

Radiation Grafting of Polymers for Advanced Application



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Md. SohelRana

B. Sc. (Hons.), M. Sc.

Roll No.: 01

Registration No.:021

Session: 2015-2016

**Department of Chemistry
University of Dhaka**

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This desertation is dedicated to my parents and all of my family member specially my younger brother Md. Razan Ali for their support and cordial help and also in memory of my grandmother, Rahatunnesa(-2019).

Declaration

This thesis work was undertaken in the Department of Chemistry, University of Dhaka and, in the Research Laboratory of Nuclear and Radiation Chemistry Division (NRCD), Institute of Nuclear Science and Technology (INST), Atomic Energy Research Establishment (AERE), Ganakbari, Savar, Dhaka, Bangladesh. To the best of my knowledge and belief, in this thesis all work contained is original and my own, except as acknowledged by appropriate references. I declare that I have not submitted this material, either in whole or in part, for a degree at this or any other university.

Md. SohelRana

Department of Chemistry
Dhaka University
Dhaka-1000
Bangladesh



Tel: +880721750041
Extn. 4107,
Fax: +880721750064

DECLARATION CERTIFICATE

We declare that the thesis entitled “**Radiation grafting of polymers for advanced application**” submitted by Md. SohelRana, in partial fulfillment of the requirement for the degree of Master of Philosophy is the candidate’s own accomplishment and is not conjoint work with anyone else. This is an authentic study of the author and no part of this thesis has been submitted to any university or any institution for any degree. The author carried out his research under our supervision and guidance in the Research Laboratory of Nuclear and Radiation Chemistry Division (NRCD), Institute of Nuclear Science and Technology (INST), Atomic Energy Research Establishment (AERE), Ganakbari, Savar, Dhaka and at the Department of Chemistry University of Dhaka, Bangladesh.

We have gone through the final draft of the thesis and approved it for submission.

Supervisor,

Joint-Supervisor,

**Professor Dr. Tofail Ahmad
Chowdhury**
Department of Chemistry
Dhaka University, Dhaka,
Bangladesh

Dr. NaziaRahman
Principal Scientific Officer
Nuclear and Radiation Chemistry
Division, Institute of Nuclear
Science and Technology (INST),
Atomic Energy Research
Establishment (AERE), Ganakbari,
Savar, Dhaka, Bangladesh.

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Abstract

The main intention of this study is to evaluate the advance application of Radiation induced grafting of polymers. For the purposes we have taken non woven polyethylene fabric as a trunk polymer and Glycidylmethacrylate (GMA) was grafted on the trunk polymer(PE) by gamma radiation(pre-irradiation technique). The GMA-g- PE film functionalized through sulfonation. The prepared sulfonated- GMA-g-non woven PE films were used as a adsorbent to remove heavy metals Cu(II) , Cr(III), Pb(II), Uranium and dyes basic fuchsin(BF), methylene blue(MB) and crystal violet(CV) from waste water. The constructed sulfonated-GMA-g-PE filmwerealso tested for fuel cell membrane. The grafting yield was calculated with various parameters radiation dose, monomer concentration and reaction time. At 30kGy radiation dose, 5% monomer concentration,adding up of 0.5% Tween-20 as an additive, 4 h reaction time, maximum 343.31% of grafting occurred. The sorbent was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Thermo-Gravimetric Analysis (TGA). We have prepared aqueous solutions of heavy metals Cu(II),Cr(III), Pb(II) and dyes basic fuchsin(BF), methylene blue(MB) and crystal violet(CV) in different concentrations and the metals and dyes uptake capacity were investigated by the developed sulfonated-GMA-g-PE sorbent. At different conditions such as contact time, pH and initial concentrations heavy metals and dyes uptake capacity were investigated. The adsorption of metals and dyes are highly pH and temperature dependent. With the increases of temperature sorption capacity of the adsorbent also increase. It is observed that the sorption capacity increases with time and sorption reached equilibrium after 48 h for all heavy metals and dyes. The sorption amount of heavy metals and dyes increases with increase of starting concentration and then reached platue value at certain elevated concentration.Pseudo-first-order and pseudo-second-order equations were used to interpret kinetics of the sorption process. The adsorption of heavy metals and cationic dyes occurs by electrostatic interaction between sulfonic group of sulfonated-GMA-g-PE sorbent and positive charge of the heavy metals and dyes. Langmuir and Fruendlich isotherm model were studied to illustrate sorption process. Between the two models Langmuir and Fruendlich, Langmuir model adjusted best with the sorption for Cu(II) , Cr(III), Pb(II) and Uranium. Among the dyes BF, MB and CV, Langmuir isotherm can interpret best the sorption of BF; while sorption of MB and CV follows Fruendlich isotherm model best as indicated by their relatively higher correlation coefficient. The uuptake ability of the sorbent for Cu(II) , Cr(III),

Pb(II), U(VI), BF, MB and CV are obtained from Langmuir model are 117.64, 151.51, 140.84, 181.82, 357.14, 344.12 and 208.33mg/g, respectively.

In addition, the sorbent could be renewed and reused repeatedly for the sorption of heavy metals and dyes. Hence, the constructed low cost sulfonated-GMA-g-PE fabric provides new outlook and posses a momentous potential for the treatment of cationic dye containing waste water.

The grafted material showed perspective properties as a fuel cell membrane. Water uptake capacity was done at different temperature 60°C, 80°C and 100°C, oxidative stability, ion exchange capacity and proton exchange capacity of the membrane were performed successfully. The ion exchange capacity of the membrane was found 1.5mmolg-1. The experimental data showed that the sulfonated-GMA-g-PE can be used as a polymeric proton exchange membrane (PEMs) for fuel cell.

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Abbreviation

GMA	Glycidyl Methacrylate
AAS	Atomic Adsorption Spectroscopy
FTIR	Fourier Transform Infrared
Fig	Figure
g	Gram
h	Hour
KJ	Kilo Joule
L	Liter
mg	Milligram
mL	Milliliter
PE	Polyethylene
Ppm	Perts Per Million
SEM	Scanning Electron Microscopy
TGA	Thermo Gravimetric Analysis
UV	Ultra Violet

Introduction and Literature Review

1.1 General Introduction

Radiation grafting of polymers by graft copolymerization is an important and essential part of modern polymer chemistry. Surface modification of polymers are performed to construct a new polymer with desired unique properties using this technique[1-2]. The majority of industrial polymers are mostly of hydrophobic character, introducing new-fangled functional groups to the backbone of polymer matrices which can import and improve characteristics such as adsorption, hydrophilicity, biocompatibility, conductivity, anti-fogging and anti-fouling. The surface modification of polymers is performed by graft copolymerization which is carried out with ionizing radiation, UV light, chemical initiators and oxidation of polymers[3-6].

Nowadays, increasing rapid industrialization, increases the use of heavy metals compound, radioactive elements and dyes globally which become a global anxiety as it possess a great threat to all forms of living life. The improper disposal of toxic heavy metals and dyes containing waste effluents from industries like plastic, tannery, pharmaceuticals, metallurgical, mining, electroplating, steel plants, battery industries, atomic and thermal power plant, textiles, dying, painting, printing, pigments and washing causes severe environmental pollution. Heavy metals, radioactive elements and dyes can easily carry on in air, water, soil and can be stored in plant and animal tissue through food chain. It can create serious harm to lungs, brain on exposure to high threshold concentration and can cause paralysis, weakness of nervous system, bone disease, dermatitis, skin irritation, allergic reactions, nausea, anemia, itai itai, glucosuria, renal failure in kidney and cancer in human body[7-9]. Several of them are even mutagenic and carcinogenic for human beings and aquatic organisms [10]. Alzheimer's disease in human body is also created by dyes [11]. On the other hand, it is seen that most of heavy metals and dyes are resistant to biodegradation and photo degradation [12-14]. So, it is very important to treat heavy metal and dye containing wastewater before discharging into environment. Up to the present time, numerous types of wastewater treatment techniques such as coagulation and flocculation, electro-coagulation, membrane separation, oxidation or ozonation and adsorption have been employed to eliminate heavy metals and dyes[15- 19]. But these methods are not always ecology friendly and cost efficient. Even these processes can be linked with difficulties like low removal rate and inadequacy of regeneration and reuse. In addition, due to comparatively lower adsorption capacity, high

cost, less possibility of regeneration and reuse and secondary contamination of adsorbents many of these methods are not appropriate [20]. So the researchers were always keen to find out an alternative way and they focused on adsorption technology. The researchers studied on cost efficient adsorbents like sawdust [21], sporopollenin [22], chitosan [23], peat [24], cellulose [25], clay material and they observed better efficiency on the removal of heavy metals and dyes in contrast to the conventional methods. One of the new advancement in the field of heavy metals, radioactive elements and dyes removal from waste water is the use of functionalized grafted polymer fiber as adsorbent [26-33]. It is seen that for eliminating heavy metals, dyes and other pollutants, adsorption is an efficient, lower cost, moderately simple and potentially useful technique [34-35]. Uses of graft polymers has become a new technique now. Elevated adsorption capacity and reusability of the adsorbent trim down the chance of creating secondary toxic waste. In case of grafting, monomers form covalent bonding to the polymer backbone and grafted monomer can incorporate different functions to parent polymer where the mechanical property of the parent polymer is conserved [36-37].

Grafting of polymers through radiation grafting are more suitable as it has high penetration power to the polymer backbone and it forms mostly homogeneous free radicals very fast [38].

Rapid increasing of population of the world the needs for energy is also increasing and the stored energy on the basis of fossil fuels are also decreasing day by day. So, it is necessary to generate alternative source of energy for proper supply of power. Fuel cell membrane is an alternative source of energy [39-40]. In the fuel cell technology polymer electrolyte proton exchange membrane are used. Till now, mostly fluorinated polymer membranes are used in fuel cell, but it is highly expensive and has relatively low proton exchange capacity. Hence, low cost non fluorinated monomer grafted polymer electrolytic membrane possesses much potential for fuel cell.

In the present study, sulfonated glycidylmethacrylate grafted non woven polyethylene(sulfonated-GMA-g-PE) adsorbent was constructed by gamma radiation induced grafting of GMA on non woven PE and the epoxy groups of GMA were functionalized through sulfonation. The adsorbent can adsorb heavy metals, radioactive elements and cationic dyes from aqueous solutions. Moreover, it is also tested for proton exchange membrane for fuel cell.

1.2. Polymers

Polymer is a larger molecule made of huge number of repeating units. In other words, when many numbers of small molecules mutually combined to make a big molecule, the small molecule from which the large molecule formed known as monomers and the large molecule called polymer. The small molecules from which the big molecules formed can be one or more chemical compounds. In the word polymer, poly meaning “many” and mer meaning “part”. Hence polymer means many repeating units. Polymers are of two types, natural polymers and artificial polymers. Natural polymers are obtained from nature and artificial polymers are synthetic. Among artificial polymers that could be able to melt and return in their initial stage are called thermoplastic polymers. It is also called linear polymers. A number of thermoplastic polymers are plastic bottles, cups, fibers and films etc. On the others, polymers that can not be melted once formed and can not be reformed called thermoset polymers. There are many numbers of thermoset polymers. Adhesives is the example of this types of polymer.

Polymers are flourished in nature. The decisive natural polymers that define life are the DNA and RNA. There are protein polymers such as albumin, casein etc. Starch and cellulose are made of from α -D(+)-glucose and β -D(+)-glucose and are the components of rice and wood. Rubber is extracted from rubber trees. Bakelite, created in 1909, the first synthetic artificial plastic. Telephone case and electric insulation materials are made from it. Rayon is synthesized from cellulose. It was invented in 1910. In 1935, Nylon was invented that is used for synthetic spider silk[41].

1.2.1. Copolymers

Copolymer is formed by the polymerization of more than one different repeating monomer unit and the properties of the resultant polymer is controlled. On the basis of this, a number of ways are applied to make out polymer in which unlike monomeric units might be integrated. The examples of a two constituent system, where the two monomer is chosen as A and B. As for example: -A-B-A-B-A-B-

Copolymer can be classified into the following classes based on distribution of monomer unit.

1. Random or statistical copolymers
2. Alternating copolymer
3. Block copolymer
4. Graft copolymer
5. Terpolymer and
6. Stereoblock copolymer

1.2.2. Graft copolymers

It is a branched copolymer where the side chains are different from the core chain. Main chain and side chain of graft copolymers may contain different homopolymers. Nevertheless, dissimilar backbone of a graft copolymer may be made by homopolymers or copolymers. It is noticeable, to make a structural distinction, sequencing of copolymer is adequate. Hence, a proper graft copolymer should have A-B di-block copolymer with A-B irregular copolymer branches.

For example, in polybutadiene that is an artificial rubber with an imprudent C=C double bond per scum. In the case of free radical polymerization of styrene-polystyrene chains rising from the both sides of the double bond and a one-carbon relocation occurred, the outcome is that polybutadiene chains budding out from the both sides of a polystyrene backbone. In the above example, consisting block copolymers, composites have property of both components and hitting of substance rubbery chains absorb energy, hence, it is greatly less fragile than usual polystyrene. The product is known as high-impact polystyrene, or HIPS.

1.2.3. Copolymer engineering

The properties of artificial plastics can be modified by copolymerization to fulfil the specific requirements, as for example crystallinity can be reduced by modifying glass transition temperature or improving solubility. By rubber galvanising mechanical properties of a polymer can be improved.

1.3. Application of Polymers [42-43]

It has a great effect of Macromolecular science on the way that we are living. How polymers affected our lives we could not imagine. Materials that we are using now has no existent before 50 years.

New research are going on globally for the upgrade applications of polymers. This effects will not stop very soon. There are so many applications of polymers, in domestic and in industries. Huge amounts of polymer plastics are used in industries now a days. In automobile and aerospace composite polymer are worn, more ordinary yield are fishing rods and bicycles. Designers got much better freedom in shaping parts of polymers for different physical properties of composites and for this reason combined products often seem to be dissimilar to usual yield. Some common applications of the polymers are given below.

1.3.1. Conductors

Insulators are mainly organic polymers, it can be assumed that there is an unusual structure in conducting polymers. It has backbone display of conjugated π -electron (i. e. system have C=C conjugated bonds) irregular electronic property as like low energy optical transition, low ionization energy and high electron affinities.

This type of polymers could be oxidized or reduced ordinarily and more reversibly compared to usual polymers. Doping is the oxidation or reduction of polymers. It convert polymer insulator to conductor.

Poly-pyrrole, poly-thiophene and poly-anilines are conducting polymers (CPs) that makes complex energetic constituents which fascinate the thoughts of individuals implicated in smart materials investigations. These complex properties can be controlled if we know, firstly, at the time of creation of the polymer conductor, the nature of processes that control them and secondly, by the application of an electrical stimulus the point to which these properties are changed. There are some important conducting polymer such as Poly-aniline and its derivatives which has a number of functions as for example application in organic light emitting diodes (OLEDs), corrosion and solar cells.

1.3.2. Elastomers



Figure1.1: Rubber

Among all elastomers, rubber is the most important polymer materials. Isoprene is the repeating unit of natural rubber. For many centuries, rubber is used by human that is obtained from the latex of the rubber trees. Before 1823, rubber was not valuable material as we know at present. On the year, by heating natural rubber with Sulfur, Charles Goodyear successfully carried out "vulcanizing" in which sulfur brings cross-linking between polymer chains. We can illustrate the cross-linking of every elastomers, the term vulcanization is often used now. Globally much of the rubber used today is an artificial rubber styrene-butadiene rubber (SBR).

1.3.3. Plastics



Figure1.2: Plastic

Every year, around 60 billion pounds of plastics are consumed globally. Thermoplastics and thermosets are two major types of plastics. On heating thermoplastics soften and solidify on cooling. In the others, on heating, thermosets flow and cross-link to appear as stiff substance that do not become softer on applying heat again. The greater part of commercial usage account for thermoplastics. With the commercial plastics polyethylene is the most important one.

There is a wide variety of applications of polyethylene, because, it can be created in many diverse forms. The primary type is the commercially exploited polythene known as LDPE or low density polyethylene. It is malleable and elastic. Its main use is plastic bags.

HDPE or High density polyethylene is linear polyethylene. It has no branching. Its key use is plastic bottles.

High and ultra-high molecular weight poly-ethylenes are the other forms of this material known as HMW and UHMW. Where extremely tough and elastic materials are needed, these are used.

1.3.4. Fibers

Among the plastics and elastics there are many important applications of fibers. For many centuries humans are using natural fibers such as cotton, wool, and silk for their needs. Nylon, polyesters are man made fibers. In modern industry, the arrangement of force, heaviness and toughness prepared these substances extremely significant. In general, it is minimum 100 times longer than its wide and its axial ratios 3000 or higher.

Nylon was developed in the 1930s and used for parachutes in world war-II. This synthetic fiber known for its strength, elasticity, toughness and resistance to abrasion, has commercial applications including clothing and carpeting. Nylon has special properties which distinguish it from other materials. One such property is the elasticity. It has turned into extremely significant in present life from textiles to bullet-proof vests.



Fig: 1.3: Fiber.

1.4. Modification of polymer[44]

It has been modifying the polymeric materials since the beginning of mankind with the functioning of animal hides and natural fibers. Though it has started earlier, potential modification occurs day by day. Polymer modification the "black art" is gradually more yielding to scientific analysis and as innovative insights turn into accessible, latest applications are initiated for this information - the advances in information and applications together.

Polymer modification is an interdisciplinary in nature cutting across traditional boundaries of chemistry, biochemistry, medicine, physics, biology and materials science and engineering.

Modifications of polymer is performed to develop the thermal stability, mechanical and biological resistance, flexibility, stiffness and degradability etc. At present polymer modification can be classified into two groups - a. physical modifications including embossment and setup and radiation induced changes and b. chemical modifications where chemical reactions on the polymer are emphasized.

1.4.1. Blending

A polymer blend or polymer mixture is a member of a class of materials analogous to metal alloys, in which at least two polymers are blended together to create a new material with different physical properties. Mixing of two or more different polymers together makes it possible to achieve various property combinations of the final material—usually in a more cost-effective way than in the case of synthesis of new polymers.

Therefore, great attention has been paid to the investigation of these systems, as well as to the development of specific materials. Recently, the problem of polymer blends has also become important for recycling industrial and/or municipal plastics scrap. A considerable amount of information has been collected during more than three decades, summarized in dozens of monographs. Basic problems associated with the equilibrium and interfacial behavior of polymers, compatibilization of immiscible components, phase structure development, and the methods of its investigation are described herein. Special attention is paid to mechanical properties of heterogeneous blends and their prediction.

1.4.2. Curing

By cross-linking of polymer chains the toughening or hardening of a polymer material called Curing and it is carried out by electron beams, heat or chemical additives. While ultraviolet radiation is in curing, the process is called UV Cure [45]. The curing process in rubber is also called vulcanization.

Types of curing:

1. UV curing
2. UV LED curing

1.4.2.1. UV curing

When ultraviolet light of high intensity is applied to make a photochemical reaction that directly cures inks. In coat, print and decorate system it is applied, it is a method of lower temperature and higher speed and in the process solvent is not needed.

1.4.2.2. UV LED curing

When monochromatic ultraviolet radiation from LED (Light Emitting Diode) is used to treat surfaces called **UV LED curing**. It is a promising technology. Ultraviolet curing is usually performed with mercury-vapor lamps. With the initiation of LEDs capable of producing UV radiation, curing devices by means of the technology have increasingly been included in industrial and commercial applications [46].

1.4.3. Grafting of polymer

The polymer grafting is a technique in which the surface modifications of a polymer backbone occurred. In the backbone of polymer chain functional monomers forms covalent bond and graft polymers are yield. It has the benefit of new functional groups arise in the backbone and it conserves mechanical character of base polymer. When two polymers can not be blended, they can be joint by means of polymer grafting. The properties of the key polymer may be improved with the micro-phase separation. When there is no chemical bonding, two polymers cannot be combined. As a result, the phase separation becomes higher with time and the benefits of blending do not appear. Considerable work has been done on techniques of graft-copolymerisation of different monomers on polymeric backbone. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting.

1.4.3.1. Grafting by chemical means

Two major paths of grafting, free radical and ionic can be accomplished by chemical means. As it indicates the path of the grafting method, the function of initiator is extremely imperative for the chemical technique. In addition, free-radical method, atom transfer radical polymerization (ATRP) and melt grafting are also attractive methods.

1.4.3.1.1. Free-radical grafting

Chemical initiators used to produce free radicals. It initiates the reaction by yielding free radicals and reaction with monomer forms graft copolymer. In general, one can consider the generation of free radicals by direct or indirect methods.

Example: Formation of polystyrene and carbon nanotubes (CNTs) from styrene follows free radical mechanism.

1.4.3.1.2. Ionic grafting

It can be done by ionic process. For this purpose, organometallic chemicals, liquid of Lewis base and sodium naphthalenide with alkali metal suspensions are useful initiators. Carbocation is formed by the reaction of halide of base polymer with alkyl aluminum and grafting occurred. The reaction follows cationic mechanism.

Example: Formation of polyethylene from ethylene follows cationic mechanism.



An anionic mechanism can also carry on through the grafting process. From methoxide of alkali metals or sodium-ammonia polymer alkoxide is formed. This alkoxide reacts with monomer.

Example: Synthetic polydiene rubber and styrene butadiene rubber (SBR) are produced by anionic polymerization.

1.4.3.2. Grafting initiated by radiation technique

Grafting by radiation technique are described below:

1.4.3.2.1. Free-radical grafting

When irradiation is exposed onto polymer matrices free radicals are produced by the homolytic fission of the covalent bond of polymer chain and free radical grafting is obtained. In this technique, the medium is important, because on the polymer matrices peroxides can be yielded in air. Free radical existence depends on the character of the base polymer. There are three ways of grafting: (a) pre-irradiation (b) peroxidation and (c) mutual irradiation technique [47–50]. In the first one, to create free radicals radiation is exposed to the main polymer in inert gas or vacuum. Monomer is reacted with the

radiation exposed polymer in an appropriate solvent. The advantages of preirradiation technique is that the grafting occurred homogeneously and formation of homopolymer is lower. In the post irradiation or mutual irradiation, irradiation is exposed to the polymer backbone and monomer simultaneously to form free radicals [51–55]. In this technique formation of homo polymer is occurred. In the peroxidation method, radiation of high energy is exposed to base polymer in oxygen or air forming diperoxide or hydroperoxides, depending on character of polymeric backbone and the irradiation process. The peroxy yield then reacts with monomer at elevated temperature, after disintegration of peroxide to radicals grafting is initiated.

Example: Grafting of acrylic acid and sodium styrene sulfonate on non woven polyethylene by gamma radiation are the example of radiation induced free radical grafting.

1.4.3.2.2. Ionic grafting

High-energy irradiation when exposed through polymer backbone, radiation grafting proceed through an ionic mode. There are two different types of ionic grafting cationic and anionic. Polymeric ion is formed with the aid of irradiation to the polymer matrices, and then treated by means of monomer. The prospective benefit of the process is that its reaction rate is high. Hence, it needs small radiation to carry out grafting.

1.4.3.3. Photochemical grafting

Absorption of light by chromophore on a macromolecule, rises to an energized state and may break into imprudent free-radicals that initiate grafting.

When bond breaking occurs free-radical sites creation does not direct by means of absorption of light, adding up of photosensitizers, (e.g. benzoin ethyl ether, dyes, as like Na-2,7 anthraquinone sulphonate or acrylated azo dye, aromatic ketones (such as benzophenone, xanthone) or metal ions) this process can be promoted. That way the grafting process by a photochemical technique can proceed in two ways: with or without a sensitizer [56-58].

1.4.3.4. Plasma radiation induced grafting

Plasma polymerization process has established growing concentration now. During planned release on the same potential as with ionizing radiation plasma situation attained [59- 60]. Electron-induced excitation, ionization and dissociation are the key processes in plasmas. Thus, plasma contains the accelerated electrons which have sufficient force to induce breaking of the chemical bonds to form macromolecule radicals in the polymeric configuration that afterward set off graft co-polymerization.

1.4.3.5. Enzymatic grafting

This is a new technique. In the method, the chemical electrochemical grafting reaction initiated by enzyme [61]. For example, tyrosinase is proficient of converting phenol into reactive o-quinone, that proceed following non-enzymatic reaction with chitosan.

1.5. Factors influencing the grafting

In the sections, a number of factors affecting the grafting process will be explained, such as the nature of the backbone, monomer, solvent, initiator, additives, temperature, etc.

1.5.1. Nature of the backbone

Grafting of polymers occurred by the formation of covalent bonding to the monomer and backbone of a polymer matrices, the nature of the backbone (viz. physical nature, chemical composition) plays an important role in the process.

1.5.2. Effect of monomer

There is a vital consequence of the reactivity of monomer on grafting yield. The reactivity of monomers depends on the different factors, viz. polar and steric nature, swellability of original polymer in the existence of the monomers and concentration of monomers.

1.5.3. Effects of solvent and monomer concentration

Grafting of monomers onto the polymer backbone depends on the character of solvent. In this case solvent is the transporter by which monomers are related to the surrounding area of the backbone. Grafting can be enhanced by the accumulation of solvent to a monomer and the specific character of the graft copolymer can be changed. It is an important factor that the incursion of the graft into the substrate which is dependent on the monomer concentration and solvent used to prepare grafted surfaces.

Trommsdorff phenomenon explains grafting of styrene to polyolefins [62] and cellulose [63]. Polymerization of bulk methyl methacrylate using benzoyl peroxide this phenomenon first noticed on that at approximately 20 – 25 % conversion the rate becomes explosively quick [64]. By the limited diffusion of the upward molecular chains this can be explained. It creates barrier of extinction by amalgamation with other growing chains, but does not perturb dispersion of the monomers significantly. In the presence of solvent when the polymerization is conceded, the rate increase is not observed. Conversely, the rate increases rapidly than the bulk polymerization and there is a higher degree of polymerization while a non-solvent system is used for poly(methyl methacrylate).

The Trommsdorff consequence has also been pragmatic in grafting reactions. It describes the graft yield with styrene concentration in methanol for grafting to pre-irradiated poly(propylene) fabric. From his explanation, the rates of propagation and initiation raise with rising monomer concentration. Though methanol is a non-solvent for polystyrene (PS), the growing chains became sufficiently powerless so that extinction by amalgamation was repressed [65-67].

1.5.4. Effect of initiator

Every chemical grafting reactions except radiation technique needs an initiator, and its nature, concentration, solubility as well as role need to be measured. There are different types of initiators: Azobisisobutyronitrile (AIBN), $K_2S_2O_8$, etc. There is an intense effect of initiator on grafting.

1.5.5. Role of additives on grafting

There is an important role of additives such as metal ions, acids, surfactants and inorganic salts on grafting yield or the amount of graft copolymer. It must compete with any reactions between the monomer and additives, except the reaction between the monomer and the polymer backbone.

1.5.6. Effects of temperature

Temperature has a key role in grafting process. It controls the kinetics of graft copolymerization. With escalating temperature grafting yield increases, until a maximum value is attained. More rapidly monomeric dispersion processes in the backbone rises with rising temperature which facilitated grafting [68-70].

1.6. Advantages of radiation grafting method

In radiation-induced grafting, the exterior and bulk property of polymer is modified by grafting of monomers onto polymer matrices using irradiation. This method has some advantages like simplicity, small price, manage over progression and amendment of substance concentration and arrangement. In addition, in the process confirms the grafting of monomers which are complicated to polymerize by conservative process with no residues of initiators and catalyst. This process undergoes on the trunk polymer irradiation is exposed to it as of monomer existence or with no monomer to produce a dynamic sites.

It enables to merge the proton-conducting character of the fluoropolymer base films together with the thermal and chemical constancy in grafted membrane appropriate for the purpose of Polymer Electrolyte Membrane Fuel Cells (PEMFC) [71-72].

1.7. Application of grafted polymers

There are numerous applications of grafted polymers now-a-days. To meet the specific needs grafting of polymers is carried out. By grafting of polymers we can improve mechanical and chemical properties of trunk polymer. It can reduce crystallinity and adjust glass transition temperature and also can improve solubility. Most of the base polymer are neutral. By grafting of polymers it can convert in ionic species through functionalisation. This cationic or anionic grafted polymer can adsorb heavy metals and

dyes which are toxic for human and animal. Heavy metals and dyes are also responsible for environmental pollution. So, grafted polymer is used for environmental purification. These polymers are also used for proton exchange fuel cell membranes which is very important for the energy sector. Grafted polymers also have a great role in medical applications, sensors and in bio-sensors.

1.8. Heavy metals and dyes

Heavy metals are the elements which have high atomic mass in the range between 63.5 and 200.6 and five times larger specific gravity than that of water [73]. The term 'heavy metals' has established priority to the environmentalists due to its devastating impact on ecosystem and human health. A group of heavy metals includes micronutrients (Fe, Mn, Cu, Zn, Mo) which is essential for metabolic processes as trace amount in living organism. But metals like chromium, cadmium, cobalt, lead, nickel, selenium, arsenic, mercury are highly toxic even at very low concentration. Heavy metal contamination has turned into a major environmental problem due to the fact that heavy metals are flexible, non-biodegradable, durable and easily added in air, water and soil [74]. Heavy metals may come into the human body through air, water, food and even sorption during skin when they come in direct contact with humans.

Heavy metal pollution occurs due to natural and anthropogenic processes. Natural emission of heavy metal can occur due to weathering of the underlying bedrock, volcanic eruptions, forest fires, biogenic sources and wind-borne soil particles. Industries, agricultural activities, mining, metallurgical processes, automobile exhaust are the major anthropogenic sources for the emission of toxic elements to the atmosphere [75-76].

The colored materials which have attraction for the substrate and absorb spectrum of visible light at a definite wavelength for this it is coloured. These colour substances are called dye. In general, a small amount of dye can generate a dramatic colour, that is related with the high molar extinction coefficients.

Dyes are colored organic substances that are used in different industries like textiles and garments factory. There are so many dyes used in the industries like acidic, basic, azo, vat, reactive, dispersed and sulphur dyes [77-78].

Commercial dyes are classified according to their application process. Depending on chemical structure the classification of dyes is shown in Figure 1.4. Dyes are also classified as cationic, anionic and non-ionic.

These dyes are constantly gone in industrial misuse and accordingly released into water body [79-80].

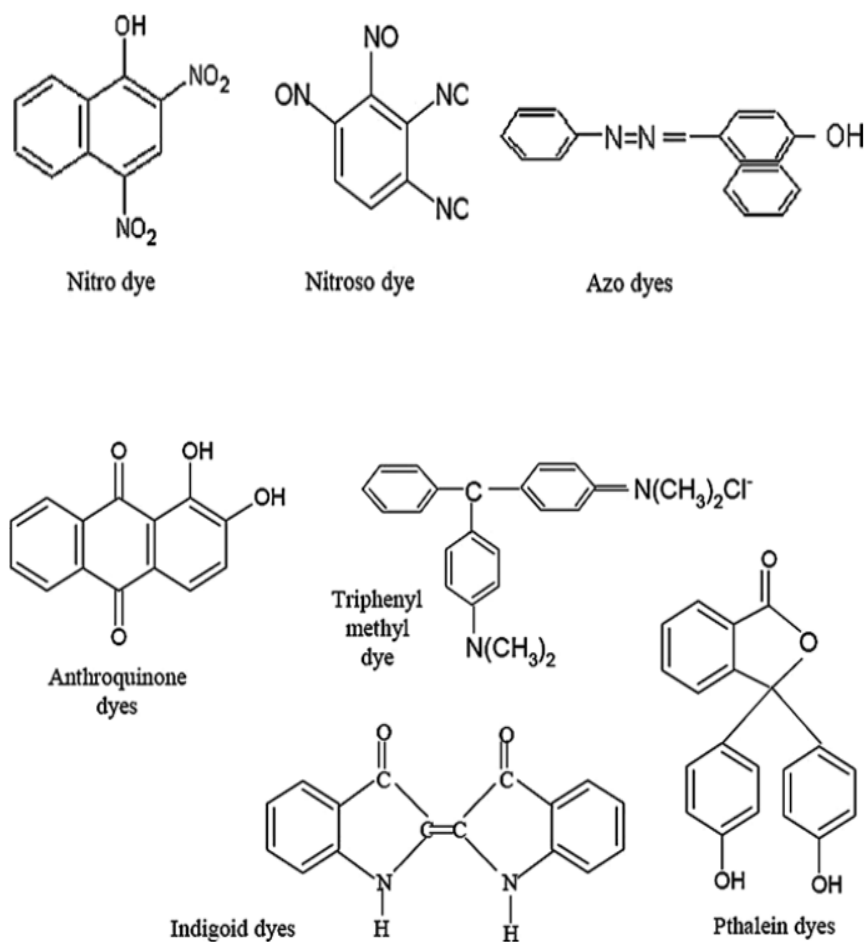


Fig. 1.4. Classification of dyes on the basis of chemical structure [81].

	Class	Application	Examples
1	Acid dyes	Nylon, wool, silk, modified acrylics, paper, leather, food, inkjet printing and cosmetics.	Acid red 88, Acid red 18
2	Cationic (Basic) Dyes	Poly acrylonitrile, paper, modified polyesters, modified nylons, cation dye able polyethylene terephthalate, wool, silk, tannin mordanted cotton and medicine.	Crystal Violet, Methylene Blue, Safranin, Basic fuschin
3	Disperse Dyes	Nylon, polyester, cellulose, acrylic fibers and cellulose acetate.	Disperse Red 1, Disperse Orange 37
4	Direct Dyes	Rayon and cotton, leather, paper and nylon.	Congo Red, Brilliant Blue, copper blue 2R
5	Reactive Dyes	Wool, nylon, cotton and other cellulosic.	Reactive Black 5, Reactive Orange 16
6	Solvent Dyes	Gasoline, plastics, oils, lubricants and waxes.	Solvent Red 1, Solvent Red 49, Solvent Red 24, Solvent Red 111
7	Sulfur Dyes	Cotton and rayon, paper, leather, silk and wood.	Sulfur Brilliant Green, Sulfur black 1
8	Vat Dyes	Cotton, rayon and wool.	Vat red 10, vat violet 13 and vat orange 1.

Fig. 1.5. Classification of dye on the basis of chemical nature [82].

1.8.1. Heavy metals and dyes in industrial waste water

Heavy metals and dyes are a prominent source of pollution both in the aquatic and soil surroundings. From thousand years it has been used in a lot of dissimilar areas. Lead is applied as building materials, water transport pipe, pigments and batteries from long ago. Many dyes are used in industries like textiles, dyeing, washing, printing, papermaking etc. Around 10,000 tones dyes are used in the world each year. basic fuchsin, methylene blue, crystal violet, methyl orange, basic red, malachite green and also many other dyes are used in the above industries. but these dyes are released mostly without pre-treatment. This dye containing wastewater mixed with river, canal and pond water and creates different diseases in like cancer, dermatitis, skin irritation in human and animal life.

Hence dyes are a threat to human and aquatic life. So it is needed to refresh wastewater containing dye.

Exposure of heavy metals continues, even rising in some areas. As for example, in wood preservatives and gold mining Arsenic and mercury is still used in a lot of parts of Latin America.

Industrial waste water effluents contain a large extent of heavy metals, there are so many industrial actions are involved in such pollution. Nuclear power plant, textiles, tanneries, metal processing and petroleum are the sources of toxic metals. A number of different metal releasing companies have no economic or technical capacity to deal with the problems and take initiative for wastewater treatment. They release mainly Zn, Cr, Cu, Ni, Pb and sometimes, Cd. This waste water generally contains relatively high concentrations of metals, ranging from 10 to 100 ppm. It has been seen that heavy metals and dyes in industrial wastewater are generally treated by adding base to precipitate as hydroxides. Conversely, because of the complexities of inorganic and organic ligands of the water, according to the thermodynamic solubility products of the precipitates the final dissolved concentrations are above of expected; such concentrations can not accomplish the maximum value of pollutants requisite by law.

Different types of wastewater treatment techniques such as adsorption, coagulation and flocculation methods, electro-coagulation, membrane separation, oxidation or ozonation, ion exchange, photocatalysis, ion floatation, hyperfiltration, precipitation and reverse osmosis are used to remove heavy metals and dyes. Among the techniques, it is seen that for removing heavy metals and dyes and other contaminants sorption is an efficient, suitable, lower cost, comparatively simple and potentially useful technique. Regarding the adsorption of metal ions a considerable amount of work has also been published in the literatures on various adsorbent surfaces such as clay, zeolite, bio-sorbents, agricultural wastes, organic/inorganic composite, alumina [83-85].

1.8.2. Adverse effect of heavy metals and dyes on human health

It has been widely known the toxicity of heavy metals and dyes to any living organisms. Heavy metals and dyes pose a serious hazard to the environment even at low concentrations due to their specific nature and multidimensional interactions and their toxic impact may persist over a long period. There is consistent evidence regarding a rise in the toxicity of heavy metals when they are oxidized or reduced. As for example, As(III) is less toxic than As(V) and the toxicity of Cr(III), is lower compared to that of Cr(VI). What is more important. Heavy metals tend to accumulate, because they cannot be chemically or biologically degraded, which may dangerously increase the presence of heavy metals in the food chain. These elevated presence of heavy metals creates serious health problem and even of consumers life. In the light of these interpretation, the issue of heavy metal contamination has taken on a sense of importance in environmental pollution control, and for that it has been given high priority on the list of problems requiring immediate solution. Heavy metals contamination with high concentrations, which noticeably exceed the toxicity threshold for living organisms, are detected, inter alia, in mine drainage waters and in industrial effluents.

Azo colors create irritation, nausea, vomiting, cancer in human body. Coloured compounds have harmful effect on microorganism. It destroys the environment of aquatic life.

There are many mechanistic aspects of heavy metal-induced toxicity and carcinogenicity, some of which are not clearly elucidated or understood. However, each of them has exceptional appearance and physico-chemical behaviour which give to its precise toxicological techniques. From this it gives an investigation of the environmental incidence, manufacture and use, prospective for human revelation, and toxic, genotoxic and carcinogenic mechanisms of Pb, Cd, Cr and Hg [86-90].

In the section it has been discussed about eight familiar heavy metals in brief chromium, arsenic, cadmium, barium, lead, silver, selenium and mercury. Each of the substances are naturally occurred that are in atmosphere at lower intensity. In bigger extents, it could be hazardous [91].

1.8.3. Copper, Chromium and Lead as Heavy Metal

Copper, Chromium and Lead occur in nature and its atomic number is 29, 24 and 82 along with an atomic weight of 64.3, 51.996 and 189.64 respectively. Copper exists as with an oxidation state +1 and +2. Chromium exists with an oxidation state ranging from +2 to +6 [92] and Lead exist +2 and +4. Copper exist in nature as mainly malachite. Chromium is found in nature as chromite ore (FeCr_2O_4) in which chromium is in the +3 oxidation state and shows greater stability than other oxidation state of chromium.

The contamination of copper, chromium and lead into various environmental elements (air, water, soil) occurs due to a large diversity of usual and anthropogenic sources [93]. Practically, the major contributor of chromium pollution is the industrial waste effluents. Metal dispensation, tannery services, chromate manufacturer release a vast amount of chromium into the environment [94]. Copper and Chromium electroplating requires enormous amount of copper and chromium. Moreover, the application of lead monochromate, potassium chromate, chrome oxide in pigment and dye formation, chromated copper arsenate as wood preservative, Fe-Cr mixed oxides, Copper chromite as catalyst for processing hydrocarbons, metallic alloy CFY (Cr-Fe-Y) as interconnector in solid oxide fuel cell are the popular industrial uses of copper, chromium and lead metal. Another important use of chromium lies in tannery industry. Chrome tanning agents are used in tanning process. Basically, chromium (III) salts like potassium chromium (III) sulfate dodecahydrate and chromium (III) sulfate dodecahydrate [$\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$] are used in tanning process. The devastating fact is that the sewage or waste from this industries carries chromium and is discharged into the environment without going through an adequate treatment. In lead storage batteries lead are used and also tetraethyl lead as an anti knocking agent of petrol [95-96].

1.8.4. Permissible limits of heavy metals in industrial waste water

As it has no clear definition of heavy metal, can be defined it by its density. Those metals of a specific density above 5 g/cm^3 . In water highest permitted maximum for Ni is 0.2 mg/l and in plants is 10mg/kg. The highest acceptable level for Cr in water is 0.1 mg/l. The acceptable limit of Cr for plants is 1.30mg/kg. The highest acceptable for Cd in water is 0.01mg/l and for plants is 0.02 mg/kg. The maximum permitted limit for Cu in water is 2 mg/l. The permitted limit of copper for plants is 10mg/kg suggested by WHO. Permitted

limit of lead in water is 0.05mg/l and plants is 2mg/kg. Iron in drinking water is 1.0 mg/L and for plants is 20 mg/kg. The acceptable of zinc is 5mg/L and plants is 50 mg/kg [97].

1.8.5. Recovery methods for heavy metals and dye removal

Heavy metals and dye pollution is a detrimental environmental evils today. As its persistence in atmosphere disposal of toxic metals and dyes is a great anxiety now. At present, different methods including adsorption, ion exchange, chemical precipitation, membrane filtration, coagulation-flocculation, flotation, electrochemical process are applied to dispose its. The processes are given below [98-107]:

1.8.5.1. Chemical precipitation

To eliminate toxic elements and dyes precipitation is a significant adsorptive method. This process is related to solubility product K_{sp} of the toxic ion, pH of aqueous media and metal and dyes concentrations. As of Matagi et al. (1998), on the basis of the equation precipitation occurs:



Precipitation occurs when product of cations and anions concentration is more than K_{sp} . As chemical precipitation is a broadly used process, it has the limitations of yielding a huge quantity of concentrated and added contaminated wastes, that creates dumping harms.

1.8.5.2. Ion exchange

In the methods, one ion can attract another dissolve ion from the liquid to solid phase and it is the broadly applied process for water treatment. It is a price efficient method and is used even for low concentrations. In the technique low cost substance are used.

Ion exchange resins (IXR) are solid materials that are water-insoluble. Positive or negative charge of from a solution it could absorb and substituted other ions.

It is not bound different ions to the energetic (functional) species with the same affinities of an ion exchanger resin. Ions of higher valency absorb more powerfully than lower valency.

1.8.5.3. Adsorption

Heavy metals and dyes in wastewater can be eliminated by adsorption on solid matrices. There are a number of adsorbent as like activated carbon, metal oxides, and agricultural products. They are used as adsorbent. Among them efficiency of sorption of activated carbon is high as a classical way and its elimination capacity is greater than 99% for a specific ions. But, it is moderately costly and could not be reformed and recycled. Scientist

are searching low price and proficient sorbent for the disposal of toxic substances. In adsorption process toxic substances are adsorbed on the surface of the sorbent.

The sorption of metal ions and dyes on sorbent surface occurred by electrostatic and van der Waals forces. Adsorption with the van der Waals forces called physical adsorption, while the adsorption occurred by electrostatic attraction called chemical adsorption.

Adsorbents are mostly collected from sources as like charcoal, zeolites, clays, ores, and other waste resources. Many of the sorbents are constructed from waste possessions.

For the disposal of heavy metals and dyes bio-sorption is the most hopeful method. It is low cost and cheapest process and obtainable dead or existing biomass which disposes heavy metals as of wastewater and sludge. This process have the compensation of metal recovery, could be renewal of bio-sorbent. It works in very dilute solution. Biomass obtained from, fungi, bacteria, sea-weeds, and some higher plants are efficiently and fruitfully uses in metal removal studies.

1.8.6 Grafted polymers as heavy metal and dye adsorbent

Grafted polymers play a major role to adsorb heavy metal and dye as they perform high chemically dynamic polymer matrix for sorption and elimination process. Polymer adsorbents can be easily prepared by direct grafting of the desired functional groups to the polymer. Ionizing radiation creates an active radical which initiate the chain propagation in the trunk polymer. Hybrid polymers that have arrangement of organic and inorganic units cooperate with mutual interaction at molecular stage. These substances are of two classes. In the first, organic and inorganic are implanted and present feeble connections, as like van der Waals, hydrogen bonding, π - π or weak electrostatic interactions between them and in the second, with strapping covalent or coordinative bonds these two components are bonded together.

1.8.7. Sulfonated glycidylmethacrylate grafted non woven polyethylene (Sulfonated-GMA-g- PE) as heavy metals and dye adsorbent

In the literature, GMA-g non-woven PE/PP adsorbent was described and functionalization was performed through amination. Sulfonated-GMA-g non-woven PE film is constructed by the grafting of GMA on non-woven PE and subsequent functionalization through sulfonation. The constructed film can adsorb cationic species like heavy metals and cationic dyes.

1.9. Mechanism and factors of metal ion adsorption [108]

Sorption is classified as physical or chemical. In case of physical adsorption (or physisorption) sharing or transfer of electrons is not occurred and is basically reversible. It is a multilayer sorption. A physico-sorbed molecule holds its character and leading desorption it come back to its initial form. In case of chemisorption chemical bonds formed and it is basically irreversible. It is a monolayer sorption. Degree of chemical sorption is related to the activity of the sorbent and adsorbate. Most of the sorption are in fact an intermediate of physical and chemical sorption, by means of mutually pore structure and imprudent functional groups are responsible for elimination.

When concentration of a certain element on the surface of a substance involving two phases called adsorption (Faust and Aly, 1998). In the circumstances, the attraction of H^+ and metal ions among the solid adsorbent and the adjoining aqueous solution is the major center of attention.

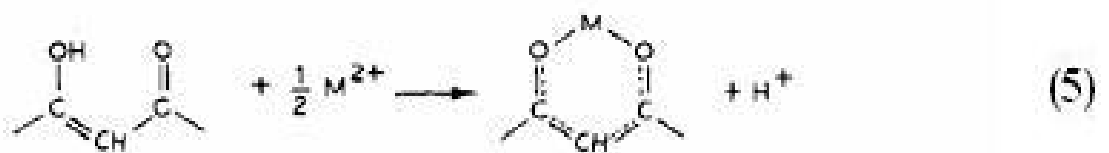
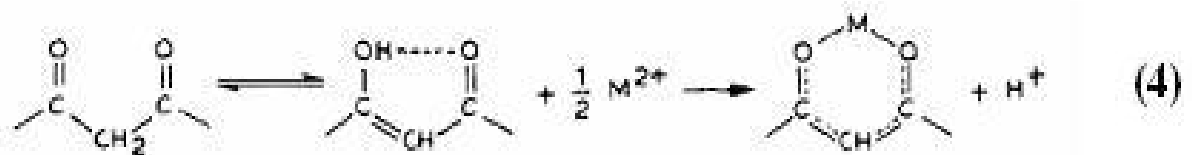
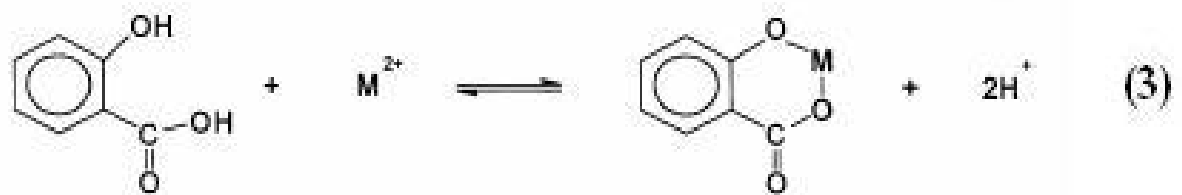
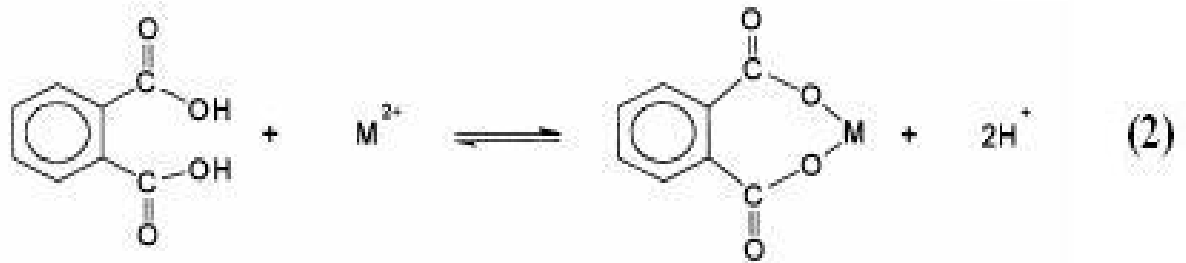


Figure 1.6: Mechanisms of complexation between metal ions and functional groups.

Metal ion sorption on adsorbent is pH dependent. The optimal pH for metal disposal from aqueous solution also varies, depends on the objective metal.

Adsorption capacity depends on initial metal ion concentrations. It is seen that with the increases of initial metal ion concentration sorption capacity of metal ions increases. Metal ion uptake ability of sorbent also depends on temperature, it increases with the increase of temperature.

1.10. Fuel cell Membrane

Fuel cell membrane is an electrolytic membrane which is used for producing energy. Due to the increasing population the needs for energy also increases. As a result the demand for fuel cell also increases worldwide. Different types of proton exchange membrane (PEMs) are available. At present fluorinated proton exchange membrane (Nafion) are mostly used in fuel cell. But, this types of proton exchange membrane are costly and relatively have low ion exchange capacity. So, researcher are searching low cost, high ion exchange capacity (IEC) non fluorinated electrolytic membrane. For this reason alternative development of PEMs in fuel cell is necessary.

Radiation grafted polymer membrane are selecting for fuel cell, because of its lower cost and a long time stability. Radiation grafting form uniform free radicals rapidly and can also incorporate with monomer uniformly. A number of grafting techniques developed, such as ionizing radiation, chemical initiator, UV light, plasma treatment, oxidation of polymers etc. Several types of radiation grafted PEMs are reported [109-110]. Due to their lower ion exchange capacity, proton conductivity and relatively higher cost they are not economically feasible at all. Therefore, a new radiation technique is applied to make a low cost and better economy perspective to power generation. Gamma radiation techniques of polymer grafting are relatively less costly and higher grafting occurs uniformly than other techniques.

1.11. Functional monomers for heavy metal adsorption

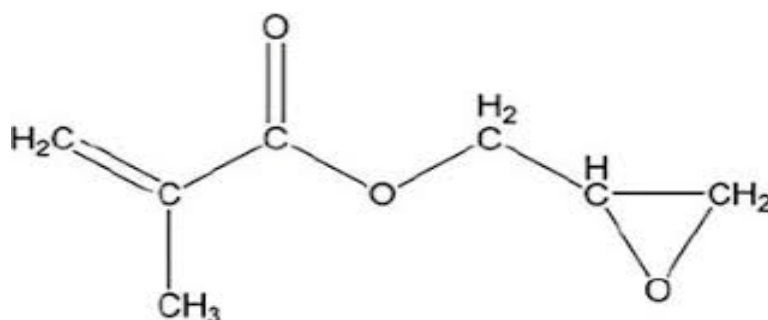
1.11.1. Glycidyl methacrylate [111]

Chemical Names: glycidylmethacrylate;

Other name : 2,3-epoxypropyl methacrylate: 2-((methacryloxy)methyl)oxirane

IUPAC Name: Oxirane-2-ylmethyl-2-methylprop2-enoate

Structural formula:



Chemical formula: $C_7H_{10}O_3$

Molar mass: 142.15 g/mol

Density : 1.05 g/cm³

Melting point: -52 °C

Boiling point: 189.0 °C

Solubility in water: 50 g/L.

Flash point: 169 F

State: liquid

Color: Clear

Water solubility: 50g/L

Viscosity: 5.481 cP

Auto-Ignition Temperature: 389 °C

Glycidyl methacrylate is an enoate ester obtained by formal condensation of the carboxy group of methacrylic acid with the hydroxyl group of glycidol. It is an enoate ester and an epoxide. It derives from a methacrylic acid and glycidol. It is used as a monomer in the production of epoxy resin. It is used to supply epoxy functionalization to polyolefins and added acrylate resins.

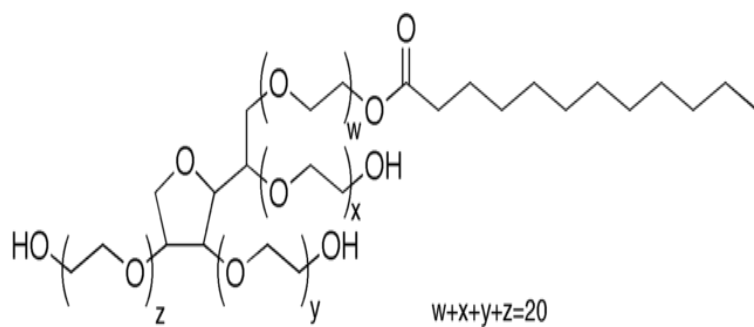
1.12. Additives and solvent for radiation induced grafting

1.12.1 Tween 20

Tween 20 is a commercial name of Polysorbate 20. It is a polysorbate type non-ionic surfactant. It is produced by the ethoxylation of sorbitan and an adding up of lauric acid in it. It is usually used as detergent and emulsifier in several domestic and scientific uses.

Chemical Name	: Polysorbate 20
IUPAC name	: Polyoxyethylene (20) sorbitan monolaurate
Other Name	: Alkest TW 20
Chemical Formula	: $C_{58}H_{114}O_{26}$

Structure :



Molar Mass	: 1227.54 g/mol
Appearance	: Clear, yellow to yellow-green viscous liquid
Density	: 1.1 g/mL
Boiling Point	: >100 °C
Flash Point	: 110 °C

1.12.2. Propanol-2

Propanol-2 or isopropanol is a secondary alcohol. It is a colorless, flammable chemicals with a strong odour used as a solvent. It's a isomer of 1-propanol.

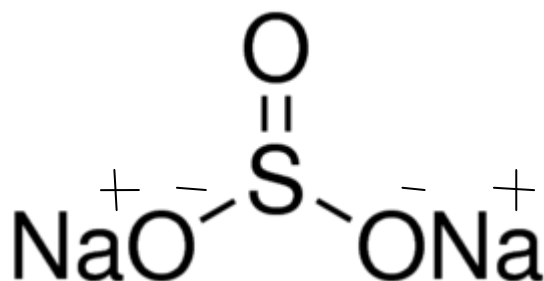
Chemical Name	: Isopropanol
IUPAC Name	: Propan-2-ol
Other Name	: Rubbing alcohol
Chemical Formula	: C ₃ H ₈ O
Appearance	: Transparent liquid, fumes in air
Odor	: Pungent alcoholic
Molar Mass	: 60.096 g/mol
Melting Point	: -89 °C
Boiling Point	: 82.6 °C
Acidity (pKa)	: -5.9
Density	: 0.786 g/ml
Viscosity	: 1.96 cP

1.12.3. Sodium Sulphite

Sodium sulphite is an inorganic compounds which is water soluble solid used as a n antioxidant and preservatives.

Chemical Name	: Sodiumsulfite
IUPAC Name	: Sodium sulfite
Other Name	: Hypo clear
Chemical Formula	: Na ₂ SO ₃
Appearance	: White solid
Odor	: Odorless
Molar Mass	: 126.043 g/mol
Melting Point	: 33.4 °C
Boiling Point	: Decomposes
Acidity (pKa)	: -9
Density	: 2.633 g/ml

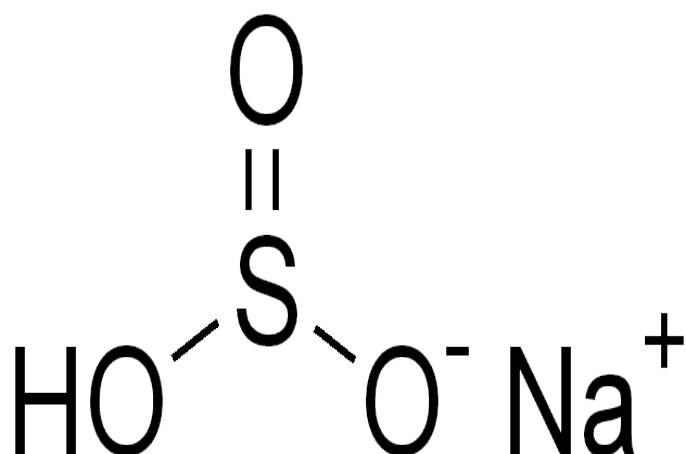
Structure :

**1.12.4. Sodium bisulphate**

Sodium bisulfate is a mixture of chemical. It's a white solids which is soluble in water.

Chemical Name	: Sodium bisulfite
IUPAC Name	: Sodium hydrogen sulfite
Other Name	: Sulfite lyes
Chemical Formula	: NaHSO ₃
Appearance	: White solid
Odor	: Sulfurous odor
Molar Mass	: 104.061 g/mol
Melting Point	: 150 °C
Boiling Point	: 315 °C
Density	: 1.48 g/ml

Structure



1.12.5. Hydrochloric Acid

It is also known as muriatic acid. It is colorless, inorganic acid with a distinctive pungent smell. It completely dissociates into aqueous solution. Hydrochloric acid is used vastly in various production-based industry.

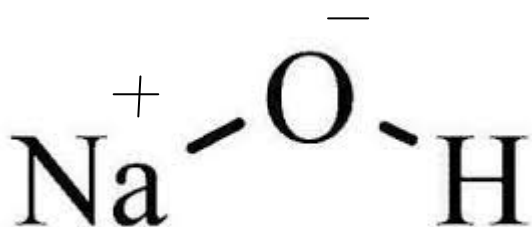
Chemical Name	: Hydrochloric Acid
IUPAC Name	: Chlorane
Other Name	: Muriatic Acid
Chemical Formula	: HCl
Appearance	: Transparent liquid, fumes in air
if concentrated	
Odor	: Pungent
Molar Mass	: 36.46094 g/mol
Melting Point	: -30 °C
Boiling Point	: 61 °C
Acidity (pKa)	: -5.9
Density	: 1.2 g/ml
Structure	



1.12.6. Sodium Hydroxide

It is an inorganic compound. It is recognized as lye and caustic soda. Soluble in water and can absorb CO₂ and moisture from the air. It is used in the production of pulp and paper, soaps and detergents.

IUPAC Name	: Sodium hydroxide
Other Name	: Caustic soda, Lye
Chemical Formula	: NaOH
Appearance	: White, waxy, opaque crystals
Odor	: odorless
Density	: 2.13 g/cm ³
Melting Point	: 323 °C
Boiling Point	: 1388 °C
Solubility in Water	: 418 g/L (0 °C)
Vapor Pressure	: <2.4 kPa (at 20 °C)
Basicity	: -0.56

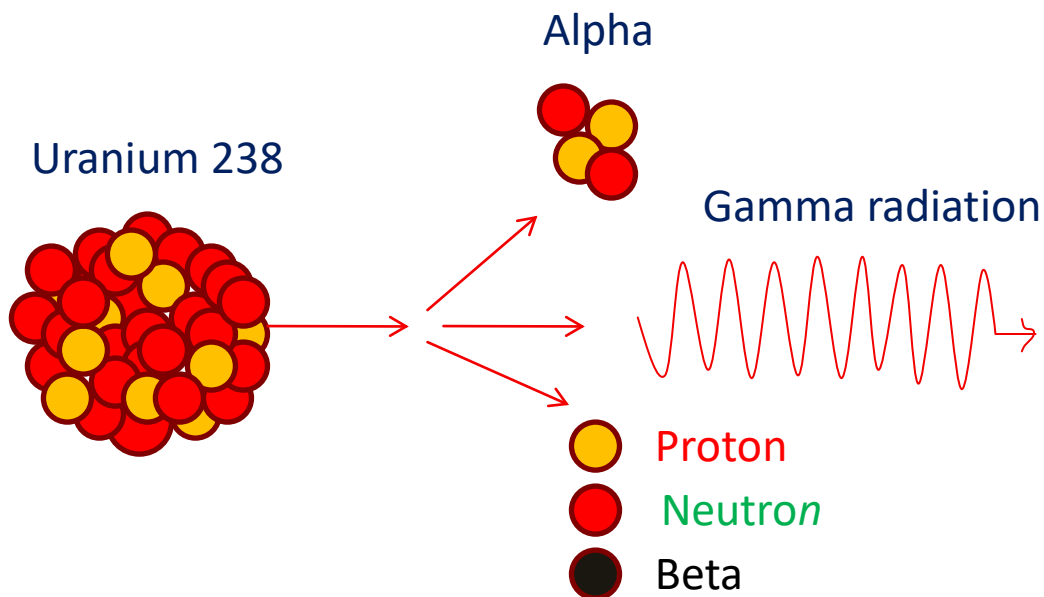
Structure**1.13. Radiation**

The release of energy in the appearance of waves or particles throughout space or a substance medium called radiation [112-113]. This includes:

- Electromagnetic radiation, as like radio waves, visible light, x-rays, and gamma radiation (γ)
- Particle radiation, as like alpha radiation (α), beta radiation, and neutron radiation (particles of non-zero rest energy)

- c) Acoustic radiation, for example, ultrasound, sound, and seismic wave (dependent on a physical transmission medium)
- d) Gravitational radiation, radiation which gains the outward appearance of gravitational waves, or ripples in the curvature of space time.

Depends on power of the radiated particles it is frequently classified as ionizing or non-ionizing. Ionizing radiation has energies more than 10 eV, that is sufficient to ionize atoms and molecules, and crack chemical bonds.



1.13.1. Gamma Radiation

It made up of photons that have wavelength less than $3 \times 10^{-11} \text{m}$ [114]. This is a nuclear progression which creates from unsteady nucleus of nuclear reactions. Alpha and beta particles contains electric charge and mass, it attracts other atoms in their path. Gamma radiation is made by photons. It has no mass and electric charge. It has penetration power higher compared to alpha or beta radiation. Thick plate of Lead can stop it.

1.13.2. Cobalt-60 Radiation

Cobalt-60, ^{60}Co , is an artificial radioactive isotope of cobalt that have a half-life of 5.2714 years. It is formed synthetically in nuclear reactors. On purpose of industrialized yield on neutron creation of massive samples of the mono-isotopic and mono-nuclidic cobalt isotope ^{59}Co [115]. In a nuclear power plant operation, considerable amounts are produced as a by-product and could be detected outwardly while leaks arise. In the final case the created ^{60}Co is largely the effect of several stages of neutron creation of iron isotopes in the reactor's steel structures [116] via the creation of ^{59}Co originator. Finally, creation of ^{58}Fe . ^{60}Co decays by beta decay to the steady isotope nickel-60 (^{60}Ni). The nickel nucleus emits two gamma rays by means of energies of 1.17 MeV and 1.33 MeV, The reaction is as follows:

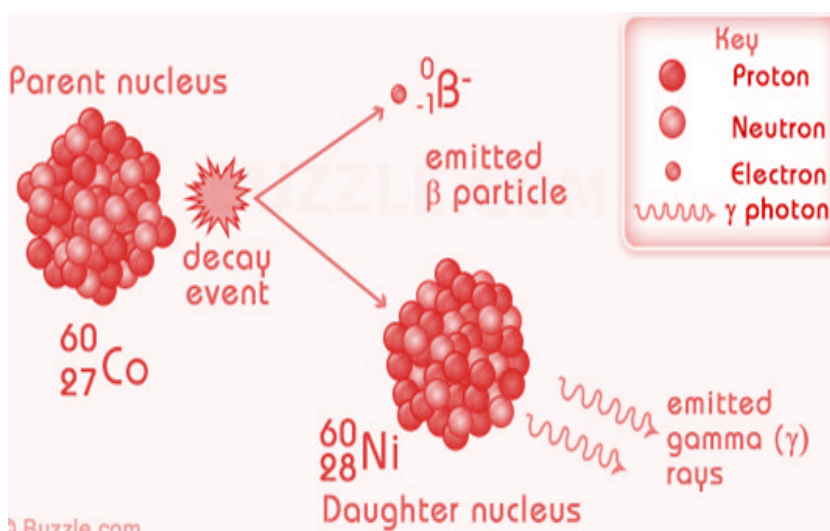
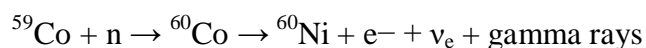


Fig. 1.7. Production of Gamma rays.

Literature Review

N. Seko et al., [117] studied elimination of hazardous metals as of streaming water and land water. Sorbent with elevated capacity could be prepared by radiation method of grafting and crosslinking. Graft sorbent could be produced by means of the usual polymer like polyethylene that have different shapes for example membrane, cloth, and fiber. Particularly, the constructed fibrous sorbent has 100% elevated rate of sorption than that of commercialized resin. Iminodiacetate sorbent was applied for the disposal of cadmium from the scallop waste. In addition, the amidoxime adsorbent is helpful for revival of rare metals such as uranium and vanadium in marine water. Original stringy sorption for arsenic was synthesized by straight grafting of phosphoric monomer and subsequent zirconium-loading. Polymers resembling carboxymethyl chitin–chitosan in the paste-like condition are applicable as the metal adsorbent. It could be biodegraded after usage.

S. Deng et al., [118] prepared *Penicillium chrysogenum* adapted by graft polymerization of acrylic acid (AAc) on the surface of biomass that are ozone-pretreated. When bigger number of carboxyl groups were present on the biomass surface, the adsorption ability for copper and cadmium improved considerably, particularly while NaOH convert carboxylic acid group to carboxylate ions. According to Langmuir isotherm, the adsorption abilities were 1.70 and 1.87 mmol/g for Cu and Cd, respectively. The used biosorbent was reformed by treating with HCl solution and can be reused over five cycles by means of small loss of sorption ability away from the second succession.

T. Sehgal et al., [119] studied in which grafted membranes were constructed by the reaction of methyl methacrylate (MMA) and polypropylene film (IPP) and yield IPP-g-MMA film. In the reaction benzoyl peroxide initiator is used and atmosphere was covered by inert nitrogen. Degree of grafting was depends on initiator and monomer concentration, reaction time and also temperature maximum grafting was 50%.

M. K. Patiet al., [120] grafted acrylic acid on chitosan. He used initiator the ceric ammonium nitrate. Grafting yield depends on initiator and monomer concentration, time & temperature of the reaction. It was characterized by FTIR, TGA, SEM and XRD

techniques. As of the FTIR information it is predicted that grafting has performed significantly. The morphology was explained by SEM. Degradation of grafted polymer at diverse state were evaluated by TGA. It is also experimented the antibacterial and antifungal behavior of the grafted polymer.

Nazia Rahman et al., [121] studied the reaction of acrylic acid (AAc) and methyl methacrylate (MMA) on polyethylene (PE) films by γ -ray induction and its appliance on the disposal of Cu (II) ions as of aqueous solution. Grafting yield depends on monomer ratio, monomer concentration, radiation dose by means of methanol/H₂O as solvent and Mohr's salt as inhibitor.

Nazia Rahman et al., [122] had developed another adsorbent by grafting Acrylic acid on irradiated polyethylene terephthalate (PET) film in order to study the selective Cu²⁺ sorption as of the aqueous solution of Cu²⁺, Co²⁺ and Ni²⁺. The grafted films were adapted by KOH conduct for the extension of the graft cuffs to make easy the entrance of metal ions to the sorbent. Sorption capacity was studied under different pH.

T.S. Anirudhan et al., [123] prepared polyacrylamide grafted sawdust to investigate the disposal of Cr (VI) ions from an aqueous solution. The method was seen to be pH, temperature and concentration dependent.

F. Madrid et al., [124] was able to graft GMA on water hyacinth fibers by radiation-induced techniques. The consequence of dissimilar grafting parameters were investigated. Absorbed dose, monomer concentration. The optimum values of solvent, absorbed dose, dose rate, and concentration of monomer were found to be 1:3 (volume/volume) water-methanol solvent, 10 kGy, 8 kGy h⁻¹ dose rate and 5% volume/volume glycidyl methacrylate, respectively. About 58% degree of grafting was achieved.

Cengiz Kavaklı et al., [125] prepared EDA functionalized PE/PP-g-PGMA and tested for the disposal of Cr (VI) ion as of the aqueous solution. Cr (VI) ion sorption was evaluated in batch approach as a purpose of pH, feed concentration, contact time, ionic strength, and coexisting anion. Desorption was carried out by 2 M HNO₃ solution.

Cengiz Kavaklı et al., [126] had also constructed Fe (III) encumbered IDA functionalized GMA-g-PE/PP non-woven fabric to dispose the phosphate ion as of the aqueous solution. Sorption investigation were carried out in batch mode at dissimilar pH (2–9) and at different phosphate concentrations.

G. Przybytniak et al., [127] studied the joint radiation grafting of acrylic acid (AAc) onto polyethylene (PE), polypropylene (PP) and polystyrene (PS). At initial stage of experiments, the power of ionizing radiation on the base polymers was evaluated, i.e. the level of radicals steady at room temperature and radiation yield of liberated hydrogen were calculated forevery polymer.

Mohamed Mahmoud Nasef et al., [128] had prepared CO₂ adsorbent by the grafting of glycidyl methacrylate (GMA) on polyethylene coated polypropylene (PE-PP) non-woven film followed by amination reaction. Grafting yield depends on monomer concentration and absorbed dose.

Masaaki Omichiet al., [129] studied the preparation of IDA functionalized GMA-g-PE/PP fabric and its function on the disposal Co ions as of the aqueous solution. The cobalt sorption ability of the PE/PP-g-GMA-IDA fabric was estemeted throughout a group sorption test.

Objectives of the Present Work

Radiation grafting of polymers is an important topic for the surface modification of polymer backbone for advanced applications. In this method functional monomer is grafted on the base polymer matrices. The grafted polymer is used for separation of toxic elements such as heavy metals and dyes. It is also used for making proton exchange membranes (PEMs) for fuel cells.

The heavy metals, dyes and radioactive elements are great concerns among the kinds of environmental pollution as of their high toxicity and other unpleasant effects on human health. These pollutants are released in the environment by various natural and industrial actions. The high exposure of heavy metals and dyes cause cough, bronchitis, asthma, lung cancer, kidney disease, headache, nausea, dizziness, tightness of chest, chest pain, vomiting, skin irritation, rapid respiration, bone disease, cyanosis and extreme weakness of nervous system. Therefore, it is essential to remove heavy metals, dyes and radioactive elements from wastewater at least below the regulatory level. Different processes have been proposed for the disposal of heavy metals and dyes from aqueous solutions. Among the separation processes coagulation, flocculation, electro-coagulation, membrane separation, oxidation or ozonation, ion exchange, chemical precipitation, reverse osmosis and adsorption. Adsorption is found to be quite suitable, cheapest and effective way to remove heavy metals from effluent. Functionalized grafted polymer as adsorbent has become very effective among adsorption technologies. From the literature studies it is seen that several types of works have also been published on the removal of toxic metals and dyes and also on the preparation of proton exchange membranes [130-131]. The grafting of glycidylmethacrylate (GMA) and its functionalisation through amination has been reported [132].

In this present study, a new adsorbent was constructed by grafting of Glycidylmethacrylate (GMA) on non-woven polyethylene film. A gamma radiation induced grafting method was adopted to make the grafted film. Functionalization of GMA-g-non woven PE film was carried out through sulfonation. Adsorption capacity of the sulfonated-GMA-g-PE film was evaluated under diverse circumstances: contact time, pH, temperature and starting metal ion concentration. The prepared film is also tested for proton exchange membrane.

The specific work plan of this present work are:

- a) Preparation of sulfonic acid functionalized GMA-g-non woven PE film.
- b) Characterization of the adsorbent through FTIR, TGA and SEM technology.
- c) Determination of the consequence of reaction time, temperature and radiation dose on degree of grafting.
- d) Studies on relation between degree of grafting and degree of sulfonation.
- e) Studies on the advanced application of sulfonated-GMA-g-PE film as heavy metals, dye adsorbent and also proton exchange membranes (PEMs) for fuel cell.
- f) Investigation the effect of initial metal ion/dye concentration on adsorption of heavy metals/dyes from aqueous medium.
- g) Determination of the Effect of pH and temperature on the sorption .
- h) Evaluation of the outcome of change of contact time on the sorption.
- i) Study of the resorption capability of the sorbent.
- j) Determination of the isotherm model and kinetics of adsorption.
- k) Evaluation of the water uptake capacity of the constructed film.
- l) Study on the oxidative properties of the PEMs.
- m) Determination of the ion exchange capacity of the PEMs.

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Experimental

2.1. Materials

2.1.1. Raw Material

Raw material: Non-oven Polyethylene

Source: Non-oven Polyethylene film manufactured by Kurashiki Textile Manufacturing Co. Ltd, Japan, was collected for the experiment.

2.1.2. Chemicals and Reagents

All the chemicals and reagents used in this investigation was of analytical grade. A list of the chemicals and reagents used in different stages in the experiment has shown in table 2.1.

Table 2.1.List of chemicals and reagents used in the experiment.

Name of Chemical	Sources
Glycidyl methacrylate (GMA)	Sigma Aldrich Co.
Tween -20	Sigma Aldrich Co.
Sodium sulphite	Sigma Aldrich(USA)
Sodium bisulphate	Sigma Aldrich(USA)
Hydrochloric Acid	Sigma Aldrich Co.
Sodium Hydroxide	Merck-Schuchardt, Schuchardt, Germany
Isopropanol	Sigma Aldrich Co.

2.1.3 Apparatus

Varieties of instrument are used in different stages of experimental work. A brief introduction of those instruments given below:

2.1.3.1. Electrical Balance

Weighing Balance of Model AR 1140 was used for measuring weight. It was supplied by SMH Engineering and Trading Co., Dhaka, Bangladesh. It's measuring range and readability is 110 g and 0.0001g, respectively.

2.1.3.2. Gravity Convention Oven

It was use for drying purpose and supplied by Memmert UM series. Its temperature range is 30-220 °C.

2.1.3.3. pH Meter

The pH meter was used for measuring pH of Cu(II),Cr(III),Pb(II),BF,MB, CV and uranium ion solution and for other experimental purpose. Its Model is Cole-Parmer-5991-81 FIB-12 and was supplied by Institute of Electronics, AERE, Dhaka, Bangladesh.



Fig.2.1. pH meter

2.1.3.4. UV-VIS Spectrophotometer

UV-VIS Spectrophotometer is used to investigate the concentration of Cu(II),Cr(III),BF,MB, CVand Uranium ion in solution. The model of the UV-VIS Spectrophotometer was UV-2401PC, SHIMADZU, Japan.



Fig. 2.2. UV spectrophotometer

2.1.3.5. Hot Plate and Magnetic Stirrer

Hot plate and magnetic stirrer was used in various stage like – monomer solution preparation, sulfonationof grafted film etc and other heating purpose. Jeo Tech TM-14SB Hot plate and magnetic stirrer from China was used.

2.1.3.6. Water Bath

Water bath is used in grafting reaction of Glycidylmethacrylate on non-woven Polyethylene film as it meets the required temperature.

2.1.3.7. Co-60 Gamma-irradiometer

The free radical site formation of non-woven polyethylene film was initiated by the Co-60 gamma-irradiator from IFRB, Atomic Energy Research Establishment, Savar, Dhaka.

2.1.3.8. FT-IR Spectrophotometer

To characterize the grafted film, FT-IR Spectrophotometer was used. The model was IRPrestige21, Shimadzu Corporation, Kyoto, Japan. This facility was used from Center for Advanced Research for Science(CARS), University of Dhaka.

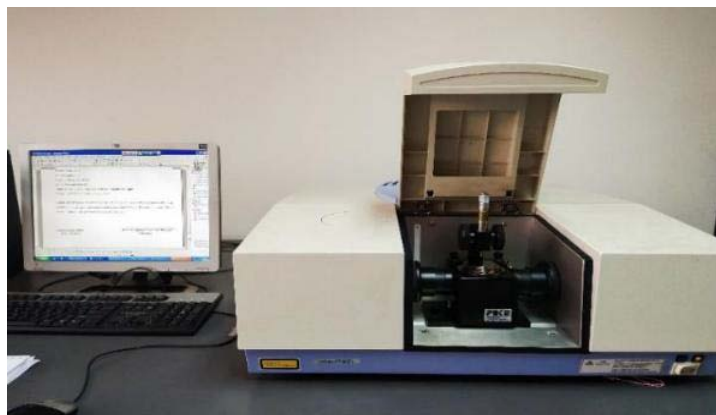


Fig.2.3: FTIR spectrophotometer.

2.1.3.9. Scanning Electron Microscope (SEM)

To study the morphology of the grafted film, SEM was used. The SEM model was JSM-6490LA, JEOL. This facility was taken from CARS, University of Dhaka.

2.1.3.10. Thermogravimetric Analyzer

Physical and chemical behaviour of grafted film are calculated as a function of rising temperature in thermogravimetric analyzer. This facility was taken from CARS, University of Dhaka.

2.1.3.11. Atomic Adsorption spectrophotometer(AAS)

To determine the concentrations of Pb(II) ion AAS is used. This facility was taken from NRCD, AERE, savar, Dhaka. The model of AAS was AA-6800, SHIMADZU, Japan.



Fig. 2.4. Atomic Adsorption spectrophotometer

2.1.3.12. Other Technical Components

For qualitative work, all the components used were of good and selective quality. SCIOLOGEX micropipette, Whatman 15cm filter paper from England, Aluminium foil paper, Beakers, Burette, Pippet, Conical flask, Volumetric flasks, Measuring cylinder, Test tubes, Petri dishes, Funnels, Gas Jar etc. of well-marked and glass bodied were used.

2.2. Methods

2.2.1. Preparation of the Adsorbent Film

2.2.1.1. Preparation of Non-woven Polyethylene Film

Non-oven Polyethylene films were composed from Kurashiki Textile Manufacturing Co. Ltd, Japan. The films were cut into the size of 8 cm × 1.5 cm. Then, it was taken weight of the non-woven polyethylene films (8 cm length and 1.5 cm width) was taken in a digital balance and kept in a small polyethylene packet.



Fig. 2.5: Non-woven polyethylene film (8 cm×1.5 cm).

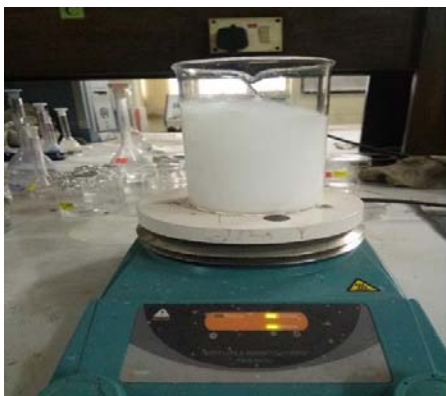
2.2.1.2. Grafting Process

Gamma radiation were exposed to the previously weighted Non-woven PE films from Co-60 gamma radiation resource at 20 KGy, 30kGy and 40KGy radiation dose at ambient temperature. The irradiated PE films were conserved at dry-ice condition until use. At room temperature (25°C), 5 wt% monomer GMA and 0.5 wt% Tween-20 as emulsifier was added to deionised water to prepare the monomer GMA emulsion by stirring with a mechanical stirrer for 0.5 h. To dispose dissolved oxygen the emulsion of GMA was bubbled for 40 minutes with Argon gas. The irradiated PE fabric was put into a glass bottle and it was fully filled by de-aerated GMA emulsion. To prevent inclusion of oxygen from air into the GMA-emulsion of bottle it was compactly closed with a lid. The grafting reaction was performed at 80°C in a water bath up to 4 h. The constructed GMA-g-PE film was washed repeatedly with deionized water to remove remaining monomer and homopolymer of GMA and dried up in a vacuum oven to steady weight. The degree of grafting was calculated as follows:

$$\text{Degree of grafting (\%)} = (W_g - W_0)/W_0 \times 100$$

Where, W_g is the dry weight of GMA grafted PE fabric and W_0 is the dry weight of PE fabric.

Illustration of the Process:



(a)



(b)



(c)



(d)



(e)



(f)

Figure 2.6: (a) Stirring of monomer solution (b) De-aeration of monomer solution using argon gas, (c) Tube containing De-aerated GMA(monomer) solution and irradiated film (d) Reaction chamber (water bath, 80 °C) (e) Drying of grafted film in an oven, (f) GMA grafted non-woven PE film.

2.2.1.3. Functionalization of GMA Grafted Non-woven PE Film

For the functionalization, GMA-g-PE fabric was deeped in sodium bisulphite, sodium sulphite, iso-propanol and water solutions at the ratio of 10:3:10:77 wt% and the reaction was carried out at 80°C with constant heating up to 6h [1]. Subsequently, sulfonated-GMA-g-PE sorbent was washed repeatedly with deionized water until neutral and desiccated in a vacuum oven to stable weight. The renovation of epoxide group (X) to sulfonate group were calculated as follows:

$$\text{Conversion (X)} = \left[\frac{W_s - W_g}{104} / \frac{W_g - W_o}{142} \right] \times 100$$

Where, W_o , W_g and W_s are the dry weight of PE fabric, GMA-g-PE fabric and sulfonated-GMA-PE sorbent respectively. 142 and 104 are the molecular weight of GMA and sodium bisulphate. Fig.2.7 shows the construction steps of sulfonated-GMA-g-PE film and Fig. 2.8 shows the picture of sulfonation of GMA-g-PE film.

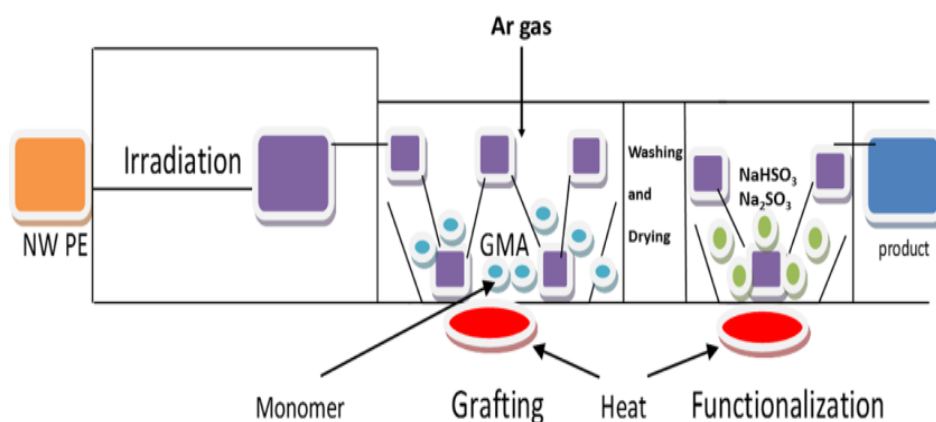


Fig.2.7.Preparation of sulfonated adsorbent from non-woven polyethylene film.



Fig.2.8: (a) Sulfonation of GMA grafted non-woven PE film at 80 °C, (b) Sulfonated GMA grafted non-woven PE film

2.2.1.4. Treatment of sulfonated film with NaOH

To enhance the adsorption capacity of the sulfonated GMA-g-non woven PE film, the films were deeped in 1M NaOH solution for several minutes.

2.2.1.5 Determination of heavy metals and dye Adsorption

The sorption behavior of the constructed sulfonated-GMA-g-PE films for heavy metals and dyes were measured by the UV spectrophotometer and Atomic Adsorption spectrophotometer(AAS) at room temperature (25°C). The heavy metals and dyes uptake ability were examined under diverse environment such as pH, contact time and starting concentration. HCl and NaOH solution was used for pH adjustment of the solutions. Aqueous heavy metals and dye solution concentrations before and after sorption were determined by a UV spectro-photometer and AAS. The heavy metals and dye sorption ability of the constructed fabric was measured using the subsequent equation:

$$Q = (C_1 - C_2)V/W$$

Where, Q is the sorption amount (mg/g) of adsorbent, W is the weight of the sulfonated-GMA-g-PE fabric(g), V is the volume of solution (L), and C_1 and C_2 are the concentrations (mg/L) of heavy metals and dye before and after sorption, respectively. Figure. 2.9 and 2.10 shows the picture of the adsorbent before and after adsorption.



Fig. 2.9. Sulfonated-GMA-PE film before adsorption

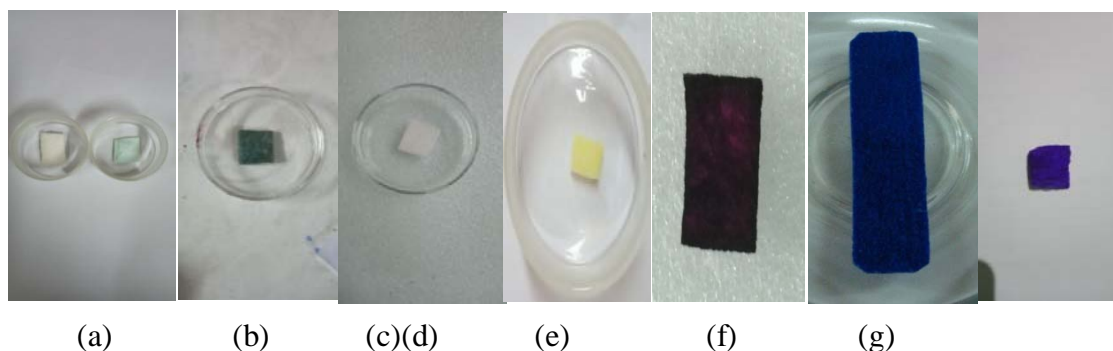


Fig.2.10. Sulfonated-GMA-g-PE film after (a) Cu(II), (b) Cr(III), (c) Pb(II), (d) U(VI), (e) BF and (f) MB (g) CV adsorption.

2.2.1.6. Desorption of adsorbed film.

The regeneration of the sorbent film was investigated by soaking in 2M aqueous HNO_3 in case of Cu(II), Cr(III), Pb(II) and dyes 24 h stirring with 300 rpm by a magnetic stirrer, 2M HCl was used for uranium for adsorption study. 0.02g of the sorbent was added to 20ml of heavy metals and dyes in aqueous solution. The desorption and repeated use was performed five consecutive cycles. Percentage of desorption was intended as follows:

Percent desorption = {Ions desorbed (mg) / Ions adsorbed by the film (mg)}

Results and Discussion

2.3. Preparation and characterizations of the Adsorbent Film

2.3.1.. Preparation of the Adsorbent Film

Sulfonated-GMA-g-PE sorbent was fabricated by exposing γ radiation (Pre-irradiation technique). Firstly, γ irradiation was subjected to the non woven PE polymer backbone to form primary free radicals. Then, a solution of GMA monomer was made by mixing in a suitable solvent and was added to the irradiated polymer for grafting. In the reaction graft growing chain and termination reaction was occurred. Finally, the graft copolymer was produced. In pre-irradiation technique, monomer is not irradiated directly and formation of homo polymer is relatively lower than simultaneous irradiation technique. The GMA grafted PE film was functionalized by sulfonation reaction and the reaction was performed at 70°C, 80°C and 90°C with constant heating up to 6 h for the determination of effect of temperature on sulfonation. It was observed that comparatively homogeneous sulfonation reaction was occurred at 80°C.

Grafting was carried out at 20kGy, 30kGy and 40kGy to study the consequence of total dose of gamma radiation. Maximum grafting and adsorption was found at 30kGy radiation dose (figure 2.11). 2.5%, 5% and 7.5% GMA solutions were used to optimize degree of grafting. Higher grafting was observed at 5% GMA solution (figure 2.12). Same activities of grafting curve against monomer concentration was found in terms of Trommsdorff effect [2]. 343.31% graft yield was obtained (favourable conditions radiation dose 30kGy, monomer concentration 5%, 0.5% adding up of Tween-20 as an additive, 4 h reaction time).

Epoxide group containing GMA-g-PE film with 343.31% degree of grafting can be easily functionalized. For functionalization purpose, sulfonation was performed in sodium bisulphite, sodium sulphite and isopropanol and water solutions in the ratio of 10:3:10:77 wt% at 80°C for 6h. The constructed sulfonated GMA grafted PE films (G-343.31%) were treated with NaOH(1M) that improved the metal ion sorption ability of the films mostly.

Table 2.2. Data for the effect of radiation dose on degree of grafting.

Radiation dose(Gry)	Degree of grafting(%)
20	180.23
30	343.31
40	460.57

Table 2.3.Data for the effect of monomer concentration on degree of grafting.

Monomer concentration(%)	Degree of grafting(%)
2.5	180.83
5.0	343.31
7.5	154.46

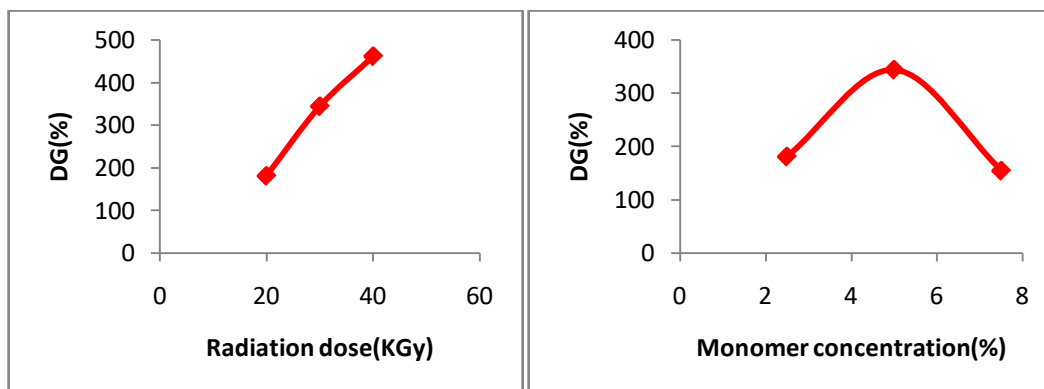


Fig 2.11.Effect of radiation dose on DG.Fig 2.12.Effect of monomer concentration on DG.

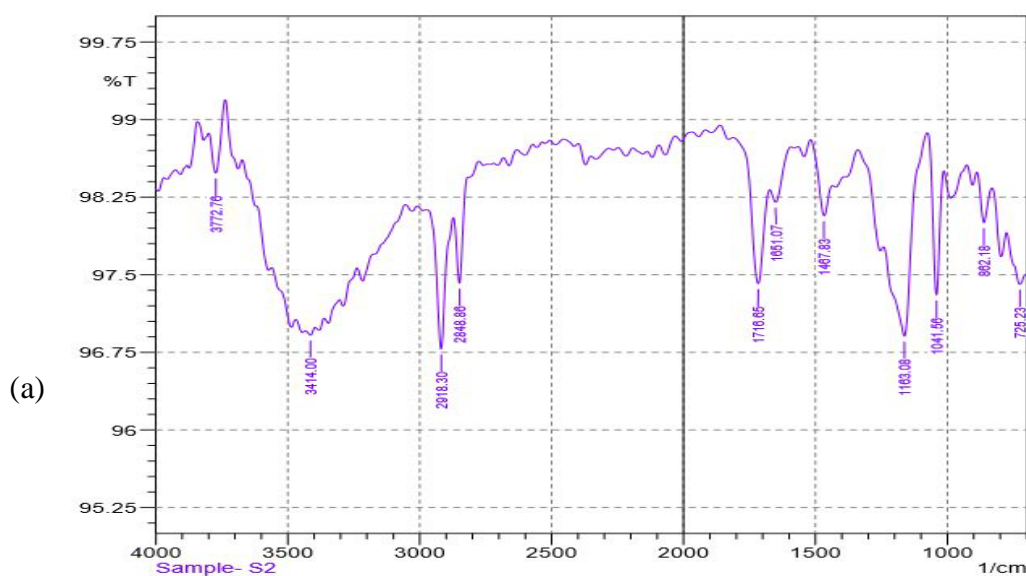
2.3.1.1. FTIR analysis

FTIR analysis of PE film, GMA grafted PE film and sulfonated-GMA-g-PE film were recorded. The spectrum of the PE film is shown in Figure 2.13(a). From IR spectrum of PE, C–H stretching and C–H deformation vibrations were found at 2910 cm^{-1} and 2845 cm^{-1} . C–H bending, wagging and rocking of CH_2 group are found at 1463 , 1369 and 721 cm^{-1} respectively.

Figure 2.13(b) shows the evidence for the grafting of GMA on PE film, peaks at 1716 cm^{-1} indicates C=O stretching vibrations, peaks at 1273 and 1147 cm^{-1} represents symmetric and asymmetric vibration of C-O in GMA and peaks for epoxy rings were appeared at 912 and 856 cm^{-1} .

Figure 2.13(c) shows the evidence for the sulfonation of GMA-g-PE film. Peaks for epoxy group at 912 cm^{-1} and 856 cm^{-1} , intensity of both peaks reduced after sulfonations in this case and a new peaks appears at 1041 cm^{-1} for sulfite. The characteristic peaks for sulfite is observed at 1030 cm^{-1} to 1060 cm^{-1} [3].

From the FTIR analysis, it can be predicted that grafting of GMA and subsequent functionalisation occurred successfully



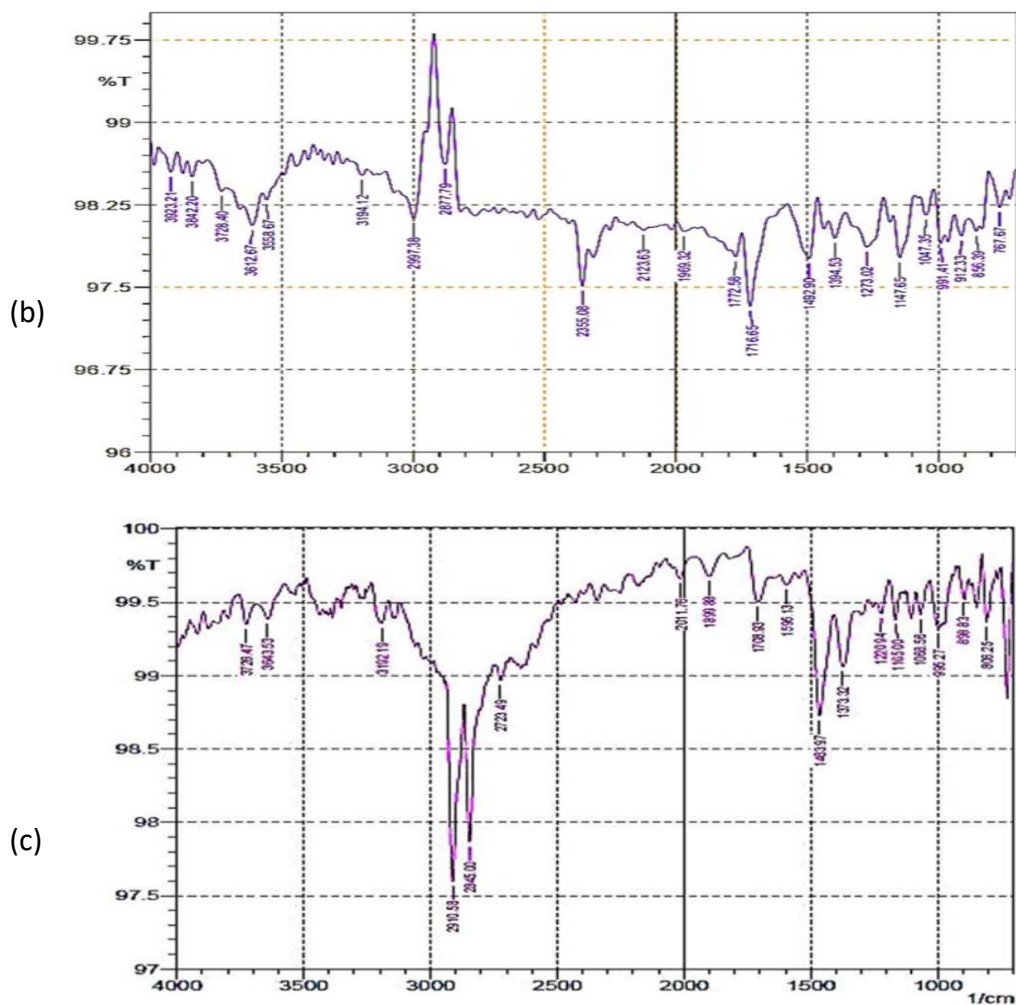


Fig 2.13.IR spectrum of (a) PE fabric (b) GMA grafted non-woven PE fabric (c) Sulfonated GMA grafted non woven PE febric.

2.3.1.2. SEM analysis of the adsorbent

The SEM image of PE and GMA-g-PE and sulfonated-GMA-g-PE fabrics are shown in Figure2.14(a),(b),(c). It showed that the morphological structure changes from PE to GMA grafted PE and sulfonated-GMA-g-PE. In the SEM image of GMA-g-PE, new graft chains and cross linked chains were found which provides proof of grafting. Functionalization through sulfonation is confirmed by the decrease of crosslinked chains and increase of diameter of the grafted chains.

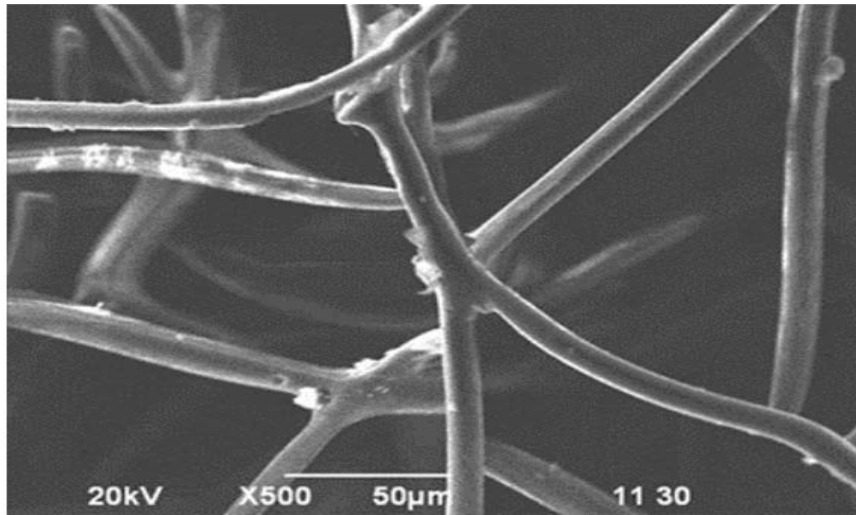


Fig. 2.14(a).SEM image of PE

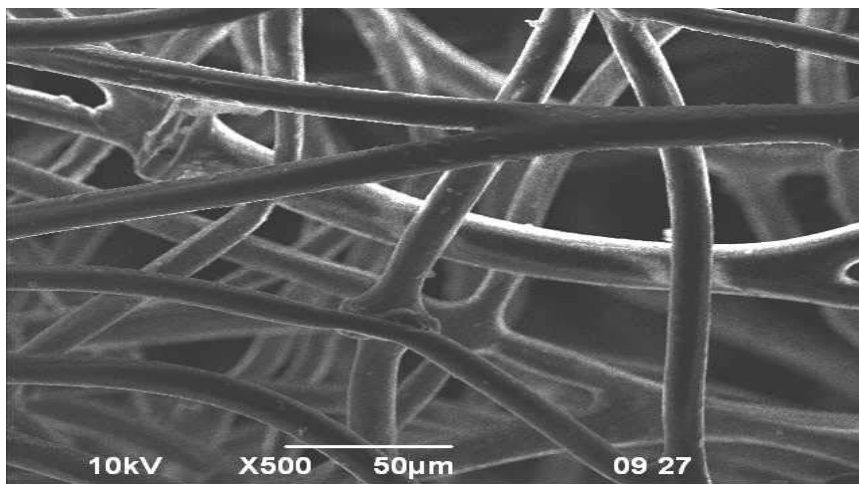


Fig.2.14(b). SEM image of GMA-g-PE

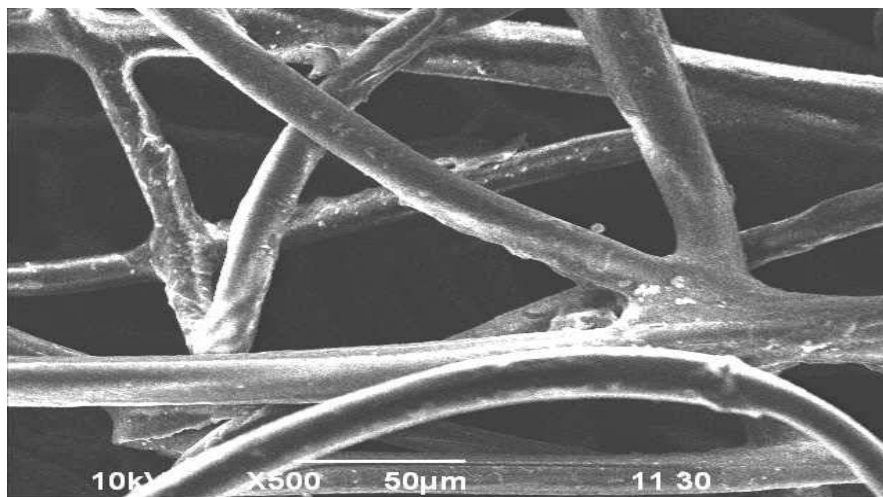


Fig.2.14(c). SEM image of Sulfonated-GMA-g-PE

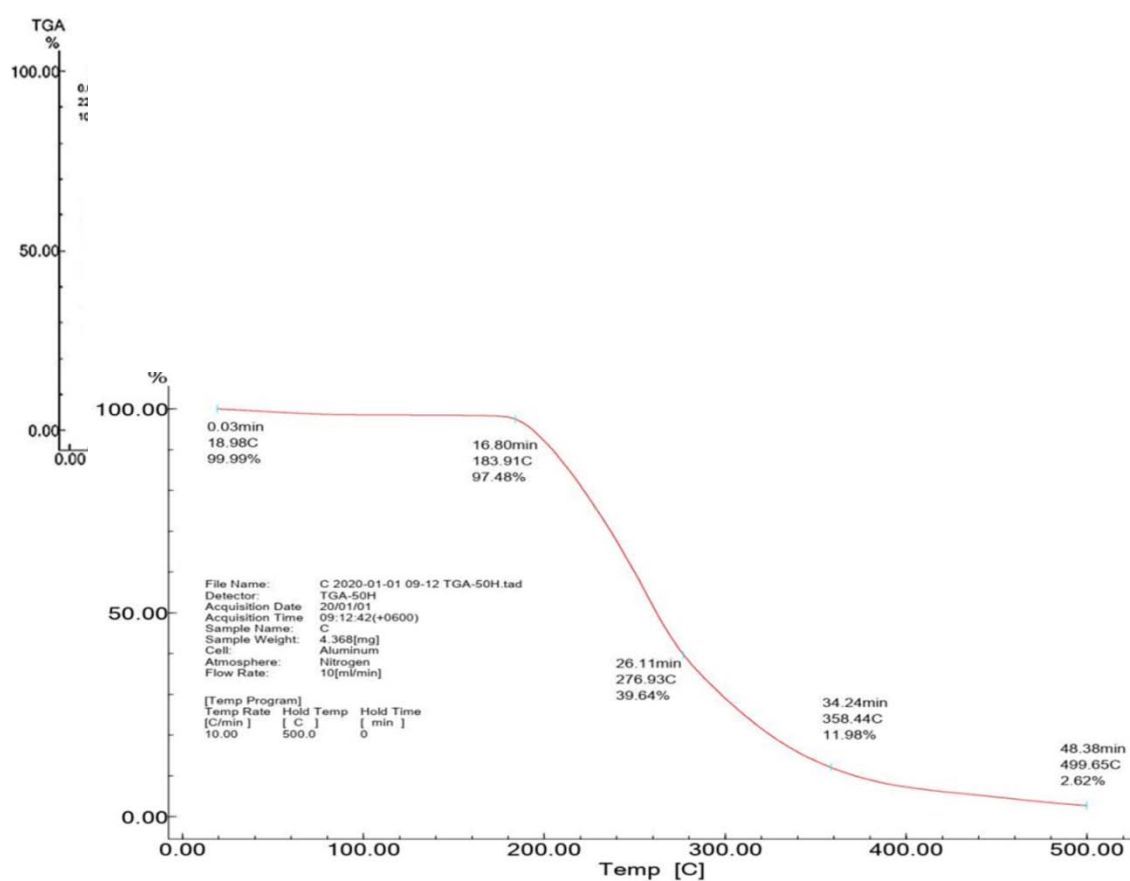
2.3.1.3. Thermo-gravimetric Analysis of the Adsorbent

The thermo-gravimetric analysis (TGA) for the non-woven PE film is presented in figure 2.15(a). Non-woven PE film shows thermal stability up to 200°C and higher than 200°C it starts to decay. It shows three decomposition steps, i.e., 200°C–255°C, 255°C–499°C and above 499°C. At 200°C–255°C, 4.81% of the PE decomposes, at 255°C–379°C, 46.33% decomposes, at 379°C–499°C, 87.08% decomposes and at above 499°C, 93.38% decomposes.

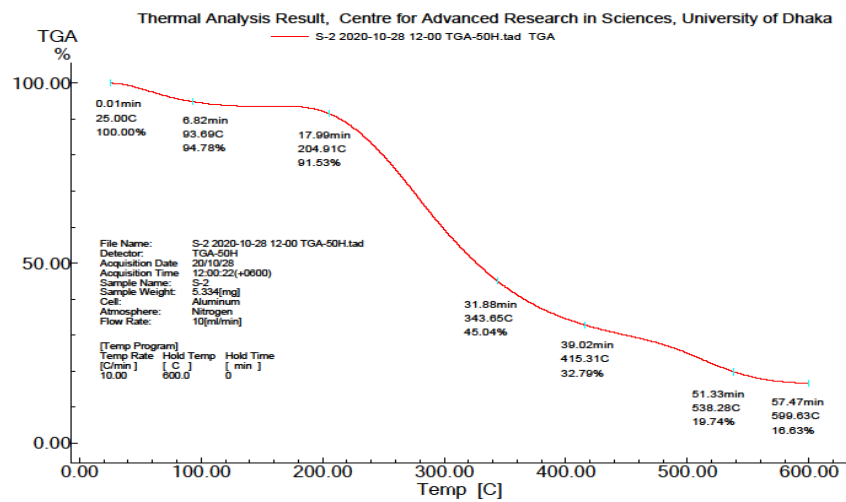
Figure 2.15(b) represents the thermo-gravimetric analysis of the GMA grafted non-woven PE film. GMA grafted non-woven PE film shows thermal steadiness up to 180°C and higher than 180°C it starts to decay. It shows four decomposition state, i.e. at 180°C–184°C, 2.52% of the grafted PE decomposes, at 184°C–277 °C, 60.36% decomposes, at 277°C–358 °C, 88.02% decomposes and above 358°C, 97.38% decomposes.

Figure 2.15(c) represents the thermo-gravimetric analysis of the sulfonated GMA grafted non-woven PE film. Sulfonated GMA grafted non-woven PE film starts to decompose around initial stage. It shows a six decomposition state, i.e. at 25°C–93°C, 5.22% of the grafted PE decomposes, at 93°C–205°C, 54.96% decomposes, at 205°C–343 °C, 55% decomposes, 343°C–415°C, 68.21% decomposes, at 415–538°C, 80% decomposes and above 538°C, 90% decomposes.

(a)



(b)



(c)

Fig. 2.15: TGA thermo-gram of (a) non-woven PE fabric (b) GMA grafted non-woven PE fabric and (c) Sulfonated-GMA grafted non woven PE.

Reference:

[1] Ke X, Drache M, Gohs U, kunz U, Beuermann S: Preparation of Polymer Electrolyte Membranes via Radiation-Induced Graft Copolymerization on Poly(ethylene-tetrafluoroethylene) (ETFE) Using the Crosslinker N-Methylenebis (acrylamide), *Membranes* 8 (4), 102, 2018 doi.org/10.3390/membranes8040102.

[2] Pengfei Zhan, Jianding Chen, Anna Zheng, Han Shi, Fuxiu Chen, Dafu Wei, Xiang Xu, Yong Guan, *The Trommsdorff effect under shear and bulk polymerization of methyl methacrylate via reactive extrusion. European polymer journal.*

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[3] W. Lee, Y. Kim, M. Jung, D. Kim, D. Cho, S. Kang

Preparation and properties of conducting polypyrrole-sulfonated polycarbonate composites, Synthetic metal.

Volume 123, Issue 2, 4 September 2001, Pages 327-333

Removal of heavy metals from aqueous solutions

3.1. Introduction

Increasing industrialization, the use of heavy metals compounds increases globally in aqueous solutions which creates much public attention as prospective hazards for human health. Heavy metals are released from paints, plastics, batteries, pigments, metallurgical, mining, tannery and electroplating industries. From these industries untreated heavy metals containing waste water are mixing in aqueous media[1]. It can create diseases such as paralysis, weakness of nervous system, irritation, nausea, anemia, itai itai, glucosuria, renal failure in kidney and cause of cancer in human body[2-4]. So, removal of heavy metal ions from aqueous solutions is necessary before discharge them into the atmospheric environment.

Methods for the elimination of heavy metal ions are precipitation, coagulation, charcoal adsorption, ion exchange, Chemical oxidation or reduction, electro-deposition, membrane operation. These methods are not suitable for high cost, low elimination rate and less possibility of renewal and reuse[5]. Hence, researchers are searching adsorbents with high separation capacity, low cost, effective and reusable for removing of hazardous heavy metals from waste water.

At present, adsorption is a common technique for the removal of heavy metal ions from wastewater. Different types of adsorbent including biomass adsorbent[6-8], inorganic minerals[9], activated carbon[10], polymer[11-12] are used to eliminate the metal ions from the wastewater. Sorption ability of an adsorbent to the metal ions mainly controlled by the surface sites of the adsorbent[13]. Physical or chemical interaction of the metal ions occurs to the surface of the adsorbent. The mechanism of the adsorption of metal ions on the surface of the adsorbent is ion exchange, coordination or electrostatic in nature. Basically, it has been reported that the groups of sulfonic acid, carboxyl, hydroxyl are enormously beneficial for the elimination of metal ions from different aqueous solutions[14-15]. Hence, to improve the capability of metal ions separation, functional group incorporation are attracted. Nevertheless, for the removing of heavy metals, an environmental friendly, efficient, low-cost and easily obtainable adsorbent is necessary. Polymer grafted adsorbent is a new approach for the elimination of toxic

substances from wastewater. In case of grafting, monomers form covalent bonding to the polymer backbone. There are several advantages of polymer grafting. Grafted monomer can incorporate different functional groups with base polymer but it conserves the mechanical property of the base polymer [16,17]. It is observed that over other methods, radiation grafting are more suitable as it has high penetration power to the polymer backbone and it forms mostly homogeneous free radicals very fast [18].

In the present study, the attraction of the constructed absorbent having sulphonate group toward copper and chromium from its aqueous solution was investigated using UV-Visible Spectrophotometer, Lead sorption was investigated through AAS technique. Langmuir and Freundlich isotherm model were used to examine the adsorption process. Regeneration and reuse of the grafted film was evaluated.

3.2. Experimental

3.2.1 Materials

Chromium Sulphate, Copper sulphate and Lead nitrate.

3.2.2. Methods

3.2.2.1. Preparation of Cu(II), Cr(III) and Pb(II) Ion Solution

A 500 ml volumetric flask was washed and dried. A weight of 1.2559g CuSO₄, 2.4048g Cr₂(SO₄)₃ and 0.7992g of Pb(NO₃)₂ were weighted in digital balance and taken in the volumetric flask. The flask was filled with distilled water up to the mark. Thus, 1000ppm concentration of Cu(II), Cr(III) and Pb(II) ion solution was prepared. This prepared solution was kept at room temperature.

Then Cu(II), Cr(III) and Pb(II) ion solution of various concentrations were prepared from the previously prepared 1000 ppm Cu(II), Cr(III) and Pb(II) ion solution. These prepared Cu(II), Cr(III) and Pb(II) ion solutions were kept at room temperature prior to testing.

Different concentrations of Cu(II), Cr(III) and Pb(II) ion solution were produced from the previously prepared 1000ppm Cu(II), Cr(III) and Pb(II) ion solution by the following formula.

Where, $V_1S_1=V_2S_2$

S_2 = Concentration of ion solution to be prepared (like 100, 200, 300, 400 ppm or even lower concentration like 1, 2, 3, 4, 5 ppm)

V_2 = Volume of Cu(II), Cr(III) and Pb(II) ion solution to be prepared

S_1 = 1000ppm

V_1 = Volume of Cu(II), Cr(III) and Pb(II) ion solution to be taken from 1000 ppm Cu(II), Cr(III) and Pb(II) ion solution.

3.2.2.2. Construction of Calibration Curve for Cu(II), Cr(III) and Pb(II) adsorption

Standard Cu(II) ion solutions of 20ppm, 40ppm, 60ppm, 80ppm, 100ppm were prepared, for Cr(III) 200ppm, 400ppm, 600ppm, 800ppm and 1000ppm solutions were prepared and for Pb(II) 0.5ppm, 2ppm, 4ppm, 6ppm, 8ppm, 10ppm and 100ppm solutions were prepared from previously prepared 1000 ppm Cu(II), Cr(III) and Pb(II) solutions. The absorbance of Cu(II) and Cr(III) solutions were measured by UV-Visible Spectrophotometer and the adsorption of Pb(II) was measured through AAS spectrophotometer. Calibration curve for the standardization of unknown copper, chromium and lead solution were ascertained. Absorbance of solution was measured at wavelength 212nm for Cu(II) and 420nm for Cr(III) and 283.3nm for Pb(II) and the spectrophotometric operation was performed in the concentration range between 0 and 100 ppm for Cu(II), 0 and 1000ppm for Cr(III) and 0 to 100ppm for Pb(II). Figure 3.1, 3.2 and 3.3 shows

the calibration curve for Cu(II), Cr(III) and Pb(II) respectively.

Table 3.1. Standardization of Cu(II) ion absorbance at different concentrations

Concentration(ppm)	Absorbance
20	0.389
40	0.789
60	1.176
80	1.544
100	1.883

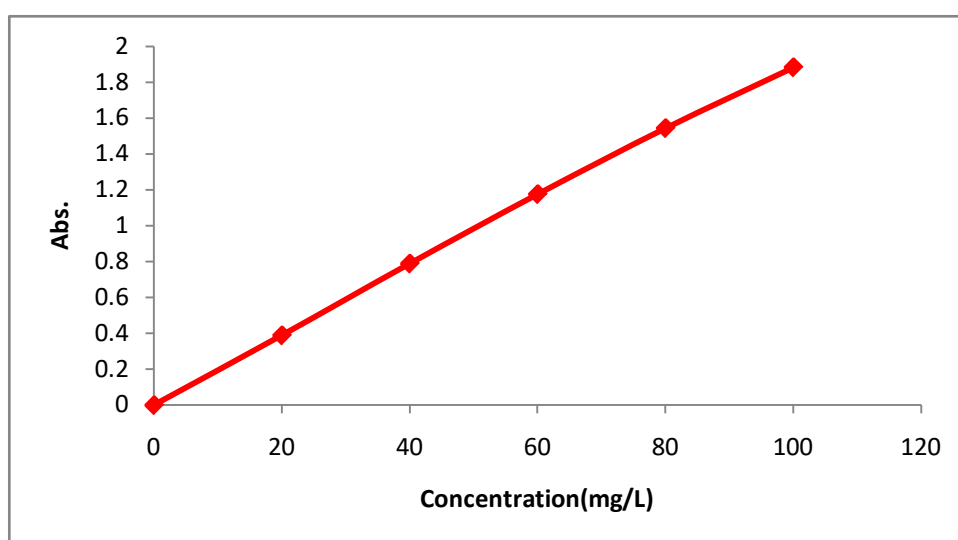


Fig.3.1. Calibration curve for Cu(II) (212nm in UV)

Table 3.2: Standardization of Cr(III) ion absorbance at different concentrations

Concentration(ppm)	Absorbance
200	0.067
400	0.133
600	0.202
800	0.267
1000	0.341

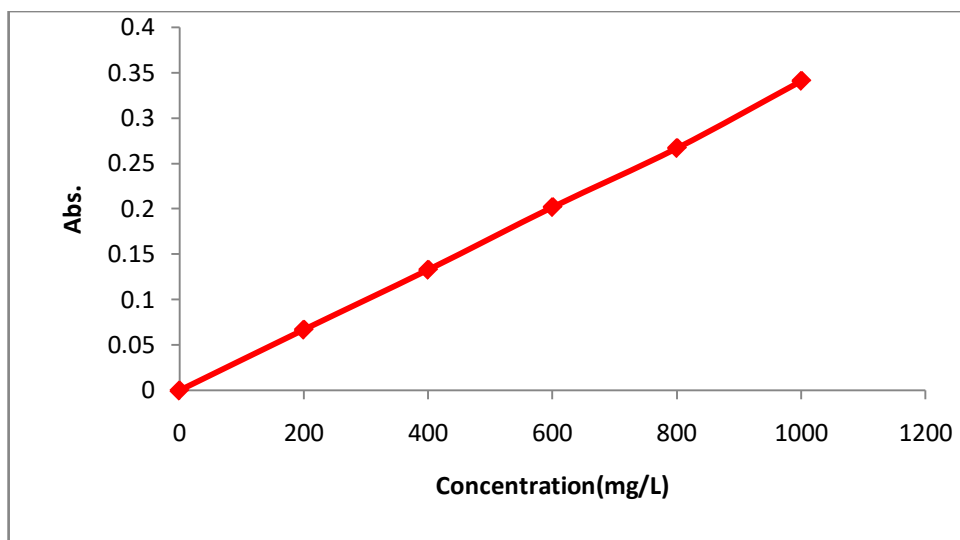


Fig.3.2. Calibration curve for Cr(III)(420nm in UV)

Table 3.3: Standardization of Pb(II) ion absorbance at different concentration

Concentration(ppm)	Absorbance
0.5	-0.0076
2	-0.0067
4	0.0016
6	0.0257
8	0.0357
10	0.0430
100	0.3979

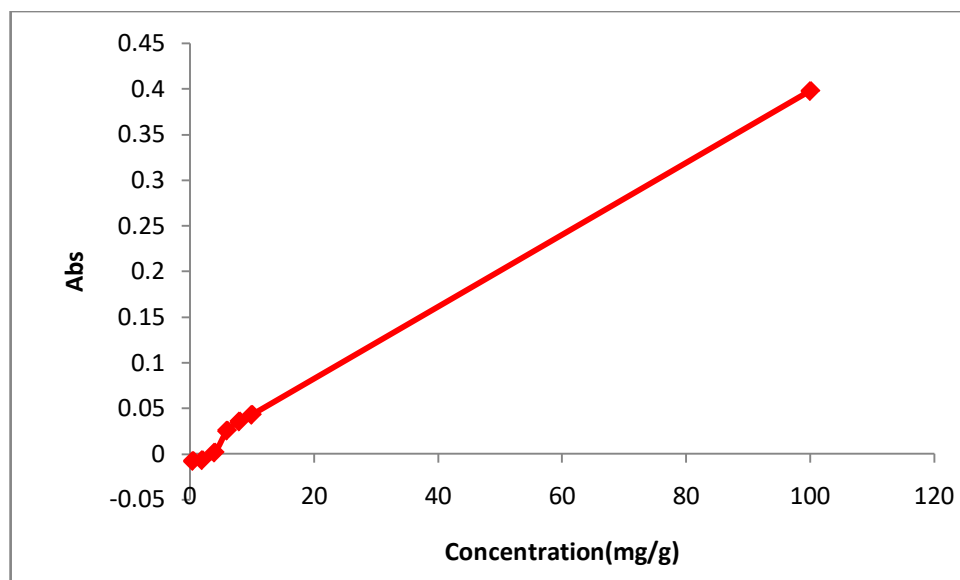


Fig.3.3. Calibration curve for Pb(II)(283.30nm in AAS)

3.2.3. Determination of Cu(II), Cr(III) and Pb(II) Adsorption

The constructed sulfonated-GMA-g-PE films were deeped into aqueous solutions of Cu(II), Cr(III) and Pb(II) at 25°C. Under different conditions such as pH, contact time and starting concentrations the sorption was pursued. HCl and NaOH solutions are used for pH adjustment of the solutions. Aqueous Cu(II) and Cr(III) solutions concentrations before and after sorption were determined by a UV spectro-photometer (wave length 212nm for Cu(II) and 420nm for Cr(III)) and Pb(II) concentration was measured by AAS at wavelength 283.3nm. The Cu(II), Cr(III) and Pb(II)sorption capability of the constructed fabric was measured using the subsequent equation:

$$Q = (C_1 - C_2)V/W$$

Where, Q is the sorption amount (mg/g) of sorbent, W is the weight of the sulfonated-GMA-g- PE fabric(g), V is the volume of solution (L), and C_1 and C_2 are the concentrations (mg/L) of metal ions before and after sorption, respectively.

3.2.4. Desorption of heavy metals Cu(II), Cr(III) and Pb(II)

Cu(II), Cr(III) and Pb(II) desorption from the sorbent fabric was determined by soaking in 2M aqueous HNO_3 for 24 h using the equation.

$$\% \text{ desorption} = \{ \text{Ions desorbed (mg)} / \text{Ions adsorbed by the film (mg)} \} \times 100$$

3.3. Results and Discussions

3.3.1. Effect of contact time on adsorption

We have studied adsorption capacity of sulfonated-GMA-g-PE films for Cu(II), Cr(III) and Pb(II) upto 51 h to illustrate the significance of contact time on the adsorption capacity. From Figure 3.4,3.5,3.6, it can be accomplished that the starting Cu(II), Cr(III) and Pb(II) uptake rate is fast, then it slows down and progressively reaches to equilibrium at 48 h with the utmost sorption of 91.72 mg/g for Cu(II), 120.23 mg/g for Cr(III) and 111.44 mg/g for Pb(II). Almost 72.68% of Cu(II), 44.73% of Cr(III) and 56.79% of Pb(II) adsorption occurred within the first 5 hours. The early fast uptake rate is related to large starting concentrations of Cu(II), Cr(III) and Pb(II) and larger number of available active sites on sulfonated-GMA-g-PE adsorbent. This fast Cu(II), Cr(III) and Pb(II) uptake rate also indicates that most of the reactive adsorption sites are to exist in front of the surface of the sulfonated-GMA-g-PE adsorbent particle and easily attracted by Cu(II), Cr(III) and Pb(II).

Table 3.4: The adsorption capacity of Cu(II), Cr(III) and Pb(II) ion for different contact time 48h at 200ppm

Time(h)	Adsorption capacity(mg/g)		
	BF	MB	CV
1	18.24	15.87	23.8
2	30.3	25.0	37.73
3	42.41	37.44	49.18
4	54.44	44.56	57.14
5	66.66	53.78	63.29
24	74.43	94.19	92.1
25	75.89	101.14	97.34
26	77.65	104.63	102.76
48	91.34	120.12	111.02
49	91.56	120.17	111.25
50	91.6	120.21	111.32

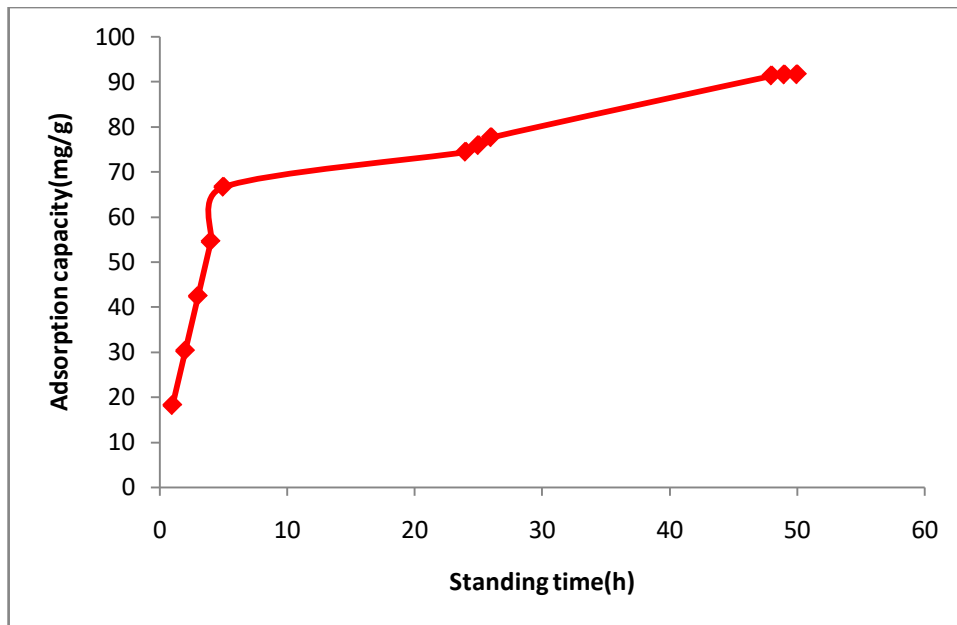


Fig.3.4: Effect of contact time of Cu(II) (Conditions: Initial Cu(II) concentration 600 mg/L; adsorbent 0.15 g, volume 150 mL, pH 4.92).

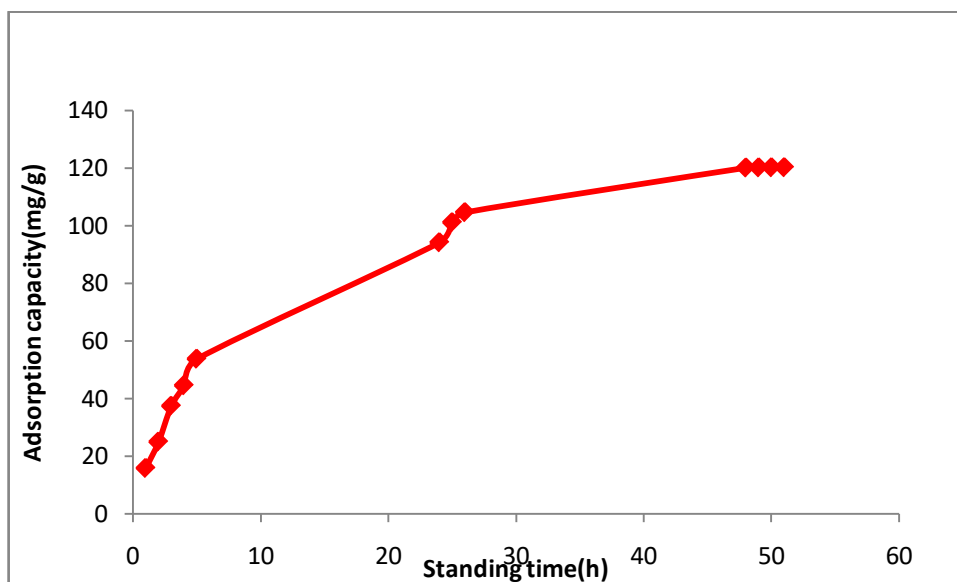


Fig.3.5: Effect of contact time on Cr(III) (Conditions: Initial Cr(III) concentration 600 mg/L; adsorbent 0.15 g, volume 150 mL, pH 4.2).

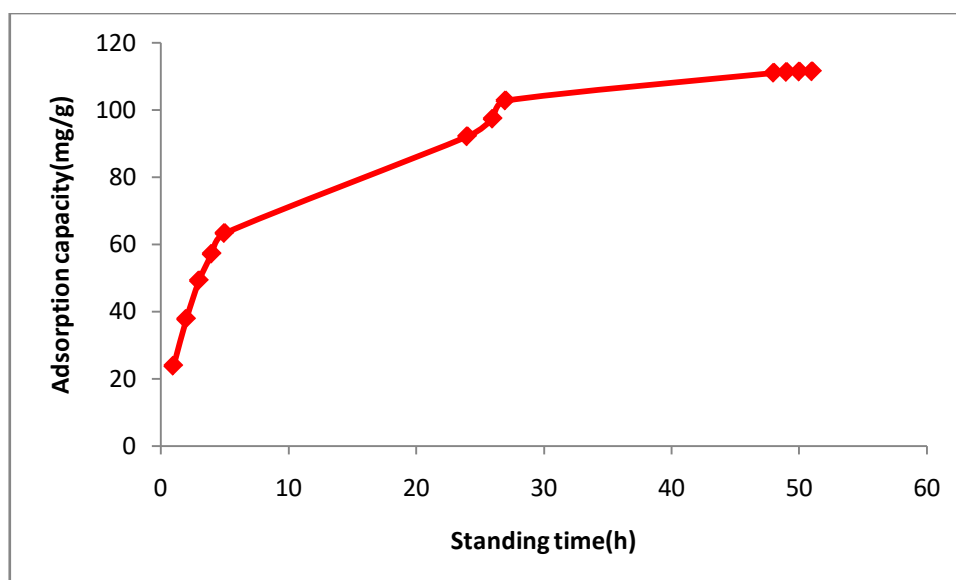


Fig.3.6: Effect of contact time Pb(II) (Conditions: Initial concentration 600 mg/L; adsorbent 0.15 g, volume 150 mL, pH 4.6).

3.3.2. Kinetic studies

To recognize the concise sorption performance of the heavy metals Cu(II), Cr(III) and Pb(II), two familiar kinetic models were used to explore sorption.

Pseudo-first-order kinetic model is expressed as:

$$\log(Q_e - Q_t) = \log Q_e - k_1/2.303 t$$

Where, Q_t and Q_e are the amount of Cu(II), Cr(III) and Pb(II) adsorbed (mg/g) at any time and at equilibrium, correspondingly, k_1 is the rate constant (h^{-1}) of the first-order sorption. The graph $\log(Q_e - Q_t)$ against t would give the value of $\log Q_e$ from intercept.

Pseudo-second-order kinetic model is expressed as:

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e$$

Where k_2 (g/h.mg) is the rate constant of the pseudo-second order adsorption. According to the pseudo-second order equation a plot of t/Q_t against t would give $1/Q_e$ from the slope. Pseudo-first order kinetic plots is presented in Figure 3.7(a) and pseudo-second-order kinetic plots is shown in Fig.3.7(b). Pseudo-first order and pseudo-second-order kinetic parameters are shown in Table 3.5.

Table 3.5: The pseudo-first-order and pseudo-second-order rate constants for Cu(II), Cr(III) and Pb(II) adsorption by sulfonated-GMA-g-PE adsorbent.

Ions	Q(cal)(mg/g)	Qe(theor.)(mgg ⁻¹)	K ₁ (h ⁻¹)	R ²	Qe (theor.) (mg/g)	k ₂ (g h ⁻¹ mg ⁻¹)	R ²
Cu(II)	91.72	89.12	0.04168	0.9859	212.76	0.0004098	0.8629
Cr(III)	120.23	121.11	0.02495	0.9953	142.85	0.0008140	0.8905
Pb(II)	111.44	68.70	0,01867	0.9691	109.89	0.0024573	0.9977

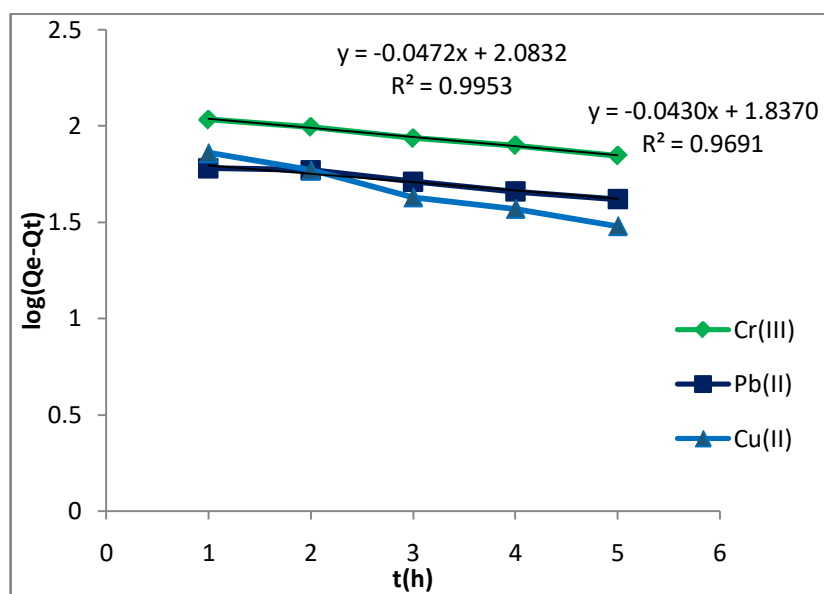


Fig 3.7(a):Pseudo first-order plot for Cu(II), Cr(III) and Pb(II) adsorption.

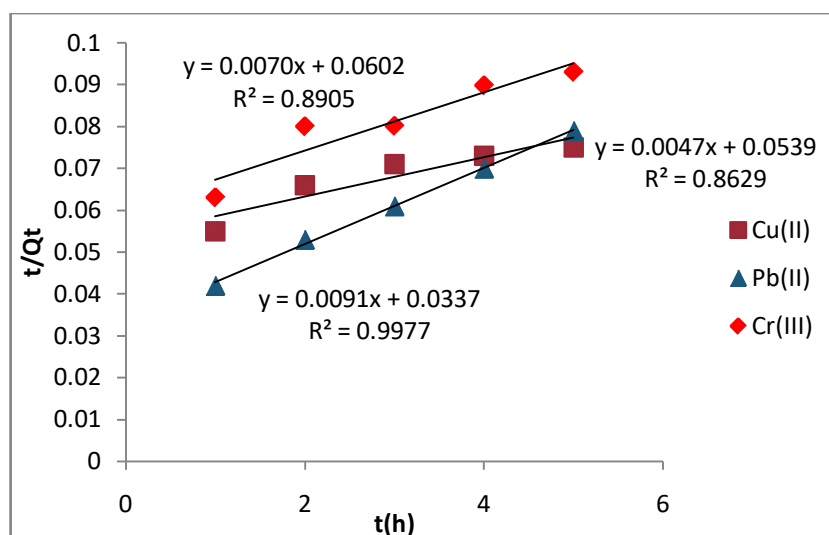


Fig3.7(b). Pseudo second-order plot for Cu(II), Cr(III) and Pb(II) adsorption.

From the Table 3.5, with respect to correlation coefficients R^2 the pseudo-first-order model gives superior description of the Cu(II) and Cr(III) adsorption on sulfonated-GMA-g-PE compared to pseudo-second-order kinetic model.

This implies that Cu(II) and Cr(III) uptake capacity of sulfonated-GMA-g-PE pursued pseudo-first order rate process and the sorption process might have occurred by both physical and chemical adsorptions. On the other hand, Pb(II) follows pseudo-second-order kinetic model as its correlation coefficient is higher than the pseudo-first-order model. So, chemical adsorption occurs in case of Pb(II).

3.3.3. Effect of pH on Cu(II), Cr(III) and Pb(II) adsorption

There is excessive impact of pH of the solution on adsorption ability of the grafted sorbent. At different pH values, because of protonation and deprotonation of sulfonate ions, the surface arrangement of the adsorbent could be altered and exist in dissimilar forms which can affect the sorption capacity. The consequence of pH on Cu(II), Cr(III) and Pb(II) sorption at initial Cu(II), Cr(III) and Pb(II) concentration 600 ppm and contact time 48h is shown in figure 3.8(a),(b),(c). It was seen that the Cu(II), Cr(III) and Pb(II) uptake of the adsorbent increases from pH range 1.25 to 5. Utmost sorption of was found at pH=4.92 for Cu(II), pH=4.2 for Cr(III) and pH=4.6 for Pb(II).

Table 3.6: The adsorption capacity of Cu(II) for different pH at 48h.

pH	Adsorption capacity(mg/g)
2.0	83.35
3.0	85.76
4.0	88.13
4.92	92.59
5.4	90.08

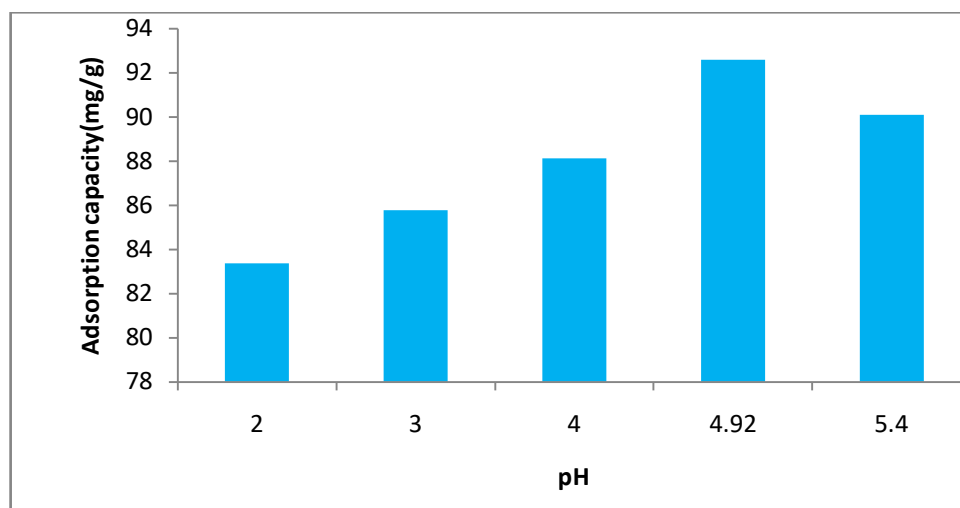


Fig.3.8(a): Effect of pH of Cu(II) on adsorption(initial conc. 600ppm, volume 20 ml, weight 0.02g ,time 48h)

Table 3.7: The adsorption capacity of Cr(III) ion for different pH at 48h.

pH	Adsorption capacity(mg/g)
1.25	16.0
2.0	32.85
3.46	56.88
4.2	64.20
4.6	63.5

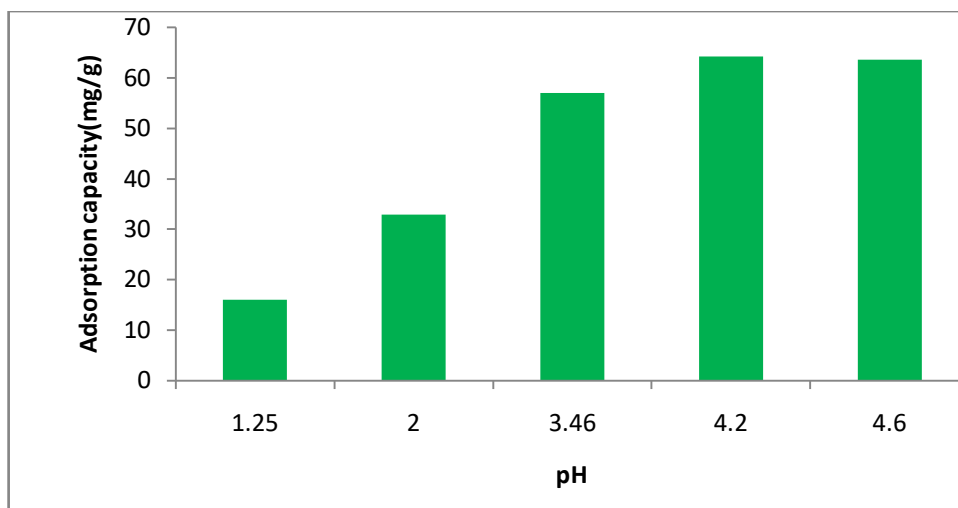


Fig.3.8(b): Effect of pH of Cr(III) on adsorption(initial conc. 600ppm, volume 20 ml, weight 0.02g ,time 24h)

Table 3.8: The adsorption capacity of Pb(II) ion for different pH at 48h.

pH	Adsorption capacity(mg/g)
2.0	55.25
3.0	78.16
4.0	102.45
4.6	112.22
5.65	108.8

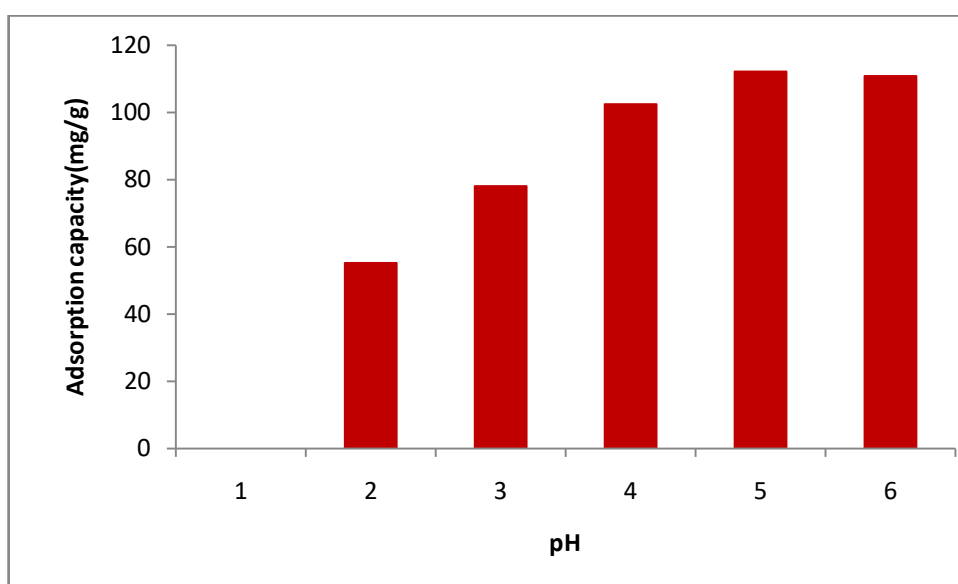


Fig 3.8(c): Effect of pH of Pb(II)on adsorption (initial conc. 600ppm, volume 20 ml, weight 0.02g ,time 48h)

3.3.4. Effect of initial Cu(II), Cr(III) and Pb(II) ions concentration on adsorption

Consequence of starting metal ion concentration on sorption power is shown in figure.3.9. We have prepared some starting concentrations of Cu(II), Cr(III) and Pb(II) and studied initial concentration effect on adsorption. It is presumed that with the increases of starting metal ion concentration sorption capacity also increases and then at specific elevated concentration the sorption reached an impediment value. It was due to saturation of chelating sites of sorbent at higher Cu(II), Cr(III) and Pb(II) concentrations.

Table 3.9: The adsorption capacity of Cu(II), Cr(III) and Pb(II) ion for different initial metal ion concentration at 48h.

Initial concentration(ppm)	Adsorption capacity(mg/g)		
	Cu(II)	Cr(III)	Pb(II)
200	54.23	87.46	70.22
400	72.92	105.99	90.38
600	91.7	126.21	111.44
800	92.14	134.0	120.25
1000		140.3	121.56

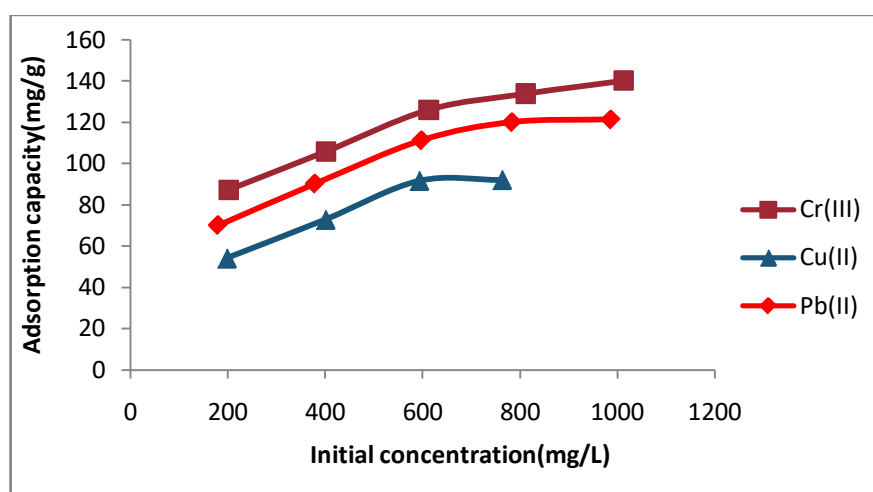


Fig.3.9. Effect of initial Cu(II), Cr(III) and Pb(II) concentration on the adsorption capacity (time 48 h, adsorbent 0.021 g, volume 20 mL).

3.3.5. Adsorption isotherms

The interactive relationship between sorbent and sorbate, surface homogeneity/heterogeneity of the sorbent can be explained by sorption isotherms. Langmuir and Freundlich isotherm models are applied to infer Cu(II), Cr(III) and Pb(II) sorption data.

Langmuir isotherm model is expressed by the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b}$$

Where, C_e is the equilibrium concentration (mg/L), Q_m is the monolayer saturation adsorption capacity of the adsorbent (mg/g), Q_e the equilibrium adsorption capacity (mg/L) and b the Langmuir adsorption constant (L/mg).

The linear correlation between C_e/Q_e and C_e indicates that the Langmuir adsorption isotherm is obeyed by the adsorption of Cu(II), Cr(III) and Pb(II) (Fig.3.10(a)). From the intercept and slope of the straight line values of Q_m, b and R^2 are presented in table 3.10. It is observed that straight lines are obtained using Langmuir isotherm model, correlation coefficient of Langmuir isotherm model is close to unity, so it is predicted that the adsorption data fits well with the Langmuir isotherm model. Hence, the sorption of Cu(II), Cr(III) and Pb(II) with the sulfonated-GMA-PE adsorbent can be strongly explained by the Langmuir isotherm model. The highest sorption capacity of the adsorbent for Cu(II) is 117.64 mg/g, for Cr(III) is 151.51 mg/g and for Pb(II) is 140.84 mg/g.

The separation factor (R_L) which is called dimensionless constant is an essential factor for Langmuir isotherm model. It describes the sorption character as favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). From the Table 3.10 it is observed that R_L value for Cu(II) is (0.185~0.467), for Cr(III) is (0.009~0.316) and for Pb(II) is (0.123~0.434) which are less than unity, indicates that the Cu(II), Cr(III) and Pb(II) uptake capacity by sulfonated-GMA-PE adsorbent is a favourable process.

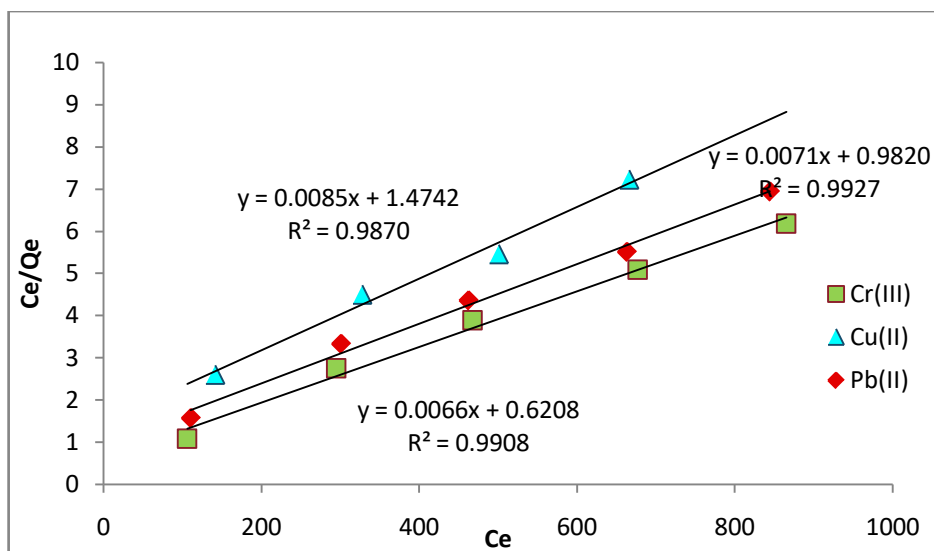


Fig.3.10(a). Langmuir isotherm model for Cu(II), Cr(III) and Pb(II) adsorption.

The Freundlich isotherm model is expressed by the following equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

Where C_e is the equilibrium concentration (mgL^{-1}), Q_e is the equilibrium sorption ability (mgg^{-1}), and n is an empirical parameter. The Freundlich isotherm model for Cu(II), Cr(III) and Pb(II) is shown in Fig.3.10(b). The K , n , and correspondence coefficients (R^2) values are given in Table 3.10.

Table 3.10: Langmuir and Freundlich isotherm parameters for Cu(II), Cr(III) and Pb(II) adsorption.

Langmuir isotherm parameters				Freundlich isotherm parameters		
Ions	Q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	$1/n$	R^2
Cu(II)	117.64	0.00576	0.9870	8.76	0.3673	0.9713
Cr(III)	151.51	0.01063	0.9908	29.20	0.2275	0.9956
Pb(II)	140.84	0.00723	0.9927	19.05	0.2791	0.9726

The data shown in the Table 3.10 indicates that there is a higher correlation coefficient of Langmuir isotherm model for Cu(II) and Pb(II), hence it is more appropriate for recitation of the sorption of Cu(II) and Pb(II) than Freundlich isotherm model. This indicates that the sorption follows monolayer mode rather than multilayer mode. Which can describe that on the surface of the adsorbent homogeneous functional sites are available. The value of correlation coefficient of Freundlich model is higher for Cr(III). So, adsorption of Cr(III) follows multilayer sorption and relatively heterogeneous. The value of $1/n$ is less than unity for the three ions which demonstrates that Freundlich

isotherm model is favorable for the adsorbent. From the data analysis of the two isotherm model it can be decided that Freundlich isotherm is more appropriate to explain the adsorption of Cr(III) on the sorbent, on the others Langmuir isotherm fitted best with the data of Cu(II) and Pb(II).

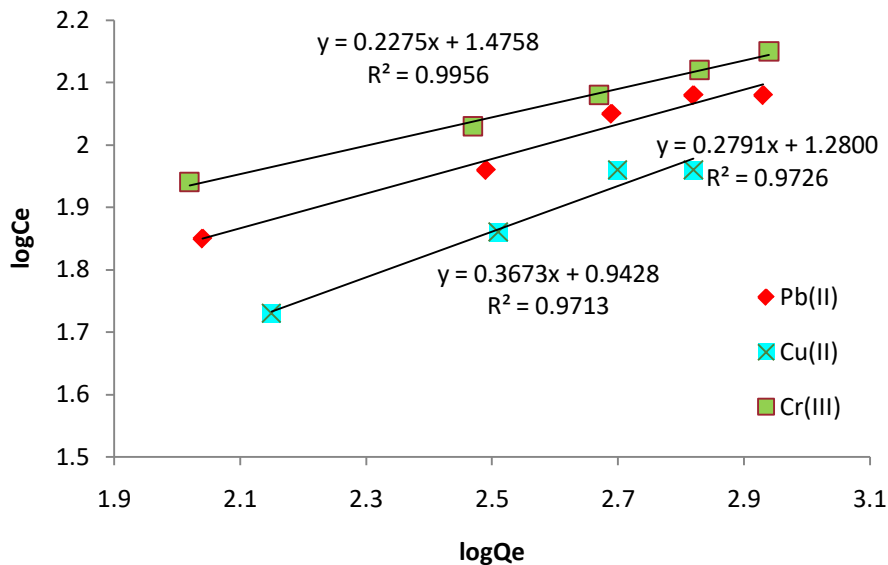


Fig. 3.10(b). Freundlich Isotherm model of Cu(II), Cr(III) and Pb(II) adsorption on sulfonated-GMA-g-PE adsorbent.

3.3.6. Effect of temperature

The influence of temperature on the sorption capacity at normal temperature (25°C), lower (9°C) and at higher temperature (60°C) was experienced (Fig. 3.11(a)). Classic Van't Hoff equation is,

$$\Delta G^\circ = -2.303RT \log K_0$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where, K_0 is the equilibrium constant at a definite temperature, and R is the molar gas constant. K_0 is defined as:

$$K_0 = Q_e / C_e$$

Where, Q_e = the amount of metal ions adsorbed by per unit mass of sorbent (mg/g)

and C_e = the equilibrium concentration of metal ions in solution.

Table 3.11: The adsorption capacity of Cu(II), Cr(III) and Pb(II) ion for different temperature at 6h.

Temperature(K)	Adsorption capacity(mg/g)		
	Cu(II)	Cr(III)	Pb(II)
282	50.23	10.0	57.26
298	65.56	47.42	71.2
333	85.31	99.5	115.11

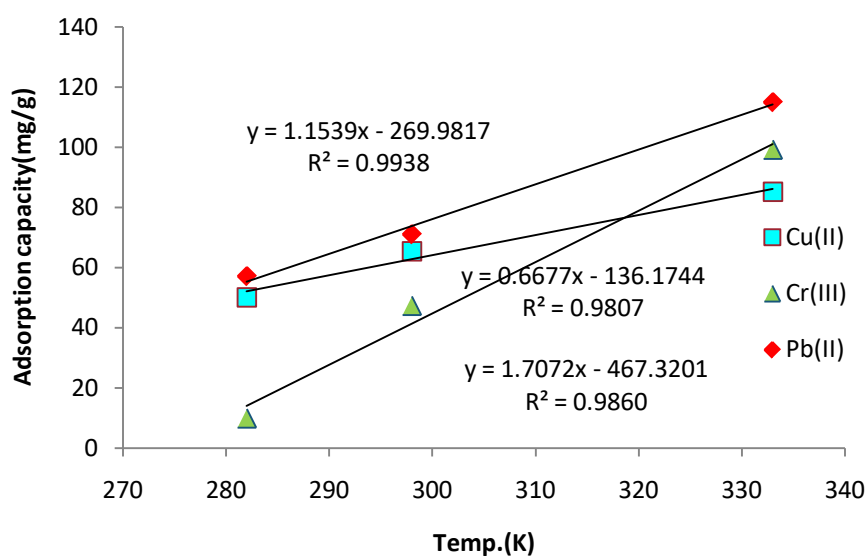


Fig.3.11(a). Adsorption capacity Vs T Curve.

The Gibbs free energy is related to the Enthalpy change (ΔH°) (i.e. heat of sorption) and Entropy change (ΔS°). From the equation:

$$\log K_0 = 2.303 \Delta S^\circ / R - 2.303 \Delta H^\circ / RT$$

$\log K$ was plotted against $1/T$ to determine ΔH° and ΔS° from the slope and intercept respectively (Fig.3.11(b)).

Table 3.12: Data for $\log C_e/Q_e$ Vs $1/T$ curve

1/T	$\log C_e/Q_e$		
	Cu(II)	Cr(III)	Pb(II)
0.0035	-1.65	-2.45	-0.97
0.0033	-1.04	-2.15	-0.87
0.003	-0.65	-1.86	-0.62

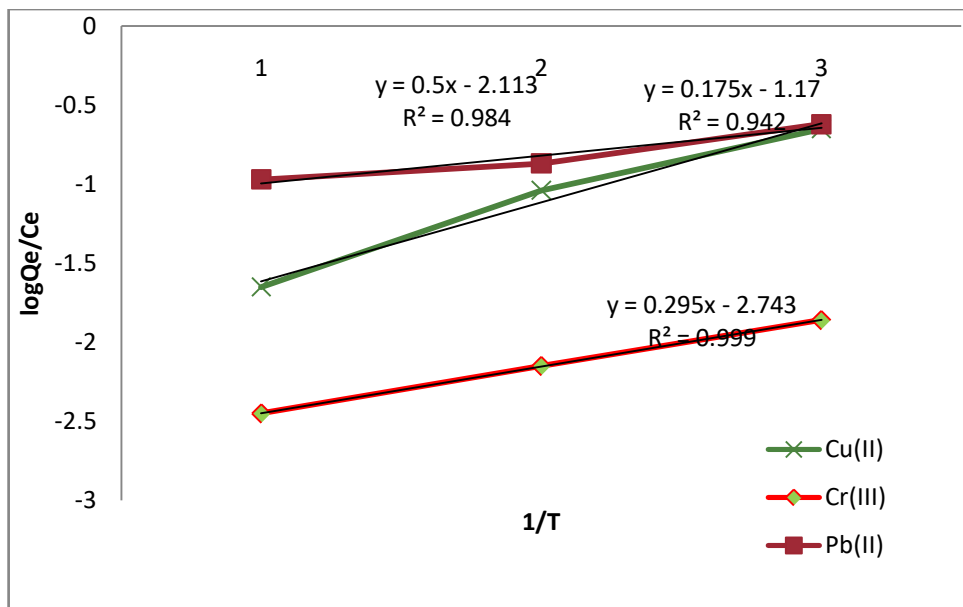


Fig.3.11(b). Plot log(Qe/Ce) vs 1/T

The value of ΔG of Cu(II), Cr(III) and Pb(II) are -5.93KJ/mol , -12.21KJ/mol and -4.96KJ/mol respectively, which are negative at 25°C and decreases with an increase of temperature. It proves that the sorption of heavy metals onto the sorbent is spontaneous and thermodynamically favorable.

3.4.Regeneration and Reusability

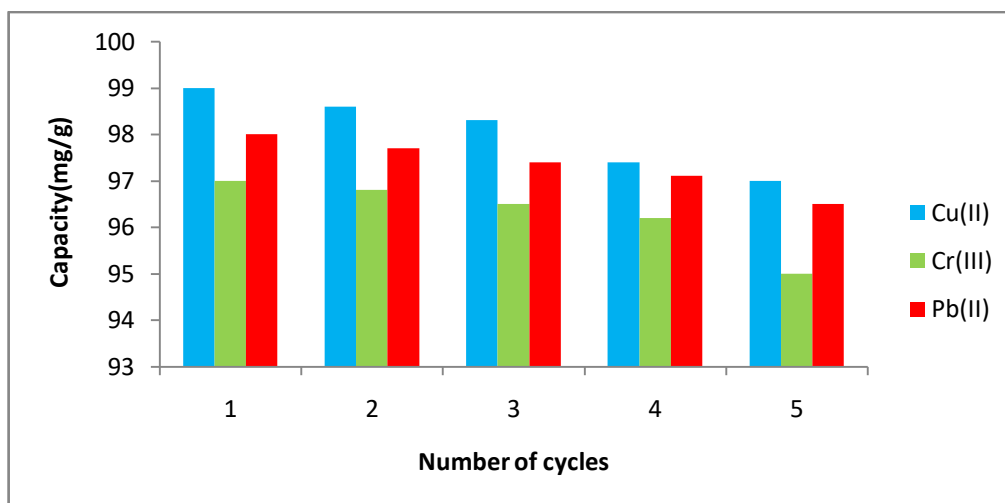


Fig.3.12. Adsorption capacity of sulfonated-GMA-g-PE adsorbent after regeneration (five consecutive cycles)

We have studied desorption and regeneration of the adsorbent film by 2M HNO_3 for 24h at room temperature. 99% desorption ratio was found for Cu(II), 97% for Cr(III) and

98% for Pb(II) uptake capacity of the sorbent in aqueous solutions is studied five consecutive cycles. There were no considerable changes of sorption efficiency for the repeated use of the sorbent. So, the sorbent can be returned to the initial state and can be reused after Cu(II), Cr(III) and Pb(II) adsorption.

3.5. Conclusions

Sulfonated-GMA-g-PE film were used to adsorb Cu(II), Cr(III) and Pb(II) from aqueous solutions. The sorbent were constructed by gamma radiation (pre-irradiation technique), grafting of glycidyl methacrylate (GMA) on non woven polyethylene fabric. At 30 kGy radiation dose, 5% monomer concentration, adding up of 0.5% Tween-20 as an additive, 4 h reaction time, utmost 343.31% of grafting occurred. The sorption performance showed excellent removal ability for heavy metals Cu(II), Cr(III) and Pb(II) ions. The experimental data fitted best with the Langmuir isotherm model for Cu(II) and Pb(II) than Freundlich model and the deliberate sorption capacity were 117.64 mg/g and 140.84 mg/g respectively. Data showed better fit with Freundlich isotherm for Cr(III). At 25°C value of ΔG is negative and the sorption process is spontaneous and thermodynamically favorable. It is concluded that the low cost and practically effectable Sulfonated-GMA-g-PE polymeric adsorbent exhibited a considerable potential in removing Cu(II), Cr(III) and Pb(II) from waste water.

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Removal of Uranium from aqueous solutions

4.1: Introduction

Efficient removal of uranium has created much public attention due to the growing demand of nuclear fuel and nuclear waste management[1]. Uses of uranium are increasing day by day due to establishment of nuclear based power plant worldwide. The radioactivity and huge amounts of uranium are discharged from this power plant into water and its radioactivity and toxicity poses severe environmental risks which makes the aquatic environment harmful for human and microorganism. It creates radiation pollution that are responsible for various diseases such as cancer, renal failure and damage of nervous system etc[2-4]. Besides, it creates additional challenges for wastewater management. So, treatment of radioactive elements is a hot topic and there is a great need to establish an efficient, cost effective technology for the removal of this radioactive elements from waste water[5-6].

There are different techniques such as adsorption[7-9], reverse osmosis[10], ion exchange[11-12], bioreduction and precipitation[13] for wastewater treatment. Among the techniques, adsorption are superior because of its low cost, high sorption capacity, simple to use and do not creating any secondary pollution. Now, radiation grafted polymers are used to remove uranium from waste water and sea water. Radiation grafted polymer adsorbent are selected for the sorption of uranium and other radioactive elements, because of its lower cost and reusability. A number of grafting techniques are arises such as ionizing radiation, chemical initiator, UV light, plasma treatment, oxidation of polymers etc. Among them radiation grafting is suitable, efficient and cost effective. Radiation grafting form uniform free radicals with monomer rapidly and uniformly. Grafted polymer has high surface area to bind the uranium from aqueous solution.

In the present study sulfonated-GMA-g-PE adsorbent was constructed by exposing gamma radiation to non woven PE and then the grafted film functionalized through sulfonation. There is a strong interaction between the negative charged sulfonated ions and the uranyl ions. For this reason sorption of uranium is relatively higher than many other adsorbents. The sorption of uranium in different conditions contact time, pH, temperature and starting metal ion concentration was studied. Regeneration and recycling of the sorbent has also been investigated in the present study.

4.2.1 Materials

Uranium nitrate($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)(Sigma Aldrich), Arsenazol(Merc, Germany) were used for the experiment.

4.2.2. Methods

4.2.2.1. Preparation of uranium Solution

A 500 ml volumetric flask was washed and dried. A definite weight of $\text{UO}_2(\text{NO}_3)_2$ measured in a digital balance and taken in the volumetric flask. Then, the flask was filled with distilled water up to the scratch. Thus, 500 ppm concentration of $[\text{UO}_2]^{2+}$ ion solution was ready. This prepared solution was kept at room temperature.

Solutions of various concentrations were prepared from the previously prepared 500 ppm uranium solution by the following formula.

Where, $V_1S_1 = V_2S_2$

S_2 = Concentration of ion solution to be prepared (like 100, 200, 300, 400 ppm or even lower concentration like 1, 2, 3, 4, 5 ppm)

V_2 = Volume of uranium solution to be prepared

$S_1 = 1000 \text{ ppm}$

V_1 = Volume of uranium ion solution to be taken from 500 ppm $[\text{UO}_2]^{2+}$ ion solution.

These prepared ion solutions were kept at room temperature prior to testing.

4.2.2.2. Preparation of colour complex of uranium.

To prepare color complex of uranium for measuring absorbance in UV spectrophotometer 4mL uranium solution, 0.5mL 1M HCl and 5mL 0.01% of arsenazol was taken in a 50mL volumetric flask and added distilled water up to the mark. Final color appears as violet. This color complex solution is used for determining absorbance of uranium.

4.2.2.2. Calibration Curve Preparation

Standard uranium solutions of 1ppm, 2ppm, 3ppm, 4ppm, 10ppm, were prepared from previously prepared 500 ppm uranium solution. The absorbance of each of the solutions was measured by UV-Visible Spectrophotometer at 652nm wavelength and a calibration curve for the standardization of unknown uranium solution was also prepared. The spectrophotometric measurement was performed within the concentration range between 0 and 10 ppm. Fig.4.1 shows calibration curve for uranium.

Table 4.1: Standardization of uranium absorbance at different concentrations

Concentration(ppm)	Absorbance
1	0.019
2	0.036
3	0.051
4	0.069
10	0.162

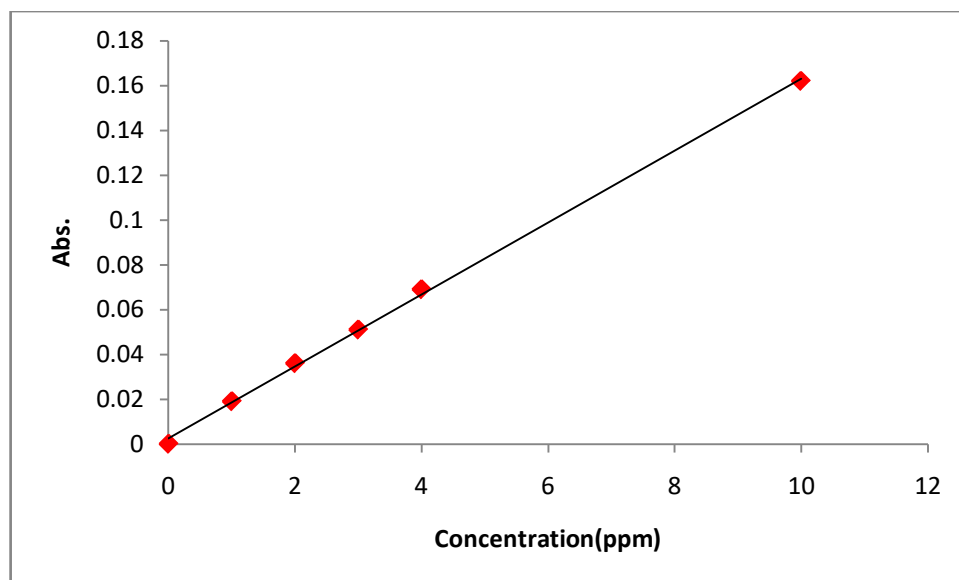


Fig.4.1. Calibration curve for Uranium adsorption.

4.2.2.3. Determination of uranium Adsorption

The constructed sulfonated-GMA-g-PE films were immersed into aqueous solutions of uranium at room temperature (25°C). Concentrations of aqueous uranium before and after sorption were determined by a UV spectro-photometer (wave length 652nm). The uranium sorption capability of the constructed fabric was investigated by the equation:

$$Q = (C_1 - C_2)V/W$$

4.2.2.4. Desorption of uranium

Uranium desorption from the sorbent fabric was determined by soaking in 2M aqueous HCl for 24 h. The desorption percentage was measured from the following equation;

$$\% \text{ desorption} = \{ \text{Ions desorbed (mg)} / \text{Ions adsorbed by the film (mg)} \} \times 100$$

4.3. Results and Discussions

4.3.1. Effect of contact time on adsorption

We studied consequence of contact time on the sorption amount of uranium up to 50 h at the starting uranium concentration 100ppm for sulfonated-GMA-g-PE films. From Figure 4.2, it can be accomplished that the starting uranium uptake rate is fast, then it slows down and gradually reaches to equilibrium at 48 h with the highest sorption of 72.2mg/g. Because of large starting concentration of uranium and large number of available active sites on sulfonated-GMA-g-PE adsorbent early fast uranium uptake rate is occurred. This first uranium uptake rate also indicates that most of the reactive adsorption sites are to be located in front of the surface of the sulfonated-GMA-g-PE sorbent particle and easily attracted by uranium.

Table 4.2: The adsorption capacity of uranium ion for different contact time 48h at 600ppm

Contact time(h)	Adsorption capacity(mg/g)
1	8.33
2	14.28
3	20.0
4	25.01
5	27.77
24	61.53
25	62.1
26	62.6
48	72.08
49	72.13
50	72.2

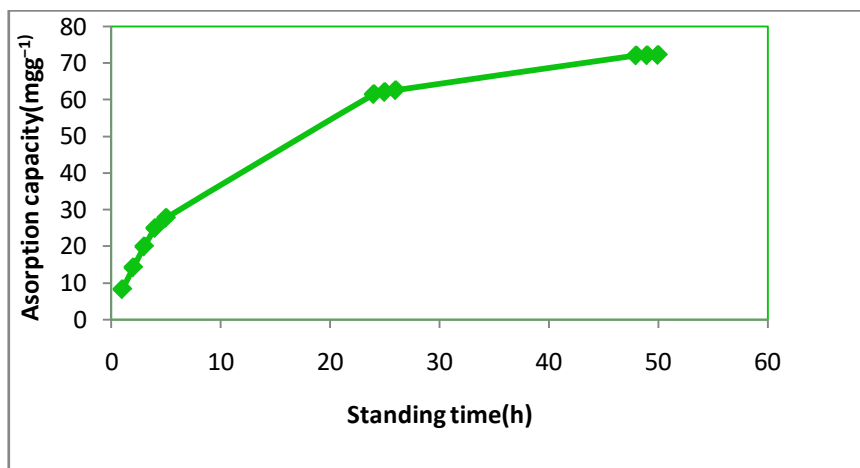


Figure 4.2.Effect of contact time on uranium adsorption by sulfonated-GMA-PE adsorbent(Conditions: Initial uranium concentration 100 mg/L; adsorbent 0.1052 g, volume 100 mL, pH 3.67).

4.3.2. Kinetic studies

To recognize the concise sorption performance of the uranium two familiar kinetic models were used to explore sorption.

Pseudo-first-order kinetic model is expressed as:

$$\log(Q_e - Q_t) = \log Q_e - k_1/2.303 t$$

The graph $\log(Q_e - Q_t)$ against t would give the value of $\log Q_e$ from intercept.

Pseudo-second-order kinetic model is expressed as:

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e$$

According to the pseudo-second order equation a plot of t/Q_t against t would give $1/Q_e$ from the slope. Pseudo-first order kinetic plots is presented in Figure 4.3(a) and pseudo-second-order kinetic plots is shown in Figure 4.3(b). Pseudo-first order and pseudo-second-order kinetic parameters are shown in Table 4.3.

Table 4.3. The pseudo-first-order and pseudo-second-order rate constants for uranium adsorption by sulfonated-GMA-g-PE adsorbent.

Q_e (exp.) (mg/g)	Pseudo-first-order rate constant			Pseudo-second-order rate constant		
	Q_e (theor.) (mg/g)	K_1 (h^{-1})	R^2	Q_e (theor.) (mg/g)	k_2 ($g\ h^{-1}\ mg^{-1}$)	R^2
72.2	47.42	0.030395	0.6950	71.43	0.02133	0.9800

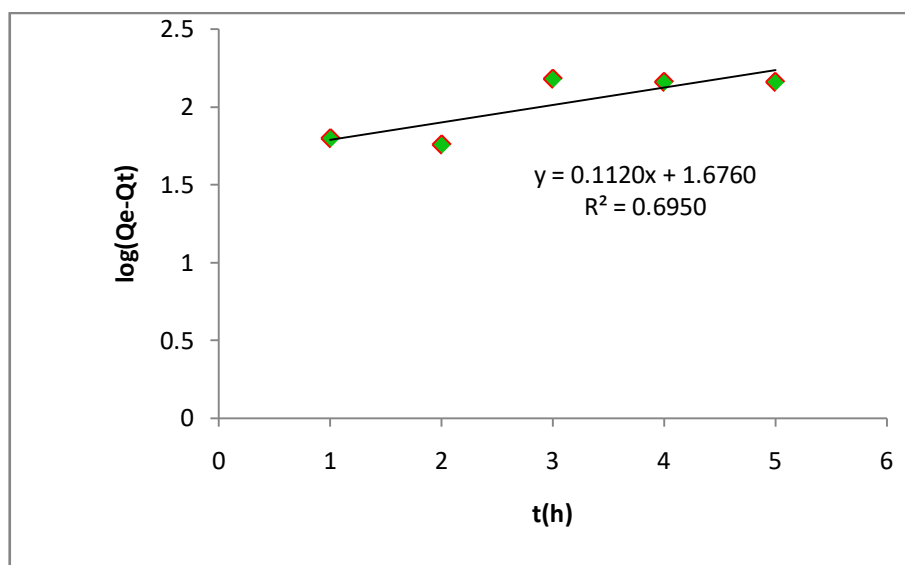


Fig. 4.3(a). Pseudo first-order plot for uranium adsorption.

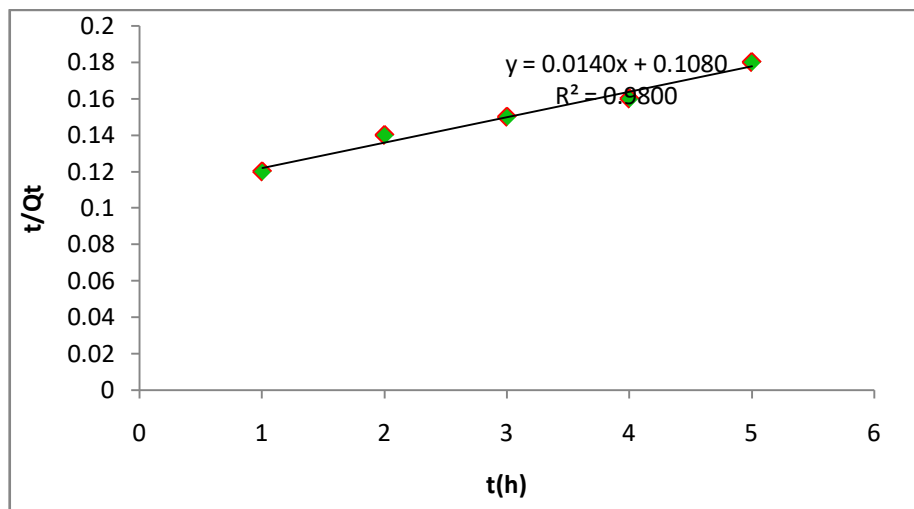


Fig. 4.3(b). Pseudo second-order plot for uranium adsorption.

Pseudo-second-order kinetic model gives better fitting of the experimental data of

uranium sorption on sulfonated-GMA-g-PE with respect to correlation coefficients R^2 (0.9800). Experimental value (72.2 mg/g) and the theoretical Q_e value designed from the pseudo-second-order kinetic model (Figure 4.3(b)) is (71.43mg/g) suits best with the investigated value (72.2 mg/g), whereas theoretical Q_e value (47.42 mg/g) calculated from the pseudo-first-order kinetic model (Fig.4.3(a)) is much less than experimental value (72.2 mg/g). This implies that uranium uptake ability of sulfonated-GMA-g-PE pursued pseudo-second-order rate process. From the point of view of the kinetics homogeneous and chemical sorption were occurred in case of uranium sorption.

It was seen that almost 38.46 % uranium adsorbed by the adsorbent within the first 5h with the starting concentration of 100mg/L. The sorption ability of the sorbent is rapid at the starting point(5h), then it slows down until it reaches steady value. This fact can be described as at the starting sorption stage large number of vacant sorption sites are accessible and later with drop of time, it is difficult to occupy rest of the vacant sites due to the repulsive force between uranium molecules on the solid and bulk phases.

4.2.3. Effect of pH on uranium adsorption

pH of sorption media plays an vital role for adsorption of uranium. Because of protonation and deprotonation of sulfonate ions, at diverse pH values the exterior arrangement of the sorbent could be altered and could subsist in disparate forms which can influence the sorption capacity. In figure 4.4, uranium adsorption consequence of pH at initial uranium concentration 100 ppm and contact time 48h is shown. We observed that the uranium uptake ability of the sorbent increases from pH range 2 to 3.67 and after pH 3.67 it decreases. At pH=3.67 maximum adsorption of uranium was observed. Due to more protonation of sulfonate ions, at low pH the sorption power of the sorbent is low. With the increases of pH adsorption of uranium increases, due to deprotonation (forming SO_3^- ions) of the modified sulfonated PE adsorbent which attracts the positively charged uranium ions. At higher pH (pH > 3.67) the sorption capacity of the sorbent decreases, as at higher pH positively charged uranium fascinated by OH^- ions and then it is less attracted by negatively charged sulfonate ions.

Table 4.4: The adsorption capacity of uranium for different pH at 48h.

pH	Adsorption capacity(mg/g)
2.0	50.44
3.0	63.31
3.67	71.98
4.32	66.76

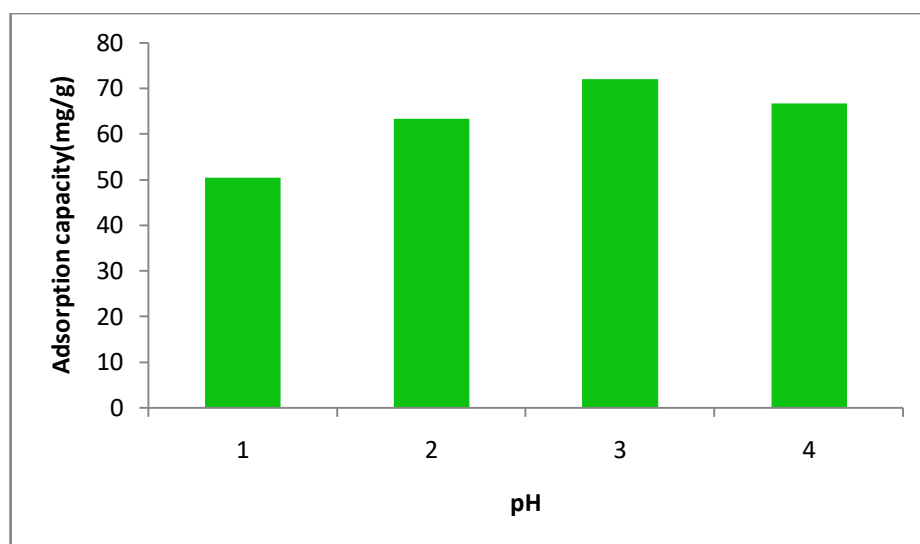


Figure 4.4.Effect of pH on adsorption (Initial uranium concentration of 100 ppm and contact time of 48h for uranium volume 20 mL).

4.2.4. Effect of initial uranium concentration on adsorption

The disparity of uranium uptake with the initial uranium concentration is shown in Figure 4.5. We have seen that with the raise of uranium concentration, the adsorption amount of uranium also raised. The reason behind this outcome is that as the concentration reaches higher value the chelation sites on the sorbent surface turn into saturated. For further sorption of uranium there remains no sites available when the chelating sites become unavailable.

Table 4.5: The adsorption capacity of uranium for different initial concentration at 48h.

Initial concentration(ppm)	Adsorption capacity(mg/g)
100	73.35
200	108.09
300	146.95
400	149.21

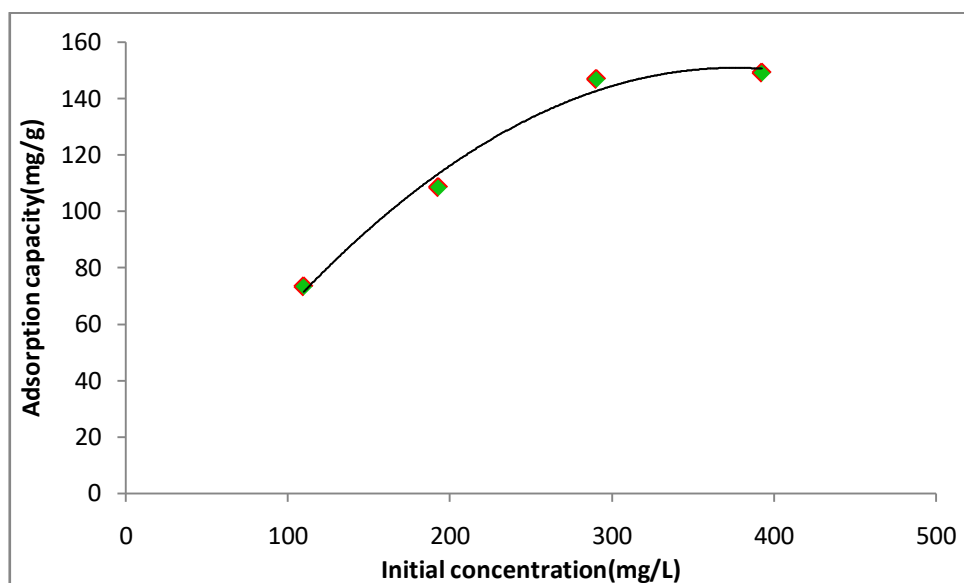


Figure 4.5.Effect of initial uranium concentration on the adsorption capacity (time 48 h, adsorbent 0.021 g, volume 20 mL, pH 3.67).

4.2.5. Adsorption isotherms

It was adopted the Langmuir and Freundlich isotherm models fitting the isotherm data and the related parameters are listed in Table 4.6. Langmuir model explain interactive relationship between adsorbent and adsorbate and also monolayer sorption process on a homogeneous surface. By the following equation the linear form of the Langmuir isotherm model is expressed:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b}$$

Investigational data plot in Langmuir model are presented in Figure 4.6(a) signifying that

fitting outcomes shows high linearity with correlation coefficient of 0.9941. It is also seen that the sorption of uranium is monolayer and homogeneous in nature. From the Langmuir isotherm model the highest sorption ability of the sorbent is 181.82 mg/g.

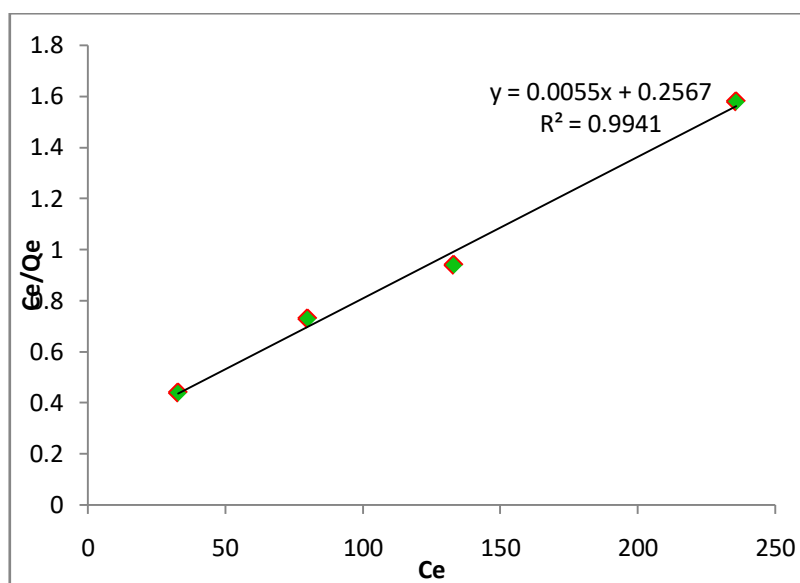


Fig 4.6(a). Langmuir isotherm model for uranium adsorption.

On contrary, the Freundlich isotherm model explain surface heterogeneity of sorption process and multilayer sorption. By the following equation the linearized form of Freundlich isotherm model is expressed as :

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

The plot of $\log Q_e$ vs $\log C_e$ shown in Figure 4.6(b). Figure 4.6(b) was drawn from the experimental data given in Figure 4.5. The K , n , and correlation coefficients (R^2) values are given in Table 4.6.

Table 4.6. Langmuir and Freundlich isotherm parameters for uranium.

Langmuir isotherm parameters			Freundlich isotherm parameters		
Q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	$1/n$	R^2
181.82	0.02029	0.9941	7.62	2.3765	0.9213

From the correlation coefficient(0.9213) of Freundlich isotherm model it can be predicted that this model fails to illustrate the investigational data for the sorption of uranium.

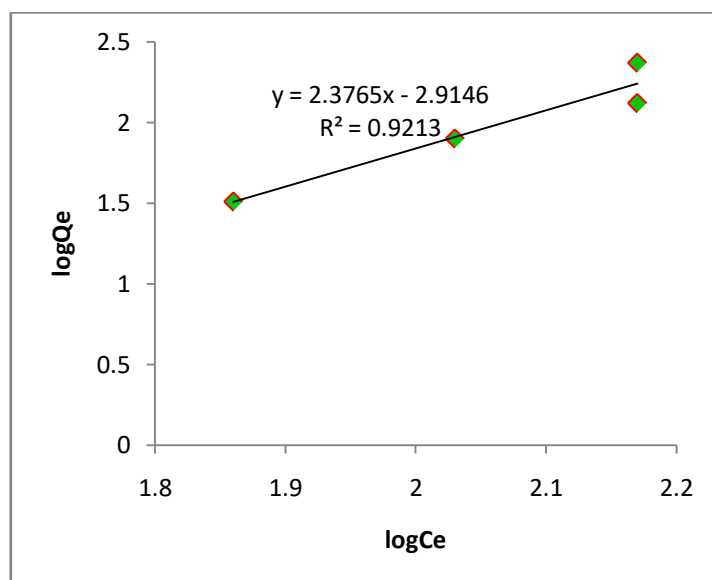


Figure 4.6(b). Freundlich Isotherm model of uranium adsorption on sulfonated-GMA-g-PE adsorbent.

The uranium uptake capacity of the sorbent obtained from Langmuir model was 181.82 mg/g.

4.2.6. Effect of temperature

The consequence of temperature on the sorption capacity at normal temperature (25°C), lower (9°C) and at higher temperature (60°C) was examined (Figure 4.7(a)). Classic Van't Hoff equation:

$$\Delta G^\circ = -2.303RT \log K_0$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where K_0 is the equilibrium constant at a certain temperature, and R is the molar gas constant. K_0 is defined as:

$$K_0 = Q_e / C_e$$

Table 4.7: The adsorption capacity of uranium for different temperature at 6h.

Temperature(K)	Adsorption capacity(mg/g)
282	50.27
298	72.88
333	110.2

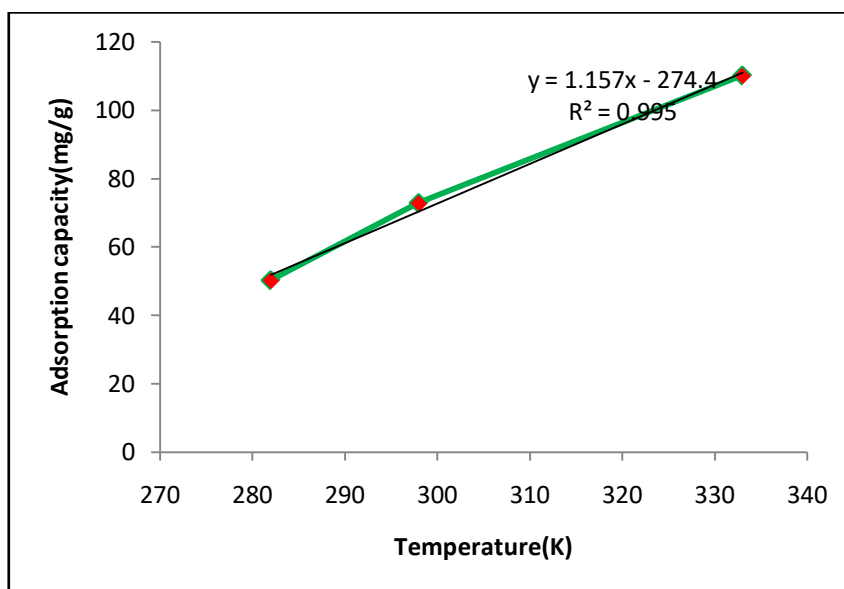


Figure.4.6(a): Adsorption capacity Vs T Curve.

The Enthalpy change ΔH° (i.e. heat of adsorption) and Entropy change ΔS° are related with the Gibbs free energy by the equation:

$$\log K_0 = 2.303 \Delta S^\circ / R - 2.303 \Delta H^\circ / RT$$

$\log K$ was plotted against $1/T$ to determine ΔH° and ΔS° from the slope and intercept respectively (Fig.4.6(b)).

Table 4.8: Data for $\log C_e/Q_e$ Vs $1/T$ curve.

$1/T$	$\log C_e/Q_e$
0.003	0.02
0.0033	-1.35
0.0035	-1.73

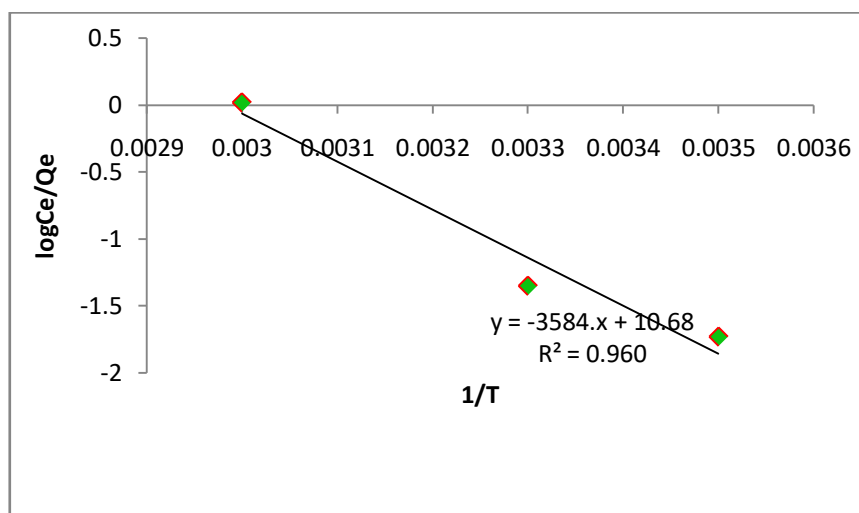


Fig.4.6(b). Plot $\log(Q_e/C_e)$ vs $1/T$

It observed that the sorption of uranium onto the sorbent is spontaneous and thermodynamically favorable.

4.3. Regeneration and Reusability

We have studied desorption and regeneration of the adsorbent film by 2M HCl for 24h at room temperature. 99% desorption ratio was found. Uranium uptake capacity of the sorbent in aqueous solutions is studied five consecutive cycles. There were no considerable changes of sorption efficiency for the repeated use of the sorbent. So, the sorbent can be returned to the initial state and reused after desorption.

4.4. Conclusions

Sulfonated-GMA-g-PE film were used to adsorb uranium from aqueous solutions. The sorbent were constructed by gamma radiation (pre-irradiation technique), grafting of glycidyl methacrylate (GMA) on non woven polyethylene fabric. The sorption performance showed excellent removal ability for uranium. The experimental data fitted best with the Langmuir isotherm model than Freundlich model and the deliberate sorption power were 181.82mg/g. At 25°C value of ΔG is -0.74KJ/mol and at higher temperature 60°C, it is -3.38KJ/mol indicates that the sorption process is spontaneous and thermodynamically favorable. It is accomplished that the low cost and practically effective Sulfonated-GMA-g-PE polymeric adsorbent exhibited a considerable potential in removing uranium from waste water.

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Removal of Cationic dyes from aqueous solutions

5.1. Introduction

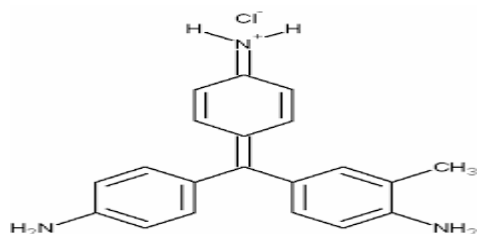
Undesirable amounts of waste water containing color effluents are released from printing cosmetics, food coloring, dyeing, textile and papermaking industries [1]. Worldwide 10,000 commercial dyes are available and approximately 7×10^5 tones different types of dyes are formed each year [2]. Annually 12% of dyes formed are released as effluents from dyeing, textiles and related industries [3]. Even in small amounts of dyes revealing into water bodies can have enormous repulsive consequence on the food web and aquatic life. It can create dermatitis and allergic reactions. Several of them are even carcinogenic for human beings and aquatic organisms [4]. Alzheimer's disease in human body is also created by dyes [5]. On the other hand, it is seen that most of dyes are resistant to biodegradation and photo degradation [6–8]. So, it is very important to treat dye containing wastewater. Up to present time, several types of wastewater treatment techniques such as coagulation and flocculation methods [9], electro-coagulation [10] membrane separation [11], oxidation or ozonation [12, 13] and adsorption have been employed to eliminate dyes. Among these techniques, it is seen that for eliminating dyes and other pollutants adsorption is an efficient, lower cost, moderately simple and potentially useful technique [14, 15]. Several types of adsorbents are developed that are used to eradicate dyes from waste water [16-23]. Due to comparatively lower adsorption capacity and secondary contamination of adsorbents many of them are not appropriate [24]. Uses of graft polymers has become new technique now. Elevated adsorption capacity and reusability of the adsorbent trim down the chance of creating secondary toxic waste. In case of grafting, monomers form covalent bonding to the polymer backbone. There are several advantages of polymer grafting. Grafted monomer can incorporate different functions with parent polymer but the mechanical property of the parent polymer is conserved [25,26]. It is seen that over other methods, radiation grafting are more suitable as it has high penetration power to the polymer backbone and it forms mostly homogeneous free radicals very fast [27].

In the present study, sulfonated-GMA-g PE adsorbent was made by radiation induced grafting of GMA on PE and later chemical treatment. The adsorbent can adsorb cationic dyes methylene blue, basic fuchsin and crystal violet as of aqueous solution. Dyes uptake capacity at dissimilar environment such as contact time, pH and starting dye concentration were identified. Kinetics and isotherm of dye adsorption were determined. Release of adsorbed dyes and more use of the adsorbent was also performed.

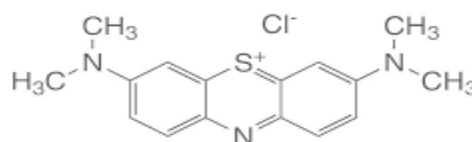
5.2. Experimental

5.2.1. Materials and reagents

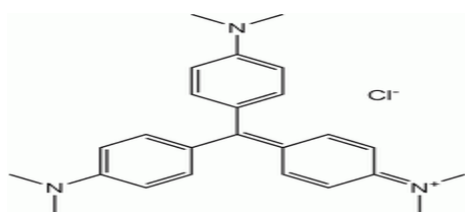
Basic Fuchsin(BF) (BDH England), Methylene Blue (MB) (Fluka, Switzerland) and Crystal Violet(CV) (Merck, Darmstadt, Germany) were used for the determination of dye uptake ability of the adsorbent.



a) Basic Fuchsin



b) Methylene Blue



c) Crystal Violet

Fig. 5.1. Structure of dyes a) Basic Fuchsin b) Methylene Blue and c) Crystal Violet

5.2.2. Construction of calibration curve

Calibration curve for BF, MB and CV is shown in Fig. 5.1, 5.2 and 5.3 respectively.

Table 5.1. Standardization of BF absorbance at different concentrations

Concentration(ppm)	Absorbance
2	0.104
5	0.294
8	0.464
11	0.688
14	0.831

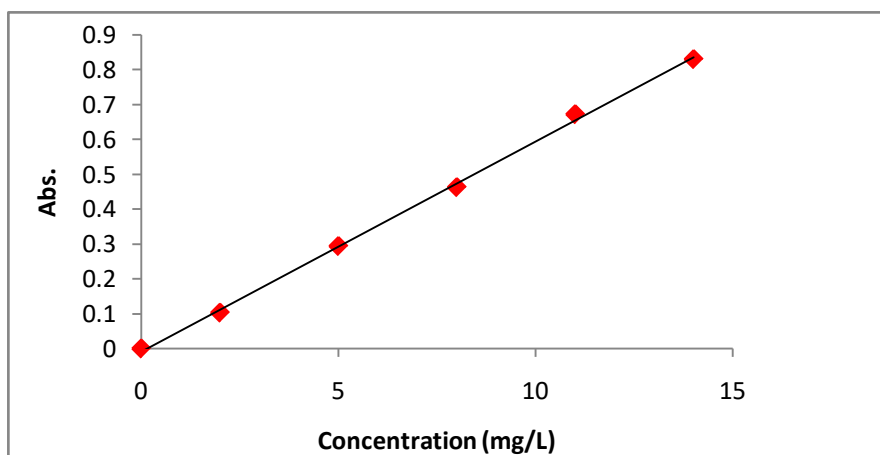


Fig.5.1. Calibration curve of BF

Table 5.2. Standardization of MB absorbance at different concentrations

Concentration(ppm)	Absorbance
1	0.206
2	0.391
3	0.572
4	0.746
5	0.935
6	1.122

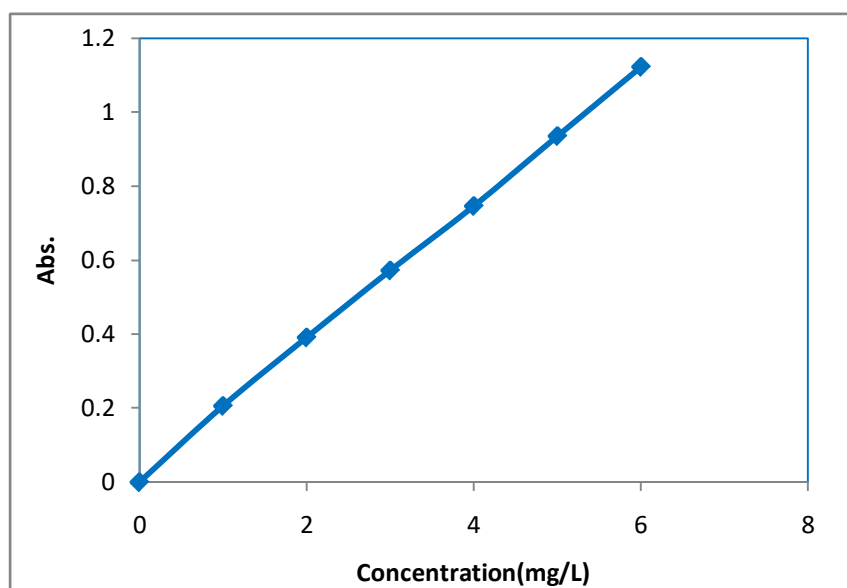


Fig.5.2. Calibration curve of MB

Table 5.3. Standardization of CV absorbance at different concentrations

Concentration(ppm)	Absorbance
1	0.373
5	1.117
10	2.102

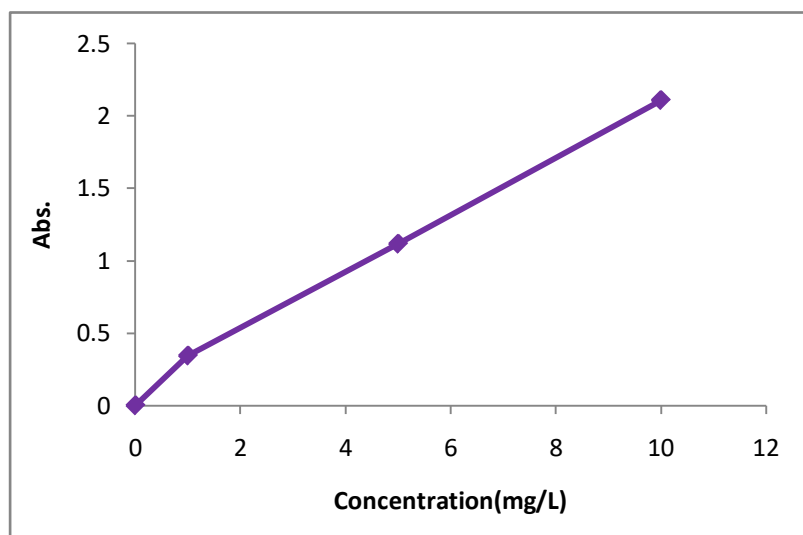


Fig.5.3. Calibration curve of CV

5.2.2. Determination of BF, MB and CV dye Adsorption

The constructed sulfonated-GMA-g-PE films were immersed into aqueous solutions of MB, BF and CV at room temperature (25°C). Aqueous BF, MB and CV solutions concentrations before and after sorption were determined by a UV spectro-photometer (wave length 545nm for BF, 663 nm for MB and 590.5nm for CV). The MB, BF and CV dye sorption ability of the constructed fabric was determined by means of the subsequent equation:

$$Q = (C_1 - C_2)V/W$$

5.2.3. Desorption of BF, MB and CV dyes

BF, MB and CV dye desorption from the sorbent fabric was determined by soaking in 2M aqueous HNO₃ for 24 h.

$$\% \text{ desorption} = \{ \text{Ions desorbed (mg)} / \text{Ions adsorbed by the film (mg)} \} \times 100$$

5.3. Result and discussions

5.3.1. Effect of adsorbent weight

The effect of sulfonated-GMA-g-PE adsorbent weight on adsorption capacity of MB is shown in figure 5.4. It was seen that the MB uptake ability of the sorbent decreases with rising of adsorbent weight at the same volume and starting concentration of the MB solution. It is due to the reduction of the external area of the reaction site in a unit weight.

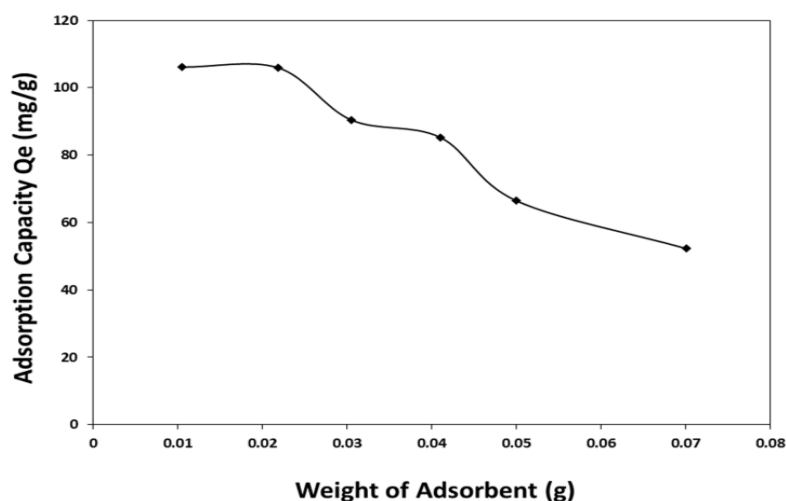


Fig.5.4. The effect of sulfonated-GMA-g-PE sorbent on sorption capacity of MB (conditions: Initial conc. 200ppm, pH 5.7, Volume 20 mL, Contact time 48h).

5.3.2. Effect of contact time on adsorption

The consequence of contact time on the sorption amount of BF, MB and CV upto 72 h at the starting dye concentration of 200ppm for BF and MB, 300ppm for CV on sulfonated-GMA-g-PE films were analysed. From Figure 5.5(a),(b),(c), it can be accomplished that the starting BF, MB and CV uptake rate is fast, then it slows down and gradually reaches to equilibrium at 48 h with the utmost sorption of 128.8mg/g for BF, 73.85 mg/g for MB and 132.2 mg/g for CV. Almost 85% for BF, 52% for MB and 23% for CV of the adsorption occurred within the first 5 hours. The early fast dye uptake rate is related to large initial concentration of dyes and large number of available active sites on sulfonated-GMA-g-PE adsorbent. This first dye uptake rate also indicates that most of the reactive adsorption sites are to be found in front of the surface of the sulfonated-

GMA-g-PE adsorbent particle and easily attracted by dyes BF, MB and CV.

Table 5.4. The adsorption capacity of BF, MB and Cv ion for different contact time 48h at 200ppm

Time(h)	Adsorption capacity(mg/g)		
	BF	MB	CV
1	87.32	23.5	9.88
2	90.53	44.42	13.7
3	94.45	55.1	18.85
4	95.01	64.1	23.19
5	96.1	67.35	29.99
24	120.57	70.2	50.13
25	120.94	71.56	55.37
26	121.51	72.7	61.92
48	128.62	75.82	132.1
49	128.75	75.83	132.12
50	128.8	75.85	132.23
72	128.82	75.86	132.25

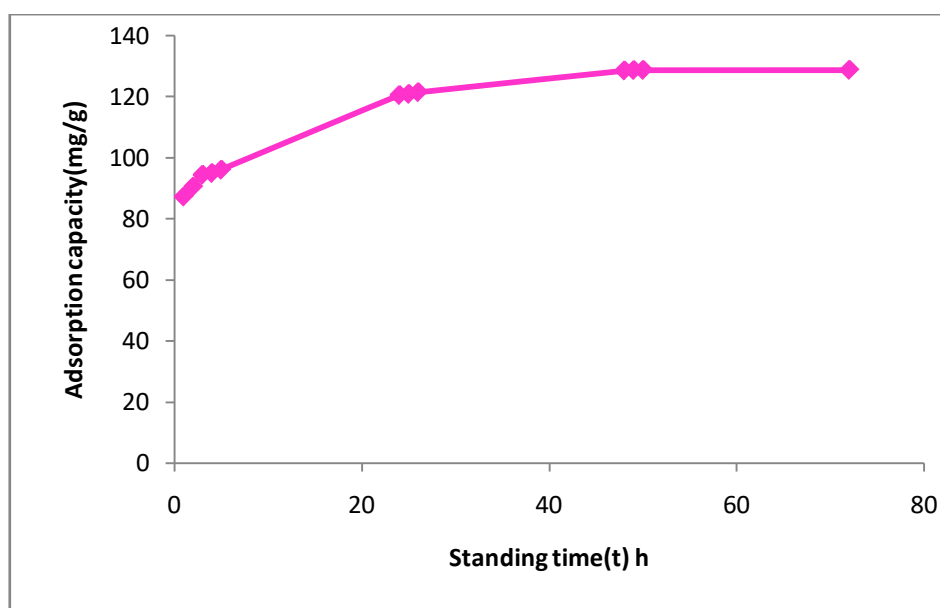


Fig.5.5(a).Effect of contact time on BF sorption by sulfonated-GMA-PE adsorbent(Conditions: Initial BF concentration 200 mg/L ;adsorbent 0.15 g, volume 150 mL).

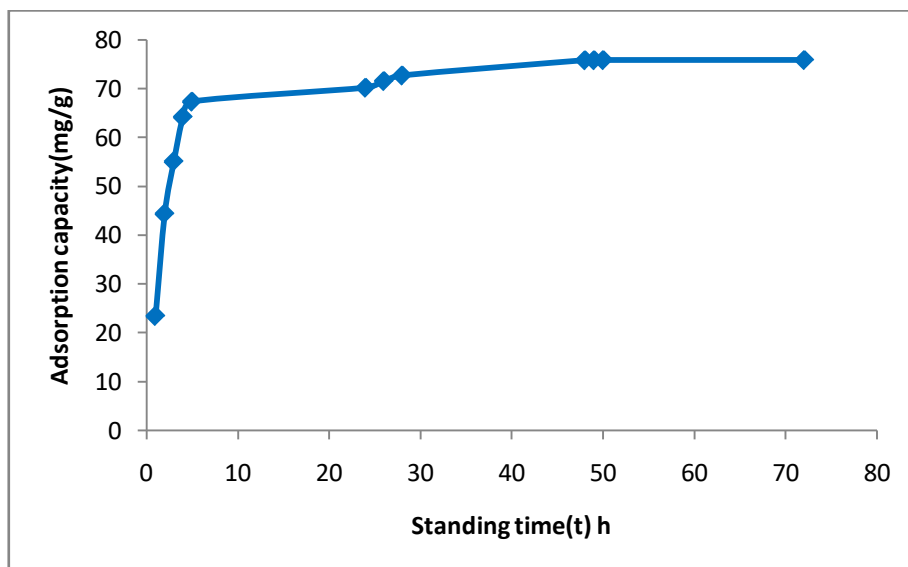


Fig.5.5(b). Effect of contact time on MB sorption by sulfonated-GMA-PE adsorbent(Conditions: Initial MB concentration 200 mg/L ;adsorbent 0.15 g, volume 150 mL).

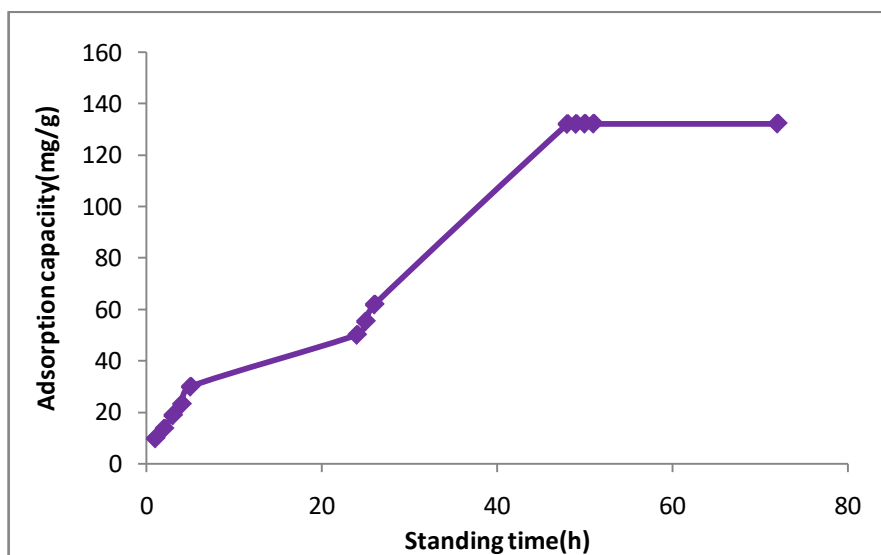


Fig.5.5(c).Effect of contact time on CV sorption by sulfonated-GMA-PE adsorbent(Conditions: Initial CV concentration 300 mg/L, ;adsorbent 0.15 g, volume 150 mL).

5.3.3. Kinetic studies

To recognize the concise sorption performance of the dyes two familiar kinetic models were used to explore sorption.

Pseudo-first-order kinetic model is expressed as:

$$\log(Q_e - Q_t) = \log Q_e - k_1/2.303 t$$

The graph $\log(Q_e - Q_t)$ against t would give the value of $\log Q_e$ from intercept.

By the following equation pseudo-second-order kinetic model is expressed:

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e$$

According to the pseudo-second order equation a plot of t/Q_t against t would give $1/Q_e$ from the slope. Pseudo-first order kinetic plots is represented in Figure 5.6(a) and pseudo-second-order kinetic plots is given in Fig. 5.6(b). Pseudo-first order and pseudo-second-order kinetic parameters are shown in Table 5.6.

Table 5. 6. The pseudo-first-order and pseudo-second-order rate constants for BF, MB and CV adsorption by sulfonated-GMA-g-PE adsorbent.

Ions Q _e (cal.)(mg/g)	Pseudo-first-order rate constant			Pseudo-second-order rate constant		
	Q _e (theor.)(mg/g)	K ₁ (h ⁻¹)	R ²	Q _e (theor.) (mg/g)	k ₂ (g h ⁻¹ mg ⁻¹)	R ²
BF 126.2	48.31	0.16121	0.9953	126.58	0.0096598	0.9957
MB 73.85	69.66	0.27866	0.9779	83.33	.0020570	0.9474
CV 130.9	128.53	0,04375	0.9691	58.82	0.0006016	0.8305

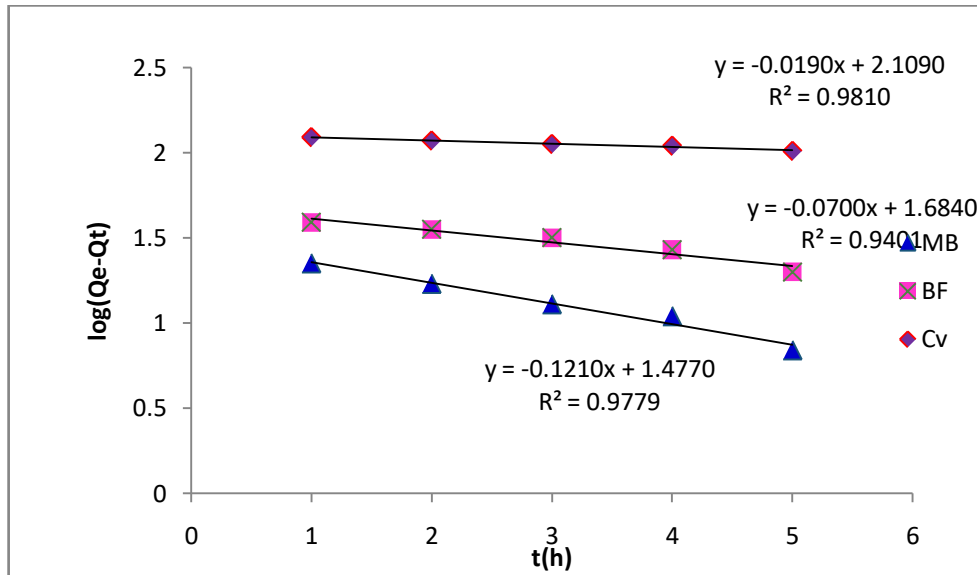


Figure 5.6(a). Pseudo first-order plot for MB adsorption.

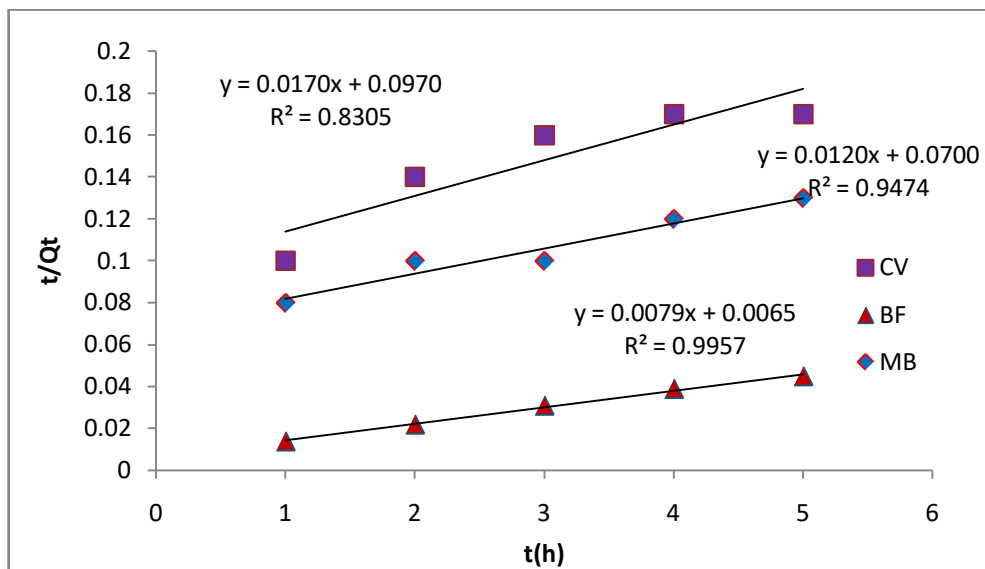


Figure 5.6(b). Pseudo second-order plot for MB adsorption

With respect to correlation coefficients R^2 the pseudo-second-order kinetic model gives a better fitting of the investigational data for BF and pseudo-first order kinetic model gives good fit for MB and CV and the calculated Q_e values ($Q_{e,cal}$) are close to the investigational values ($Q_{e,exp}$). This implies that BF uptake capacity of sulfonated-GMA-g-PE pursued pseudo-second-order rate process and the sorption process might have occurred by chemical adsorptions and pseudo-first-order rate process follows sorption for MB and CV that occurred by both physical and chemical sorptions.

5.3.4. Effect of pH on dye adsorption

There is great impact of pH of the medium on sorption ability of the grafted sorbent. At unlike pH values, because of protonation and deprotonation of sulfonate ions, the surface arrangement of the sorbent could be altered and could exist in dissimilar forms which can affect the sorption capacity. The effect of pH on BF, MB and CV adsorption at initial dye concentration 200 ppm is shown in figure 5.7(a),(b),(c). It was seen that the BF, MB and CV dye uptake of the adsorbent increases from pH range 1 to 7. At pH=7 utmost sorption of BF, MB and CV was pragmatic. At low pH the sorption power of the adsorbent is low, because of more protonation of sulfonate ions. With the increases of pH adsorption of BF, MB and CV increases, because of the deprotonation (forming SO_3^- ions).

Table 5.7: Data for the adsorption capacity of BF for different pH at 48h.

pH	Adsorption capacity(mg/g)
2.0	83.35
3.0	85.76
4.0	88.13
4.92	92.59
5.4	90.08

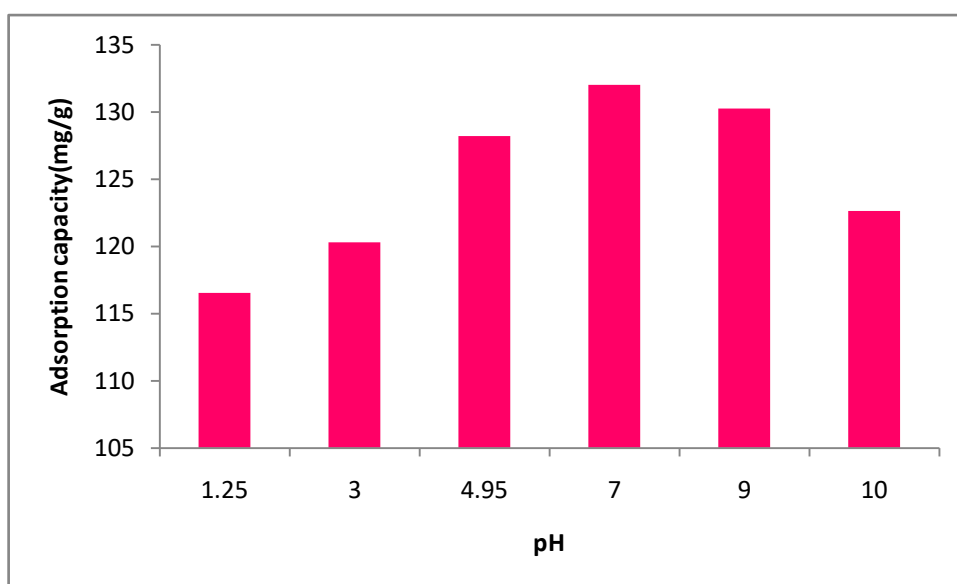


Figure 5.7(a). Effect of pH on BF dye sorption (Initial BF concentration of 200 ppm and

contact time of 48 h for BF each volume 20 mL).

Table 5.8. The adsorption capacity of MB for different pH at 48h.

pH	Adsorption capacity(mg/g)
2	28.21
4	38.12
6	39.02
7	62.67
8	39.96
10	32.34

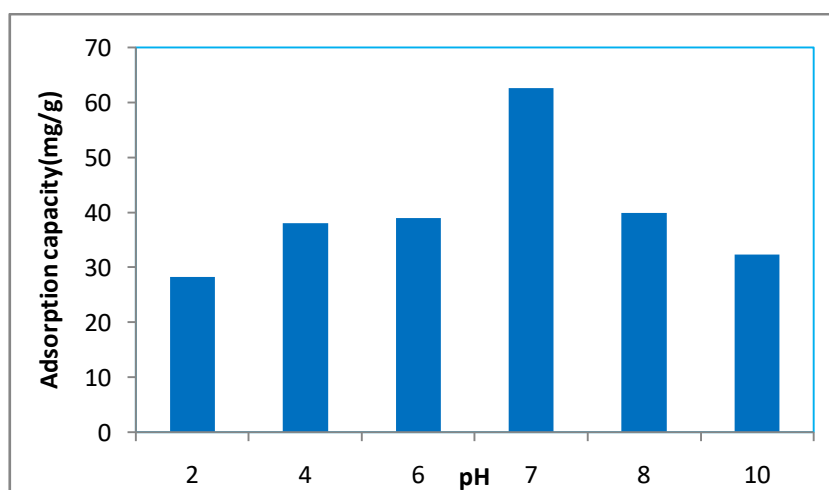


Figure 5.7(b). Effect of pH on MB dye sorption (Initial MB concentration of 200 ppm and contact time of 24 h , each volume 20 mL).

Table 5.9.: The adsorption capacity of CV ion for different pH at 48h.

pH	Adsorption capacity(mg/g)
2.1	68.23
3.3	79.45
5.63	93.88
7.2	116.39
8.42	100.91
10.03	73.44

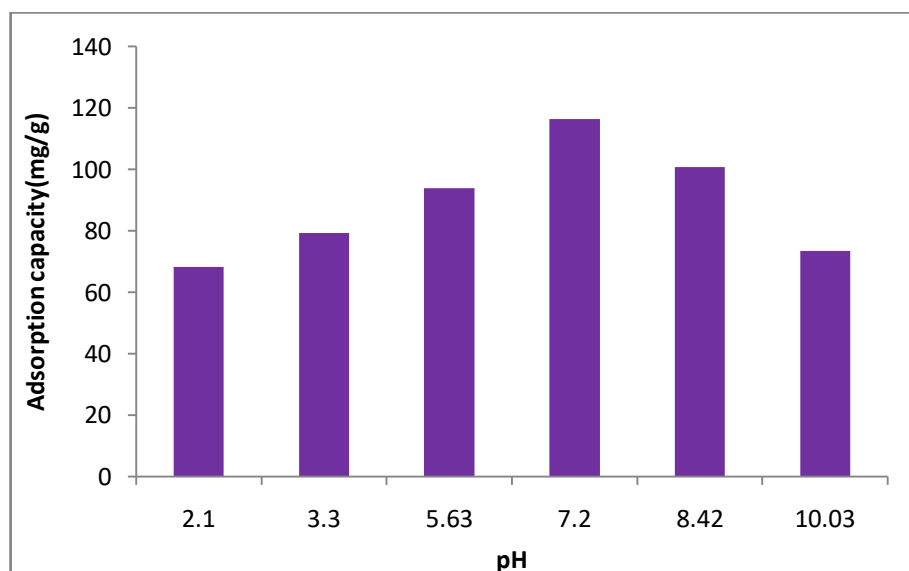


Figure 5.7(c). Effect of pH on CV dye sorption (Initial CV concentration of 300 ppm and contact time of 48 h , each volume 20 mL).

5.3.5. Effect of initial BF, MB and CV dye concentration on adsorption

Figure 5.8 shows the variation of BF, MB and CV dye uptake with the initial dye concentration. It can be illustrated that with the raise of dye concentration, the adsorption amount of dyes BF, MB and CV also raised. The reason behind this outcome is that the sites of chelation on the sorbent surface become saturated while the concentration reaches higher value. When the chelating sites become occupied there remains no sites unoccupied for further sorption of dye.

Table 5.10: The adsorption capacity of BF, MB and CV dye for different initial concentrations at 48h.

Initial concentration(ppm)	Adsorption capacity(mg/g)		
	BF	MB	CV
200	71.6	53.3	62.65
400	126.2	98.98	93.47
600	167.87	134.471	130.9
800	199.16	153.53	153.47
1000	221.67	194.77	173.16

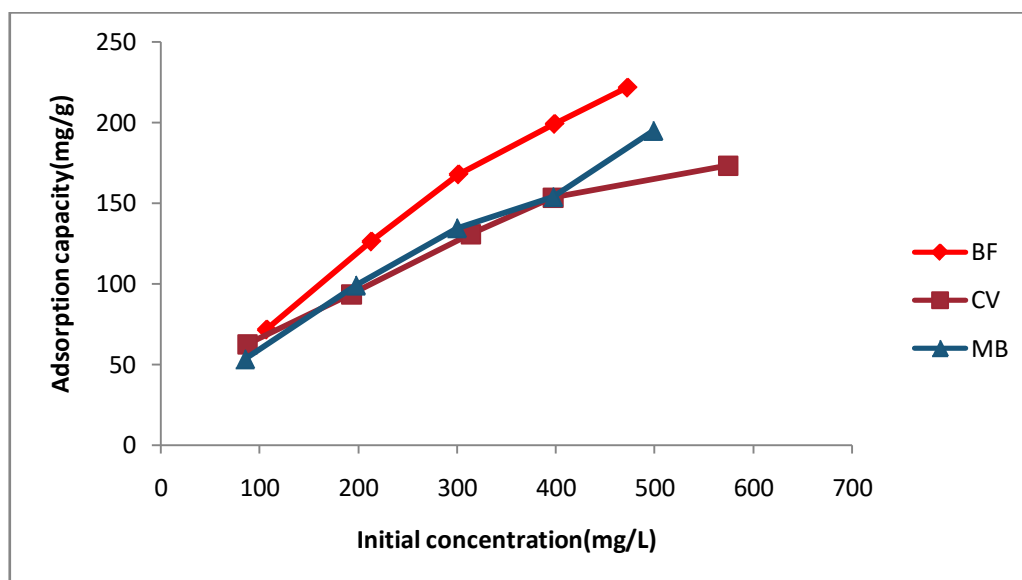


Fig.5.8.Effect of initial BF, MB and CV concentration on the adsorption capacity (time 48 h, adsorbent 0.022 g, volume 20 mL).

5.3.6. Adsorption isotherms

The interactive relationship between sorbent and sorbate, surface homogeneity/heterogeneity of the sorbent could be explained by sorption isotherms. Langmuir and Freundlich isotherm models are applied to infer dye BF, MB and CV sorption data.

Langmuir isotherm model is expressed by the subsequent equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b}$$

Figure 5.9(a) shows the plot of C_e/Q_e Vs C_e drawn from the investigational data shown in Figure 5.8. The correlation between C_e/Q_e and C_e is linear and it indicates that the Langmuir sorption isotherm is obeyed by the sorption characteristics. The measured values of Q_m , b and R^2 obtained from the intercept and slope of the straight line are shown in table 5.11. From the straight line of the Langmuir isotherm model it is predicted that the sorption data suits the Langmuir isotherm model as its correlation coefficient is close to unity. Overall, the Langmuir isotherm model can explain the sorption of BF, MB and CV dye by the sulfonated-GMA-PE adsorbent. The maximum BF, MB and CV sorption capability of the sorbent is 357.14 mg/g, 344.82 mg/g and 208.33 mg/g, respectively.

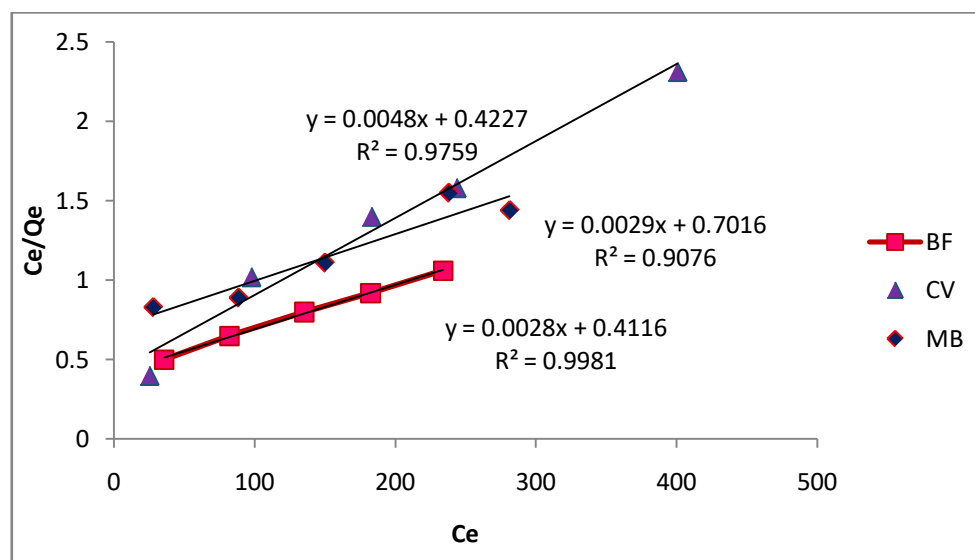


Fig.5.9(a). Langmuir isotherm model for BF, MB and CV adsorption.

The Freundlich isotherm model is expressed by the following equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

The plot of $\log Q_e$ versus $\log C_e$ shown in Figure 5.9(b). Figure 5.9(b) was drawn from the investigational data given in Figure 5.8. The K , n , and correlation coefficients (R^2) values are given in Table 5.11.

Table 5.11. Langmuir and Freundlich isotherm parameters for BF, MB and CV dye adsorption.

Ions	Langmuir isotherm parameters			Freundlich isotherm parameters		
	Q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	$1/n$	R^2
BF	357.14	0.00680	0.9981	427.56	-0.1710	0.9394
MB	344.12	0.00414	0.9076	9.21	0.5297	0.9884
CV	208.33	0.01135	0.9759	17.95	0.3815	0.9852

The data shown in the Table 5.11 indicates that in case of MB and CV there is a higher correlation coefficient (R^2 , 0.9884 for MB and 0.9852 for CV) for Freundlich model. Hence it is more appropriate for recitation of the sorption of MB and CV than Langmuir isotherm model. This indicates that the sorption follows multilayer mode rather than

monolayer mode. It describes that on the surface of the sorbent heterogeneous functional sites are shown. The value of $1/n$ is less than unity (0.5297 for MB and 0.3815 for CV) which demonstrates that Freundlich isotherm model is favorable for the sorbent. Hence, it can be decided that Freundlich isotherm is more suitable to explain the sorption of MB and CV dyes on the sorbent. Freundlich model fails to describe the experimental data of BF, that indicates the homogeneous sorption of BF onto the sulfonated-GMA-g-PE adsorbent.

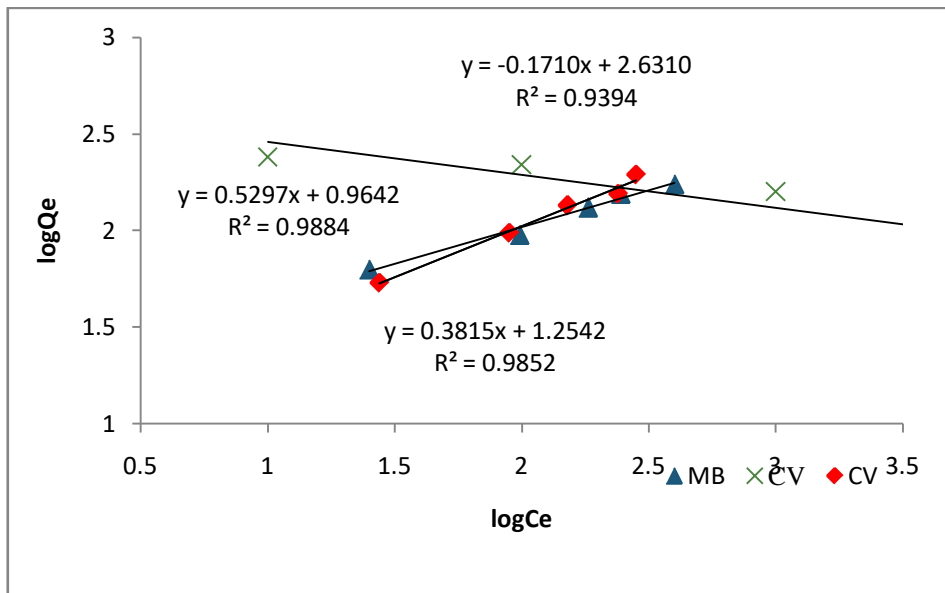


Figure 5.9(b). Freundlich Isotherm model of BF, MB and CV adsorption on sulfonated-GMA-g-PE adsorbent.

The BF, MB and CV sorption ability of the adsorbent obtained from Langmuir model was 357.14 mg/g, 344.12mg/g and 208.33mg/g, respectively.

5.3.7. Effect of temperature

The consequence temperature on the adsorption capacity at normal temperature (25°C), lower (9°C) and at higher temperature (60°C) was examined (Fig. 5.10(a)). The Gibbs free energy change (ΔG°) of the sorption progression can be determined as of classic Van't Hoff equation:

$$\Delta G^\circ = -RT \log K_0$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Where, K_0 is the equilibrium constant at a certain temperature, and R is the molar gas constant. K_0 is defined as:

$$K_0 = Q_e / C_e$$

Table 5.12: The adsorption capacity of BF, MB and CV dye for different temperature at 6h.

Temperature(K)	Adsorption capacity(mg/g)		
	BF	MB	CV
282	90.42	78.91	26.43
298	97.04	91.05	41.65
333	128.78	109.42	75.56

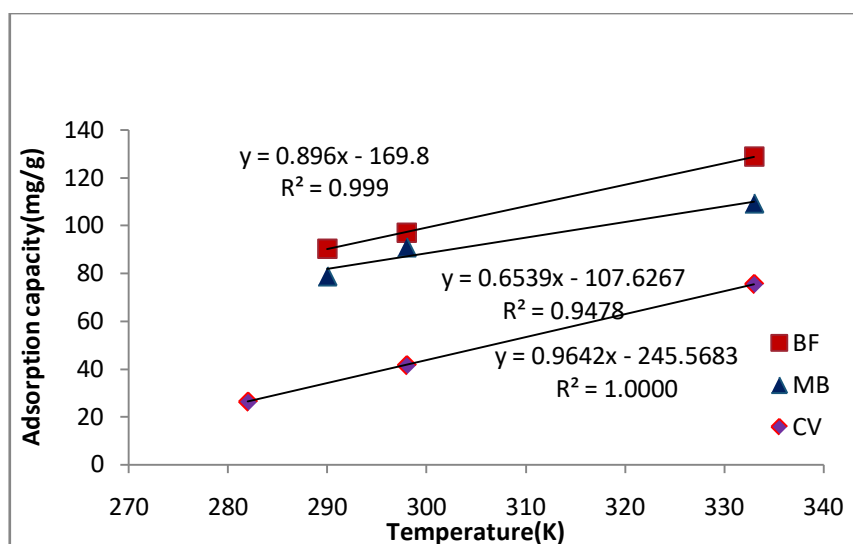


Figure.5.10(a):Adsorption capacity Vs T Curve.

The Gibbs free energy are associated with the Enthalpy change (ΔH°) (i.e. heat of sorption) and Entropy change (ΔS°) by the equation:

$$\log K_0 = \Delta S^\circ / R - \Delta H^\circ / RT$$

$\log K$ was plotted against $1/T$ to determine ΔH° and ΔS° from the slope and intercept, respectively (Fig.5.10(b))

Table 5.13: Data for $\log C_e/Q_e$ Vs $1/T$ curve for BF, MB and CV dye.

1/T	$\log C_e/Q_e$		
	BF	MB	CV
0.0035	0.06	-0.017	-0.069
0.0033	0.14	-0.062	-0.049
0.003	0.5	0.017	0.012

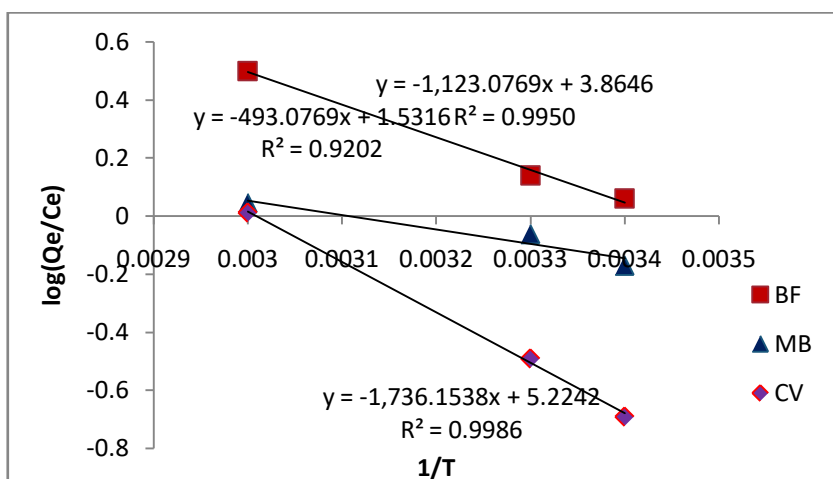


Fig.5.10(b): Plot Log(Qe/Ce) vs 1/T

The value of ΔG (-0.741KJ/mol) are negative for BF at 25°C, and decreases with the raise of temperature. This shows that at higher temperature enhanced sorption is produced. ΔS° is used to illustrate the randomness throughout sorption process, the positive value of ΔS° (73.99J/mol) shows the attraction of the sorbent for particular BF and confirms the increased randomness at the solid–solution edge throughout the sorption. The value of ΔH (21.5J/mol) is positive which indicates the sorption of BF by the sorbent is endothermic and it can predict that with increase of the temperature sorption of sorbent increases. The value of ΔG is positive for MB and CV(0.353KJ/mol for MB and 2.79KJ/mol for CV) at 25°C, but at higher temperature it is negative(-0.28KJ/mol for MB and -0.068KJ/mol for CV) and the adsorption increase.

Proposed adsorption Mechanism for dye Adsorption: The following suggested Mechanism for dye adsorption is shown in figure 5.11.

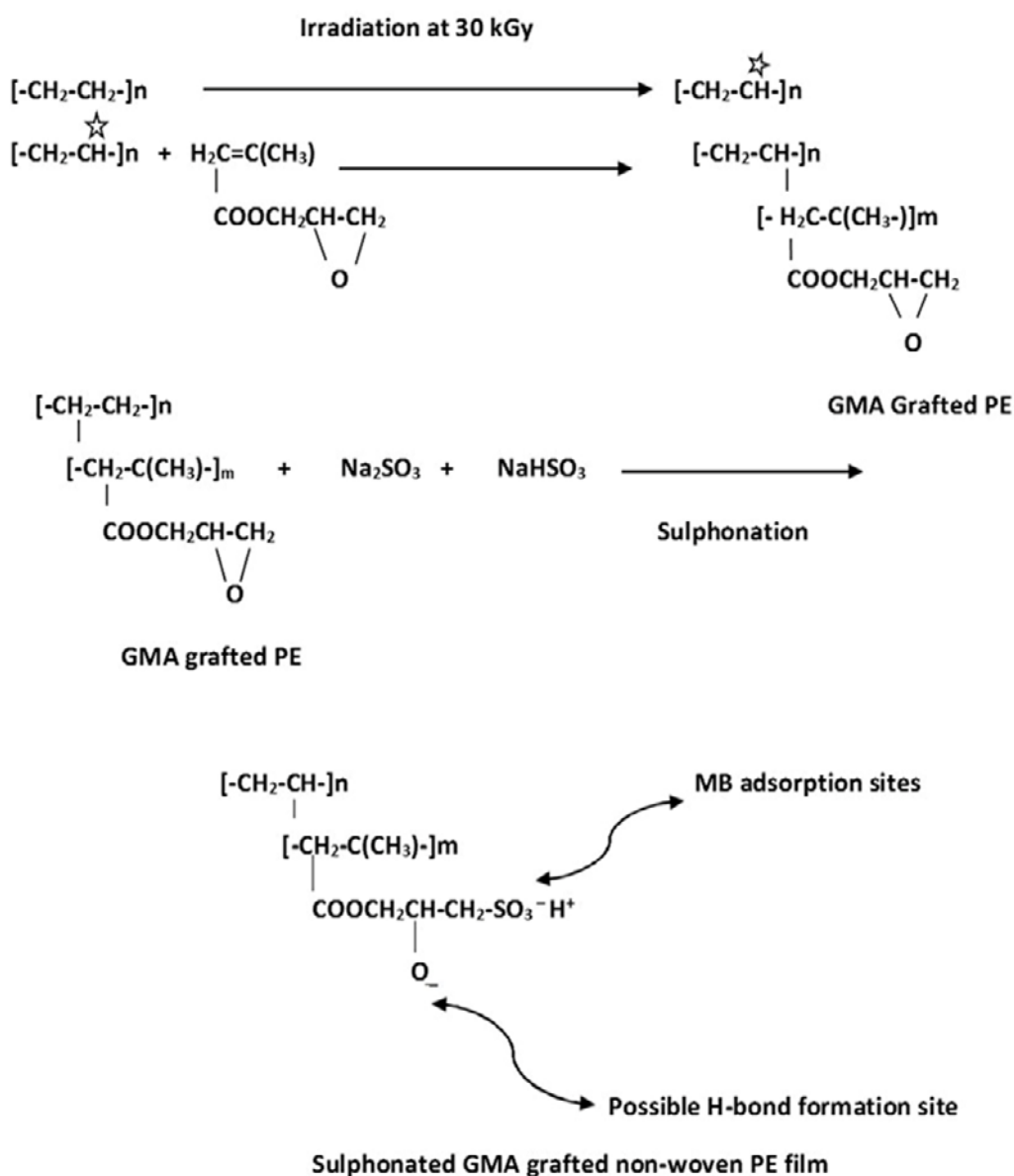


Figure 5.11. Suggested mechanism for dye adsorption

5.4. Regeneration and Reusability

We have studied desorption and regeneration of the adsorbent film by 2M HNO₃ for 24h at room temperature. Desorption ratio was found 99%, 95% and 94% for BF, MB and CV, respectively. BF, MB and CV uptake capacity of the sorbent in aqueous solutions was studied in five consecutive cycles. There were no considerable changes of sorption

efficiency for the repeated use of the sorbent. So, the sorbent can be returned to the initial state and reused after BF, MB and CV dye adsorption.

5.5. Conclusions

Sulfonated-GMA-g-PE film were used to adsorb basic fuchsin (BF), methylene blue(MB) and crystal violet(CV) dye from waste water. The sorbent were constructed by gamma radiation(pre-irradiation technique), grafting of glycidyl methacrylate(GMA) on non woven polyethylene fabric. At 30 kGy radiation dose, 5% monomer concentration,adding up of 0.5% Tween-20 as an additive, 4 h reaction time, utmost 343.31% of grafting was occurred. The sorption performance showed excellent removal ability for cationic dyes BF, MB and CV. The experimental data fitted best with the Langmuir isotherm model for BF than Freundlich model.The sorption ability of BF, MB and CV are 357.14 mg/g, 344. 82 mg/g and 208.33 mg/g respectively.On the others MB and CV dye follows Fruendlich isotherm model than Langmuir isotherm model. At 25 °C value of ΔG is -0.74KJ/mol, 0.353KJ/mol and 2.795KJ/mol for BF, MB and CV respectively and at higher temperature 60°C, it is -3.38KJ/mol, -0.28KJ/mol and -0.068KJ/mol that indicates the sorption process is spontaneous and thermodynamically favorable. It is concluded that the low cost and practically effectiveSulfonated-GMA-g-PE polymeric adsorbent exhibited a considerable potential in removing cationic dyes BF, MB and CV from waste water.

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Application of the constructed sulfonated-GMA-g-PE for Proton Exchange Fuel Cell Membrane.

6.1 Introduction

Recently, radiation grafted sulfonic acid functionalized membranes have created much attention as attractive and alternative Proton Exchange Membrane for Fuel Cells (PEMFCs) [1]. This substitution of energy producing sector can reduce utilization of fossil fuel and also shrink carbon dioxide emission [2]. Due to the rapid increase of population, demand for energy also increases. To fulfill this demand of energy researcher are searching efficient and low cost alternating fuel cell membranes. Polymer electrolytic membranes used in fuel cell are environmentally friendly and it significantly influence the performance of fuel cell. Now, Nafion is widely used in fuel cell due to high mechanical and electrical stability and proton conductivity [3-5], but it is highly expensive, proton conductivity drops above 100° C and relatively low ion exchange capacity (IEC is 0.9 meqg⁻¹) [6-9]. For this reason alternative development of PEMs in fuel cell is necessary.

Radiation grafted polymer membrane are selected for fuel cell, because of its lower cost and long time stability. Starting polymer matrices form uniform free radicals rapidly and monomer can incorporate uniformly. A number of grafting processes arise such as ionizing radiation, chemical initiator, UV light, plasma treatment, oxidation of polymers etc. There are several types of radiation grafted PEMs are reported [10-17]. Due to their lower ion exchange capacity, proton conductivity and relatively higher cost they are not economically feasible at all. Therefore, radiation technique is applied to make a low cost and better economy perspective to power generation. Gamma radiation techniques for polymer grafting is relatively lower cost and higher grafting occurs uniformly than other techniques.

In the present study, we have grafted GMA onto non woven PE fabric by gamma irradiation technique and the grafted film are modified through sulfonation. The constructed sulfonic acid membrane shows higher grafting of GMA and highly stable at higher temperature (above 120 °C). It also shows better ion exchange capacity than Nafion (0.9 meqg⁻¹). Water uptake capacity, oxidative property, ion exchange capacity were performed. The prepared membrane were characterized by TGA, SEM and FTIR technology.

6.2. Experimental

6.2.1. Materials and Reagent

Hydrogen peroxide (Merc Germany), Phenolphthaline (sigma Aldrich) and Sodium chloride (Sigma Aldrich) were used for the experiment.

6.2.2. The Ion-exchange Capacity (IEC)

We were performed the ion-exchange capacity of the constructed PEM by titrimetic investigation. The developed membrane was protonated by 1N HCl, then washed by distilled water and dried. At room temperature, the dried membrane was deeped in 0.1 mol/L NaCl aqueous solution for 24 h. H^+ ions, of membrane were released into the solution. After that H^+ ions containing NaCl solution was titrated by 0.05 mol/L NaOH solution. The IEC of the sulfonated-GMA-g-PE membrane was determined by means of the following equation:

$$IEC = (C \times V) / W_{dry} \quad (1)$$

C is the concentration of NaOH, V is the volume of NaOH and W_{dry} is the dry weight of the membrane.

6.2.3. The Water Uptake capacity

By the following equation the water uptake of the sulfonated-GMA-g-PE membrane was determined:

$$\text{Water uptake (\%)} = 100 \times (W_{wet} - W_{dry}) / W_{dry} \quad (2)$$

Where, W_{wet} = the weight of PEMs after immersing the dry membrane in water at different temperatures for different times

W_{dry} = the weight of the dry PEM

6.2.4. Oxidative Stability

The Oxidative Stability of the sulfonated-GMA-g-PE membranewas determined by calculating weight loss of the membrane in different concentrations of H₂O₂ solution. By the following equation weight loss was calculated:

$$\text{Weight loss (\%)} = 100 \times (W_{\text{dry}} - W_{\text{H}_2\text{O}_2}) / W_{\text{H}_2\text{O}_2} - (3)$$

Where, W_{H₂O₂} = weight of PEMs after immersing the dry membrane in H₂O₂ at dissimilar temperatures for diverse time

W_{dry}= weight of the dry PEM.

6.3.Result and discussion

6.3.1.The Ion Exchange Capacity

The ion exchange capacity (IEC) is very important in case of proton exchange membrane for fuel cell. It plays a key part in calculating the proton conductivity of the membrane[18]. In the present study, IEC increased with rising S (%) (Fig. 6.1) as the integrationof improved number of SO₃H groups into the grafted sulfonated-GMA-g-PE film. It is desirable to have high value of IEC in proton exchange membranes to accomplish higher proton conductivity. At 55.26% degree of sulfonation maimum IEC of the constructed PEM was set up1.45mmol g⁻¹. The IEC of the sulfonated-GMA-g-PE membrane is higher than that of some other non fluorinated membrane such as AA-g-PET etc.

Table 6.1: Data for Ion Exchange Capacity of Proton Exchange Membrane.

Degree of sulfonation	IEC (mmol g ⁻¹)
28.72	1.18
35.13	1.26
40.35	1.36
46.0	1.40
55.26	1.45

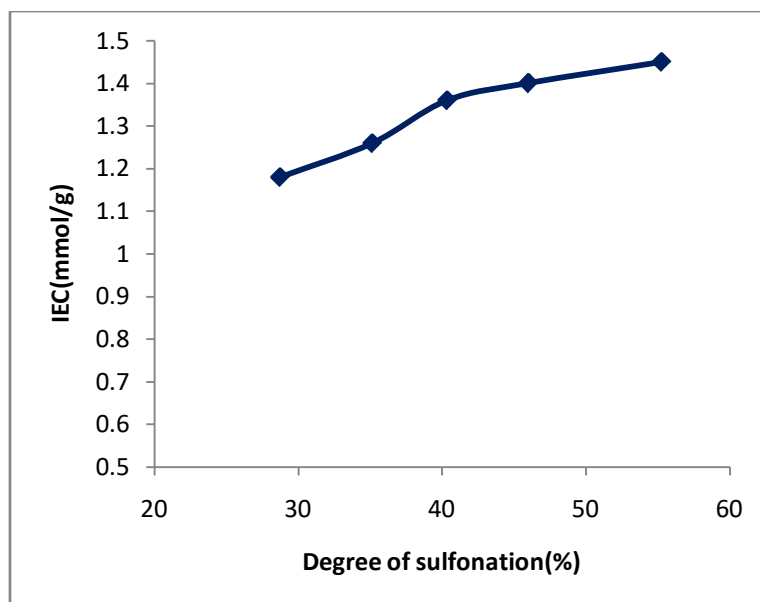


Fig.6.1. Ion exchange capacity (IEC) of the membrane as a function of the degree of sulfonation, S (%).

6.3.2. Water Uptake Capacity

The water uptake capacity is the another key parameter for determining the performance of fuel cell membrane. The constructed sulfonated-GMA-g-PE membrane show high proton conductivity. The water uptake capacity of the membrane was performed at different temperature (60°C, 80°C, 100°C) as a function of soaking time (1-9 h). The highest water uptake capacity for the equipped PEM were found to be 85.15% at 100°C for 9 h soaking time (Fig.6.2). It is significant that all the membranes maintained their dimensional solidity at 80°C. This implies that at eminent temperatures it could assemble the demands for function as PEMs for using in fuel cell [19].

Table 6.2: Data for Water Uptake Capacity of Proton Exchange Membrane.

Time(day)	Water uptake capacity		
	60	80	100
1	52	57	73.0
3	59	63	78.0
5	65	67	80.61
7	68	70	82.76
9	71	78	85.15

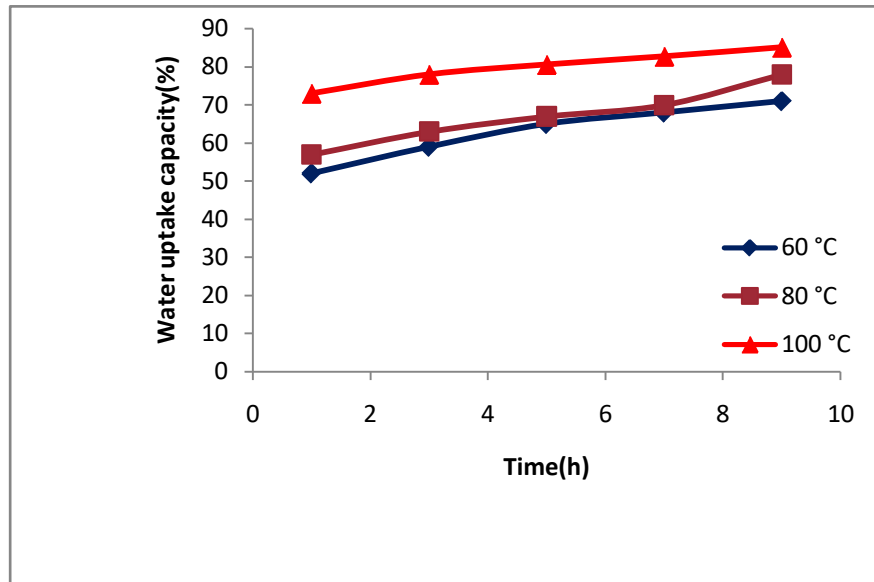


Fig. 6.2. Water uptake of the sulfonated membrane as a function of soaking time at 60°C, 80°C and 100°C.

6.3.3. Oxidative Stability

In hydrogen fuel cell, H_2O_2 can be formed at a very low concentration, so in case of proton exchange membrane the oxidative stability is particularly important for applications in fuel cell. Hence, the stability of the constructed sulfonated membrane in such a surroundings was identified by means of unlike concentrations of H_2O_2 at 80°C for 10 days (Fig. 6.3). In the prepared sulfonated membrane there were moderate changes (at most 53.12 % weight loss) of weight even after treatment with 0.05 mol/L H_2O_2 for 10 days that confirm the significant oxidative stability.

Table 6.3: Data for Oxidative stability of Proton Exchange Membrane.

Time (h)	Oxidative Stability		
	0.01M	0.02 M	0.05M
2	6.66	8.1	13.09
4	20.21	25.7	35.22
6	28.53	33.31	45.37
8	30.74	40.13	52.56
10	31.13	42.09	53.12

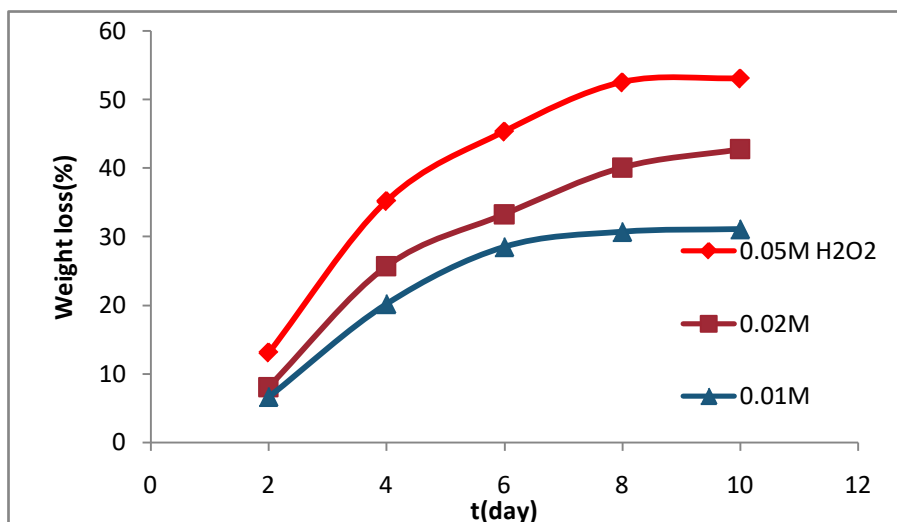


Fig.6.3. The stability of the sulfonated membranes in unlike concentrations of H_2O_2 as a function of reaction time

6.4. CONCLUSIONS

Gamma radiation induced sulfonic acid functionalized GMA-g-non woven PE membrane is constructed successfully for the use as proton exchange membrane for fuel cell. We have investigated the electrolyte character of the sulfonated membranes where highest IEC was $1.45 \text{ mmol }^{-1} \text{ g}^{-1}$, water uptake (at 100°C for 9 h) was 85.15%. Besides, the constructed membranes were set up with high thermal stability from the TGA experiment (at upto 600°C). The PEMs were found to hold moderate oxidative stability (max. weight loss 53.12% in 0.05 mol/L H_2O_2 at 80°C for 10 days). It can be concluded that the constructed PEMs can be used in fuel cells as a substitute of Nafion and it can be a potential addition in the non fluorinated membrane technology.

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Overall Conclusions and Outlook

Gamma radiation induced grafting of GMA on non-woven polyethylene and subsequent functionalization through sulfonation was investigated. Grafting was carried out at 20kGy, 30kGy and 40kGy radiation dose to study the effect of total dose of gamma radiation. Maximum grafting and adsorption was found at 30kGy radiation dose. To study the effect of monomer concentrations on degree of grafting, 2.5%, 5% and 7.5% GMA solutions were used. Higher grafting was observed at 5% GMA solution. At 30KGy radiation dose, 5% monomer concentration, adding up of 0.5% Tween-20 as an additives and 4 h reaction time maximum 343.31% graft yield was obtained. The GMA grafted PE film functionalized using sodium sulfite, sodium bisulfite, iso-propanol and water solutions at the ratio of 10:3:10:77 wt% and the reaction was carried out at 80°C with constant heating up to 6h.

The sorbent was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Thermo-Gravimetric Analysis (TGA) technology. We have prepared aqueous solutions of heavy metals Cr(III), Cu(II), Pb(II) and dyes basic fuchsin (BF), methylene blue (MB) and crystal violet (CV) in different concentrations. Metals and dyes uptake capacity were performed by the developed sulfonated-GMA-g-PE sorbent. The constructed sulfonated-GMA-g-PE films were used to study the sorption of heavy metals Cu(II), Cr(III), Pb(II), uranium and dyes Basic Fuchsin (BF), Methylene Blue (MB) and Crystal Violet (CV). The film was also studied for Proton Exchange Fuel Cell Membranes (PEMFCs). Adsorption capacity of the prepared film was calculated under different conditions such as contact time, starting metal ion concentrations, pH and temperature. The main features of this thesis work are:

It is observed that the sorption capacity of heavy metals and dyes raises with rising of time and the sorption reached equilibrium after 48 h.

Results shows that the adsorption of Cu(II), Cr(III), Pb(II) and uranium increases significantly with rising pH from 1.25 to 7 and highest adsorption was observed at pH=4.92 for Cu(II), pH=4.2 for Cr(III), pH=4.6 for Pb(II) and pH 3.67 for uranium. Adsorption capacity of BF, MB and CV increases significantly with growing pH from 2 to 7. At pH=7, maximum adsorption of BF, MB and CV was observed.

The adsorption amount of heavy metals and dyes increases with increasing initial ion concentration then attain plateau value at elevated concentration. This is due to the fact that the chelating sites of the adsorbent turn into saturated at higher concentrations.

The adsorption of metals and dyes are highly temperature dependent. The value of ΔG of Cu(II), Cr(III) and Pb(II) are -5.93KJ/mol, -12.21KJ/mol and -4.96KJ/mol respectively which are negative at 25°C, and decreases with an increase of temperature. The value of ΔG (-0.741KJ/mol) is also negative for BF at 25°C, and decreases with the increase of temperature, that are positive for MB and CV (0.353KJ/mol for MB and 2.79KJ/mol for CV) at 25°C, but at higher temperature it is negative(-0.28KJ/mol for MB and -0.068KJ/mol for CV).

It proves that the adsorption amount of heavy metals and dyes increases with increase of temperature of the solutions.

The resorption and reuse of the films were also effectively carried out. The outcome indicate that the sulfonated-GMA-g-PE film can be used for the elimination of heavy metals and cationic dyes from industrial wastewater for environmental purifications.

The prepared film shows good ion exchange capacity for proton exchange fuel cell membranes. The investigated IEC of the membrane is 1.45mmol g⁻¹. So, it can be used also as proton exchange membrane in fuel cell.

In this work, grafting of GMA onto non woven PE film occurred successfully by gamma radiation and the grafted film properly functionalized through sulfonation. The constructed sulfonated-GMA-g-PE film has been used for the removal of heavy metals and textile dyes from waste water. It also shows good ion exchange capacity. So, it can be used in fuel cell as a proton exchange membrane. As Bangladesh has huge number of tannery and textile industries that discharging heavy metals and dyes continuously into the water. So, the film could be practically used in this sector for environmental purification.

From the above discussion, it is concluded that the developed low cost and practice ally effective sulfonated-GMA-g-PE film is a new addition in adsorption and energy technology which exhibited a considerable potential in removing heavy metals and cationic dyes from waste water.

List of publications from this research:

1. Applications of Sulfonated-GMA-g-PE film for the efficient removal of methylene blue dye from wastewater. American Journal of Polymer Science and Technology 2021; 7(1): 1-9 <http://www.sciencepublishinggroup.com/j/ajpst> doi: 10.11648/j.ajpst.20210701.11 ISSN

Conference proceedings(oral presentation):

Rapid and Efficient adsorption of Cationic Dyes Using Sulfonated GMA-grafted- Non Woven PE Adsorbent. ICSTB-2021.Dhaka.