	0.6964	5.6117
6	63.53	65.27	67.15	0.4570	5.2469	0.4799	5.1070	0.5074	4.9640
7	54.82	56.45	58.15	0.3162	5.2119	0.3280	5.0614	0.3414	4.9134
8	46.88	48.22	49.72	0.2353	5.3328	0.2414	5.1846	0.2486	5.0282
9	42.33	43.81	44.94	0.1927	5.2500	0.1977	5.0724	0.2018	4.9449
10	41.28	42.12	43.23	0.1703	4.8450	0.1728	4.7483	0.1765	4.6264

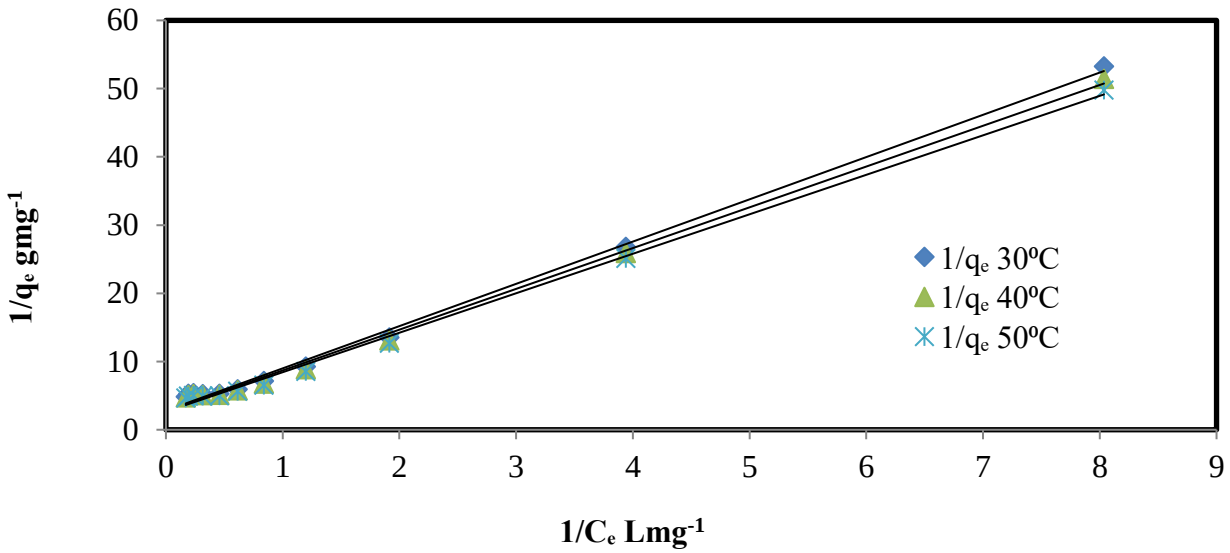

Figure 2.3.7(a) Graphical presentation on Langmuir curve for the biosorption of phenol onto bagasse; phenol conc.: 0.5-10.0 mg/L; bagasse dose: 2.0 g; p. size: 150 µm; cont. time: 90 min and pH 6.5 at 30-50˚C

2.3.4.2 Freundlich isotherm model for biosorptionof phenol onto bagasse

Freundlich isotherm is employed based on sorption on to a heterogeneous surface of varied affinities[28].

The linear form of the Freundlich isotherm model is given by the following relation[8,23].

$\ln q_e = \ln k_f + (1/n) \ln C_e$

Where q_e (mg/g) is the amount of sorbed phenol at equilibrium (mg/g), C_e (mg/L) is the equilibrium concentration of the phenol (mg/L) and k_F and 1/n is the Freundlich constants related to sorption capacity and sorption intensity of the sorbent respectively. The values of K_f and 1/n can be obtained from the intercept and slope of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$[8,28] respectively, has been shown in figure 2.3.7(b) and Table 2.3.8(b). At all temperatures,1/n values have been found less than unity indicating thereby the biosorption process favorable are shown in Table 2.3.8(d).

Table 2.3.8(b) Experimental data for study on Freundlich isotherm model

Concentration of phenol mg/L)	Biosorption of phenol (%)			30°C		40°C		50°C	
	30°C	40°	50°C	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$
0.5	75.11	77.81	80.35	-2.0839	-3.9751	-2.1988	-3.9398	-2.3202	-3.9077
1	74.62	77.22	79.65	-1.3712	-3.2885	-1.4793	-3.2542	-1.5921	-3.2233
2	73.89	76.41	78.82	-0.6543	-2.6036	-0.7512	-2.5716	-0.8590	-2.5406
3	72.18	75.33	77.91	-0.2212	-2.2080	-0.3010	-2.1804	-0.4114	-2.1467
4	70.23	74.18	76.63	0.1051	-1.9348	0.0323	-1.9081	-0.0674	-1.8756
5	67.4	69.29	71.28	0.4886	-1.7808	0.4289	-1.7532	0.3619	-1.7249
6	63.53	65.27	67.15	0.7831	-1.6576	0.7342	-1.6306	0.6785	-1.6022
7	54.82	56.45	58.15	1.1514	-1.6509	1.1147	-1.6216	1.0748	-1.5920
8	46.88	48.22	49.72	1.4468	-1.6739	1.4213	-1.6457	1.3919	-1.6151
9	42.33	43.81	44.94	1.6468	-1.6582	1.6208	-1.6238	1.6005	-1.5984
10	41.28	42.12	43.23	1.7702	-1.5780	1.7558	-1.5578	1.7364	-1.5318

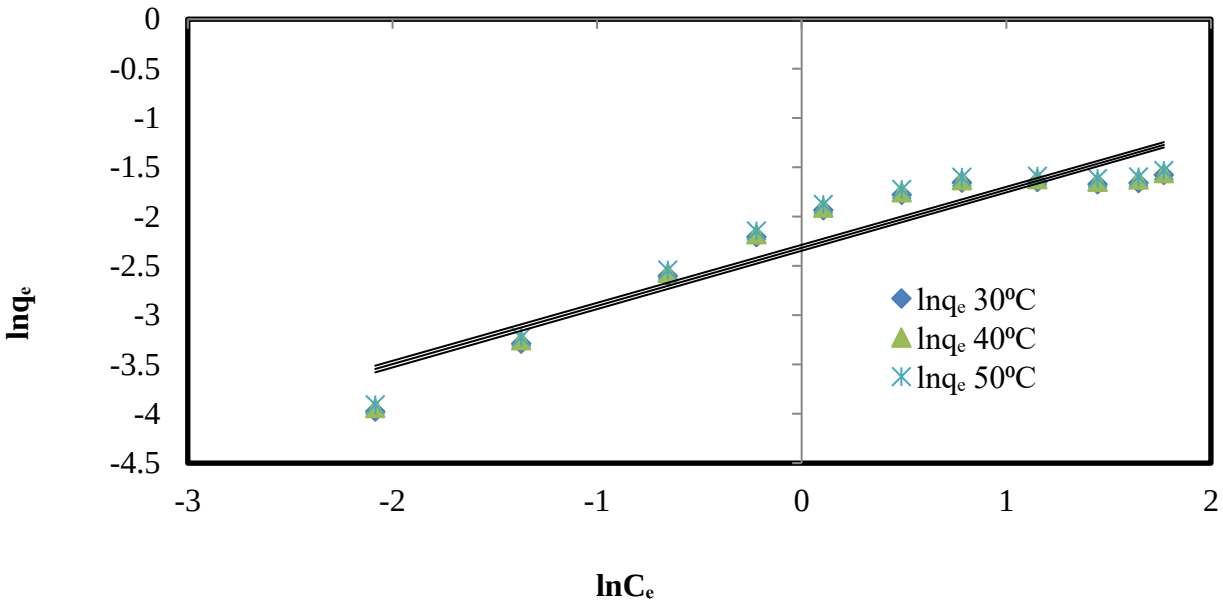

Figure2.3.7(b) Graphical presentation on Freunlich curve for the biosorpt[n] of phenol onto bagasse; phenol conc.:0.5-10.0 mg/L; bagasse dose: 2.0 g; p. size:150 µm; cont. time:90 min and pH 6.5 at 30-50˚C

Table 2.3.8(c): Parameters of Freundlich and Langmuir isotherm models

Sorbents	Freundlich			Langmuir			Reference
	k_F	*1/n*	R^2	q°	b	R^2	
Rice Husk	0.00092	0.195	0.96	0.0022	30.720	0.87	Mahvi et al, 2004
Barley straw	0.032	0.389	0.99	0.067	1.017	0.98	Maleki et al. 2010
Bagasse	0.096	0.59	0.88	0.357	0.452	0.99	Present study

Table 2.3.8(d) Isotherm constants for biosorption of phenol onto bagasse

Name of compound	**Phenol**		
Temperature	30 °C	40°C	50°C
Constants Langmuir isotherm equation: $1/q_e = 1/q° + 1/(bq°c_e)$			
q°	0.3571	0.3687	0.3785
b	0.452	0.454	0.457
$R_L=1/(1+k_LC_o)$	0.1811	0.1806	0.1796
R^2	0.996	0.996	0.996
Freundlich isotherm equation $lnq_e = lnk+(1/n)lnC_e$			
1/n	0.591	0.589	0.588
N	1.692	1.698	1.701
K_f	0.0957	0.0986	0.1016
R^2	0.887	0.888	0.887

2.3.4.3 Isotherm models on biosorption of phenol onto bagasse

The data of experiments have been applied to the Langmuir and Freundlich isotherm models and the obtained parameters are given in Table 2.3.8(d) and Figure 2.3.7(a-b). Inspection of Table and figuresreveal that (i) the regression coefficients (R^2) 0.99 obtained from the Langmuir model is closer to 1 than that R^2 (0.88) of the Freundlich model, in all cases suggesting that the Langmuir isotherm fits better with the biosorption of phenol onto bagasse; (ii) the R_L values obtained are in all cases lie between 0 and 1 confirming that the biosorption is a favorable process. Hence, it can be concluded that the monolayer Langmuir biosorption isotherm is more suitable to explain the biosorption of phenol onto bagasse; (iii) the values of 1/n are less than 1 indicating that the biosorption of phenol on the surface of bagasse is a favorable process follows physical biosorption technique. It is observed that the equilibrium data are very well represented by the Langmuir isotherm equation when compared to the

Freundlich isotherm. The biosorption equilibrium data fitted the Langmuir equations with correlation coefficients (R^2), which are a measure of goodness-of-fit. The higher value of b=0.452-0.457>k_F=0.0957- 0.102; the Langmuir constant showed easy uptake of phenol from aqueous solution[13-15]. The *n* value, which reflects the intensity of the biosorption, presents the opposite trend, but as seen from Table 2.3.8(d) for the sorbents and pollutants, *n* values were found high enough for separation. The higher fractional value of *1/n* ($0 < 1/n < 1$) signifies that the surface of the sorbent is heterogeneous in nature[28]. However, the Langmuir isotherm model fits the best for the estimation of maximum sorption capacity corresponding to complete monolayer coverage on the agro wastes biosorbent bagasse[26]. The maximum sorption capacity q° is 0.357 mg/g for phenol–bagasse system in table 2.3.8(c), which appears to be significantly higher in comparison with barley straw[4] 0.067 mg/g and with rice husk[29] 0.0022 mg/g. Hence, the biosorption process of phenol using sugarcane bagasse as biosorbent followed the Langmuir isotherm. Moreover, this also suggested that physicosorption might be the rate-limiting step that controlled the overall biosorption process which indicated goodness-of-fit for the Langmuir model.

2.3.5 Kinetics studies on biosorption of phenol onto bagasse from the aqueous system

Biosorption is often studied as a potential tool for the purification of water and industrial effluents. In general, works in this field report of experimental results about the sorption capacity of solutes at equilibrium, and about the kinetics of biosorption. The data are then described using various models or empirical formulas. Two types of kinetic models are generally used, namely the pseudo-first order and pseudo-second order rate laws. Pseudo-first order kinetics was first proposed at the end of the 19th century by Lagergren[30]. Pseudo-second order kinetics was introduced in the middle of the 80's[31]. However, it was not very popular until 1999 when Ho and McKay[32] analyzed several experimental results were taken from the literature, and arrived at the conclusion that for all of the systems studied, in the vast majority of studies in which comparison have been done, superiority between 1st order and 2nd order rate constants has been found[33]. It is explained that there are two main issues in the statistical treatment generally used in the literature and that the method systematically tends to favor either the pseudo-first order or pseudo-second order rate law. The remainder of this work is divided into three main sections. In the next section, the basic formulas for the statistical analysis of experimental data and model comparison are presented. The third section is dedicated to the presentation of results and to their discussion. The two issues met in analyses used in the literature are exposed and they are illustrated in the case of data obeying first-order kinetics. Then a re-examination of the experimental data treated in the original paper by Ho and McKay[32] is carried out, a sample of data reported in the current literature is analyzed, and

a few diffusion-controlled processes are examined. Finally, a conclusive summary has been directed that the main results of this work present some prospects. The kinetic studies of biosorption kinetic describe the phenol uptake rate which controls the residence time of sorbate uptake at the solid/solution interface[26]. The Kinetic studies are set up in the laboratory in batch method by adding a known amount of phenol to a required number of flasks which contain 100 ml of sample solution. Initial variable phenol concentrations are from 2.0 to 5.0 mg/L at constant temperature 30˚C. The sorbent is 2.0 g and the pH value of the system solution is 6.5. The bottles are subsequently capped and shaken in a rotary shaker up to equilibrium time 90 minutes. This has been also done at variable temperatures 30-50˚C and constant phenol concentration (5.0 mg/L) and is also shaken for upto equilibrium time 90 minutes. The data from the experiments are employed in both the pseudo-first-order and pseudo-second-order kinetic models.

Table 2.3.9(a) Conditions of biosorption for experimental data to apply on kinetic models

1	Initial concentration of phenol	2.0-5.0 mg/L
2	pH of system solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanidesolution	0.7 ml
5	Volume of 4-AAPsolution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Biosorbent bagasse dose	2.0 g
8	Contact time of phenol solution and bagasse	Upto 90 minutes
9	Temperature effect	30-50 ˚C

2.3.5.1 Pseudo first order kinetic (FOK) model for biosorption of phenol onto bagasse

The equation for pseudo-FOK was introduced initially by Lagergren[30]. In the literature[11,14] it is generally used in the form proposed by Ho and McKay[32]. The Pseudo-first-order kinetic model is widely used to predict the sorption kinetic and is defined as:

$\ln (q_e - q_t) = \ln q_e - k_{FO}t$

Where, q_e and q_t (mg/g) are the sorption capacities at equilibrium and at any given time, t (min) respectively. K (min^{-1}) is the biosorption rate constant. Graphs of $\ln(q_e-q_t)$ versus t is plotted and shown in Figure 2.3.8(a) at variable phenol concentrations (2.0-5.0 mg/L) and constant temperature(30˚C) and in Figure 2.3.8(b) at variable temperature (30-50˚C) and constant concentration of phenol, (5.0 mg/L) in aqueous system separately. The data from experiments are cited in Table 2.3.9(b-c).

Table 2.3.9(b) Experimental data of biosorption of phenol onto bagasse from (2.0- 5.0 mg/L) aqueous solution to apply on the pseudo FOK model at 30˚C

Time	Biosorption (%)				Time	$\ln(q_e-q_t)$			
	2ppm	3ppm	4ppm	5ppm	t	2ppm	3ppm	4ppm	5ppm
0	0	0	0	0	0	-2.6106	-2.2231	-1.9628	-1.7808
5	9.55	9.38	9.11	8.61	5	-2.7498	-2.3623	-2.1018	-1.9175
10	20.69	20.28	20.05	19.52	10	-2.9412	-2.5530	-2.2990	-2.1228
15	30.83	30.36	29.98	29.75	15	-3.1545	-2.7689	-2.5195	-2.3631
20	41.15	40.41	39.53	38.52	20	-3.4315	-3.0438	-2.7903	-2.6283
30	50.31	49.41	48.42	46.43	30	-3.7645	-3.3768	-3.1322	-2.9484
45	59.51	58.46	56.91	54.82	45	-4.2701	-3.8834	-3.6253	-3.4594
60	64.81	63.69	62.41	59.96	60	-4.7467	-4.3634	-4.1579	-3.9846
75	69.01	67.82	66.16	63.39	75	-5.4081	-5.0298	-4.8110	-4.6027
90	73.49	72.18	70.23	67.40	90				

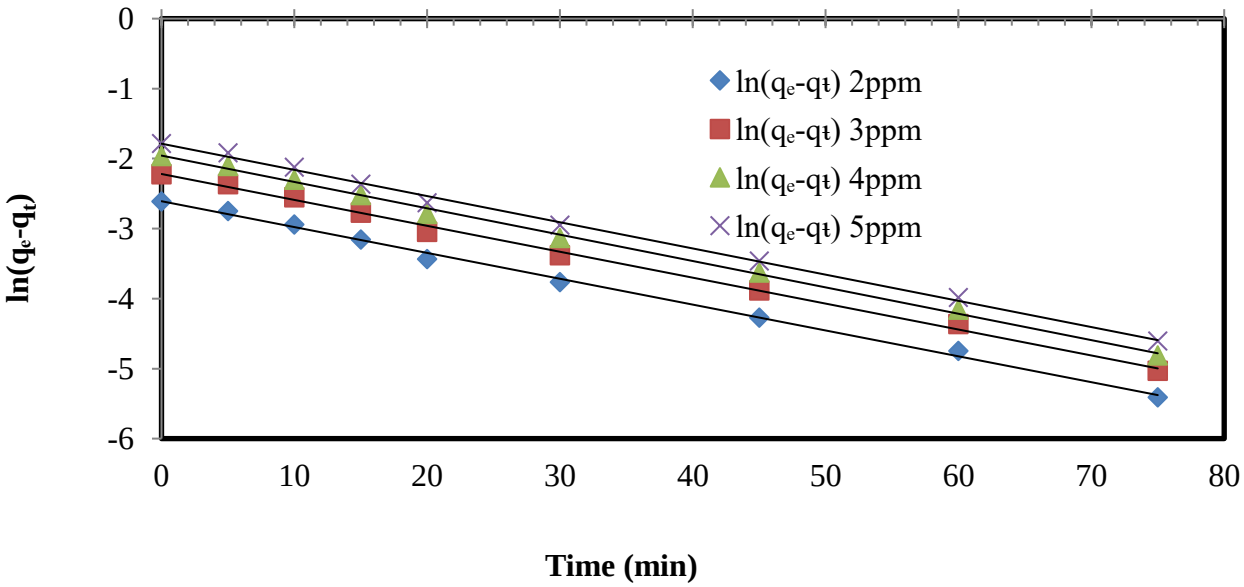

Figure 2.3.8(a) Graphical presentation on Pseudo FOK model for biosorption of phenol onto bagasse from (2.0-5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; particle size: 150 µm; cont. time: 90 min and pH 6.5 at 30°C.

Table 2.3.9(c) Experimental data of biosorption of phenol onto bagasse from (5.0 mg/L) aqueous sol^{n}to apply on the pseudo-FOK model at 30-50 ^{o}C

Time	Biosorptionof phenol (%)			Sorption capacity of phenol q_t			Time	$\ln(q_e-q_t)$		
	30^0C	40^0C	50^0C	30^0C	40^0C	50^0C		30^0C	40^0C	50^0C
0	0	0	0	0	0	0	0	-1.7808	-1.7360	-1.6832
5	8.61	8.98	9.43	0.0215	0.0225	0.0236	5	-1.9175	-1.8723	-1.8189
10	19.52	20.35	21.18	0.0488	0.0509	0.0530	10	-2.1228	-2.0767	-2.0187
15	29.75	31.08	32.11	0.0744	0.0777	0.0803	15	-2.3631	-2.3174	-2.2490
20	38.52	40.27	42.41	0.0963	0.1007	0.1060	20	-2.6283	-2.5830	-2.5289
30	46.43	48.52	51.16	0.1161	0.1213	0.1279	30	-2.9484	-2.9018	-2.8495
45	54.82	57.27	60.24	0.1371	0.1432	0.1506	45	-3.4594	-3.4097	-3.3474
60	59.96	62.69	66.05	0.1499	0.1567	0.1651	60	-3.9846	-3.9373	-3.8800
75	63.39	66.25	69.84	0.1585	0.1656	0.1746	75	-4.6027	-4.5469	-4.4941
90	67.4	70.49	74.31	0.1685	0.1762	0.1858	90			

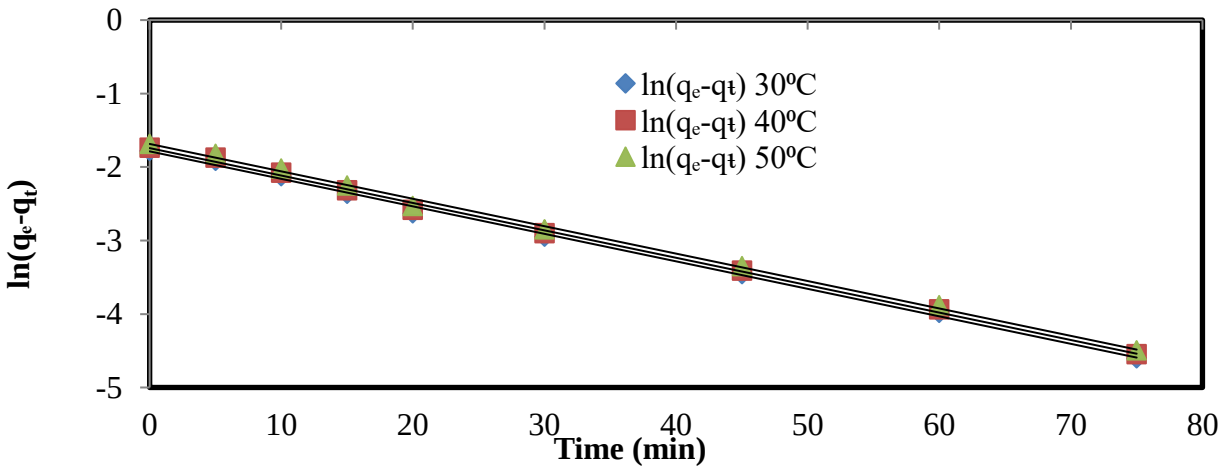

Figure 2.3.8(b) Graphical presentation on Pseudo FOK model for biosorption of phenol onto bagasse from (5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; p. size: 150 µm; cont. time: 90 min and pH: 6.5 at 30- 50°C

2.3.5.2 Pseudo second-order kinetic (SOK) model for biosorption of phenol

Ho[33] proposed the second-order model employed for the biosorption of phenol onto bagasse based on the sorption capacity of the sorbents to differentiating the kinetics of a second-order rate expression. The formula for pseudo-second order kinetics is literaturally employed in the form proposed by Ho. The linearized form of the pseudo-second-order model is defined as follows:

$t/q_t = 1/(kq_e^2) + t/q_e$

Where k is the rate constant of the pseudo-second-order model, q_e is the amount of phenol sorbed onto the sorbent (mg/g) at equilibrium, and q_t is the amount of phenol sorbed onto the

sorbent (mg/g) at any time, t can be calculated from the slope and intercept of the plot of t/q_t against t. The graphical presentations are shown as in Figure2.3.8(c) at initial phenol concentration, (2.0-5.0 mg/L) and constant temperature, (30˚C) and in Figure 2.3.8(d) at variable temperature, (30-50˚C) and constant concentration, (5.0 mg/L) separately. The data from experiments are cited in Table 2.3.9 (d-e)

Table 2.3.9(d)Experimental data of biosorption of phenol onto bagasse from (2.0-5.0 mg/L) aqueous solution applied on the pseudo SOK model at 30°C

Time	Biosorption of phenol (%)				Time	t/qt			
	2ppm	3ppm	4ppm	5ppm		2ppm	3ppm	4ppm	5ppm
5	9.55	9.38	9.11	8.61	5	523.5602	355.366	274.4237	232.288
10	20.69	20.28	20.05	19.52	10	483.3253	328.7311	249.3766	204.918
15	30.83	30.36	29.98	29.75	15	486.5391	329.3808	250.1668	201.6807
20	41.15	40.41	39.53	38.52	20	486.0267	329.9513	252.9724	207.6843
30	50.31	49.41	48.42	46.43	30	596.3029	404.7764	309.7893	258.4536
45	59.51	58.46	56.91	54.82	45	756.1754	513.1714	395.3611	328.3473
60	64.81	63.69	62.41	59.96	60	925.7831	628.0421	480.6922	400.2668
75	69.01	67.82	66.16	63.39	75	1086.799	737.2457	566.8077	473.2608
90	73.49	72.18	70.23	67.4	90	1224.656	831.2552	640.7518	534.1246

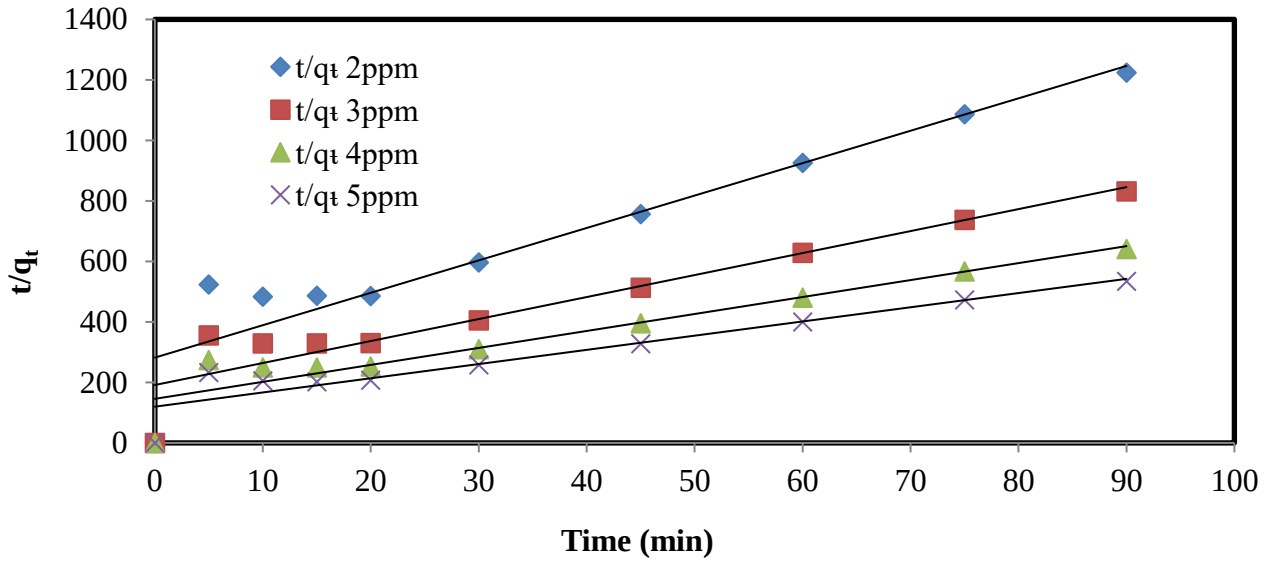

Figure 2.3.8(c) Graphical presentation on Pseudo SOK model for biosorption of phenol onto bagasse from (2.0- 5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; p. size: 150 µm; cont. time: 90 min and pH: 6.5 at 30°C

Table 2.3.9(e) Experimental data of sorption phenol onto bagasse from (5.0 mg/L) aqueous system toapply on the pseudo SOK model at 30-50 ºC

Time	Biosorptionof Phenol (%)			q_t			Time	t/q_t		
	30^0C	40^0C	50^0C	30^0C	40^0C	50^0C		30^0C	40^0C	50^0C
5	8.61	8.98	9.43	0.0215	0.0225	0.0236	5	232.288	222.7171	212.0891
10	19.52	20.35	21.18	0.0488	0.0509	0.0530	10	204.918	196.5602	188.8574
15	29.75	31.08	32.11	0.0744	0.0777	0.0803	15	201.6807	193.0502	186.8577
20	38.52	40.27	42.41	0.0963	0.1007	0.1060	20	207.6843	198.6591	188.6348
30	46.43	48.52	51.16	0.1161	0.1213	0.1279	30	258.4536	247.3207	234.5582
45	54.82	57.27	60.24	0.1371	0.1432	0.1506	45	328.3473	314.3007	298.8048
60	59.96	62.69	66.05	0.1499	0.1567	0.1651	60	400.2668	382.8362	363.3611
75	63.39	66.25	69.84	0.1585	0.1656	0.1746	75	473.2608	452.8302	429.5533
90	67.4	70.49	74.31	0.1685	0.1762	0.1858	90	534.1246	510.7107	484.457

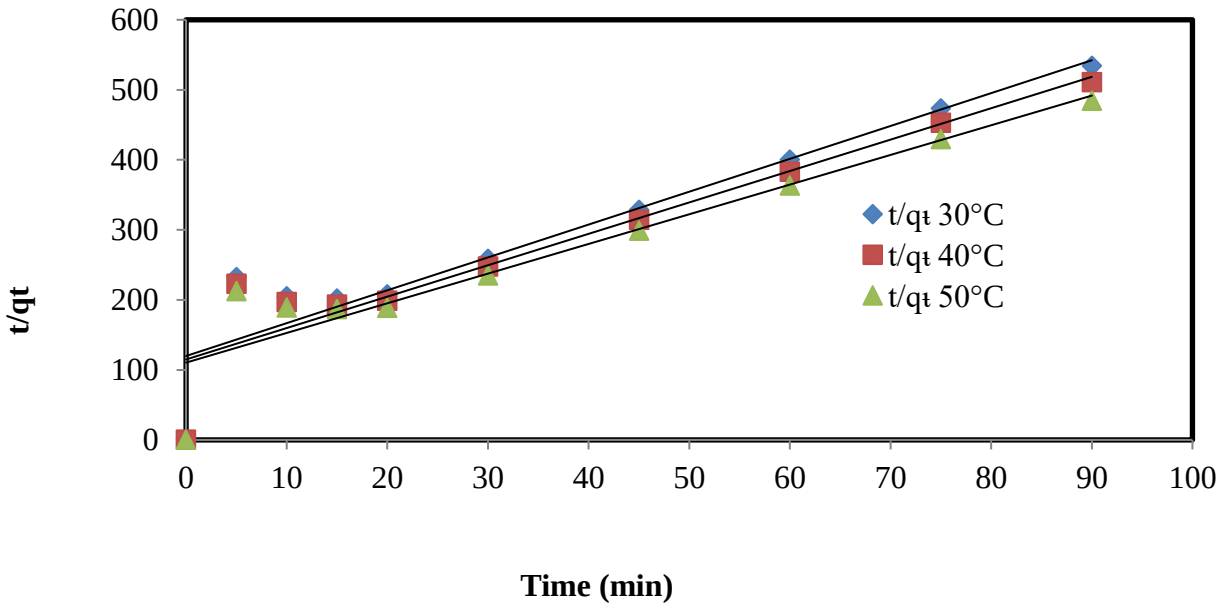

Figure2.3.8 (d) Graphical presentation on Pseudo SOK model for biosorption of phenolonto bagasse from (5.0 mg/L) aqueous systems at 30-50˚C; bagasse dose: 2.0 g; p. size: 150 µm; cont. time: 90 min at pH 6.5

By comparing the two groups of graphical charts in Figure 2.3.5(a-b) and Figure 2.3.5(c-d) are observed that the correlation coefficients (R^2) for pseudo-first order model are in the range of 0.99 in all cases which were higher than the R^2 values of the pseudo-second order 0.885 to 0.889 which indicated a better fit for the pseudo-first-order kinetic model. Hence, the sorption process of phenol using sugarcane bagasse followed the pseudo-first-order kinetic model. The kinetic isotherm rate constants are shown in Table 2.3.5(f) and graphical charts are in Figure 2.3.5(a-b) and Figure 2.3.5(c-d). It is observed that the experimental data are very well

represented by the Pseudo First order kinetic studies when compared to the Pseudo second order kinetics.

Table 2.3.9 (f) Kinetic constants for the biosorption of phenol onto bagasse

Phenol							
	Pseudo first order kinetic equation $\ln(q_e-q_t) = \ln q_e - kt$						
Constants	Conc. of system solution (mg/L)				Temp. of system solution		
	2	3	4	5	30˚C	40˚C	50˚C
K_{FO}	0.036	0.037	0.037	0.037	0.037	0.037	0.037
$q_{e\ FOK}$ cal.	0.0736	0.1170	0.1414	0.1676	0.1676	0.1752	0.1854
q_{eFOK} exp.	0.0735	0.1083	0.1405	0.1685	0.1685	0.1762	0.1858
R^2_{FOK}	0.997	0.997	0.997	0.997	0.997	0.997	0.997
Pseudo second order kinetic equation $t/q_t = 1/(kq_e^2) + t/q_e$							
K_{SOK}	0.4066	0.2761	0.2159	0.1838	0.1838	0.1750	0.1626
q_{eSOK} Cal.	0.0934	0.1376	0.1783	0.2131	0.2131	0.2230	0.2360
q_{eSOK} Exp.	0.0735	0.1083	0.1405	0.1685	0.1685	0.1762	0.1858
R^2_{SOK}	0.888	0.888	0.889	0.889	0.889	0.888	0.885

2.3.6 Application of the developed treatment system

The textile industries are known to be one of the largest polluting industries in Bangladesh and the effluent of these industry contain above the maximum permissible limit of the phenol. The utility of the locally available bagasse has been tested with effluent of two textile industries and one agro-chemical industry around Dhaka City, Bangladesh. Three industrial effluent samples are collected in a glass collection bottle with Teflon-lined caps directly from the outlet of a textile (Padma Poly Cotton Ltd.), industry located at 131 Tejgaon I/A, Dhaka-1208, Dhaka, Bangladesh, dyeing industry (Color Thread Company) located at Plot No-23, Shampur, Kadamtali I/A, Dhaka, Bangladesh and Agro chemical industries (EH & agro vet. ltd,) located at Dilhaj mansion plot#151/ka, Pisiculture H.S. Shyamoli Dhaka-1207 Dhaka during operation of the plant. The samples are immediately brought to the laboratory to be placed in a cool place. The phenol contents have been analyzed by the modified 4-AAP method and found to be sample 1, 2, and 3 are 10.02, 7.65, and nil mg/L, respectively. The characteristics of the effluents and treatment results are shown in Table 2.3.10(b-c). The pH of the effluents is adjusted to 6.5, and bagasse dose of 2.0 g/100 ml has been taken and the agitated time is 90 minutes. The biosorption efficiency of phenol using bagasse is satisfactory and is about 88 and

90% for samples 1 and 2, respectively. The desorption efficiencies of sorbed phenol with 100 ml of 1M NaOH are 92 and 89%, respectively. These results indicate that the biosorption can eliminate phenol successfully from practical phenol containing aqueous effluent, and the sorbed phenol can be recovered satisfactorily from the surface of bagasse which can be regenerated in the biosorption system.

Table 2.3.10(a) Conditions on application of developed system on biosorption of phenol

1	Particle size of bagasse	150 µm
2	Volume of potassium ferricyanidesolution	0.7 ml
3	Volume of 4-AAP solution	0.9 ml
4	Volume of buffer solution (pH 10)	1.0 ml
5	Bagasse dose	2.0 g
6	Contact time of phenol solution and bagasse	90 minutes
7	Temperature effect	30^{o}C
8	Concentration of phenol in the effluents from different industries	Unknown conc.
9	pH	6.5

Table 2.3.10(b) Effluent treatment

Sample No	Concentration of phenol (mg/L)
Sample 1 (Padma Poly Cotton Ltd.)	10.02
Sample 2 (Color Thread Company)	07.65
Sample 3 (EH & agro vet. ltd,)	BDL (Below Detection Limit)
Sample 1 1 (After one time treatment of sample 1)	1.2
Sample 12 (After one time treatment of sample 2)	0.76

Table 2.3.10(c) Desorption of sorbed phenol from bagasse (After biosorption).

	Sample -1	Sample -2
pH	7.3	7.9
Initial concentration of phenol (mg/L)	10.02	07.65
Final concentration of phenol (mg/L)	1.20	0.76
Biosorption (%)	88	90
Desorption (%)	92	89

2.3.7 Desorptionof phenol and regeneration of biosorbent bagasse

Desorption of the biosorbed material and regeneration of the biosorbent is also an important aspect of wastewater treatment. Attempts have been made to desorbed phenol from bagasse surface with various eluents, such as hydrochloric and nitric acid solutions and base solution sodium hydroxide. This desorption process has been performed using the batch method. 2.0 g of spent sorbent bagasse after sorption at pH 6.5 for three times have been shaken with 100 ml of 1M NaOH, 1M HCl, and 1M HNO_3 respectively for regeneration, which are shaken for 90 minutes equally. The determination of phenol 81.44, 67.98, and 52.64% are desorbed from the sorbed phenol (sorbed from the initially present 5.0 mg/L phenol solution) onto the bagasse in a single step, respectively. Although the achievement of arsenic elution using strong acidic or alkaline solutions has been reported in the literature, the present work showed that effective desorption is obtained with an alkaline solution. These phenomena are consistent with the results observed for the effect of pH. In general, the desorption efficiency of phenol tends to increase with increasing desorption time. Consequently, sodium hydroxide solution is more useful for desorption of phenol from the surface of bagasse.

Desorption efficiency of phenol is calculated using the equation,

$$\text{Percentage of desorbed phenol} = \frac{\text{Amount desorbed after Desorption}}{\text{Amount Biosorbed before Desorption}} \times 100$$

Table 2.3.11(a)Condition on the desorption of sorbed phenol from sorbent bagasse

1	Initial concentration of phenol	5.0 mg/L
2	pH of solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of phenol solution and bagasse	90 min
9	Temperature	30 ºC

Table 2.3.11(b) Biosorption of phenol onto bagasse (before desorption):

Initial conc. (mg/L)	Absorbance	Concentration (mg/L)	% biosorption	% remaining
5	0.1876	1.63	67.40	32.60

Table 2.3.11(c) Biosorbed phenol desorption from sorbent bagasse (after desorption):

Desorbing agent	Initial conc (mg/L)	Absorbance	Conc. (mg/L)	% Regenerated
1N NaOH	3.37	0.3077	2.75	81.44
1N HCl	3.37	0.2561	2.29	67.98
1N HNO_3	3.37	0.2039	1.77	52.64

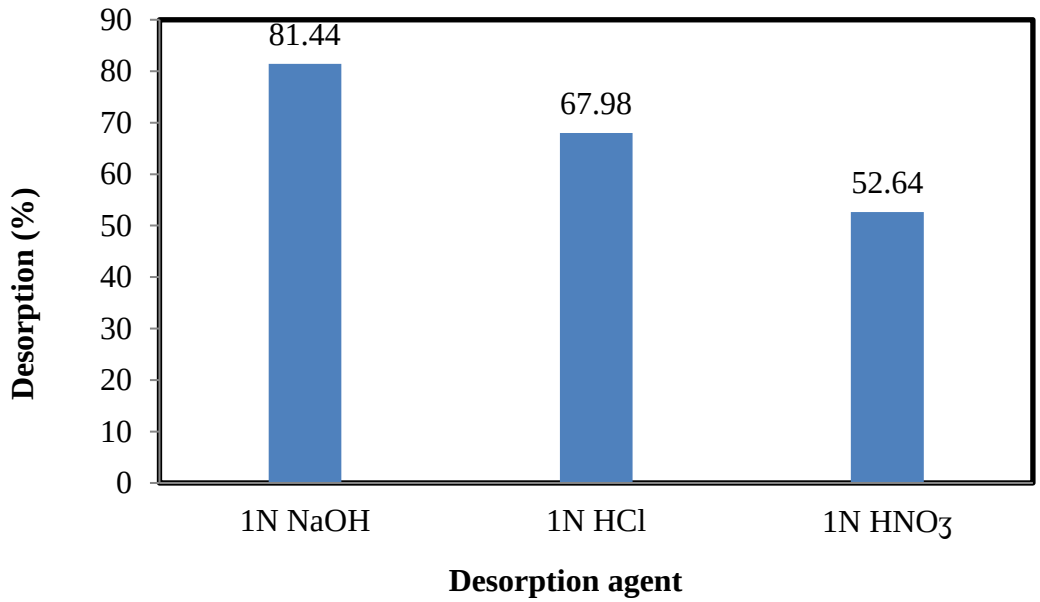

Figure 2.3.9 Graphical presentation on recover of phenol from biosorbent bagasse; phenol: 5.0 mg/L; bagasse: 2.0 g; particle size: 150 µm; contact time: 90 min; and pH: 6.5 at 30 °C

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Chapter 3

Biosorption of 2-chlorophenol from aqueous system using agricultural waste bagasse

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3.1 Introduction

Ortho-chlorophenol is treated as an organic pollutant imparts potential toxicity of carcinogenicity, mutagenicity, poor biodegradation, high stability, and widespread pollution[1,2]. It is a classical pollutant in a watery environment. It has acute toxicity, mutagenic activities, and carcinogenic nature. It also damages lives in water bodies and human health through the food chain. 0.01 mg/L ortho-chlorophenol (o-CPh) imparts disagreeable taste and odor to water. In drinking water maximum allowable limit of o-CPh is 10.0 μg/L[3]. The compound has high solubility in a watery environment[4]. The sources of the o-CPh to the natural water system are from petrochemical refineries, leather, and textile industries and manufacturing of pharmaceuticals, plastic, paint, paper industry, pesticides chemical industries, herbicides, and wood preservative industries[5] which are environmental concern.

Commonly used techniques for the biosorption of o-CPh is electrochemical conversion, coagulation, flocculation, microbial decomposition, biosorption, and adsorption[6,7]. Recycling of biowaste sorbent is an economical safety for sorption of the o-CPh and can confirm pure water. The use of low cost and available agro-waste materials in water and wastewater treatment have directed to take a competent effort[8].

However, activated carbon (AC) is widely used for the sorption of o-CPh. AC removes many of the impurities like o-CPh existing in water and wastewater. Though AC is reliable for sorption, but its high cost and variable performances of carbon regeneration, researchers desire for single-use materials[9]. So, research workers are looking for more economic, practical, and efficient sorbents for biosorption processes. As substituted of AC; rice straw, rice husk, fly ash, sewage sludge, sawdust, various seeds, eggshell, tree bark, nutshell, plant leaves, algae, coconut fiber, coconut coir, pulse straw, pulse husk, peanut straw, garlic husk etc can be used for mitigation of organic pollutants[9] like o-CPh. However, the biosorption behavior of o-CPh onto agricultural wastes available in Bangladesh has not been extensively studied. The present study is to intend to make a venture to develop a very simple but highly efficient for the biosorption of o-CPh along with other organic pollutants from industrial effluents using locally available as a cheap agricultural waste material like eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw and rice husk. These agricultural wastes have been investigated to observe their efficiency and it is revealed that bagasse is comparatively efficient than the rest of those materials.

It is revealed that agricultural waste bagasse can be used for wastewater treatments. Bagasse is an extremely inhomogeneous material comprising around 30-40% of “pith’’ fiber, which is derived from the core of the sugarcane plant. Bagasse contains cellulose fiber that can be processed in a sugar mill. Moreover, bagasse can be regenerated and it can also be used as fuel. In this study, o-CPh is considered as an organic-based typical pollutant. It is also well known that o-CPh and its derivates represent a serious class of pollutants for the aqueous environment and it has been found that most o-CPh are present in wastewater from many industries. As these compounds have high toxicity and a carcinogenic character even at low concentrations, it is necessary to eliminate o-CPh from industrial effluents and water bodies.

3.2. Materials and Methods

The contents of sub-para 3.2.1 on Materials, 3.2.2 on apparatus and equipments, 3.2.3 on experimental procedures and 3.2.4 on preparation of solutions have been mentioned in para 2.2 of chapter 2.

3.2.5 Operational procedures

The estimation of 2-chlorophenol (2-CP) is done spectrophotometrically by the modified 4-aminoantipyrine (4-AAP) method using Shimadzu UV-1700 double beam spectrophotometer. For the modification of the process detailed experiments are carried out varying all parameters as follows:

Introductory experiments:

These experiments are implemented by spectrophotometer for estimation of 2-CP following the modified 4-AAP method with solution at pH 10.0 and absorbance is estimated at 510.5 nm respectively did not give satisfactory results. Maximum absorption is at 510.5 nm and the required time to reach a point of maximum color is 20 minutes. It is therefore decided to modify the method first and then to apply the modified method for the estimation of 2-CP. Attempt is taken to modify the 4-AAP method for the spectrophotometric measurement of 2-CP. Total studies are implemented with including the investigations making the color using the absorption spectra, optimum solution media, suitable reagent concentration, adherence to Beer's law etc. As a result, the modified method may be applied for the estimation of the trace amount of 2-CP in solution.

General Procedure (Direct Spectrophotometry):

An appropriate aliquot of the test solution containing a definite amount a 5.0 mg/L (w/v) of 2-CP is taken in a 25 ml flask three times. This is followed by the addition of 0.1 ml, 0.8 ml, 1.1 ml buffer concentrate (pH 10) solution; and then the addition of 0.8 ml 4-AAP and 0.7 ml potassium ferricyanide solutions each time. The samples are then diluted with double distilled water, up to the mark (25ml) and then pH is measured. A blank of reagent is prepared according to identical conditional situations, against which absorbance is measured at the wavelength of maximum absorption (A max) after 15 minutes.

Color Reaction:

In the experiments, 2-CP offers brownish-red color with 4-AAP in presence of potassium ferricyanide in alkaline medium instead of an acidic medium. In alkaline medium color intensity gradually increases with the increasing volume of buffer concentrate (pH 10) solution up to 1.1 ml, beyond which the intensity decreases quickly. This is the reason to modify the spectrophotometric method for detection of trace amount of 2-CP.

3.2.6 Modification of 4-AAP method for determination of 2-CP

Effect of potassium ferricyanide solution on color development:

The result of the potassium ferricyanide (2% W/V) solution is shown in Table 3.1(b) which indicates that 0.7 ml of potassium ferricyanide (2% W/V) tincture is enough to develop maximum color in the arrangement of 5.0 mg/L 2-CP solution. The results are graphically represented in Figure 3.1. This indicates that volume beyond 0.7 ml of the potassium ferricyanide (2% W/V) solution decreases the color intensity of the system. Therefore, 0.7 ml potassium ferricyanide (2% W/V) solution is used for the optimum color development of the system containing 5.0 mg/L 2-CP solution.

Table 3.1(a) Condition on the effect of potassium ferricyanide for color development

Volumeof 4-AAP solution	1.0 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 2-CP	5.0 mg/L
Volume of potassium ferricyanide solution (ml)	Different Volume
Color development time	20 minutes
Total volume of the solution	25 ml

Table 3.1(b)Effect on volume of potassium ferricyanide solution for color intensity

Volume of potassium ferricyanide solution (ml)	λ_{max}(nm)	Absorbance
0.2	510.5	0.4853
0.4		0.5491
0.5		0.5654
0.6		0.5791
0.7		**0.5821**
0.8		0.5635
0.9		0.5377
1.0		0.5291
1.2		0.5021
1.3		0.4906
1.4		0.4715

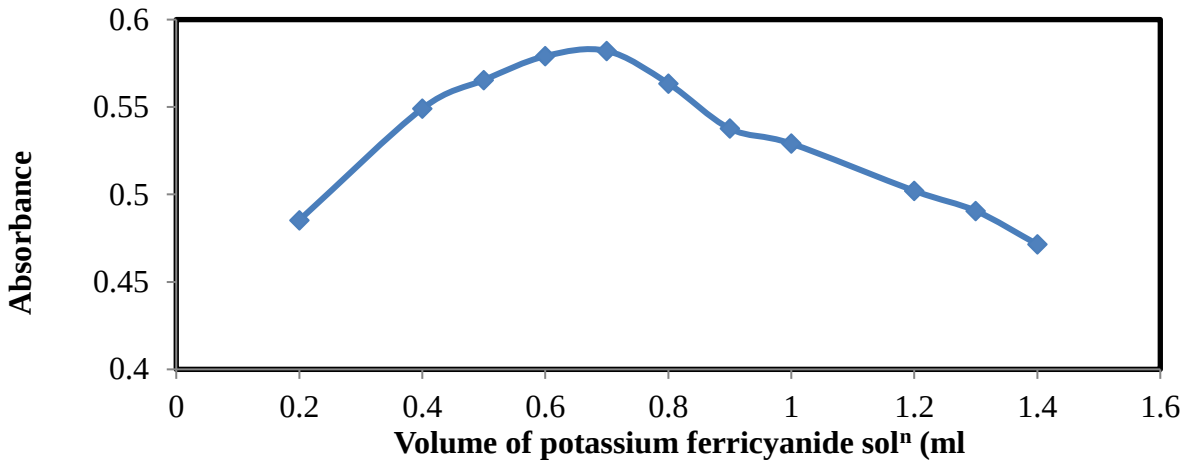

Figure 3.1 Effect of volume of potassium ferricyanide (2.0%W/V) solution on maximum color intensity; 2-CP conc.: 5.0 mg/L; 4-AAP (0.5%w/v) soln: 1.0 ml; buffer (pH 10) soln: 1.0 ml and time: 20 min at λ_{max}: 510.5 nm

Effect of 4-AAP solution on color development:

The result of the 4-AAP (0.5% W/V) tincture is shown in Table 3.2(b) which denotes that 0.8 ml of 4-AAP (0.5% W/V) tincture is enough to develop maximum color of the arrangement having 5.0 mg/L of 2-CP tincture. The results are graphically represented in Fig. 3.2. The graph depicts that volume beyond 0.8 ml of 4-AAP solutions decreases the color intensity of the system. Therefore, 0.8 ml of 4-AAP (0.5% W/V) solutions is used for the optimum color development of the arrangement having 5.0 mg/L of 2-CP.

Table 3.2 (a) Condition on the effect of 4-AAP solution for color development

Volume of 4-AAP solution (ml)	Different volume
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 2-CP	5.0 mg/L
Volume of potassium ferricyanide solution	0.7 ml
Color development time	20 minutes
Total volume of the solution	25 ml

Table 3.2(b) Effect of volume of 4-AAP solution for maximum color intensity

Volume of 4-AAP(ml)	λ_{max} (nm)	Absorbance
0.4	510.5	0.4603
0.5		0.4908
0.6		0.5279
0.7		0.5679
0.8		**0.5973**
0.9		0.5895
1.0		0.5821
1.2		0.5408
1.3		0.5143
1.4		0.4768

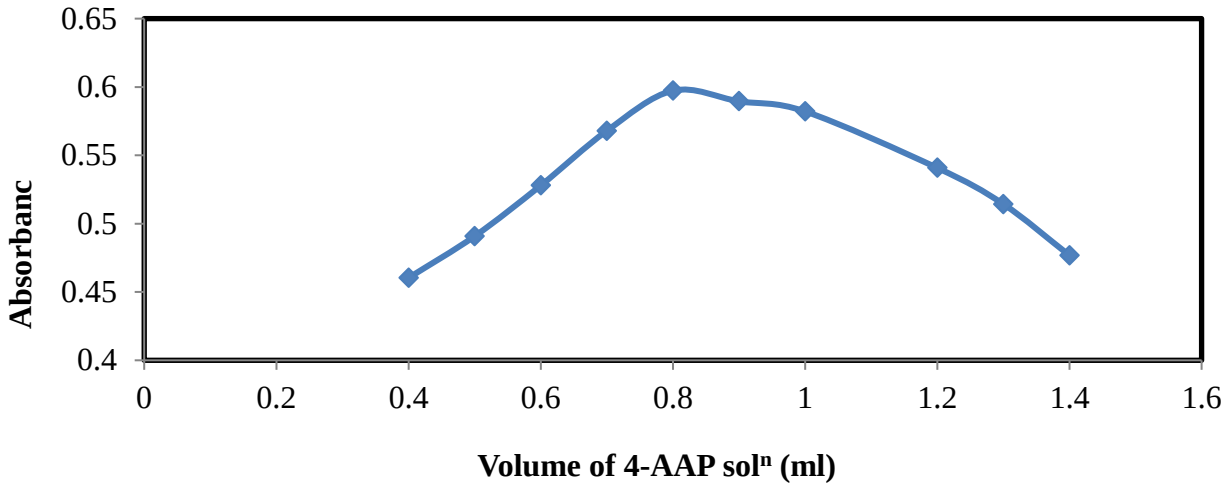

Figure3.2 Effect of volume of 4-AAP solution (0.5%W/V) for maximum color intensity; 2-CP conc.: 5.0 mg/L; PFC (2.0%w/v) soln: 0.7 ml; buffer (pH10) soln: 1.0 ml; λ_{max}: 510.5 nm and time: 20 min at 30°C

Effect of volume of buffer solution (pH 10) on maximum color development:

Buffer solution (pH 10) 1.1 ml is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L o-CP in water. The results are graphically represented in Figure3.3 which depicts that volume beyond 1.1 ml of buffer (pH10) solution decreases the color intensity of the system solution. Therefore, 1.1 ml of buffer solution (pH10) is required for the optimum color development of the system containing 5.0 mg/L of 2-CP solution.

Table 3.3(a) Condition on effect of buffer solution (pH 10) for color development

Volume of 4–AAP solution	0.8 ml
Volume of buffer solution (pH 10) (ml)	Different volume
Concentration of 2-CP	5.0 mg/L
Volume of potassium ferricyanide solution	0.7 ml
Color development time	20 minutes
Total volume of the solution	25 ml

Table 3.3(b) Effect on volume of buffer solution for maximum color intensity

Volume of buffer solution (pH 10) ml	λ_{max}(nm)	Absorbance
0.4	510.5	0.4107
0.5		0.4601
0.6		0.5026
0.7		0.5352
0.8		0.5531
0.9		0.5704
1.0		0.5973
1.1		**0.6035**
1.2		0.5762
1.3		0.5139
1.4		0.4507
1.5		0.3935
1.7		0.3151

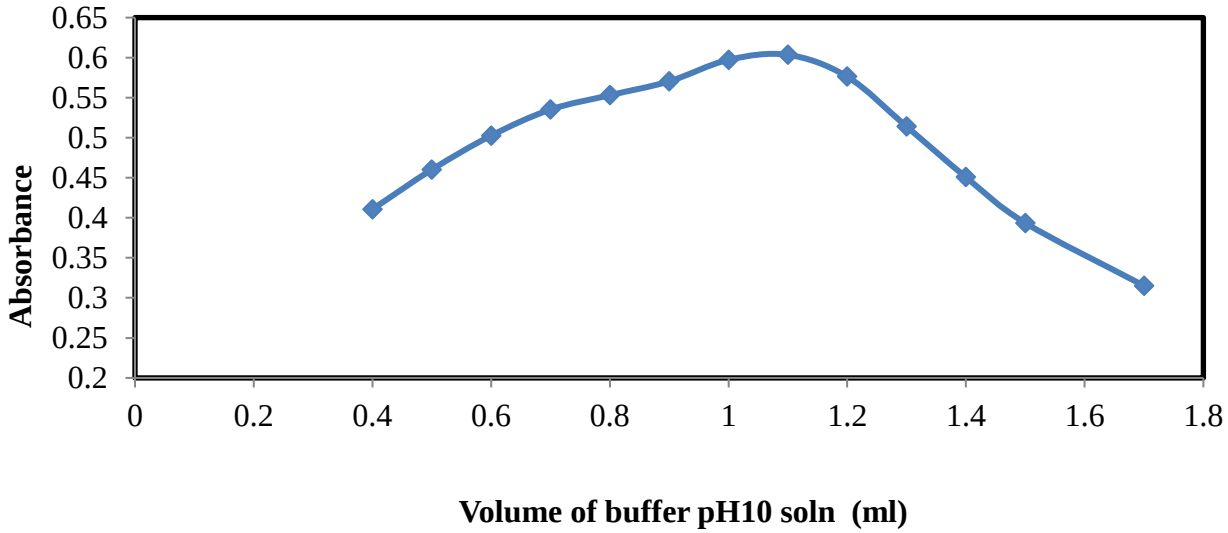

Figure 3.3 Effect of volume of buffer (pH10) sol^n on maximum color intensity; 2-CP conc.: 5.0 mg/L; 4-AAP (0.5%w/v) sol^n: 0.8 ml; PFC (2.0%w/v) sol^n: 0.7 ml; λ_{max}: 510.5 nm and time: 20 min at 30 °C

Effect of time for color formation reaction to reach equilibrium:

The result of time variation is shown in Table 3.4(b) which indicates that 20 minutes is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L 2-CP solution with 0.7 ml potassium ferricyanide solution, 0.8 ml 4-AAP, 1.1 ml buffer solution (pH 10). The results are graphically represented in Figure 3.4. This indicates that 20 minutes are necessary for stable color intensity of the system and after 20 minutes, the color intensity of the system remains constant and falls on equilibrium. Therefore, 20 minutes are used for the optimum color development of the system containing 5.0 mg/L of 2-CP solution.

Table 3.4(a) Condition on effect of reaction time for color development

Volume of 4-AAP solution	0.8 ml
Volume of buffer solution (pH 10)	1.1 ml
Concentration of 2-CP	5.0 mg/L
Volume of potassium ferricyanide solution	0.7 ml
Color development time (minute)	Different time
Total volume of the solution	25 ml

Table 3.4(b) Effect on time for development of color intensity

Time (minutes)	λ_{max} (nm)	Absorbance
5	510.5	0.4303
10		0.4934
15		0.5616
20		**0.6035**
23		0.5985
25		0.5952
30		0.5917
35		0.5851
40		0.5814

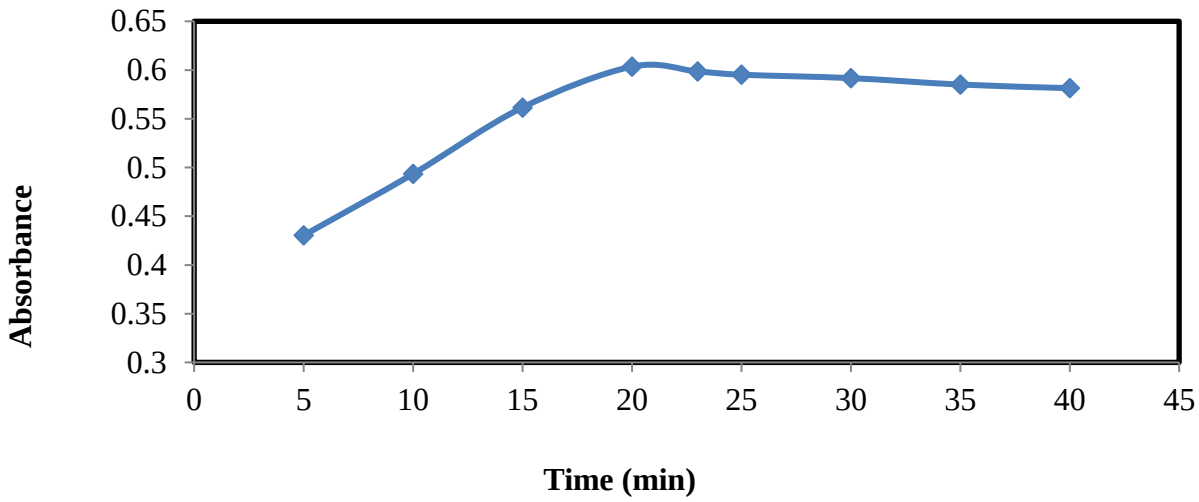

Figure 3.4 Effect of reaction time for maximum color intensity; 2-CP: 5.0 mg/L; 4-AAP (0.5%w/v) sol^n: 0.8 ml; PFC (2.0%w/v) sol^n: 0.7 ml; buffer (pH10) sol^n: 1.1 ml and λ_{max}: 510.5 nm at 30°C

3.2.7 Preparation of standard calibration curve for determination of 2-CP

A standard curve is a graph relating to a measured optical density to concentration of the substance of interest in "known" samples. The standard calibration curve has been drawn by plotting absorbance (on the Y-axis) versus concentration (on the X-axis). The result of the standard calibration curve is shown in Table 3.5(b). The standard curve has been determined by the system containing 5.0 mg/L of 2-CP solution with 0.7 ml potassium ferricyanide

solution, 0.8 ml 4-AAP solution, 1.1 ml buffer solution (pH 10), and the color development reaction time 20 minutes. The results are graphically represented in Figure 3.5.

Table 3.5(a) Condition on preparation of standard calibration curve

Volume of 4-AAP solution	0.8 ml
Volume of buffer solution (pH 10)	1.1 ml
Concentration of 2-CP	Different concentration
Volume of potassium ferricyanide solution	0.7 ml
Clor development time	20 Minutes
Total volume of the solution	25 ml

Table 3.5(b) Evaluating the optimum value for standard calibration curve

Concentration of 2-CP (mg/L)	λ_{max}(nm)	Absorbance
1	510.5	0.1269
2		0.2204
3		0.3615
4		0.4757
5		0.6035
6		0.7066
7		0.8149
8		0.9021
9		1.0212
10		0.1269

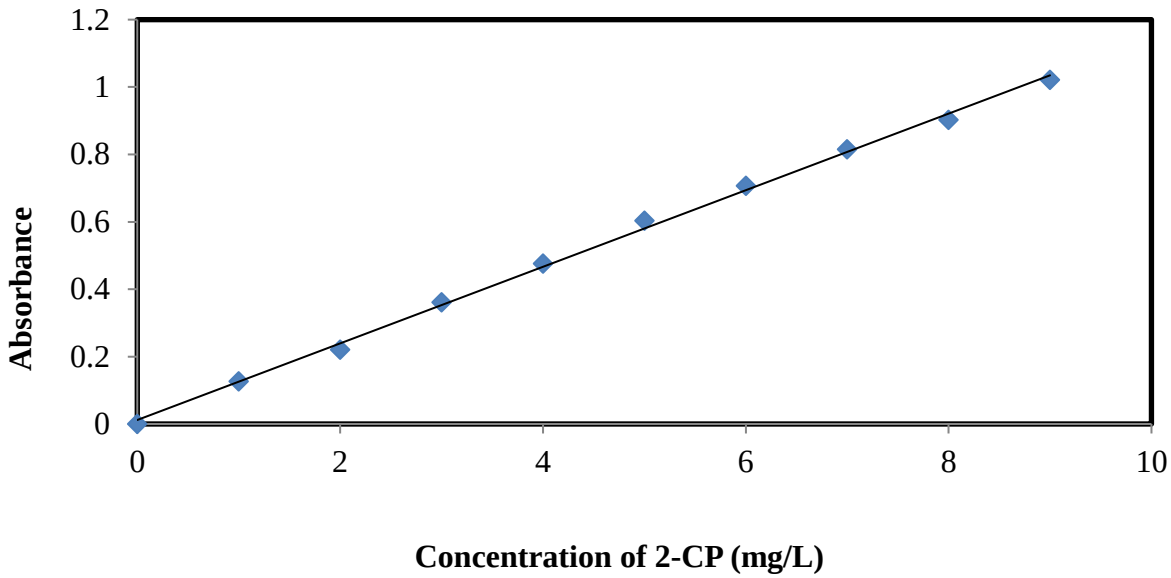

Figure 3.5 Standard calibration curve for determination absorbance of 2-CP. Concentration of 2-CP: 1.0 -10.0 mg/L; 4-AAP (0.5%w/v) solution: 0.8 ml; PFC (2.0%w/v) sol^{n}: 0.7 ml; buffer (pH10) solution: 1.0 ml; time: 25 min and λ_{max}: 500nm at 30°C

3.3 Results and Discussion

3.3.1 Performances of biosorbents

Preliminary evaluation of performances of nine agricultural wastes (Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk) were taken for the biosorption of 2-CP from system solutions. The biosorption of 2-CP has been performed by the conditions: 2-CP concentration, 5.0 mg/L; temperature (ambient temperature), 30^{o}C; amount of sorbent, 1.0 g; contact time, 60 minutes; particle size 150 µm and pH value 6.5. The studies indicate for sorption effectiveness of 2-CP with Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw and rice husk are 15.1%, 14.5%, 14.9%, 30.5%, 15.7%, 33.5%, 19.1%, 31.06%, and 30.9% respectively. Among these, eight sorbents have lesser sorption efficiencies from bagasse. So, those are not selected for the next experiments. Hence, agro-waste bagasse is taken as a comparatively more efficient biosorbent for the biosorption of 2-CP from water system.

3.3.2.1 Effect of bagasse dose on biosorption of 2-CP

Biosorbent bagasse dose study is an important parameter because it determines the efficiency of bagasse for biosorption of a given initial concentration of the 2-CP solution[11]. The biosorption of 2-CP onto bagasse is carried out at different bagasse dose by keeping other parameters constant. Biosorbent bagasse dose has been varied from 0.5 to 5.0 g. The batch experiments are performed with an initial concentration of 5.0 mg/L of 2-CP, the pH of the system solution is 6.5, and the agitation time is 60 minutes. The relationship between biosorption of substrate and bagasse dose for the same initial concentration of 2-CP has been presented in Figure 3.3.1. The figure depicts that the biosorption is increasing with the increase in bagasse dose, up to 2.0 g, beyond which the sorption efficiency is negligible, and in this connection, biosorption is marginal and becomes almost constant[12]. Biosorption percentage of 2-CP is increasing with the increase in bagasse dose and after a certain dose (2.0 g) of bagasse, sorption does not increase. The increase of biosorption seems that there are still active sites on the surface of the sorbent bagasse that are unsaturated. If the bagasse dose is more than the optimum amount (2.0 g) in the process unit, stoichiometrically, the dose is more than the equivalent amount of 2-CP in the solution. For this reason, biosorption does not increase with the increase of biosorbent bagasse dose[13]. These phenomena are attributed due to a large availability of sorption sites with higher sorbent dose on the initial rate of 2-CP uptake up to 2 g then the sorption reach to the saturation situation and remained constant[14] up to 2.0-5.0 g. With increasing sorbent dose from 0.5 to 2.0 g, the biosorption is increased from 16.06 to 60.98%. An increase in the biosorption with the increase in sorbent doses can be attributed to greater surface area and the availability of more sorption sites[15]. Therefore, the optimum biosorbent dose is taken as 2.0 g/0.1 L for subsequent experiments.

Table 3.3.1(a) Experimental condition on effect of bagasse doses for sorption of 2-CP

1	Initial concentration of 2-CP	5.0 mg/L
2	Operational temperature	30°C
3	pH of the system solution	6.5
4	Volume of potassium ferricyanide	0.7 ml
5	Volume of 4-AAP solution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Contact time of 2-CP solution and bagasse	60 minutes
8	Parlicle size of bagasse	250 µm
9	Bagasse dose, g	Different dose

Table 3.3.1(b) Effect of sorbent dose on sorption of 2-CP in aqueous system

Weight of bagasse(g)	Absorbance	Concentration (mg/L)	Biosorption of 2-CP (%)
0.5	0.4991	4.20	16.06
1.0	0.3733	3.325	33.50
1.5	0.2481	2.22	55.53
2.0	0.2127	1.95	60.98
2.5	0.2127	1.95	60.98
3.0	0.2127	1.95	60.98
3.5	0.2127	1.95	60.98
4.0	0.2127	1.95	60.98
4.5	0.2127	1.95	60.98
5.0	0.2127	1.95	60.98

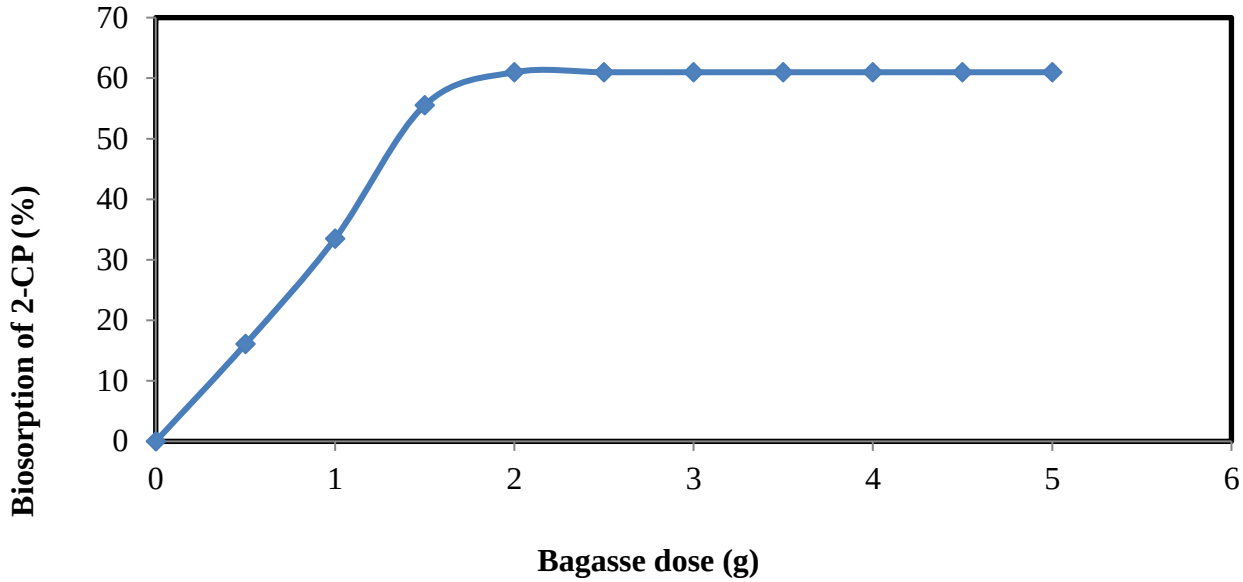

Figure 3.3.1 Graphical presentation on the effect of biosorbent bagasse dosesforthe biosorption of 2-CP from aqueous system; 2-CP: 5.0 mg/L; particle size: 150 µm; time: 60 min and pH: 6.5 at 30 °C

3.3.2.2 Effect of contact time on biosorption of 2-CP onto bagasse

The effects of time on the biosorption process have been evaluated and determine the equilibrium point. Batch experiments are carried out to investigate the effects of the biosorption time of 2-CP onto bagasse, which is shown in Figure 3.3.2. Results show that the equilibrium time required for the sorption of 2-CP onto bagasse is almost 90 minutes. No significant change in 2-CP sorption has been observed[16] after 90-300 minutes. Available sorption results reveal fast uptake of 2-CP species at the initial stages of the contact period. As shown, the sorption process is completed through three stages: (1) an initial stage with biosorption occurs rapidly, (2) subsequently, slow biosorption, and (3) a final stage with sorption reaches to the equilibrium and remains constant. The first stage can be attributed to the rapid attachment of 2-CP to the surface of the bagasse by surface mass transfer. At this stage, (up to 61% of 2-CP can be sorbed within 60 minutes of total sorption of 69%) above 80% of 2-CP sorption has been occurred in all cases cited in Table 3.3.2(b). It has been observed that an increase in the rapid biosorption with the increase in contact time can be attributed to greater surface area and the availability of more sorption sites[15]. The second stage is slower, possibly because biosorption sites become lower along with many of the available external sites are already occupied system then a slow diffusion of 2-CP molecules observed into the network of the bagasse. An asymptotic trend is found after approximately 90 minutes regardless of the initial concentration of 2-CP has been applied to the biosorption system. The biosorption is not significant at contact times longer than the equilibrium time of 90 minutes. Such findings reveal the benefits of using this low-cost biosorbent or so-called eco-sorbent for the treatment of aqueous solutions rich in chlorophenols/pesticides in general and 2-CP in particular[17]. These results also indicate that the sorption process can be considered very fast because of the expectable amount of 2-CP attached to the sorbent within the first 60 minutes of the sorption period from an aqueous system containing a low amount of organic pollutants like 2-CP[18].

Table3.3.2 (a) Condition on contact time for sorption of 2-CPonto bagasse

1	Initial concentration of 2-CP	5.0 mg/L
2	Operational temperature	30 ˚C
3	pH of the solution	6.5
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Bagasse dose	2.0 g
8	Contact time of 2-CP solution and bagasse (minutes)	Different time
9	Particle size of bagasse	150 µm

Table 3.3.2(b) Effect of contacttime on biosorption of 2-CP onto bagasse

Time	Absorbance	Concentration of 2-CP (mg/L)	Biosorption of 2-CP (%)
5	0.5650	4.560	8.73
10	0.4755	4.002	19.96
15	0.4122	3.470	30.68
20	0.3507	2.950	40.95
30	0.3319	2.640	47.12
45	0.2759	2.190	56.13
60	0.2454	1.950	60.98
75	0.2203	1.750	65.01
90	**0.1673**	**1.560**	**68.82**
120	0.1673	1.560	68.82
150	0.1673	1.560	68.82
180	0.1673	1.560	68.82
210	0.1673	1.560	68.82
240	0.1673	1.560	68.82
270	0.1673	1.560	68.82
300	0.1673	1.560	68.82

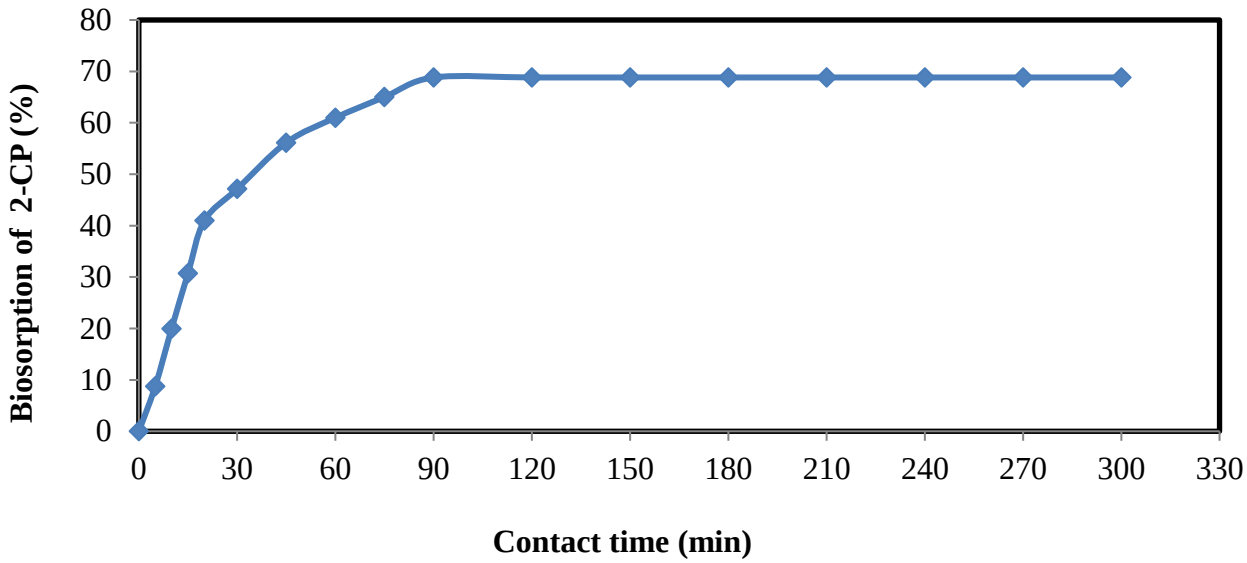

Figure 3.3.2 Graphical presentation on the effect of cont. time on biosorpt^{n} of 2-CP onto bagasse from aqueous system; 2-CP conc.: 5.0 mg/L; bagasse dose: 2.0 g; particle size: 150 µm; and pH: 6.5 at 30 °C

3.3.2.3 Effect of particle size of bagasse on biosorption of 2-CP

Batch experiments of the biosorption have been carried out for the removal of 2-CP from aqueous sample solution using six different particle size fractions (average diameters of 50, 70, 100, 150, 200, and 250 µm). With decreasing bagasse particle size , the biosorption of 2-CP is increased from 61 to 78%. These phenomena might be attributed because the smaller particles offer comparatively larger surface areas and greater numbers of sorption sites[19]. The same amounts of biosorbent of different particle sizes are introduced in separate 2-CP solutions of the same volume and same initial concentration[12]. The biosorption of 2-CP is measured after

90 minutes. The results are as shown in figure 3.3.3. We selected 150 µm of bagasse particle size to run the subsequent experiments for better convenience.

Table 3.3.3(a) Conditionof effect on particle size for biosorption of 2-CP

1	Initial concentration of 2-CP	5.0 mg/L
2	Operational temperature	30˚C
3	pH of the solution	6.5
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAPsolution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Bagasse dose	2.0 g
8	Contact time of 2-CP solution and bagasse	90 minutes
9	Particle sizeof bagasse (µm)	Different size

Table 3.3.3(b) Effect of particle size on biosorption of 2-CP

Particle size (µm)	Absorbance	Concentration of 2-CP (mg/L)	Biosorption of 2-CP (%)
50	0.1394	1.11	77.82
70	0.1408	1.18	76.32
100	0.153683	1.29	74.16
150	0.167326	1.56	68.82
200	0.221184	1.76	64.81
250	0.245951	1.96	60.87

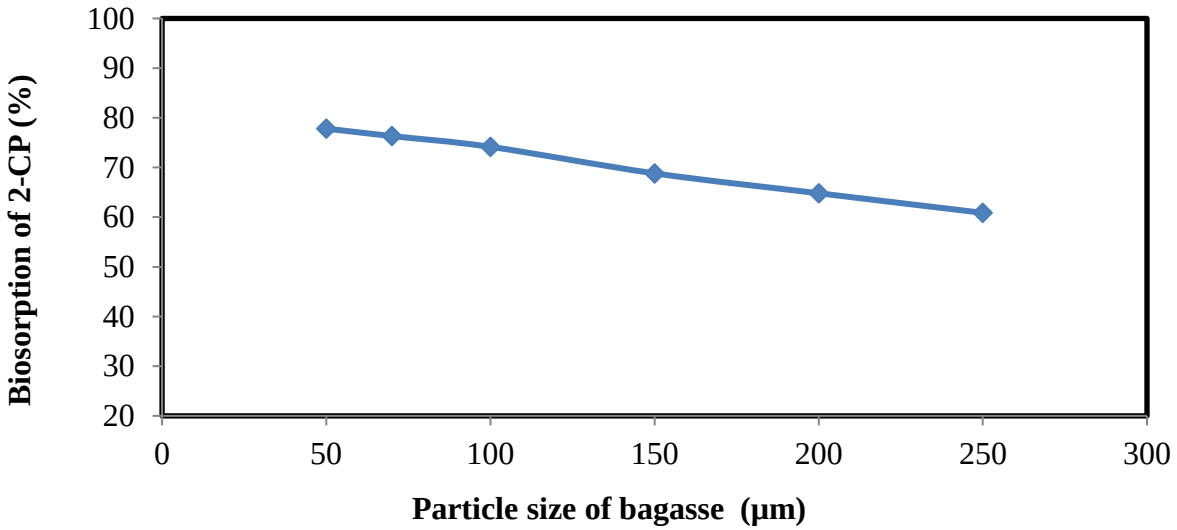

Figure 3.3.3 Graphical presentation of effect of bagasse particle size on the biosorption of 2-CP from aqueous system; 2-CP conc.: 5.0 mg/L; bagasse dose: 2.0 g; cont. time: 90 min and pH: 6.5 at 30 °C

3.3.2.4 Effect of initial concentration onbiosorption of 2-CP onto bagasse

The effects of initial concentrations of 2-CP on biosorption efficiency are represented in Figure 3.3.4. It is evident from the figure that, biosorption efficiency of 2-CP decreases with the increase in initial concentration[16]. When the initial concentration of 2-CP is increased from 0.5 to 10.0 mg/L in the aqueous sample solution, the biosorption efficiency is decreased from 75 to 41%. In the case of lower concentrations of 2-CP, the ratio of the available surface area of biosorbent bagasse to the initial number of moles of 2-CP is larger and subsequently, the fractional sorption becomes independent at initial concentration. However, at higher 2-CP concentrations, the available sorption sites become fewer, and hence the biosorption percentage of 2-CP decreases[20]. The figure is also revealed that all 2-CP ions present in the solution have interacted more with the binding sites at lower concentrations than at higher concentrations. Furthermore, initially, the number of sorption sites available and the driving force for the mass transfer is greater. Therefore, the sorbate 2-CP reaches the sorption site with ease. On the contrary, with the increase of initial concentration, the numbers of active sites become less along with the addition of many external influences and impeding the movement of the sorbate 2-CP species. This can be accounted for by the decrease in sorption rate with the increase in concentration. Therefore, a higher percentage of sorption is obtained at a lower initial concentration and a lower percentage of sorption is obtained at a higher initial concentration of 2-CP. Finally, it is concluded that the initial concentration provides an important driving force to overcome all mass transfer resistances of 2-CP between the aqueous and solid phases[18]. Increasing the mass transfer driving force, the rate at which 2-CP molecules pass from the bulk solution to the particle surface, and the equilibrium uptake and sorption yield are highest and expectable, because of the greater specific surface area and the microporous structure of bagasse[21].

Table 3.3.4(a) Condition on effect of initial concentrations on sorption of 2-CP

1	Initial concentration of 2-CP (mg/L)	Different concentration
2	Operational temperature	30˚C
3	pH of the system solution	6.5
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAPsolution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Bagasse dose	2.0 g
8	Contact time of 2-CPsolution and bagasse	90 minutes
9	Particle size of bagasse	150 µm

Table 3.3.4 (b): Effect of initial concentration on biosorption of 2-CP onto bagasse

Ini. conc. of 2-CP (mg/L)	Absorbance	Final Conc.of 2-CP (mg/L)	Biosorpt^{n} of 2-CP (%)
0.5	0.0152	0.12	75.34
2	0.0645	0.51	74.34
3	0.1018	0.81	73.14
4	0.1448	1.15	71.25
5	0.1673	1.56	68.82
6	0.3012	2.40	59.98
8	0.5121	4.31	46.12
10	0.6184	5.88	41.18

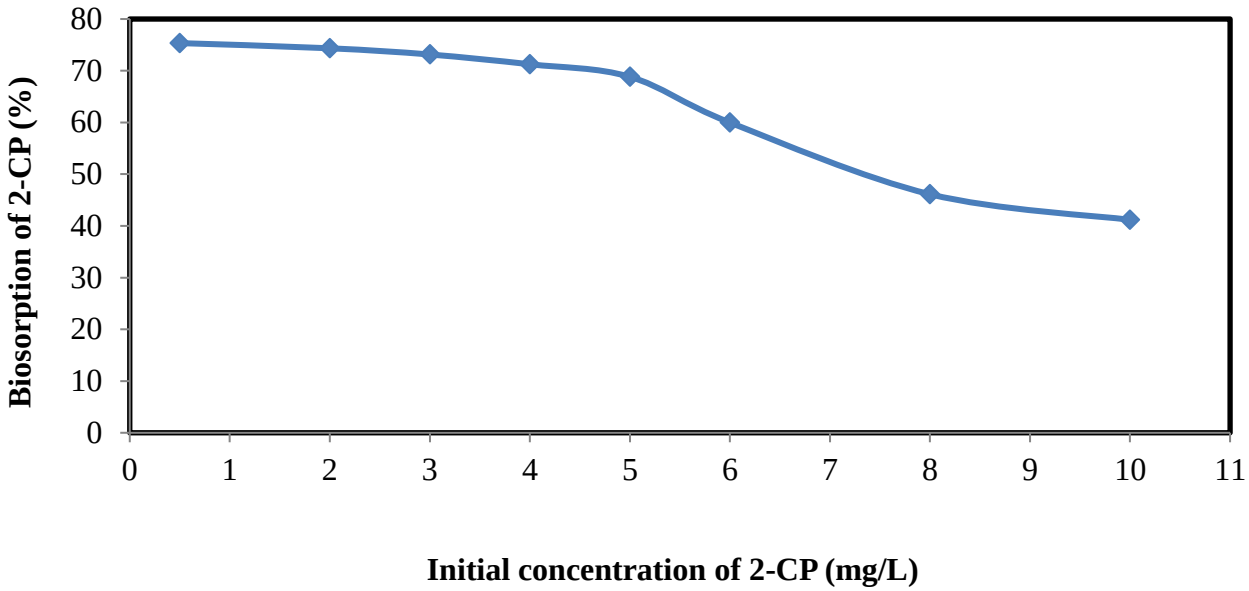

Figure3.3.4 Graphical presentation on effect of initial concentration on biosorption of 2-CP onto bagasse; bagasse dose: 2.0 g; particle size: 150 µm; contact time: 90 min and pH: 6.5 at 30 °C

3.3.2.5 Effect of pH on biosorption of 2-CP onto bagasse

The biosorption of the 2-CP from aqueous solution is dependent on the pH of the system solution. pH affects the surface charge of the biosorbent bagasse, degree of ionization, and speciation of 2-CP. The biosorption of 2-CP onto bagasse has been studied at various pH values from 3 to 12. The biosorption percentage increases with increasing the pH up to 6.5 and dramatic decrease in sorption with further increasing the pH value[21] up to 12. The results have been displayed in Figure 3.3.5. The mechanism of the decrease in biosorption can be attributed to the depending of 2-CP ionization; loss of a hydrogen cation (H^{+}) from the hydroxyl group of 2-CP forms a corresponding negative 2-chlorophenolateion or 2-chlorophenoxide ion, and the corresponding salts are called 2-chlorophenolates or 2-chlorophenoxide, although the term aryloxides are preferred according to the IUPAC (Gold Book.) on the pH value. Accordingly, 2-CP, which is a weak acid, has to be sorbed to a lesser extent at higher pH>6.5 values due to the repulsive force[22] between the negative groups on the bagasse surface and 2-

chlorophenolate or 2-chlorophenoxide ion. However, as seen in Figure 3.3.5, the biosorption of 2-CP is increased from 51 to 69% with an increase in pH from 3 to 6.5 and then a dramatic decrease in 2-CP sorption from 69.00 to 19.00% with an increase in the pH from 6.5 to 12. The biosorption values are attained at equilibrium after 90 minutes period of time with a 5.0 mg/L concentration of 2-CP solution[23]. The lower biosorption of 2-CP at a very lower pH system solution is probably due to the presence of excess H^+ ions competing with 2-CP molecules for the sorption sites of bagasse. Furthermore, at lower pH values (below the pH<<6.5) -COO- group in bagasse is protonated to -COOH group, and the hydrogen bonds are formed with -COOH groups resulting in a decrease of 2-CP uptake[5]. On the other hand, at higher pH (>6.5), the OH^- ion concentration is increased and this ion repulse with the negative active sites on the sorbent leading to a decrease[24] in 2-CP sorption. The difference in sorption efficiency of bagasse at different pHs may be due to the difference in the concentrations of H^+ and OH^- ionsin the solutions. Sorbent particles have active sites with negative charges. The H^+ ions within low pH≤ 6.5 environments can neutralize those negative particles, reduce the hindrance to diffusions of chlorophenolate ions and consequently increase the chances of their sorption. High pH environments led to the high concentration of OH^- ion, which can increase the hindrance to the diffusions of chlorophenolate ions and thus reduce the chances of their sorption[25]. The variation in the 2-CP uptake concerning the initial solution pH can be explained based on the structure of the 2-CP molecule and the point of zero charge of bagasse. For this bagasse carbon, the point of zero charge is estimated to be at 6.5. Above this pH, the carbon of bagasse acquires a negative surface charge leading to a lesser uptake since the 2-CP molecule becomes neutral at that pH. At a pH lower than 6.5 the surface of the bagasse carbon acquires a positive charge and 2-CP molecules also become positive charge. Due to this, there is an electrostatic repulsion between 2-CP molecules and bagasse carbon that causes a decrease in the 2-CP uptake[26]. Finally, it is concluded that both the bagasse and the 2-CP have functional groups that are subjected to protonation/deprotonation depending on the solution pH; therefore, the negative effect of increasing and decreasing pH with compare to pH at 6.5 on 2-CP sorption is likely due to the charge properties of both sorbate and sorbent. The concomitant build-up of net negative charges on the surfaces of the bagasse led to an enhanced electrostatic repulsion between the sorbate and sorbent, resulting in a dramatic decrease in 2-CP sorption at pH >6.5. When the neutral 2-CP that has no charge is predominant at low pH≤ 6.5, electrostatic interactions are insignificant even though the surfaces of the sorbent particles are positively charged. Thus, the biosorption of neutral 2-CP is determined by sorbate-sorbent interactions other than electrostatic attraction. On the other hand, electrostatic repulsion prevails when the relative content of the anionic 2-CP is high and when negative charges of the sorbent surfaces build up. This study found that maximum sorption 69% at pH 6.5. Thus, pH 6.5 is chosen as the optimum, and all the subsequent experiments have been carried out at this pH 6.5.

Table 3.3.5(a) Condition on effect of pH on biosorption of 2-CP onto bagasse

1	Initial concentration of 2-CP	5.0 mg/L
2	Operational temperature	30˚C
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Bagasse dose	2.0 g
8	Contact time of 2-CP solution and bagasse	90 minutes
9	pH value of system solution	Different value

Table 3.3.5(b) Effect of pH on biosorption of 2-CP onto bagasse from aqueous system

pH	Absorbance	Concentration of 2-CP (mg/L)	Biosorption of 2-CP (%)
3.0	0.3054	2.43	51.35
4.0	0.2765	2.20	55.93
5.0	0.2551	2.03	59.45
6.0	0.2150	1.71	65.78
6.5	0.1669	1.56	68.82
7.0	0.2225	1.77	64.56
8.0	0.2790	2.22	55.59
9.0	0.3043	2.56	48.81
10.0	0.3053	2.97	40.52
11.0	0.3988	3.49	30.14
12.0	0.4828	4.06	18.84

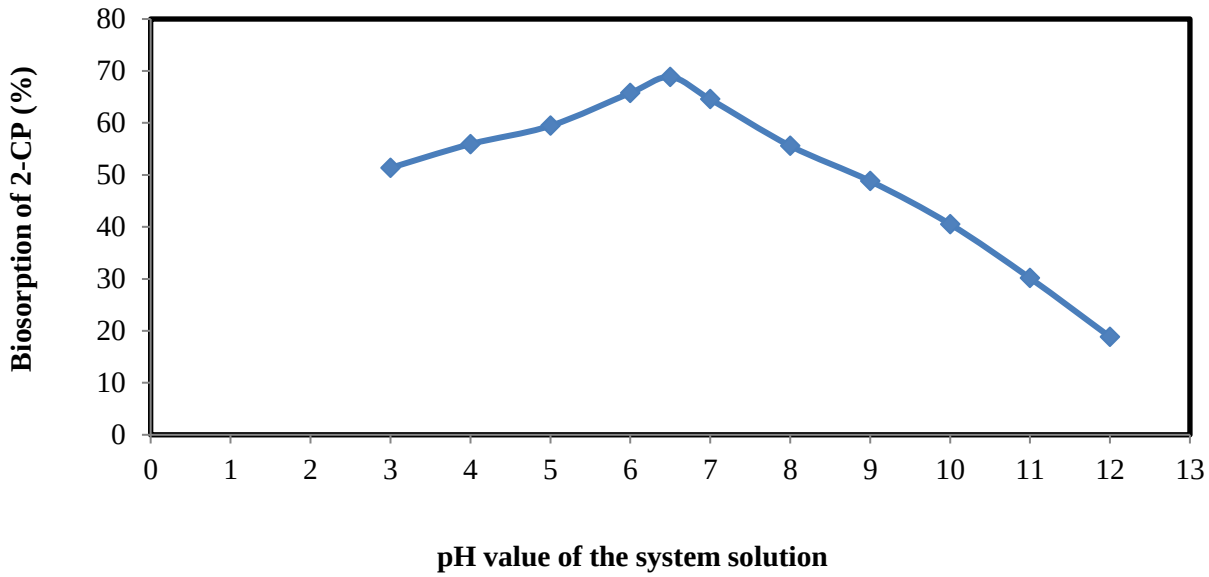

Figure 3.3.5 Graphical presentation on effect of pH of the system sol^{n} for the sorption of 2-CP onto bagasse; 2-CP conc.: 5.0 mg/L; bagasse dose: 2.0 g; particle size: 150 µm and cont. time: 90 min at 30°C

3.3.2.6 Effect of temperature on the biosorption of 2-CP onto bagasse

Temperature is an indicator for the biosorption nature whether it is an exothermic or endothermic process. It is also an important parameter for any separation process. Biosorption of 2-CP onto bagasse has been studied at different temperatures; 30 (room temperature) 35, 40, 45, and 50˚C. Besides, temperature has not been raised beyond 50˚C for formation of color is observed in the test solution. The plot of biosorption efficiency as a function of temperature is shown in Figure 3.3.6. The biosorption of 2-CP onto bagasse is increased from 69 to 73%, when temperature goes from 30 to 50 ˚C, suggesting that the process is endothermic. Higher temperatures reduce the thickness of the outer surface of the sorbent and increase the kinetic energy of 2-CP molecules. As a result, 2-CP molecules are easily sorbed on the biosorbent surface[27,28]. Increasing temperature may increase the biosorptive forces between the 2-CP species and the active sites on the bagasse surface as a result of increasing biosorption efficiency. The increase in biosorption with an increase in temperature is partly due to the intraparticle diffusion rate of sorbate 2-CP ions into the pores has to be intensified as temperature increases, as diffusion is the endothermic process. So, the sorption increases with an increase in temperature[17]. Temperature has a pronounced effect on the sorption efficiency of the sorbents. Since sorption is an endothermic process, it would be expected that an increase in temperature of the sorbate-sorbent system would result in increased sorption efficiency as shown in all of the results. The results confirm the endothermic nature of the biosorption process. Higher temperature reduces the thickness of the outer surface of the bagasse and increases the kinetic energy of 2-CP molecules. Hence a higher temperature is favorable for the biosorption and 2-CP molecules are easily sorbed on the bagasse surface[22]. It is investigated that at higher temperature, the hydrogen bonding (intra and intermolecular) becomes weak, which makes 2-CP molecules freely available, and hence, biosorption intends to increases at higher temperature[18]. Since biosorption of 2-CP onto bagasse is enhanced a little bit from 69 to 73% at the higher temperature due to lignin and other inactive matters in cellulose of sorbent have not been separated. The intraparticle diffusion rate of sorbate ion is a little into the pores as the pores fill up and covered active sites. However, room temperature, 30˚C has been chosen for subsequent experiments for economy and convenience.

Table3.3.6(a) Condition on effect of temperature on 2-CP sorption onto bagasse

1	Initial concentration of 2-CP	5.0 mg/L
2	pH value of system solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAPsolution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Bagasse dose	2.0 g
8	Contact time of 2-CP solution and bagasse	90 minutes
9	Temperature of the system (˚C)	Different temperature

Table 3.3.6(b) Effect of temperature on 2-CP biosorption onto bagasse in aqueous system

Temperature (°C)	Absorbance	Conc. of 2-CP (mg/L)	Biosorption of 2-CP (%)
30	0.1673	1.56	68.82
35	0.1917	1.52	69.71
40	0.1847	1.47	70.67
45	0.1780	1.42	71.68
50	0.1693	1.35	72.98

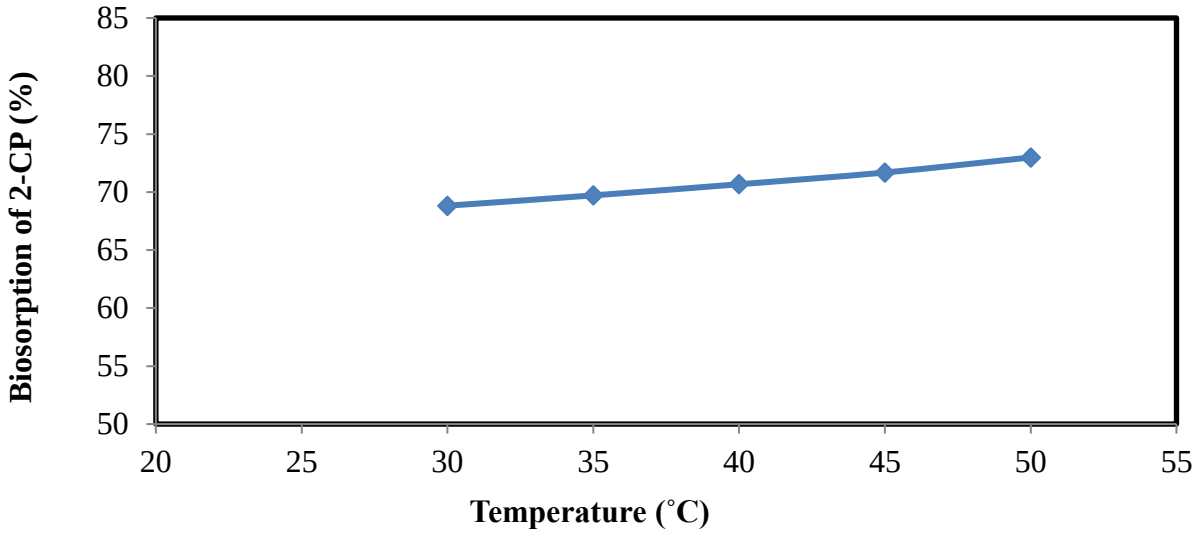

Figure 3.3.6 Graphical presentation on effect of Temperature on 2-CP sorptiononto bagasse; 2-CP concentration: 5.0 mg/L, bagasse dose: 2.0 g; particle size: 150 µm and contact time: 90 min at pH 6

3.3.3 FTIR spectroscopy studies

The infrared spectra were used to determine changes in the structure of cellulose, hem cellulose, and lignin during the sequence of treatments subjected to bagasse (native). Table 3.3.7 shows the FTIR spectrum of natural sugarcane bagasse. The band at 1162 cm^{-1} is characteristic of C-

O-C asymmetrical stretching, 1335 cm^{-1} is characteristic of C-O aromatic ring, 1423 cm^{-1} is characteristic of CH_2 symmetrical stretching, 1732 cm^{-1} is characteristic of C=O unconjugated stretch, 2885 cm^{-1} is characteristic of C-H symmetrical stretching, and 3300 cm^{-1} is characteristic of O-H linked shearing.

Table 3.3.7 Structural characterization of the bagasse

Wave number (cm^{-1})	Vibration
3300	O-H linked shearing
2885	C-H symmetrical stretching
1732	C=O unconjugated stretch
1423	CH_2 symmetrical stretching
1335	C-O aromatic ring
1162	C-O-C asymmetrical stretching

3.3.4.1 Langmuir isotherm model for biosorption of 2-CP onto bagasse

The Langmuir isotherm assumes that the surface of any sorbent material contains several active sites where the sorbate attaches itself. This attachment can either be physical or chemical. When the attachment is via Van der Waals interactions it is known as physicosorption and when via covalent bond it is known as chemisorptions. Langmuir model indicates that there is not much interaction between the sorbate molecules and sorbent bagasse and once a saturation value has been reached no further biosorption would take place[30]. The experimental data for the Langmuir model in Table 3.3.8(a) employed to reveal the isotherm constants

The linear form of the Langmuir isotherm model can be represented by the following relation[22]

$1/q_e = 1/q^\circ + 1/(bq^\circ C_e)$

Where q° (mg/g) and b (L/mg) are the Langmuir constants related to the maximum biosorption capacity and the energy of biosorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ and are shown in Figure 3.3.7(a)

The essential feature of the Langmuir isotherm can be expressed using dimensionless separation factor R_L which is calculated using the following equation:

$R_L = 1/ (1+bC_o)$

Where b denotes the Langmuir constant and C_o is the initial concentration[31] of 2-CP in an aqueous system. At all temperatures, R_L values have been found less than unity and showed in Table 3.3.8(d) indicating that the sorption process is favorable.

Table 3.3.8(a) Experimental data for applying on Langmuir isotherm model

Conc. of 2-CP (mg/L)	Biosorption of 2-CP (%)			30˚C		40˚C		50˚C	
	30˚C	40˚C	50˚C	$1/c_e$	$1/q_e$	$1/C_e$	$1/q_e$	$1/c_e$	$1/q_e$
0.5	75.34	78.64	81.87	8.1103	53.0927	9.3633	50.8647	11.0314	48.8580
1	74.95	77.98	80.96	3.9920	26.6850	4.5413	25.6476	5.2521	24.7036
2	74.34	76.84	79.64	1.9486	13.4517	2.1589	13.0141	2.4558	12.5565
3	73.14	75.33	77.98	1.2410	9.1149	1.3512	8.8499	1.5138	8.5492
4	71.25	73.24	75.74	0.8696	7.0175	0.9342	6.8269	1.0305	6.6015
5	68.82	70.67	72.98	0.6414	5.8123	0.6819	5.6601	0.7402	5.4810
6	59.98	61.68	63.43	0.4165	5.5574	0.4349	5.4042	0.4558	5.2551
7	51.51	53.12	54.72	0.2946	5.5467	0.3047	5.3787	0.3155	5.2214
8	46.12	47.07	48.52	0.2320	5.4206	0.2362	5.3112	0.2428	5.1525
9	42.05	43.36	44.68	0.1917	5.2847	0.1962	5.1251	0.2009	4.9736
10	41.18	42.41	43.65	0.1700	4.8567	0.1736	4.7159	0.1775	4.5819

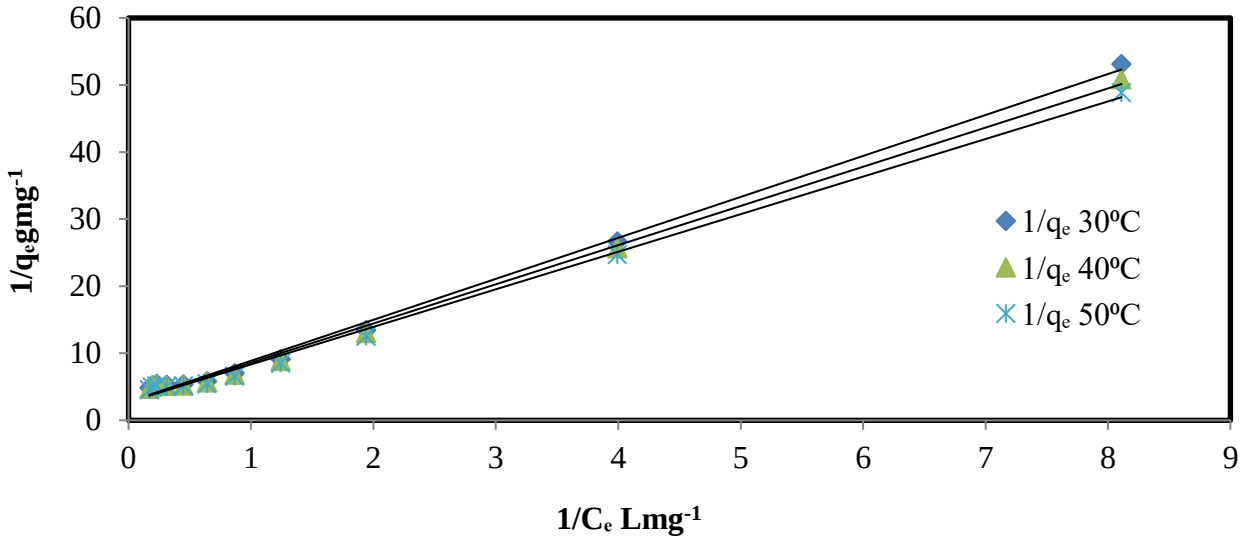

Figure3.3.7(a) Graphical presentation on Langmuir isotherm curve for the biosorption of 2-CP onto bagasse; 2-CP conc.: 0.5-10.0 mg/L; bagasse dose: 2.0 g; particle size: 150 µm; contact time: 90 min and pH: 6.5 at 30-50 °C

3.3.4.2 Freundlich isotherm model for biosorption of 2-CP onto bagasse

Freundlich isotherm is based on the sorption on a heterogeneous surface of varied affinities. This model can be applied for non-ideal sorption on a heterogeneous surface of the sorbent[32]. The experimental data for the Freundlich model in Table 3.3.8(b) employed to reveal the isotherm constants.

The linear form of the Freundlich isotherm model is given by the following relation[33].

$\ln q_e = \ln k_F + (1/n)\ln C_e$

Where, q_e (mg/g) is the biosorption capacity of 2-CP, at equilibrium time, C_e (mg/L) is the equilibrium concentration of the 2-CP k_F and 1/n is the Freundlich constants related to biosorption capacity and intensity, respectively. The values of K_F and 1/n can be obtained from the intercept and slope of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$, respectively. At all temperatures, 1/n values have been found less than unity indicates that the biosorption process favorable are shown in Table 3.3.8(d)

Table 3.3.8(b) Experimental data for applying on Freundlich isotherm model

Conc. of 2-CP (mg/L)	Biosorptionof 2-CP (%)			30˚C		40˚C		50˚C	
	30˚C	40˚C	50˚C	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$
0.5	75.34	78.64	81.87	-2.0931	-4.1952	-2.2368	-4.1523	-2.4008	-4.1121
1	74.95	77.98	80.96	-1.3843	-3.5072	-1.5132	-3.4676	-1.6586	-3.4301
2	74.34	76.84	79.64	-0.6671	-2.8223	-0.7696	-2.7892	-0.8985	-2.7534
3	73.14	75.33	77.98	-0.2159	-2.4331	-0.3010	-2.4036	-0.4146	-2.3690
4	71.25	73.24	75.74	0.1398	-2.1716	0.0680	-2.1440	-0.0301	-2.1105
5	68.82	70.67	72.98	0.4441	-1.9831	0.3829	-1.9566	0.3009	-1.9244
6	59.98	61.68	63.43	0.8760	-1.9383	0.8326	-1.9103	0.7858	-1.8824
7	51.51	53.12	54.72	1.2221	-1.9364	1.1883	-1.9056	1.1536	-1.8759
8	46.12	47.07	48.52	1.4610	-1.9134	1.4432	-1.8930	1.4155	-1.8626
9	42.05	43.36	44.68	1.6516	-1.8880	1.6288	-1.8573	1.6052	-1.8273
10	41.68	42.41	43.65	1.7719	-1.8035	1.7508	-1.7741	1.7290	-1.7453

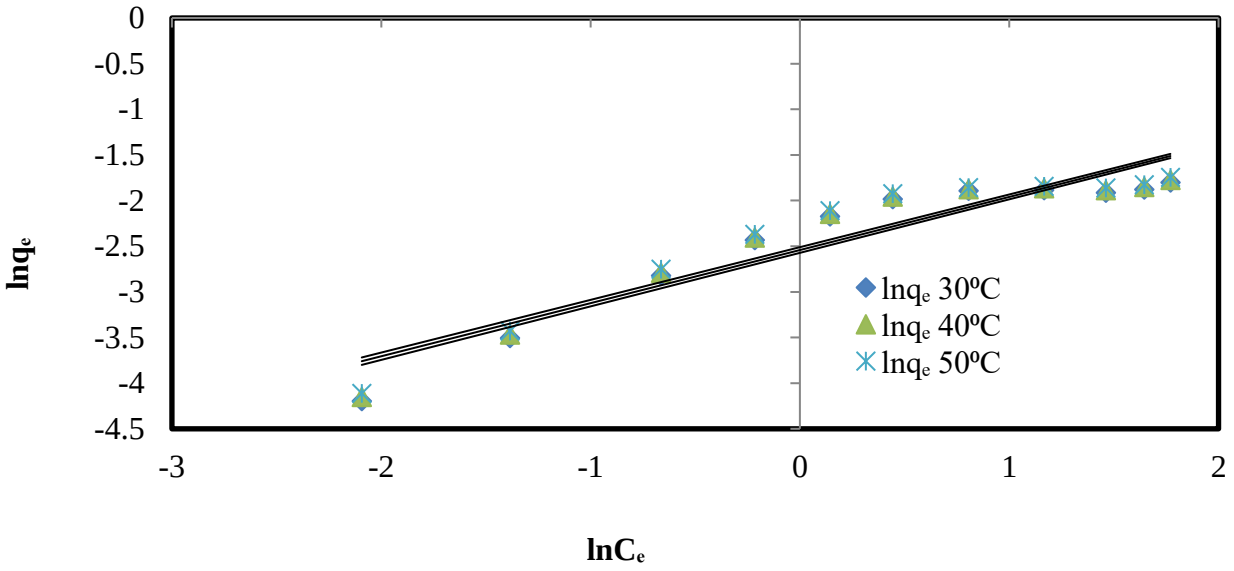

Figure 3.3.7(b) Graphical presentation on Freundlich isotherm curve for the sorption of 2-CP onto bagasse; 2-CP conc.: 0.5-10.0 mg/L, bagasse dose: 2.5 g; p. size: 150 µm; cont. time: 90 min and pH: 6.5 at 30-50°C

Table 3.3.8(c) Parameters of Freundlich and Langmuir isotherm models

Sorbents	Freundlich constants			Langmuir constants			Reference
	K_F	*1/n*	R^2	q°	*b*	R^2	
Modified fly ash	4.07	0.362	0.906	0.042	0.074	0.80	Moh. Malakootian 2015
Bagasse	0.075	0.577	0.88	0.36	0.47	0.99	Present study

Table 3.3.8(d) Isotherm constants for the biosorption of 2-CP onto bagasse

Name of compound	**2-CP**		
Temperature	30 °C	40°C	50°C
constants	Langmuir isotherm equation $1/q_e = 1/q° + 1/(bq°C_e)$		
q°mg/g	0.3613	0.3628	0.3672
b_L	0.4531	0.4719	0.4860
$R_L = 1/(1+bC_0)$	0.1808	0.1749	0.1706
R^2	0.995	0.995	0.995
Freundlich isotherm equation $\ln q_e = \ln k_F + (1/n) \ln C_e$			
1/n	0.586	0.581	0.577
N	1.704	1.721	1.733
K_f	0.0764	0.0788	0.0813
R^2	0.888	0.889	0.889

3.3.4.3 Isotherm models on the biosorption of 2-CP onto bagasse

The parameters obtained by applying experimental data to the Langmuir and Freundlich models are given in Table 3.3.8 (a-b) and Figure 3.3.7(a-b). Inspection of Tables 3.3.8(d): (i) the regression coefficients (R^2) 0.99 obtained from the Langmuir model is closer to 1 than that R^2(=88) of the Freundlich model in all cases, suggesting that the Langmuir isotherm fits better with the biosorption of 2-CP onto bagasse; (ii) the R_L values obtained are in all cases lie between 0 and 1 confirming that the biosorption is a favorable process. Hence, it can be concluded that the monolayer Langmuir isotherm is more suitable to explain the biosorption of 2-CP onto bagasse; (iii) the values of 1/n are less than 1 indicating that sorption of 2-CP on the surface of the bagasse is a favorable process. It is observed that the equilibrium data are very well represented by the Langmuir isotherm equation when compared to the Freundlich isotherm equation. The sorption equilibrium data fitted the Langmuir with correlation

coefficients (R^2), which are a measure of goodness-of-fit. The higher value of (b_L=0.45-0.48>k_F=0.076-0.081) b in all cases; the Langmuir constant, showed easy uptake of 2-CP from aqueous solution[22]. The sorption capacity q˚ is higher for the 2-CP-bagasse system (present study) than the 2-CP-modified fly ash system is shown in Table3.3.8(c). The *n* value, which reflects the intensity of biosorption, presents the opposite trend, but as seen from Table 3.3.8(d) for the sorbents and pollutants, *n* values were found high enough for separation. The higher fractional value of 1/n (0 <1/n < 1) signifies that the surface of the sorbent is heterogeneous in nature[33]. However, the Langmuir isotherm model is chosen for the estimation of maximum biosorption capacity corresponding to complete monolayer coverage on the agro wastes bagasse. Moreover, this also suggested that physisorption might be the rate-limiting step that controlled the overall sorption process which indicated goodness-of-fit for the Langmuir biosorption model. The maximum sorption capacity q˚ is 0.36 mg/g for the 2-CP-bagasse system, which appears to be significantly higher in comparison with modified fly ash[34]0.042 mg/g in table 3.3.8(c). Hence, the biosorption process of 2-CP using agricultural waste SCB as biosorbent proved the better performances.

3.3.5 Kinetics studies on biosorption of 2-CP onto bagasse

Experimental results of biosorption of 2-CP up to equilibrium point can be applied to study various models or empirical formulas like kinetics. Two types of kinetics are generally used, namely the pseudo-first order and pseudo-second order rate laws. Pseudo-first order kinetic hasbeen proposed by Lagergren[35]and Pseudo-second order kinetichas been introduced by Y. S Ho[36]. The kinetic rate laws become popular when Ho and McKay[37] analyzed several experimental results taken from the literature. They have concluded that for all of the systems are studied, in the vast majority in which comparison has been done about the superiority between 1st order and 2nd order rate constants[36]. It is explained that there are two main issues in the statistical treatment generally used in the literature and that the method systematically tends to favor either the pseudo-first order or pseudo-second order rate law. The remainder of this work is divided into three main sections. In the next section, the basic formulas for the statistical analysis of experimental data and model comparison are presented. The third section is dedicated to the presentation of results and their discussion. The two issues meet in analyses used in this literature are exposed and they are illustrated in the case of data obeying first-order kinetics. Then a reexamination of the experimental data treated in the original paper by Ho and McKay[37] is carried out a sample of data reported in the current literature is analyzed. Finally, a conclusion summarizes the main results of this work and presents some prospects. The studies of biosorption kinetic describe the 2-CP uptake rate which controls the residence time of sorbate uptake at the solid/solution interface. The Kinetic studies are set up in the laboratory in

batch method by adding a known amount of 2-CP to a required number of flasks that containing 100 ml of solution. Initial 2-CP solutions concentrations are 2.0-5.0 mg/L at 30 ˚C with 2.0 g bagasse. The pH of the system solutions is 6.5 for all experiments. The flasks are subsequently capped and shaken in a rotary shaker up to equilibrium time, 90 minutes. The experiments have been also done at 30-50˚C and constant concentration of 2-CP, 5.0 mg/L at the equilibrium time, 90 minutes. The experimental data have been employed in both the Pseudo-first-order and Pseudo-second-order kinetic models for the distinguished results cited in Table 3.3.9(f)

Table 3.3.9(a) Condition on kinetics studies of experimental data related to biosorption

1	Initial concentration of 2-CP	2.0-5.0 mg/L
2	pH Value of system solution	6.5
3	Particle size of the bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2-CP solution and bagasse	Up to 90 minutes
9	Operational temperatures	30-50˚C

3.3.5.1 Pseudo First-order kinetic (FOK) model for biosorption of 2-CP onto bagasse

The equation for pseudo-first order kinetics was introduced initially by Lagergren[35]. In the literature, it is generally used in the form proposed by Ho and McKay[37].

The pseudo-first-order kinetic model is widely used to predict the sorption kinetic and is defined as:

$$\ln (q_e - q_t) = \ln q_e - kt$$

Where q_e and q_t (mg/g) are the biosorption capacities of bagasse at equilibrium time and at any given time, t (minutes), respectively. K_{FOK} (min^{-1}) is the biosorption rate constant. To determine the constants of the pseudo-first-order kinetic model, a graph of $\ln(q_e - q_t)$ versus t is plotted as shown in Figure 3.3.8(a) at initial concentration of 2, 3, 4, and 5.0 mg/L and constant temperature, 30˚C and in Figure.3.3.8 (b) at 5.0 mg/L constant concentration and temperature 30, 40 and 50˚C. The experimental data are sited in Table 3.3.9 (b-c) and the constants are cited in Table 3.3.9(f).

Table 3.3.9(b) Experimental data of sorption 2-CP (2.0-5.0 mg/L) from aqueous solutiononto bagasse to apply on the pseudo FOK model at 30˚C

Time	Biosorption of 2-CP (%)				Time	$\ln(q_e-q_t)$			
	2ppm	3ppm	4ppm	5ppm		2ppm	3ppm	4ppm	5ppm
0	0	0	0	0	0	-2.5991	-2.2099	-1.9484	-1.7600
5	9.78	9.62	9.23	8.73	5	-2.7402	-2.3509	-2.0872	-1.8956
10	20.64	20.36	20.21	19.96	10	-2.9243	-2.5362	-2.2820	-2.1025
15	31.28	31.27	30.63	30.68	15	-3.1452	-2.7677	-2.5104	-2.3502
20	42.63	42.09	41.47	40.95	20	-3.4511	-3.0667	-2.8208	-2.6639
30	51.78	51.06	49.78	47.12	30	-3.7916	-3.4076	-3.1480	-2.9142
45	60.63	59.51	58.03	56.13	45	-4.2896	-3.8900	-3.6329	-3.4507
60	65.75	64.61	63.01	60.98	60	-4.7572	-4.3587	-4.1056	-3.9322
75	70.15	69.01	67.25	65.01	75	-5.4751	-5.0840	-4.8283	-4.6538
90	74.34	73.14	71.25	68.82	90				

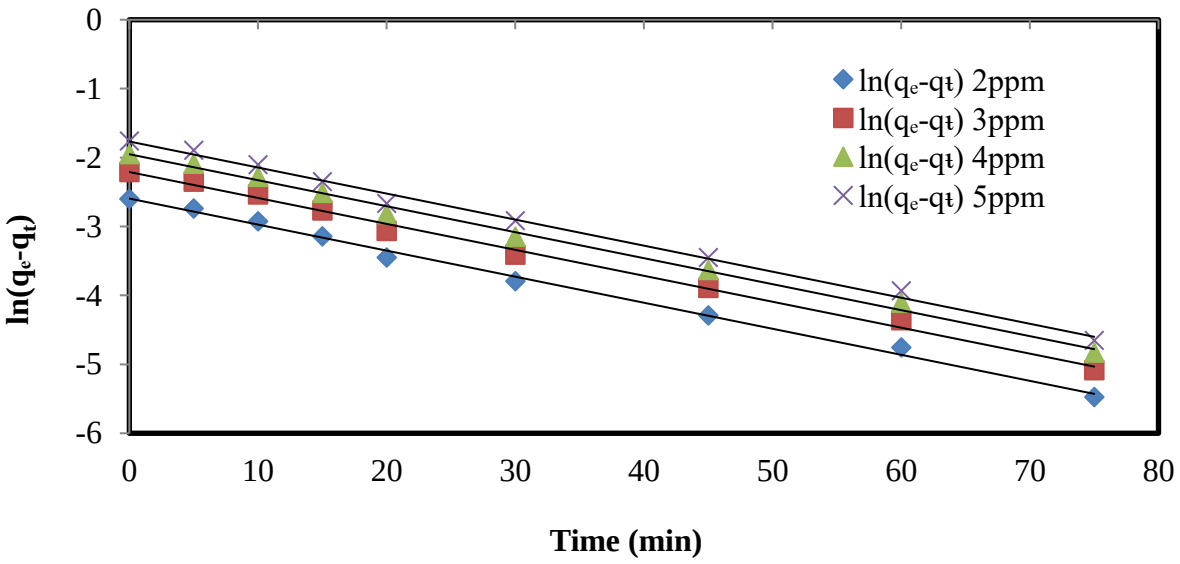

Figure 3.3.8(a) Graphical presentation on Pseudo FOK model for biosorption of 2-CP onto bagasse from (2.0-5.0 mg/L) aqueous systems; bagasse dose 2.0 g, p. size 150 µm, cont. time 90 min and pH 6.5 at 30ºC

Table 3.3.9(c) Experimental data on biosorption of 2-CP from (5.0 mg/L) aqueous solution onto bagasse to apply on the pseudo FOK model at 30-50 ºC

Time	Biosorptⁿof 2-CP (%)			Biosorptⁿ capacity of 2-CP (q_t)			Time	ln(q_e-q_t)		
	30˚C	40˚C	50˚C	30˚C	40˚C	50˚C		30˚C	40˚C	50˚C
0	0	0	0	0	0	0	0	-1.7600	-1.7233	-1.6742
5	8.73	9.18	9.29	0.0218	0.0230	0.0232	5	-1.8956	-1.8610	-1.8065
10	19.96	20.51	20.68	0.0499	0.0513	0.0517	10	-2.1025	-2.0620	-1.9969
15	30.68	31.21	31.69	0.0767	0.0780	0.0792	15	-2.3502	-2.2981	-2.2235
20	40.95	41.65	42.14	0.1024	0.1041	0.1054	20	-2.6639	-2.5990	-2.4998
30	47.12	48.11	49.76	0.1178	0.1203	0.1244	30	-2.9142	-2.8439	-2.7638
45	56.13	58.31	60.15	0.1403	0.1458	0.1504	45	-3.4507	-3.4204	-3.2948
60	60.98	63.25	65.18	0.1525	0.1581	0.1630	60	-3.9322	-3.8947	-3.7091
75	65.01	67.42	69.63	0.1625	0.1686	0.1741	75	-4.6538	-4.6127	-4.3144
90	68.82	71.39	74.98	0.1721	0.1785	0.1875	90			

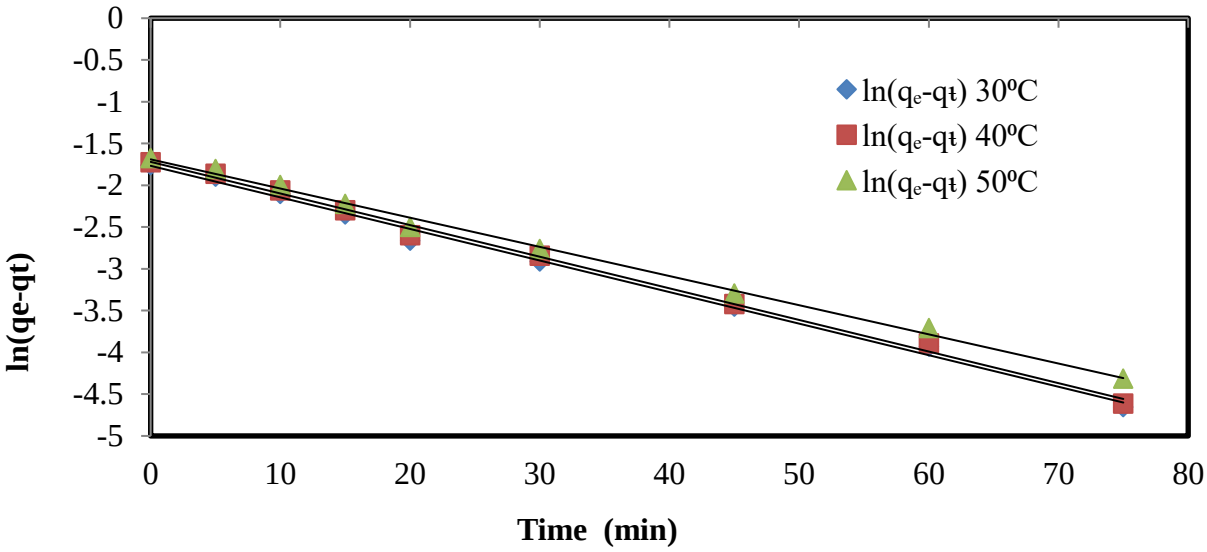

Figure 3.3.8 (b) Graphical presentation on Pseudo FOK model for biosorption of 2-CP onto bagasse from (5.0 mg/L) aqueous systems at 30- 50°C; bagasse dose 2.0 g, p. size 150 µm, cont. time min at pH 6.5

3.3.5.2 Pseudo second-order kinetic (SOK) model for biosorption 2-CP onto bagasse

Ho's proposed second-order modelhas been employed in the literature[35,] for the biosorption of 2-CP onto bagasse based on the biosorption capacity to differentiate the kinetics of a second-order rate expression.

The linearized form of the pseudo-second-order model is defined as follows:

$t/ q_t = 1/ (kq_e^2) + t/ q_e$

Where k is the rate constant of the pseudo-second-order, q_e (mg/g) is the amount of sorbed 2-CP by per unit of biosorbent at equilibrium time, and q_t is the amount of sorbed 2-CP by the sorbent at any time, t. k can be calculated from the slope and intercept of the plot of t/q_t against t. The graphical representations are shown in Figure 3.3.8(c) at initial concentration 2.0-5.0 mg/L of 2-CPand constant temperature 30˚C and in Figure 3.3.8(d) at variable temperatures are 30-50˚C and constant concentration, 5.0 mg/L. The experimental data are cited in table 3.3.9(d-e).

Table 3.3.9(d) Experimental data on biosorption of 2-CP from (2.0-5.0 mg/L) aqueous sol^{n}onto bagasse for apply on the Pseudo SOK model at 30˚C

Time	Biosorption of 2-CP (%)				Time	t/q_t			
	2ppm	3ppm	4ppm	5ppm		2 ppm	3 ppm	4 ppm	5 ppm
5	9.78	9.62	9.23	8.73	5	511.2474	346.5003	270.8560	229.0951
10	20.64	20.36	20.21	19.96	10	484.4961	327.4394	247.4023	200.4008
15	31.28	31.27	30.63	30.68	15	479.5396	319.7953	244.8580	195.5671
20	42.63	42.09	41.47	40.95	20	469.1532	316.7815	241.1382	195.3602
30	51.78	51.06	49.78	47.12	30	579.3743	391.6960	301.3258	254.6689
45	60.63	59.51	58.03	56.13	45	742.2068	504.1170	387.7305	320.6841
60	65.75	64.61	63.01	60.98	60	912.5475	619.0992	476.1149	393.5717
75	70.15	69.01	67.25	65.01	75	1069.138	724.5327	557.6208	461.4675
90	74.34	73.14	71.25	68.82	90	1210.654	820.3445	631.5790	523.1037

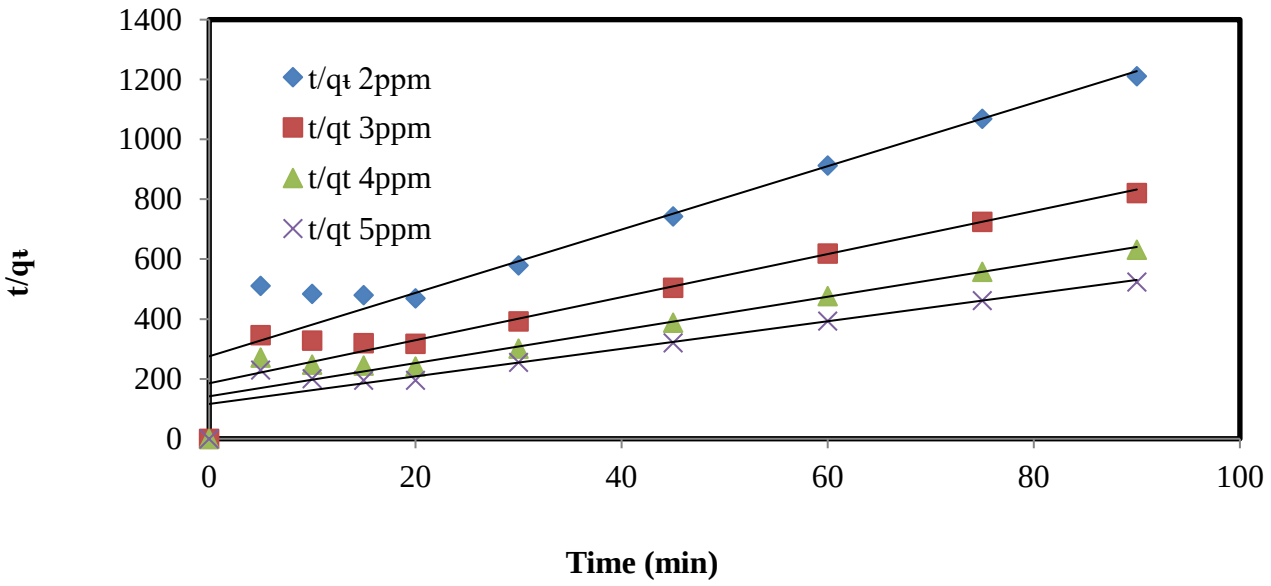

Figure3.3.8(c) Graphical presentation on Pseudo SOK model for biosorption of 2-CP onto bagasse from (2.0- 5.0 mg/L) aqueous systems; bagasse dose 2.0g, p. size 150 µm, cont. time 90 min and pH 6.5 at 30ºC

Table 3.3.9(e) Experimental data on biosorption of 2-CP from (5.0 mg/L) aqueous solution onto bagasse to apply on the pseudo SOK model at 30- 50˚C

Time	Biosorptionof 2-CP (%)			q_t			Time	t/q_t		
	30˚C	40˚C	50˚C	30˚C	40˚C	50˚C		30˚C	40˚C	50˚C
5	8.73	9.18	9.29	0.0218	0.0230	0.0232	5	229.0951	217.8649	215.2853
10	19.96	20.51	20.68	0.0499	0.0513	0.0517	10	200.4008	195.0268	193.4236
15	30.68	31.21	31.69	0.0767	0.0780	0.0792	15	195.5671	192.2461	189.3342
20	40.95	41.65	42.14	0.1024	0.1041	0.1054	20	195.3602	192.0768	189.8434
30	47.12	48.11	49.76	0.1178	0.1203	0.1244	30	254.6689	249.4284	241.1576
45	56.13	58.31	60.15	0.1403	0.1458	0.1504	45	320.6841	308.6949	299.2519
60	60.98	63.25	65.18	0.1525	0.1581	0.1630	60	393.5717	379.4466	368.2111
75	65.01	67.42	69.63	0.1625	0.1686	0.1741	75	461.4675	444.9718	430.8488
90	68.82	71.39	74.98	0.1721	0.1785	0.1875	90	523.1037	504.2723	480.1280

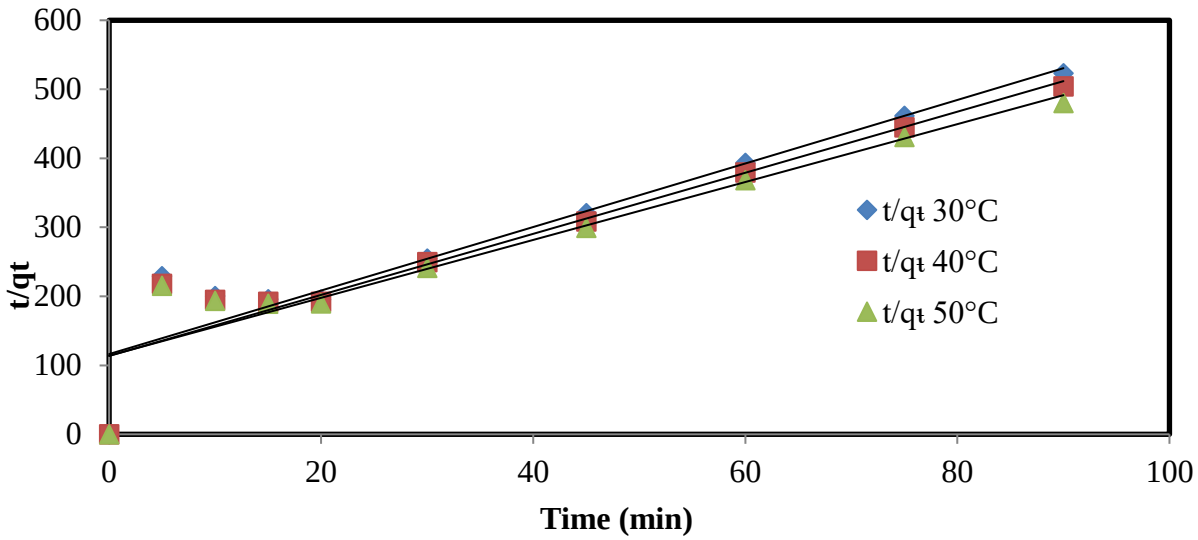

Figure 3.3.8 (d) Graphical presentation on Pseudo FOK model for biosorption of 2-CP onto bagasse from (5.0 mg/L) aqueous systems at 30- 50˚C; bagasse dose 2.0 g, p. size 150 µm, contact time 90 min at pH 6.5

By comparing the two groups of graphical charts in Figure 3.3.8(a-d) have been observed that the correlation coefficients (R^2) 0.99 for pseudo-first order model were higher than the R^2 (= 0.88) values of the pseudo-second order and experimental equilibrium sorption capacity q_e is closer to calculated values for pseudo first-order kinetic model than that of Second order kinetic in all cases which indicated a better fit for the pseudo-first-order kinetic model. Hence, the adsorption process of 2-CP using sugarcane bagasse followed the pseudo-first-order kinetic model. The kinetic isotherm rate constants are shown in Table 3.3.9(e); graphical charts in Figure 3.3.8(a-b) and Figure 3.3.8(c-d). It is observed that the experimental data are very well represented by the Pseudo first-order kinetic studies when compared to the Pseudo second order kinetics.

Table 3.3.9(f) Kinetics constants for the biosorption of 2-CP onto bagasse

Pseudo first order biosorption kinetic equation $\ln(q_e-q_t) = \ln q_e - kt$							
Constants	Concentration of 2-CP (mg/L)				Temp. of the systemsolution		
	2	3	4	5	30 °C	40 °C	50 °C
K_{FO}	0.037	0.037	0.037	0.037	0.037	0.037	0.034
q_{eFOK} cal.	0.0747	0.1098	0.1421	0.1710	0.1710	0.1792	0.1847
q_{eFOK} exp.	0.0743	0.1097	0.1425	0.1720	0.1720	0.1785	0.1875
R^2_{FOK}	0.995	0.995	0.994	0.994	0.994	0.996	0.996
Pseudo second order kinetic equation, $t/q_t = 1/(kq_e^2) + t/q_e$							
K_{SOK}	0.4068	0.2793	0.2163	0.1823	0.1823	0.1725	0.1544
q_{eSOK} cal.	0.0945	0.1390	0.1805	0.2173	0.2173	0.2260	0.2384
q_{eSOK} exp.	0.0743	0.1097	0.1425	0.1720	0.1720	0.1785	0.1875
R^2_{SOK}	0.888	0.889	0.889	0.888	0.888	0.889	0.878

3.3.6 Application of the developed treatment system

The textile and agrochemical industries are known to be the largest polluting industries in Bangladesh and effluents of the industries contain a large amount of chlorinated phenolic compounds. The utility of the locally available bagasse has been tested with industrial effluents around Dhaka City, Bangladesh. Two industrial effluent samples have been collected in a glass collection bottle with Teflon-lined caps directly from the outlet of a dying industry (Color Thread Company) located at Plot No-23, Shampur, Kadamtali I/A, Dhaka and Agrochemical industries (EH & agro vet. Ltd), Dlhaj mansion plot#151/ka, Pisciculture H.S. Shyamoli Dhaka-1207, Dhaka, Bangladesh during operation of the plant. The samplesare immediately brought to the laboratory to be placed in a cool place. The 2-CP contents have been analyzed by the modified 4-aminoantipyrine method. It is found that the contents in samples 1 and 2 are 6.95 and 9.72 mg/L 2-CP, respectively. The characteristics of the effluents and treatment results have been shown in Table 3.3.10(b-c). The pH of the effluent has been adjusted to 6.5, bagasse dose 2.0 g/100 ml is taken at equilibrium time, 90 minutes. The sorption efficiency of 2-CP using bagasse is found satisfactory and are about 90 and 88% sorption occur for samples 1 and 2, respectively. The desorption efficiencies with 100 ml of 1M NaOH are 89 and 93% respectively of sample 1 and 2 respectively. These results indicate that the 2-CP is successfully removed from practical 2-CP containing effluent, and the sorbed 2-CP has been recovered from the surface of bagasse. Based on the present treatment system, wastewater treatment of 20 L of 2-CP containing effluent will be achievable with 400 g of bagasse in about 90 minutes of treatment time.

Table: 3.3.10 (a): Condition of biosorption to apply on developed system

1	Particle size of bagasse	150 µm
2	Volume of potassium ferricyanide solution	0.7 ml
3	Volume of 4-AAP solution	0.8 ml
4	Volume of buffer solution (pH 10)	1.1 ml
5	Bagasse dose	2.0 g
6	Contact time of solution and bagasse	90 minutes
7	Temperature of the system solution	30˚C
8	Concentration of 2-CP in effluents from different industries	Unknown conc.
9	pH value	6.5

Table 3.3.10(b): Effluent treatment data

Sample No	Concentration (mg/L)
Sample 1 (Color Thread Company)	6.95
Sample 2 (EH & agro vet.ltd)	9.72
Sample 1 1 (After one time treatment of sample 1)	0.70
Sample 12 (After one time treatment of sample 2)	1.17

Table 3.3.10(c): Effluent treatment results on biosorption and desorption

	Sample -1	Sample -2
pH	7.9	7.3
Initial concentration of 2-CP (mg/L)	6.95	9.72
Final concentration of 2-CP (mg/L)	0.70	1.17
Biosorption (%)	90	88
Desorption (%)	89	93

3.3.7 Desorption of 2-CP and regeneration of biosorbent

Recovery of the sorbed material and regeneration of the biosorbent are also important aspects of wastewater treatment. Attempts were made to desorbed 2-CP from bagasse surface with various eluents, such as hydrochloric and nitric acid solutions and base solution sodium hydroxide. This desorption process has been performed using the batch method. 2.0 g of spent sorbent bagasse after sorption at pH 6.5 is shaken with 100 ml of 1M NaOH, 1M HCl, and 1M HNO_3 for regeneration, which were shaken for 90 minutes equally and about 83.45, 70.32, and 57.48% desorbed of the sorbed 2-CP (sorbed from the initially present 5.0 mg/L 2-CP solution) from the sorbent bagasse in a single step, respectively. Although the achievement of arsenic,

elution using strong acidic or alkaline solutions has been reported in the literature[25], the present work showed that effective desorption has been obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. In general, the desorption efficiency of 2-CP tended to increase with increase in desorption time. Consequently, solution of sodium hydroxide is useful for the 2-CP desorption from the surface of bagasse.

The removal (adsorption) efficiency was calculated using the equation,

Percentage of desorbed 2-CP= $\frac{\text{Amount desorbed after Desorption}}{\text{Amount biosorb before Desorpton}} \times 100$

Table 3.3.11(a) Conditions on the desorption of 2-CP from bagasse

1	Initial concentration of 2-CP	5.0 mg/L
2	pH of solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.7 ml
5	Volume of 4-AAP solution	0.8 ml
6	Volume of buffer solution (pH 10)	1.1 ml
7	Bagasse dose	2.0 g
8	Contact time of solution and bagasse	90 minutes
9	Temperature effect	30˚C

Table 3.3.11(b) Before desorption

Initial conc. 2-CP (mg/L)	Absorbance	Concentration (mg/L)	% removal	% remaining
5.0	0.1723	1.559	68.82	31.18

Table 3.2.11 (c) After Desorption

Desorbing agent	Initial conc of 2-CP (mg/L)	Absorbance	Concentration (mg/L)	% Regenerated
1N NaOH	3.441	0.3177	2.87	83.45
1N HCl	3.441	0.2690	2.42	70.32
1N HNO_3	3.441	0.2213	1.98	57.48

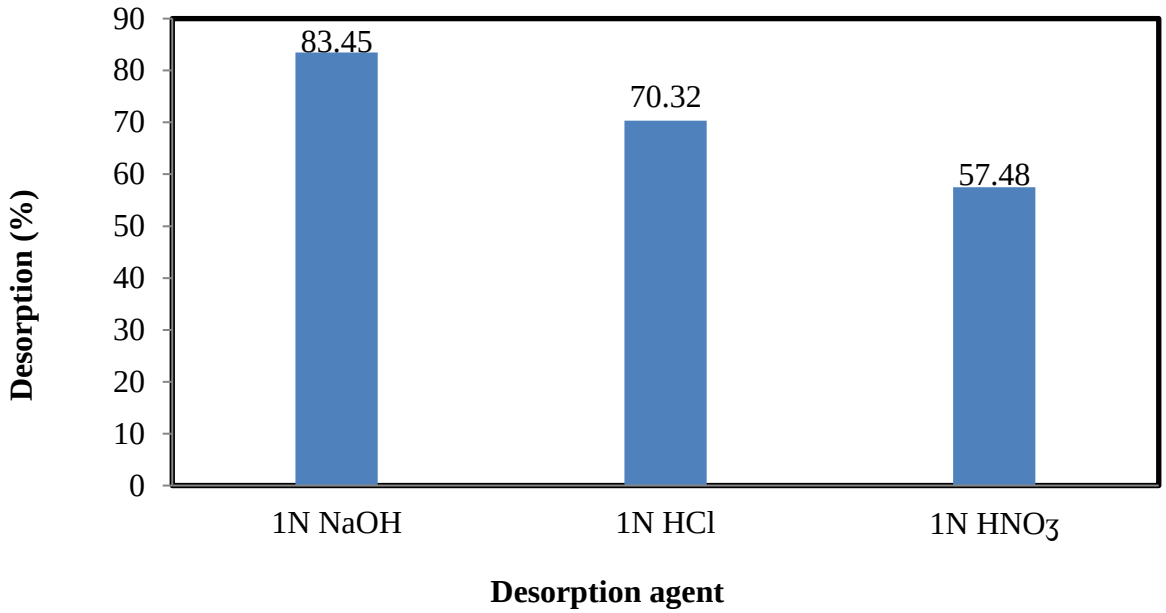

Figure 3.3.9: Graphical presentation on recover of 2-CP from biosorbent bagasse 2-CP: 5.0 mg/L; bagasse: 2.0 g; particle size 150 µm; contact time: 90 min and pH: 6.5 at 30°C

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Chapter 4

Biosorption of 4-chlorophenol from aqueous system using agricultural wastes bagasse

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Biosorption of 4-chlorophenol from aqueous system using agricultural waste bagasse

4.1 Introduction

The principal sources of environmental pollution with chlorophenols are effluent from petrochemical units, coal gasification sites, oil refineries, textiles, pesticides, and pharmaceutical industries[1]. Para-chlorophenol (p-CPh) is a phenolic compound recognized as a priority pollutant by the United States Environment Protection Agency (USEPA) due to its toxicity, carcinogenicity, and mutagenicity to living organisms[1-3]. The maximum allowable limit of p-CPh in potable water is 0.5 mg/L[1]. The used methods for remediation of this pollutant are electrochemical oxidation, photocatalytic degradation, ultra-filtration, wet oxidation, solvent extraction, adsorption, biosorption, and membrane filtration[4,5]. Among the physicochemical methods, biosorption process has been widely applied as a treatment technique for organic pollutants[6,7]. This method is one of the best treatment alternatives for the mitigation of pollutants like p-CPh from industrial effluents and wastewater, because it is possible to recover the sorbent and sorbate. Since sorption onto activated carbon commonly used technique for the removal of toxic organic pollutants but commercial activated carbon is expensive and performs variance in use. So, attempts have been taken to utilize low cost, naturally occurring biosorbents including rice straw, rice husk, fly ash, orange peels, algae, bagasse, coconut fiber, coconut coir, pulse straw, pulse husk, maize cob, maize husk/maize ear, garlic husk etc for mitigation of organic pollutants[8,9] like p-CPh.

Sugarcane bagasse (SCB) is one of the most cost-effective and available agro-industrial waste, is a product of tropical regions[9]. Bangladesh is one of the top sugarcane production countries and by-product bagasse is available here[10]. In Bangladesh, every year 1.5 lakh tons of sugar and 8.0 lakh tons of SCB is found as by-product[10]. SCB can be used as biosorption of targeted p-CPh sorbates from aqueous system, including toxic heavy metals, dyes, petroleum, organic nutrients[9], and other chlorinated phenolic compounds[11]. Bagasse is a fibrous waste that contains various functional groups that can bind pollutant ions onto the bagasse surface. Chemically modified forms of SCB are time and energy consumed and comparatively expensive and is not eco-friendly. So, the present work has been done without using any chemical to modify bagasse for biosorption of p-CPh.

The biosorption efficiency depends on the bagasse dose, contact time, bagasse particle size, and initial p-CPh concentration, pH, and temperature of the system solution. Many of review

articles have discussed the various low-cost biosorbents; most of them can sorb sorbate p-CPh as well as focusing on metals, dyes, or phenol. In this work, we aim to present SCB as an eco-friendly, low-cost biosorbent along with describing the techniques utilized for biosorption of the p-CPh pollutant from an aqueous system using no chemical. Moreover, the present article provides an extensive use of the literature regarding the biosorption potentiality of SCB in this relative topic which will guide a wide range of research in this area.

4.2 Materials and Methods

The contents of sub-para 4.2.1 onmaterials, 4.2.2 on apparatus and equipments, 4.2.3 on experimental procedures and 4.2.4 on preparation of solutions have been mentioned in para 2.2 of chapter 2.

4.2.5 Operational procedures

The estimation of 4-chlorophenol (4-CP) has been done spectrophotometrically by the modified 4-aminoantipyrine (4-AAP) method using Shimadzu UV-1700 double beam spectrophotometer. For the modification of the process detailed experiments are carried out varying all parameter as follows:

Preliminary experiments:

Preliminary experiments are carried out for the spectrophotometric estimation of 4-CP following the modified 4-AAP method with pH 10.0 solutions and absorbance has been measured at 506 nm which does not give a satisfactory result. Investigation on absorbance revealed that the maximum absorption is at 506 nm and the required time for full-color development is 25 minutes. It is therefore decided to modify the procedure first and then to apply the modified method for the estimation of 4-CP. In an attempt to modify the 4-AAP method for the spectrophotometric estimation of 4-CP, detailed studies have been carried out including the investigations on the development of color using the sorption spectra, optimum solution media, suitable reagent concentration, adherence to Beer's law etc, so that the modified method may be applied for the estimation of trace amount of 4-CP in the system solution.

General Procedure (Direct Spectrophotometry):

An appropriate aliquot of the test solution containing a definite amount of 4-CP is taken in a 25 ml volumetric flask. This is followed by the addition of 0.2 ml, 0.7 ml, 1.1 ml buffer concentrate (pH10) solution, and 0.9 ml 4-AAP and 0.6 ml potassium ferricyanide solutions in the system solution. The samples are then diluted with double distilled water, up to the mark

(25 ml). A reagent blank is prepared under identical conditions, against which the absorbance is measured at the wavelength of maximum absorption (A max) after 15 minutes.

Color Reaction:

Preliminary experiment has showed that 4-CP does not give any appreciable color with 4-AAP in presence of potassium ferricyanide in an acidic medium. But in alkaline medium 4-CP gives a deep-brownish red color whose intensity gradually increases with the increasing amount of buffer concentrate (pH 10) solution up to 1.1 ml, beyond which the intensity sharply decreases. This is the reason to modify the spectrophotometric method for the detection of trace amounts of 4-CP.

4.2.6 Modification of 4-AAP method for determination of 4-CP

Effect of volume of potassium ferricyanide (2% W/V) solution on color development:

The result of potassium ferricyanide (2%W/V) solution is shown in Table 4.1(b) which indicates that 0.6 ml of potassium ferricyanide solution is sufficient for the development of maximum color intensities of the aqueous system containing 5.0 mg/L 4-CP solution. The results are graphically represented in Figure 4.1. This indicates that an amount higher than 0.6 ml of the potassium ferricyanide solution decreases the color intensity of the system. Therefore, 0.6 ml potassium ferricyanide (2% W/V) solution is used for the optimum color development of the system containing 5.0 mg/L 4-CP solution.

Table 4.1 (a) Conditions on the effect of potassium ferricyanide for maximum color

Volume of 4-AAP solution	1.0 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 4-CP	5.0 mg/L
Volume of potassium ferricyanide solution (ml)	Different Volume
Color development time	20 minutes
Total volume of system solution	25 ml

Table 4.1(b) Effect of volume of potassium ferricyanide solution for development of maximum color intensity

Volume of potassium ferricyanide (ml)	λ_{max}(nm)	Absorbance
0.2	506	0.3591
0.4		0.4912
0.5		0.5298
0.6		**0.5378**
0.7		0.5301
0.8		0.5213
0.9		0.5138
1.0		0.4968
1.2		0.4527
1.3		0.4328
1.4		0.3977

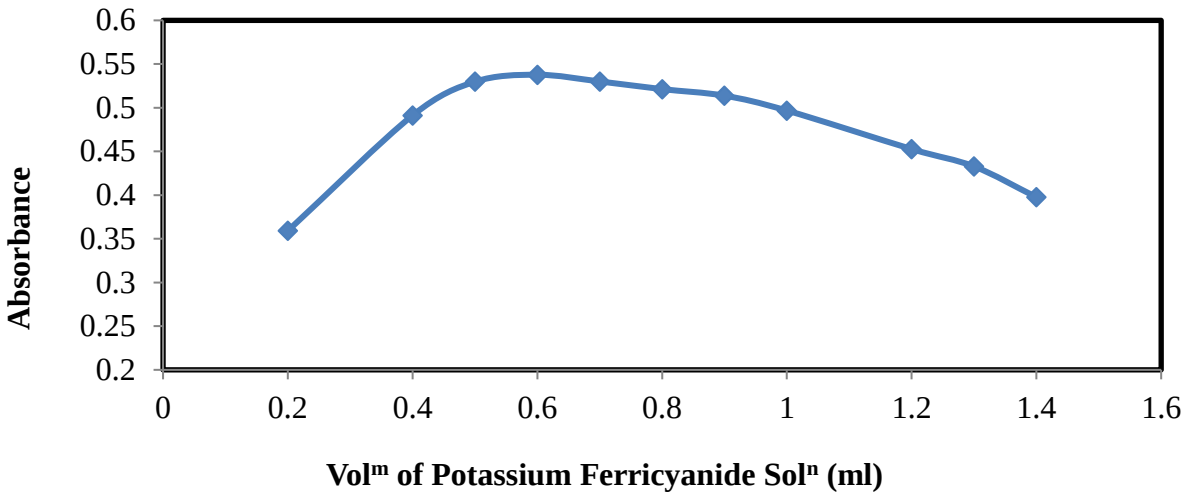

Figure4.1 Effect on volume of potassium ferricyanide (2.0% W/V) solution for maximum color intensity; 4-CP concentration: 5.0 mg/L; 4-AAP (0.5% W/V) solution: 1.0 ml; buffer (pH10) solution: 1.0 ml; time: 20 min at λ_{max}: 506 nm

Effect of 4-AAP solution on color development with 4-CP

The result of the 4-AAP (0.5% W/V) solutions is shown in Table 4.2(b) which indicates that 0.9 ml of 4-AAP (0.5%W/V) solution is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L of 4-CP solution. The results are graphically represented in Figure 4.2. This indicates that an amount higher than 0.9 ml of 4-AAP solutions decreases the color intensity of the system. Therefore, 0.9 ml of 4-AAP (0.5% W/V) solution has been used for the maximum color development of the system containing 5.0 mg/L of 4-CP solution.

Table 4.2(a) Condition on effect of 4-AAP for color development

Volume of 4-AAP solution (ml)	Different volume
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 4-CP	5.0 mg/L
Volume of potassium ferricyanide solution	0.6 ml
Color development time	20 minutes
Total volume of aqueous system	25 ml

Table 4.2(b) Effect on volume of 4-AAP solution (0.5% W/V) for maximum color intensity

Volume of 4-AAP solution (ml)	λ_{max} (nm)	Absorbance
0.4	506	0.3275
0.5		0.3741
0.6		0.4311
0.7		0.4817
0.8		0.5233
0.9		**0.5409**
1.0		0.5378
1.2		0.5181
1.3		0.4919
1.4		0.4667

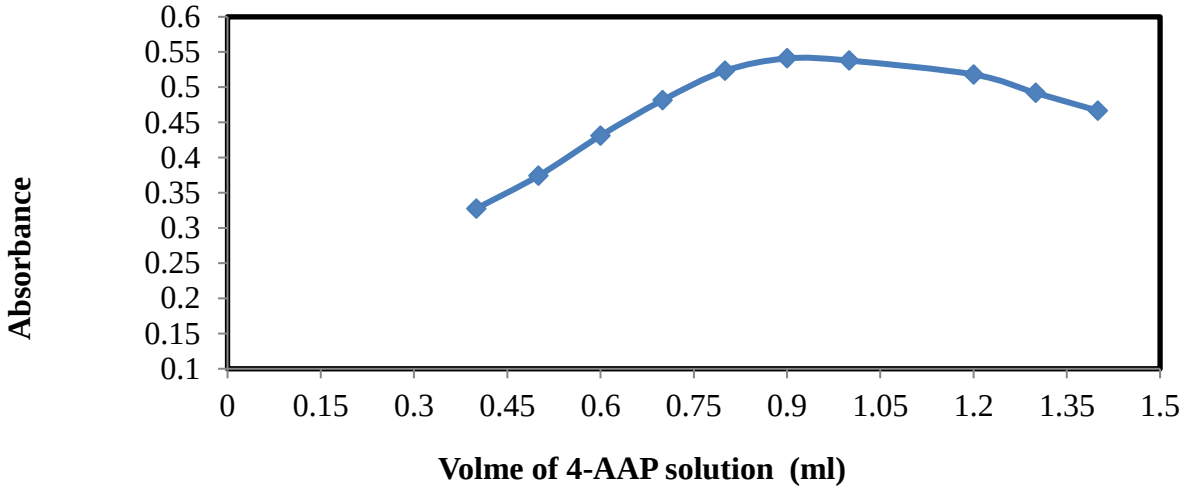

Figure4.2 Effect of volume of 4-AAP sol^n (0.5% W/V) on development of maximum color intensity; 4-CP conc.: 5.0 mg/L; PFC (2.0% w/v) sol^n: 0.6 ml; buffer (pH10) sol^n: 1.0 ml; reaction time: 20 min at λ_{max}: 506 nm

ESffect of buffer solution (pH 10) for maximum color development with 4-CP

The result of the buffer solution (pH10) is shown in Table 4.3(b) which indicates that 1.0 ml of buffer solution (pH10) is sufficient for the development of maximum color intensity of an aqueous system containing 5.0 mg/L 4-CP solution. The results are graphically represented in Figure 4.3. The figure depicts that volume beyond 1.0 ml of buffer solution (pH10) decreases

the color intensity of the system solution. Therefore, 1.0 ml of buffer solution (pH10) is used for the optimum color development of the system containing 5.0 mg/L solution of 4-CP.

Table 4.3(a) Condition on effect of buffer solution (pH 10) for color development

Volume of 4-AAP solution	0.9 ml
Volume of buffer solution (pH 10), ml	Different volume
Concentration of 4-CP	5.0 mg/L
Volume of potassium ferricyanide solution	0.6 ml
Color development time	20 min
Total volume of the aqueous solution	25 ml

Table 4.3(b) Effect on volumeof buffer solution (pH 10) for maximum color intensity

Volume of buffer solution (pH 10) ml	λ_{max} (nm)	Absorbance
0.4	506	0.3887
0.5		0.4191
0.6		0.4481
0.7		0.4829
0.8		0.5165
0.9		0.5291
1.0		**0.5409**
1.2		0.5185
1.3		0.5073
1.4		0.4909
1.5		0.4803
1.7		0.4511

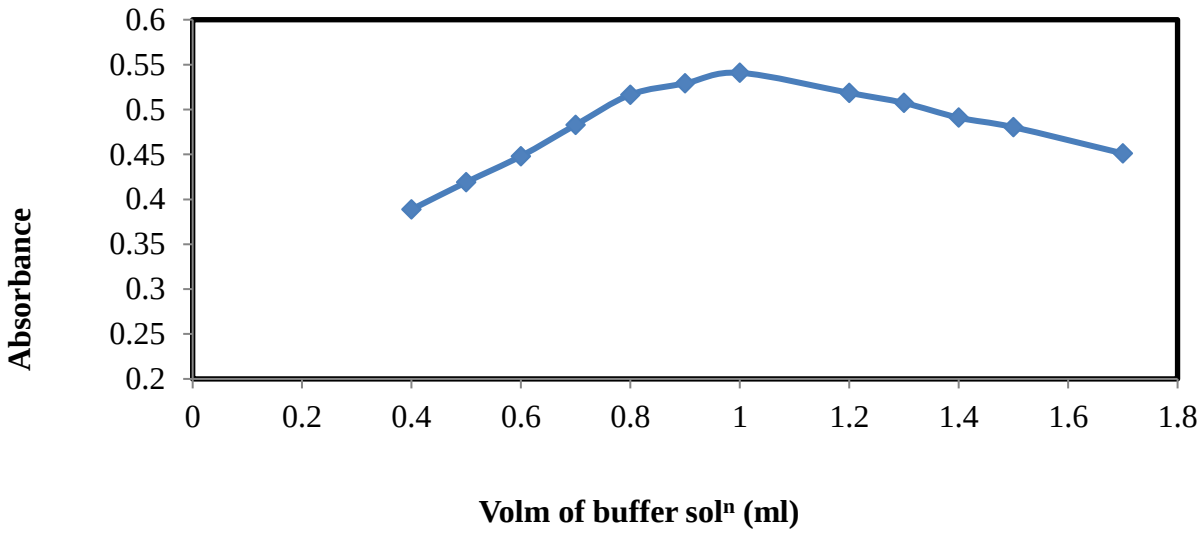

Figure 4.3 Effect on volume of buffer (pH 10) soln for maximum color intensity; 4-CP conc.: 5.0 mg/L; 4-AAP (0.5% W/V) soln: 0.9 ml; PFC (2.0% W/V) soln: 0.6 ml; color development time: 20 min and λ_{max}: 506 nm at 30°C

Effect of time for color development of 4-CP to reach equilibrium

The result of time variation is shown in Table 4.4(b) which indicates those 25 minutes is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L 4-CP solution with 0.6 ml potassium ferricyanide solution, 0.9 ml 4-AAP, 1.0 ml buffer solution (pH10). The results are graphically represented in Figure 4.4. The figure indicates that 25 minutes is sufficient for the stable color intensity of the system solution. Therefore, 25 minutes is used for the optimum color development of the system containing 5.0 mg/L of 4-CP solution.

Table 4.4(a) Condition on effect of reaction time for color development

Volume of 4-AAP solution	0.9 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 4-CP	5.0 mg/L
Volume of potassium ferricyanide solution	0.6 ml
Color development time (minutes)	Different time
Total volume of the system solution	25 ml

Table 4.4(b) Effect on reaction time for maximum color intensity

Time (minutes)	λ_{max} (nm)	Absorbance
10	506	0.4809
15		0.5106
20		0.5409
23		0.5499
25		**0.5563**
30		0.5358
35		0.5119
40		0.4978

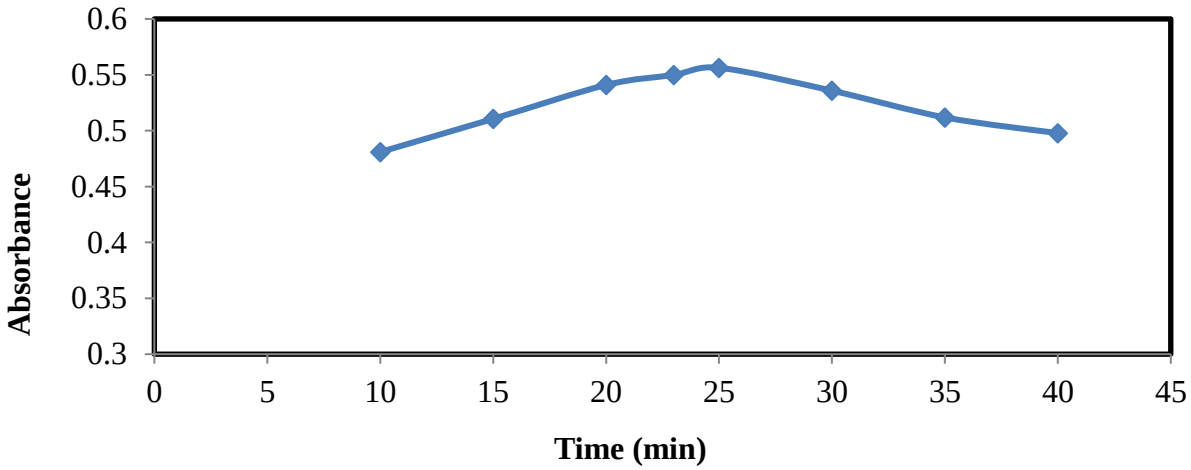

Figure4.4 Effect of reaction time on color intensity; 4-CP conc.: 5.0 mg/L; 4-AAP (0.5% w/v) sol^n: 0.9 ml; PFC (2.0% w/v) sol^n: 0.6 ml; buffer (pH 10) sol^n: 1.0 ml and λ_{max}: 506 nm at 30°C

4.2.7 Preparation of a standard calibration curve for determination of 4-CP

A standard curve is a graph relating a measured optical density to the concentration of the substance of interest in "known" samples. The standard calibration curve is drawn by plotting absorbance (on the Y-axis) versus concentration (on the X-axis). The result of a standard calibration curve is shown in Table 4.5(b). Standard curve is determined in an aqueous system containing 5.0 mg/L of 4-CP solution with 0.6 ml potassium ferricyanide solution 2% (W/V), 0.9 ml, 4-AAP solution 0.5% (W/V) and 1.0 ml buffer (pH 10) at room temperature. The results are graphically represented in Figure 4.5.

Table 4.5(a) Experimental condition for preparation of standard calibration curve

Volume of 4-AAP solution	0.9 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 4-CP (mg/L)	Different concentration
Volume of potassium ferricyanide solution	0.6 ml
Color development time	25 Minutes
Total volume of the solution	25 ml

Table 4.5(b) Evaluating the optimum value for standard calibration curve

Concentration 4-CP (mg/L)	λ_{max} (nm)	Absorbance
1	506	0.1265
2		0.2329
3		0.3594
4		0.4258
5		0.5563
6		0.6188
7		0.6985
8		0.7597
9		0.9111
10		1.0346

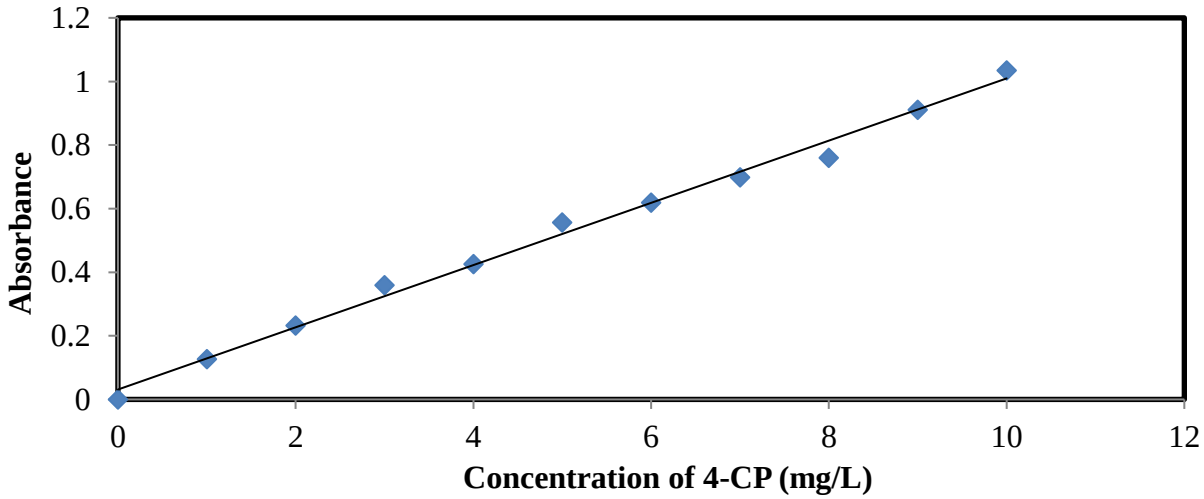

Figure 4.5 Standard calibration curve for determination of 4-CP concentration of 1.0-10.0 mg/L; 4-AAP (0.5% w/v) sol^n: 0.9 ml; PFC (2.0 %w/v) sol^n: 0.6 ml; buffer (pH10) sol^n: 1.0 ml and time: 25 min at λ_{max}: 506

4.3 Results and Discussion

4.3.1 Performances of biosorbents

Preliminary evaluation of performances of nine agricultural wastes (Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk) has been taken for the biosorption of 4-CP from system solutions. The biosorption of 4-CP has been performed with 5.0 mg/L concentrate 4-CP, 1.0 g sorbent of 150 µm particle size, maintaining pH value at 6.5 for 60 minutes contact time at 30˚C (ambient temperature). The biosorption efficiency of 4-CP onto eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw and rice husk are 15.8%, 14.92%, 16.0%, 31.05%, 16.5%, 34.1%,17.7%, 31.1% and 31.3% respectively. Among these, eight sorbents have lesser sorption efficiencies from bagasse. So, those are not selected for further experiments. Hence, agro-biowaste bagasse is taken as a comparatively more efficient biosorbent for the biosorption of 4-CP from the water system.

4.3.2.1 Effect of bagasse dose on biosorption of 4-CP

Study on biosorbent doses is an important parameter because it determines the efficiency of sorbent for a given initial concentration of the sorbate solution[12]. The biosorption of 4-CP onto bagasse has been carried out at different sorbent doses keeping other parameters constant. biosorbent dose has been varied from (0.5-5.0) g/0.1L. These experiments have been performed with an initial concentration of 5.0 mg/L of 4-CP and the pH of the solution is 6.5 at 30^{o}C. The relationship between sorbent dose and substrate removal for the same initial concentration of 4-CP is presented in figure 4.3.1. The figure depicts that with increase in the biosorbent doses upto 2.5 g reveals a higher biosorption of 4-CP, but with an increase in biosorbent dose higher than the 2.5 g, the biosorption efficiencies are negligible and the sorptions are marginal and become almost constant[13]. The biosorption of 4-CP increases with an increase in biosorbent dose up to 2.5 g and after this certain dose (2.5 g) biosorption does not increase. The increase of biosorption seems that there are still active sites on the surface of the sorbent that are unsaturated[13]. If the dose is more than the optimum amount (2.5 g) in the process unit, stoichiometrically, the dose is more than the equivalent amount of 4-CPin the system solution. For this reason, biosorption does not increase with the increase in sorbent dose. With increasing sorbent dose from 0.5 to 2.5 g, the sorption is increased from 13.62 to 60.04%. Since an increase in the sorption with the increase of sorbent doses up to 2.5 g/0.1 L and this can be attributed to a greater surface area and the availability of more sorption sites with completion of sorption saturation mode[14]. Therefore, the optimum biosorbent dose has been taken as 2.5 g/0.1 L for subsequent experiments.

Table 4.3.1(a) Condition on effect of sorbent bagasse dose for biosorption of 4-CP

1	Initial concentration of 4-CP	5.0 mg/L
2	Operational temperature	30 ˚C
3	pH Value of the system solution	6.5
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Contact time of solution and bagasse	60 minutes
8	Parliclesize size of bagasse	150 µm
9	Bagasse dose (g)	Different dose

Table 4.3.1(b) Effect of bagasse dose on biosorption of 4-CP from aqueous system

Bagasse dose (g)	Absorbance	Concentration (mg/L)	Bi**o**sorption of 4-CP (%)
0.5	0.4601	4.319	13.62
1.0	0.3953	3.295	34.10
1.5	0.3064	2.559	48.83
2.0	0.2545	2.188	56.25
2.5	0.2326	1.998	60.04
3.0	0.2720	1.998	60.04
3.5	0.2720	1.998	60.04
4.0	0.2720	1.998	60.04
4.5	0.2720	1.998	60.04
5.0	0.2720	1.998	60.04

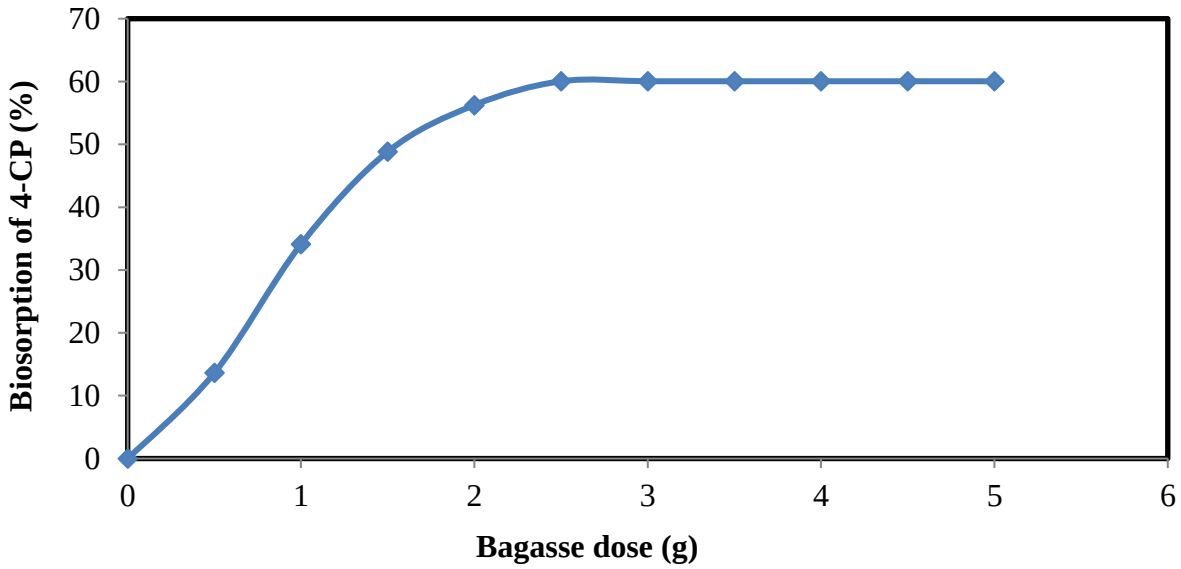

Figure 4.3.1 Graphical presentation of effect of sorbent bagasse doses for biosorption of 4-CP; 4-CP conc.: 5.0 mg/L; particle size: 150 µm; contact time: 60 min and pH: 6.5 at 30 °C

4.3.2.2 Effect of contact time on biosorption of 4-CP onto bagasse

Batch experiments have been carried out to investigate the effect of contact time on biosorption of 4-CP onto bagasse. The biosorption percentage versus contact time for the uptake of 4-CP onto bagasse waste-based functional group is indicated in figure 4.3.2. The figure depicts that the required equilibrium time for the biosorption of 4-CP onto bagasse is almost 120 minutes. No significant change in biosorption of 4-CP has been observed after 120 to 300 minutes. Therefore, the equilibrium point for the biosorption process has been determined 120 minutes. Characterization of the contact time is denoted by the rapid increase in the biosorption of 4-CP at the beginning 60 minutes, followed by a slower uptake till reach to equilibrium. At the equilibrium point where the rate of biosorption onto the bagasse surface is equal to the desorption from the same surface. The dynamic equilibrium stage acts as the determinant time to evaluate the biosorption efficiency of bagasse for the 4-CP[15]. It can be seen that the initial biosorption is attributed to the rapid attachment of 4-CP to the surface of the bagasse by surface mass transfer. At this stage biosorption of 4-CP is detrmined at about 80% in all cases. The fast uptake of 4-CP at the beginning of the biosorption time can be due to the availability of large numbers of vacant sites on the biosorbent surface[9]. With the increase of initial contact time, these vacant sites are saturated with 4-CP and biosorption efficiency is high[16]. The second stage is slower; possibly because biosorption sites become in lesser along with available external sites are already occupied the system. An asymptotic trend prevails after 120 minutes regardless of the initial concentration of 4-CP applied to the system. Such findings reveal the benefits of using this low-cost biosorbent or so-called eco-sorbent for the treatment of industrial aqueous effluents rich in organic pollutants in general and 4-CP in particular. Therefore, in this study, the equilibrium contact time, 120 minutes is selected for the subsequent experiments.

Table 4.3.2(a) Condition on contact time for sorption of 4-CP onto bagasse

1	Initial concentration of 4-CP	5.0 mg/L
2	Operational temperature	30˚C
3	pH value of the system solution	6.5
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Contact time of 4-CP solution and bagasse (minutes)	Different time
9	Particle size of bagasse	150 µm

Table 4.3.2(b) Effect of time on the biosorptionof 4-CP onto bagasse

Time, minutes	Absorbance	Concentration of 4-CP (mg/L)	Biosorptionof 4-CP (%)
5.0	0.5113	4.60	8.05
10	0.4547	4.27	14.65
15	0.4097	3.85	22.99
20	0.3609	3.39	32.13
30	0.3589	2.99	40.17
45	0.2801	2.34	53.18
60	0.2348	2.00	60.04
75	0.2205	1.89	62.16
90	0.2032	1.74	65.12
120	**0.1784**	**1.51**	**69.74**
150	0.1784	1.51	69.74
180	0.1784	1.51	69.74
210	0.1784	1.51	69.74
240	0.1784	1.51	69.74
270	0.1784	1.51	69.74
300	0.1784	1.51	69.74

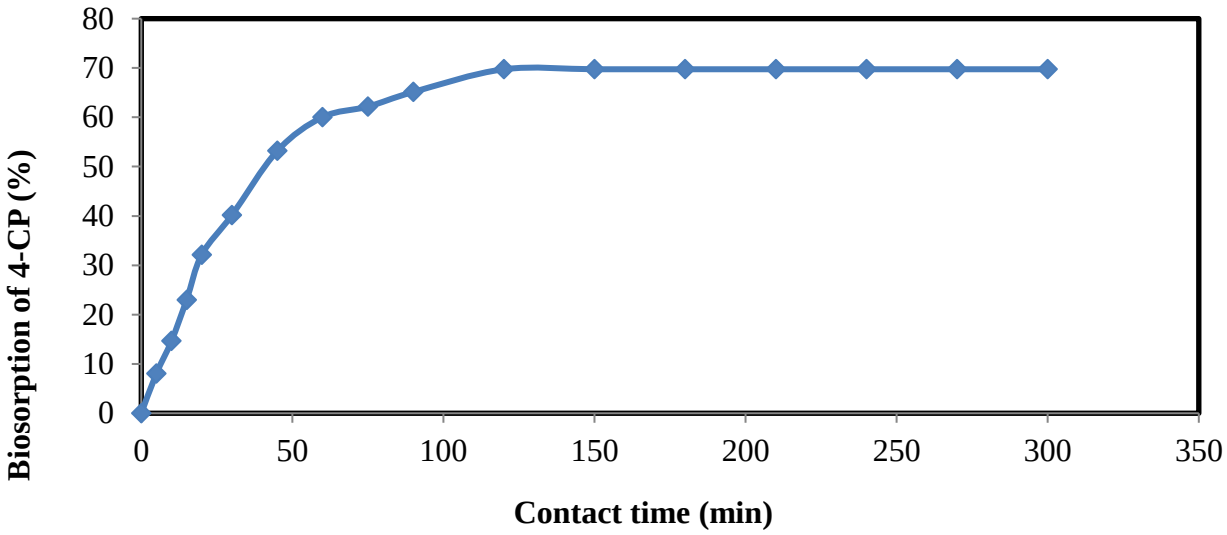

Figure 4.3.2 Graphical presentation of the effect of contact time on biosorption of 4-CP onto bagasse; 4-CP conc: 5.0 mg/L; bagasse dose: 2.5 g particle size: 150 µm; and pH: 6.5 at 30 °C

4.3.2.3 Effect of particle size of bagasse on the biosorption of 4-CP

Batch experiments have been carried out for biosorption of 4-CP from aqueous solution using six different particle sizes of biosorbent bagasse (average diameters of 50, 70, 100, 150, 200, and 250 µm). The results are graphically represented in Figure 4.3.3. With decreasing particle size from 250 to 50 µm (micrometer), the biosorption of 4-CP is increased[17] from 65.84 to 80 % cited in Table 4.3.3(b). The phenomena might be since the smaller particles offer comparatively larger surface areas and biosorption sites[14]. Different particle sizes with the same amount of biosorbent bagasse are introduced in the system solution of 4-CP of the same volume

and same initial concentration separately. Particles size, 150 µm has been selected for subsequent experiments for better convenience.

Table 4.3.3(a) Condition on effect of bagasse particle sizes for biosorption of 4-CP

1	Initial concentration of 4-CP	5.0 mg/L
2	Operational temperature	30˚C
3	pH of the system solution	6.5
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Contact time of solution of 4-CP and bagasse	120 minutes
9	Particle size of bagasse (µm)	Different sizes

Table 4.3.3(b) Effect of particle sizes of bagasse on sorption of 4-CP from aqueous system

Particle size (µm)	Absorbance	Concentration (mg/L)	Biosorptionof 4-CP (%)
50	0.1178	0.99	80.13
70	0.1390	1.17	76.53
100	0.1558	1.32	73.61
150	0.1784	1.51	69.74
200	0.1923	1.62	67.52
250	0.1987	1.71	65.84

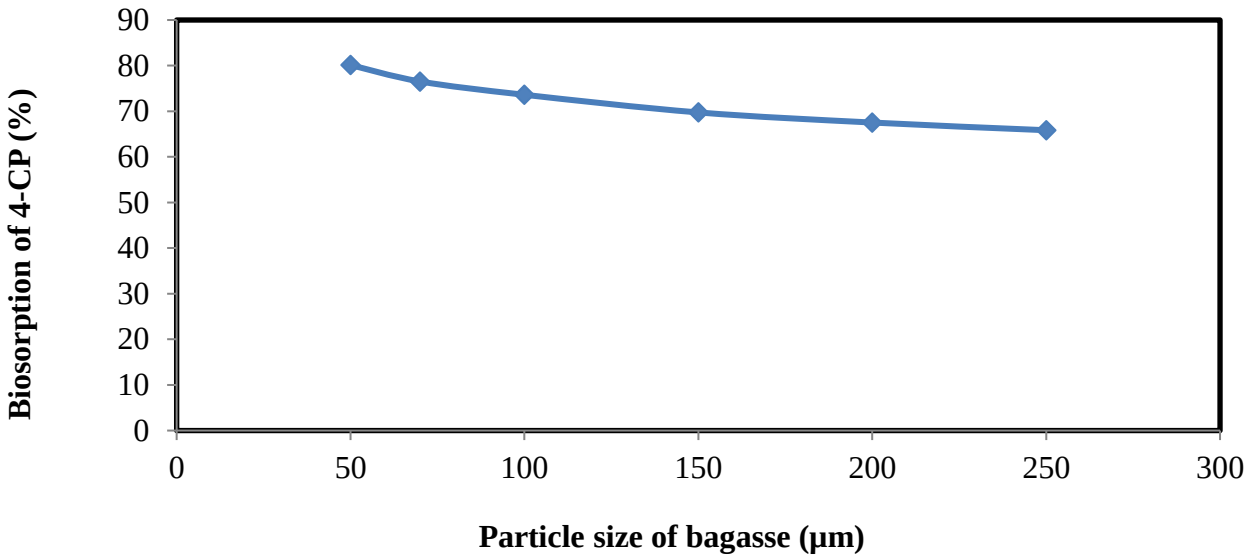

Figure 4.3.3 Graphical presentation of effect of bagasse particle size on the biosorption of 4-CP; 4-CP conc.: 5.0 mg/L; bagasse dose: 2.5 g; contact time: 120 min and pH: 6.5 at 30 °C

4.3.2.4 Effect of initial concentration on biosorption of 4-CP onto bagasse

Biosorption efficiency is highly dependent on the initial concentration of 4-CP in the aqueous system. The results are graphically represented in Figure 4.3.4. The figure depicts that the biosorption efficiency of the bagasse is decreased with increasing 4-CP concentration[18]. When the initial concentration of 4-CP is increased from 0.5 to 10.0 mg/L in the aqueous system, the biosorption percentage is decreased from 77 to 42 % and is cited in Table 4.3.4(b). In case of lower concentrations of 4-CP, the ratio of the available surface area of biosorbent bagasse to the initial number of moles of 4-CP is large and subsequently, the fractional biosorption becomes independent. It is evident that initially the number of biosorption sites is available and the driving force for the mass transfer is greater. Therefore, the 4-CP reaches the biosorption sites with ease[19]. However, at a higher concentration of 4-CP, the available biosorption sites become fewer, and hence the percentage of biosorption of 4-CP is decreased[19]. Besides this, with the increase of initial concentration, the number of active sites becomes less and the movement of the sorbate 4-CP comes to be slow down. This can be accounted for by the decrease in sorption rate with the increase in concentration of 4-CP. On a relative basis, however, the percentage of biosorption of 4-CP decreases as the initial concentration increases. It is also concluded that the initial concentration of sample solution of 4-CP provides an important driving force to overcome all mass transfer resistances of the 4-CP between aqueous and solid phase[20]. The equilibrium uptake and sorption yield are higher for the bagasse, which is expected, because of the greater specific surface area and the microporous structure of the bagasse. Since the highest allowable limit of 4-CP in the effluent is 5.0 mg/L; therefore, 5.0 mg/L is considered for subsequent experiments.

Table 4.3.4(a) Condition on effect of initial concentration for biosorption of 4-CP

1	Initial concentration of 4-CP (mg/L)	Different concentration
2	Operational temperature	30°C
3	pH of the system solution	6.5
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Contact time of 4-CP solution and bagasse	120 minutes
9	Particle size of bagasse	150 µm

Table 4.3.4(b) Effect of initial concentration on the biosorption of 4-CP onto bagasse

Conc. of 4-CP (mg/L)	Absorbance	Final conc. of 4-CP (mg/L)	Sorption of 4-CP (%)
0.5	0.0142	0.12	76.81
2	0.0574	0.49	75.65
3	0.0896	0.76	74.59
4	0.1289	1.10	72.61
5	0.1784	1.51	69.74
6	0.2653	2.28	62.01
8	0.5038	4.20	47.51
10	0.6424	5.78	42.21

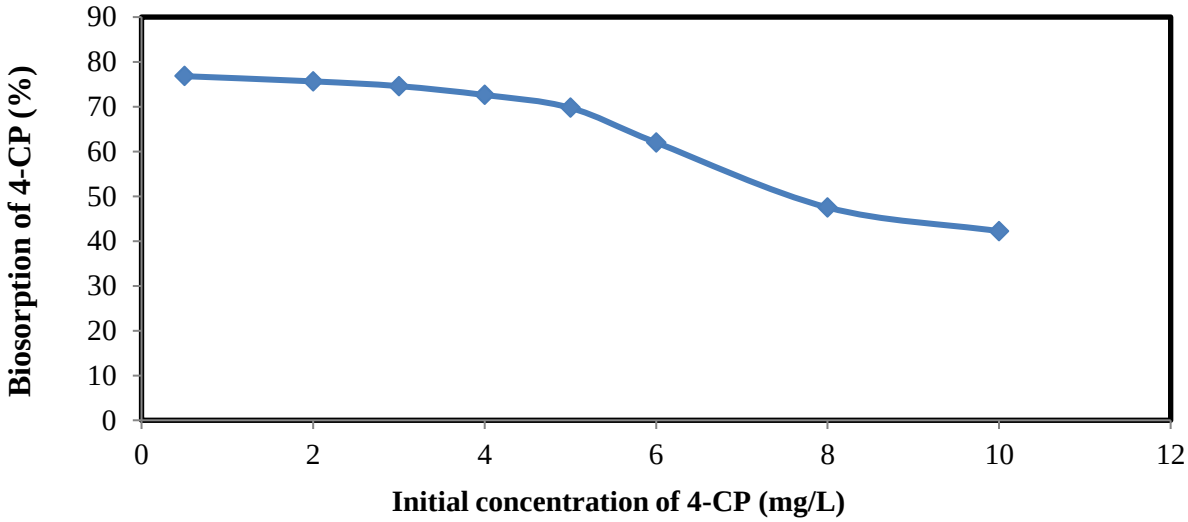

Figure 4.3.4 Graphical presentation on effect of initial concentration on sorption of 4-CP onto bagasse; bagasse dose: 2.5 g; particle size: 150 µm; contact time: 120 min and pH: 6.5 at 30 °C

4.3.2.5 Effect of pH on the biosorption of 4-CP onto bagasse

pH of the solution is an important operational parameter that governs the biosorption process of organic chemicals in the aqueous system. This is because it affects the solubility of the chemical ions concentration of the counter ions on the functional groups of the biosorbent and the degree of ionization of sorbate during the sorption process[21]. In the present work Figure 4.3.5 depicts the effects of pH on the biosorption of 4-CP onto bagasse. At the range of pH 3 to 12, the percentage of 4-CP sorption is increased from 46% at pH 3 to 70.0% at pH 6.5 and is decreased to 29.0 % at pH 12. This seems that the high biosorption of 4-CP at lower pH at ≤6.5 is due to high electrostatic attraction between the negatively charged 4-CP molecules and positively charged biosorption sites. As the pH is increased, there are fewer H^+ ions present in the solution and consequently more negatively charged sites are made available and this facilitated decreasing 4-CP sorption due to electrostatic repulsion. It can be noticed that 4-CP uptake increases with increasing pH from 3 to till it reaches its maximum at pH 6.5 and then 4-CP uptake sharply decreases at higher pH from 6.5-12.0. The lower 4-CP removal at acidic (pH≤3) is probably due to the presence of excess H^+ ions competing with 4-CP molecules for the sorption sites of the sorbent. Furthermore, at lower pH values (below the pKa of carboxylic groups, approximate 4.6), the -COO- groups in bagasse are protonated to -COOH groups and

the hydrogen bonds with -COOH groups are formed resulting in a decrease of 4-CP uptake. On the other hand, at higher pH (>6.5), the OH^- ions concentration increase, and these ions repulse with the negative active sites on the sorbent leading to a decrease in 4-CP sorption[22]. Also, at higher pH, 4-CP dissociates to 4-chlorophenolate anions that form negative charges in sorbate solution resulting in high repulsion forces between sorbate and sorbent which decreases the 4-CP uptake and hence its remove from aqueous solution[23].

Table 4.3.5(a) Condition on effect of pH for biosorption of 4-CP onto bagasse

1	Initial concentration of 4-CP	5.0 mg/L
2	Operational temperature	30˚C
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Contact time of solution and bagasse	120 minutes
9	pH of system solution	Different pH

Table 4.3.5(b) Effect of solution pH on the biosorption of 4-CP onto Bagasse

pH	Absorbance	Concentrationof 4-CP (mg/L)	Biosorption of 4-CP (%)
3	0.3786	3.1600	46.00
4	0.3081	2.6472	58.82
5	0.2784	2.3916	65.21
6	0.2667	2.2628	68.43
6.5	**0.2607**	**2.2104**	**69.74**
7	0.2714	2.3024	67.44
8	0.2927	2.5072	62.32
9	0.3226	2.7636	55.91
10	0.3672	3.0620	48.45
11	0.3987	3.3908	40.23
12	0.4103	3.8556	28.61

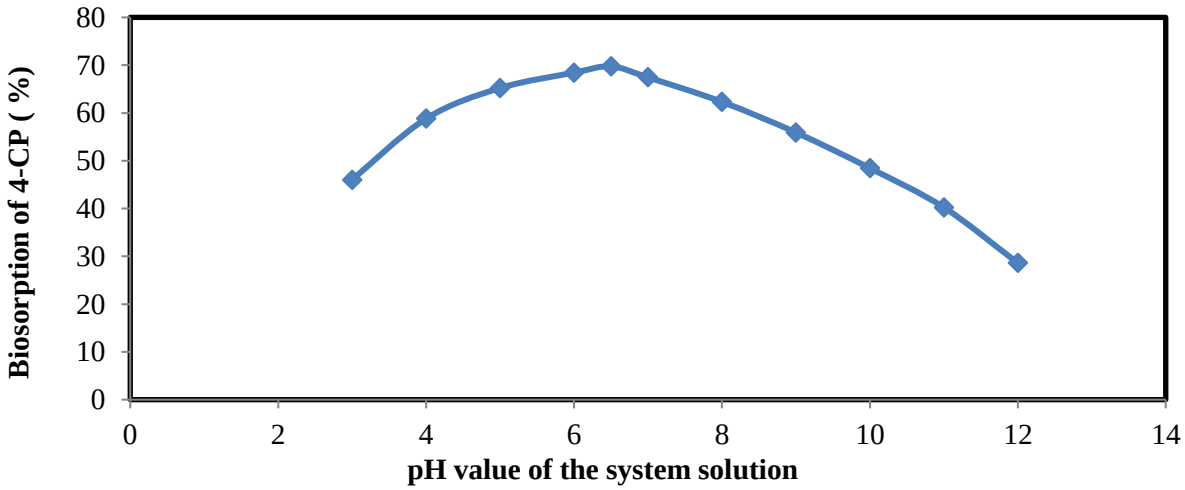

Figure 4.3.5 Graphical presentation of effect of pH of the system solution on the sorption of 4-CP onto bagasse; 4-CP concentration: 5.0 mg/L; bagasse dose: 2.5 g; p. size: 150 µm and time: 120 min at 30 °C

4.3.2.6 Effect of temperature on the biosorption of 4-CP onto bagasse

Temperature is an important parameter for any separation process. Biosorption of 4-CP onto bagasse has been studied at different temperatures: 30 (room temperature), 35, 40, 45, 50˚C. The plot of biosorption efficiency as a function of temperature is shown in Figure 4.3.6. The figure indicates that the biosorption of 4-CP onto bagasse is enhanced a little from 70-74%, when temperature goes from 30°C to 50°C, suggesting that the process is endothermic[20]. Hence a higher temperature is favorable for the biosorption of 4-CP. This is for the higher temperature reduces the thickness of the outer surface of the bagasse and increases the kinetic energy of 4-CP molecules. As a result, 4-CP molecules are easily sorbed on the bagasse surface[23]. The increase in biosorption a little bit with increase in temperature, it may due to lignin in cellulose of sorbent bagasse which has not been separated. The intraparticle diffusion rate of sorbate ions a little into the pores as the pores fills up and insisted by lignin when increasing temperature and intensifies the pore area. However, increase in biosorption with increasing temperature, the process is endothermic. It is investigated that at higher temperature, the hydrogen bonding (Intra and intermolecular) becomes weak, which makes 4-CP molecules freely available, and hence, biosorption intends to increases at higher temperature[20]. The room temperature at about 30˚C is selected for subsequent experiments for convenience and economy.

Table 4.3.6(a) Condition on effect of temperature for sorption of 4-CP onto bagasse

1	Initial concentration of 4-CP	5.0 mg/L
2	pH of system solution	6.5
3	Particle sizeof bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Contact time of solution of 4-CP and bagasse	120 minutes
9	Temperature effect (°C)	Different temperature

Table 4.3.6(b) Effect of temperature on the biosorption of 4-CP onto Bagasse

Temperature (°C)	Absorbance	Conc. of 4-CP (mg/L)	Biosorption of 4-CP (%)
30	0.1784	1.51	69.74
35	0.1747	1.48	70.35
40	0.1670	1.42	71.71
45	0.1592	1.36	72.72
50	0.1521	1.30	73.92

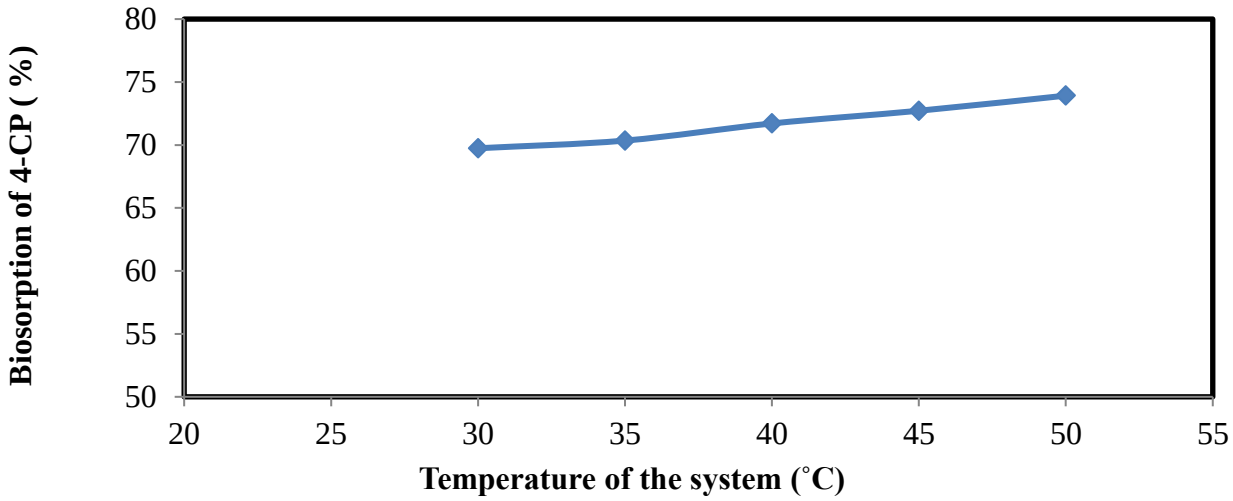

Figure 4.3.6 Graphical presentation of effect of temperature on biosorption of 4-CP onto bagasse; 4-CP conc.: 5.0 mg/L; bagasse dose: 2.5 g; particle size: 150 µm and cont. time: 120 min at pH: 6.5

4.3.3 FTIR spectroscopy studies

The infrared spectra have been used to determine changes in the structure of cellulose, hemicelluloses, and lignin during the sequence of treatments subjected to bagasse (native). Table 4.3.7 shows the FTIR spectrum of natural sugarcane bagasse. The band at 1162 cm^{-1} is characteristic of C-O-C asymmetrical stretching, 1335 cm^{-1} is characteristic of C-O aromatic ring, 1423cm^{-1} is characteristic of CH_2 symmetrical stretching, 1732 cm^{-1} is characteristic of C=O unconjugated stretch, 2885cm^{-1} is characteristic of C-H symmetrical stretching, and 3300 cm^{-1} is characteristic of O-H linked shearing.

Table 4.3.7 Structural characterization of the bagasse

Wavenumber (cm^{-1})	**Vibration**
3300	O-H linked shearing
2885	C-H symmetrical stretching
1732	C=O unconjugated stretching
1423	CH_2 symmetrical stretching
1335	C-O aromatic ring
1162	C-O-C asymmetrical stretching

4.3.4.1 Langmuir model for biosorption of 4-CP onto the bagasse

The Langmuir biosorption model serves to estimate the maximum uptake values where they cannot be reached in experiments. This model does not take into account the variation in sorption energy, but it is the simplest description of the biosorption process[24]. It is based on the physical hypothesis that the maximum sorption capacity consists of a monolayer biosorption. There has been no interaction between biosorbed molecules and the biosorption energy is distributed homogeneously over the entire coverage surface[25]. It is the isotherm model that can be successfully applied to many pollutants for biosorption processes and can be used widely to describe the biosorption of a solute from an aqueous system. A basic assumption of the Langmuir theory is that the biosorption takes place at specific homogeneous sites on the surface of the biosorbent. It is then assumed that once a sorbate molecule occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force and area. The driving force is the concentration of a solute in the system solution, and the area is the amount of bare surface[26]. The monolayer biosorption on a surface with a finite number of identical sites is validated by Langmuir isotherm[27]. This isotherm model predicts the maximum sorption capacity of 4-CP on the surface of bagasse carbon.

The linear form of the Langmuir model can be represented by the following relation[18,28].

$1/q_e = 1/q^\circ + 1/(bq^\circ C_e)$

Where q_e (mg/g) is the amount of biosorption of 4-CP onto per unit weight of biosorbent bagasse (mg/g) at equilibrium, C_e (mg/L) is the equilibrium concentration of sorbate 4-CP in the sample system, and q^o and b are Langmuir constants related to biosorption capacity and energy of biosorption obtained from the intercept and slope of the graph respectively. The equilibrium data for the sorption of 4-CP over the entire concentration range were fitted to the Langmuir isotherm. The Langmuir model parameters are given in Table 4.3.8(d). The biosorption process confirms to the Langmuir model when the value of the correlation coefficient (R^2) is 0.99 closer[26] to 1.

The essential feature of the Langmuir isotherm can be expressed employing dimensionless separation factor constant which is calculated using the following equation;

$R_L=1/(1+b_L C_\circ)$

Where k is the Langmuir constant and $C_\circ$ is the initial sorbate concentration (Langmuir isotherm). The value of R_L demonstrates that the sorption system is unfavorable whether $R_L > 1$, irreversible whether $R_L = 0$, linear whether $R_L = 1$, and favorable whether $0 < R_L < 1$). Based on the value in Table 4.3.8(c) of $R_L = 0.1095$, the sorption system of 4-CP on the bagasse surface is favorable.

Table 4.3.8(a) Experimental data for applying on Langmuir isotherm model

Con. of 4-CP (mg/L)	Biosorption of 4-CP (%)			30˚C		40˚C		50˚C	
	30˚C	40˚C	50˚C	$1/C_e$	$1/q_e$	$1/C_e$	$1/q_e$	$1/C_e$	$1/q_e$
0.5	76.81	80.32	83.39	8.6244	65.0957	10.1626	62.2510	12.041	59.9592
1	76.32	79.67	82.53	4.2230	32.7568	4.9188	31.3794	5.7241	30.2920
2	75.65	78.82	81.55	2.0534	16.5235	2.3607	15.8589	2.7100	15.3280
3	74.59	77.45	80.05	1.3118	11.1722	1.4782	10.7596	1.6708	10.4102
4	72.61	75.02	77.45	0.9127	8.6076	1.0008	8.3311	1.1086	8.0697
5	69.74	71.71	73.92	0.6609	7.1695	0.7070	6.9725	0.7668	6.7641
6	62.01	63.58	65.45	0.4387	6.7193	0.4576	6.5534	0.4824	6.3662
7	54.23	55.31	57.07	0.3121	6.5857	0.3197	6.4571	0.3328	6.2580
8	47.51	48.79	50.14	0.2381	6.5776	0.2440	6.4050	0.2507	6.2325
9	43.03	44.43	45.49	0.1950	6.4554	0.1999	6.2520	0.2038	6.1063
10	42.21	43.11	44.01	0.1730	5.9228	0.1758	5.7991	0.1786	5.6805

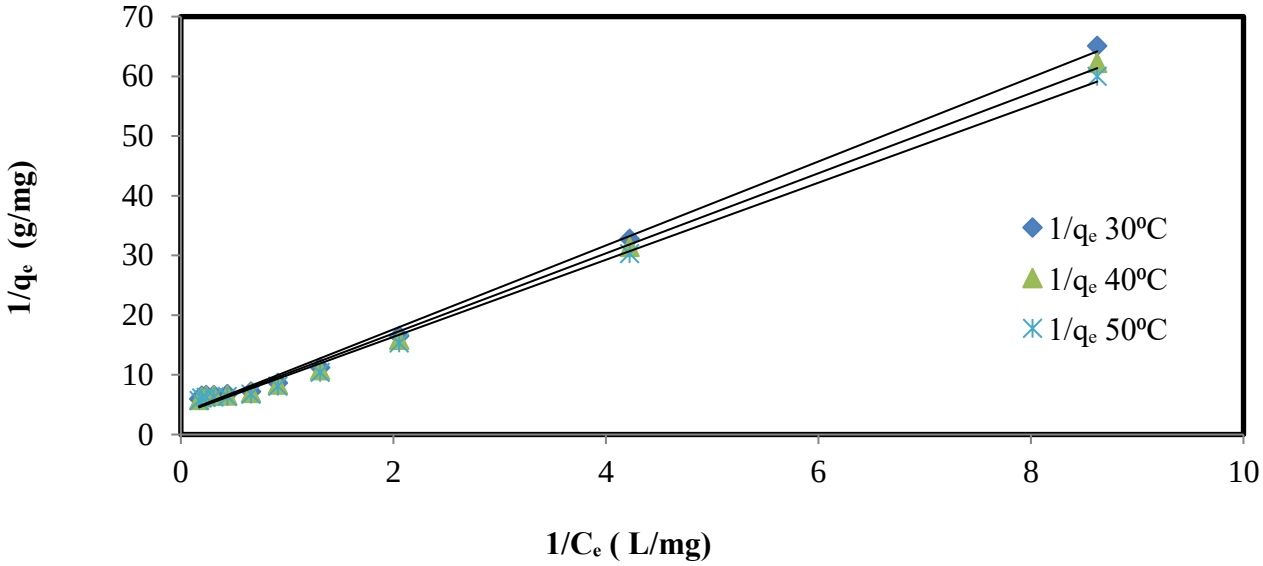

Figure4.3.7(a) Graphical presentation of Langmuir isotherm curve for the sorptⁿ of 4-CP onto bagasse; 4-CP conc.: 0.5-10.0 mg/L; bagasse dose: 2.5 g; p. size: 150 µm; cont. time: 120 min and pH: 6.5 at 30-50 °C

4.3.4.2 Freundlich isotherm model for biosorption of 4-CP onto the bagasse

Freundlich isotherm is based on the biosorption on a heterogeneous surface of varied affinities[27]. An empirical equation has been developed by Freundlich to describe the sorption process. The isotherm model is the most widely applicable non-linear model for describing the dependence of sorption on the sorbate concentration. This model represents proper sorption data at low and intermediate concentrations for several kinds of sorption sites on solid heterogeneous surfaces[29]. In this model, the ratio of the amount of solute sorbed onto a given mass of a sorbent to the concentration of the solute in the solution is not constant at different solution concentrations. This isotherm does not predict any saturation of the sorbent by the

sorbate; thus, infinite surface coverage is predicted mathematically, indicating multilayer sorption of the surface.

The linear form of the Freundlich isotherm model is given by the following relation[18,28]

$\ln q_e = \ln k_F + (1/n) \ln C_e$

Where q_e (mg/g) is the sorption capacity of 4-CP onto biosorbent bagasse at equilibrium time (amount of 4-CP sorbed per unit mass sorbent bagasse), C_e (mg/L) is the equilibrium concentration of 4-CP in the system. K_F (L/g) is a constant related to the extent of biosorption and n is a constant related to the intensity of biosorption or the degree of dependence of biosorption on concentration of 4-CP. The values of K_F and n depend on temperature, the nature of the biosorbent, and the substance 4-CP to be sorbed[26]. The values of K_F and n are also presented in Table 4.3.8(c). Found from the relation of the intercept and slope of the graph.

Table 4.3.8(b) Experimental data for applying on Freundlich isotherm model

Conc. of 4-CP (mg/L)	Biosorptionof 4-CP (%)			30˚C		40˚C		50˚C	
	30˚C	40˚C	50˚C	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$
0.5	76.81	80.32	83.39	-2.1546	-4.1759	-2.3187	-4.1312	-2.4883	-4.0937
1	76.32	79.67	82.53	-1.4405	-3.4891	-1.5931	-3.4462	-1.7447	-3.4109
2	75.65	78.82	81.55	-0.7195	-2.8048	-0.8590	-2.7637	-0.9970	-2.7297
3	74.59	77.45	80.05	-0.2714	-2.4134	-0.3908	-2.3758	-0.5133	-2.3428
4	72.61	75.02	77.45	0.0913	-2.1527	-0.0008	-2.1200	-0.1031	-2.0881
5	69.74	71.71	73.92	0.4141	-1.9698	0.3468	-1.9420	0.2654	-1.9116
6	62.01	63.58	65.45	0.8239	-1.9050	0.7817	-1.8800	0.7290	-1.8510
7	54.23	55.31	57.07	1.1644	-1.8849	1.1404	-1.8652	1.1003	-1.8339
8	47.51	48.79	50.14	1.4349	-1.8837	1.4102	-1.8571	1.3754	-1.8218
9	43.03	44.43	45.49	1.6346	-1.8649	1.6097	-1.8329	1.5904	-1.8093
10	42.21	43.11	44.01	1.7542	-1.7788	1.7385	-1.7577	1.7226	-1.7370

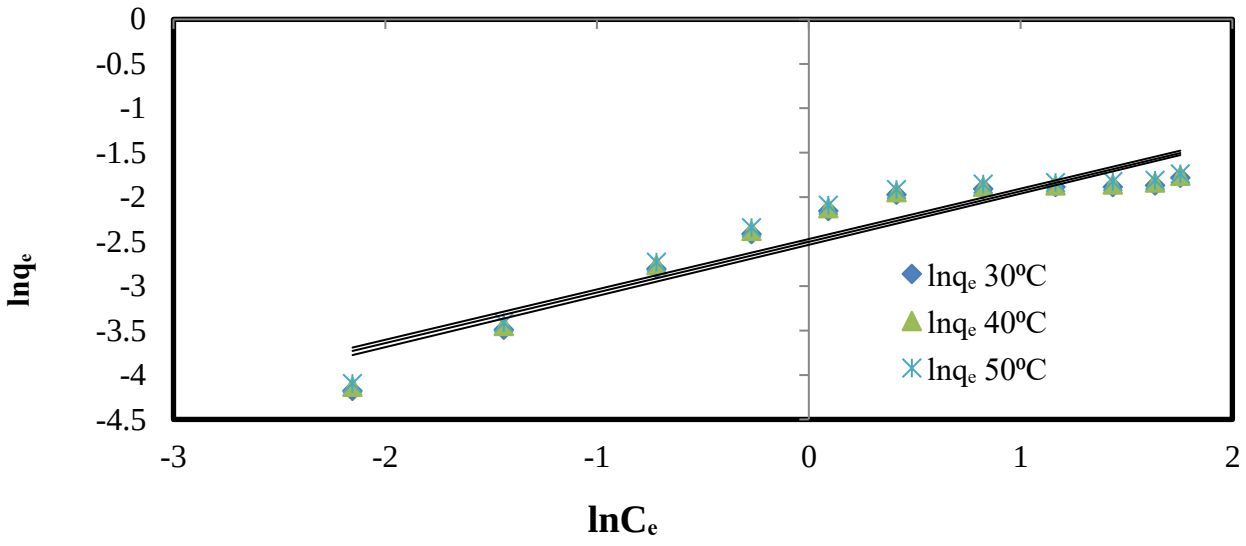

Figure4.3.7(b) Graphical presentation on Freundlich isotherm curve for the biosorption of 4-CP ontobagasse; 4-CP conc.: 0.5-10.0 mg/L; bagasse dose: 2.5 g; p. size: 150 µm; Contact time: 120 min and pH: 6.5 at 30-50°C

Table 4.3.8(c) Isotherm constants for biosorption of 4-CP onto the bagasse

Name of compound	4-CP		
Temperature	30℃	40℃	50℃
Constants	Langmuir adsorption isotherm equation $1/q_e = 1/q^\circ + 1/(bq^\circ c_e)$		
q^o	0.2821	0.2851	0.2904
b	0.5042	0.5229	0.5335
R_L	0.1655	0.1605	01579
R^2	0.995	0.995	0.995
Constants	Freundlich adsorption isotherm equation $\ln q_e = \ln k + (1/n) \ln C_e$		
1/n	0.575	0.569	0.566
N	1.7391	1.7575	1.7668
K_f	0.0793	0.0819	0.0846
R^2	0.889	0.888	0.886

4.3.4.3 Isotherm models on the biosorption 4-CP onto the bagasse

Isotherms describe the relationship between the biosorption quantity of sorbate 4-CP onto the bagasse and the concentration of dissolved sorbate 4-CP in the aqueous system at equilibrium[30]. The equilibrium biosorption isotherm is fundamentally very crucial in the design of sorption systems. Biosorption is usually described by an isotherm equation characterized by certain parameters whose values express the surface properties of the sorbent and its affinity to the sorbate[26]. Two important isotherms; the Freundlich and Langmuir models have been employed for the present study. When $\ln q_e$ has been plotted against $\ln C_e$, a straight line with the slope of 1/n is obtained from Figure 4.3.7(b). Whether n<1, it would show that the biosorption would be chemical in nature[22]. But in this study n> 1 indicates that biosorption is physical in nature and the sorbate 4-CP is favorably sorbed onto the biosorbent bagasse surface. However, the correlation coefficient R^2 of Freundlich isotherm is less than that of Langmuir also indicates that the biosorption of 4-CP onto bagasse is a physical sorption. In general, as the K_F value increases, the biosorption capacity also increases. The Freundlich constant n should have values lying in the range of 1-10 for classification as favorable sorption[25,31]. The 1/n values are between 0 and 1, indicating that the biosorption of 4-CP onto the bagasse biomass is favorable in the studied conditions. The isotherm constants and correlation coefficients are shown in Table 4.3.8(d) and in Figure 4.3.7(a-b). It is observed that the equilibrium data are very well represented by the Langmuir isotherm equation when compared to the Freundlich. The biosorption equilibrium data fitted the Langmuir isotherm equation with correlation coefficient (R^2), which are a measure of goodness-of-fit, R^2 values of 0.99 for Langmuir and 0.88 for

Freundlich, at all temperatures (30-50˚C) respectively. The higher value of b in the Langmuir constant, showed easy uptake of 4-CP from aqueous solution[28,32]. The *n* value, which reflects the intensity of sorption, presents the opposite trend, but as seen from Table 5.3.8(c) for the sorbents and pollutants, *n* values are found optimum for separation. The higher fractional value of 1/n (0 <1/n < 1) signifies that the surface of the sorbent is heterogeneous in nature[33.] However, the Langmuir isotherm model is chosen for the estimation of maximum biosorption capacity corresponding to complete monolayer coverage on the agricultural waste bagasse. The maximum biosorption capacity q˚ is 0.282, 0.285 and 0.290 mg/g for 4-CP–bagasse system at temperature 30-50˚C respectively cited in Table 5.3.8(c), which appear to be significant

Effects of temperature on isotherm model for biosorption

The temperature has also been evaluated as one of themost important factors affecting the biosorption capacity. The calculations of Langmuir and Freundlich isotherm constants of biosorption of 4-CP onto bagasse as a function of temperature and the corresponding coefficient of correlation values are shown in Table 5.3.8(c). According to Table 5.3.8(c) the optimum biosorption temperature, at which the sorption capacity of 4-CP on the biomass is the higher, at 50˚C of the temperature ranges studied. Besides, temperature has not been raised beyond 50˚C for formation of color is observed in the test solution. The coefficient of the Langmuir model indicates that b lies between zero and one, suggesting that the biosorption of 4-CP by bagasse is favorable. The values of q˚, which is defined as the maximum biosorption capacity of biosorbents, are also calculated from the Langmuir plots. Concerning the coefficients of the Freundlich model, K_F increased with a rise in the temperatures, revealing that the biosorption capacity of 4-CP by bagasse increased with the increase in temperature. This indicates that the biosorption of 4-CP by bagasse might be endothermic (ΔH• is a positive value) in nature and the biosorption is favored at a higher temperature. Since the biosorption process, is controlled by the diffusion process (Intra particle transport–pore diffusion), the sorptive capacity is increased with an increase in temperature due to the endothermicity of the diffusion process. An increase in the temperature involves an increased mobility of 4-CP and a decrease in the retarding forces acting on the diffusing ions. These result in the enhancement in the sorptive capacity of the sorbent[33]. The highest value of n for 4-CP at 50˚C, represents favorable biosorption at higher temperature. If the value of n is below one, then the biosorption is a chemical process; otherwise, the biosorption is a physical process. All values of n exceed one, suggesting the biosorption of 4-CP onto bagasse is a physical process. On the other hand, the Freundlich exponent of 1/n gives information about surface heterogeneity and surface affinity for the solute. The Freundlich exponent 1/n between 0 and 1 indicates favorable biosorption and a high affinity of bagasse for 4-CP[34].

4.3.5 Kinetic studies on biosorption of 4-CP onto the bagasse from aqueous system

The experimental data of biosorption are described using various models or empirical formulas. The process is controlled by the sorption mechanism at the liquid/solid interface and an

excellent review about slow sorption (and desorption) is available in the literature[35]. Two types of kinetics are generally used, namely the pseudo-first order proposed by Lagergren[34] and pseudo-second order rate law is introduced by Y. S Ho[35]. The rate law has become very popular when Ho and McKay[37] analyzed some experimental results have taken from the literature and arrived at the conclusion that for all of the systems studied explain to compare about superiority between 1st order and 2nd order rate constants[36]. The study also explained on two main issues in the statistical treatment generally used in the literature and that the method systematically tends to favor either the pseudo-first order or pseudo-second order rate law. The remainder of this work is divided into three main sections. In the next section, the basic formulas for the statistical analyses of experimental data and model comparison are presented. The third section is dedicated to the presentation of results and their discussion. The two issues that have met in analyses used in the literature are exposed and they are illustrated in the case of data obeying first-order kinetics. Then a re-examination of the experimental data treated in the original paper by Ho and McKay[37] is carried out, a sample of data reported in the literature is analyzed, and a few diffusion-controlled processes are examined. Finally, a conclusion summarizes the main results of this work and presents some prospects. The studies on biosorption kinetic describe the 4-CP uptake rate which controls the residence time of sorbate uptake at the solid/solution interface. The Kinetic studies are set up in the laboratory in batch method by adding a known amount of 4-CP to a required number of flasks which contain 100 ml of solution. Initial 4-CP solution concentrations are 2.0-5.0 mg/L at pH 6.5 and the amount of sorbent required 2.5 g at constant temperature 30˚C. The bottles were subsequently capped and shaken up to an equilibrium time of 120 minutes. This has been also done at variable temperatures 30, 40, and 50˚C with constant 4-CP concentration 5.0 mg/L and has been shaken up to that of equilibrium 120 minutes. The experimental data have been employed in both the pseudo-FOK and pseudo-SOK models and the finding constants are cited in Table 4.3.9(f)

Table 4.3.9(a) Condition on kinetics studies of experimental data for biosorption of 4-CP

1	Initial concentration of 4-CP	2.0-5.0 mg/L
2	pH of the system solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Equlibrium time of 4-CP solution and bagasse	120 minutes
9	Operational temperatures	30-50ºC

4.3.5.1 Pseudo First order Kinetic (FOK) on biosorption of 4-CP onto bagasse

The equation of pseudo FOK was introduced initially by Lagergren[38]. In the literature[18,20], it is generally used in the form proposed by Ho and McKay[37].

The pseudo FOK model is widely used to predict the biosorption kinetic and is defined as:

$\ln (q_e - q_t) = \ln q_e - kt$

Where q_e and q_t (mg/g) are the biosorption capacities of bagasse at equilibrium time and at any given time, t (minutes), respectively. K (min^{-1}) is the biosorption rate constant. The constants q_e and k of the model are found from the intercept and slope of the graphs of $\ln(q_e-q_t)$ versus t at different concentrations and temperatures. To determine the constants of the pseudo-first-order kinetic model, graphs of $\ln(q_e-q_t)$ versus t are plotted as shown in Figure 4.3.8(a) at initial concentration 2.0-5.0 mg/L of 4-CP and temperature 30˚C and in Figure4.3.8 (b) at 5.0 mg/L concentration of 4-CP at 30-50˚C. The experimental data are sown in Table 4.3.9 (b-c) and the kinetic constants are shown in Table 4.3.9(f)

Table 4.3.9(b) Experimental data of biosorption of 4-CP onto bagasse from (2.0- 5.0 mg/L) aqueous solution to apply on pseudo FOK model at 30ºC

Time	Biosorption of 4-CP (%)				Time	$\ln(q_e-q_t)$			
	2ppm	3ppm	4ppm	5ppm		2ppm	3ppm	4ppm	5ppm
						-2.8048	-2.4134	-2.1540	-1.9698
5	8.61	8.43	8.28	8.05	5	-2.9256	-2.5333	-2.2753	-2.0925
10	15.97	15.78	15.36	14.65	10	-3.0419	-2.6511	-2.3921	-2.2056
15	24.83	24.37	23.87	22.99	15	-3.2026	-2.8090	-2.5533	-2.3698
20	33.76	33.21	32.23	32.13	20	-3.3958	-3.0026	-2.7419	-2.5873
30	44.67	44.06	42.67	40.17	30	-3.6976	-3.3067	-3.0419	-2.8279
45	55.75	55.01	53.43	53.18	45	-4.1402	-3.7509	-3.4891	-3.4076
60	63.51	62.66	61.02	60.04	60	-4.6344	-4.2464	-3.9963	-3.9425
75	67.44	66.52	64.43	62.16	75	-5.0256	-4.6373	-4.3484	-4.1891
90	70.45	69.46	67.42	65.12	90	-5.4822	-5.0903	-4.8105	-4.6842
120	75.65	74.59	72.51	69.74	120				

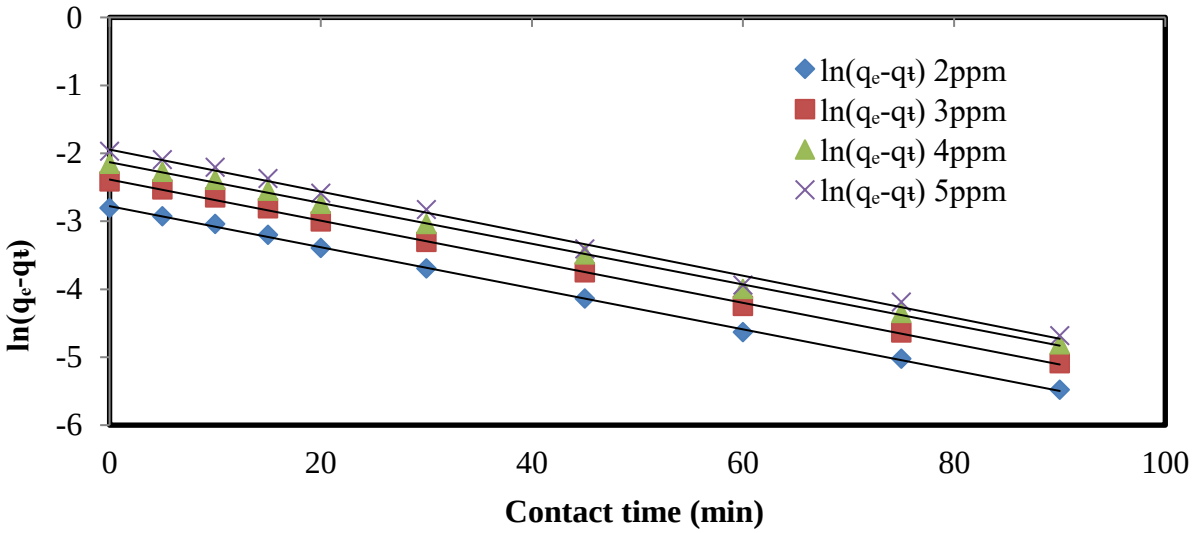

Figure 4.3.8(a): Graphical presentation on Pseudo FOK model for sorptⁿ of 4-CP onto bagasse from aqueous systems of 2.0-5.0 mg/L of 4-CP; bagasse dose 2.5 g, p. size 150 µm, cont. time 120 min, pH 6.5 at 30˚C

Table 4.3.9(c) Experimental data of biosorption of 4-CP onto bagasse from 5.0 mg/L aqueous solution to apply on pseudo FOK model at 30- 50 ˚C

Time	Adsorptionof 4-CP (%)			Biosorption capacity of 4-CP (q_t)			Time	$\ln(q_e-q_t)$		
	30˚C	40˚C	50˚C	30˚C	40˚C	50˚C		30˚C	40˚C	50˚C
0	0	0	0	0	0	0	0	-1.9698	-1.9295	-1.9100
5	8.05	8	8.27	0.0161	0.0163	0.01654	5	-2.0925	-2.0486	-2.0284
10	14.65	14.75	15.01	0.0293	0.0295	0.03002	10	-2.2056	-2.1566	-2.1366
15	22.99	23.14	24.89	0.04598	0.04628	0.04978	15	-2.3698	-2.3132	-2.3197
20	32.13	33.53	34.23	0.06426	0.06706	0.06846	20	-2.5873	-2.549	-2.5305
30	40.17	42.12	43.72	0.08034	0.08424	0.08744	30	-2.8279	-2.7972	-2.8028
45	53.18	55.62	54.78	0.10636	0.11124	0.10956	45	-3.4076	-3.3820	-3.2566
60	60.04	61.11	62.26	0.12008	0.12222	0.12452	60	-3.9425	-3.7723	-3.7482
75	62.16	64.09	65.13	0.12432	0.12818	0.13026	75	-4.1891	-4.0722	-4.0274
90	65.12	67.21	68.12	0.13024	0.13442	0.13624	90	-4.6842	-4.5282	-4.4363
120	69.74	72.61	74.04	0.13948	0.14522	0.14808	120			

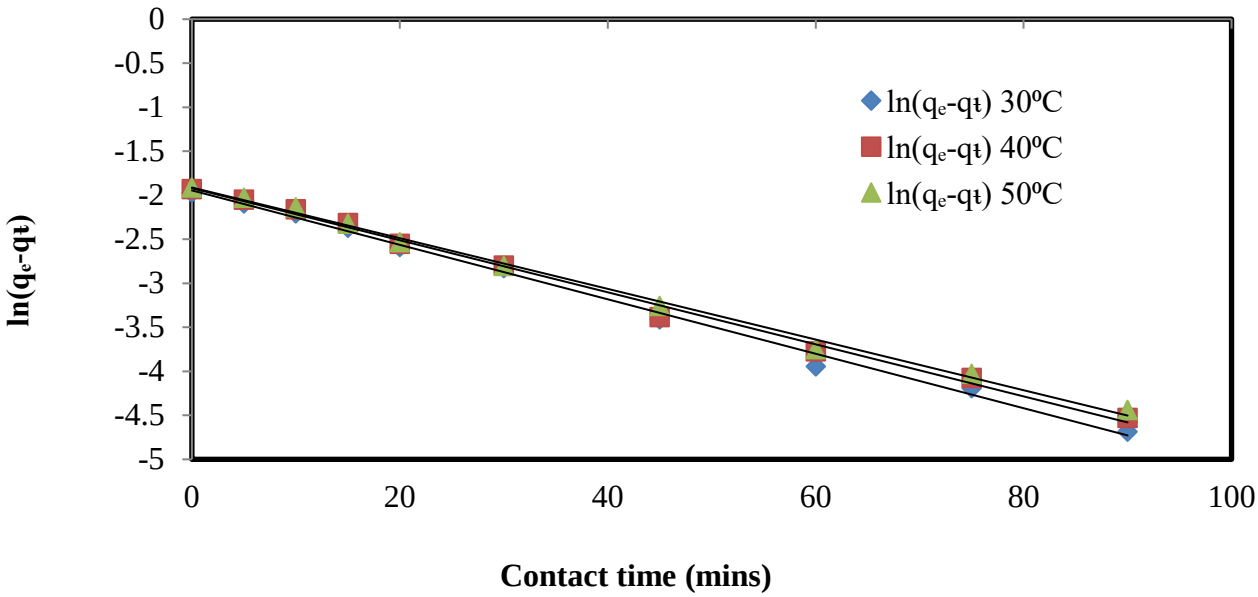

Figure4.3.8(b) Graphical presentation on Freundlich isotherm curve for the biosorption of 4-CP onto bagasse; 4-CP conc.: 0.5-10.0 mg/L; bagasse dose: 2.5 g; p. size: 150 µm; Cont. time: 120 min and pH: 6.5 at 30-50°C

4.3.5.2 Pseudo second order kinetic model (SOK) of 4-CP onto bagasse

Ho[38] proposed the second order model for the biosorption of 4-CP onto bagasse based on the biosorption capacity of the biosorbent to differentiate the kinetic of a second-order rate expression based on the concentration of 4-CP from an aqueous system.

The linearized form of the pseudo-second-order model defined by Ho[35] is as follows:

$t/q_t = 1/(kq_e^2) + t/q_e$

Where k ($gmg^{-1}min^{-1}$) is the rate constant of the pseudo-second order equation, $q_e$and q_t (mg/g) are the quantity of the biosorption of 4-CP onto the bagasse at equilibrium time, and at any

given time, t. q_e and k can be calculated from the slope and intercept of the plot of t/q_t against t respectively. To determine the constants of the pseudo-second-order kinetic model, graphs of t/q_t versus t are plotted as shown in Figure 4.3.8(c) at initial concentration 2.0-5.0 mg/L and 30˚C and in Figure 4.3.8(d) at concentration, 5.0 mg/L and 30-50˚C. The experimental data are sown in Table 4.3.9 (d-e) and the constants are shown in Table 4.3.9 (f)

Table 4.3.9 (d) Experimental data of biosorption of 4-CP onto bagasse from (2.0-5.0 mg/L) aqueous solution to apply on pseudo SOK model at 30˚C

Time	Biosorption (%)				Time	t/q_t			
	2ppm	3ppm	4ppm	5ppm		2ppm	3ppm	4ppm	5ppm
5	8.61	8.43	8.28	8.05	5	725.9001	494.2665	377.4155	310.5590
10	15.97	15.78	15.36	14.65	10	782.7176	528.0946	406.9010	341.2969
15	24.83	24.37	23.87	22.99	15	755.1349	512.9257	392.7524	326.2288
20	33.76	33.21	32.23	32.13	20	740.5213	501.8569	387.8374	311.2356
30	44.67	44.06	42.67	40.17	30	839.4896	567.4081	439.4188	373.4130
45	55.75	55.01	53.43	53.18	45	1008.9690	681.6942	526.3897	423.0914
60	63.51	62.66	61.02	60.04	60	1180.9160	797.9572	614.5526	499.6669
75	67.44	66.52	64.43	62.16	75	1390.1250	939.5670	727.5338	603.2819
90	70.45	69.46	67.42	65.12	90	1596.8770	1079.7580	834.3222	691.0319
120	75.65	74.59	72.51	69.74	120	1982.8160	1340.6620	1034.3400	860.3384

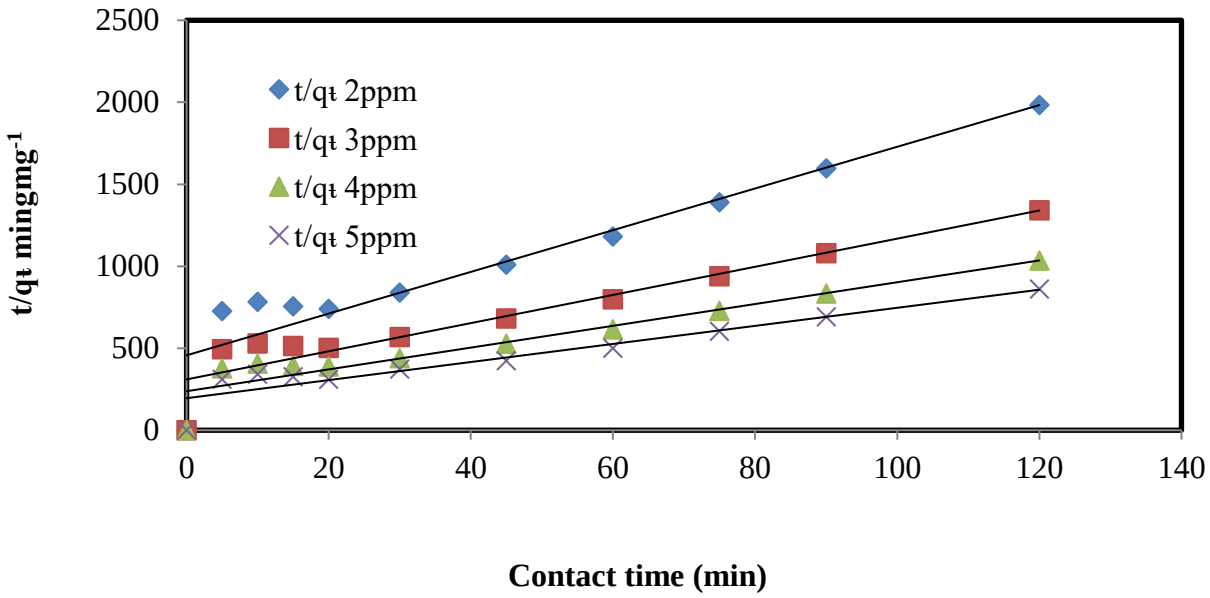

Figure 4.3.8(c) Graphical presentation of Pseudo FOK model for sorptⁿ of 4-CP onto bagasse from aqueous systems; 4-CP conc.: 2.0-5.0 mg/L; bagasse dose: 2.5 g; P. size: 150 µm; Cont. time: 120 min and pH: 6.5 at 30 °C

Table 4.3.9 (e) Experimental data of biosorption of 4-CP onto bagasse from 5.0 mg/L aqueous system to apply on the pseudo SOK model at 30-50˚C

Time	Biosorptionof 4-CP (%)			q_t			Time	t/q_t		
	30˚C	40˚C	50˚C	30˚C	40˚C	50˚C		30˚C	40˚C	50˚C
5	8.05	8	8.27	0.0161	0.0163	0.0165	5	310.5590	306.7485	302.2975
10	14.65	14.75	15.01	0.0293	0.0295	0.0300	10	341.2969	338.9831	333.1113
15	22.99	23.14	24.89	0.0460	0.0461	0.0498	15	326.2288	324.1141	301.3258
20	32.13	33.53	34.23	0.0643	0.0671	0.0685	20	311.2356	298.2404	292.1414
30	40.17	42.12	43.72	0.0803	0.0842	0.0874	30	373.4130	356.1254	343.0924
45	53.18	55.62	54.78	0.1064	0.1112	0.1096	45	423.0914	404.5307	410.7338
60	60.04	61.11	62.26	0.1201	0.1222	0.1245	60	499.6669	490.9180	481.8503
75	62.16	64.09	65.13	0.1243	0.1282	0.1303	75	603.2819	585.1147	575.7715
90	65.12	67.21	68.12	0.1302	0.1344	0.1362	90	691.0319	669.5432	660.5989
120	69.74	72.61	74.04	0.1395	0.1452	0.1481	120	860.3384	826.3325	810.3728

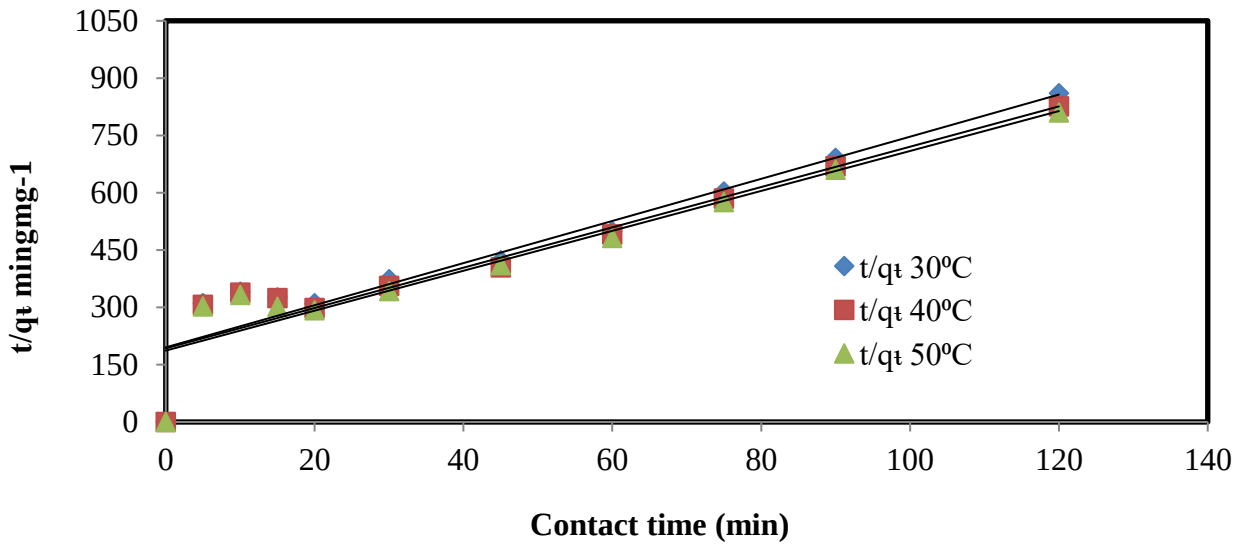

Figure 4.3.8 (d) Graphical presentation of Pseudo FOK model for sorption of 4-CP onto bagasse from aqueous systems; 4-CP conc.: 5.0 mg/L; bagasse dose: 2.5 g; p. size: 150 µm; Cont. time: 120 min and pH: 6.5 at 30-50 °C

By comparing the two groups of graphical charts from Figure 4.3.8 (a-b) and Figure 4.3.8 (c-d) sited in Table 4.3.9(f) have been observed that the correlation coefficients (R^2) for pseudo-first order kinetic model are above 0.99, which are higher than the R^2 values of the pseudo-second order 0.88 in all cases which indicated a better fit for the pseudo-first-order kinetic model. Hence, the biosorption process of 4-CP using sugarcane bagasse followed the pseudo-firsr-order kinetic model. Furthermore, the percentage difference between experimental and calculated biosorption capacity of 4-CP onto bagasse are very close to each other in the first order kinetic model than that of second order also proof that the physical biosorption is favorable in the followed method. Therefore, it is concluded that the experimental data from Table 4.3.9 (b-e), applying in kinetics models have been found the rate constants are shown in Table 4.3.9(f), corresponding from the graphical charts in Figures 4.3.8 (a-b) and

Figures4.3.5(c-d) which remark that the experimental data of biosorption of 4-CP are very well represented by the Pseudo First Order kinetic studies when compared to the Pseudo Second Order kinetic.

Table 4.3.9(f) Pseudo FOK and SOK constants for the biosorption of 4-CP

4-CP							
Pseudo first order kinetic equation $\ln(q_e-q_t) = \ln q_e - kt$							
Constants	Conc. of 4-CP (mg/L)				Temp. of the 4-CP solution		
	2	3	4	5	30°C	40°C	50°C
K_{FOk}	0.030	0.030	0.030	0.030	0.030	0.029	0.028
q_{eFOk} cal.	0.0622	0.0921	0.1188	0.1430	0.1430	0.1466	0.1478
q_{eFOk} exp.	0.0605	0.0895	0.1160	0.1395	0.1395	0.1452	0.1481
R^2_{FOk}	0.999	0.999	0.998	0.995	0.995	0.995	0.996
Pseudo second order kinetic equation $t/q_t = 1/(kq_e^2) + t/q_e$							
K_{SOk}	0.3581	0.2403	0.1837	0.1588	0.1588	0.1444	0.1459
q_{eSOk} cal.	0.0787	0.1165	0.1505	0.1814	0.1814	0.1895	0.1915
q_{eSOk} exp.	0.0605	0.0895	0.1160	0.1395	0.1395	0.1452	0.1481
R^2_{SOk}	0.889	0.888	0.887	0.889	0.889	0.881	0.886

4.3.6 Application of the developed treatment system

The textile and pesticide industries are known to be the most polluting industries in Bangladesh and the effluents of these industries contain crossing the permissible limit of phenolic compounds like 4-CP. The utility of the locally available bagasse has been tested with the effluents of two industrial effluents around Dhaka City, Bangladesh. The effluent samples are collected in glass collection bottles with Teflon-lined caps directly from the outlet of a textile (Bijoy Textile Industries Ltd.), phenolic-based industry located at Plot No-23, Shampur, Kadamtali I/A, Dhaka, Bangladesh, and Agrochemical industries (EH & agro vet. Ltd), Dilhaj mansion plot#151/ka, Pisciculture H.S. Shyamoli Dhaka-1207, Dhaka, Bangladesh, during operation of the plant. The samples have been immediately brought to the laboratory to be placed in a cool place. The 4-CP contents have been analyzed by the modified 4-AAP method and found 7.62 and 9.05 mg/L 4-CP in samples 1 and 2 respectively. The characteristics of the effluents and treatment results are shown in Table5.2.9. The pH of the effluents system samples adjusted to 6.5, and bagasse doses are 2.5 g/100 ml is taken and contact time for biosorption is

120 minutes. The biosorption efficiencies of 4-CP using bagasse are found satisfactory and they are about 86 and 84% for samples 1 and 2, respectively. The desorption efficiencies with 100 ml of 1M NaOH are 90 and 92% respectively. These results indicate that the 4-CP is successfully removed from practical 4-CP containing effluents, and the sorbed 4-CP can be recovered from the surface of the bagasse. Based on the present treatment system, wastewater treatment of 20 L of 4-CP containing effluent will be achievable with 500 g of bagasse in about 120 minutes of treatment time.

4.3.10(a) Condition for the application on biosorption of 4-CP in the developed system

1	Particle size of bagasse	150 µm
2	Volume of potassium ferricyanide solution	0.6 ml
3	Volume of 4-AAP solution	0.9 ml
4	Volume of buffer solution (pH 10)	1.0 ml
5	Biosorbent bagasse dose	2.5 g
6	Contact time of 4-CP solution and biosorbent	120.0 minutes
7	Operational temperature	30 °C
8	Effluent concentration from different industries (mg/L)	Unknown concentration
9	pH	6.5

Table 4.3.10(b) Effluent treatment

Sample No	Concentration of 4-CP (mg/L)
Sample 1 (Bijoy Textile Industries Ltd)	7.62
Sample 2 (EH & agro vet.ltd.)	9.05
Sample 1 1 (After one-time treatment of sample 1)	1.04
Sample 12 (After one-time treatment of sample 2)	1.45

Table 4.3.10(c):Effluent treatment data on sorption and desorption

	Sample -1	Sample -2
pH	7.5	8.0
Initial concentration of 4-CP (mg/L)	7.62	9.05
Final 4-CP concentration (mg/L)	1.04	1.45
Removal (%)	86	84
Desorption (%)	90	92

4.3.7 Desorption of 4-CP and regeneration of bagasse

Recovery of the biosorbed material and regeneration of the biosorbent bagasse are also important aspects of wastewater treatment. Attempts are made desorption of biosorbed 4-CP from bagasse surface with various eluents, such as hydrochloric and nitric acid solutions and base solution sodium hydroxide. This desorption process is performed using the batch method using 2.5 g of spent bagasse after biosorption at pH 6.5 is shaken with 100 ml of 1M NaOH, 1M HCl, and 1M HNO_3 for regeneration, which is completed within 120 minutes. The desorbed efficiencies are 85.46, 74.20, and 59.30% from bagasse which are earlier sorbed onto bagasse from 5.0 mg/L of 4-CP in system solution. Although the achievement of arsenic, elution using strong acidic or alkaline solutions has been reported in the literature[84], the present work has been shown that effective desorption is obtained with 1M NaOH solution. These phenomena are consistent with the results observed for the effect of pH. In general, the desorption efficiency of 4-CP tended to increase with increasing desorption time. Consequently, sodium hydroxide solution is useful for desorption of 4-CP from the surface of bagasse.

The desorption (after biosorption) efficiency of 4-CP is calculated using the equation,

$$\text{Percentage of desorption 4-CP} = \frac{\text{Amount desorbed after Desorption}}{\text{Amount sorbed before Desorption}} \times 100$$

Table 4.3.11 (a) Condition on sorption 4-CP from bagasse

1	Initial concentration of 4-CP	5.0 mg/L
2	pH of solution	6.5
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.6 ml
5	Volume of 4-AAP solution	0.9 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.5 g
8	Contact time of 4-CP solution and bagasse	120 minutes
9	Operational temperature	30 ˚C

Table 4.3.11 (b): Biosorption of 4-CP onto bagasse (before desorption):

Initialconc. mg/L	Absorbance	Conc. of 4-CP (mg/L)	% sorption	% remaining
5	0.1805	1.513	69.74	30.24

Table 4.3.11 (c): Sorbed 4-CP desorption from bagasse (after desorption):

Desorbing agent	Biosorbed 4-CP (mg/L)	Absorbance	4-CP recovered (mg/L)	% recovered
1N NaOH	3.487	0.3571	2.98	85.46
1N HCl	3.487	0.3099	2.59	74.20
1N HNO_3	3.487	0.2472	2.07	59.30

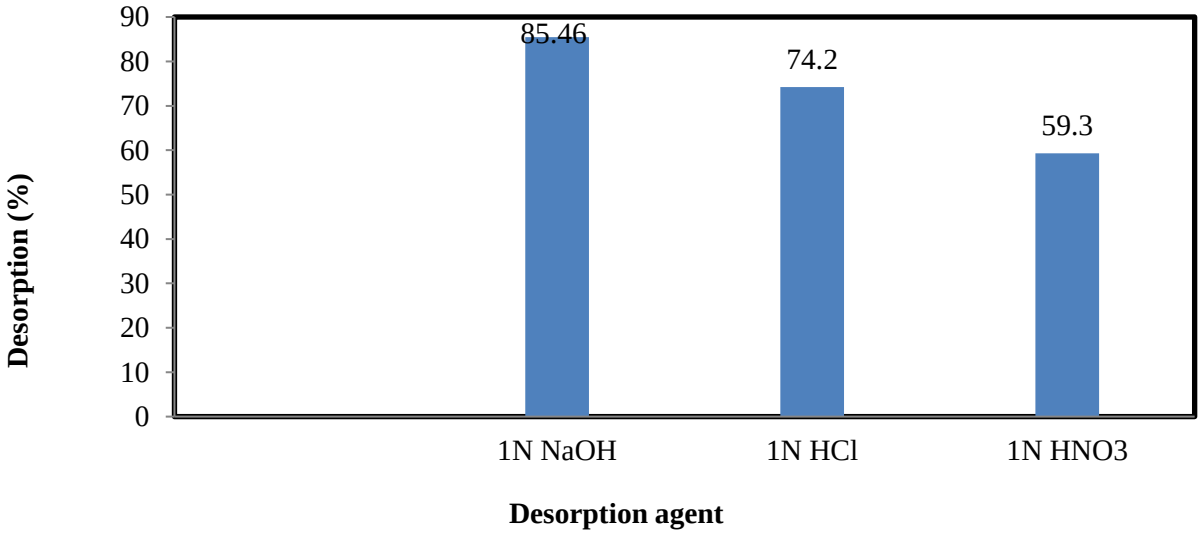

Figure4.3.9 Graphical presentation on recover of 4-CP from biosorbent bagasse (4-CP conc: 5.0 mg/L; bagasse: 2.5 g; particle size 150 µm; contact time: 120 min and pH: 6.5 at 30 ˚C)

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Chapter 5

Biosorption of 2, 4-dichlorophenol from aqueous system using agricultural waste bagasse

Chapter 5

Biosorption of 2,4-dichlorophenol from aqueous system using agricultural waste bagasse

5.1 Introduction

The disposal of ortho, para-dichlorophenol (o, p-DCPh) with industrial effluent is of serious issue from the viewpoint of environmental protection because it is a frequent and toxic byproduct in industrial processes. Herbicide ortho, para-dichloro-phenoxiacetic acid (o, p-D) is prepared using o, p-DCPh as an intermediate reactant. The total production of o, p-DCPh is 40 thousand tons per year in the world. Sources of the compound in the water are from pulp and paper industries, petrochemicals, agrochemicals, plastic, and preservative industries are the major. The compound is also used in the manufacturing of pesticides, herbicides, insecticides, etc, and comes to the water body from various related industrial effluent directly and by decomposition of pesticides, herbicides from agricultural activities, indirectly. The decomposed o, p-DCPh first mixes with soil, then wash away with rainwater to the surface water and through aquifer reach to groundwater. It is hazardous to the ecosystem and living organs. It renders acute and chronic toxicity to freshwater creatures with concentration of 2,020 and 365µg/L respectively. World health organization (WHO) and environment protection agency (EPA) have recommended 0.001 and 3.09 mg/L o, p-DCPh respectively for potable water to protect the publichealth. So, it is necessary for involving treatment of the industrial effluents containing o, p-DCPh at their discharge point. Oxidation, coagulation, chlorination, solvent extraction, liquid membrane permeation, and biosorption are the several mitigation methods of the o, p-DCPh from the industrial effluents and water bodies[1]. Biosorption is an easy and low-cost eco-friendly process. Sorption of o, p-DCPh onto activated carbon (AC) acts as the best water purification process but due to its high cost with variance in carbon generation, low cost and available agro-industrial biosorbents can be expected[2].

Recently, the biosorption process is treated as a low-cost and effective process for mitigating phenolic pollutants in the industrial effluents containing organic pollutants like o, p-DCPh. The agricultural wastes eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, rice husk, etc are available in the rural area of Bangladesh can be used as biosorbent for the purification of water and industrial wastewater. Among these biosorbents, bagasse is comparatively high in biosorption efficiency and it can be used for the treatment of water and industrial effluents containing the o, p-DCPh. Many countries along with Bangladesh produce sugarcane and based on this sugarcane sugar and bioethanol industries have been established and produce byproduct bagasse is known as agricultural waste. Bangladesh is one of the highest populated countries with limited land areas but produces 8.0 lakh tons bagasse

per year[3] at almost districts all over the country. However, the biosorption behavior of o, p-DCPh onto native sugarcane bagasse (SCB) does not yet study extensively. So, the present work is selected to explore an eco-friendly biosorption technique using agricultural waste bagasse.

5.2 Materials and Methods

The contents of sub-para 5.2.1 on materials, 5.2.2 on apparatus and equipments, 5.2.3 on experimental procedures and 5.2.4 on preparation of solutions have been mentioned in para 2.2 of chapter 2.

5.2.5 Operational procedures

The estimation of 2, 4 -dichlorophenol (2,4-DCP) has been done spectrophotometrically by the modified 4-aminoantipyrine (4-AAP) method using Shimadzu UV-1700 double beam spectrophotometer. For the modification of the process detailed experiments are carried out varying all parameters as follows:

Preliminary experiments:

Preliminary experiments are carried out for the spectrophotometer estimation of 2, 4-DCP following the modified 4-AAP method with solution at pH 10.0 and absorbance measured at 503 nm respectively did not give satisfactory results. Investigation on absorbance revealed that the maximum absorption is at 503 nm that the time required for full-color development is 25 minutes. Therefore, it is decided to modify the procedure first and then to apply the modified method for the estimation of 2, 4-DCP. In an attempt to modify the 4-AAP method for the spectrophotometric estimation of 2, 4-DCP, detailed studies have been carried out which include the investigations on the development of color using the absorption spectra, optimum solution media, suitable reagent concentration, adherence to Beer's law etc; so that the modified method can be applied for the estimation of trace amount of 2, 4-DCP in the aqueous system.

General Procedure (Direct Spectrophotometry):

An appropriate aliquot of the test solution containing a definite amount of 2, 4-DCP is taken in a 25 ml volumetric flask. This is followed by the addition of 0.4 ml, 0.8 ml, 1.0 ml buffer concentrate (pH 10) solution, 1.0 ml 4-AAP and 0.8 ml, potassium ferricyanide solutions. The sample is then diluted with double distilled water, up to the mark (25ml). A reagent blank is prepared under identical conditions, against which the absorbance has been measured at the wavelength of maximum absorption (A max) after 15 minutes.

Color Reaction:

Preliminary experiments showed that 2, 4-DCP does not give any appreciable color with 4-AAP in presence of potassium ferricyanide in an acidic medium. But in alkaline medium 2,4-DCP gives a deep brownish-red color whose intensity gradually increases with the increasing the volume of buffer concentrate (pH 10) solution up to 1.0 ml beyond which the intensity sharply decreases. This color system is made the basis for the development of the modified spectrophotometric method for the determination of trace amount of 2, 4-DCP.

5.2.6 Modification of 4-AAP method for determination of 2, 4-DCP

Experiment on the effect of volume ofpotassium ferricyanide solution:

The Results of the potassium ferricyanide (2%W/V) solutions are shown in Table 5.1(b) which indicates that 0.8 ml of potassium ferricyanide solution is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L 2,4-DCP solution. The results are graphically represented in Figure 5.1. The figure depicts that volume beyond the 0.8 ml of the potassium ferricyanide (2%W/V) solution decreases the color intensity of the system. Therefore, 0.8 ml potassium ferricyanide (2% W/V) solution is used for the optimum color development of the system containing 5.0 mg/L 2,4-DCP solution.

Table 5.1(a) Condition on the effect of potassium ferricyanide for color development

Volume of 4-AAP solution	1.0 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 2, 4-DCP	5.0 mg/L
Volume of potassium ferricyanide solution	Different Volume
Color development time	20 minutes
Total volume of the system solution	25 ml

Table 5.1(b) Effect on vol^{m} of potassium ferricyanide sol^{n} for maximum color intensity

Volume of potassium ferricyanide (ml)	λ_{max}(nm)	Absorbance
0.2	503	0.1912
0.4		0.2578
0.5		0.3131
0.6		0.3555
0.7		0.3917
0.8		**0.4202**
0.9		0.3191
1.0		0.2671
1.2		0.2185
1.3		0.1911
1.4		0.1701

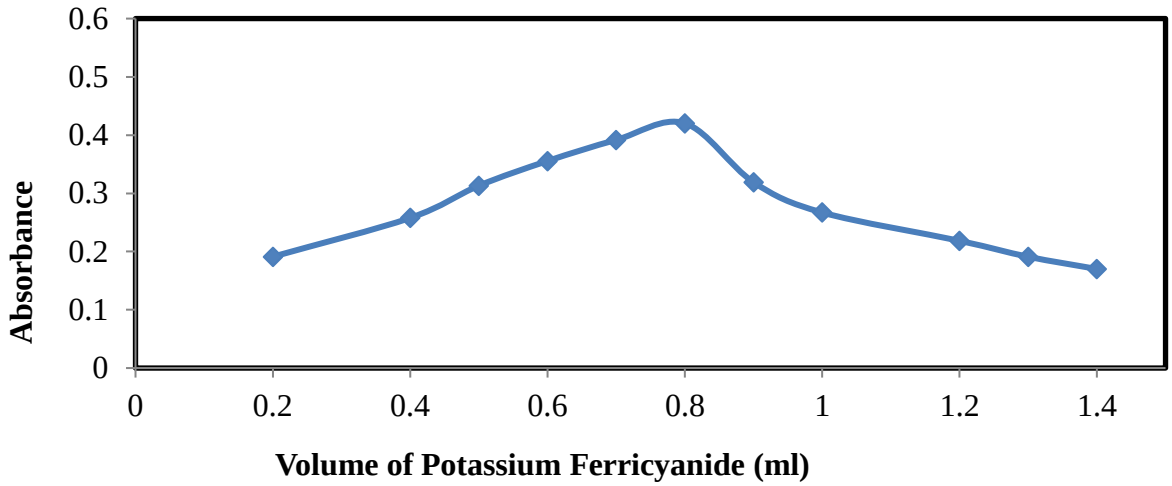

Figure 5.1 Effect on volume of potassium ferricyanide (2.0%W/V) solution for maximum color intensity; 2,4-DCP conc.: 5.0 mg/L; 4-AAP (0.5% w/v) sol^{n}: 1.0 ml; buffer (pH10) sol^{n}: 1.0 ml; time: 20 min at λ_{max}: 503 (nm)

Effect of volume of 4-AAP solutionon color development:

The results of the 4-AAP (0.5% W/V) solutions are shown in Table 5.2(b) which indicates that 1.0 ml of 4-AAP (0.5%W/V) solution is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L of 2,4-DCP solution. The results are graphically represented in Figure5.2. The figure depicts that amount beyond 1.0 ml of 4-AAP solutions decreases the color intensity of the system. Therefore, volume of 1.0 ml of 4-AAP solution is used for the optimum color development of the system containing 5.0 mg/L of 2, 4-DCP.

Table 5.2(a) Condition on effect of 4-AAP for color development

Volume of 4-AAP solution (ml)	Different volume
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 2,4-DCP	5.0 mg/L
Volume of potassium ferricyanide solution	0.8 ml
Color development time	20 minutes
Total volume of the system solution	25 ml

Table 5.2(b) Effect of volume of 4-AAP solution on maximum color intensity

Volume of 4-AAP (ml)	λ_{max} (nm)	Absorbance
0.4	503	0.2685
0.5		0.3093
0.6		0.3455
0.7		0.3767
0.8		0.3956
0.9		0.4082
1.0		**0.4202**
1.2		0.3797
1.3		0.3619
1.4		0.3495

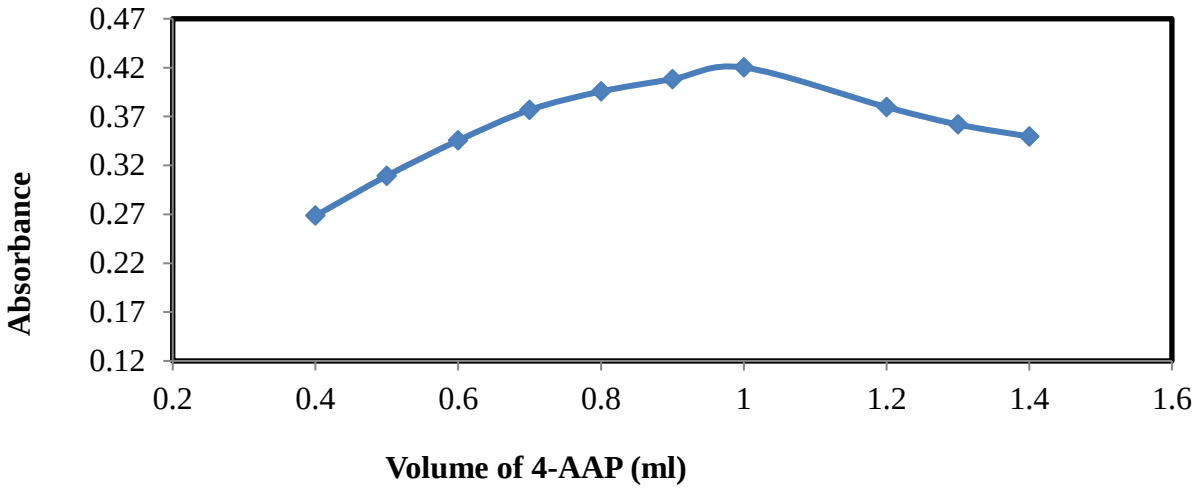

Figure 5.2 Effect on volume of 4-AAP solution (0.5% W/V) for maximum color intensity; 2, 4-DCP conc.: 5.0 mg/L; PFCN (2.0%w/v) sol^n: 0.8 ml; buffer (pH10) sol^n: 1.0 ml; time: 20 min at λ_{max}: 503 (nm)

Effect on volume of buffer solution (pH 10) for color development of the system

The result of the buffer solution (pH 10) is shown in Table 5.3(b) which indicates that 1.0 ml of buffer solution (pH 10) is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L 2, 4-DCP solution. The results are graphically represented in Figure 5.3. The figure reveals that the beyond 1.0 ml of buffer solution (pH 10) decreases the color intensity of the system. Therefore, 1.0 ml of buffer solution (pH 10) is used for the optimum color development of the system containing 5.0 mg/L of 2, 4-DCP solution.

Table 5.3(a) Condition on effect of buffer solution (pH 10) for color development

Volume of 4–AAP solution	1.0 ml
Volume of buffer solution (pH 10) (ml)	Different volume
Concentration of 2, 4-DCP	5.0 mg/L
Volume of potassium ferricyanide solution	0.8 ml
Color development time	20 minutes
Total volume of the system solution	25 ml

Table 5.3(b) Effect on volumeof buffer solution for maximum color intensity

Volume of buffer solution pH 10 (ml)	λ_{max}(nm)	Absorbance
0.4	503	0.2524
0.5		0.3051
0.6		0.3485
0.7		0.3627
0.8		0.3819
0.9		0.4027
1.0		**0.4202**
1.2		0.3691
1.3		0.3250
1.4		0.2922
1.5		0.2551
1.7		0.2121

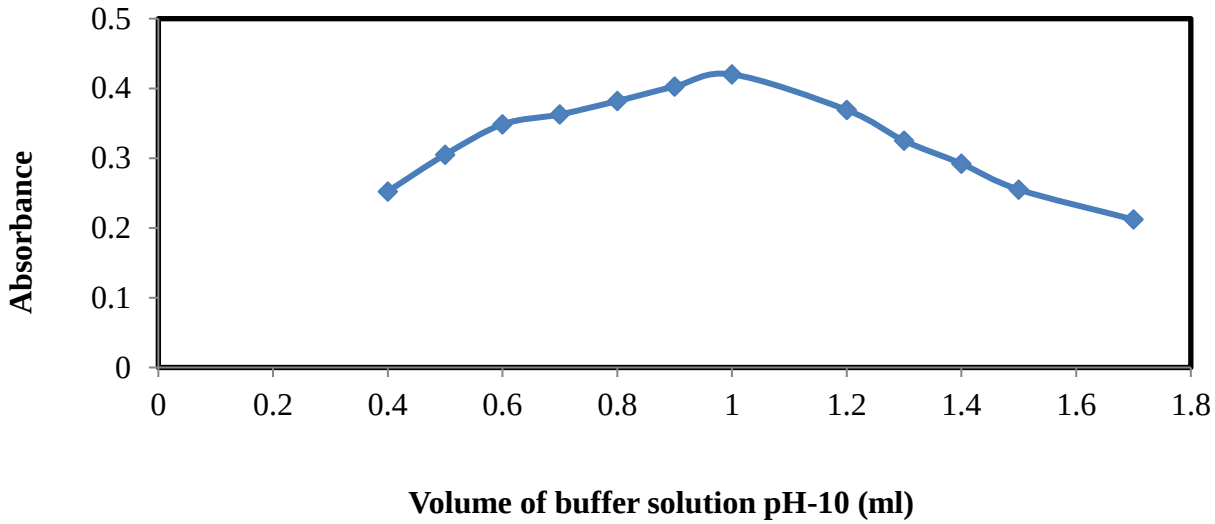

Figure 5.3 Effect on volume of buffer (pH10) solution for maximum color intensity; 2, 4-DCP conc.: 5.0 mg /L; 4-AAP (0.5% W/V) sol^n: 1.0 ml; PFCN (2.0%W/V) sol^n: 0.8 ml; time: 20 min at λ_{max}: 503 (nm)

Effect of time on color development of 2, 4-DCP:

The result of time variation is shown in Table 5.4(b) from which it is observed that 25 minutes is sufficient for the development of maximum color intensities of the system containing 5.0 mg/L 2,4-DCP solution with 0.8 ml potassium ferricyanide solution, 1.0 ml 4-AAP, 1.0 ml buffer solution (pH 10). The results are graphically represented in Figure 5.4. This indicates that 25 minutes are necessary for stable color intensity of the system. Therefore, 25 minutes are used for the optimum color development of the system containing 5.0 mg/L of 2, 4-DCP solution.

Table 5.4(a) Condition on effect of reaction time for color development

Volume of 4-AAP solution	1.0 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 2,4-DCP	5.0 mg/L
Volume of potassium ferricyanide solution	0.8 ml
Color development time (minutes)	Different time
Total volume of the solution	25 ml

Table 5.4(b) Effect on reaction time for maximum color intensity

Time (min)	λ_{max} (nm)	Absorbance
10	503	0.3088
15		0.3815
20		0.4202
23		0.4438
25		**0.4583**
30		0.4413
35		0.4003
40		0.3812

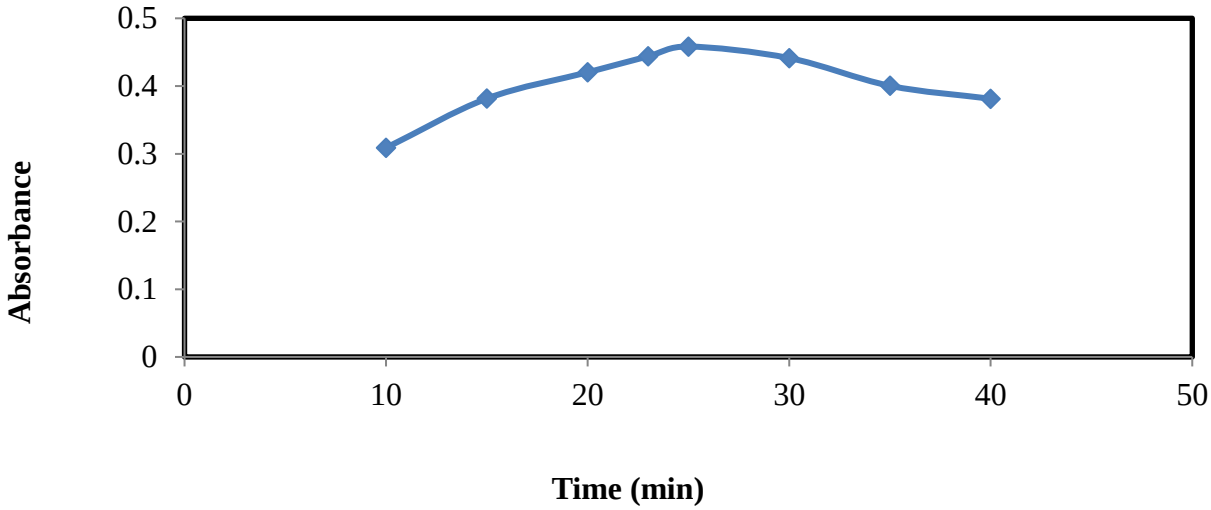

Figure 5.4 Effect of reaction time for development of maximum color intensity; 2,4-DCP conc.: 5.0 mg/L; 4-AAP (0.5% W/V) sol^n: 1.0 ml; PFCN (2.0%W/V) sol^n: 0.8 ml; buffer (pH10) sol^n: 1.0 ml at λ_{max}: 503 (nm)

5.2.7 Preparation of a standard calibration curve for determination of the 2, 4-DCP

A standard calibration curve is a graph relating a measured optical density to a concentration of the substance of interest in "known" samples. The curve is drawn by plotting absorbance (on the Y-axis) versus concentration (on the X-axis). Results of the curve are shown in Table 5.5(b). Standard curve is determined by the system containing 5.0 mg/L of 2,4-DCP solution with 0.8 ml potassium ferricyanide solution (2% w/v), 1.0 ml 4-AAP solution 0.5% (W/V), 1.0 ml buffer

solution (pH 10) and reaction time is 25 minutes. The results are graphically represented in Figure 5.5.

Table 5.5(a) Experimental condition on standard calibration curve

Volume of 4-AAP solution	1.0 ml
Volume of buffer solution (pH 10)	1.0 ml
Concentration of 2,4-DCP (mg/L)	Different concentration
Volume potassium ferricyanide solution	0.8 ml
Time required for maximum color intensity	25 Minutes
Total volume of the system solution	25 ml

Table 5.5 (b) Evaluating the optimum value for standard calibration curve

Concentration of 2, 4-DCP (mg/L)	λ_{max} (nm)	Absorbance
1	503	0.0966
2		0.1702
3		0.2613
4		0.3544
5		0.4583
6		0.5432
7		0.6345
8		0.7234
9		0.8156
10		0.9032

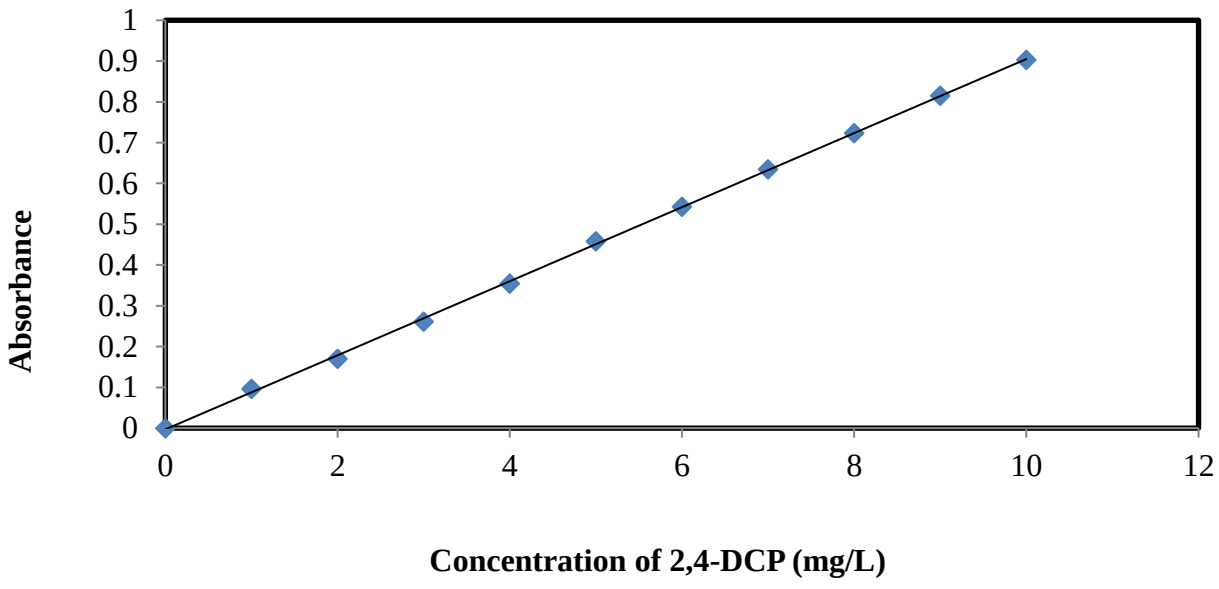

Figure 5.5 Standard calibration curve fordet^{n} absorbance of 2,4-DCP; 2, 4-DCP conc.: 1.0- 10.0 mg/L; 4-AAP (0.5% W/V) sol^{n}: 1.0 ml; PFC (2.0% W/V) sol^{n}: 0.8 ml; buffer (pH10) sol^{n}: 1.0 ml and react^{n} time: 25 min at λ_{max}: 503 nm

5.3 Results and Discussion

5.3.1 Performances of agricultural wastes biosorbents

Preliminary evaluation of performances of nine agricultural wastes (Eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw, and rice husk) have been taken for the biosorption of 2, 4-DCP from system solutions. The biosorption of 2, 4-DCP was performed by conditions: 2, 4-DCP concentration, 5.0 mg/L; temperature (ambient temperature), 30^{o}C; amount of sorbent, 1.0 g; contact time, 60 minutes; particle size 150 µm and pH value 6.0. The studies indicate for biosorption effectiveness of 2, 4-DCP with eggshell, used tea leaves, orange peel, coconut husk, maize husk, bagasse, banana peel, rice straw and rice husk are 16.0%, 15.2%, 16.3%, 31.9%, 16.8%, 34.94%, 18.1%, 31.5%, and 31.7% respectively. Among these, eight adsorbents have lesser sorption efficiencies from bagasse. So, those are not selected for extra experiments. Hence, agro-biowaste bagasse is taken as a comparatively more efficient biosorbent for the biosrption of 2, 4-DCP from system water.

5.3.2.1 Effect of bagasse dose on biosorption of 2, 4-DCP

The biosorption efficiency based on the amount of bagasse has been studied. Different doses of bagasse are introduced in different solutions of 2, 4-DCP of the same volume and same initial concentration. Sorbent bagasse doses are varied from 0.5 to 5.0 g with 100 ml solution of 5.0 mg/L 2, 4-DCP where pH is 6.0, contact time is 60 minutes at 30˚C (room temperature). Results are shown in Figure 5.3.1. The figure indicates that the biosorption efficiency of 2, 4-DCP increases from 14.78 to 60.49% with the increase of bagasse dose from 0.5 to 2.0 g/0.1L and after the certain dose (2.0 g) of the sorbent bagasse, biosorption does not increase. An increase in the biosorption with the bagasse doses can be attributed to greater surface area and the availability of more sorption sites are unsaturated[4]. If the bagasse dose is more than the optimum amount (2.0 g) in the process unit, stoichiometrically, the dose is more than the equivalent amount of 2, 4-DCP in the solution. For this reason, biosorption does not increase with the increase of bagasse dose from 2.0-5.0 g[2,4]. It is revealed that 2.0 g/0.1L bagasse is required for subsequent experiments.

Table 5.3.1(a) Condition on effect of bagasse dose for biosorption of 2, 4-DCP

1	Initial concentration of 2,4-DCP	5.0 mg/L
2	Operational temperature	30˚C
3	pH value of the system solution	6.0
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Contact time of 2, 4-DCP solution and bagasse	60 minutes
8	Particle size of bagasse	150 µm
9	Bagasse dose (g)	Different doses

Table 5.3.1(b) Effect of bagasse dose on biosorption of 2,4-DCP from aqueous system

Bagasse dose (g)	Absorbance	Conc. of 2, 4-DCP (mg/L)	Biosorptionof 2, 4-DCP (%)
0.5	0.3775	4.26	14.78
1.0	0.2789	3.20	34.94
1.5	0.2119	2.49	50.19
2.0	0.1765	1.98	60.49
2.5	0.1765	1.98	60.49
3.0	0.1765	1.98	60.49
3.5	0.1765	1.98	60.49
4.0	0.1765	1.98	60.49
4.5	0.1765	1.98	60.49
5.0	0.1765	1.98	60.49

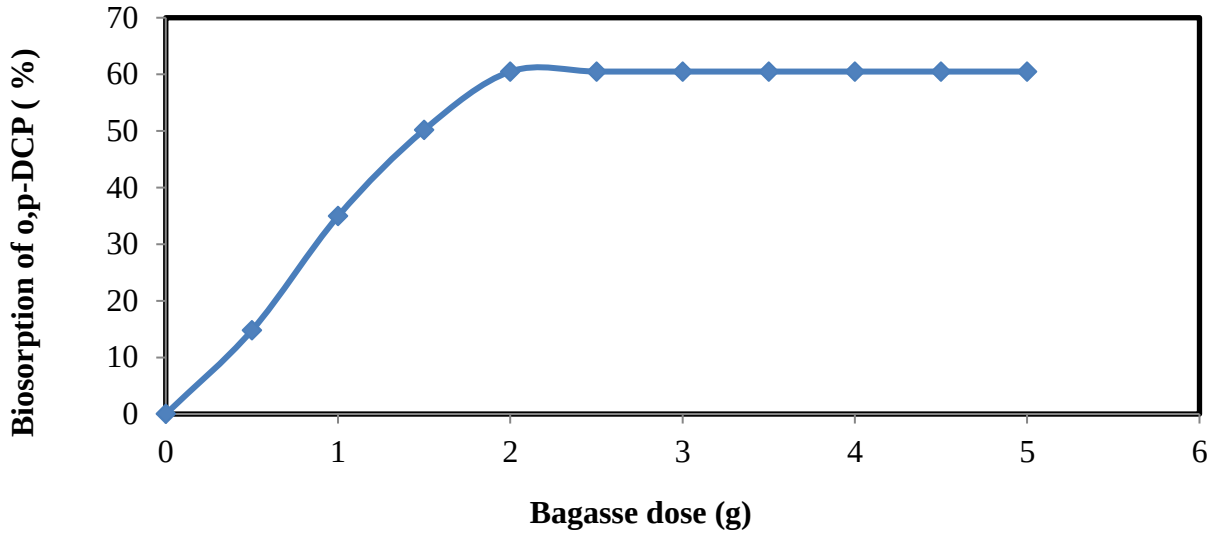

Figure 5.3.1 Graphical presentation on the effect of sorbent bagasse doses on 2, 4-DCP sorption from aqueous system; 2, 4-DCP conc.: 5.0 mg/L; bagasse particle size: 150 µm; cont. time: 60 min and pH: 6.0 at 30 °C

5.3.2.2 Effect of contact time on biosorption of 2, 4-DCP onto bagasse

The effect of time on the biosorption process has been evaluated to determine the equilibrium point. Batch experiments have been carried out to investigate the effect of time on the biosorption of 2, 4-DCP onto bagasse, which is shown in Figure 5.3.2. The figure depicts that the biosorption process is divided into three stages, an initial stage biosorption is occurring rapidly[5,6], subsequently the biosorption is slow and a final stage in which the biosorption reaching equilibrium and remains constant. The fast uptake (more than 80% 2,4-DCP sorption occurs within 60 minutes) occurs at the beginning of the sorption time can be due to the availability of large numbers of vacant sites on the bagasse surface and the rapid attachment of 2,4-DCP to the surface of the bagasse by surface mass transfer[9]. The second stage is slower, as biosorption sites gradually become lower; on the contrary, it is possible many of the available external sites are already occupied and prevails slower biosorption of 2, 4-DCP molecules into the network of the bagasse. An asymptotic trend is found after approximately 120 minutes regardless of the

initial 2, 4-DCP concentration applied to the biosorption system. In this stage biosorption of 2, 4-DCP is not significant at contact times longer than the equilibrium point (120 minutes). The dynamic equilibrium stage acts as the determinant time to evaluate the biosorption efficiency of a sorbent for the 2, 4-DCP. It is concluded to express in simplified mode that at the first initial biosorption of 2, 4-DCP occurs rapidly and then gradually slower up to equilibrium is obtained at a contact time of 120 minutes and at this stage the biosorption efficiency is 73.25% and remains at fixed state during the remaining time from 120-300 minutes. With the increasing of contact time, the vacant sites are become saturated with 2, 4-DCP, and the biosorption efficiency is gradually decreased[8]. Such findings reveal the benefits of using the low-cost biosorbent or so-called eco-friendly biosorbent for the treatment of aqueous solutions rich in pesticides industries in general and 2, 4-DCP in particular. Since after 120 minutes, the biosorption efficiency becomes constant and the biosorption reach to the equilibrium point. Therefore, 120 minutes has been selected as the contact time for the biosorption of 2, 4-DCP onto the SCB under the experimental condition.

Table 5.3.2(a) condition on contact time for biosorption of 2, 4-DCP onto bagasse

1	Initial concentration of 2, 4-DCP	5.0 mg/L
2	Operational temperature	30˚C
3	pH value of the system solution	6.0
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2,4-DCP solution and bagasse (minutes)	Different time
9	Particle size of bagasse	150 µm

Table 5.3.2(b) Effect of contact time on biosorption of 2, 4-DCP onto bagasse

Cont. time	Absorbance	Concen of 2,4-DCP (mg/L)	Biosorption of 2, 4-DCP (%)
5	0.4215	4.60	8.08
10	0.3727	4.20	15.95
15	0.3399	3.83	23.32
20	0.3014	3.47	30.69
30	0.2534	2.91	41.89
45	0.2017	2.37	52.52
60	0.1761	1.98	60.49
75	0.1560	1.84	63.25
90	0.1418	1.65	66.98
120	0.1290	1.34	**73.25**
150	0.1290	1.34	73.25
180	0.1290	1.34	73.25
210	0.1290	1.34	73.25
240	0.1290	1.34	73.25
270	0.1290	1.34	73.25
300	0.1290	1.34	73.25

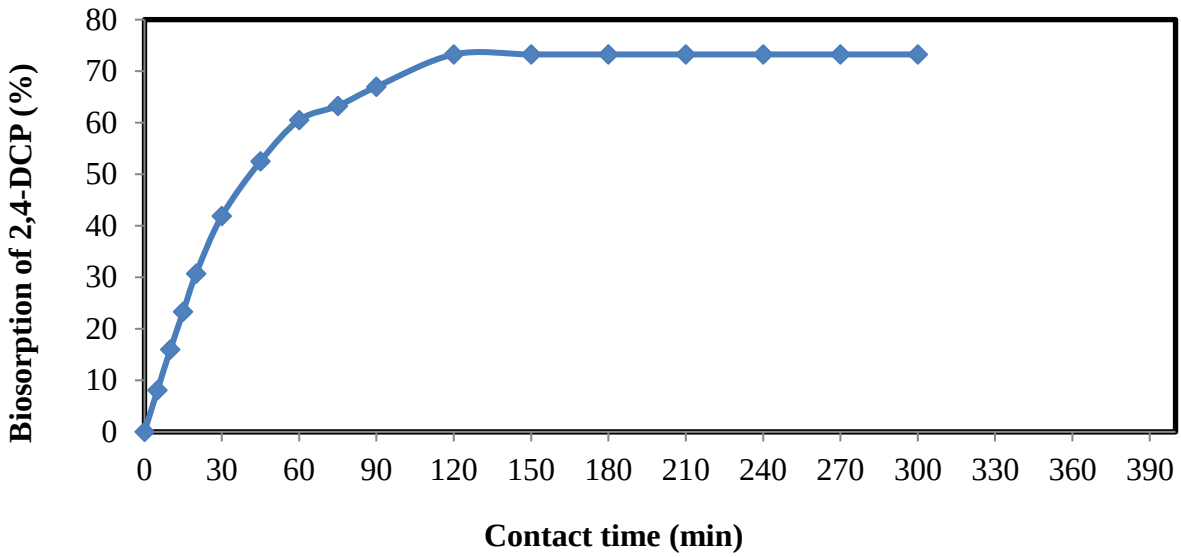

Figure 5.3.2 Graphical presentation on effect of contact time on biosorption of 2, 4-DCP onto bagasse; 2, 4-DCP conc.: 5.0 mg/L, bagasse dose: 2.0 g, particle size: 150 µm; and pH: 6.0 at 30 °C

5.3.2.3 Effect of particle size of bagasse on biosorption of 2, 4-DCP

The particle size of SCB is very important for the biosorption of 2, 4-DCP. In this study, the same amount of bagasse of different particle sizes has been introduced[9] in different solutions of 2, 4-DCP of same volume and same initial concentration at room temperature. The biosorption of 2, 4-DCP is measured after the same time[10] of 120 minutes at the equilibrium point. Batch experiments have been carried out for the 2, 4-DCP sorption from aqueous solution using six different particle size fractions (average diameters of, 50, 70, 100, 150, 200, and 250

μm) which have shown variable efficiency in Figure 5.3.3. The figure indicates that with decreasing particle sizes from 250 to 50 μm, the biosorption is increased from 66.41 to 82.98% with the same bagasse dose 2.0 g. These phenomena might be attributed because the smaller particles offer comparatively larger surface areas and greater numbers of biosorption sites[11]. It is also reported that increasing the surface area of sugarcane bagasse by milling increases the biosorption efficiency[12] of 2, 4-DCP. The selected particle size for subsequent experiments is 150 μm for better convenience.

Table 5.3.3 (a) Condition on effect of particle size of bagasse for biosorption of 2, 4-DCP

1	Initial concentration of 2, 4-DCP	5.0 mg/L
2	Operational temperature	30 ˚C
3	pH of the aqueous system	6.0
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2, 4-DCP solution and bagasse	120.0minutes
9	Particle size of bagasse (μm)	Different size

Table 5.3.3(b) Effect of particle sizeof bagasse on biosorption of 2, 4-DCP

particle sizeof SCB (μm)	Absorbance	Conc. of 2,4-DCP (mg/L)	Biosorptionof 2, 4-DCP (%)
50	0.0822	0.85	82.98
70	0.0937	0.97	80.61
100	0.1066	1.10	77.92
150	0.1292	1.34	73.25
200	0.1313	1.54	69.15
250	0.1429	1.68	66.41

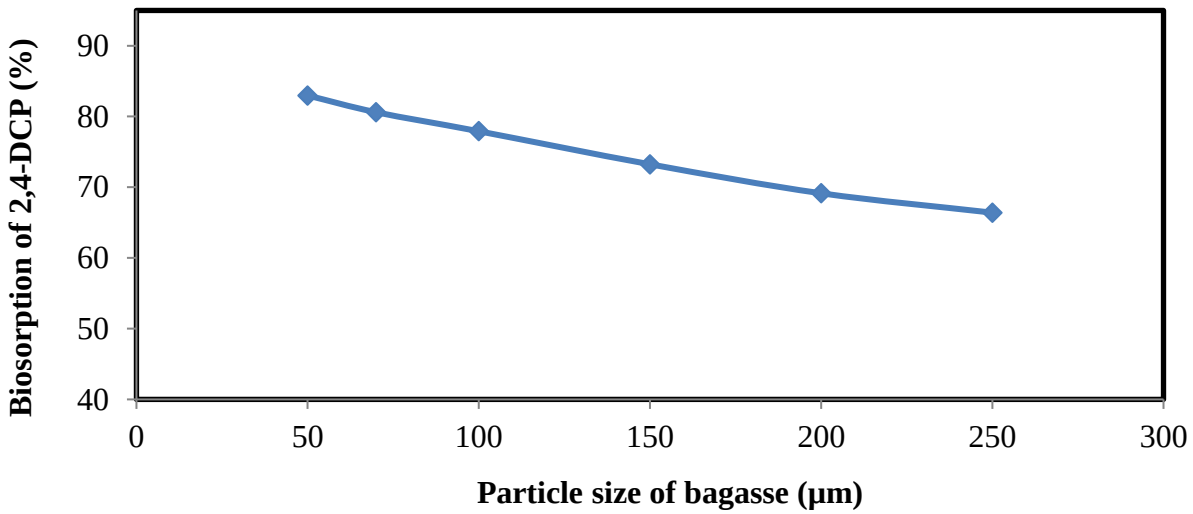

Figure 5.3.3 Graphical presentation of effect of bagasse particle size on the biosorption of 2, 4-DCP from aqueous system; ; 2, 4-DCP concentration: 5.0 mg/L; bagasse dose: 2.0 g; contact time: 120 min and pH: 6 at 30 °C

5.3.2.4 Effect of initial concentration on biosorption of 2, 4-DCP onto bagasse

The same amount and same particle size of bagasse are introduced in 2, 4-DCP solutions of different initial concentrations and the biosorption of 2, 4-DCP is measured at an equilibrium time of 120 minutes. Biosorption decreases with an increasing initial concentration of 2, 4-DCP[13]. For this, the biosorption efficiency is highly dependent on the initial concentration of 2, 4-DCP in the aqueous system. The effects of the initial concentration on the biosorption of 2, 4-DCP onto bagasse are presented in Figure 5.3.4. As seen from the figure, the biosorption percentage of the bagasse decreases with increase in 2, 4-DCP concentration. When the initial 2,4-DCP concentration is increased from 0.5-10.0 mg/L with 2.0g bagasse, the biosorption percentage decreases from 81.0 to 44.0% for 2,4-DCP. Increasing the mass transfer driving force, the rate at which 2, 4-DCP molecules pass from the bulk solution to the particle surface. It is evident that initially the number of bagasse surface sorption sites is available and the driving force for the mass transfer is greater. Therefore, the 2, 4-DCP reaches to the sorption site with ease. With the increase in 2, 4-DCP concentration, increase competition for the active sorption sites and the biosorption becomes to be slowing down[14]. On the other side, with the increase of initial concentration, the number of active sites becomes less and impeding the movement of the 2, 4-DCP. Thus, the initial 2, 4-DCP concentration provides an important force to overcome all mass transfer resistances of the 2, 4-DCP between aqueous and solid phase[5]. In the case of lower 2, 4-DCP concentrations, the ratio of the initial number of moles of 2, 4-DCP to the available surface area of bagasse is large and subsequently, the fractional sorption becomes independent of initial concentration. However, at higher 2, 4-DCP concentrations, the available sorption sites become fewer, and hence the biosorption percentage of 2, 4-DCP decreases[13]. On a relative basis 2, 4-DCP sorption percentage decreases as the initial 2, 4-DCP concentration increases. However, the equilibrium uptake and sorption yield are significant for the bagasse, which is expected, because of the greater specific surface area and the microporous structure of the bagasse[15].

Table 5.3.4 (a) Condition on effect of initial conc. for biosorption of 2, 4-DCP onto bagasse

1	Initial concentration of 2, 4-DCP (mg/L)	Different concentration
2	Operational temperature	30 ˚C
3	pH of the system solution	6.0
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of solution and bagasse	120 minutes
9	Particle size of bagasse	150 µm

Table 5.3.4(b) Effect of initial concentration on biosorption of 2, 4-DCP onto bagasse

Initial conc. (mg/L)	Absorbance	Conc of 2, 4-DCP (mg/L)	Biosorptionof 2, 4-DCP (%)
0.5	0.0091	0.0974	80.52
2	0.0407	0.4218	78.91
3	0.0639	0.6621	77.93
4	0.0910	0.9396	76.51
5	0.1290	1.3375	73.25
6	0.1567	1.8408	69.32
8	0.3460	3.9712	50.36
10	0.5113	5.579	44.21

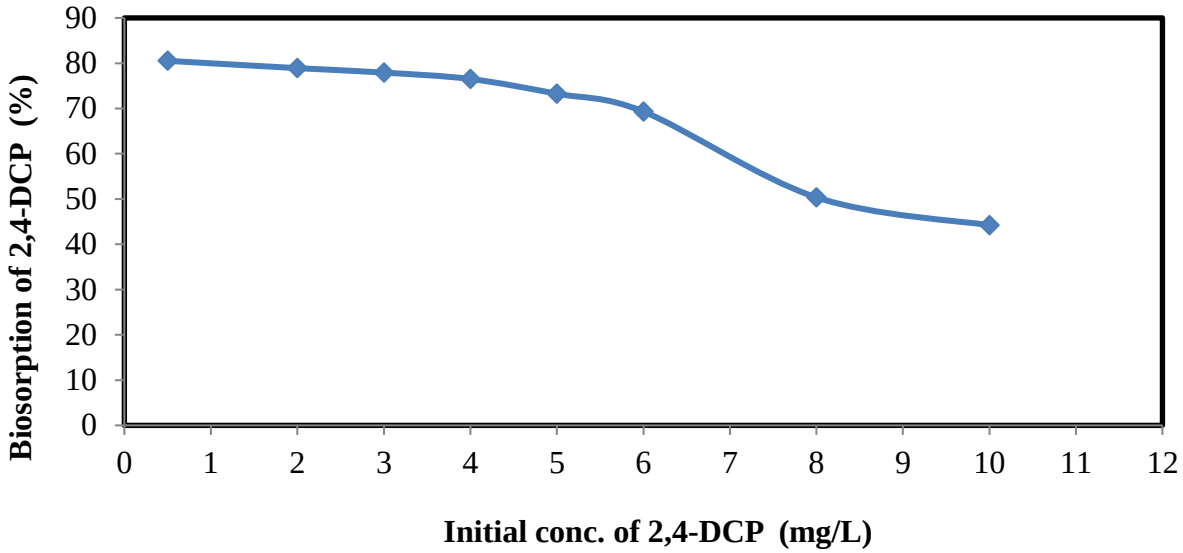

Figure5.3.4 Graphical presentation on effect of initial concentration on biosorption of 2, 4-DCP onto bagasse; bagasse dose: 2.0 g; particle size: 150 µm; contact time: 120 min and pH: 6.0 at 30 °C

5.3.2.5 Effect of pH on biosorption 2, 4-DCP onto bagasse

The solution pH plays a significant role in the biosorption uptake of 2, 4-DCP by SCB. The biosorption of 2, 4-DCP from an aqueous system is dependent on the pH of the system solution, which affects the surface charge of the biosorbent, degree of ionization, and speciation of the sorbate 2, 4-DCP species. The effect of solution pH is investigated between 3 and 12 and the results are displayed in Figure 5.3.5. The figure depicts that the biosorption efficiency of 2, 4-DCP is increased with increase in the pH value up to 6.0 and dramatic decrease in biosorption of 2, 4-DCP with further increase in the pH value. Both the sorbent bagasse and the sorbate 2, 4-DCP have functional groups that are subjected to protonation/deprotonation depending on the solution pH; therefore, the negative effect of increasing pH on biosorption of 2, 4-DCP is likely due to the charge properties of both sorbate and sorbent. The compound 2, 4-DCP is a weak acid. Thus, 2, 4-DCP is in its neutral form at pH ≤6, and the content of anionic species is negligible which has been shown in Figure 5.3.5. The relative content of the anionic 2, 4-DCP

increases as pH increases and becomes prevalent when pH>6. At pH>6, the anionic form of 2, 4-DCP is predominant, and the relative content of the neutral form is negligible. Since the 2, 4-DCP exists in the neutral species at pH 6.0 and there is nearly no electrostatic repulsion between the sorbent and the sorbate[17]. The lower biosorption of 2, 4-DCP at acidic (pH<6) environment is probably due to the presence of excess H^+ ions which competing with 2, 4-DCP molecules for the biosorption sites of bagasse. Furthermore, at lower pH values of carboxylic groups, approximate pH at 4.6, the -COO- groups in bagasse are protonated to -COOH group, and the hydrogen bonds are formed with -COOH group resulting in a decrease of 2, 4-DCP uptake. On the other hand, at higher pH (>6), the OH^- ions concentration increase, and these ions repulse with the negative active sites on the sorbent leading to a decrease in biosorption of 2, 4-DCP[18]. Furthermore, at higher pH, 2,4-DCP dissociates to 2, 4-dichlorophenolate anions that form negative charges in the sample solution. Since the neutral 2, 4-DCP has no charge is predominant at neutral pH (=6.0), electrostatic interactions are not significant even though the surfaces of the bagasse are positively charged. Thus, the biosorption of neutral 2, 4-DCP is determined by sorbate-sorbent interactions other than electrostatic attraction. On the other hand, electrostatic repulsion prevails when the relative content of the anionic 2, 4-DCP is high and when negative charges of the sorbent surfaces build up. As the pH is increased above 6.0, the anionic form of 2, 4-DCP becomes predominant to its neutral counterpart. The concomitant build-up of net negative charges on the surfaces of the bagasse carbon led to an enhanced electrostatic repulsion between the sorbate and sorbent, is resulting in a dramatic decrease in 2, 4-DCP sorption[19] at pH >6. From the study it is found that maximum biosorption 73.25% at pH 6.0. Thus, pH 6.0 has been chosen as the optimum, and at all the subsequent experiments are carried out at this pH.

Table 5.3.5 (a) Condition on effect of pH on biosorption 2, 4-DCP onto bagasse

1	Initial concentration of 2,4-DCP	5.0 mg/L
2	Operational temperature	30 ˚C
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2, 4-DCP solution and bagasse	120 minutes
9	pH value of the system solution	Different value

Table 5.3.5 (b) Effect of pH of the system solution on the biosorption 2, 4-DCP

pH	Absorbance	Concentration of 2, 4-DCP (mg/L)	Biosorption of 2, 4-DCP (%)
3	0.2242	2.57	48.53
4	0.1724	2.03	59.48
5	0.1391	1.63	67.31
6	**0.1292**	**1.34**	**73.25**
6.5	0.1346	1.39	72.13
7	0.1428	1.48	70.43
8	0.1439	1.67	66.64
9	0.1731	2.03	59.33
10	0.2114	2.48	50.32
11	0.2551	2.93	41.43
12	0.3253	3.67	26.57

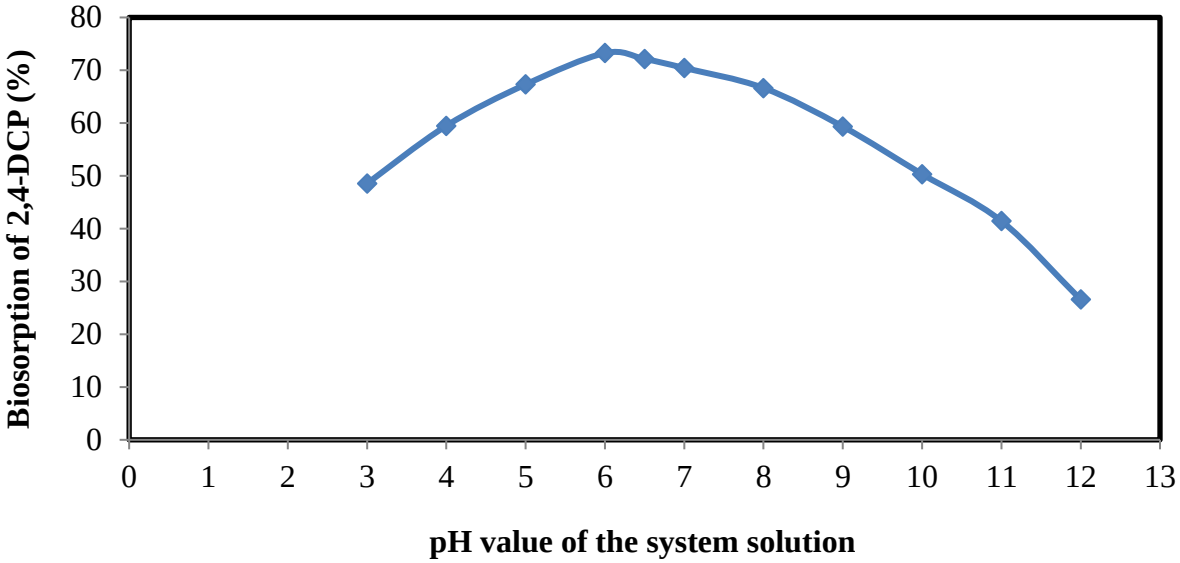

Figure5.3.5 Graphical presentation on effect of pH in thesolution of 2, 4-DCP sorption onto bagasse; 2, 4-DCP conc.: 5.0 mg/L; bagasse dose: 2.0 g; p. size: 150 µm and contact time: 120 min at 30 °C

5.3.2.6 Effect of temperature on sorption of 2, 4-DCP onto bagasse

Temperature is an important parameter for any separation process. Biosorption of 2, 4-DCP onto bagasse has been studied at various temperatures: 30 (room temperature), 35, 40, 45, and 50. The plot of biosorption efficiency as a function of temperature is shown in Figure 5.3.6. The figure indicates that biosorption of 2, 4-DCP onto bagasse is enhanced a little from 73.25-82.43%, when temperature goes from 30-50˚C, suggesting that the process is endothermic[5]. Hence a higher temperature is more favorable for the biosorption of 2, 4-DCP. The higher temperature also reduces the thickness of the outer surface of the bagasse and increases the kinetic energy of 2, 4-DCP molecules. As a result, 2, 4-DCP molecules are easily sorbed on the bagasse surface[20]. The increase in biosorption a little bit with increase in temperature due to lignin in cellulose of sorbent would not be separated. The intraparticle diffusion rate of

sorbate ions are a little into the pores as the pores fill up with lignin and insist sorption when increasing temperature intensifies the pore area. However, increase in biosorption with an increase in temperaturethe process is endothermic[5]. It is investigated that at higher temperature, the hydrogen bonding (Intra and intermolecular) becomes weak, which makes 2, 4-DCP molecules freely available, and hence, biosorption intends to increase at higher temperature. The room temperature at 30˚C is selected for subsequent experiments for convenience.

Table 5.3.6 (a) Condition on effect of temperature for biosorption of 2, 4-DCP onto bagasse

1	Initial concentration of 2,4-DCP	5.0 mg/L
2	pH value of system solution	6.0
3	Particle size of bagasse	150µm
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2,4-DCP solution and bagasse	120 minutes
9	Temperature effect on biosorption of 2,4-DCP (˚C)	Different temperature

Table 5.3.6 (b) Effect of temperature on the biosorption of 2, 4-DCP onto bagasse

Temperature (˚C)	Absorbance	Conc of 2, 4-DCP (mg/L)	Biosorption of 2, 4-DCP (%)
30	0.1292	1.3375	73.25
35	0.1169	1.2105	75.79
40	0.1014	1.0675	78.65
45	0.0977	0.974	80.52
50	0.0848	0.8785	82.43

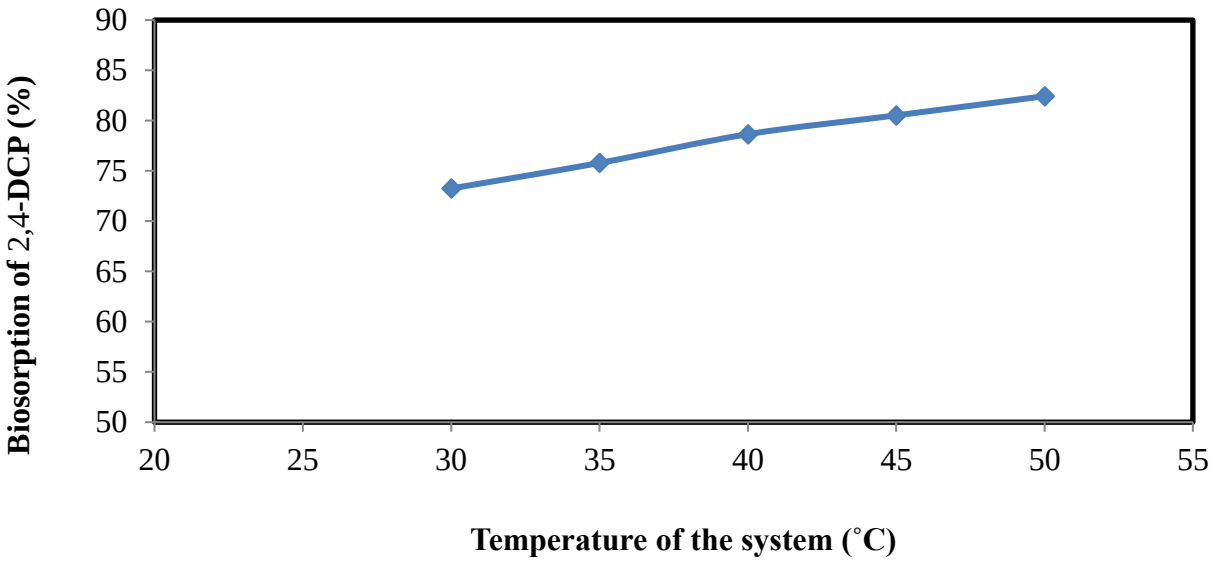

Figure 5.3.6 Graphical presentation on effect of temperature (30 to 50°C) on sorption of 2, 4-DCP onto bagasse; 2, 4-DCP conc.: 5.0 mg/L; bagasse dose: 2.0 g; p. size: 150 µm and contact time: 120 min at pH: 6.0

5.3.3 FTIR spectroscopy studies

The infrared spectra were used to determine changes in the structure of cellulose, hemicelluloses, and lignin during the sequence of treatments subjected to bagasse (native). Table 4.3.3 shows the FTIR spectrum of natural sugarcane bagasse. The band at 1162 cm^{-1} is characteristic of C-O-C asymmetrical stretching, 1335 cm^{-1} is characteristic of C-O aromatic ring, 1423 cm^{-1} is characteristic of CH_2 symmetrical stretching, 1732 cm^{-1} is characteristic of C=O unconjugated stretch, 2885cm^{-1} is characteristic of C-H symmetrical stretching, and 3300 cm^{-1} is characteristic of O-H linked shearing.

Table 5.3.7 Structural characterization of the bagasse

Wavenumber (cm^{-1})	Vibration
3300	O-H linked shearing
2885	C-H symmetrical stretching
1732	C=O unconjugated stretch
1423	CH_2 symmetrical stretching
1335	C-O aromatic ring
1162	C-O-C asymmetrical stretching

5.3.4.1 Langmuir isotherm model for biosorption of 2, 4-DCP onto the bagasse

The monolayer biosorption on a surface with a finite number of identical sites is validated by Langmuir isotherm[21]. Langmuir isotherm assumes that monolayer uptake occurs at binding sites with homogenous energy levels[22,23]. This isotherm model predicts the maximum sorption capacity of 2,4-DCP on the homogenous surface of bagasse carbon.

The linear form of the Langmuir isotherm model can be represented by the following relation[24].

$1/q_e = 1/q^\circ + 1/ (bq^\circ C_e)$

Where C_e (mg/L) is the equilibrium concentration of 2, 4-DCP, q_e (mg/g) is the biosorption capacity of bagasse carbon in during the equilibrium time and q° (mg/g) and b (L/mg) are the Langmuir constants related to the maximum biosorption capacity and the energy of biosorption, respectively. These constants q° (mg/g) and b (L/mg) can be evaluated from the intercept and slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$.

The essential property of the Langmuir isotherm model is a dimensionless constant separation factor, R_L, or equilibrium parameter[30] and is defined by the following equation:

$R_L=1/(1+bC_o)$

Where b denotes the Langmuir constant and C_o is the initial concentration[25] of 2, 4-DCP in the aqueous system. At all temperatures, R_L values have been found less than unity showed in Table 5.3.8(c) indicating that the biosorption process is favorable.

Table 5.3.8(a) Experimental data to apply on Langmuir isotherm model

Con. of 2,4-DCP (mg/L)	Sorptionof 2, 4-DCP (%)			30˚C		40˚C		50˚C	
	30˚C	40˚C	50˚C	$1/C_e$	$1/q_e$	$1/C_e$	$1/q_e$	$1/C_e$	$1/q_e$
0.5	80.52	83.53	85.82	10.2669	49.6771	12.1433	47.8870	14.1044	46.6092
1	79.75	82.69	84.93	4.9383	25.0784	5.7770	24.1867	6.6357	23.5488
2	78.91	81.76	83.95	2.3708	12.6727	2.7412	12.2309	3.1153	11.9120
3	77.93	80.69	82.81	1.5104	8.5547	1.7262	8.2621	1.9391	8.0506
4	76.51	79.15	81.22	1.0643	6.5351	1.1990	6.3171	1.3312	6.1561
5	73.25	75 .75	77.63	0.7477	5.4608	0.8016	5.3298	0.89415	5.1527
6	69.32	71.66	73.42	0.5432	4.8086	0.5881	4.6516	0.6270	4.5401
7	59.21	61.36	62.79	0.3502	4.8254	0.3697	4.6564	0.3839	4.5503
8	50.36	51.98	53.28	0.2518	4.9644	0.2603	4.8095	0.2675	4.6922
9	46.65	47.97	49.09	0.2083	4.7636	0.2136	4.6325	0.21825	4.5268
10	44.21	45.36	46.38	0.1792	4.5239	0.1830	4.4092	0.1865	4.3122

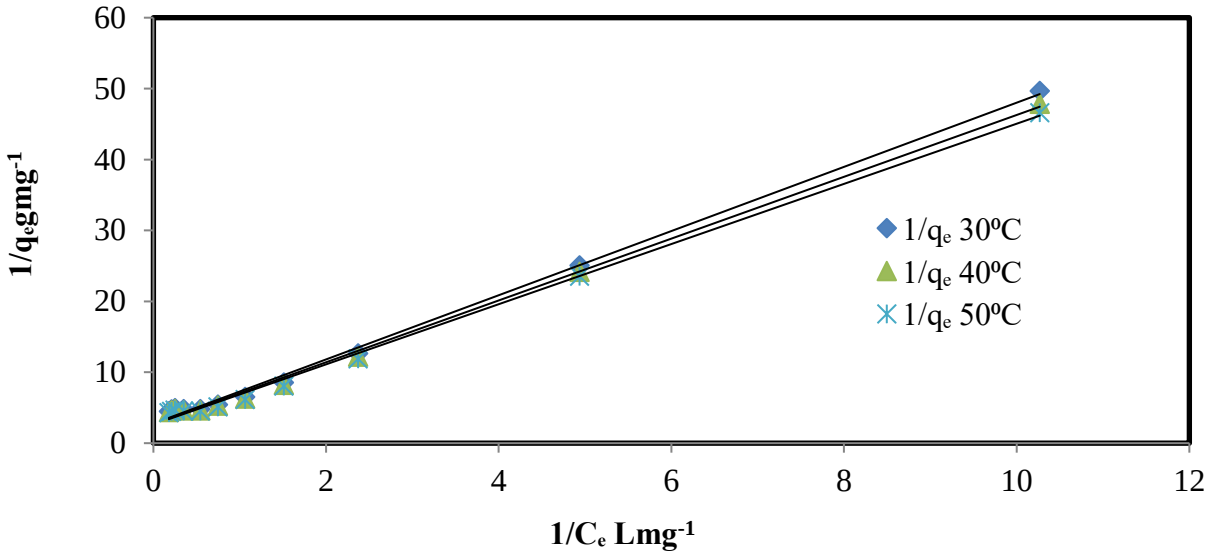

Figure5.3.7(a) Graphical presentation on Langmuir isotherm curve for the sorption of 2, 4-DCP onto bagasse; 2,4-DCP conc.: 0.5-10.0 mg/L; bagasse dose: 2.0 g; p. size: 150 µm; cont. time: 120 min and pH: 6.0 at 30-50 °C

5.3.4.2 Freundlich isotherm model for biosorption of 2, 4-DCP onto bagasse

Freundlich isotherm is based on the biosorption on a heterogeneous surface of varied affinities[26]. This model can be applied for non-ideal sorption on a heterogeneous surface of biosorbent[27,28].

The linear form of the Freundlich isotherm model is given by the following relation[29].

$\ln q_e = \ln k + (1/n) \ln C_e$

Where q_e (mg/g) is the biosorption capacity of 2, 4-DCP at equilibrium, C_e (mg/L) is the equilibrium concentration of the 2, 4-DCP and k and 1/n are the Freundlich constants related to biosorption capacity and intensity, respectively. The values of k and 1/n can be obtained from the intercept and slope of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$ respectively are shown in Figure 5.3.8. For n <1, it indicates chemical biosorption but while for n>1, it shows that the biosorption occures is in physical and the sorbate is favorably sorbed onto the sorbent[30].

Table 5.3.8(b) Experimental data for study on Freundlich isotherm model

Conc 2, 4-DCP (mg/L)	Sorptionof 2, 4-DCP (%)			30˚C		40℃		50℃	
	30˚C	40℃	50℃	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$	$\ln C_e$	$\ln q_e$
0.5	80.52	83.53	85.82	-2.3289	-3.9055	-2.4968	-3.8688	-2.6465	-3.8418
1	79.75	82.69	84.93	-1.5970	-3.2220	-1.7539	-3.1858	-1.8925	-3.1591
2	78.91	81.76	83.95	-0.8632	-2.5395	-1.0084	-2.5040	-1.1363	-2.4775
3	77.93	80.69	82.81	-0.4123	-2.1465	-0.5459	-2.1117	-0.6622	-2.0857
4	76.51	79.15	81.22	-0.0623	-1.8772	-0.1815	-1.8433	-0.2861	-1.8175
5	73.25	75 .75	77.63	0.2908	-1.6976	0.2211	-1.6733	0.1120	-1.6395
6	69.32	71.66	73.42	0.6102	-1.5704	0.5309	-1.5372	0.4668	-1.5130
7	59.21	61.36	62.79	1.0492	-1.5739	0.9950	-1.5382	0.9573	-1.5152
8	50.36	51.98	53.28	1.3791	-1.6023	1.3459	-1.5706	1.3184	-1.5459
9	46.65	47.97	49.09	1.5689	-1.5610	1.5439	-1.5331	1.5221	-1.5100
10	44.21	45.36	46.38	1.7190	-1.5094	1.6982	-1.4837	1.6793	-1.4615

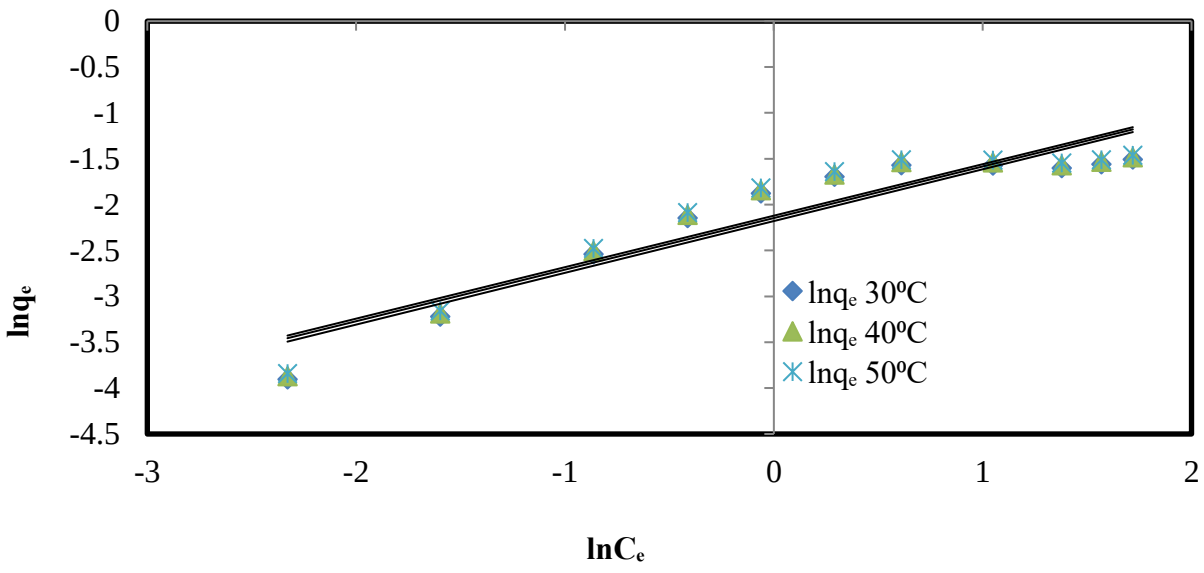

Figure5.3.7(b) Graphical presentation on Freundlich isotherm curve for the sorption of 2,4-DCP onto bagasse; 2, 4-DCP conc.: 0.5-10.0 mg/L, bagasse dose: 2.0 g; p. size: 150 µm; cont. time: 120 min and pH: 6.0 at 30-50 ºC

Table 5.3.8(c) Isotherms constants for biosorption of 2, 4-DCP onto bagasse

Name of compound	2,4-DCP		
Temperature	30˚C	40˚C	50˚C
Constants Langmuir isotherm equation $1/q_e = 1/q^\circ + 1/(bq^\circ C_e)$			
q°	0.3625	0.3717	0.3807
b	0.6096	0.6172	0.6192
R_L	0.1409	0.1394	0.1390
R^2	0.996	0.996	0.996
Freundlich isotherm equation $\ln q_e = \ln k + 1/n \ln C_e$			
1/n	0.564	0.562	0.561
N	1.773	1.779	1.783
K_F	0.1132	0.1170	0.1200
R^2	0.880	0.879	0.877

5.3.4.3 Isotherm models on the biosorption of 2, 4-DCP onto bagasse

The experimental data has been applied to the Langmuir and Freundlich isotherm models and the obtained parameters are given in Table 5.3.8(c) and Figure 5.3.7(a-b). Inspection of the Table 2.3.8(a-b): reveals that: (i) the regression coefficients (R^2) 0.99 obtained from Langmuir model is closer to 1 than that of R^2 (0.880-0.877) at all temperatures respectively of the Freundlich model, suggesting that the Langmuir isotherm fits better with the biosorption of 2, 4-DCP onto bagasse; (ii) the R_L values obtained are in all cases lie between 0 and 1 (0.141-0.139) confirming that the sorption is a favorable process. Hence, it can be concluded that the monolayer Langmuir biosorption isotherm is more suitable to explain the biosorption of 2, 4-DCP onto bagasse; (iii) the values of 1/n are less than 1 (0.564-0.561) indicating that sorption of 2, 4-DCP on the surface of bagasse is a favorable process follows physical sorption technique. However, it is observed that the equilibrium data are very well represented by the Langmuir isotherm model when compared to the Freundlich model. The sorption equilibrium data fitted the Langmuir correlation coefficients (R^2), which are a measure of goodness-of-fit. The higher value of (b= 0.6096-0.6192> k_F= 0.1132-0.1200) b, the Langmuir constant, showed easy uptake of 2, 4-DCP from aqueous solution[24,31]. The biosorption capacity q° (=0.3625-0.3807) is higher for the 2, 4-DCP-bagasse system is expected. Moreover, this is also suggested that physisorption might be the rate-limiting step that controlled the overall biosorption process which is also indicated goodness-of-fit for the Langmuir isotherm model.

Effects of temperature on isotherm model for biosorption

The temperature has also been evaluated as one of themost important factors affecting the biosorption capacity. The calculations of Langmuir and Freundlich isotherm constants for biosorption of 2, 4-DCP onto bagasse as a function of temperature and the corresponding coefficient of correlation values are shown in Table 5.3.8(d). According to Table 5.3.8(d) the optimum biosorption temperature, at which the sorption capacity of 2, 4-DCP on the biomass bagasse is the higher at 50˚C of the temperature ranges studied. Besides, temperature cannot be raised beyond 50˚C for color formation has been observed in the test solution. The coefficient of the Langmuir model indicates that b lies between zero and one, suggesting that the biosorption of 2, 4-DCP by bagasse is favorable. The values of q°, which is defined as the maximum capacity of biosorbents, have also been calculated from the Langmuir plots at higher temperatures. For the coefficients of the Freundlich model, K_F increased with a rise in the temperatures, reveal that the biosorption capacity of 2, 4-DCP onto bagasse increased with the increase in temperature. This indicates that the biosorption of 2, 4-DCP by bagasse might be endothermic (ΔH• was a positive value) in nature and the biosorption is favored at a higher temperature. Since the biosorption process is controlled by the diffusion process (intraparticle transport–pore diffusion), the sorptive capacity is increased with an increase in temperature due to the endothermicity of the diffusion process. An increase in the temperature involves an increased mobility of 2, 4-DCP and a decrease in the retarding forces acting on the diffusing ions. These are the results in the enhancement in the sportive capacity of the biosorbent bagasse[32]. The highest value of n in Table 5.3.8(c) for 2, 4-DCP at 50˚C, represents favorable biosorption at high temperature. If the value of n is below one, then the biosorption is a chemical process; otherwise, the biosorption is a physical process. All values of n exceed one, suggesting the biosorption of 2, 4-DCP by bagasse is a physical process. On the other hand, the Freundlich exponent of 1/n gives information about surface heterogeneity and surface affinity for the solute. The Freundlich exponent 1/n between 0 and 1 indicates favorable biosorption and a high affinity of bagasse for chlorophenol[33].

5.3.5 Kinetics studies on biosorption of 2, 4-DCP onto bagasse from the aqueous system

To understand the interactions between the targeted 2, 4-DCP and the sugarcane bagasse as biosorbent, the biosorption rates, rate constants, dynamics of sorption, and reaction mechanisms have been studied based on Lagergren pseudo first order and Ho's pseudo second order kinetic models. The studies of biosorption kinetic describe the 2, 4-DCP uptake rate which controls the residence time of sorbate uptake at the solid/solution interface[34]. The residence time of 2, 4-DCP on the bagasse surface is significant in finding whether the process is completed or not and also to estimate the total uptake capacity. These are key parameters in

designing an actual treatment plant used for wastewater treatment. To analyze the biosorption kinetics of 2, 4-DCP onto bagasse, Pseudo first and second order models are applied to analyze the experimental data. The kinetic studies are set up in the laboratory in batch method by adding a known amount of 2, 4-DCP to a required number of flasks which contain 100 ml of solution. Initial 2, 4-DCP solution concentrations are 2.0-5.0 mg/L at pH 6.0 and the amount of biosorbent bagasse is 2.0 g at constant temperature 30 ˚C. The bottles are subsequently capped and shaken in a rotary shaker for 120 minutes, the equilibrium time. The Process is also done for different temperatures at 30-50˚C with a constant 2, 4-DCP concentration of 5.0 mg/L and has been shaken for up to equilibrium time 120 minutes separately. The experimental data are employed in both the pseudo-first-order and pseudo-second-order kinetic models.

Table 5.3.9(a) Condition on kinetic model for biosorption of 2, 4-DCP

1	Initial concentration of 2,4-DCP	2.0-5.0 mg/L
2	pH value of system solution	6.0
3	Particle size of bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2,4-DCP solution and bagasse	120 minutes
9	Operational temperature	30-50˚C

5.3.5.1 Pseudo First order kinetic (FOK) studies for sorption 2, 4-DCP onto bagasse

The pseudo-first-order kinetic model[35] is widely used to predict the biosorption kinetics of 2, 4-DCP and can be illustrated by the following equation:

$$\ln (q_e - q_t) = \ln q_e - kt$$

Where q_e and q_t (mg/g) are the values of sorbed 2, 4-DCP onto the bagasse surface at equilibrium time and at any time t (minute), respectively. Moreover, k (min^{-1}) is the biosorption rate constant of the pseudo-first order kinetic model. To determine the suitability of the pseudo-first-order kinetic model, a graph of $\ln (q_e - q_t)$ versus t is plotted and is as shown in Fig. 5.3.5(a) at initial concentration 2.0-5.0 mg/L and constant temperature at 30˚C and in Figure 5.3.7(b) at constant concentration, 5.0 mg/L and variable temperature 30-50˚C separately. The graphical representations are shown in figure 5.3.7(a-b) from which q_e and k has been estimated from the relation of intercept and slope.

Table 5.3.9(b) Experimental data of biosorption 2,4-DCP onto bagasse from (2.0-5.0 mg/L) aqueous solution to apply on the pseudo FOK model at 30˚C

Time	Biosorption of 2, 4-DCP (%)				Time	$\ln(q_e-q_t)$			
	2ppm	3ppm	4ppm	5ppm		2ppm	3ppm	4ppm	5ppm
0	0	0	0	0	0	-2.5395	-2.1465	-1.8772	-1.6976
5	8.69	8.57	8.41	8.08	5	-2.6561	-2.2630	-1.9936	-1.8145
10	17.15	16.95	16.64	15.95	10	-2.7845	-2.3917	-2.1224	-1.9432
15	25.08	24.75	24.34	23.32	15	-2.9219	-2.5286	-2.2601	-2.0808
20	33.05	32.65	32.07	30.69	20	-3.0822	-2.6894	-2.4205	-2.2406
30	45.12	44.57	43.73	41.89	30	-3.3876	-2.9949	-2.7248	-2.5459
45	56.56	55.88	54.85	52.52	45	-3.8009	-3.4090	-3.1391	-2.9599
60	64.08	63.25	62.12	60.49	60	-4.2111	-3.8158	-3.5481	-3.4452
75	68.13	67.27	66.07	63.25	75	-4.5301	-4.1358	-3.8690	-3.6889
90	72.15	71.27	69.93	66.98	90	-4.9967	-4.6062	-4.33057	-4.1557
120	78.91	77.93	76.51	73.25	120				

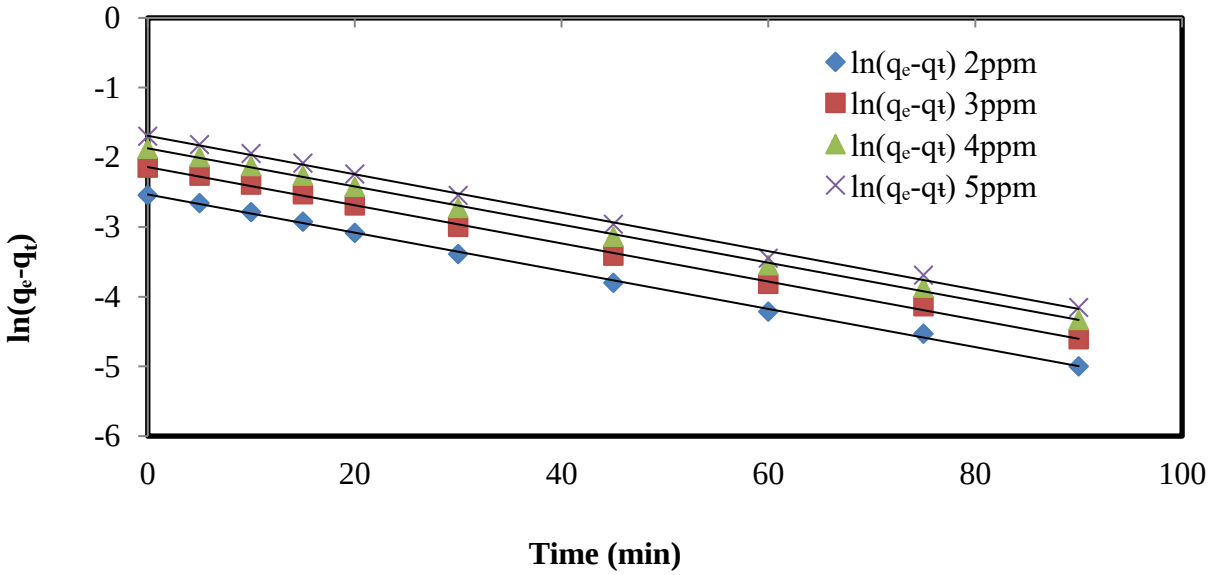

Figure 5.3.8(a) Graphical presentation on Pseudo FOK model for biosorption of 2, 4-DCP onto bagasse from (2.0- 5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; p. size: 150 µm; contact time: 120 min and pH: 6 at 30 °C

Table 5.3.9(c) Experimental data on biosorption of 2, 4-DCP onto bagasse from (5.0 mg/L) aqueous solution to apply on the pseudo FOK model at 30-50 ˚C

Time	Sorptionof 2, 4-DCP (%)			q_t			Time	$\ln(q_e-q_t)$		
	30˚C	40˚C	50˚C	30˚C	40˚C	50˚C		30˚C	40˚C	50˚C
0	0	0	0	0	0	0	0	-1.6976	-1.6639	-1.6395
5	8.08	8.31	8.52	0.0202	0.0208	0.0213	5	-1.8145	-1.7801	-1.7558
10	15.95	16.43	16.98	0.0399	0.0411	0.0425	10	-1.9432	-1.9084	-1.8863
15	23.32	24.14	24.73	0.0583	0.0604	0.0618	15	-2.0808	-2.0476	-2.0231
20	30.69	31.75	32.54	0.0767	0.0794	0.0814	20	-2.2406	-2.2071	-2.1828
30	41.89	43.37	44.38	0.1047	0.1084	0.1110	30	-2.5459	-2.5136	-2.4874
45	52.52	54.33	55.65	0.1313	0.1358	0.1391	45	-2.9599	-2.9267	-2.9013
60	59.49	61.52	63.03	0.1487	0.1538	0.1576	60	-3.3697	-3.3354	-3.3104
75	63.25	65.39	67.08	0.1581	0.1635	0.1677	75	-3.6889	-3.6526	-3.6353
90	66.98	69.25	70.97	0.1675	0.1731	0.1774	90	-4.1557	-4.1181	-4.0954
120	73.25	75 .75	77.63	0.1831	0.1894	0.1941	120			

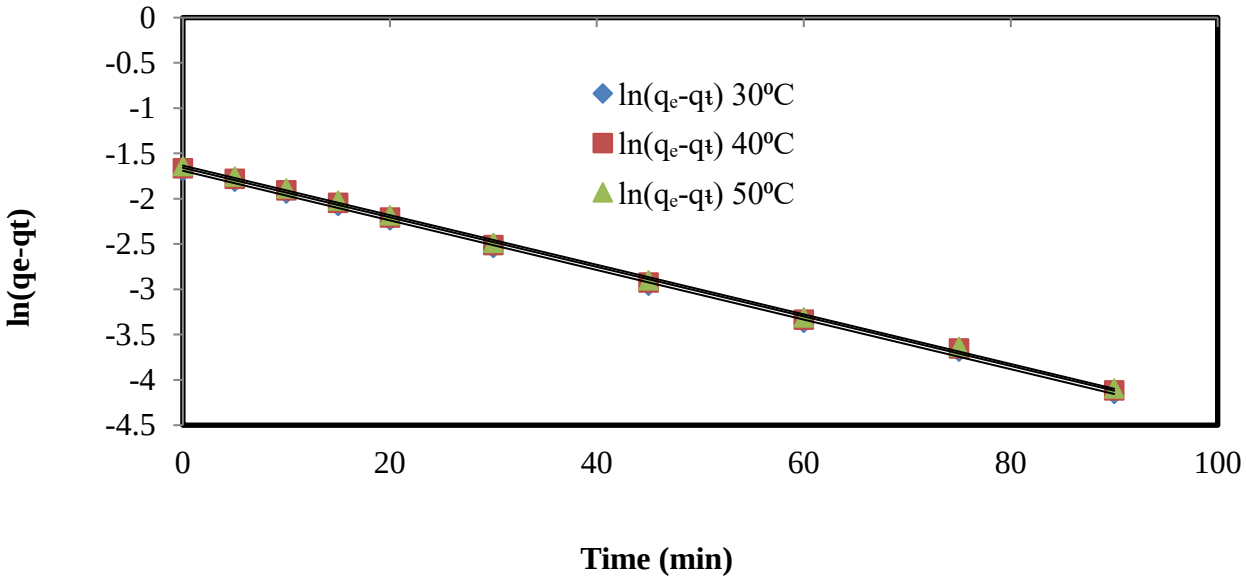

Figure 5.3.8(b) Graphical presentation on Pseudo FOK model for biosorption of 2, 4-DCP onto bagasse from (5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; p. size: 150 µm; time: 120 min at pH: 6.0 at 30- 50 °C

5.3.5.2 Pseudo second order kinetic (SOK) studies for sorption of 2, 4-DCP onto bagasse

Ho proposed a second order model for the biosorption of 2, 4-DCP onto bagasse based on the sorption capacity of the sorbents to differentiate the kinetics of a second-order rate expression based on the sorbate concentration from models that are based on the solute concentration and represent a pseudo-second-order rate expression.

The linearized form of the pseudo-second-order model as given by Ho[36] is as follows

$t/q_t = 1/(kq_e^2) + t/q_e$

Where k is the rate constant of the pseudo-second-order adsorption, q_e is the amount of 2, 4-DCP sorbed on the biosorbent at equilibrium (mg/g), and q_t is the amount of 2, 4-DCP sorbed on the biosorbent at any time, t (mg/g). K and q_e can be calculated from the intercept and slope of the plot of t/q_t against t. The graphical representations are shown in figures 5.3.8(c-d).

Table 5.3.9(d) Experimental data on biosorption of 2,4-DCP from (2.0- 5.0 mg/L) aqueous solution onto bagasse to apply on the Pseudo SOK model at 30˚C

Time	Sorption of 2, 4-DCP (%)				Time	t/q_t			
	2ppm	3ppm	4ppm	5ppm		2ppm	3ppm	4ppm	5ppm
5	8.69	8.57	8.41	8.08	5	575.374	388.9537	297.2652	247.5248
10	17.15	16.95	16.64	15.95	10	583.0904	393.3137	300.4808	250.7837
15	25.08	24.75	24.34	23.32	15	598.0861	404.0404	308.1348	257.2899
20	33.05	32.65	32.07	30.69	20	605.1437	408.3716	311.8179	260.6712
30	45.12	44.57	43.73	41.89	30	664.8936	448.7323	343.0139	286.4646
45	56.56	55.88	54.85	52.52	45	795.6153	536.8647	410.2097	342.7266
60	64.08	63.25	62.12	60.49	60	936.3296	632.4111	482.9363	403.4291
75	68.13	67.27	66.07	63.25	75	1100.8370	743.2734	567.5798	474.3083
90	72.15	71.27	69.93	66.98	90	1247.4010	841.8689	643.5006	537.4739
120	78.91	77.93	76.51	73.25	120	1520.7200	1026.5620	784.2112	655.2901

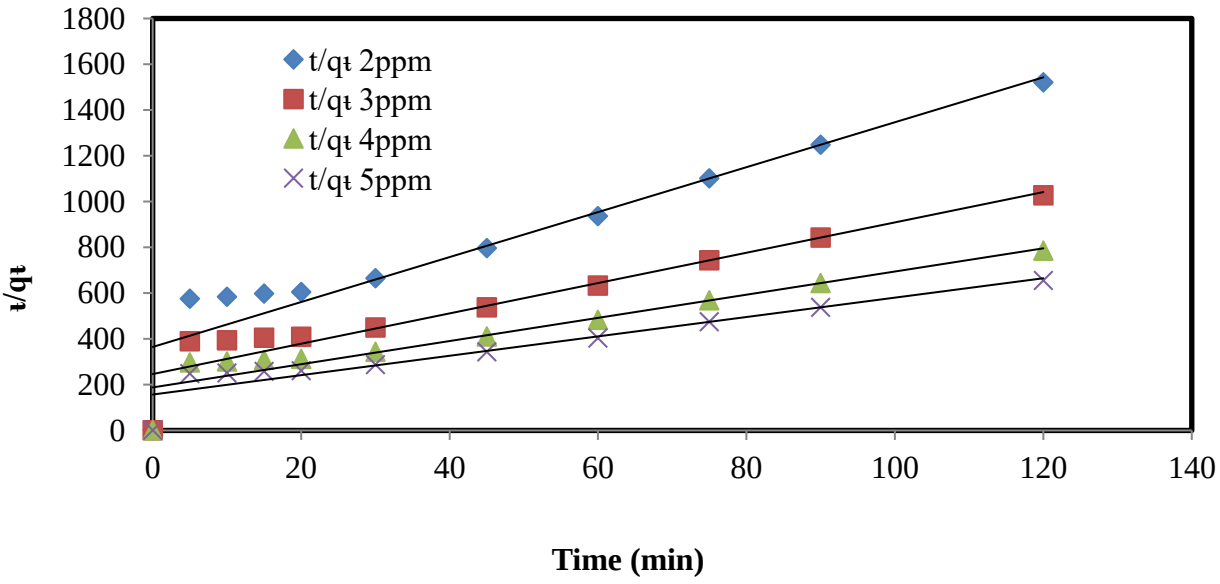

Figure 5.3.8(c) Graphical presentation on Pseudo SOK model for biosorption of 2, 4-DCP onto bagasse from (2.0-5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; particle size: 150 µm; time: 120 min and pH: 6.0 at 30 °C

Table 5.3.9 (e) Experimental data on biosorption of 2, 4-DCP from (5.0 mg/L) aqueous solution onto bagasse to apply on the pseudo SOK model at 30-50˚C

Time	2, 4-DCP sorption (%)			Sorption capacity of 2,4-DCP (q_t)			Time	t/q_t		
	30˚C	40˚C	50˚C	30˚C	40˚C	50˚C		30˚C	40˚C	50˚C
5	8.08	8.31	8.52	0.0202	0.0208	0.0213	5	247.5248	240.6739	234.7418
10	15.95	16.43	16.98	0.0399	0.0411	0.0425	10	250.7837	243.4571	235.5713
15	23.32	24.14	24.73	0.0583	0.0604	0.0618	15	257.2899	248.5501	242.6203
20	30.69	31.75	32.54	0.0767	0.0794	0.0814	20	260.6712	251.9685	245.8513
30	41.89	43.37	44.38	0.1047	0.1084	0.1110	30	286.4646	276.6890	270.3921
45	52.52	54.33	55.65	0.1313	0.1358	0.1391	45	342.7266	331.3087	323.4501
60	59.49	61.52	63.03	0.1487	0.1538	0.1576	60	403.4291	390.1170	380.7711
75	63.25	65.39	67.08	0.1581	0.1635	0.1677	75	474.3083	458.7857	447.2272
90	66.98	69.25	70.97	0.1675	0.1731	0.1774	90	537.4739	519.8556	507.2566
120	73.25	75 .75	77.63	0.1831	0.1894	0.1941	120	655.2901	633.5797	618.3177

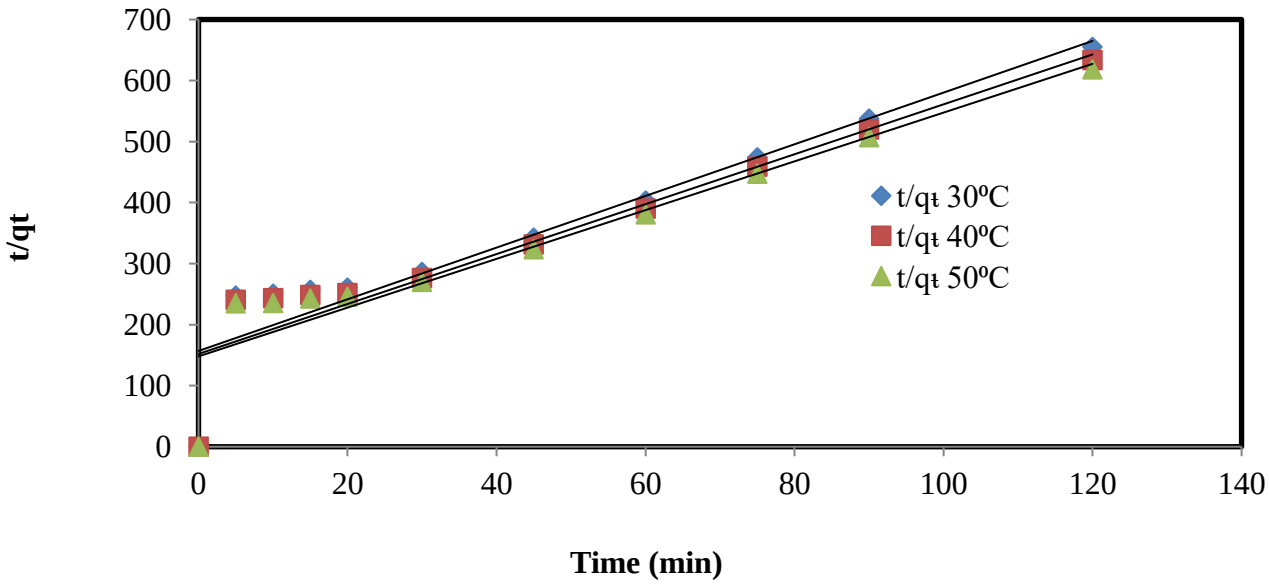

Figure 5.3.8(d) Graphical presentation on Pseudo SOK model for biosorptⁿ of 2, 4-DCP onto bagasse from (5.0 mg/L) aqueous systems; bagasse dose: 2.0 g; p. size: 150 µm; time: 120 min and pH: 6 at 30-50 °C

By comparing the two groups of graphical charts in Figure.5.3.8 (a-b) and Figure 5.3.8(c-d) are observed that the correlation coefficients (R^2) for pseudo-first order model are in the range of 0.99 which are higher than the R^2 values of the pseudo-second order 0.88 in all cases which indicate a better fit for the pseudo-first-order kinetic model. Hence, the biosorption process of 2, 4-DCP using raw sugarcane bagasse followed the pseudo-first-order kinetic model. The kinetic isotherm rate constants are shown in Table 5.3.9(e); graphical charts in Figure 5.3.8(a-b) and 5.3.8(c-d). It would observe that the experimental data are very well represented by the Pseudo First order kinetic studies when compared to the Pseudo second order kinetic.

Table 5.3.9(f) Kinetics constants for the biosorption of 2, 4-DCP onto bagasse

Pseudo first order kinetic equation $\ln(q_{eFO}-q_t) = \ln q_{eFO} - k_{FO}t$							
Constants	Concentration of 2,4-DCP (mg/L)				Temp. of the 2,4-DCPsolution		
	2	3	4	5	30˚C	40˚C	50˚C
K_{FOk}	0.027	0.027	0.027	0.027	0.027	0.027	0.027
q_{eFOk} cal.	0.0794	0.1178	0.1540	0.1843	0.1843	0.1905	0.1953
q_{eFOk} exp.	0.0789	0.1169	0.1530	0.1831	0.1831	0.1894	0.1941
R^2_{FOk}	0.998	0.998	0.998	0.997	0.997	0.998	0.998
Pseudo second order sorption kinetic equation $t/q_t = 1/k_{SO}q^2_{eSO} + 1/q_{eSO}t$							
K_{SOk}	0.2640	0.1783	0.1363	0.1142	0.1142	0.1100	0.1078
q_{eSOk} cal.	0.1019	0.1509	0.1975	0.2362	0.2362	0.2446	0.2504
q_{eSOk} exp.	0.0789	0.1169	0.1530	0.1831	0.1831	0.19663	0.2060
R^2_{SOk}	0.889	0.889	0.889	0.889	0.889	0.888	0.889

5.3.6 Application of the developed treatment system

The pesticides and textile industries are known to be the largest industries for the pollution of the aqueous environment in Bangladesh and effluents of these industries contain a large amount of phenolic compounds like 2,4-DCP. The utility of the locally available bagasse has been tested for biosorption of the effluents of pesticide and textile industries around Dhaka City, Bangladesh. Industrial effluent samples are collected in a glass collection bottle with Teflon-lined caps directly from the outlet of a Pesticide effluent (Runner Agro products Ltd) Tejgaon Industrial Area, Dhaka 1208, Bangladesh, and textile effluent (Bijoy Textile Industries Ltd.), located at Plot No-23, Shampur, Kadamtali I/A, Dhaka, Bangladesh within the operating duration of the plant. The sample is immediately brought to the laboratory to be placed in a cool place. The 2, 4-DCP contents are analyzed by the modified 4-AAP method and found 8.72 and 6.12 mg/L of 2, 4-DCP from samples 1 and 2, respectively. The characteristics of the effluents and treatment results are shown in Table 5.3.10(c). The pH of the effluent is adjusted to 6.0, and the bagasse dose is of 2.0 g/100 ml is taken and the agitated duration is 120 minutes. The removal efficiencies of 2, 4-DCP using bagasse are found satisfactory and are about 89 and 88% for samples 1 and 2, respectively. The desorption efficiencies with 100 ml of 1M NaOH are 90 and 92% from bagasse for sample 1 and 2 respectively. These results indicate that the 2, 4-DCP is successfully removed from practical effluents containing 2, 4-DCP, and the biosorbed 2, 4-DCP can be recovered from the surface of bagasse. Based on the present treatment system, wastewater treatment of 20 L of 2, 4-DCP containing effluent may be achievable with 400 gm of bagasse in about 120 minutes of treatment time.

Table 5.3.10 (a) Condition of the application of developed treatment system

1	Particle size of bagasse	150 µm
2	Volume of potassium ferricyanide solution	0.8 ml
3	Volume of 4-AAP solution	1.0 ml
4	Volume of buffer solution (pH 10)	1.0 ml
5	Bagasse dose	2.0 g
6	Contact time of solution and bagasse	120 minutes
7	Operational temperature	30˚C
8	Conc. of 2, 4-DCP (mg/L) in effluent from different industries	Unknown concentration
9	pH	6.0

Table 5.3.10(b) Effluent treatment

Sample No	Concentration of 2,4-DCP (mg/L)
Sample 1 Runner Agro products Ltd.	8.72
Sample 2 (Bijoy Textile Industries Ltd.)	6.12
Sample 1 1 (After one time treatment of sample 1)	0.95
Sample 12 (After one time treatment of sample 2)	0.73

Table 5.3.10(c)Industrial effluents treatment results on biosorption and desorption

	Sample -1	Sample -2
pH	7.0	7.5
Initial concentrationof 2,4-DCP (mg/L)	8.72	6.12
Final concentration of2,4-DCP (mg/L)	0.96	0.73
Removal (%)	89	88
Desorption (%)	90	92

5.3.7 Desorptionof 2, 4-DCP and regeneration of bagasse

Recovery of the sorbed material and regeneration of the sorbent are also important aspects of wastewater treatment. Attempts are made to desorb 2,4-DCP from bagasse surface with various eluents, such as hydrochloric and nitric acid solutions and base solution sodium hydroxide. This desorption process has been performed using the batch method. 2.0 g of spent bagasse after biosorption at pH 6 is shaken with 100 ml of 1M NaOH, 1M HCl, and 1M HNO_3 for regeneration, which has been completed within 120 min duration andabout 86, 75, and 60% of the sorbed quantity of 2, 4-DCP from the initially present 5.0 mg/L is desorbed from the bagasse in a single step, respectively. Although the achievement of arsenic elution using strong acidic or alkaline solutions has been reported in the literature (Lorenzen et al. 1995), the present

work showed that effective desorption is obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. In general, the desorption efficiency of 2, 4-DCP is tended to increase with increasing desorption time. Consequently, sodium hydroxide solution is useful for the desorption of 2,4-DCP from the surface of bagasse.

The removal (sorption) efficiency has been calculated using the equation,

$$\text{Percentage of desorbed 2,4-DCP} = \frac{\text{Amount desorbed after Desorption}}{\text{Amount Biosorbed before Desorption}} \times 100$$

Table 5.3.11(a) Coonditions on the desorption 2,4-DCPfrom bagasse

1	Initial concentration of 2,4-DCP	5.0 mg/L
2	pH value of system solution	6.0
3	Particle size of the bagasse	150 µm
4	Volume of potassium ferricyanide solution	0.8 ml
5	Volume of 4-AAP solution	1.0 ml
6	Volume of buffer solution (pH 10)	1.0 ml
7	Bagasse dose	2.0 g
8	Contact time of 2,4-DCP solution and bagasse	120 minutes
9	Operational temperature	30 ˚C

Table 5.3.11(b) Biosorption of 2,4-DCP (Before desorption) onto bagasse

Initial conc. (mg/L)	Absorbance	Concentration (mg/L)	Biosorption (%)	Remaining (%)
5.0	0.1292	1.34	73.25	26.75

Table5.3.11 (c) Desorption of 2,4-DCP from biosorbent bagasse

Desorbing agent	Initialconc. (mg/L)	Absorbance	Conc.of 2,4-DCP (mg/L)	Desorption (%)
1N NaOH	3.66	0.2745	3.15	86.07
1N HCl	3.66	0.2396	2.75	75.23
1N HNO_3	3.66	0.1970	2.21	60.38

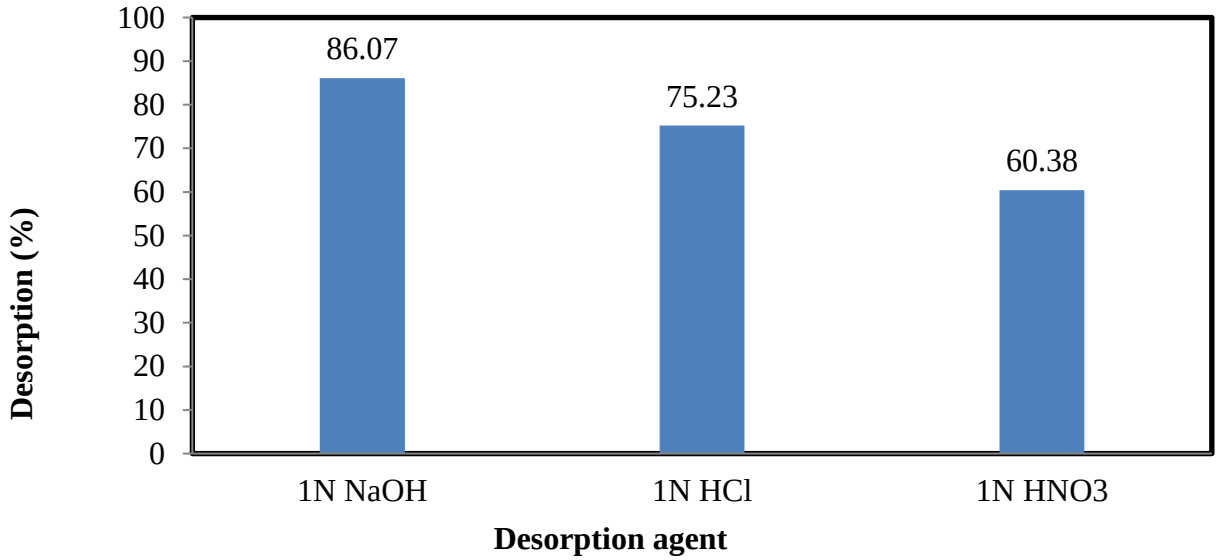

Figure 5.3.9 Graphical presentation on recovery of 2, 4-DCP from biosorbent bagasse; 2, 4-DCP concentration: 5.0 mg/L; bagasse dose: 2.0 g; particle size 150 µm; time: 120 min and pH: 6.0 at 30 ˚C

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Chapter 6

Conclusion

Conclusion

The present study shows that the bagasse is an effective adsorbent for the removal of phenol and phenolic compounds (Phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol) from aqueous solutions. Moreover, in the context of the present efforts for the diversified uses of bagasse, a new field will be opened if bagasse is taken as a biosorbent. Bagasse has been used as a biosorbent of the phenolic compounds sorption in a wide pH range from 3.0-12.0. The maximum biosorption of phenols has been occurred in the pH range 6.0-6.5. Langmuir isotherm model is the most suitable model to describe the biosorption of phenols onto bagasse. The positive value of ΔH° indicates the spontaneous and endothermic nature of the biosorption process. Successful desorption and regeneration of bagasse indicate its economic value for the industrial effluent treatment process and adds value to agricultural wastes. The initial pH of the solution influences the biosorption process. The maximum monolayer biosorption capacity (2,4-dichlorophenol > 2-chlorophenol > phenol > 4-chlorophenol) of sugarcane bagasse has been calculated by the Langmuir isotherm equation at the pH range 6.0-6.5 at 30˚C. The pseudo-first-order kinetic model is more applicable than the pseudo-second-order model. A single batch biosorption system has been designed to predict the mass of sorbent required for desired phenolic compounds removal efficiency at a given initial concentration. Adsorbed phenolic compounds could be regenerated by desorption with the help of 1M NaOH. The proposed batch treatment systems showed that the bagasse can be used as an efficient, appropriate, and suitable sorbent material for the removal of organic compounds containing phenol and phenolic compounds in the industrial wastewater recommended by Bangladesh because of the simplicity, easy operation, and easy handling. Moreover, bagasse after desorption process can be used as a fuel source because they do not contain harmful substances.