REMOVAL OF HEAVY METALS FROM AQUEOUS MEDIUM AND THEIR IMPACT ON BIOLOGICAL SYSTEM

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SEPTEMBER 2015

THESIS SUBMITTED FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF APPLIED CHEMISTRY
AND CHEMICAL ENGINEERING
UNIVERSITY OF DHAKA
DHAKA, BANGLADESH

Dedicated to the soul of my late father

ACKNOWLEDGEMENT

First of all, the author is thankful to the Almighty Allah for His blessings in the successful completion of this research work.

The author would like to express her profound and deepest sense of gratitude to the respective supervisors Prof. Dr. Nurul Amin and Prof Dr. Ahmad Ismail Mustafa, Department of Applied Chemistry and Chemical Engineering, University of Dhaka and Dr. Shamshad Begum Quraishi, Chief Scientific Officer, Chemistry Division, Atomic Energy Centre, Dhaka for their successful guidance, valuable suggestions and ideas, fruitful discussions, encouragement and cordial dealings throughout the work.

The author is indebted to Dr. Bilkis Ara Begum, Head, Chemistry Division, Atomic Energy Centre, Dhaka for her kind cooperation, valuable suggestions, encouragement during the work.

My deepest gratitude goes to Prof. Dr. A.M. Sarwaruddin Chowdhury, Department of Applied Chemistry and Chemical Engineering, University of Dhaka for giving untiring support and inspiration for completing this thesis work.

The author is grateful to Dr. Syed M. Shamsuddin, Professor and Chairman, Department of Applied Chemistry and Chemical Engineering, University of Dhaka for his cooperation during the whole tenure.

The author is proud to acknowledge Md. Azizul Maksud, Muhammad Shahidur Rahman Khan, and Lutfun Naher Lutfa, Chemistry Division, Atomic Energy Centre, Dhaka for their support and inspiration during this research work.

The author express her deepest sense of gratitude to her lovely kids Samir Anowar and Sahil Anowar have been a source of joy and inspiration for her to achieve the progress the research work.

Last but not the least, the author would like to express her special thanks and extreme gratitude to her family members for everlasting encouragement understanding and support during the period of this research work.

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ABSTRACT

The presence of arsenic in groundwater has been recognized as a major problem for Bangladesh. Due to its high toxicity, even in low concentrations, it is a threat to human health. There are many techniques, which can be effectively applied to remove arsenic from water streams. Many technologies, including co precipitation with iron or alum, adsorption onto coagulated floc, ion-exchange resin, reverse osmosis, and membrane techniques, have been used to remove arsenic from aqueous solution. Moreover, these existing techniques are costly and they are not economically applicable in small community systems. Therefore, there is a need for developing cheap efficient methods for the removal of arsenic from drinking water. Adsorption techniques are simple and convenient and have the potential for regeneration and sludge free operation. The present work was performed to evaluate the use of duckweed *(Lemna minor)* and neembark *(Azadirachta indica)* without any pretreatment as alternate adsorbents for removing arsenic (III) from aqueous mediums. Moreover, the duckweed and neem bark were applied to the removal of arsenic from Bangladeshi As-contaminated drinking water samples in a single-step column operation.

For the removal of arsenic (III) using duckweed, various parameters were investigated that affect arsenic adsorption/desorption. Optimum arsenic (III) removal was obtained under the following conditions: initial As (III) concentration, 100 μg/L; duckweed amount, 3 g; average particle size, 0.595 mm; treatment flow rate, 1.67 mL/min; and pH, 5.5,respectively. The desorption efficiencies with 1M H_2SO_4 was observed 97.67%.

The adsorption characteristics of arsenic on neem bark, a low-cost natural adsorbent, were studied in the laboratory scale using real-life sample. Neem bark has tremendous potential as a remediation material for the removal of arsenic from groundwater. The present work investigates the possibility of the use of neem bark adsorption technology without any pretreatment in the removal of arsenic from aqueous media. Various conditions that affect the adsorption/desorption of arsenic are investigated. Adsorption

column methods show the optimum removal of As (III) under the following conditions: initial arsenic concentration, 100 μg/L; neembark amount, 5 g; average particle size, 0.595 mm; treatment flow rate, 1.67 mL/min; and pH, 6.9; respectively. The desorption efficiencies with 1M of HCl after the treatment of groundwater were in the range of 79%. The present study might provide new avenues to achieve the arsenic concentration for drinking water recommended by Bangladesh and the World Health Organization (WHO).

Tanning industries are one of the main economic activities in Bangladesh. It has been well documented that waste water discharged from tanneries without appropriate treatment that results in detrimental effects on the ecosystem. No eco-toxicity evaluation of any aquatic environment in Bangladesh has been conducted so far. There are various methods to remove Cr (III) and Cr (VI) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis. These methods are non economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of chromium because of its efficiency and low cost. In this study, groundnut shell (*Arachis hypogaea)* and flax (*Linum usitatissimum)* have been used for Cr (III) and Cr (VI) removal from aqueous solution. The present study is intended to use of these locally available as conventional cheap materials as chromium adsorbents.

Adsorption and de-sorption of chromium (III) ions on groundnut shell from aqueous solutions have been studied using batch adsorption techniques with respect to the influence of contact time, pH, adsorbent dose, initial chromium concentration and particle size. Appropriate adsorption isotherm and kinetic parameters of chromium (III) adsorption on groundnut shell have also been determined. The results of this study showed that adsorption of chromium (III) by groundnut shell reached to equilibrium after 360 minutes of the experiment and after that a little change of chromium removal efficiency was observed. Maximum chromium removal (87.5 %) was obtained at pH 7.0. The adsorption of chromium by groundnut shell was found to decrease with the higher chromium concentrations in aqueous solutions, lower adsorbent doses and higher particle sizes. The desorption efficiencies with 0.5M KOH was observed 78%. It is observed that the adsorption of chromium (III) by groundnut shell follows Langmuir and Freundlich isotherm equation. The kinetic of the adsorption process follows the first order kinetics with a rate constant of 0.01min^{-1}. The results indicate that groundnut shell can be employed as a low cost alternative to commercial adsorbent in the removal of chromium (III) from water and wastewater.

The removal of hexavalent chromium from aqueous solution using nutshell has been best suited for the treatment of real tannery effluents since Cr salt is used for tanning. Batch adsorption studies were carried out under varying experimental conditions of contact time, pH, adsorbent dose, initial chromium concentration and particle size. Appropriate adsorption isotherm and kinetics parameters of chromium (VI) adsorption on nutshell have also been determined. The adsorption followed first order rate expression. The equilibrium data fit well into Langmuir and Freundlich isotherms. Adsorption was maximum at an initial pH of 2.0. The desorption efficiencies with 1 M KOH was observed 87%. It is expected that the developed rate equation could likely be used for design and performance predictions of adsorption processes for treating chromate wastewaters.

Furthermore, adsorption of chromium (III) on flax from aqueous solutions has been studied using batch adsorption techniques. Batch adsorption studies were carried out under varying experimental conditions of contact time, pH, adsorbent dose, initial chromium concentration and particle size. Appropriate adsorption isotherm and kinetics parameters of chromium (III) adsorption on flax have also been determined. The results of this study showed that adsorption of chromium (III) by flax reached to equilibrium after 420 minutes. Maximum chromium removal (70 %) was obtained at pH 2.0. The adsorption of chromium by flax was found to decrease with the higher chromium concentrations in aqueous solutions, lower adsorbent doses and higher particle sizes. The desorption efficiencies with 0.5M KOH was observed 90%. It is observed that the adsorption of chromium (III) by flax fitted Langmuir and Freundlich isotherm equation. The kinetic of the adsorption process follows the first order kinetics with a rate constant of 0.01min^{-1}. The results indicate that flax can be employed as a low cost adsorbent for the removal of chromium (III) from water and waste water.

A 60-day experiment was conducted to compare the accumulation and toxicological effects of arsenic in muscle, intestine and liver of shingi fish, *H. fossilis* (Bloch) after exposure to two concentrations (7.0 and 20.0 ppm) of arsenic trioxide. The highest/maximum level of accumulation of arsenic was observed in the liver whereas the lowest level of arsenic was found to accumulate in the muscle tissues at the end of exposure period. It is apparent from the study that the damage of the liver of test fish due to 15 days exposed period was less compared to the damage caused by 60 days exposure periods. The intensity of histological alterations was observed to increase gradually with the arsenic concentration and the exposure time.

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CHAPTER 1: INTRODUCTION

CHAPTER TWO: ANALYTICAL FRAMEWORK OF THE RESEARCH

CHAPTER ONE: INTRODUCTION

1.1 General Background and Aim of the present Study

General background

Over the past 20 years, a number of legislations have come into force to control pollution. Problems associated with wastewater disposal in developing countries (especially in Bangladesh) can be attributed to lack of adequate treatment/management policies coupled with ineffective legislation on the part of entrusted government agencies. The discharge of heavy metals into aquatic ecosystems has become a matter of concern in Bangladesh over the last few decades because their presence and accumulation have a toxic effect on living species. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. Such pollutants include heavy metals (arsenic, chromium, mercury, lead, cadmium, copper and nickel) which endanger public health after being incorporated in food chain. Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. Some of the heavy metals are toxic to aquatic organisms even at low concentration. The problem of heavy metal pollution in water and aquatic organisms including fish, needs continuous monitoring and surveillance as these elements do not degrade and tend to biomagnify in man through food chain. Therefore, the study of the existing effluent disposal methods, facilities, and attitudes is essential in order to make a positive impact on our environmental hygiene. Hence there is a need to remove the heavy metals from the aquatic ecosystems.

Research and development, therefore focuses on sector-specific methods and technologies to remove heavy metals from different kinds of waste streams. In view of the above toxicological effects of heavy metals on environment, animals and human beings, it becomes imperative to treat these toxic compounds in wastewater effluents before they are discharged into freshwater bodies. Over the last few decades, several methods have been devised for the treatment and removal of heavy metals from aqueous solution including chemical precipitation, lime coagulation, ion exchange, electrodialysis, ultrafiltration, reverse osmosis, solvent extraction and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials.

Therefore, there is currently a need for a cost-effective treatment method that is capable of removing toxic substances from aqueous effluents.

In these methods, however, the adsorption techniques are simple and convenient and have the potential for regeneration and sludge-free operation. Adsorptions by commercial adsorbent materials have various disadvantages, and hence many low cost adsorbents are increasingly used as biosorbents. Biosorption has advantages compared with conventional techniques. Some of these are listed below:

- Cheap: the cost of the biosorbent is low since they often are made from abundant or waste material.

- Metal selective: the metal sorbing performance of different types of biomass can be more or less selective on different metals. This depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physicochemical treatment.

- Regenerative: biosorbents can be reused, after the metal is recycled.

- No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.

- Metal recovery possible: In case of metals, it can be recovered after being sorbed from the solution.

- Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor.

Aim of the present Study

In Bangladesh, ground water used for drinking purpose has been highly contaminated with naturally occurring inorganic arsenic. The literature review shows many methods of arsenic removal from ground water. But socio-economic conditions of Bangladesh demands economic, suitable, reliable method that could be implemented at household level. However, in rural areas of Bangladesh, the method which is cheap and easy to operate may attain sustainable acceptance. Almost all the methods now available, suffer from high cost. The people of Bangladesh are not able to buy any chemical for disinfection of surface water or purifying arsenic tainted water. On the other hand, all chemical methods produce highly concentrated arsenic containing sludge, which is another problem. If a method can be derived, which can be affordable to all the people of Bangladesh and uses only the available local material, then the people can easily fabricate it for their own use. The present work tries to see, if the adsorption method using low cost adsorbents can achieve this aim.

The column of impregnated adsorbents was used for their ability to remove arsenic (by controlling flow rate) from actual water sample collected from a contaminated tube well and arsenic has been removed successfully. The present work describes all the procedure for adsorption of arsenic from ground water using column experiments.

The application of chromium, a heavy metal in various industries, especially in leather tanning has gained a negative impact in the society with respect to its pollution potential. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production .Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. There are various methods to remove chromium including chemical precipitation, membrane process, ion exchange, liquid extraction and electro dialysis. These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost .For this purpose, investigations have been carried out for the effective removal of chromium from solution using natural adsorbents. The present study is intended to use of this locally available as a conventional cheap material as a chromium adsorbents.

For these adsorbents, adsorption efficiency was studied as a function of contact time, pH, particle size, adsorbent dose and adsorbate concentration. Different adsorption isotherms were employed in order to evaluate the optimum adsorption conditions. From the experimental results, the best adsorbents were chosen considering the metal loading capacity. It was found that the adsorption capacity of the adsorbents studied was well compared to the other adsorbents reported in literature.

The present work is to study the removal of arsenic and chromium by low cost adsorbents such as duckweed, neembark, nutshell, flax etc from aqueous mediums and to offer this biosorbent as local replacement for existing commercial adsorbent materials. The objective of this preliminary study is to determine the effects of chronic exposure of arsenic on the biological bodies as well as development of a simple and cost effective technology for efficient and selective removal of arsenic from ground and chromium from waste water.

1.2. Arsenic and Chromium Pollution

1.2.1 Arsenic Scenario

1.2.1.1 Arsenic Catastrophe in Bangladesh: The Scale of the Problem

Bangladesh is very much dependent on ground water both for drinking and irrigation purposes. Ground water from shallow aquifers contaminated by naturally occurring arsenic (As) is widely used as source of drinking water in Bangladesh (BGS/DPHE, 2001)

Until the discovery of Arsenic, groundwater was considered safe for drinking. Tubewells have, in the majority, replaced the traditional surface water sources and diarrhoeal disease has reduced significantly. An estimated 97% of drinking water of the rural population in Bangladesh is now supplied by groundwater. About 80% of the population is covered by manually operated shallow tube wells and 6% by manually operated deep tubewells. It has been estimated that about 8.0 million hand pump tubewells have been installed under private initiatives and government has sunk about 1.2 million tube-wells (NAISU, 2003)

Comprehensive database of As available for groundwater composition in Bangladesh showed that the average As concentrations is 199±1.66 μg/L. The World Health Organisation's guideline for maximum arsenic concentration in drinking is currently 10 ppb (WHO, 2006). However, the US Environmental Protection Agency had lowered its maximum allowed arsenic concentration in drinking water from 50 ppb to 10 ppb in 2001 (WHO, 2004).

Arsenic enrichment in drinking water-supplies poses a serious concern for the public health in many countries around the world including the Ganges–Brahmaputra–

Meghna (GBM) Delta in Bangladesh and West Bengal, India where tens of millions of people are currently exposed to dangerous levels of the As (Stuben et al., 2003). The health-affect of As poisoning is felt more severely in Bangladesh due to its high population density (~1000 person per km^2) (BBS, 2008). Studies of groundwater As over the last few decades (BGS and DPHE, 2001 and Ahmed et al., 2004) have brought researchers to a general consensus that the occurrence of elevated As (>50 μg/L; Bangladesh drinking water standard is 50 μg/L) in alluvial aquifers in the Bengal Basin is geogenic and reductive dissolution of Fe (III)-oxyhydroxide minerals due to microbial metabolism releases As into groundwaters. Excessive As in groundwater, 10–100 times the WHO guideline for drinking water (10 μg/L), threatens human health and the yield of irrigated crops across the extensive floodplains of the Ganges, Brahmaputra and Meghna rivers of the Bengal Basin in West Bengal and Bangladesh (Brammer et al.,2009). It is estimated that approximately 57 million people in Bangladesh currently drink water with As levels exceeding the World Health Organization (WHO) drinking water quality guideline of 10 μ/L (Rahman et al., 2009).

In 1993, DPHE first identified high concentration of arsenic in shallow tube-well in Chapai Nawabganj adjacent to an area of West Bengal which had been found to be extensively contaminated in 1988· Extensive contamination was confirmed in 1995 when additional surveys showed contamination of shallow tube-wells across much of southern and central Bangladesh. WHO declared arsenic contamination as a ' Major Public Health Issue' in 1996 and informed Bangladesh Government to deal with emergency basis.

Department of Public Health Engineering (DPHE), British Geological Survey (BGS) and Mott MacDonald Ltd. survey (approximately 3500 samples) throughout Bangladesh, but excluding the Chittagong Hill Tracts, revealed that 27% of the shallow tube-wells are contaminated with arsenic above the level of 0.05 mg/l (50 ppb) and 46% of the shallow tube-wells tested are contaminated with arsenic above the WHO guideline 0.01 mg/l (10 ppb). Eight of the 61 sampled districts had no samples exceeding the Bangladesh standard for arsenic (0.05 mg/l) and all districts except Thakurgaon had at least one well exceeding WHO guideline value (NAISU, 2003).

According to the study finding the worst affected districts (percent of sampled wells with greater than 0.05 mg/l arsenic) were:

Chandpur (90%), Munshiganj (83%), Gopalganj (79%), Madaripur (69%), Noakhali (69%), Satkhira (67%), Comilla (65%), Faridpur (65%), Shariatpur (65%), Meherpur (60%), Bagerhat (60%) and Lakshmipur (56%). The least affected districts were Thakurgoan, Barguna, Jaipurhat, Lamonirhat, Natore, Nilphamari, Panchagar, Patuakhali (and 0%), Rangpur (1%), Dinajpur (2%), Noagoan (2%).

Most of the arsenic has been found in the shallow aquifer, with only 1% of the deep tubewells (greater than 150m) tested in the BGS study having arsenic greater than 50 ppb and 5% greater than 10ppb. However there are some concerns regarding future arsenic contamination of the deep aquifer, particularly where the shallow and deep water is not separated by an aquitard. The population exposed to arsenic contamination more than 0.05 mg/l (>50 ppb) would lie in the range 18.5-22.7 million (DPHE /BGS/ MML in phase 1).

However the BGS-DPHE studies finally gave an estimation of the number of population exposed to arsenic concentration above 0.05 mg/l (50 ppb) and 0.01 mg/l (10 ppb) to be 35 million and 57 million respectively. (Based on upazilla-averaged statistics the exposure levels to arsenic exceeding 0.05 mg/l (50 ppb) and 0.01 mg/l (10 ppb) were computed as 28 million and 46 million respectively, but the BGS report states that they consider the larger figures to be more reliable).

School of Environmental Studies (SOES), Jadavpur University, Calcutta and Dhaka Community Hospital Trust tested water from 64 districts of Bangladesh. Their finding up to February 2000 shows that in 47 districts arsenic in ground water is above 0.05 mg/l and in 54 districts above 0.01 mg/l.

In a report WHO has predicted that in most of the southern part of Bangladesh almost 1 in every 10 adult deaths will be a result of cancer triggered by Arsenic poisoning in the next decade. From the experience of Taiwan it has been forecasted that almost two million of people are at risk of developing cancer in the next decades.

An estimate of Department of Public Health Engineering (DPHE) and DGHS reveals:

Total Arsenic Contaminated Districts: 61

Total Upazillas contaminated with Arsenic: 268

Total number of Patients: 13333

The current arsenic situation of Bangladesh has been considered as the greatest environmental disaster of the world. So effective and appropriate mitigation program is urgently warranted for tackling this catastrophe in Bangladesh. Tube-well switching and re-installation of tube-wells in As-safe sediments is strongly encouraged as an approach to provide safe drinking water supplies to rural communities (Jakariya et al., 2007)

Table 1. Statistics of Arsenic Calamity in Bangladesh (Chakraborti et al., 1996)

Parameter	Value
Total number of districts in Bangladesh	64
Total area of Bangladesh	147,570 km^2
Total population of Bangladesh	153 Million
WHO standard for arsenic in drinking water	0.01 µg/L
WHO-recommended maximum permissible limit for arsenic in drinking water	0.05 µg/L
Bangladesh standard for arsenic in drinking water	0.05 µg/L
Total number of tube-wells in Bangladesh	5 million
Total number of affected tube-wells	3 million
Number of districts surveyed for arsenic contamination of groundwater	64
Number of districts having arsenic above	61
Population at risk	> 80 million

Population potentially exposed	> 30 million
Number of patients suffering from arsenicosis	> 38000

A map showing the intensity of arsenic contamination of ground water in different parts of Bangladesh is shown in figure. The map has been updated on the basis of information available from arsenic analysis conducted by BGS and DPHE (2001).

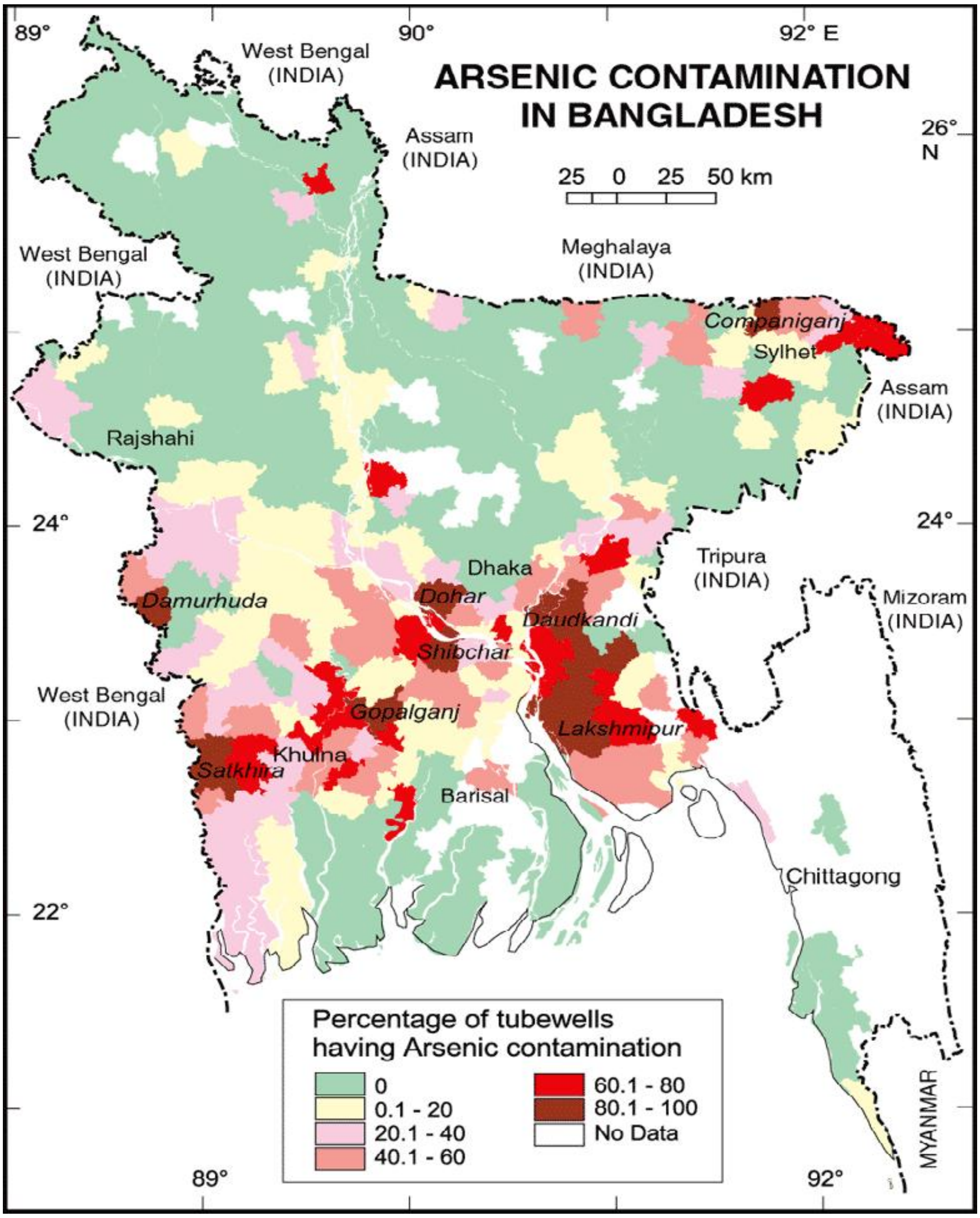

Fig 1: **Arsenic contaminated region of Bangladesh with arsenic level in ground water**

The following table shows a summary of the present status of As contamination and its associated health effects in Bangladesh and a comparison of the present status of As contamination as of 2009 and the initial survey results published in 1997, illustrating the changing arsenic situation over the past 14 years.

Table 2: Distribution of Hand Tubewells against Concentration Range (μ/L) of Arsenic in All 64 districts of Bangladesh: Source (Chakraborti et al.,2010)

Division	District	Maximum concentration detected (μ/L)
Rajshahi	Bogra	1040
	Dinajpur	77
	Gaibanda	512
	Joypurhat	32
	Kurigram	50
	Lalmanirhat	50
	Naogaon	22
	Natore	63
	Nawabganj	1600
	Nilphamari	50
	Pabna	2108
	Panchagarh	15
	Rajshahi	524
	Rangpur	939
	Sirajganj	216
	Thakurgaon	130
Khulna	Bagherhat	958
	Chuadangm	841
	Jessore	1120
	Jhenaidaha	592
	Khulna	3143
	Kushtia	2190
	Meherpur	1230
	Magura	1050
	Narail	375
	Satkhira	750
Barisal	Barguna	15
	Barisal	1770
	Bhola	50
	Jhalakati	310
	Patuakhali	10

	Pirojpur	731
Sylhet	Habiganj	100
	Moulavi	133
	Bazar	302
	Sunamganj	177
	Sylhet	
Dhaka	Dhaka	352
	Faridpur	1630
	Gazipur	533
	Gopalganj	920
	Jamalpur	1172
	Kishoreganj	365
	Madaripur	1200
	Manikganj	586
	Munshiganj	529
	Mymensingh	330
	Narayanganj	1750
	Narshingdi	1000
	Netrokona	580
	Rajbari	714
	Shariatpur	580
	Sherpur	275
	Tangail	224
Chittagong	Bandarban	-
	Brahmanbaria	210
	Chandpur	1318
	Chittagong	275
	Comilla	1769
	Cox's Bazar	-
	Feni	1000
	Khagrachari	-
	Lakshmipur	2030
	Noakhali	-
	Rangamati	4730

The maximum As concentration detected in a hand tubewell was 4730 µg/L of the village Chiladi in Noakhali district (Chakraborti et al., 2010). Many villages in the As-affected areas of Bangladesh surveyed over the past 14 years were found to have 70-

100% of the hand tubewells contaminated with As above 50 µg/L. It is possible that Chiladi (Thana: Senbagh, District: Noakhali) is the village with the most severe As contamination in the world, where people were drinking from contaminated sources for extended periods of time. Out of 73 hand tubewells analyzed from Chiladi, only one tubewell contained As between 10 and 50 µg/L (depth of this tubewell is 190 m) and the remaining 72 tubewells contained As above 100 µg/L. It was also found that 21 tubewells from this village had As above 1000 µg/L.

1.2.1.2 Arsenic Contamination of Ground Water

Before 2000, there were five major incidents of arsenic contamination in groundwater in Asian countries: Bangladesh, West Bengal, India, and sites in China. Between 2000 and 2005, arsenic-related groundwater problems have emerged in different Asian countries, including new sites in China, Mongolia, Nepal, Cambodia, Myanmar, Afghanistan, DPR Korea, and Pakistan (Mukherjee et al.,2006). A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water. Arsenic contamination of ground water is found in many countries throughout the world, including the USA (Smedley et al.,2002).

Approximately 20 incidents of groundwater arsenic contamination have been reported from all over the world (Mukherjee et al.,2006). Of these, four major incidents were in Asia, including locations in Thailand, Taiwan and Mainland Chaina (Chowdhury et al.,2000).

In South America, Argentina and Chile are affected. There are also many locations in the United States where the groundwater contains arsenic concentrations in excess of the Environmental Protection Agency standard of 10 parts per billion adopted in 2001. According to a recent film funded by the US Superfund, "In Small Doses" millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that are not safe.

Fig 2: Groundwater arsenic contamination areas

Table 3: Concentrations of arsenic in groundwater of the arsenic-affected countries (Mandal and Suzuki, 2002)

Location	Concentration (µg/L)[a]
Hungary	68 (1–174)
South-west Finland	17–980 (range)
New Jersey, USA	1 (median) 1160 (maximum)
Western USA	48,000 (maximum)
South-west USA	16–62 (range)
Southern Iowa and western Missouri, USA	34–490 (range)
Northeastern Ohio, USA	<1–100 (range)
Lagunera region, northern Mexico	8–624 (range)
Cordoba, Argentina,Chile	>100
Pampa, Cordoba, Argentina	100–3810 (range)
Kuitun-Usum, Xinjiang, PR China	0.05–850 (range)
Shanxi, PR China	0.03–1.41 (range)
Hsinchu, Taiwan	<0.7
West Bengal, India	0.003–3700 (range)
Calcutta, India	<50–23,080 (range)
Bangladesh	<10–>1000 (range)
Nakhon Si Thammarat Province, Thailand	503.5 (1.25–5114)
Fukuoka, Japan	0.001 1994 –0.293 (range)
Hanoi, Vietnam	159 (1–3050)

[a] Mean and ranges of total arsenic unless stated otherwise

1.2.1.3 Sources of Arsenic

Minerals

The most abundant Arsenic ore mineral is arsenopyrite, FeAsS

Table 4: Major arsenic minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays or limestones, also hot-spring deposits
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly mineral veins
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	Hydrothermal veins
Enargite	Cu_3AsS_4	Hydrothermal veins
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Scorodite	$FeAsO_42H_2O$	Secondary mineral

Rocks, sediments and soils

Earth's crust Few estimates exist for the concentration of arsenic in the earth's crust. However, the concentration is generally taken to be low.

Igneous rocks

Arsenic concentrations in igneous rocks are generally similar to those found in the crust. Overall, there is relatively little difference between the different igneous rock types.

Metamorphic rocks

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most contain around 5 mg kg–1 or less.

Sedimentary rocks

The concentration of Arsenic in sedimentary rocks is typically in the range 5–10 mg kg^{-1}.

Unconsolidated sediments Concentrations of Arsenic in unconsolidated sediments are typically 3–10 mg kg^{-1}, depending on texture and mineralogy.

Soils Baseline concentrations of Arsenic in soils are generally of the order of 5–10 mg kg^{-1}. Peats and bog soils can have higher concentrations (average 13 mg kg^{-1}).

The atmosphere

The concentrations of arsenic in the atmosphere are usually low but as noted above, are increased by inputs from smelting and other industrial operations, fossil-fuel combustion and volcanic activity. Concentrations amounting to around 10^{-5}–10^{-3} μg m^{-3} have been recorded in unpolluted areas, increasing to 0.003–0.18 μg m^{-3} in urban areas and greater than 1 μg m^{-3} close to industrial plants (WHO, 2001). Much of the atmospheric arsenic is particulate. Total arsenic deposition rates have been calculated in the range <1–1000 μg m^{-2} yr^{-1} depending on the relative proportions of wet and dry deposition and proximity to contamination sources. Airborne arsenic is transferred to water bodies by wet or dry deposition.

1.2.1.4 Mechanism of Arsenic Contamination

There are several hypotheses, regarding ground water arsenic contamination in Bangladesh:

Oxidation of pyrites and arsenopyrites

The oxidation theory is so far the accepted theory. The oxidation of arseno-pyrite could be the main mechanism for the groundwater arsenic contamination in Bangladesh.

According to this theory, arsenic is released from the sulfide minerals (arseno-pyrite) in the shallow aquifer due to oxidation. The lowering of water table owing to over exploitation of groundwater for irrigation has initiated the release of arsenic. The large-scale withdrawal of groundwater has caused rapid diffusion of oxygen within the pore spaces of sediments as well as an increase in dissolved oxygen in the upper part of groundwater. As long as the arsenic materials called Arsenopyrites (FeAsS) were submerged in ground water, they remained inert. The newly introduced oxygen oxidizes the arseno-pyrite and forms hydrated iron arsenate compound known as pitticite in presence of water (Karim, 1997). This is very soft and water-soluble compound. The light pressures of tube-well water break the pitticite layer into fine particles and make it readily soluble in water. Then it seeps like drops of tea from the teabag and percolates from the subsoil into the water table. Hence, when the tube-well is in operation, it comes out with the extracted water. The portrayed of the mechanisms are as follows:

$$\mathrm{FeAsS} \xrightarrow{\text{oxidized in air}} \mathrm{As_2O_3 + H_2O} \longrightarrow \mathrm{H_3AsO_3}$$

$$\mathrm{FeAsS} \xrightarrow{\text{oxidized in air}} \mathrm{As_2O_5 + H_2O} \longrightarrow \mathrm{H_3AsO_4}$$

As monsoon replenished the water table, the arsenic seeped into the tube well (Chakraborti, 1996).

Reduction of Oxyhydroxides

The arsenic may be released from iron oxide coatings on grains of sand through reduction that is electrons may be added to the iron compound (Bangla and Kaiser, 1996).

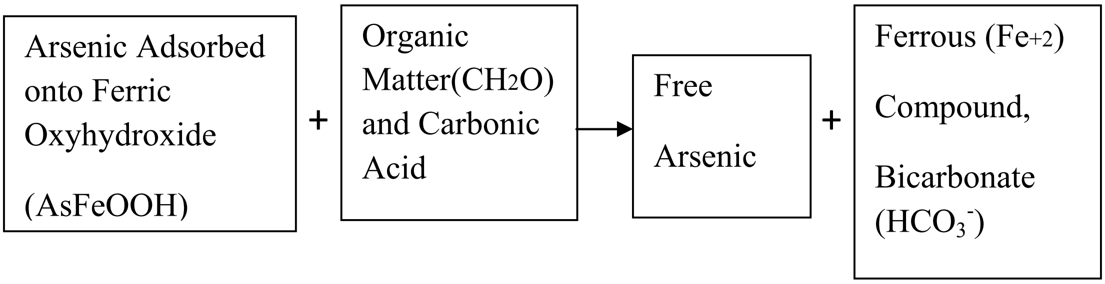

Fig 3: Arsenic release according to hydroxide reduction hypothesis (Bangla and Kaiser, 1996)

Oxidation and Reduction

Unconfined aquifers subjected to oxidation and reduction and underlain by peaty clay and/or clay layer is responsible for arsenic contamination (Bangla and Kaiser, 1996). The continued abstraction of water from unconfined aquifers releases pentavalent arsenic and transformed into trivalent and mobile into water.

1.2.1.5 Chemical Forms of Concern of Arsenic

Arsenic is a ubiquitous chemical element in the biosphere and it occurs naturally in both inorganic and organic forms.

Table 5: **Chemical forms of arsenic found in aquatic systems**

Name	Abbreviation	Formula
	Inorganic arsenicals	
Arsenious acid or arsenite	As^{III}	$As^{3+}(OH)_3$
Arsenic acid or arsenate	As^{V}	$H_3As^{5+}O_4$
	Methylated arsenicals	
Monomethylarsonous acid	$MMAA^{III}$	$CH_3As(OH)_2$
Dimethylarsinous Acid	$DMAA^{III}$	$(CH_3)_2AsOH$
Monomethylarsonic acid	$MMAA^{V}$	$AsO(OH)_2CH_3$

Dimethylarsinic acid	DMAA^{V}	$AsO(OH)(CH_3)_2$
Trimethylarsine acid	TMAA	$(CH_3)_3As$
Thioarsenicals		
Monomethyl-monothio arsenate	MMMTAs^{V}	$(CH_3)AsO_2S^{2-}$
Monomethyl-dithio arsenate	MMDTAs^{V}	$(CH_3)AsOS_2^{2-}$
Dimethyl-monothio arsenate	DMMTA^{V}	$(CH_3)_2AsOS$
Dimethyl-dithi oarsenate	DMDTA^{V}	$(CH_3)_2AsS_2^{-}$
Organoarsenic compounds		
Arsenocholine	AsC	$(CH_3)_3As^{+}CH_2CH_2O$
Arsenobetaine	AsB	$(CH_3)_3As^{+}CH_2COO^{-}$

Most cases of human toxicity from arsenic have been associated with exposure to inorganic arsenic. A number of studies have noted differences in the relative toxicity of these compounds, with trivalent arsenites tending to be somewhat more toxic than pentavalent arsenates.

1.2.1.6 Use of Arsenic Compounds

Arsenic compounds are mainly used in agriculture, livestock, medicine, electronics, industry and metallurgy etc (Ngubane et al.,1994) which are described below-

Field	Use
Agriculture	Pesticides (e.g, Organoarsenicals), insecticides, wood preservatives (arsenates of Cu, Zn, Pb), herbicides, debarking of trees, soil sterling, defoliants
Livestock	Feed additives, disease prevention (Swine dysentery, heartworm infection), cattle and sheep dips, removal of fungus, algaecides.
Medicine	[As(III)] anticancer agent used to treat patients suffering from acute promyelocytic leukemia.
Electronics	Solder cells, opto-electronicdevices, semi-conductor (Gallium arsenic), light-emiting diodes.
Industry	Glassware, electrophotography, catalysts, pyrotecniques, anti-fouling points, dyes and soaps, ceramics, pharmaceutical substances.
Metallurgy	Alloys (automatic body solder and radiators), battery plates (hardening agents).

1.2.1.7 Effects of Arsenic in Human Body

Much smaller amounts of inorganic arsenic in the range of millionths of a gram, if ingested or breathed for years, are sufficient to cause each one of the diseases that kill most in the world, including cerebrovascular disease, cancer, diabetes, dementia and many others

Respiratory effects

Humans exposed to inorganic arsenic naturally and occupationally experience laryngitis, tracheae bronchitis, rhinitis, pharyngitis, shortness of breath, chest sounds (crepitations and/or rhonchi), nasal congestion and perforation of the nasal septum.

Pulmonary effects

Exposure to arsenic increase the risk of chronic lung diseases, including Chronic obstructive pulmonary diseases (COPD) and higher risk for the occurrence of acute coronary syndrome, which represents a set of different clinical conditions induced by a rupture of atherosclerotic plaque in coronary artery, with accompanying thrombosis, inflammation, vasoconstriction and micro embolization .

Hematological effects

The hematopoietic system is also affected by both short- and long-term arsenic exposure. Normocytic and normochromic anemia as well as a significant increase in hemolysis, TBARS production and catalase activity in the blood of arsenic intoxicated pups. Moreover, arsenic produce a significant increase of serum cholesterol, triglicerids and urea levels whereas the proteins diminishes

Anemia and Leukopenia (granulocytopenia, thrombocytopenia, myeloid, myelodysplasia) are common effects of poisoning and is reported as resulting from acute, intermediate and chronic oral exposures. These effects may be due to direct hemolytic or cytotoxic effects on the blood cells and a suppression of erythropoiesis. Relatively high doses of arsenic are reported to cause bone marrow depression in human (EPA, 2007).

Fig 4: Hematologic malignancy

Cardiovascular effects

Cardiovascular diseases such as hypertension, QT prolongation, peripheral arterial disease, atherosclerosis, impaired microcirculation, coronary heart disease, and stroke are well recognized in relation to dose and duration of arsenic exposure. These manifestations may be classified as cardiac and vascular diseases. Also haematopoietic and cardiac stress occurs.

Gastrointestinal effects

The efficiency of absorption of inorganic arsenicals from the gastrointestinal tract depends on their water solubility. Several gastrointestinal symptoms are common and salient features of arsenic intoxication due to ingestion of heavy doses of arsenic. Sub-acute arsenic poisoning from lesser doses of arsenic may manifest as dry mouth and throat, heartburn, nausea, abdominal pains and cramps, and moderate diarrhea. Chronic low dose arsenic ingestion may be without symptomatic gastrointestinal irritation or may produce a mild esophagitis, gastritis, or colitis with respective upper and lower abdominal discomfort. Anorexia, malabsorption and weight loss may be present.

Hepatic effects

Long-term exposure of arsenic leading to hepatic damage

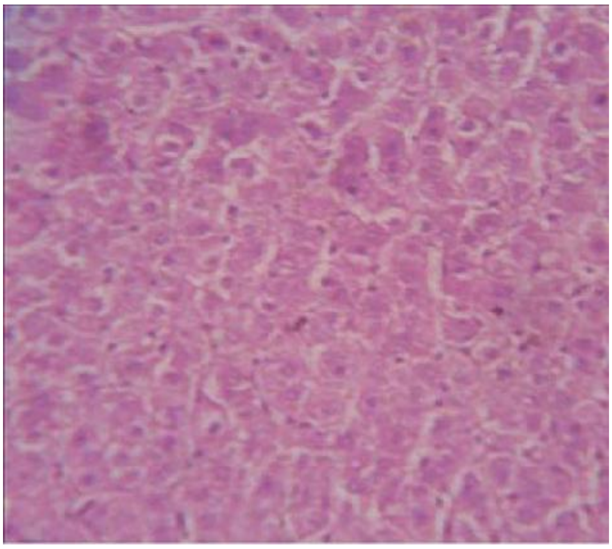

Fig 5: Cross section of liver showing diffused fatty changes in the hepatocytes

Arsenic intoxication leads to hepatocellular injury, fatty degeneration and progressive fibrosis**.** Patients may come to medical attention with bleeding esophageal varices, ascites, jaundice, or simply an enlarged tender liver, mitochondrial damage, impaired mitochondrial functions, and porphyrin metabolism, congestion, fatty infiltration, cholangitis, cholecystitis and swollen and tender liver.

Renal effects

Like the liver, the kidneys will accumulate inorganic arsenic in the presence of repeated exposures. The kidneys are the major route of arsenic excretion, as well as a major site of conversion of pentavalent arsenic. In humans, the kidneys seem to be less sensitive to arsenic than most other organ systems. Sites of arsenic damage in the kidney includes capillaries, tubules and glomeruli, which leaded to hematuria and proteinuria, oliguria, shock and dehydration with a real risk of renal failure, cortical necrosis, and cancer.

Dermal effects

Chronic exposures to arsenic by either ingestion or inhalation will produce a variety of skin insignia of arsenic toxicity (i.e. diffused and spotted melanosis, leucomelanosis, keratosis, hyperkeratosis, dorsum, Bowen's disease, and cancer). Skin disorders are documented in several epidemiological studies in which people consumed drinking water that contained arsenic at the doses of 0.01–0.1 mg As kg^{-1} per day or more. Hyperpigmentation may occur, particularly in body areas where the skin tends to be a little darker.

Fig 6: Hyperpigmentation

Fig 7: Skin disorders in hands

Fig 8: Skin disorders in hands

Neurological effects

The neurobehavioral dysfunction is induced by arsenite exposure. Acute high exposure (1 mg As kg^{-1} per day or more) often causes encephalopathy with symptoms as headache, lethargy, mental confusion, hallucination, seizures. Intermediate and chronic exposures (0.05–0.5 mg As kg^{-1} per day) cause a painful ‘pins and needles’ sensation, wrist or ankle drop, asymmetric bilateral phrenic nerve.

Reproductive effects

Inorganic arsenic readily crosses the placental barrier and affects fetal development. There is an extensive documentation of experimental induction of malformations in a variety of species with increased fetal, neonatal and postnatal mortalities, and elevations in low birth weights, spontaneous abortions, still-birth, pre-eclampsia and congenital malformations.

Immunologic effects

As (III) impairs functions of several key immune cells. At high doses of arsenite (1.9×10^{-5} M) and arsenate (6×10^{-4} M), phytohemagglutinin (PHA)-induced stimulation of human lymphocytes is completely inhibited with an impairment of immune response. Particularly, As (III) inhibits proliferation of T cells, independently of IL-2, and alters the pattern of cytokines secreted by human activated T cells.

Genotoxic effects

The trivalent forms are far more potent and genotoxic than the pentavalent forms, whereas DMA is genotoxic in assays using mammalian and human cells. Enhancing any genotoxicity of As would be the impairment of DNA repair capabilities.

Carcinogenic effects

Arsenical skin cancers commonly occur in the presence of dermatologic manifestations of arsenicism, but there are reports of elevated cancer risks at multiple sites (notably lung, skin, bladder, kidney and liver) from parts of the world including Japan, Bangladesh, West Bengal-India, Chile and Argentina where subsets of the population are exposed to arsenic-contaminated drinking water. Exposure to arsenic compounds can induce changes in global levels of posttranslational histone modifications in peripheral blood mononuclear cells.

Biochemical effects

Arsenic compounds are known to inhibit more than 200 enzymes in humans. Kulanthaivel et al. noted the catalytic action of vicinal thiol groups and that phenylarsine oxide (PAO) inhibited Na^+ and H^+ efflux of human placental Na^+–H exchanger.

As a phosphate analog, arsenate competes with phosphate a enters cells via phosphate transporters arsenate esters hydrolyse many orders of magnitude faster than the equivalent phosphate esters, which results in wasteful ‘futile’ cycles in metabolic pathways, uncoupled oxidative phosphorylation, and extreme DNA instability.

1.2.1.8 Theoretical Aspects for Arsenic

Adsorption

Among other processes for removal of As (III) from ground water, adsorption process is an economically feasible alternative. *Adsorption* is a process in which a single or a group of ions compounds get accumulated on the surface of another solid or liquid.

The substance on which the adsorption takes place is known as adsorbent and the substance, which gets adsorbed, is called adsorbate.

Based on the extent of attraction between the adsorbent and adsorbate, the adsorption process can be classified into two types:

Physical adsorption or vanderWaal's adsorption

Adsorption, which can result from the vander Waal's force of interaction, is known as physical adsorption or vander Wall's adsorption. In this type of adsorption, the process heat is of the order of 20-40 kJ/mol. Physical adsorption process is reversible and established rapidly. Physical adsorption can be of two types, i.e., monolayer adsorption and multi-layer adsorption.

Chemisorption

In chemisorption, the chemical interaction electrostatic force of attraction occur between the adsorbent surface and adsorbate molecules. In this process, the heat of adsorption usually varies from 40 to 400kJ/mol. It is associated with appreciably high activation energy and therefore termed as activated adsorption. It is a relatively slow process.

Physical adsorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. On the other hand chemisorption, in general, is an irreversible process because of strong electrostatic force of interaction between the adsorbent and adsorbate molecules.

Physical adsorption is very effective, particularly at a temperature close to the critical temperature of a given fluid. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physical adsorption, is a specific process, which can only take place on some solid surface for a given fluid.

Contrary to physical adsorption, chemisorption leads to monolayer adsorption. Under favorable conditions, both the processes can occur simultaneously or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic in nature.

Most of the adsorbents possess a complex porous structures that consist of pores of different sizes and shapes. The total porosity is usually classified into three groups:

- micro pores (diameter, d<2 nm),
- meso pores (2<d<50 nm) and
- macro pores (d>50 nm).

The significance of pore size in the adsorption process is well known. Because the size of micro pores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. This is the fundamental difference between adsorption in micro, meso and macro pores. Consequently, the adsorption in micro pore is essentially a pore filling process in which the pore volume is the main controlling factor .In case of mesopores whose walls are formed by a large number of adsorbent atoms or molecules, the boundary of the inter-phase has a distinct physical meaning. That means the adsorbent surface area has a physical meaning. The adsorption forces do not occur throughout the void volume in macro pores but at a close distance from their walls. Therefore, the mono and multilayer adsorption take place successively on the surface of meso-pores and their final fill proceeds according to the mechanism of capillary adsorbent condensation.

The basic parameters characterizing meso-pores are: specific surface area, pore volume and pore size or pore-volume distribution. The mechanism of adsorption on the surface of macro pores does not differ from that of the flat surfaces. The specific surface area of macro-porous solid is very small; that is why adsorption on this surface is usually neglected. The capillary adsorbate condensation does not occur in macro pores. Various forms of chemical adsorbents and materials of biological origin or biosorbents have been shown to be effective metal removers from mining wastewater.

1.2.2 Chromium pollution

1.2.2.1 World Chromite Scenario

The largest proven deposits of chromite are found in South Africa, Zimbabwe and former Soviet Russia. Country-wise data on reserves and production are shown in Table 6.

Table 6: Chromium reserve in world

Country	Chromite (tons)
Albania	20,000
Brazil	9,000
Finland	29,000
India	88,350
South Africa	57,00,000
United States of America	70,000
U. S. S. R.	10,000
Zimbabwe	7,50,000
All World	68,00,000

1.2.2.2 Sources of Chromium

The application of chromium, a heavy metal in various industries, especially in leather tanning has gained a negative impact in the society with respect to its pollution potential. Chromium has several oxidation states ranging from Cr (II) to Cr (VI), but the trivalent and the hexavalent states are the most stable. Cr (VI) is toxic, carcinogenic, and mutagenic to animals as well as humans and is associated with decreased plant growth and changes in plant morphology.Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production (Gao et al., 2007). Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (EPA, 2007).

1.2.2.3 Uses of Chromium Compounds

Due to increase in population coupled with mining, extraction and use of various metals as different industrial and household materials, the load of toxic metal pollution in the environment is increasing. The waste from metallurgical mining sectors, in general, creates destabilization in the ecosystem, as most of the heavy metal ions are toxic to the living organisms. But some of these heavy metals, in traces, play significant role in the human metabolism. The demand of chromium has been increasing globally due to its extensive use in various metallurgical, chemical and leather tanning industries due to its various physic-chemical properties. Some of its important applications are enumerated below:

- Corrosion resistance property of chromium expanded its application in hardened steel, stainless steel and alloys.
- Use in electro-plating to produce a hard, shining surface and prevent corrosion.
- Use to impart a greenish tint to glass.
- Wide use in catalysts preparation.
- Use of $K_2Cr_2O_7$ as an oxidizing agent.
- Use in the textile as a mordant.
- Use as yellow pigments(e.g. lead chromate)
- Use in the aircraft and other industries for anodizing and corrosion resistance.
- Use as chromate in refractory for aluminum forming bricks to give a defined shape as it has a high melting point, moderate thermal expansion and stable crystalline structure.
- Use in open-hearth steel melting furnaces as a major component due to its high melting point ($1700\text{-}1900^0$c) and neutrality, being ideal for separating acidic and basic refractory in wall linings.
- Use in leather tanning.
- Use in industrial chemical synthesis.

Apart from industrial uses, Cr (III) plays an important role in our body (Wang, 2004). Without Cr (III) in our diet, the body loses its ability to use sugar, protein and fat properly, which may result in weight loss or impaired growth, improper function of nervous system and imbibe diabetic conditions. The best-known nutritional effect of chromium is to assist insulin in regulating blood sugar (glucose) levels in human body as established through radio tracing. Insulin is a protein hormone that is released in to the blood when blood glucose level gets high. Insulin then binds to the receptor cells outside, causing to absorb more glucose from blood, returning blood glucose levels to normal.

Due to its strategic importance in different metallurgical processing, chromite is traded in world market either as high-grade ore or intermediate like ferrochrome charge chrome. The finished products of modern technology use ferrochrome of various grades worldwide. There have been attempts to replace chromium by other metals like cobalt, nickel vanadium, molybdenum and columbium in the manufacture of alloy steels. But these are not universally accepted due to their higher cost and marginal advantages over chromium. Therefore, chromium is still the most sought after metal in alloy steel production in addition to its traditional outlets like stainless steel or refractory bricks. A brief list of important uses of chromium for different purposes is given in Table 7.

Table 7: Application of chromium and chromium chemicals in different sectors

SI. No.	Use	Percentage of total consumption
1	Metal finishing and corrosion control	37
2	Pigment and allied products	26
3	Leather tanning and textiles	20
4	Wood preservatives	5
5	Drilling mud	4
6	Catalyst/batteries/ magnetic tapes etc	8

1.2.2.4 Effects of Chromium in Human Body

Chromium occurs in the environment primarily in two valence states, trivalent chromium Cr (III) and hexavalent chromium Cr (VI). Exposure may occur from natural or industrial sources of chromium. Chromium (III) is much less toxic than chromium (VI). The respiratory tract is also the major target organ for chromium (III) toxicity, similar to chromium (VI). Chromium (III) is an essential element in human body. The body can detoxify some amount of chromium (VI) to chromium (III).

The respiratory tract is the major target organ for chromium (VI) toxicity for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure.

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (IV); hexavalent chromium. For most people eating food that contains chromium (III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food in stores in steel tanks or cans chromium concentrations may rise.

Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes.

Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium.

Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium (VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium (VI) are:

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity- Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate and zinc chromate. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.

1.2.2.5 Environmental effects of chromium

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities.

The main human activities that increase the concentrations of chromium (III) are steal, leather and textile manufacturing. The main human activities that increase chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils.

Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water chromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve.

Chromium (III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer.

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops.

Plants usually absorb only chromium (III). This may be the essential kind of chromium. But when concentrations exceed a certain value, negative effects can still occur.

Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation.

1.2.2.6 Theoretical considerations for Chromium

This section describes the various theories based on which our experimental 2 or 3 bands results are interpreted.

Adsorption isotherm model equations

Adsorption isotherm helps in determining the properties of the adsorbents such as pore volume, pore size or energy distribution and specific surface area. The isotherm curve can also be utilized to obtain information concerning the desorption mechanism strictly connected with interaction between the adsorbent and adsorbate molecules. Therefore, the efficiency of an industrial adsorbent can be assessed through this curve. The correct interpretation of experimental adsorption isotherm can be realized in terms of some mathematical equations called adsorption isotherm model equations. Such equations are derived assuming an ideal physical model for the adsorption system. The model assumptions are usually a result of experimental observations. The experimental results allow for the formulation of a hypothesis about the character of the adsorption process. This hypothesis can be tested experimentally and if found suitable, could be developed into a theory, i.e., a suitable adsorption isotherm equation. The adsorption isotherm thus developed provides useful information for estimating performance in a full-scale process stream. Firstly, they help to determine, the possibility to reach a desired purity level for a given adsorbent. This is important when multiple impurities are present and one or more impurities are poorly adsorbed. Secondly, the isotherm allows calculation of uptake (qe) at equilibrium, which has a major impact on the process economy. It can also be used to predict the relative performance of different types of adsorbents.

Prior to 1914 only a few theoretical interpretations of adsorption isotherms were in use. But thereafter, a number of isotherm equations were proposed by different investigators. Some of those in frequent use are:

- Freundlich adsorption isotherm
- Langmuir adsorption isotherm
- Brunneuer-Emmeth-Teller adsorption isotherm
- Temkin adsorption isotherm

Here Freundlich and Langmuir adsorption are described.

a. Freundlich isotherm

Freundlich adsorption isotherm was proposed by Boedecker in 1895 as an empirical equation. Later Freundlich made some useful modifications as a result of which, it assumed great importance.

The Freundlich adsorption equation can be written as:

$$\frac{x}{m}=q_e=kc^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Taking the logarithm of both sides,

$$\text{Log } q_e = \log k + \frac{1}{n}\log c \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where ‘q_e’ is equilibrium adsorption capacity (mg/g), ‘Ce’ is the equilibrium concentration of the adsorbate in solution, ‘K’, and ‘n’ are constants related to the adsorption process such as adsorption capacity and intensity respectively.

b. Langmuir adsorption isotherm

The Langmuir adsorption isotherm was based on the following assumptions:

- Fixed number of adsorption sites: at equilibrium, at any temperature, a fraction of the adsorbent surface sites (θ) is occupied by adsorbed molecules and the rest (1- θ) is free.
- All sorption processes are homogeneous.
- There is only one sorbate
- One sorbate molecule reacts with only one active site.
- No interaction between the sorbate species.
- A monolayer surface phase is formed.

The equation proposed by Langmuir was universally applicable to chemisorption with some restrictions involving physical adsorption. This equation is applicable to the physical or chemical adsorption on solid surface with one type of adsorption active center. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems or for varied conditions within any given system. The Langmuir equation is given by:

$$\frac{Ce}{qe}=\frac{1}{Qeb}+\frac{Ce}{Qe} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where ‘Ce’ is the equilibrium concentration and ‘qe’ is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g); 'Q_0' and 'b' are Langmuir constants related to the sorption capacity and intensity respectively.

Adsorption kinetic models

The study of adsorption kinetics in wastewater is significant as it provides valuable insight into the reaction pathways and into the mechanism of the reaction. Further, it is important to predict the time at which the adsorbate is removed from aqueous solution in order to design an appropriate sorption treatment plant. Any adsorption process is normally controlled by three diffusive transport processes for the adsorbate:

- From bulk solution to the film surrounding the adsorbent.
- From the film to the adsorbent surface
- From the surface to the internal sites followed by binding of the metal ions onto the active sites

But in kinetic modeling, all these three steps are grouped together and it is assumed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for adsorption. Further, it is established from the experimental observations that at optimum agitation speed, the external boundaries have hardly any effect. So application of the kinetic model depends only on the initial and final concentrations of the solution at different time intervals. It is incorrect to apply simple kinetic model such as first and second order rate equations to a sorption process with solid surface, which is rarely homogenous. Secondly, the effects of transport and chemical reaction are often experimentally inseparable.

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto an adsorbent:

- Pseudo first order/Lagergren kinetic model
- First order reversible kinetic model
- Ritchie's second order kinetic model
- Pseudo second order kinetic model

1.3 Literature Review

Over the past few decades, many remediation technologies were applied all over the world to deal with the contaminated aquifers. Many documents and reviews on these technologies for remediating inorganic pollutants are available. A document, summarizing all the applied and emerging technologies for arsenic removal from groundwater, along with their scopes, advantages and limitations will come handy for the scientific research community for designing newer technologies as well as in the decision making process of the heavy metal affected community trying to fish out a suitable solution for their problem. So, in this review, I have focused on the removal of arsenic from groundwater.

As per WHO limit of Chromium in drinking standards, permissible limit of chromium in water is 0.05 mg/litre. According to the Bangladesh standards, the permissible limit of Cr is 0.05 and 0.1 mg/L for potable and industrial discharge water respectively. Most of the chromite mine discharge water in the world contains 2 to 5 mg/L and the effluent from electroplating; ferrochrome and leather tanning industries contain 50 to 100 mg/L of Cr (VI), which is much higher than the permissible limit. So Cr (III) and Cr (VI) removal or reduction in mining and industrial effluents is important before discharge into the aquatic environment. There are various physical and chemical methods used to treat Cr (III) and Cr (VI) contaminated mining and industrial effluents.

All the reviewed technologies have been classified under three categories viz Chemical Technologies, Biological/Biochemical/Biosorptive Technologies, Electrolytic methods and Physico-Chemical Technologies. In some cases, these technologies overlapped. However, this is the consequence of the changing face of the science and technology in the modern world, where interdisciplinary studies are gaining ground over compartmentalized field of studies.

In this review, I have divided the treatment technologies into the following classes:

1.3.1. Chemical Treatment Technologies

1.3.2. Biological/Biochemical/Biosorptive Treatment Technologies,

1.3.3. Electrolytic Methods
1.3.4. Physico-Chemical Treatment Technologies.

1.3.1. Chemical treatment technologies

1.3.1. A. Chemical treatment technologies for Arsenic

Groundwater contaminants are often dispersed in plumes over large areas, deep below the surface, making conventional types of remediation technologies difficult to apply. In those cases, chemical treatment technologies may be the best choice. Chemicals are used to decrease the toxicity or mobility of metal contaminants by converting them to inactive states. Oxidation, reduction and neutralization reactions can be used for this purpose (Evanko and Dzombak,1997). Reduction is the method most commonly used (Yin and Allen, 1999).

In-situ treatment by using reductants

When groundwater is passed through a reductive zone or a purpose-built barrier, metal reductions may occur. Based on both laboratory and field studies, an appropriately created reduced zone can remain in reducing conditions for up to a year (Fruchter et al.,1997). Manipulation of sub-surface redox conditions can be implemented by injection of liquid reductants, gaseous reductants or reduced colloids.

Reduction by using Fe base technology

Ponder suggested that the As (III) removal was mainly due to the spontaneous adsorption and coprecipitation of As (III) with Fe (II) and Fe (III) oxides/hydroxides formed in-situ during ZVI oxidation (corrosion). The oxidation of ZVI by water and oxygen produces Fe(II) (Ponder et al.,2000):

$^{0}Fe+2H_2O\rightarrow 2Fe^{2+}+H_2+2OH^{-}$

$^{0}Fe+O_2+2H_2O\rightarrow 2Fe^{2+}+4OH^{-}$

Fe(II) further reacts to give magnetite (Fe_3O_4), ferrous hydroxide ($Fe(OH)_2$) and ferric hydroxide ($Fe(OH)_3$) depending upon redox conditions and pH:

$6Fe^{2+}+O_2+6H_2O\rightarrow 2Fe_3O_4(s)+12H^{+}$

$Fe^{2+}+2^{-}OH\rightarrow Fe(OH)_2(s)$

$6Fe(OH)_2(s)+O_2 \rightarrow 2Fe_3O_4(s)+6H_2O$

$Fe_3O_4(s)+O_2(aq)+18H_2O \leftrightarrow 12Fe(OH)_3(s)$

Recent research suggests that the formation of Fe^{2+} and H_2O_2 on the corroding Fe^0 surface in turn forms OH• radical (Joo et al.,2004).

$^0Fe+O_2+2H^+ \rightarrow Fe^{2+}+H_2O_2$

$Fe^{2+}+H_2O_2 \rightarrow Fe(OH)_2+OH\bullet$

The As (III) oxidation reaction then proceeds as:

$$2OH\bullet + H_3AsO_3 \rightarrow H_2AsO_4^- + H_2O + H^+$$

1.3.1. B Chemical methods for Chromium

Amongst the chemical methods, the use of $FeSO_4$ for reduction of Cr (VI) is by far the easiest and efficient process. Apart from the ease of process, the chemical is cheap and available in plenty. Water treatment plants in industrial belts use FeSO4 extensively. Some industrial effluents like those from leather tanning plants contain very high levels of Cr (III) as well as Cr (VI). These are usually precipitated after reducing Cr (VI) to Cr (III) as hydroxides (at pH ~9.0) by the application of alkali and slight heating (60-80 ^0C) to coagulate the precipitate. Iron scraps are most devoured as reducing agent followed by neutralization and precipitation of Cr (VI) from electroplating wastes. At times, iron scraps are deliberately put into effluent treatment ponds to facilitate reduction. Polymeric ferrous sulphate is also used along with polyacrylamide as a coagulant for tannery wastewater treatment. Ferric hydroxides have been found to catalyze the reduction of Cr (VI) to Cr (III). Some of the exogenous heavy metal ions including Cr (VI) have been found to be retained by the iron oxide present in soil fraction.

1.3.2. Biological, biochemical and biosorptive treatment technologies

1.3.2. A. Biological, biochemical and biosorptive treatment technologies for Arsenic

Biological activity in the sub-surface

Potentially useful phyto remediation technologies for remediation of As-contaminated sites include phytoextraction, phytostabilization and rhizofiltration (Evanko and Dzombak, 1997) evaluated the feasibility of using biological methods for the remediation of As contaminated groundwater.

Enhanced biorestoration

Many of the biorestoration processes first pumped out the leaked contaminants as far as possible. Some of them have been discussed here.

In-situ bioprecipitation process (ISBP)

In situ bioprecipitation (ISBP), involves immobilizing the As in groundwater as precipitates (mainly sulphides) in the solid phase. Carbon sources such as molasses, lactate, acetate and composts are injected in the aquifer where they undergo fermentation and trap the metal ions in an organic matrix. The ISBP process was investigated for stabilizing As and was shown to be feasible as a strategy for improving groundwater quality (Navarro and Alguacil, 2002). However, the stability of As precipitates in the ISBP remains to be a questionable issue.

In-situ As removal from contaminated groundwater by ferrous oxides and micro-organisms

The micro-organisms *Gallionellaferruginea* and *Leptothrixochracea* were found to support biotic oxidation of iron, where iron oxides and these micro-organisms were deposited in the filter medium, offering a favorable environment for arsenic adsorption. These micro-organisms probably oxidized As (III) to As (V), which got adsorbed in Fe (III) resulting in overall arsenic removal of up to 95% even at high initial As concentrations of 200 $\mu g\ L^{-1}$.

Biosorption

Experiments with various biosorbents showed promising results.

Metal uptake by organisms

The involvement of hydroxyl (–OH), alkanes (–CH), nitrite (–NO_2) and carboxyl group (–COO) chelates in metal binding was indicated by the FTIR analysis. The presence of common ions viz. Ca^{2+}, Mg^{2+}, Cl^{-}, $SO_4^{=}$, $PO_4^{=}$did not significantly interfere with metal uptake properties even at higher concentrations. Isolated fifteen fungal strains from soils of West Bengal, India can test the biological removal of As. The *Trichoderma* sp., sterile mycelial strain, *Neocosmospora* sp. and *Rhizopus* sp. fungal strains were found to be most effective in biological uptake of As from soil, the removal rate ranging between 10.92 and 65.81% depending on pH.

1.3.2. B. Biological or microbial treatment methods for Chromium

The use of biological process to treat wastewater containing heavy metal ions is a recent development although the technique has been extensively used in chemical and pharmaceutical industries in a commercial scale. The knowledge gained in these industries is now being extended to address various problems related to environment. The use of biotechnology is slowly gaining importance due to the advanced knowledge as well as sufficient availability of waste biomass for further use. A chromium resistance Shwanella algae bry was reported to remove Cr (VI) and Cr (III) from wastewater under anaerobic conditions (Verma et al., 2006) reported the use of microorganisms to remove Cr (VI) and Cr (III) from solution. Chromate bearing cooling tower wastewater was purified in 20 L continuous stirred tank reactor using Psedominant mendocina. The process efficiency was found to be more than 99.9% in when the Cr (VI) and Cr (III) concentration varied in the range 25 to 100 mg/L and the retention time varied between 4.5 to 8 h. The microorganism efficiently withstood wide variation in pH (6.5-9.5) and heat (25-40 0C). Batch reduction and adsorption of Cr (VI) from aqueous solutions by Corncob under highly acidic conditions (pH~1) was reported . A two-stage process was developed to treat Cr (VI) contaminated water using E. coli strain. In the first step, the microorganisms were grown in a chemostat and after the growth; the bacterial solution was pumped into a plug flow reactor operated under anaerobic condition. The flow rate and retention time was regulated to maximize the conversion. Peat moss was also used to treat Cr (VI) contaminated water. The peat moss was found to adsorb Cr (VI) at a pH of 2.0. Initially the Cr (VI) was reduced to Cr (III) followed by biosorption and the total process was carried out at pH 2.0. Bio-sorption of heavy metal ions under acidic conditions from industrial wastewater using the green algae Cladophora crispate was also reported (Ozer, 2006). The optimum conditions for adsorption also have been established.Sulphate reducing bacterial strains isolated from a metal finishing waste to treat Cr (VI) contaminated water, (Li et al., 2007) also used sulfate reducing microorganisms to treat Cr (VI) contaminated solutions. The microbial/biological processes are inexpensive and pollution free. But the technique is relatively new and requires special skill in handling the microbe strains for treating the metal contaminated solution. Since long-term impacts of most of the strains are not yet known, many are skeptical and advocate further intensive studies before employing such microorganisms in environmental processes.

1.3.3. Electrolytic methods for Chromium treatment

An innovative technique of Cr (VI) reduction is the in-situ electrolytic generation of ferrous ion from consumable anodes immersed in feed water so that instantaneous reaction takes place. It is the most suitable method since the current applied and potential difference is very low. Consumable electrode is inexpensive. It does not add any undesirable ion into the downstream water. The acidification of the waste in an anode compartment followed by reduction in the cathode compartment. The cathode used was porous carbon in which instantaneous reduction took place. Simultaneously, the reduced chromium was precipitated as insoluble chromium compound within the pores. After separating the sludge, the water was recycled. The removal of Cr (VI) from partially saturated kaolinite clay soil using an electro-kinetic process. An electroplating wastewater containing Cr (VI) in the concentration range of 0.2 to 3.8 g/L and pH ~1.5 was subjected to electrochemical precipitation at 75 V, 4.8 A with 50 minutes retention time. The resultant concentration could be brought down to < 0.2 mg/L. The process economy showed good comparison with the conventional process. Reaction kinetics of the iron solution from consumable anode was reported to be of third to first order. The mechanism was reported to be the adsorption of various trace metal ions (like Cr, Fe, Zn, Bi and Sb) on ferrihydrite produced by the hydrolysis of the electrolytic iron. Wastewater samples containing heavy metals, suspended solids, oils, colloids and organics are subjected to direct current to neutralize the ionic and other charged particles before coagulation.

1.3.4. Physico-chemical treatment technologies

1.3.4. A Physico-chemical treatment technologies for Arsenic

The techniques are dependent upon physical processes or activities such as civil construction of barriers, physical adsorption or absorption, mass transfer as well as harnessed chemical or biochemical processes are discussed here. Most of the times, two or more processes are coupled together to deal with the contamination problem.

Adsorption

Adsorption by commercial and synthetic activated carbon

Commercial activated carbons was extensively used for As (III) and As(V) adsorption from water (Navarro and Alguacil, 2002). GAC provided support for ferric ions that were impregnated on it using aqueous ferrous chloride ($FeCl_2$) followed by NaOCl oxidation. Prepared iron containing mesoporous carbon (IMC) from a silica template (MCM-48) and used it for As removal from drinking water. The IMC had a BET (Brunauer, Emmett and Teller) surface area of 401 m^2 g^{-1} while mesoporous carbon had 503 m^2 g^{-1}. The maximum adsorption capacities were 5.96 mg As g^{-1} for arsenite and 5.15 mg As g^{-1} for arsenate.

Adsorption in industrial byproducts and wastes

They were found to be good substitutes for activated carbons. Bio-char from fast wood/bark pyrolysis were effectively investigated as adsorbents for As^{3+} from water (Mohan and Chander, 2006). Maple wood ash without any chemical treatment could also be utilized to immobilize As (III) and As (V) from contaminated aqueous streams in low concentrations (Rahman et al., 2004). Static tests removed ≤80% As, while dynamic column experiments reduced the As concentration from 500 ppb to <5 ppb.

Use of ferrous materials as adsorbents

Some researchers proposed the use of Fe oxides, oxyhydroxides and sulphides to sorb or immobilize a range of heavy metals from groundwater and wastes (Mohan and Chander, 2006).

Using different mineral derived products for heavy metal adsorption

Table 8: Overview of the traditional arsenic removal methods (Freenstra et al., 2007)

Techniques	Advantages	Disadvantages
Oxidation/Precipitation		
• Air oxidation	relative simple, low-cost	partial removal of arsenic slow process
• chemical oxidation	relative simple and rapid process, oxidizes other impurities and kills microbes	
Coagulation/Co-precipitation	no monitoring of break through is required low costs and simple chemicals	toxic sludge is produced operation requires training
• Alum coagulation	chemicals normaly available low capital costs	pre-oxidation is a must, low removal of Asproduces toxic sludges
• Iron coagulation	efficient at low costs simple operation common chemicals	medium removal of As (III) pre-oxidation may be required
• Lime softening	common chemicals	re-adjustment of pH is required large waste
• Enhanced Coagulation	high removal efficiency of As,organic matterand metal hydroxides	emerging technique, not proven on practical

Sedimentation Oxidation/Filtration	simple	low reduction
• Adsorption	no daily sludge problem	requires monitoring break throughrequires periodical regeneration or medium shift
• Activated Alumina	well known, commercially available, very efficient removal, low maintenance, no daily sludge	re-adjustment of pH required toxid solid waste monitoring is difficult

Compared to the other water treatment processes, the adsorption process has many advantages such as:

- Low cost of adsorbent
- Easy availability of adsorbent
- Utilization of industrial, biological and domestic wastes as adsorbent
- Low operational cost
- Ease of operation compared to other processes
- Re-use of adsorbent after regeneration
- Capacity of removing heavy metal ions over a wide range of pH and to a much lower level
- Ability to remove complex form of metals that is generally not possible by other conventional method
- Environment friendly, cost effective and technically feasible alternative due to utilization of biomaterials.

The major advantages of biosorption over other conventional treatment methods are:

- Low cost,
- High efficiency of metal removal from dilute solution,
- No additional nutrient requirements

- Regeneration and recycling of the biosorbent and
- Possibility of metal recovery

1.3.4. B. Adsorption treatment methods for chromium

Among other processes for removal of Cr (III), Cr (VI) from industrial mining wastewater, adsorption process is an economically feasible alternative. Adsorption is a process in which a single or a group of ions compounds get accumulated on the surface of another solid or liquid. The substance on which the adsorption takes place is known as adsorbent and the substance, which gets adsorbed, is called adsorbate. Based on the extent of attraction between the adsorbent and adsorbate, the adsorption process can be classified into two types:

- Physical adsorption or vanderWaal's adsorption
- Chemisorption

Adsorption, which can result from the VanderWaal's force of interaction, is known as physical adsorption or VanderWall's adsorption. In this type of adsorption, the process heat is of the order of 20-40 kJ/mol. Physical adsorption process is reversible and established rapidly. Physical adsorption can be of two types, i.e., monolayer adsorption and multi-layer adsorption. In chemisorption, the chemical interaction electrostatic force of attraction occur between the adsorbent surface and adsorbate molecules. In this process, the heat of adsorption usually varies from 40 to 400kJ/mol. It is associated with appreciably high activation energy and therefore termed as activated adsorption. It is a relatively slow process. Physical adsorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. On the other hand chemisorption, in general, is an irreversible process because of strong electrostatic force of interaction between the adsorbent and adsorbate molecules. Physical adsorption is very effective, particularly at a temperature close to the critical temperature of a given fluid. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physical adsorption, is a specific process, which can only take place on some solid surface for a given fluid. Contrary to physical adsorption, chemisorption leads to monolayer adsorption (Malik, 2004),. Under favorable conditions, both the processes can occur simultaneously or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, there by, this process is exothermic in nature. Most of the adsorbents in industrial possess have a complex porous structures that consist of pores of different sizes and shapes. The total porosity is usually classified into three groups: micro pores (diameter, $d<2$ nm), meso pores ($2<d<50$ nm) and macro pores ($d>50$ nm). The significance of pore size in the adsorption process is well known. Because the size of micro pores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. This is the fundamental difference between adsorption in micro, meso and macro pores. Consequently, the adsorption in micro pore is essentially a pore filling process in which the pore volume is the main controlling factor. In case of mesopores whose walls are formed by a large number of adsorbent atoms or molecules, the boundary of the inter-phase has a distinct physical meaning. That means the adsorbent surface area has a physical meaning. The adsorption forces do not occur throughout the void volume in macro pores but at a close distance from their walls. Therefore, the mono and multilayer adsorption take place successively on the surface of meso-pores and their final fill proceeds according to the mechanism of capillary adsorbent condensation. The basic parameters characterizing meso-pores are: specific surface area, pore volume and pore size or pore-volume distribution. The mechanism of adsorption on the surface of macro pores does not differ from that of the flat surfaces. The specific surface area of macro-porous solid is very small; that is why adsorption on this surface is usually neglected. The capillary adsorbate condensation does not occur in macro pores. Various forms of chemical adsorbents and materials of biological origin or biosorbents have been shown to be effective metal removers from the industrial and mining wastewater. The adsorption process has many advantages such as:

- Low cost of adsorbent
- Easy availability of adsorbent
- Utilization of industrial, biological and domestic wastes as adsorbent
- Low operational cost

- Ease of operation compared to other processes
- Re-use of adsorbent after regeneration
- Capacity of removing heavy metal ions over a wide range of pH and to a much lower level
- Ability to remove complex form of metals that is generally not possible by other conventional method
- Environment friendly, cost effective and technically feasible alternative due to utilization of biomaterials.

Due to ease of techniques operation, the adsorption has been used widely to treat metal ion containing wastewater. Nut shell and flax, being cheap and easily available, are used widely either as such or in treated from to remove metal ions from wastewater (Argun et al., 2006). Sorption studies were carried out mostly in batch scale and various adsorption parameters affecting the overall process were studied. Use of nut shell and flax were also reported to remove metal ions from wastewater.

Nut shell can be used widely to treat wastewater to remove organic or inorganic pollutants because of their large specific surface area, high adsorption capacity and special surface chemical properties. These physical and chemical properties of nut shell depend on pore size, pore distribution and number of surface oxygen groups. The pore size and pore volume can be controlled during the activation process such as activation time, activation agent and temperature. The surface oxygen also can be changed by using suitable oxidizing agents and thermal treatment in order to get the surface functional groups such as carboxyl, phenolic and lactonic group attached to carbon. These groups can improve the adsorption capacity and selectivity on a certain adsorbate in the gaseous or liquid phase.

Waste microorganisms usually in the form of dead cells are also used as an alternative adsorbent for the treatment of heavy metal containing wastewater. In this process biological materials accumulate heavy metals from wastewater by either metabolically mediated or purely physico-chemical pathways of uptake. The major advantages of biosorption over other conventional treatment methods are:

- Low cost,

- High efficiency of metal removal from dilute solution,
- No additional nutrient requirements
- Regeneration and recycling of the biosorbent and
- Possibility of metal recovery

The bioadsorbents (nut shell and flax) can take up metal ion in numerous pathways. The mechanisms of biosorption have been discussed and reviewed the unknown ways in which bioadsorbents can take up toxic metals. The uptake of heavy metal ions can take place by entrapment in the cellular structure and subsequent sorption on to the binding sites present in the cellular structure.

1.4 Instrumentation

1.4.1 Atomic Absorption Spectrophotometry (AAS)

Atomic absorption spectrophotometry (AAS) today has become one of the most routinely used analytical methods for the determination of about 70 trace elements in a variety of sample matrices. The commonly used technique of atomization in this method is the use of air acetylene and N_2O- acetylene flame. The main limitation of flame AAS technique is its limited sensitivity. After the introduction of graphite furnace – AAS (GFAAS) for the atomization of large number of trace elements, particularly the refractory elements like Al, Mo, B, Co etc. The sensitivity of detection has been significantly improved. Although solid samples can be analyzed by GFAAS method, it is desirable that all analyte samples are introduced into the analytical system in the solution form. And in some specific cases like As, Se, etc if required to be analyzed GFAAS technique (especially for small analyte samples). Matrix modifier is to be used to minimize analyte loses at high temperature. Otherwise, such elements are analyzed by hydride vapour generator and flame or electrothermal atomization technique (HVG-AAS). AAS is one of the advanced instrumental analytical methods. Modern AAS instruments are fully computerized. The purpose of this manual is therefore, to provide instructions on the basic principle of AAS, its instrumentations and how to safely use this instrumental analytical method for solving analytical problems of diverse nature.

1.4.1.1 Analytical Principle of FAAS

Beer’s – Lambert Law

Atomic Absorption Spectrophotometry (AAS) is basically an analytical spectroscopic method. It is based on the principle of quantitative measurement of light absorption by atomic species present in an atomic vapor cloud known as the plasma formed by atomizing the analyte substance at high temperature. Though this plasma when a monochromatic light beam passes, some portion of the light is absorbed by the chemical species in the atomic state present in the plasma. The Beer’s Lambert law of light absorption as stated below is used for analytical quantification of the atomic species.

According to Beer’s – Lambert Law

$A = -\log (I/I_\circ) = -\log T = abc$

Where, A = total absorption of light

a= absorptivity co-efficient

b = light path

c = the concentration of the absorbing species in the light path, that is analyte concentration.

T = Transmittance

$I_\circ$ = Incident light intensity

I = transmitted light intensity

According to the fundamental principle of AAS, a particular energy level of an atom is excited to the higher energy level by a monochromatic light beam of the same energy, emitting from the light source consisting of the same element in an inert atmosphere.

The absorbing atomic species in the light path exist in the form of a cloud known as atomic plasma of the element of interest.

Since the wavelength of the light source, selected by the monochromator is the same as that of the excited level, the absorbance is maximum. Such an absorbance is known as the resonance absorbance. Because of these two factors, AAS is highly selective and sensitive. The energy level diagram of excited atom in both the absorption and emission modes of AAS in shown in following figure:

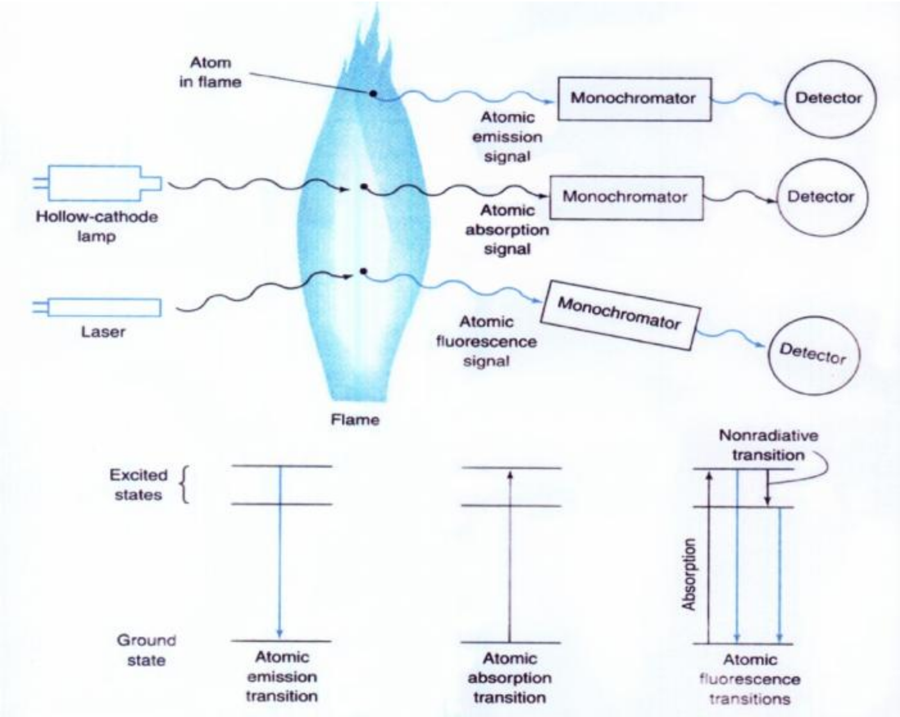

Figure 9: Schematic representation of absorption, emission and fluorescence by atoms in a flame

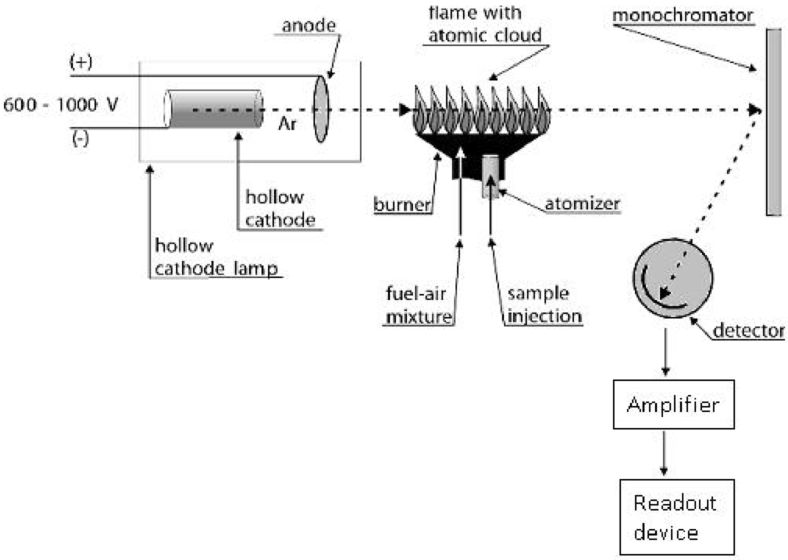

Figure 10: Block diagram of spectrometer

1.4.1.2 Hydride Generation AAS:

Atomic absorption absorption spectroscopy (AAS) is one of the commonest instrumental methods for analyzing for metals and some metalloids. But because of interferences, poor reproducibility, and poor detection limits an alternative method for some elements--mostly metalloids--has been developed.

Hydride generation atomic absorption spectroscopy (HGAAS) is available via an option for many modern AAS instruments. It "only" requires the hydride generation module. Metalloids like antimony, arsenic, selenium, and tellurium are now routinely analyzed by HGAAS (see www.shsu.edu/~chm_tgc/sounds/sound.html). Inductively coupled plasma (ICP) is also a powerful analytical, instrumental method for these elements but at this point its much higher cost limits it widespread use as compared to AAS or HGAAS. As the animation on HGAAS here shows, many of the main parts of the HGAAS system are identical to that of AAS: a hollow cathode lamp, air/acetylene flame, and optical system but include (in most systems) an optical cell and the relatively complex hydride generation system.

The nebulizer required in AAS is not used in HGAAS. The system described here is a continuous flow system, but batch flow systems have been used in the past. The job of each component is detailed below:

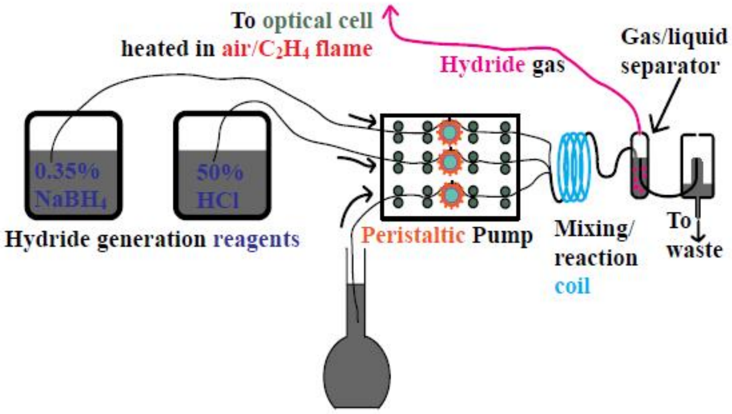

Fig 11: Hydride Generator

The process of lighting the AAS flame involves first putting the optical cell in place and connecting the hydride gas transfer line. Next the fuel and the oxidant are turned on and then the flame is lit with the instrument's auto ignition system (a small flame or red-hot glow plug). After only a few minutes the flame is stable. Deionized water or a dilute acid solution can be aspirated between samples (but experimentation is required to ascertain what produces the best reproducibility). An aqueous solution with the correct amount of acid and no analyte is often used as the blank. To stabilize the HGAAS system the acidic blank is often flowed through the sample inlet tube for 5 or 10 minutes; although the longer this goes on, the more acidic waste is produced. Careful control of the fuel/air mixture is important because each element's response depends on successful decomposition of the volatile hydride in the heated optical cell. Remember that the flame's heat must break down the hydride and reproducibly create the elemental form of the analyte atom. Optimization is accomplished by aspirating a solution containing the element (with analyte content about that of the middle of the linear response range) and then adjusting the fuel/oxidant mix until the maximum light absorbance is achieved. Also the position of the burned head, optical cell, and sample uptake rate are similarly "tuned." Most computer controlled systems can save variable settings so that methods for different elements can be easily saved and reloaded.

Shut down involves aspirating deionized water through all three inlet tubes (borohydride, acid, and sample inlets) for a short period and then closing the fuel off first. Most modern instruments control the ignition and shutdown procedures automatically. The plastic tubing that is stretched around the peristaltic pump head is loosened to length its lifetime. Finally the purge gas is turned off.

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CHAPTER TWO: ANALYTICAL FRAMEWORK OF THE RESEARCH

2.1 Materials and Methods

2.1.1 Collection of Adsorbents

Collection of Adsorbents for Arsenic Removal

Collected adsorbents which are available in our country are shown in table 9.

Table 9: Collection sites of the adsorbent

Adsorbents	Collection Site
Jute Stalk	Faridpur
Cotton Stalk	Mirpur Ceramic Factory, Dhaka
Cotton Seed Hull	Kapasia, Gazipur, Dhaka
Wheat Husk	Comilla
Saw Dust of Burmatic Tree	Chittagong
Baggase	Kustia
Banana Pith	Narsingdi
Coir Pith	Comilla
Flax	Mirpur Ceramic Factory, Dhaka
Nut Shell	Comilla
Water Hycinth	Mirpur, Dhaka
Duck Weed	Mirpur, Dhaka
Rice Straw from Jhum Culture	Chittagong

Collection of Adsorbents for Chromium Removal

Collected adsorbents for removal of chromium are mentioned in the table 10.

Table 10: Collection sites of the adsorbent

Adsorbents	Collection site
Coconut fibre	Brahmanbaria
Rice straw	Brahmanbaria
Neem bark	Brahmanbaria
Orange peel	Sylhet
Nut shell	Brahmanbaria
Pomelo peel	Brahmanbaria
Water hyacinth	Brahmanbaria
Rice husk	Brahmanbaria
Saw dust	Dhaka
Coconut coir	Brahmanbaria
Flax(Shawn)	Brahmanbaria
Baggage	Gazipur

2.1.2 Digestion of Adsorbents

Sample Preservation

All the adsorbents available in our country were firstly collected and dried in an oven at a temperature of 100 – 105 ^{0} C for an hour. Then the adsorbents were ground to fine powder (80 mesh size) using a moter and stored in a polyethylene bag until used for the acid microwave digestion.

Sample Digestion in Microwave Accelerated Reaction System (MARS)

Digestion of adsorbents was carried out in Microwave Accelerated Reaction System (MARS), model no-MARS 5, supplier- Pinnacle Associates Limited. Duplicate samples (0.5g) of each adsorbent were weighted in the XP-1500 digestion vessel that were soaked in 20% HNO_3 for 24 hours and washed with distilled water and then dried properly. Then the 6ml of HNO_3 was added to the sample drop by drop to wet the sample.

Vessels were then covered with Teflon cover and pushed it by end and checked that the cover fitted well into the vessel. The vessels were then kept for 7-10 minutes for marinating the solid with acid. Then the XP -1500 linear vessels were placed into the support module and placed the disk plate on the Teflon cover, with the flat part of it facing downwards. The safety membrane was also placed properly and then tightens the screw. Now the vessels were taken into the support module and all the support modules were tighten in the same way. The complete vessels module was then placed onto turntable motor assembly of the plant. Then the door of MARS -5 was closed.

Heating Program of MARS

Temperature	75% of 1600w that means 180°C
Ramping Time	15 minutes (time taken to raise the temperature from the room temperature to 180°C)
Holding Time	10 minutes (after raising the temperature from 0-180°C then hold it for 10 minutes)
Cooling Time	15 minutes (time required to cold down from 180°C -60°C or less)

Sample Preparation after Digestion

After completion of digestion it is necessary to cool down the rotor before opening the vessel. The rotor assembly was then move from MARS-5 to fume hood where temperature goes down to 60°C. Under the fume hood loosen the screw of the vent to release the pressure and loosen the upper screw carefully with the torque wrench. The XP-1500 vessels were taken out from the support modules and finally the vessels were opened and the digested samples were rinsed with deionized water repeatedly which were collected into the polyethylene vial separately .The final volume of the sample solution were made up at 10ml.

Analysis of sample by MARS

The solution was further diluted if required for analysis. The solution was then analysis by using an Atomic Adsorption Spectrometer (AA240) to determine the arsenic content and Atomic Adsorption Spectrometer (AA240FS) to determine chromium content in the adsorbents before adsorption experiment. From this analysis we get the following contents of arsenic and chromium in different adsorbents:

Fig 12: Microwave Digester (Microwave Accelerated Reaction System)

Table 11: As content in different adsorbents

Name of the adsorbent	Arsenic content (ppm)
Jute Stalk	0.084±0.003
Cotton Stalk	0.107±0.002
Cotton Seed Hull	0.050±0.001
Wheat Husk	0.023±0.001
Saw Dust of Burmatic Tree	0.474±0.011
Baggase	0.114±0.003
Banana Pith	0.063±0.001
Dhoincha	0.112±0.001
Coir Pith	0.112±0.007
Flax	0.159±0.001
Nut Shell	0.312±0.001
Water Hycinth	0.136±0.0013
Duck Weed	0.098±0.001
Rice Straw from Jhum Culture	0.035±0.0048
Neem bark	4±0.3

Table 12: Cr content in different adsorbents

Name of the adsorbent	Chromium content (ppm)
Coconut fiber	0.78± 0.001
Rice straw	<o.o1
Neem bark	0.02±0.001
Orange peel	<o.o1
Nut shell	<o.o1
Pomelo peel	<o.o1
Water hyacinth	0.74±0.001
Rice husk	<o.o1
Saw dust	<o.o1
Coconut coir	<o.o1
Flax	<o.o1
Baggage	1.54±0.001

2.1.3 Preparation of adsorbents

Preparation of adsorbent for As removal (Duck Weed and Neembark)

Duck weed

Duckweed (khudipana) common name for a group of angiospermic plants of family Lemnaceae under the group Monocotyledons. Lemna minor L. is the scientific name of common duckweed, is a small, free floating aquatic plant fast growing, adapt easily to various aquatic conditions and play an important role in extraction and accumulation of pollutants from waters.

Duckweeds are so named because they are eaten efficiently by waterfowls. The plants also possess characteristics of a weed. They proliferate quickly as feed in aquaculture and livestock farming. Duckweed acts as an excellent biofilter to treat domestic wastewater.

Fig13: Duckweed

Duck weed is available in our country. The duck weed contains various organic functional groups, which are good chelating agents and thus good binder for various metal ions. Therefore, it has the potential to treat ground water containing heavy metal ions. Interest in the use of duck weed as an adsorbent has been stimulated by the good results obtained by other investigators. This duck weed collected from Mirpur, Dhaka, Bangladesh, has been used in this experiment. The duck weed is particularly interesting in Bangladesh because of its high availability and low cost as compared to the other adsorbents.

The duck weed used in the present work was obtained from a local pond in Bangladesh. The chemical composition has been reported as 86% and 97% water, Nitrogen (0.8—7.8%), Carbon(30.5—43.7) and organic matter.

Table 13: Organic composition (% of dry weight)

Component	% of dry weight
protein	6.8 — 45.0
lipid	1.8 — 9.2
crude fiber	5.7 — 16.2
carbohydrate	14.1 — 43.6
ash	12.0 — 27.6

The collected materials were washed with pure water several times to remove dust and fines. The washing process was repeated until the color of the wash water was transparent. The washed materials were then dried in a hot-air oven at 60º C for 24 h. The dried material was sieved into the following five size fractions: 1.68, 1.41, 0.595, 0.250 and < 0.105mm. The materials were used for the removal of arsenic without further physical or chemical treatment.

Neem Bark

Fig 14: Neem Bark

Composition of Neem bark

Protein-3.43%

Alkaloids-.68%

Mineral-4.16%

The neem bark was collected from Netrakona district of thana Purbadhola and the village of Ghagra.

Classification of neem tree:

Classification :

Kingdom : Plantae

Division : Magnoliophyta

Class: Magnoliopsida

Order : Sapindales

Family : Meliaceae

Genus : Azadirachta

Species : A. indica

Scientific Name : Azadirachta indica

Cultivation:

Neem tree can easily be grown in the dry, stony, shallow and clayey soils. It needs very little water and plenty of sunlight. It grows slowly during the first year of planting. It can be propagated through the seeds and cuttings. Young Neem tree can not tolerate excessive cold.

Medicinal uses:

The indigenous people of Nilgiris consume the dried and powered tubulers of the terrestrial orchids as an energizing tonic. Neem also holds medicinal value. Each part of neem is used in the medicines. It has been used in Ayurvedic medicines for more than 4000 years. Neem oil extracted from its seeds is used in medicines, pest control and cosmetics etc. Its leaves are used in the treat Chickenpox. According to the Hindus, it is believed that the Goddess of the chickenpox, Sithala lives in the Neem tree. Neem tea is usually taken to reduce the headache and fever. Its flowers are used to cure intestinal problems. Neem bark acts as an analgesic and can cure high fever as of malaria. Even the skin diseases can be cured from the Neem leaves. Indians even believe that the Neem can even purify diseases.

Other Uses:

People in India use its twigs to brush their teeth. Neem is considered as the useful tree in rehabilitating the waste land areas. Neem seed pulp is useful for methane gas production. It is also useful as carbohydrate which is rich base for other industrial fermentations. Neem bark contains tannins which are used in tanning and dyeing. In south India its wood is used to make the furniture. The bark of the yields the fiber that is woven into ropes. Neem cake is widely used in India as fertilizer for sugarcane, vegetable and other cash crops. Many countries have been consistently growing the Neem tree against the global warming. The worldwide Neem Foundation has helped in making the people aware about the importance of Neem and its uses globally.

Preparation of adsorbents for Chromium removal (Nut shell and Flax)

Nutshell preparation

Nut shell is an agricultural waste material which is available in our country. The waste material is either stockpiled or used as fuel in cooking. The availability of nut shell is quite high and has practically very little commercial value. The nut shell contains various organic functional groups, which are good chelating agents and thus good binder for various metal ions. Therefore, it has the potential to treat wastewater containing heavy metal ions. Interest in the use of nut shell as an adsorbent has been stimulated by the good results obtained by other investigators. This nut shell collected from Brahmanbaria, Bangladesh, has been used in this experiment. It is available in plenty and was collected from a local field. The nut shell is particularly interesting in Bangladesh because of its high availability and low cost as compared to the other adsorbents. The collected nut shell was dried in sunlight until almost all the moisture evaporated. It was ground to a powder and sieved to 20 to 240 mesh.

Flax preparation

Flax is an agricultural waste material which is available in our country. The waste material is used as fuel in cooking. The availability of flax is quite high and has practically very little commercial value. The flax contains various organic functional groups, which are good chelating agents and thus good binder for various metal ions. Therefore, it has the potential to treat wastewater containing heavy metal ions. Interest in the use of flax as an adsorbent has been stimulated by the good results obtained by other investigators. This flax collected from Brahmanbaria, Bangladesh, has been used in this experiment. It is available in plenty and was collected from a local field. The flax is particularly interesting in Bangladesh because of its high availability and low cost as compared to the other adsorbents. The collected flax was dried in sunlight until almost all the moisture evaporated. It was ground to a powder and sieved to 20-240 mesh size.

2.1.4 Adsorption experiments

Column experiments for Arsenic removal

The Duckweeds and Neembark were washed with pure water several times to remove dust and fines until the color of the wash water was transparent. The washed materials were then dried in an oven at 60°C for 24 h. The dried materials were sieved into particle size of 0.105−2.3 mm. Adsorbents kept to the treatment glass columns (2 x 30 cm). The arsenic adsorption was carried out in columns with a stopper for controlling the column eluate flow rate. The adsorption factors including duckweed and Neembark amount, particle size, pH, initial sample concentration, and treatment flow rate were evaluated. The sample solution was passed through the adsorption column, after the pH had been fixed with HCL and NaOH, at a given flow rate. The flow rates of 0.41, 0.55, 0.83, 1.67 and 3.3 mL/min correspond to 3g (Duckweed) and 5g (neembark) of adsorbents. During the treatment, a small piece of tissue paper was inserted in the bottom of the column to prevent loss of adsorbent and kept constant the flow rate with the controlling of the stopper valve. The treatment was performed at ambient temperature. Analyses were performed using Varian Atomic Absorption Spectrometer (Model SpectrAA 240) with a Hydride generation system which is controlled with software Version 5.01 and ICP-MS(BRUKER 820MS). During the analysis time, acid container contains 5M HCl and reductant container contain 0.6% sodium borohydride in 0.5% (w/v) sodium hydroxide of the hydride generation-AAS system.

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

$$\text{Removal (adsorption) efficiency (\%)} = \frac{Co - Ct}{Co} \times 100$$

where C_0 and C_t are the concentration of As in the sample solution before and after treatment, respectively.

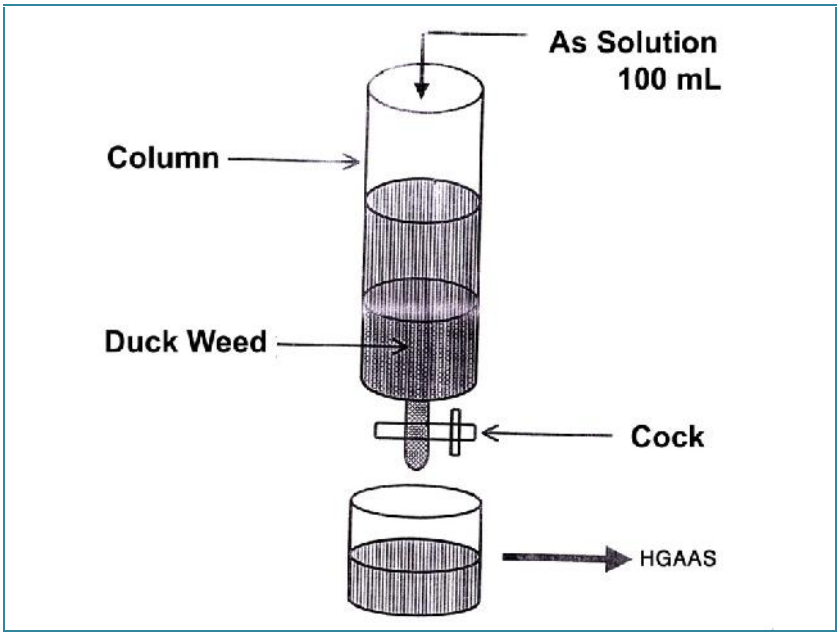

Figure 15: Schematic diagram of column method

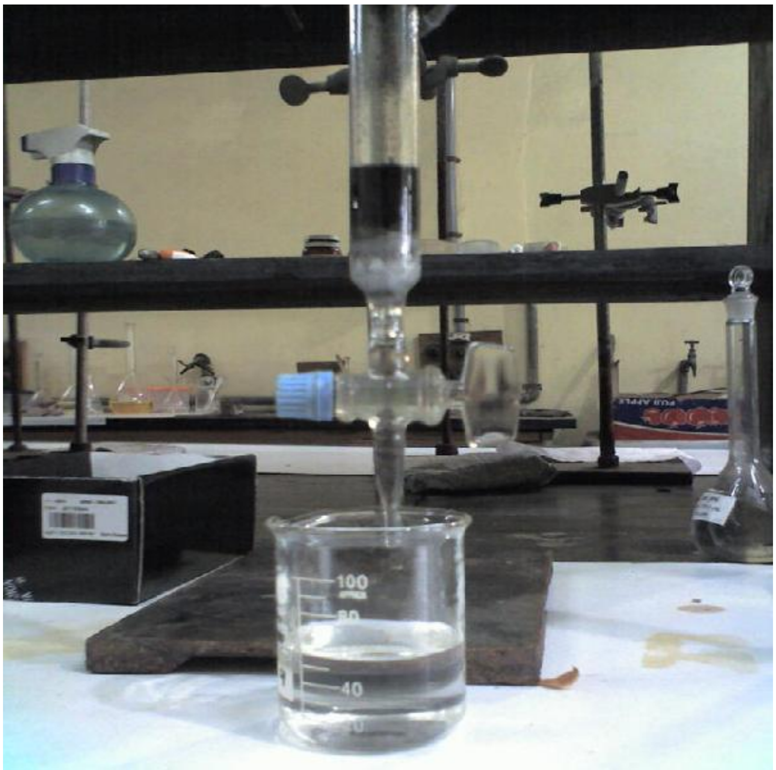

Figure 16: Adsorption Column with adsorbent.

Batch adsorption experiment for Chromium removal:

The sorption studies were carried out at 25±1°C. Solution pH was adjusted with H_2SO_4 or NaOH. A known amount of adsorbent was added to the samples and was agitated by a shaker (Labtech, Korea) at 60 rpm agitation speed, allowing sufficient time for adsorption equilibrium. Then, the mixtures were filtered through filter paper, and the Cr (III) ions concentration were determined in the filtrate using Atomic Absorption Spectrophotometer (Varian AA240FS). The effects of various parameters on the rate of adsorption process were observed by varying contact time, t (30,60, 120, 180, 240, 300, 360, 420 and 480 min), initial concentration of chromium ion, Co (100, 200, 400, 800 and 1600 µg/L), adsorbent concentration, W (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 g/100 mL) and initial pH of solution (1.5, 2, 4, 6, 7, 8, 10 and 12). The solution volume (V) was kept Constant (100 mL).

Fig 17: Shaker (Labtech, Korea)

The chromium removal (%) at any instant of time was determined by the following equation:

$$\text{Chromium removal }(\%) = \frac{Co - Ct}{Co} \times 100$$

Where, Co and Ct are the concentration of chromium at initial condition and at any instant of time, respectively. To increase the accuracy of the data, each experiment was repeated 3 times. Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 10 g/100 mL while maintaining the initial chromium concentration at 200 µg/L.

2.1.5 Standard and sample solution Preparation

Standard Solution and Sample preparation for Arsenic

Reagents

All chemicals used were of analytical-reagent grade. Arsenic standard solutions were prepared immediately before use by appropriate dilution of the 1000 ppm stock solution from Spectropure, USA. Extra pure grade 0.6 % Sodium borohydride ($NaBH_4$) was used to prepare a stabilized solution in 0.5 % (w/v) sodium hydroxide.

Standard arsenic solution preparation

The supplied standard arsenic solution was a solution of 1000 ppm. The solution was diluted to 10 ppm then to required concentrations (100 ppb,200ppb, 400ppb, 800ppb, 1600ppb, 3200ppb) by using the theory of dilution ($V_1S_1 = V_2S_2$), where V_1 is the initial volume , S_1 is the initial concentration , V_2 is the final volume and S_2 is the final concentration of the solution. The standard solution was prepared in desired volumetric flasks.

Sample preparation

The samples and standards were prepared by using 1% KI and 3M HCl and kept for 2 hrs to complete the reduction.

Sample Analysis

Analyses were performed by Atomic Absorption Spectrometer (Model VarianAA 240) and ICP-MS (BRUKER 820MS). The AAS instrument is equipped with a Hydride generation system (Model VGA-77) and controlled with software Version 5.01. Samples were analyzed with HG-AAS using three-point calibration. In the analysis time, acid container contains 5M HCl and Reductant container contain 0.6 % Sodium borohydride ($NaBH_4$) in 0.5 % (w/v) sodium hydroxide.

Optimized conditions for hydride generation

Sample solution acidity: 3.0 M HCl;

Sample solution flow rate: 7 ml/min;

$NaBH_4$ concentration: 0.6 % (w/v) in 0.5 % (w/v) NaOH;

$NaBH_4$ solution flow rate: 1 ml/min;

HCl flow rate: 1 ml/min.

Quality assurance

Quality assurance measures included the calculation of method detection limit, inclusion of recovery and analysis of standard reference materials. Procedural blanks were used throughout sample preparation and analysis to evaluate contamination from reagent, container etc. Procedures for sample preparation and analysis were validated by carrying out analysis in triplicate of water samples, reference material, blank and spike samples. Method accuracy was assessed by analysis of a certified Standard Reference Material (NIST 1640). This Standard Reference Material (SRM) is intended primarily for use in evaluating methods used in the determination of trace elements in fresh water. SRM 1640 is composed of natural fresh water collected from Clear Creek, CO, which has been filtered and stabilized with nitric acid at a concentration of 0.5 mol/L. The average percentage recoveries for the spiked samples were also satisfactory with the falling between 87-102 % (Table 14). Method detection limits (DL) were calculated from the standard deviation of twenty replicates of a low level standard multiplied by 2.539 (In the present case, t test value is 2.539

for degree of freedom 19 at 99% confidence level), and these are also listed in Table 14.

Table 14: Analysis results of Standard Reference Material NIST 1640, % recovery of spikes of the samples with metals, method detection limits

Metal	Reference Water results		Spike Recovery (%)	DL (μg/l)
	Analysed (μg/l)	Certified (μg/l)		
As	26.2	26.67±0.41	95	1.0

Standard Solution preparation for Cr

The supplied standard chromium solution was a solution of 1000 ppm, spectropure, USA. The solution was diluted to 10 ppm then to required concentrations (100 ppb,200ppb, 400ppb, 800ppb, 1600ppb, 3200ppb) by using the theory of dilution ($V_1S_1 = V_2S_2$), where V_1 is the initial volume , S_1 is the initial concentration, V_2 is the final volume and S_2 is the final concentration of the solution. The standard solution was prepared in desired volumetric flasks.

2.1.6 Analytical Condition for Flame Atomic Absorption Spectrometer (VARIAN AA240FS)

The sample solution is aspirated into a flame and the sample element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state. These ground-state atoms can absorb radiation of a particular wavelength that is produced by a special source made from that element. The wavelengths of radiation given off by the source are the some as those absorbed by the atoms in the flame.

Fig 18: Flame Atomic Absorption Spectrophotometer

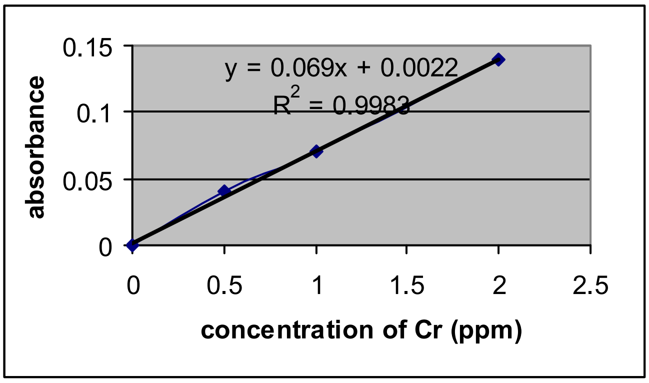

Fig 19: Calibration curve for Atomic Absorption Spectroscopy (AAS)

Condition used in Flame Atomic Absorption Spectrometer:

1. Sampling mode . . . . Manual

2. Instrument mode . . . . Absorbance

3. Flame type and Gas flow (L/min)

a) Fame type . . . . Air / acetylene

b) Air flow 13.50

c) Acetylene flow 2.90

4. Measurement mode . . . . Integration

a) Time (s)

Measurement 7

Read delay 10

b) HC lamp

Lamp Current (mA) 7.0

c) Monochromator

Wavelength (nm) 357.9

Slit with (nm) 0.2

5. Nebulizer Uptake Rate - 5ml/min

6. Sampler

a) Sampling Set up

Probe Height 150mm

Rinse Rate 10

Rinse Time 5

2.1.7 Hydride –Generation Atomic Absorption Spectrometer (Varian AA240)

Fig 20: Atomic Absorption Spectrophotometer

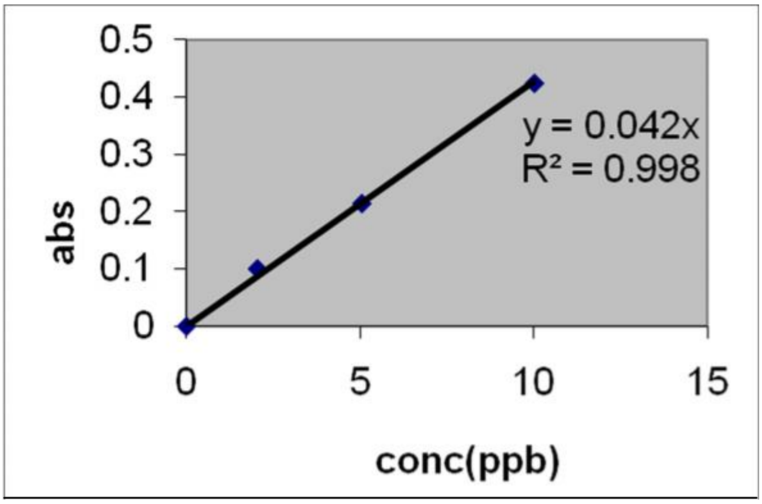

Fig 21: Calibration curve for Atomic Absorption Spectroscopy (AAS)

Condition used in Atomic Absorption Spectrometer

1. Sampling mode . . . . Manual
2. Instrument mode . . . . Absorbance
3. Flame type and Gas flow (L/min)
    a) Fame type . . . . Air / acetylene
    b) Air flow 3.50
    c) Acetylene flow 1.5
4. Measurement mode . . . . Integration
    a) Time (s)
        Measurement 7
        Read delay 45
    b) HC lamp
        Lamp Current (mA) 10
    c) Monochromator
        Wavelength (nm) 193.7nm
        Slit with (nm) 0.5nm

Reagent flow rate------------------------------2.5ml/min

Sample flow rate-------------------------------3.5ml/min

2.1.8 Fourier Transform Infrared Spectroscopy (FTIR) Studies

FTIR analysis of the adsorbents was carried out using JASCO make FTIR-3500 spectrophotometer. Pellets (press disk) were used for measuring absorption spectra. The samples were ground with 200 mg of KBr (spectroscopic grade) in a mortar and pressed into 10 mm diameter disks under 10 tons of pressure and high vacuum for FT-IR analysis. The conditions used were 16 scans at a resolution of 4 cm-1 measured between 600 and 4000 cm-1.

2.1.9 Scanning Electron Microscopy (SEM)

The surface morphology of prepared adsorbents as well as after adsorption of metal ions was investigated from the micrographs of the porous structure by scanning electron microscopy (SEM) (Analytical Scanning Electron Microscope; Model No. JEOL JSM-6490 LA). The SEM was carried out by the bombardment of electrons of 30 KeV on target sample particle which was spread earlier over an aluminum stub with the help of a doubled edged tape followed by coating the surface with Platinum film. Electrons that are emitted from the specimen with energy of less than 50 eV are defined as secondary electrons and are used for specimen investigation.

2.1.10 Real sample processing

For Arsenic Removal

The arsenic contaminated ground water collected from different places of Bangladesh was first allowed to sediment for removing suspending materials. Then the partially clarified effluent is filtered through filter paper of Whatman No-44. The clarified solution was stored in refrigeration system at a temperature of 0-50 C. From here, 100ml solution in each column for optimized amount of adsorbents were used to testify the efficiency of adsorbent in the real sample.

For Chromium Removal

The effluent (mainly tannery effluent) collected from Hazaribag was first sediment to remove suspending materials. Then the partially clarified effluent is filtered through filter paper of Whatman No-44. The clarified solution was stored in refrigeration system at a temperature of $0\text{-}5^0$ C. From here 100ml solution in each batch for 5g of adsorbent was used to testify the efficiency of adsorbent in the real sample.

2.1.11 Materials and methods for the effects of Arsenic in tissues of Singi Fish

Materials for the Study

Shingi fish *H. fossilis* (Bloch, 1772) was used as experimental fish in the present study. The present experiment was performed during the period of March 2010 to February 2011.

Description of the Fish Species under Study

Heteropneustes fossilis has several common names like Asian stinging cat fish or Fossil cat but in our country this fish is locally called Shing fish. In many Asian countries this fish is commercially as well as aquaculturally an important species. It is an indigenous species to Indo-Pak-Bangladesh sub-continent. This cat fish used to belong to the family Heteropneustidae for many years but very recently it has been moved into the Clariidae family.

Scientific Name*: Heteropneustes fossilis (*Bloch)

Local Name: Shingi

Order: Siluriformes

Family: Clariidae

Brief Description

Elongate compressed body. Head depressed with top and sides covered with osseous plates. Occipital process short. 4 pairs of barbels; maxillary pairs extend to end of pectorals or to commencement of anal. Teeth in villiform bands in jaws. On vomer in two narrow patches converging or touching anteriorly.

Fish Sample Collection

Shingi fish, *Heteropneustes fossilis* was used as experimental fish in the present study. The test animal (fish) were obtained from the local markets of Dhaka City (Hatirpul Bazar, Ananda Bazar, Polashi Bazar etc.) in live condition. The fishes were brought to the Aquarium house in oxygenated Polythene bags as recommended by Jhingran (1985). Attempts were taken to use more or less uniform sized fish for this particular experiment.

Special care was taken to make sure that the fish were approximately of similar size and weight. The mean weight and the length of the fish are shown in Table-15.

Table 15: The mean length and weight of *H. fossilis*.

Shingi	Range	Mean
Length (cm)	7.50-8.80	8.15
Weight (gm)	5.50-7.01	6.25

2.1.12 Methods for the study

Techniques for heavy metal analyses

Sample Preparation

The fish samples were cleaned and washed with deionized water. Different organ of fish sample such as gill, liver, stomach, intestine, muscle were collected and frozen.The muscle tissue (edible portion) were taken after removal of internal organs.These frozen samples were cleaned and washed with deionized water.Sample tissue were chopped into pieces with the aid of a stainless steel knife which had been cleaned by acetone and hot distilled water prior to use. These samples were dried in an oven at 65^0C for 48 hours. The dried samples were powdered and homogenized with morter. The sample powders were dried at 105^0C in an oven untill a constant weight was obtained (dry weight). The sample powder was finally preserved in clean and dry polyethene bottle for the consequent analyses.

Reagents

Acids used, namely hydrochloric acid, nitric acid and perchloric acid were of analytical grade and were procured from BDH. Pure metal powder or suitable metal salts available in the purest grade were used for the purpose of elemental analysis. Distilled and deionized water were used throughout the work for sample dilution. Acetylene and nitrous oxide gases were procured from Bangladesh Oxygen Ltd., Dhaka. Air was made available from the atmosphere with the help of an Air-Compressor of Pyc Unicam.

Procedure

The fish samples for atomic absorption spectrometric measurements were prepared by digestion with nitric acid perchloric acid mixture according to the following procedure:

Two grams of the fish power was added to a mixture of 10 ml of 65% nitric acid (HNO_3), 5ml of 70-72% perchloric acid ($HClO_4$) and 5 ml deionized water in Teflon vessel .The vessel was placed in a sealed stainless steel container and heated at $150^{O}C$ for 2 hours in an oven. After cooling the vessel was taken out and the sample solution were transferred to a Teflon beaker containing 25 ml distilled water. The solution was further heated at $100^{o}C$ for 15-20 min. in a hot plate to reduce its volume to about 5 ml. The resulting solution was then filtered: the filtrated was diluted to 100 ml with deionized water and stored in a plastic bottle. This was used as the stock solution for further analysis. An analytical blank was prepared in the similar manner without the sample. Arsenic and cadmium were determined from this solution. Lead, Zinc, Cromium, and copper were determined from diluted stock solution. The determination of metals in fish tissue were carried out by atomic absorption spectrometry (AAS) using an air acetylene flame. Standard stock solution 1000 ppm of each element)were prepared either by dissolving high purity metal powders in appropriate acids or by dissolving high purity metal salts in distilled water.

A series of individual standard working solutions were prepared by appropriate dilution of the 1000 ppm stock solution . The ranges of the standard working solution were chosen to encompass the concentrationsin the fish flesh solution.

Quality Control

All non-acid reactive apparatus were carefully cleaned with hot nitric acid followed by thorough rinsing with deionized water immediately before use. Digestion apparatus was dried at 105ºC in an open air oven. Samples were handled with polythylene gloves and dissection carried out with acid washed stainless steel tweezers, spatulas and knives. Pyrex glassware were used to minimize contamination. Standard reference materials were used to ensure analytical quality.

Analysis of certified sample

The analytical procedure was checked using standard reference materials DORM-2 (dogfish muscle). These fish sample prepared and provided by the National Research Council (NRC), Canada.The results obtained are summarized in Table-2 from which it can be seen that the procedure followed gave analogous results and werein excellent agreement with the certified values if the precision and accuracy of the determination is taken into account.

Table 16: Comparision of our values analysis of standard reference materials DORM-2 (Dog fish muscle) (µg/gm dry weight basis)

Metal	**Concentration**	**µg/gm**	**Deviation (%)**
	Certified value	Our value*	
Pb	0.065±0.007	0.067 ± 0.021	2.99
Zn	25.06±2.30	26.37 ± 2.65	2.92
Cu	2.34 ± 0.16	2.30 ± 0.15	1.74
Cd	0.043 ± 0.008	0.041 ± 0.014	4.88
Cr	34.70 ± 5.50	35.53 ± 4.50	2.39
As	18.00 ± 1.10	17.56 ± 0.52	2.51

* Average of three determination

2.1.13 Techniques for arsenic accumulation in *Heteropneustes fossilis*

Acclimation of experimental fish

On arrival at the laboratory the fish were immediately released into a large glass aquarium containing tap water and maintained there after about seven days static condition. The fish were fed with artificial feed twice daily. The water medium was changed at 24 hours interval to remove the metabolic pollutants. Air compressor with stones was used for oxygenation of water.

The water quality parameter of the acclimation tank was monitored at times. However after acclimation, only healthy fishes of approximately similar size were transferred to the experimental system. During this time length and weight of fishes were noted.

Experimental water

Tap water was the main source of water for all the experimental work and acclimation. The physiological characteristics of test water such as pH, alkalinity, hardness, oxygen concentration, temperature were conducted frequently following the standard procedure.

The toxicant used

In this experiment Arsenic (III) trioxide was selected for the present experiment for its negative impact on both human and animal (fish).

Place and Period of the Study

The experiment was earned out in the Anima! House of the department of Zoology, University of Dhaka located at the animal garden of the department. Analytical and other laboratory works were done both in the Laboratory of the Department of Applied Chemistry and Department of Zoology. The present experiment was performed during the period of March 2010 to February 2011.

Concentration of toxicant used

Three concentration of Arsenic trioxide used in different experimental group of fish.

Table 17: The concentration used in different experimental group of fish

Concentration used	Length (cm)	Weight (gm)
3 ppm	7.50	5.50
7 ppm	8.0	6.20
20 ppm	8.80	7.01

Preparation of toxicant concentrations

Test solution of arsenic (As_2O_3) were made by adding requisite amount of chemical, calculated in terms of active ingredient to tap water. The test chemicals were measured by micropipette. Initially stock solution of dilation was prepared. Calculated amount of stock solution was then added to the experimental tanks to obtain the desired concentrations of the chemical.

Experimental system

The experimental trials were conducted in a laboratory bioassay system. The system consist a no. of glass aquaria each with 20 litter capacity. Before and after each bioassay trial, the aquaria were washed with commercial detergent and then ringed thoroughly with tap water. The aquaria were then sun dried before the fish were exposed to the toxicant and placed on a steel platform serially. Draining of water from the aquaria was done by siphoning. Air compressors with stones were also arranged to ensure oxygenation of water.

Measurement and Analysis of Water Quality

The physical chemical characteristics of test water were measured before and during the experimental trial. Temperature was measured by an N-filled mercury thermometer in °C dissolved -oxygen, P^H, total hardness of water was measured by using portable water kit (F.F-2.HACH, U.S.A).

Fig 22: HACHKIT used for water quality monitoring

Tissue sample collection after exposed to arsenic

Dead fish collected from the aquaria of different experimental group of fish after exposed to As_2O_3. Then the dead fishes were dissected and collect the selected tissue (gills, liver, stomach, intestine muscle).

Water Sample Collection

Water sample were also collected in polythene bottles which were washed and cleaned with deionized water.

Fig 23 (a): Dead fish collected from the Aquaria after exposed to Arsenic

Fig 23 (b): Tissue sample collected from the dead fish.

Fig 24 (a): Aquarium for fish preservation

Fig 24 (b): The experimental system of the aquarium

2.1.14. Procedure for histopathological studies of arsenic exposed tissues

Apparatus

- Oven
- Automatic tissue processor
- Paraffin dispenser
- Ribbon cutting machine (820, ROTARY MICROTOME)
- Warmer/stressor

Reagents

1. Bouins fixative

- Picric acid, saturated aqueous solution- 75ml
- Formalin (40% formaldehyde)- 25ml
- Glacial Acetic Acid- 5ml

2. Wash with 70% alcohol

3. Alcohol (50%, 70%, 80%, 90%, 95% and 100%)

4. Paraffinwax

5. Haematoxyline

6. Eosin

7. DPX

8. Mayor's egg albumen

9. Acetone

10. Xylene

Permanent slides of test *H. fossilis* were prepared by the following methods for histological studies. Histopathological investigation was carried out for 1% formalin treated (for 1 hour) Shingi on thin sections muscle of dorsal side (up to 5 mm thick).

Preparation of sample

The fishes which were treated with 1% formalin (for 1 hour) used for histological studies. After treating with formalin, muscle tissue was taken from dorsal side of the fishes during observations at 6th hour, 12th hour, 16th hour, 20th hour, and 24th hour.

Fixation of Tissue Sample

After dissection the collected tissue were quickly washed with physiological saline solution (0.75%) and then fixed in Bouins fluid. Next they were washed with 70% alcohol (ethanol).

Processing of Tissue

a. Dehydration

The tissue is left in alcohol in the following way:

Alcohol 50% for 15 mins,

Alcohol 70% for 45 mins,

Alcohol 90% for 15-20 mins,

Alcohol 100% for 15 mins.

b. Clearing

After dehydration the tissue were cleared in xylene.

c. Paraffin impregnation

Paraffin bath with temperature range of 60°C-70°C was used. The melting point of the paraffin was 58°C-62°C. The tissue was treated in molten paraffin for 1-2 hours.

d. Paraffin embedding

Embedding in melted was for 30-45 minutes. The tissue was boiled with paraffin was in incubator at 60^0C- paraffin the tissue became rousted.

e. Block making

Paraffin dispenser was used for block making. Molten paraffin was then pored into a block of the iron blocked plate. The tissue was carefully embedded in a paper plane. The blocked plate was allowed to harden in the ice chamber of a refrigerator.

f. Trimming

The blocks were then trimmed properly to the size of the tissue by cutting off the extra paraffin and were kept in the ice chamber for sometime before cutting the section.

g. Section cutting

The block was fitted to the microtome for sectioning. A sharpened microtome knife was used for cutting sections. The temperature of the water bath was maintained between 45°C-50°C for stretching the ribbon on it. Sections were cut at 4-5 micron in thickness.

h. Affixing

The ribbon of tissue was attached on the slide by means of Mayer's albumen. Mayer's albumen:

- Fresh egg's white 50 ml
- Glycerin 50 ml
- Sodium Sal icy late. 5 ml

In 20cc distilled water 3-5 drop of Mayer's albumen was shacked and used.

i. Mayer's albumen

Mayer's albumen was put in the slide. The ribbon of the tissue was arranged in rows putting the slides. The slides were then kept in standing position for some time to drain out the water and then allowed to dry at 25°C-34°C in warmer.

j. Deparaffinization

The slides with ribbons containing tissue were kept in the warmer for melting at 60°C for ten minutes. This was followed by immersing the slides in xylene for ten minutes to remove the wax.

k. Rehydration of tissue

The slides with section of tissue were gradually re hydrated in descending concentration of ethyl alcohol from absolute alcohol to 70% keeping ten minutes in each. At the end of this process tap water was used to remove alcohol.

l. Staining

For staining the following procedure were used-

Dipped in Haematoxyline- 5 minutes washed properly with running water.

Dipped in 0.5% alcohol-15 second, washed again with running water.

Dipped in Ammonia- 1 minute washed with running water.

Dipped in Eosin- 01 to 02 minutes.

m. Dehydration

The slides were then dehydrated gradually with alcohol in the following ways. Alcohol- 70% for 5 minutes, Alcohol- 90% for 3-5 minutes & Alcohol- 100% for 15 minutes.

n. Cleaning

The stained tissues were cleaned in Xylene-1, Xylene-11, and Xylene-111 for two minutes each.

o. Mounting

After cleaning permanent mounting of the slides was made by using Canada balsam.

p. Labeling

Finally the slides were labeled according to the samples and then the slides were ready for observing under compound microscope and photomicrograph.

2.1.15 Photomicrography

The photomicrographs were taken by using a digital microscopic camera. Micrographs of desired muscle tissues were taken at different magnifications using eye piece 10 and objectives 3.5, 10 or 20 as was observed in the laboratory of the Department of Zoology, University of Dhaka. The present experiment was performed during the period of March 2010 to February 2011.

2.2 Removal of Arsenic (III) from Groundwater by Adsorption onto Duckweed *(Lemna minor)*

2.2.1 Introduction

Arsenic (As) is a naturally occurring element, due to the presence of arsenical minerals, (e.g., arsenolite, arsenopyrite, enargite, tennantite etc.), volcanic emissions and inputs from geothermal sources, as well as a consequence of anthropogenic activities, such as mining activities, combustion of fossil fuels and the use of arsenical pesticides (Biterna et al., 2010). A large number of sites worldwide have been contaminated by arsenic from natural and anthropogenic sources (Mandal and Suzuki, 2002). Global concern as a pollutant of drinking water and groundwater, which has been reported in Bangladesh, India, Taiwan, Argentina, Mexico, Hungary, and Chile (Smeldy et al.,2002; Nicolaidis et al.,2004). Increased usage of groundwater for drinking has caused serious health problems (Nickson et al.,1998), because arsenic is known to be highly detrimental to human beings and animals. They include several neurological (Shungi et al.,2003), dermatological (Ayotte et al.,2003), gastrointestinal (Hughes, 2002) and cardiorenal diseases (Chakravarty et al.,2002); arsenic also is a suspected carcinogen (Thommas et al.,2001). Furthermore, recent research has suggested that As is toxic to living organisms at high concentration, and inorganic arsenicals are proven carcinogens to human (Ng JC, 2005). Recently, because of its high nuisance value, various regulatory agencies have revised the maximum contaminant arsenic level 50 to 10 μg/L in drinking water (EPA, 1999; NAPW 2001). This situation will require the development of simple and low-cost methods for the removal of As from groundwater for drinking water.

Arsenic toxicity depends on its speciation, and generally inorganic arsenic species are more toxic than organic species (Ng JC, 2005; Meharg et al.,2002). Arsenic (III) is more toxic than Arsenic (V), and dimethylarsinic acid (DMAA) and mono methyl-arsonic acid (MMAA) are more toxic than their parent compounds (Petrick et al.,2000). In general, in anaerobic ground waters, arsenite [As (III)] predominates, whereas arsenate [As (V)] is more prevalent in surface waters. The As(V) species exists as oxyanions ($H2AsO_4^-$ and $HAsO_4{}^{2-}$) at neutral pH, whereas the predominant

As(III) species is neutral H_3AsO_3 (Ghimire et al.,2003). As (III) is more toxic and more difficult to remove with the conventionally applied physicochemical treatment methods than As(V). Coprecipitation with iron or alum, ion-exchange resin, adsorption onto coagulated floc, reverse osmosis and membrane techniques are widely used to remove As from aqueous solution(Katsoyiannis and Zouboulis, 2004; Kim and Benjamin, 2004; Jay at el, 2004; Maeda et al.,1992). Among these methods, the adsorption techniques are simple and convenient. This method also have the potential for regeneration and sludge-free operation. Metal-loaded coral limestone, activated carbon, activated alumina, reverse osmosis and hydrous zirconium oxide, etc. adsorbents are used for arsenic removal (Maeda et al.,1992; Ohki et al.,1996; Manjare et al.,2005; Hege et al.,2004; Ghosh and Yuan, 1987; Suzuki et al.,1997). But most of these adsorbents are expensive and several problems in terms of efficiency. The purpose of this study was to evaluate the feasibility of using of duckweed without any pretreatment as an alternate adsorbent for removing arsenite from Bangladeshi As-contaminated drinking water samples in a single-step column operation.

2.2.2 Materials and Methods

Reagent

All reagents are analytical grade (Merck, Germany) were used in this study. Standard As (III) solution was supplied by Varian Inc, USA with highest purity level (99.98%). Stock solutions (1000mg/L) of As (III) was prepared by dissolving appropriate weighed quantity of solid $KAsO_2$ in distilled water. Standard dilute solutions were prepared daily before use. Water was purified with an ultrapure water making system (Advantec MFS, Inc., Tokyo, Japan) with a resistivity of >18 MΩ cm.

Preparation of Adsorbent

The dhoincha, duckweed, water hyacinth and wheat husk were collected from local area of Bangladesh. The proximate analysis of dry duckweed is as follows (wt.%): moisture − 3.7; total volatiles (120−950°C) − 78.0 (including volatiles evolved at 120−650°C − 67); fixed carbon − 8.8; ash − 9.5. The ultimate analysis of a dry duckweed is as the following (%): C − 39.11; H − 6.13; O − 37.74; N − 5.52; S −

0.67; balance − mineral matter(Muradov et al.,2010). The Duckweeds were washed with pure water several times to remove dust and fines until the color of the wash water was transparent. The washed materials were then dried in an oven at 60°C for 24 h. The dried material was sieved into particle size of 0.105−2.3 mm. The materials were used for the removal of arsenic without further treatment.

Adsorption and Analytical Procedures

The Duckweeds were washed with pure water several times to remove dust and fines until the color of the wash water was transparent. The washed materials were then dried in an oven at 60°C for 24 h. The dried material was sieved into particle size of 0.105−2.3 mm. Duckweed kept to the treatment glass columns (2 x 30 cm). The arsenic adsorption were carried out in columns with a stopper for controlling the column eluate flow rate. The adsorption factors including duckweed amount, particle size, pH, initial sample concentration, and treatment flow rate were evaluated. The sample solution was passed through the adsorption column, after the pH had been fixed with HCL and NaOH, at a given flow rate. The flow rates of 0.41, 0.55, 0.83, 1.67 and 3.3 mL/min correspond to 3 g of adsorbent. During the treatment, a small piece of tissue paper was inserted in the bottom of the column to prevent loss of adsorbent and kept constant the flow rate with the controlling of the stopper valve. The treatment was performed at ambient temperature. Five experiments for the removal of As. Analyses were performed using Varian Atomic Absorption Spectrometer (Model SpectrAA 240) with a Hydride generation system and controlled with software Version 5.01. During the analysis time, acid container contains 5M HCl and reductant container contain 0.6% sodium borohydride in 0.5% (w/v) sodium hydroxide.

The adsorption efficiency was calculated as the following equation,

$$\text{Removal (adsorption) efficiency} = \frac{Co - Ct}{Co} \times 100$$

Where Co and Ct are the concentration of As (III) in the sample solution before and after treatment, respectively.

Regeneration of Adsorbent

Recovery of the adsorbed material and regeneration of As (III) is also an important aspect of wastewater treatment. Attempt was made to desorb of As (III) from duck weed surface with acid solutions of sulfuric, nitric acid, and hydrochloric and base solutions of sodium hydroxide and potassium hydroxide. This desorption process was performed by the column method. 100 mL of desorption solution was added to the column and was kept for a fixed period of time for each experiment. The solution was passed through the column after the fix time.

2.2.3 Results and Discussion

First, the performances of four adsorbents (Dhoincha, Duckweed, Water hyacinth and Wheat husk) were evaluated for the removal of As (III) from aqueous solutions. The removal efficiencies with Dhoincha, Duckweed, Water hyacinth and Wheat husk were 3.31%, 22.72%, 7.03%and 3.74%, respectively. The adsorbents Dhoincha, Water hyacinth and Wheat husk had lower removal efficiencies than duck weed. Therefore, they were not considered for further investigations. The duck weed used was an available material in the local pond. Because the main component of duck weed is carbon, duckweed has the potential to be used as an adsorbent. Duck weed was chosen for use as an adsorbent material because of its ability to absorb metals and accumulated their tissues.

Effect of Adsorbent Amount

The effect of the amount of Duck weed on the removal of As (III) was investigated. The results are presented in Figure 1. The removal efficiencies of As (III) increased gradually with increasing amount of Duck weed. It is readily understood that the adsorption capacity of Duck weed depends on the surface activity, that is, the specific surface area available for As-surface interactions that is accessible to the As. Hence, increasing the amount of Duck weed will increase removal capacity of As. Until now, various kinds of adsorbents have been studied for the removal of arsenic. The maximum As(III) removal efficiency achieved was 99% for iron oxide-coated sand at an adsorbent dose of 20 g/L with an initial As concentration 100 μg/L in batch studies (Gupta et al.,2005). The removal efficiencies for As(III) from an aqueous solution

(100 μg/L, 100 mL) by 0.1 g of modified fungal biomass were 75%, respectively, after a 12-h batch treatment (Pokhrel and Viraraghavan, 2006). When an aqueous As(III) solution of 10 mg/L concentration was stirred in the presence of both 1.0 g/L TiO_2 and 1.0 g/L activated alumina under sunlight irradiation, the arsenic removal increased with time and reached 89% after 24 h (Nakajima et al.,2005). Although the removal efficiencies in the proposed system were similar to those obtained with the other adsorbents, the treatment time was very short because of the flow method (column system).

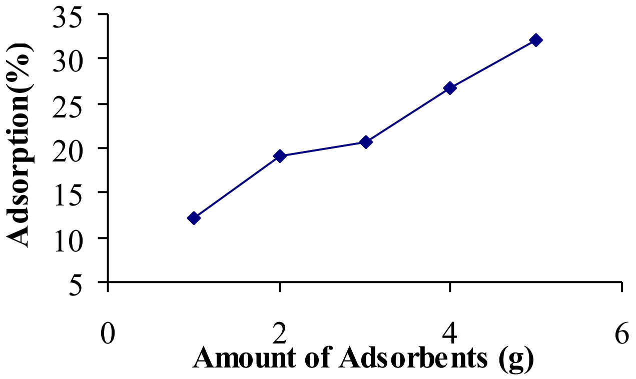

Figure1: Effect of adsorbent amount on the removal of As (III) by adsorption onto duckweed (initial As concentration, 100 µg/L; pH, 5.5; Treatment flow rate 1.67 mL/min)

Effect of Flow Rate

The treatment flow rate is one of the effective factors in column adsorption process. The effect of the treatment flow rate on the removal of As (III) is illustrated in Figure 2. The removal efficiency for As (III) increased gradually with decreasing treatment flow rate. This is because, when the flow rate was slow, As (III) in the sample solution got more contact time with the active surface of the adsorbents.

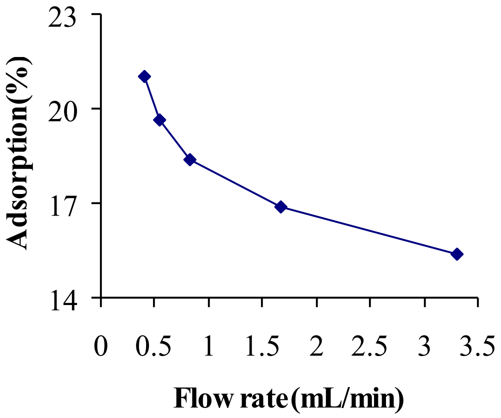

Figure 2: Effect of treatment flow rate on the removal of As (III) by adsorption onto duck weed (initial As concentration, 100 µg/L; pH, 5.5; amount of adsorbent 3g)

Effect of Particle Size

Column adsorption experiments were carried out for the removal of arsenic from aqueous solution using five different particle sizes (0.105 mm, 0.25 mm, 0.595 mm, 1.41 mm, and 2.3 mm). The results are shown in Figure 3. With decreasing particle size, the removal increased from 19.84% to 80.86% for As (III). Munaf and Zein reported that, when the size of adsorbent particles increased, the adsorption of metal ions decreased (Munaf and Zein, 1997). Similar trends have been reported by Wong et al.,2003. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites.

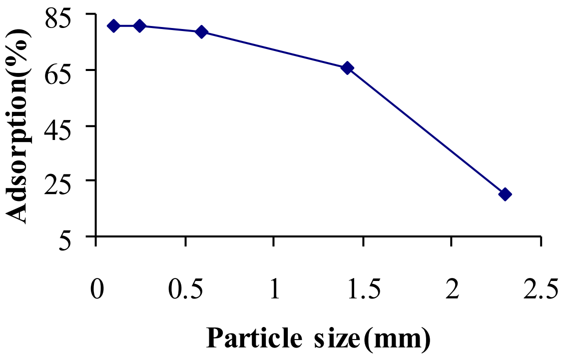

Figure 3: Effect of particle size on the removal of As (III) by adsorption onto duck weed (initial As concentration, 100 µg/L; pH, 5.5; amount of adsorbent 3g; Treatment flow rate, 1.67 mL/min)

Effect of Initial Concentration.

The removal efficiency is highly dependent on the initial concentrations of As (III) in the sample solution. The effect of the initial sample concentration on the removal of arsenic with duckweed was investigated. The initial concentration was evaluated in the range of 50-500 µg/L, and the results are illustrated in Figure 4. The removal efficiency decreased with increasing adsorbate concentration in the solutions. It is because, at low concentration, most of As (III) in the sample solution get contact with active sites. With increasing arsenic concentration in solution, active sites on the adsorbents were not increased. Therefore arsenic removal efficiencies were decreased.

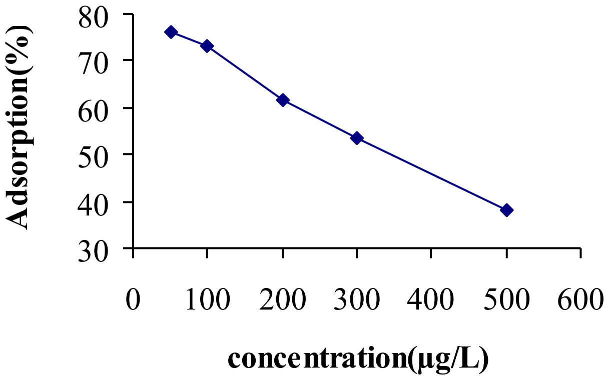

Figure 4: Effect of initial adsorbate concentration on the removal of As (III) by adsorption onto duck weed (Particle size 0.595 mm; pH, 5.5; amount of adsorbent 3g; treatment flow rate 1.67 mL/min)

Effect of pH

pH is one of the most important parameters controlling the metal ion sorption process [39-40]. Figure 5 depicts the effect of pH on As (III) removal with Duck weed. The removal efficiency of As (III) tended to decrease with increasing pH and then decreased markedly at pH 12. At low pH values, i.e., higher hydrogen ion concentration, the negative charge at the surface of internal pore were neutralized and some more new adsorption sites were developed which provided a positive charge for anionic As(III) complex to get adsorbed on the surface. Again it is observed that the final pH of the solution was always greater than the initial pH of the solution, which confirmed the neutralization of H^+ ions with the negative charge at the surface and envelopment of more H^+ ions in formation of positively charged surface. As a result, the concentration of H^+ ions decreased in the solution and hence the pH of the solution increased. Many authors also reported similar results (Yu et al.,2003). The removal efficiency for As (III) observed in the range 75-76% was in comparatively neutral regions (at pH 7.0). As it is shown, the optimum pH of solution was observed at pH of 7.0 and removal is 76%. These results should be of great advantage for the practical implementation of arsenic removal from groundwater.

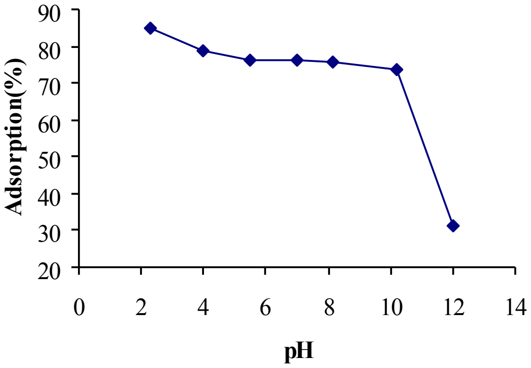

Figure 5: Effect of pH on the removal of As (III) by adsorption onto duckweed (initial As (III) concentration, 100 µg/L; particle size, 0.595 mm; amount of adsorbent 3g; treatment flow rate 1.67 mL/min)

Adsorption Mechanism

Arsenic removal by adsorption onto duck weed can be supposed to occur mainly through two routes: (i) affinity adsorption and (ii) anion exchange between the arsenic in the water and the carbon surface of the duck weed. Affinity adsorption is related to the surface behavior of duck weed, whereas anion exchange relates to the existing forms of the arsenic species. OH groups are created on the carbon surface during the activation process (Corapcioglu and Haung, 1987; Manju et al.,,1998). The mechanism of adsorption of metal anions onto activated carbon is generally well explained by electrochemical theory: Carbon in contact with water reduces oxygen to a hydroxyl group (Navarro and Alguacil, 2002).

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

And thus, the carbon loses electrons and become positively charged. Electrical neutrality is maintained with hydroxyl ions, resulting in their adsorption. Although the duck weed used in the present work was not subjected to any chemical or physical activation treatment, a large number of OH groups will remain on the surface of the duck weed after the drying process. The physical adsorption and interaction between the H_3AsO_3 species and the duck weed surface might be partly responsible for the removal of As (III).

Desorption

The results are illustrated in Table 1. It has been reported that although arsenic elution obtained using strong acidic or alkaline solutions (Lorenzen et al.,1995) , the present work showed that effective desorption was achieved with acidic solutions. These phenomena are consistent with the results observed due to the effect of pH. Consequently, sulfuric acid solution was useful for the desorption of arsenic from the surface of duckweed in the present study.

Table1: Influence of the Eluent on the Desorption of As (III)

Desorption agent	Desorption (%)
NaOH (1M)	72.0 ± 0.05
KOH(1M)	57.42 ± 0.01
HCl(1M)	84.84 ± 0.03
H_2SO_4(1M)	97.67 ± 0.01
HNO_3(1M)	58.13 ± 0.02

Adsorption process: initial As (III) concentration, 100 µg/L; duck weed 3g; average particle size, 0.595 mm; treatment flow rate, 1.67 mL/min. Volume of desorption agent, 100 mL.

2.2.4 Scanning Electron Microscope (SEM)

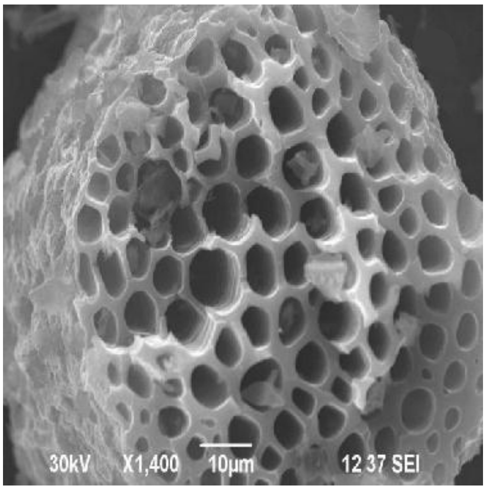

Fig 6 (a): Duckweed

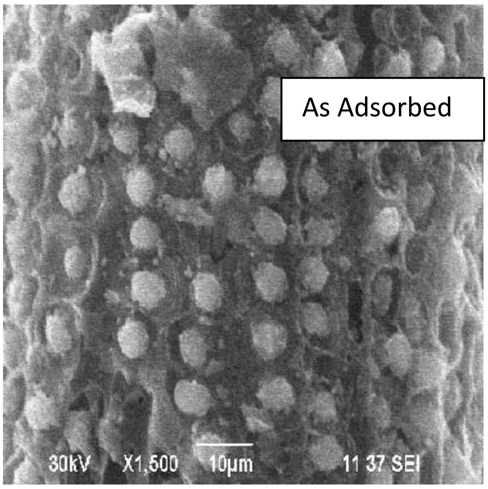

Fig 6 (b): Arsenic adsorbed Duckweed

The SEM picture of the thermally activated Duckweed is shown in Fig 6 (a). Arsenic adsorbed adsorbents were showed in Fig 6 (b). From the SEM pictures of Duckweed, there is a little bit of uniform and well developed pore structure on the surface of the Thermal-active Duckweed. Physically and chemically Duckweed shows tremendous, perfect and constructed pore structures on the surface [Fig 6 (a)]. High surface area and pore structure are the basic parameters for an effective adsorbent. When the porosity increases the surface area also increases. The surface modification of adsorbents led to variation in morphology, like the structure of the surface and crystalline pattern, and hence the difference in adsorption capacity was observed for Arsenic onto two biomaterials.

2.2.5 FTIR analysis of Duckweed

Apart from electrostatic force of attraction, the adsorption might be due to formation of complex in the legends available in the adsorbents.

The infrared spectrum was taken for duckweed in 3412.01, 2926.11 and 2856.67 cm $^{-1}$ which refers to group (-OH), identical alkyl group (-CH_2-) and aldyhid group (-CHO), respectively (Stuart, 1996). Also, the spectrum cleared bands at 1660.77 and 1095.60 cm^{-1} were to be the presence of (C=C) and (C-O), respectively.

The As (III) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups. Therefore FTIR studies showed the vital role played due to chelation. Chelation is favoured at lower pH and so the adsorption efficiency was more.

The surface IR-characterization of duckweed indicated the presence of many of function groups were able to join with binding the metals cations.

Table 2: FTIR peaks and group assignment (duckweed)

Peak at wave length cm^{-1}	Assign to
1095.60	C-O bending
1660.77	C=C bending
2856.67	-CHO
2926.11	($-CH_2-$) deformation
3412.01	-OH group

2.2.6 Application of the Developed Treatment System

The utility of the duck weed was evaluated for the treatment of As contaminated Bangladeshi groundwater samples. The concentrations of total arsenic in the samples was 233.032 μg/L. It has been reported that the total arsenic concentration in the tubewell water is in the range 0.25-1 mg/L, with 60-90% of the arsenic present as As (III) species [37]. Because the pH of these groundwater samples was around 7, the arsenic species might be H_3AsO_3 for As (III) (Ghimire et al.,2003; Wickramasinghe et al.,2004). The treatment results are presented in Table 2. Although 3 g of adsorbent was applied in the treatment, the concentration of arsenic in the treated sample water could be lowered to 54 µg/L. The desorption efficiencies with 100 mL of 1 M H_2SO_4 was 96.53%. From the present results, the arsenic was successfully removed from practical As-contaminated groundwater, and the adsorbed As could be recovered from the surface of duck weed.

Table 3: Removal and Desorption of As from the Contaminated Groundwater of Bangladesh

	Sample
pH	7.5
initial As conc. (µg/L)	233.032 ± 0.05
final As conc. (µg/L)	54.71 ± 0.01
removal[a] (%)	76.51 ± 0.03
desorption[b] (%)	96.53 ± 0.5

[a] Removal: Duck weed 3g, treatment flow rate 1.67mL/min, average particle size 0.595mm [b]Desorption: 1M H_2SO_4, 100mL, flow rate 1.67mL/min.

2.2.7 Conclusion

The proposed column treatment systems are appropriate and suitable homemade approaches to arsenic removal in local areas, because of their simplicity and easy operation and handling.The present method is effective for a wide range of concentrations(i.e., 50-500 μg/L), which were quite similar to those observed in contaminated Bangladeshi groundwater. No secondary-pollution problem will occur, because desorption of the arsenic is possible. Direct removal of arsenic (III) can be achived without first oxidizing arsenite to arsenate,whereas the traditional methods require the oxidation process.Based on the results of this research, duck weed can be considered as low cost, effective, available and natural adsorbent for removing arsenic from ground water.

2.2.8 References

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2.3 Arsenic Removal from Real-life Ground water by Adsorption on Neem Bark (*Azadirachta indica*)

2.3.1 Introduction

Arsenic (As) is mostly found in the earth's core and in clay- and sulphide-rich portions of the earth's crust (Henken, 2009b). Being a metalloid in group 15 on the periodic table (along with antimony, bismuth, nitrogen and phosphorus), arsenic is well known for its chronic toxicity, particularly when exposure occurs over prolonged periods (Katherine et al., 2011). Arsenic exposure via drinking-water is related to lung, kidney, bladder and skin cancer. For example, drinking-water arsenic concentrations in excess of 50 μg/L have been associated with increased risks of cancer in the bladder and lung, whilst drinking-water arsenic levels even below 50 μg/L have been associated with precursors of skin cancer (IPCS, 2001). Therefore, the presence of arsenic in water supply poses a serious risk to human health. Surface and ground waters in many parts of the world have been found to naturally contain As concentrations that make these waters unsuitable for human use. Significant concentrations of Arsenic have been reported in various countries such as Bangladesh, Chile, USA, China, and India. In Bangladesh, for example, about 100 million people currently drink water with Arsenic concentrations up to 100 times the World Health Organisation (WHO) drinking water guideline, which is 10 μg/L (Mohan and Pittman Jr., 2007).

To remove Arsenic from potential drinking water sources, a variety of conventional and non-conventional technologies have been studied, and these technologies have been reviewed by several authors (Mohan and Pittman Jr., 2007). However, it is known that conventional engineered treatment technologies are costly and create problems of sludge generation and disposal (Kosolapov et al., 2004; Cohen, 2006; Nelson et al., 2006). In addition, these systems often become sources of As-rich effluents and are typically located in remote isolated areas (such as mining sites), thus precluding the transportation of the effluents to large centralized treatment facilities. As such, to prevent As pollution of water courses, it is essential to find onsite, decentralized treatment systems that are robust and have low maintenance requirements and operating costs.

Many technologies, including co precipitation with iron or alum, adsorption onto coagulated floc, ion-exchange resin, reverse osmosis, and membrane techniques, have been used to remove As from aqueous solution (Katsoyiannis et al., 2004;Kim and Benjamin,2004, Jay et al.,2004;Hege et al.,2004; Balasubramanian and Madhavan,2001). In these methods, however, the adsorption techniques are simple and convenient and have the potential for regeneration and sludge-free operation. So far, various adsorbents for arsenic removal have been developed that include such materials as metal-loaded coral limestone, (Maeda et al.,1992;Ohki et al,. 1996) hematite and feldspar, (Singh et al.,1996) activated carbon, (Manjare et al.,2005; Huang and Fu,1984) activated alumina, (Ghosh and yuan,1987; Hathaway and Rubel,1987) and hydrous zirconium oxide (Suzuki et al.,1997).However, most of these adsorbents entail several problems in terms of efficiency and cost. The present work was performed to evaluate the use of neem bark without any pretreatment as an alternate adsorbent for removing arsenite from aqueous mediums. Moreover, the neem bark was applied to the removal of arsenic from Bangladeshi As-contaminated drinking water samples in a single-step column operation.

2.3.2 Arsenic Chemistry

Arsenic is a highly reactive metalloid that can be found in oxidation states -3, 0, +3 and +5. In natural waters, arsenic occurs as arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}), referred to as As (III) and As (V). As (III) mostly exists in reducing groundwaters and hydrothermal waters, whilst As (V) is more often present in surface waters and oxidising groundwaters (Henken and Hutchison, 2009). The main factors that control arsenic speciation are the oxidation state and pH. As (III) commonly hydrates to arsenious acid; therefore its chemistry depends strongly on pH. The predominant As (III) species is arsenious acid, H_3AsO_3, due to the high value of pKa_1 (pKas values reported by Wolthers et al. 2005) under the condition of 25 ˚C and 1 bar pressure). The reactions of the dissociation of arsenious acid and its respective anions are shown below, along with with the associated pKas values (where pKa = -log (Ka), and Ka = equilibrium constant of the reaction):

$H_3AsO_3 \leftrightarrow H_2AsO_3^{-} + H^{+}$ $pKa_1 = 9.24$ ... … (1)

$H_2AsO_3^{-} \leftrightarrow HAsO_3^{-2} + H^{+}$ $pKa_2 = 10.99$... … (2)

$HAsO_3^{-2} \leftrightarrow AsO_3^{-3} + H^+$ $pKa_3 = 13.47$ ... … (3)

As (V) commonly hydrates to arsenic acid, and its chemistry also depends on pH. The most common species are $H_2AsO^-_4$ and $HAsO_4^{-2}$, due to the low pKa_1 value (pKas values reported by Wolthers et al., 2005). The reactions of dissociation of arsenic acid and its respective anions are shown below along with the associated pKas values:

$H_3AsO_4 \leftrightarrow H_2AsO^-_4 + H^+$ $pKa_1 = 2.25$ ... … (4)

$H_2AsO^-_4 \leftrightarrow HAsO_4^{-2} + H^+$ $pKa_2 = 6.83$ ... … (5)

$HAsO_4^{-2} \leftrightarrow AsO_4^{-3} + H^+$ $pKa_3 = 11.52$ ... … (6)

The toxicity of arsenic depends on its speciation; for example, arsenite is significantly more toxic than arsenate (APHA et al., 2005). It is typically more difficult to remove arsenite than arsenate from contaminated water; this is because in natural waters, under normal pH conditions (6)–(9), arsenite is mostly found as an uncharged species (H_3AsO_3), and negatively charged species ($H_2AsO_3^-$, $HAsO_3^{-2}$ and AsO_3^{-3}) are found only at high pH (>9). On the other hand, arsenate is commonly found as negatively charged species ($H_2AsO_4^{-2}$ and $HAsO_4^{-2}$); which are easier to remove than are uncharged species, because the charges of the As(V) oxyanions allow them to be removed by sorption, anion exchange or precipitation/coprecipitation (Henken and Hutchison, 2009).

2.3.3 Materials and Methods

Reagent

All reagents used throughout this work were of analytical-grade purity. NaOH, KOH, KI, HCl, HNO_3, and H_2SO_4 were obtained from E. Merck, Germany. Individual standard solution of As (III) was supplied by Varian Inc, USA with highest purity level (99.98%). Dilute standard solutions were prepared daily before use. Pure water was purified with an ultrapure water system (Barnsted E-Pure, USA) resulting in a resistivity of >18 MΩ cm.

Preparation of Adsorbent

The Neem bark used in the present work was obtained from Bangladesh. The chemical composition of Neem bark has been reported as 3.43 wt % protein, 0.68 wt

% Alkaloids, 4.16 wt % Mineral,. The collected materials were washed with pure water several times to remove dust and fines. The washing process was repeated until the color of the wash water was transparent. The washed materials were then dried in a hot-air oven at 60° C for 24 h. The dried material was sieved into the following five size fractions: 0.105 mm, 0.25 mm, 0.595 mm, 1.41 mm, and 2.3 mm. The materials were used for the removal of arsenic without further physical or chemical treatment.

Adsorption and Analytical Procedures

Neem bark was added to the treatment glass columns (2 x 30 cm). The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column eluate flow rate (treatment rate). Adsorption factors including the amount of duckweed (1-5 g), average particle size (0.105-2.3mm), treatment flow rate (3.3-0.41 mL/min), initial sample concentration (50-500 μg/L), and pH (2.3-12) were evaluated. After the pH had been adjusted to the desired value with HCl and NaOH solutions, the sample solution (100 mL) was passed through the adsorption column at a given flow rate. The treatment flow rates of 0.41, 0.55, 0.83, 1.67and 3.3, mL/min correspond to 5 g of neem kark. The packing density of the treatment column was 0.32 g/cm^3. A small piece of tissue paper was inserted into the bottom of the column to prevent the loss of neem bark during the treatment. The flow rate was kept constant by controlling the stopper valve. The removal treatment was performed at ambient temperature. The number of experiments for the removal of As was greater than five. Analyses were performed by Varian Atomic Absorption Spectrometer (Model SpectrAA 240). The instrument is equipped with a Hydride generation system (Model VGA-77) and controlled with software Version 5.01. Samples were analyzed with HG-AAS using three-point calibration.

In the analysis time, acid container contains 5M HCl and reductant container contain 0.6 % Sodium borohydride ($NaBH_4$) in 0.5 % (w/v) sodium hydroxide.

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

$$\text{Removal (adsorption) efficiency} = \frac{Co - Ct}{Co} \times 100$$

Where Co and Ct are the concentration of As in the sample solution before and after treatment, respectively.

2.3.4 Results and Discussion

First, the performances of eight adsorbents (Coconut shell, Neem bark, Orange peel, Nut shell, Flax, Saw dust, Wheat stalk, News paper) were evaluated for the removal of As (III) from aqueous solutions. The removal efficiencies with coconut shell, Neem bark, Orange peel, Nut shell, Flax, Saw dust ,Wheat stalk and Newspaper were 18.79%, 19.23%, 3.8%, 14.26%, 12.89%, 14.2%, 12.3%, 32.3% respectively. Although the absorption capacity of news paper was highest, neem bark was taken as adsorbent because the main component of neem bark is carbon, neem bark has the potential to be used as an adsorbent. It was chosen for use as an adsorbent material because of its granular structure, insolubility in water, chemical stability, and high mechanical strength. Neem bark was selected as a suitable adsorbent. Of the adsorption neem bark gives the highest desorption and regeneration. Apart from this neem bark is widely available through the country.

Effect of Adsorbent Amount

The effect of the amount of neem bark on the removal of As (III) was investigated. The results are presented in Figure 1. The removal efficiencies of As (III) increased gradually with increasing amount of neem bark. It is readily understood that the adsorption capacity of neem bark depends on the surface activity, that is, the specific surface area available for As-surface interactions that is accessible to the As. Hence, increasing the amount of neem bark will increase removal capacity of As. Until now, various kinds of adsorbents have been studied for the removal of arsenic. The maximum As(III) removal efficiency achieved was 99% for iron oxide-coated sand at an adsorbent dose of 20 g/L with an initial As concentration 100 µg/L in batch studies (Gupta et al.,2005)The removal efficiencies for As(III) from an aqueous solution (100 µg/L, 100 mL) by 0.1 g of modified fungal biomass were 75%, respectively, after a 12-h batch treatment(Pokhrel and Viraraghavan,2006) When an aqueous As(III) solution of 10 mg/L concentration was stirred in the presence of both 1.0 g/L TiO_2 and 1.0 g/L activated alumina under sunlight irradiation, the arsenic removal increased with time and reached 89% after 24 h(Nakajima et al.,2005). Although the removal efficiencies in the proposed system were similar to those obtained with the other adsorbents, the treatment time was very short because of the flow method (column system).

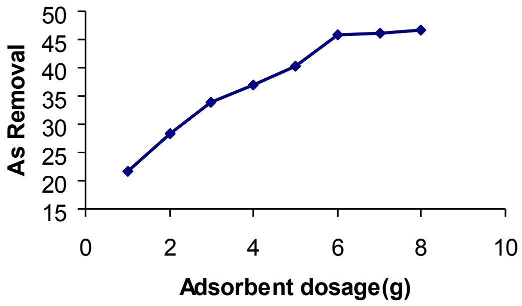

Figure1: Effect of adsorbent amount on the removal of As (III) by adsorption onto neem bark (initial As concentration, 100 µg/L; pH, 2.36; treatment flow rate, 1.67 mL/min)

Effect of Flow Rate

Flow rate is one of the effective factors in column adsorption process. The effect of the treatment flow rate on the removal of As (III) is illustrated in Figure 2. The removal efficiency for As (III) increased gradually with decreasing treatment flow rate. This is because, when the flow rate was slow, As (III) in the sample solution got more contact time with the active surface of the adsorbents.

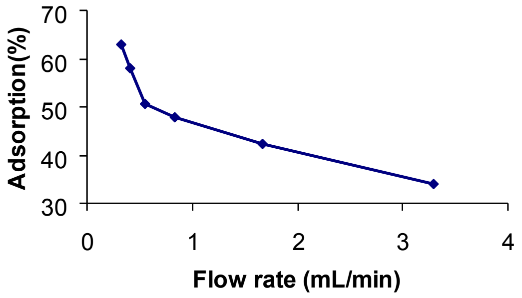

Figure 2: Effect of treatment flow rate on the removal of As (III) by adsorption onto neem bark (initial As concentration, 100 µg/L; pH 2.36; Amount of adsorbent, 5g)

Effect of Initial Concentration

The removal efficiency is highly dependent on the initial concentrations of As (III) in the sample solution. The effect of the initial sample concentration on the removal of arsenic with neem bark was investigated. The initial concentration was evaluated in the range of 50-500 µg/L, and the results are illustrated in Figure 3. The removal efficiency decreased with increasing adsorbate concentration in the solutions. It is because, at low concentration, most of As (III) in the sample solution gets contact with active sites. With increasing arsenic concentration in solution, active sites on the adsorbents were not increased. Therefore arsenic removal efficiencies were decreased.

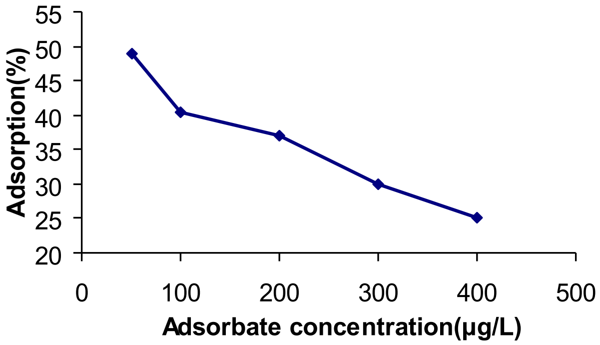

Figure 3: Effect of initial adsorbate concentration on the removal of As (III) by adsorption onto neem bark (pH 2.36; Amount of adsorbent, 5g; Treatment flow rate 1.67 mL/min)

Effect of pH

pH is one of the most important parameters controlling the metal ion sorption process (Munaf and Zein,1997; Wong et al.,2003). Figure 4 depicts the effect of pH on As(III) removal with neem bark. For the removal of As (III), the efficiency curve was essentially nearly a plateau in the pH range of 4-7, and then, the efficiency tended to decrease with increasing pH. The poor As removal efficiencies at high pH can be attributed to the following factors: First, chemical species for As (III) in this pH region are oxyanions. Next, hydroxyl groups are more plentiful on the surface of neem bark with increasing pH. The maximum removal efficiency for As (III) was observed in comparatively neutral region (at pH 7). This result should be of great advantage for the practical implementation of arsenic removal from groundwater.

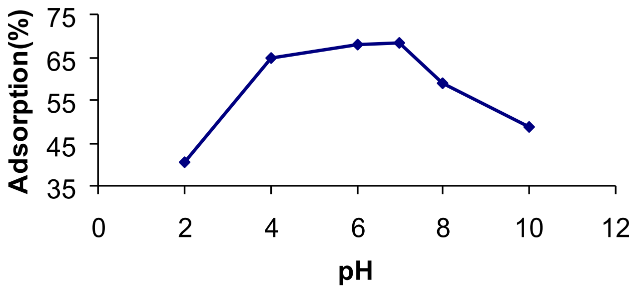

Figure 4: Effect of pH on the removal of As (III) by adsorption onto neem bark (initial As (III) concentration, 100 µg/L; Amount of adsorbent, 5g; Treatment flow rate 1.67 mL/min)

Effect of Particle Size

Column adsorption experiments were carried out for the removal of arsenic from aqueous solution using five different particle sizes (0.105 mm, 0.25 mm, 0.595 mm, 1.41 mm, and 2.3 mm). The results are shown in Figure 5. With decreasing particle size, the removal increased from 68.23% to 96% for As (III). Munaf and Zein reported that, when the size of adsorbent particles increased, the adsorption of metal ions decreased (Munaf and Zein, 1997). Similar trends have been reported by Wong et al. (Wong et al., 2003). These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites.

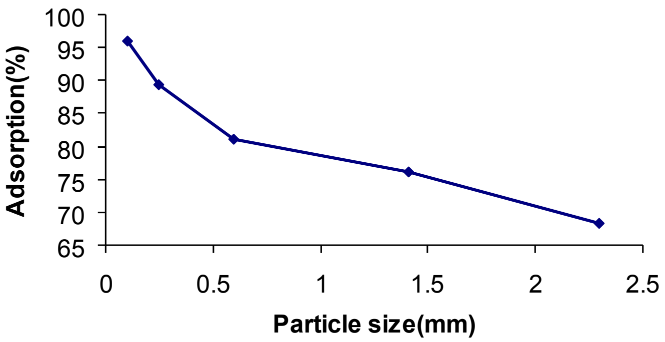

Figure 5: Effect of particle size on the removal of As (III) by adsorption onto neem bark (initial As concentration, 100 µg/L; pH, 7; amount of adsorbent 5g; treatment flow rate 1.67 mL/min)

Adsorption Mechanism

Arsenic removal by adsorption onto neem bark can be supposed to occur mainly through two routes: (i) affinity adsorption and (ii) anion exchange between the arsenic in the water and the carbon surface of the neem bark. Affinity adsorption is related to the surface behavior of neem bark, whereas anion exchange relates to the existing forms of the arsenic species. OH groups are created on the carbon surface during the activation process (Corapcioglu and Huang, 1987; Manju et al., 1998). The mechanism of adsorption of metal anions onto activated carbon is generally well explained by electrochemical theory: Carbon in contact with water reduces oxygen to a hydroxyl group

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

And thus, the carbon loses electrons and become positively charged. Electrical neutrality is maintained with hydroxyl ions, resulting in their adsorption. Although the neem bark used in the present work was not subjected to any chemical or physical activation treatment, a large number of OH groups will remain on the surface of the neem bark after the drying process. The physical adsorption and interaction between the H_3AsO_3 species and the neem bark surface might be partly responsible for the removal of As (III).

Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb As (III) from the neem bark surface with various eluents, such as hydrochloric, sulfuric, and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide.

This desorption process was performed using the column method. For each experiment, 100 mL of desorption solution was added to the column and held there for a fixed period of time. After the standing time, the solution was passed through the column.The results are presented in Table 1. Although the achievement of arsenic elution using strong acidic or alkaline solutions has been reported in the literature, (Lorenzen et al.,1995) the present work showed that effective desorption was obtained with acidic solutions. These phenomena are consistent with the results observed for the effect of pH. Consequently, hydrochloric acid solution was useful for the desorption of arsenic from the surface of neem bark.

Table1: Influence of the Eluent on the Desorption of As (III)

Desorption agent	Desorption (%)
NaOH (1M)	38.0±0.02
KOH(1M)	42±.0.01
HCl(1M)	79±0.03
H_2SO_4(1M)	48.08±0.03
HNO_3(1M)	51.63±0.01

Adsorption process: initial As(III) concentration, 100 μg/L; neem bark 5g; average particle size, 0.595 mm; treatment flow rate, 1.67 mL/min.Volume of desorption agent, 100 mL.

2.3.5 Application of the Developed Treatment System

The utility of the neem bark was evaluated for the treatment of As contaminated Bangladeshi groundwater samples. The concentrations of total arsenic in the samples was 233.032 μg/L. It has been reported that the total arsenic concentration in the tubewell water is in the range 0.25-1 mg/L, with 60-90% of the arsenic present as As (III) species (Khoe et al., 1997). Because the pH of these groundwater samples was around 7, the arsenic species might be H_3AsO_3 for As (III) (Meng et al., 2000; Ghimire et al., 2003; Wickramasinghe et al., 2004).The treatment results are presented in Table 2. Although 10 g of adsorbent was applied in the treatment, the concentration of arsenic in the treated sample water could be lowered to 60μg/L. The desorption efficiencies with 100 mL of 1 M HCLwas 89.63%. From the present results, the arsenic was successfully removed from practical As-contaminated groundwater, and the adsorbed As could be recovered from the surface of neem bark.

Table 2: Removal and Desorption of As from the Contaminated Groundwater of Bangladesh

	Sample
pH	7.5
initial As conc. (µg/L)	233.032 ± 0.05
final As conc. (µg/L)	60 ± 0.03
removal[a] (%)	74.25 ± 0.04
desorption[b] (%)	89.63 ± 0.02

[a] Removal: neem bark 10g, treatment flow rate 1.67 mL/min, average particle size 0.595 mm [b]Desorption: 1M HCL, 100 mL, flow rate 1.67 mL/min.

2.3.6 SEM

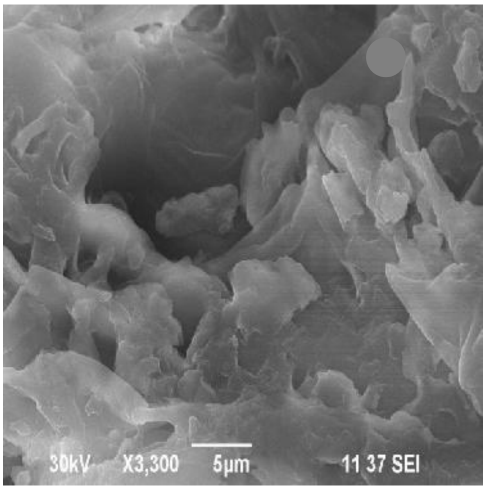

Fig 6 (a). Neem bark

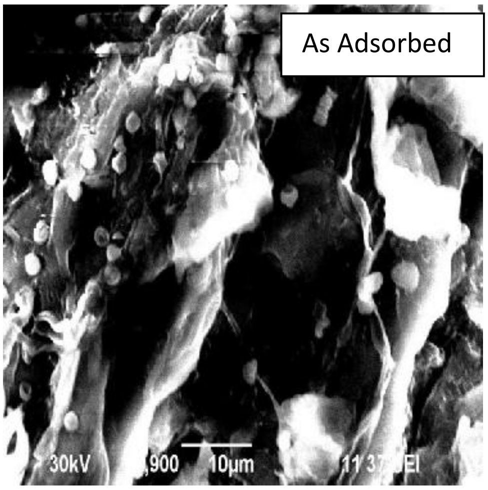

Fig 6 (b). Arsenic adsorbed Neem bark

The SEM picture of the thermally activated Neem bark is shown in Fig 6 (a). Arsenic adsorbed adsorbent was compared also in Fig 6 (b). The surface modification of adsorbents led to variation in morphology, like the structure of the surface and crystalline pattern, and hence the difference in adsorption capacity was observed for Arsenic onto neem bark.

2.3.7 Fourier Transform Infrared Spectroscopy (FTIR) Studies

Apart from electrostatic force of attraction, the adsorption might be due to formation of complex in the ligands available in the adsorbents.

The infrared spectrum was taken for Neembark in 3412.01, 2926.11 and 2856.67 $^{-1}$ which refers to group (-OH), identical alkyl group (-CH_2-) and aldyhid group (-CHO), respectively (Stuart, 1996). Also, the spectrum cleared bands at 1660.77 and 1095.60cm^{-1} were to be the presence of (C=C) and (C-O), respectively (Stuart, 1996).

The As (III) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups. Therefore FTIR studies showed the vital role played due to chelation. Chelation is favoured at lower pH and so the adsorption efficiency was more.

The surface IR-characterization of duckweed indicated the presence of many of function groups were able to join with binding the metals cations.

Table 16: FTIR peaks and group assignment

Peak at wave length cm^{-1}	Assign to
1095.60	C-O bending
1660.77	C=C bending
2856.67	-CHO
2926.11	(-CH_2-) deformation
3412.01	-OH group
1032.91	S=O stretching

2.3.8 Conclusion

The presence of arsenic in groundwater has been recognized as a major problem for Bangladesh. Due to its high toxicity, even in low concentrations, it is a threat to human health. There are many techniques, which can be effectively applied to remove arsenic from water streams. Moreover, some of the existing techniques are costly and they are not economically applicable in small community systems. Therefore, there is a need for developing cheap efficient methods for the removal of arsenic from drinking water. The proposed column treatment systems are appropriate and suitable home made approaches to arsenic removal in local areas, because of their simplicity and easy operation and handling. The present method is effective for a wide range of concentrations (i.e., 10-500 μg/L), which were quite similar to those observed in contaminated Bangladeshi groundwater. No secondary-pollution problem will occur, because desorption of the arsenic is possible. Direct removal of arsenic (III) can be achived without first oxidizing arsenite to arsenate, whereas the traditional methods require the oxidation process. Based on the results of this research, neem bark can be considered as low cost, effective, available and natural adsorbent for removing arsenic from ground water.

2.3.9 References

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2.4 Adsorption of Chromium (III) from Aqueous Solution by Groundnut Shell

2.4.1 Introduction

Chromium is one of the main toxic heavy metals in the environment. In the recent years, a large quantity of wastes containing chromium has been directly discharged into the environment without treatment [Wang et al., 2011]. Chromium (III) is an essential microelement that can be toxic in large doses (Khawaja, 1998). Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive under normal conditions. However, all forms of chromium can be toxic at high levels. Chromium has been considered as one of the top 16th. toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern (Torresdey et al., 2000). Chromium can be released to the environment through a large number of industrial operations, including tannery industry, metal finishing industry, iron and steel industries and inorganic chemicals production (Gao et al., 2007). Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (EPA, 2007). Adsorption process is considered very effective in textile and tannery waste water treatment. Most of the chemical methods used in cleaning up of heavy metals are not effective (Idris et al., 2012). There are various methods to remove Cr (III) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis (Verma et al., 2006). These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost (Li et al., 2007). For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using natural adsorbents which are economically viable such as agricultural wastes including sunflower stalks (Sun and Shi, 1998), Eucalyptus bark (Sarin and Pant, 2006), maize bran (Singh et al., 2006), coconut shell, waste tea, rice straw and tree leaves. In this study, ground nut shell has been used for Cr (III) removal from aqueous solution. The aims of this study are to 1) investigate the chromium adsorption from aqueous solution and desorption from the adsorbent by ground nutshell 2) study the effect of different parameters such as contact time, pH, adsorbent dose, initial chromium concentration and particle size on adsorption process and 3) find optimum adsorption isotherm as well as the rate of adsorption kinetics.

2.4.2 Material and Methods

Preparation of adsorbent:

All the reagents and chemicals used were of A.R grade (Merck,Germany).The solutions were prepared in double-distilled water. The groundnut shell was ground and its particle sizes between 0.063 and 0.841mm were obtained by passing the milled material through standard steel sieves. Then, these particular groundnut shells were used for experiments without any physical or chemical treatments as adsorbents.

Batch sorption experiments

The sorption studies were carried out at 25±1 °C. Solution pH was adjusted with H_2SO_4 or NaOH. A known amount of adsorbent was added to samples and was agitated by a shaker (Labtech, Korea) at 60 rpm agitation speed, allowing sufficient time for adsorption equilibrium. Then, the mixtures were filtered through filter paper, and the Cr (III) ions concentration were determined in the filtrate using Atomic Absorption Spectrophotometer (Varian AA240 FS).Batch adsorption studies were carried out under varying experimental conditions of contact time, initial chromium concentration, adsorbent dose, pH and particle size. The chromium removal (%) at any instant of time was determined by the following equation:

$$\text{Chromium removal (\%)} = \frac{Co - Ct}{Co} \times 100$$

Where, Co and Ct are the concentration of Cr (III) in the sample solution before and after the treatment. Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 10 g per 100 mL while maintaining the initial chromium concentration at 200 µg/L.

2.4.3 Results and Discussion

The performances of eight adsorbents (Coconut fibre, rice straw, neem bark, orange peel, groundnut shell, rice husk, sawdust and coconut coir) were evaluated for the removal of chromium (III) from aqueous solutions. The removal efficiencies with coconut fibre, rice straw, neem bark, orange peel, rice husk, saw dust, coconut coir and groundnut shell were 28%, 30%, 17%, 9%, 23%, 4.5%, 28%, and 70% respectively. Based on this results groundnut shell has been considered for further investigation.

Effect of adsorbent dose on chromium adsorption

The effect of adsorbent dose on the adsorption of Cr (III) by nutshell is presented in Fig.1. It is evident from Fig.1 that chromium removal efficiency increases with increase in adsorbent dose, as contact surface of adsorbent particles and the availability of more binding sites increase for adsorption (Garg,U.K.,2004).

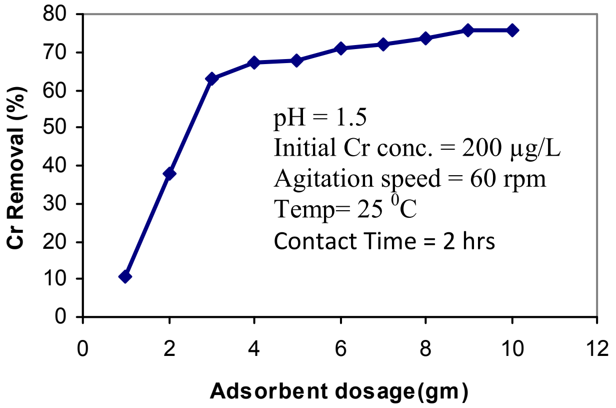

Fig. 1: Effect of adsorbent dose on Cr (III) removal

Effect of contact time on chromium adsorption

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Therefore, it is important to study its effect on the capacity of retention of chromium (III) by groundnut adsorbent. The effect of contact time on Cr (III) adsorption efficiency is shown in Fig. 2. It is evident from this study that, Cr uptake is rapid at the initial stage of contact time and slowly increases at higher contact time until saturation. This may be due to the available free space for adsorption. In this experiment, adsorption rate initially was increased rapidly, and the removal efficiency was reached at maximum (80.1%) within about 360 min. There was no significant change in equilibrium concentration after 360min. to 480 min. After some time, the remaining vacant surface sites may be difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Thus, the driving force for the mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to traverse farther distance and deeper into the pores encountering much larger resistance (Srivastava, V. C., 2006). This results in the slowing down of the adsorption during the later phase.

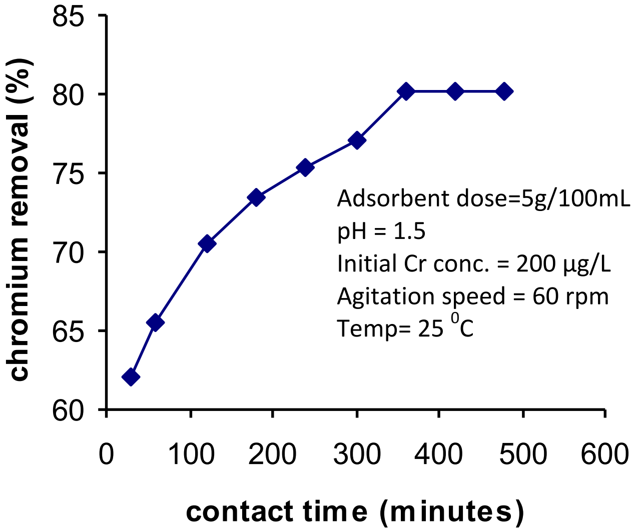

Fig 2: Effect of contact time on adsorption process efficiency

Effect of initial chromium concentration on adsorption process

Initial chromium concentration is one of the effective factors on adsorption efficiency. The experiments were done with variable initial chromium concentration (100, 200, 400, 800 and 1600 µg/L), remaining other parameters constant such as temperature (25 °C), pH (1.5), agitation speed (60 rpm), contact time (120 min) and 5 g of adsorbent dose (5 g/100 mL). The experimental results of the effect of initial chromium concentration on removal efficiency are presented in Fig. 3. It is evident from this figure that, Cr (III) removal efficiency decreases with the increase in initial chromium concentration. In case of lower chromium concentrations, the ratio of the initial number of moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher chromium concentrations, the available sites of adsorption become fewer, and hence the percentage removal of Cr (III) decreases (Yu *et al.,* 2003)

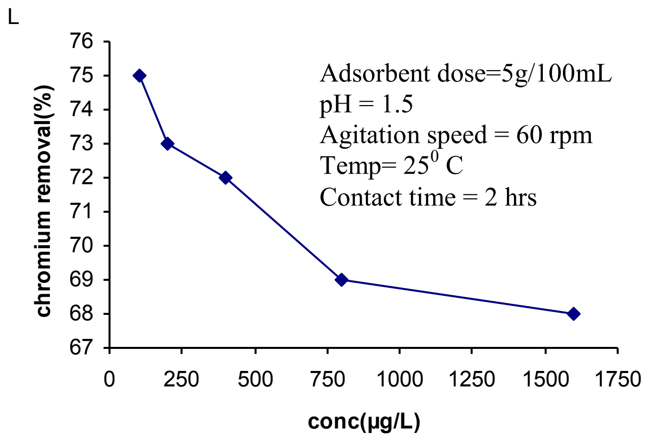

Fig 3: Effect of initial chromium concentration on adsorption process

Effect of pH on chromium adsorption

The pH is an important controlling parameter in aqueous adsorption process. The experiments were done under different pH values remaining other parameters constant. The experimental results are presented in Fig. 4. It is observed that the chromium removal efficiency (87.5%) was optimum at pH 7. By increasing pH, decrease in adsorption percentage was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately lead to the reduction in sorption capacity (Baral et al., 2006). As the maximum removal efficiencies for chromium observed in neutral region, this study should be of great advantage for the practical implementation of chromium removal from water and waste water.

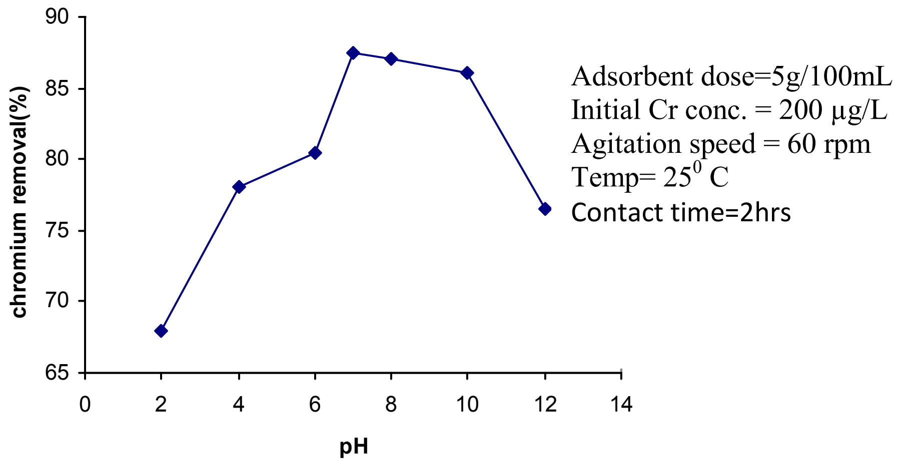

Fig 4: Effect of pH on Cr (III) removal

Effect of particle Size:

Batch adsorption experiments were carried out for the removal of Cr (III) from aqueous solutions using groundnut shell of six different particle sizes (0.063, 0.074, 0.125, 0.177, 0.42, 0.841 mm). The results are shown in Figure 5. The lower the particle size the higher the percent chromium removal has been observed. With decresing particle size, the % removal of chromium III was increased from 74% to 97.5%. Munaf and Zein reported that, when the size of the adsorbents particles increased, the adsorption of metal ions decreased. Similar trends have been reported by Wong et al. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites.

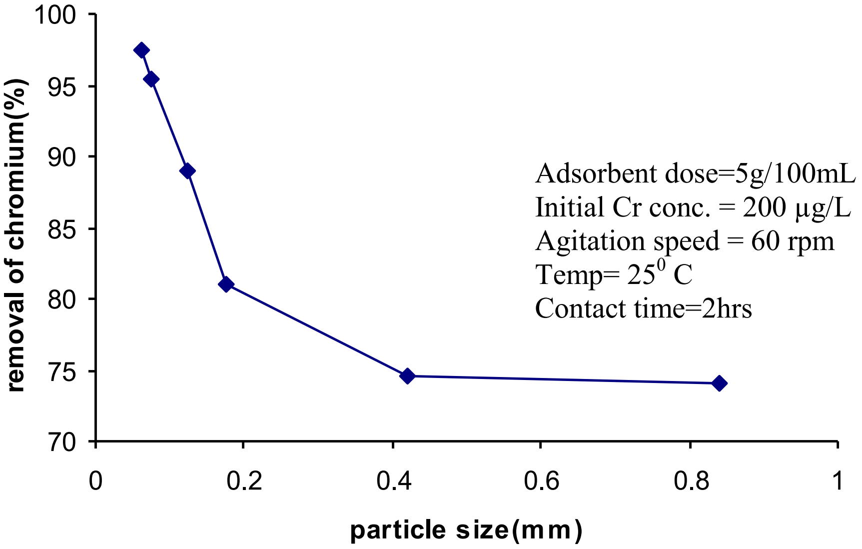

Fig 5: Effect of particle size on removal of Cr (III)

Adsorption isotherms

The distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir, and Freundlich. The Langmuir isotherm equation can be expressed as $q_e = \frac{\theta.b.C_e}{1+b.C_e}$, where, C_e: the equilibrium Concentration (mg/L), q_e: the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), θ: (mg/g) and b (L/mg): the Langmuir constant related to the maximum sorption capacity and energy of adsorption, respectively. K (mg/g): an indicator of the adsorption capacity. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

The Freundlich isotherm equation may also be given as $q_e = KC_e^{1/n}$, Where, $\frac{1}{n}(mg/L)$: adsorption intensity and K: constant related to the adsorption energy (mol^2/KJ^2)

However, the Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption (Bulut and Baysal, 2006).

In order to find the most appropriate model for the chromium adsorption, the data were fitted to each isotherm model. The constant Parameters of Langmuir isotherm model are θ= 384.6 (μg/g), and b=0.0016 (L/μg) and the Freundlich isotherm model are K=0.87, n=1.13.

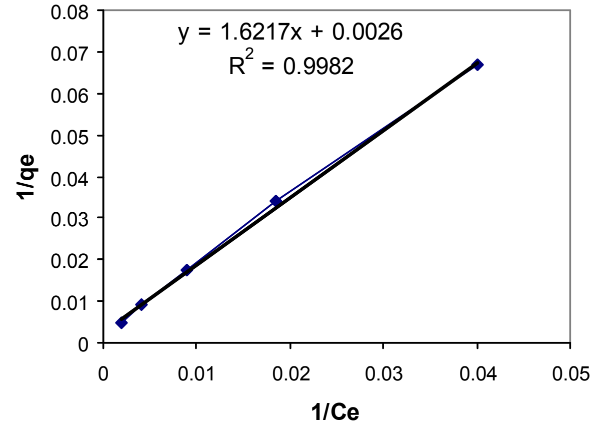

Fig 6: Langmuir isotherm (pH = 1.5, Temp= 25^0 C, C_0= 200 μg/L)

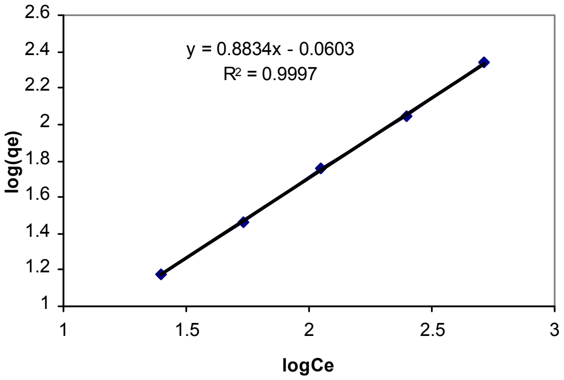

Fig 7: Freundlich isotherm (pH = 1.5, Temp= 25^0 C, C_0= 200 μg/L)

The isotherms for groundnut shell at 25±1°C are given in Fig. 6 and Fig 7. The results indicate that the Langmuir and Freundlich adsorption isotherms were best fitted models for the Cr (III) adsorption on groundnut shell with R^2 values of 0.9982 and 0.9997 respectively. The essential features of Langmuir and Freundlich adsorption isotherms can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (*R*L), which is defined by the following relationship (Hall *et al.,*1966; Malik, 2004):

$$R_L = \frac{1}{1 + bC_0}$$

where, *C*o is the initial Cr(III) concentration (μg/L). The *R*L value indicates the shape of the isotherm to be irreversible (*R*L = 0), favorable (0 <*R*L <1), linear (*R*L = 0) or unfavorable (*R*L >1) (Mckay *et el.,* 1982; Malik, 2004). Through the above-mentioned equation, *R*L value for investigated Cr-adsorbent system is found to be 0.76. From the value of *R*L, it is confirmed that groundnut shell is desirable for adsorption of Cr (III) from wastewater under the conditions used in this study. For Freundlich isotherm, n is equal to 1.13. The situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that cause a decrease in adsorbent-adsorbate interaction with increasing surface density (Reed and Matsumoto, 1993) and the values of *n* within the range of 2-10 represent good adsorption (Mckay *et el.,* 1980; Ozer and Pirincci, 2006).

Adsorption kinetics

In order to define the adsorption kinetics of heavy metal ions, the kinetics parameters for the adsorption process were studied for contact times ranging from 1 to 480 min by monitoring the removal percentage of the Cr (III). The data were then regressed against the Lagergren equation (Eq. *), which represents a first order kinetics equation (Namasivayam and Yamuna, 1995).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \ldots\ldots\ldots\ldots\ldots (*)$$

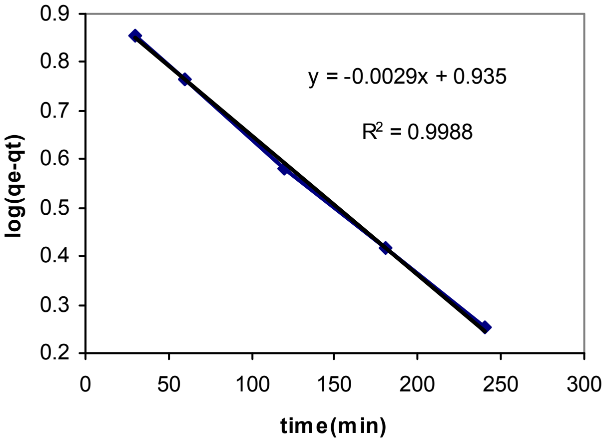

Fig 8: First-order kinetics plot for adsorption of chromium on Nut shell

where, qt is the Cr (III) uptake per unit weight of adsorbent (µg/g) at time t, q_e is the metal uptake per unit weight of adsorbent (µg /g) at equilibrium, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order (Argun *et al.,* 2006). The slopes and intercepts of these curves were used to determine the values of K_1, as well as the equilibrium capacity (q_e).

The first-order kinetic constants for adsorption of chromium on are rate constant (K=0.01 (1/ min) and correlation factor (R^2 = 0.9988). The results indicated that the adsorption process follows first-order model. The plot of log (q_e-q_t) versus t gives a straight line as shown in Fig. 8.

Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorbs chromium (III) from the groundnut shell surface with various eluents, such as hydrochloric, sulfuric and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. For each experiment, after adsorption, 100mL of desorption solution was added to the adsorbent and was shook for two hours with an RPM 60. The results are presented in Table 4. The present work indicates that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was useful for the de sorption of chromium from the surface of Nutshell and the desorption efficiencies with 0.5M KOH was 78%.

Table 1: Influence of the Eluent on the desorption of Cr (III) (shaking time-2 hours)

desorption agent	Desorption (%)
NaOH (0.5M)	68 ± 0.04
KOH(0.5M)	78 ± 0.03
HCl(0.5M)	16 ± 0.02
H_2SO4(0.5M)	18 ± 0.02
HNO3(0.5M)	12 ± 0.01

Adsorption process: initial Cr concentration, 200 µg/L, nutshell 5gm, volume of desorption agent, 100mL.

2.4.4 FTIR Analysis for Ground Nutshell

Apart from electrostatic force of attraction, the adsorption might be due to formation of complex in the ligands available in the adsorbents. The adsorbent as such showed peaks at 3420, 2927, 1535, 1261 and 1058 cm^{-1} which correspond to bonded OH group, aliphatic C-H group, NH_2 scissoring, C-O stretching and C-N stretching respectively. The Cr (III) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups. Therefore FTIR studies showed the vital role played due to chelation. Chelation is favoured at lower pH and so the adsorption efficiency was more. The results are shown in Table 2

Table -2: FTIR peaks and group assignment

Peak at wave length cm	Assign to
1058	C-N
1261	O-C
1375	O-H bending in plane
1417	CH2 and CH4 deformation
1535	N-H (-amide) II band
1631	N-H (-amide) II band
2927	SP3 stretching
3420	O-H (H-bonded), usually broad

2.4.5 Application of the Developed Treatment System

Tanning industries are one of the main economic activities in Bangladesh. It has been well documented that waste water discharged from tanneries without appropriate treatment that results in detrimental effects on the ecosystem. No eco-toxicity evaluation of any aquatic environment in Bangladesh has been conducted so far. In this study Chromium analysis were carried out from water samples obtained from two sampling spots: Kalo Nagar, Hazaribug (Sample1), where different effluents of tanneries are flowing and effluent discharging site on River Buriganga (Sample 2), in the Hazaribagh tannery area of Dhaka City, Bangladesh. The concentrations of chromium in the samples were 3.1 mg/L and 1.46 mg/L respectively. The treatment results are presented in Table 5. Although 20g of adsorbent was applied in the treatment, the concentrations of chromium in the treated sample water could be lower to 131 μg/L and 50 μg/L. The desorption efficiencies with 100 mL of 0.5M KOH were 100%. From the present results, the chromium was successfully removed from practical chromium contaminated water and adsorbed chromium could be recovered from the surface of Nutshell.

Table 3: Removal and Desorption of Chromium from the contaminated water of Bangladesh

	Sample1	Sample2
pH	7.5	8
initial Cr conc. (μg/L)	3100 ± 3.0	1460 ± 2.0
final Cr conc. (μg/L)	131 ± 0.5	50 ± 0.01
removal[a] (%)	98.83 ± 0.02	96.58 ± 0.02
desorption[b] (%)	100 ± 0.1	100 ± 0.1

[a] Removal: groundnut shell 20 gm, [b]Desorption: 0.5M KOH, 100mL

2.4.6 Conclusion

The present research showed that groundnut shell can be effectively used as an excellent alternative for the removal of Cr (III) from aqueous solutions. The adsorption of Cr (III) was found to depend on pH, particle size, contact time, adsorbent dosage and initial metal concentration. Both Langmuir and Freundlich isotherms were followed by the adsorption of Cr (III). The kinetics analysis of the study showed that the adsorption of Cr (III) ions onto groundnut shell could be well described with the first-order kinetics model. As the maximum removal efficiency of chromium was observed in neutral pH, this study can be effectively applied for the removal of chromium from water and wastewater.

2.4.7 References

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2.5 Adsorption, Desorption and Kinetic Study on Hexavalent Chromium Removal from Aqueous Solution using Groundnut Shell

2.5.1 Introduction

The application of chromium, a heavy metal in various industries (Bai and Abraham 2001), especially in leather tanning has gained a negative impact in the society with respect to its pollution potential. Chromium has several oxidation states ranging from Cr(II) to Cr(VI), but the trivalent and the hexavalent states are the most stable (Yadav et al. 2005). Cr (VI) is toxic, carcinogenic, and mutagenic to animals as well as humans and is associated with decreased plant growth and changes in plant morphology (James and Bartlett 1984; Costa 2003).Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production (Gao et al., 2007). Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (EPA, 2007). Most of the chemical methods used in cleaning up of heavy metals are not effective (Idris et al., 2012) There are various methods to remove Cr(VI) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis (Verma et al., 2006). These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost (Li et al., 2007). For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using natural adsorbents which are economically viable such as agricultural wastes including sunflower stalks (Sun and Shi, 1998), Eucalyptus bark (Sarin and Pant, 2006), maize bran (Singh et al., 2006), coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks (Karthikeyan et al., 2005). In this study, groundnut shell has been used for Cr (VI) removal from aqueous solution. The present study is intended to use of this locally available as a conventional cheap material as a chromium adsorbent.

2.5.2 Materials and Methods

Preparation of adsorbent:

All the reagents and chemicals used were of A.R grade (Merck,Germany). The solutions were prepared in double-distilled water (Barnsted E-Pure, USA) resulting in a resistivity of >18 MΩ cm. The groundnut shell was ground and particle sizes between 0.063 and 0.841mm were obtained by passing the milled material through standard steel sieves. Then, they used for experiments without any physical or chemical treatments.

Batch sorption experiments

The sorption studies were carried out at 25±1°C. Solution pH was adjusted with H_2SO_4 or NaOH. A known amount of adsorbent was added to samples and was agitated by a shaker (Labtech, Korea) at 60 rpm agitation speed, allowing sufficient time for adsorption equilibrium. Then, the mixtures were filtered through filter paper, and the Cr (III) ions concentration were determined in the filtrate using Atomic Absorption Spectrophotometer (Varian AA240 FS).Batch adsorption studies were carried out under varying experimental conditions of contact time, initial chromium concentration, adsorbent dose, pH and particle size. The chromium removal (%) at any instant of time was determined by the following equation:

$$\text{Chromium removal }(\%) = \frac{Co - Ct}{Co} \times 100 \ldots\ldots\ldots\ldots..\ (1)$$

Where, Co and Ct are the concentration of Cr (III) in the sample solution before and after the treatment. Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 10 g/100 mL while maintaining the initial chromium concentration at 200 µg/L.

2.5.3 Results and Discussion

Effect of adsorbent dose on chromium (VI) adsorption

The effect of adsorbent dose on the adsorption of Cr (VI) by ground nut shell is presented in Fig.1. It is evident from Fig.1 that chromium removal efficiency increases with increase in adsorbent dose, as contact surface of adsorbent particles and the availability of more binding sites increase for adsorption (Garg,U.K.,2004).

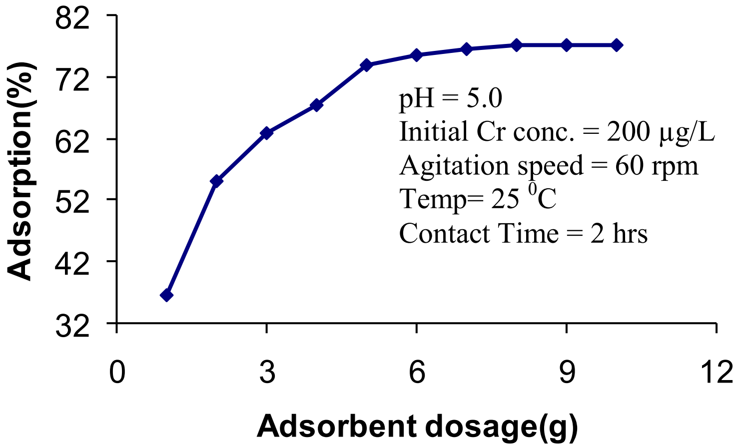
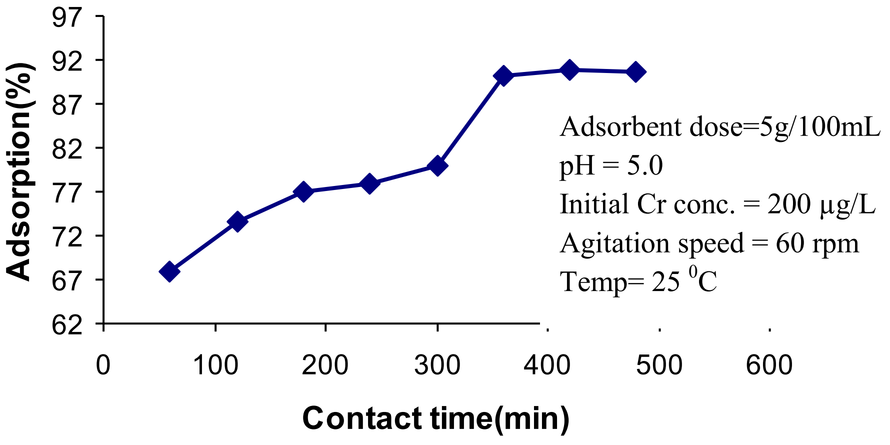


Fig. 1: Effect of adsorbent dose on Cr (VI) removal

Effect of contact time on chromium (VI) adsorption

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Therefore, it is important to study its effect on the capacity of retention of chromium (VI) by groundnut shell adsorbent. The effect of contact time on Cr (VI) adsorption efficiency is shown in Fig. 2. It is evident from this study that, Cr uptake is rapid at the initial stage of contact time and slowly increases at higher contact time until saturation. This may be due to the available free space for adsorption. In this experiment, adsorption rate initially was increased rapidly, and the removal efficiency was reached at maximum (90.1%) within about 360 min. There was no significant change in equilibrium concentration after 360 min. to 480 min. After some time, the remaining vacant surface sites may be difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Thus, the driving force for the mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to traverse farther distance and deeper into the pores encountering much larger resistance. This results in the slowing down of the adsorption during the later phase.

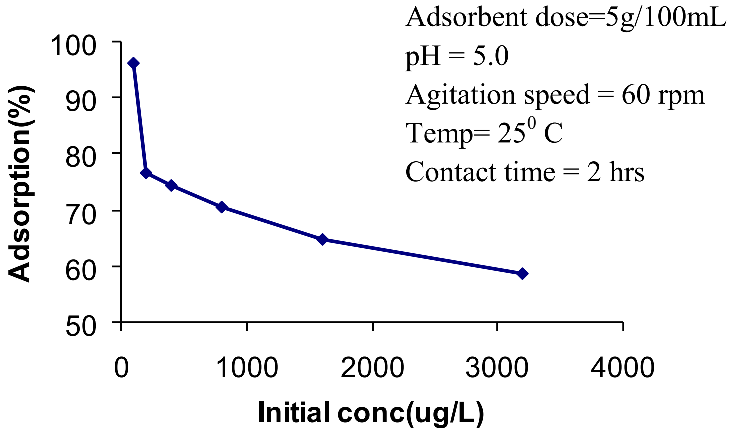


Adsorbent dose=5g/100mL
pH = 5.0
Initial Cr conc. = 200 µg/L
Agitation speed = 60 rpm
Temp= 25 ^{0}C

Fig 2: Effect of contact time on Cr(VI) removal

Effect of initial chromium (VI) concentration on adsorption process

Initial chromium concentration is one of the effective factors on adsorption efficiency. The effect of initial chromium concentration on removal efficiency are presented in Fig. 3. It is evident from this figure that, Cr (VI) removal efficiency decreases with the increase in initial chromium concentration. In case of lower chromium concentrations, the ratio of the initial number of moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher chromium concentrations, the available sites of adsorption become fewer, and hence the percentage removal of Cr (VI) decreases (Yu *et al.,* 2003).



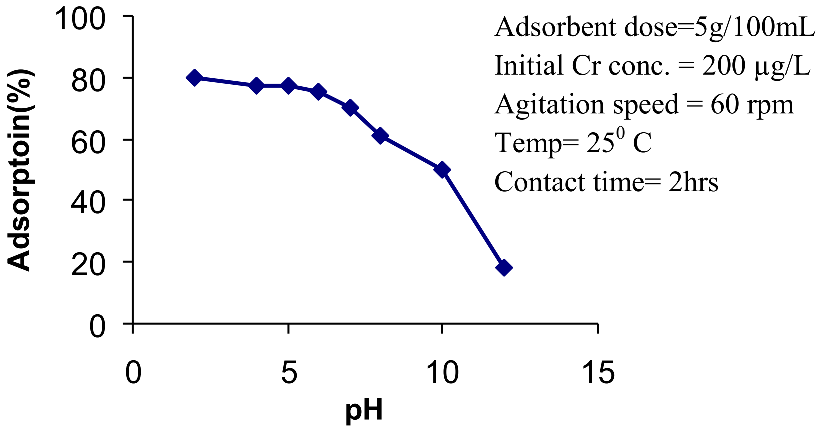
Adsorbent dose=5g/100mL
pH = 5.0
Agitation speed = 60 rpm
Temp= 25^0 C
Contact time = 2 hrs

Fig 3: Effect of initial chromium concentration on Cr (III) removal

Effect of pH on chromium (VI) adsorption

The pH is an important controlling parameter in aqueous adsorption process. The experiments were done under different pH values remaining other parameters constant. The experimental results are presented in Fig. 4. It is observed, the optimum pH of solution was observed at pH of 2 and by increasing pH, decrease in adsorption percentage was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately lead to the reduction in sorption capacity (Baral *et al.,* 2006). Adsorption of hexavalent chromium varies as a function of pH with H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$and CrO_4^{2-} ions appear as dominant species (Gaballah and Kilbertus, 1998). At pH of 2, $HCrO_4^-$ is the dominant species. The surface charge of nut shell is positive at low pH, and this may promote the binding of the negatively charged $HCrO_4^-$ ions. The $HCrO_4^-$ species are most easily exchanged with OH^- ions at active surfaces of adsorbent under acidic conditions as shown in Eq. 2 (Ar is adsorbent surface) (Argun *et al.,* 2006):

$\mathrm{Ar\,OH + HCr\,O_4^- + H^+ \rightarrow ArHCr\,O_4 + H_2O}$…………….. (2)



Adsorbent dose=5g/100mL
Initial Cr conc. = 200 µg/L
Agitation speed = 60 rpm
Temp= 25^0 C
Contact time= 2hrs

Fig 4: Effect of pH on Cr (VI) removal

Effect of particle Size on Cr (VI) adsorption

Batch adsorption experiments were carried out for the removal of Cr (VI) from aqueous solutions using groundnut shell of six different particle sizes (0.063, 0.074, 0.125, 0.177, 0.42, 0.841 mm). The results are shown in Figure 5. The result shows that decreasing particle size, the % removal of chromium (VI) was increased from 58.22% to 80.65%. Munaf and Zein reported that, when the size of the adsorbents particles increased, the adsorption of metal ions decreased. Similar trends have been reported by Wong et al. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites.

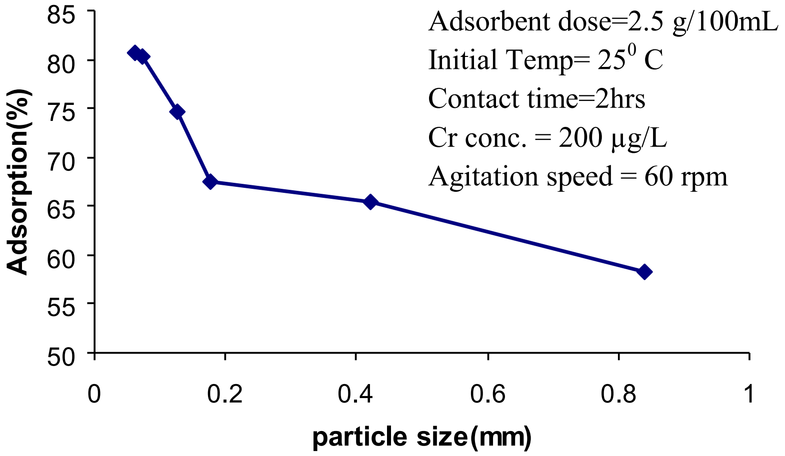


Fig 5: Effect of particle size on Cr (VI) removal

Adsorption isotherms

The distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir, and Freundlich. The Langmuir isotherm equation can be expressed as $q_e = \frac{\theta.b.C_e}{1+b.C_e}$, where, C_e: the equilibrium Concentration (mg/L), q_e: the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), θ: (mg/g) and b (L/mg): the Langmuir constant related to the maximum sorption capacity and energy of adsorption, respectively. K (mg/g): an indicator of the adsorption capacity. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Freundlich isotherm equation may also be given as $q_e = KC_e{}^{1/n}$, where, $\frac{1}{n}(mg/L)$: adsorption intensity and K: constant related to the adsorption energy (mol^2/KJ^2)

However, the Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption (Bulut and Baysal, 2006).

In order to find the most appropriate model for the chromium adsorption, the data were fitted to each isotherm model. The constant parameters of Langmuir isotherm model are θ= 370.37(μg/g), and b=0.00204 (L/μg) and the Freundlich isotherm model are K=2.022, n=1.37.

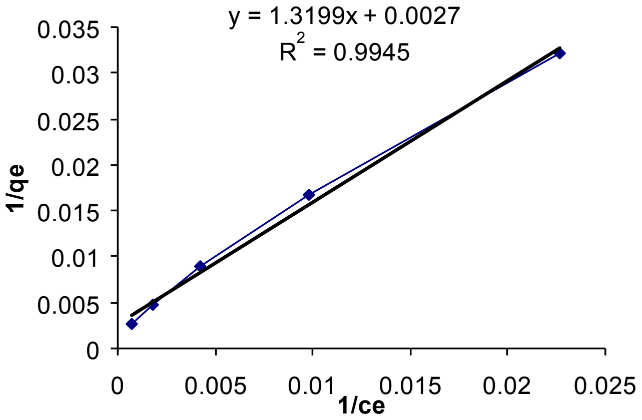


Fig 6: Langmuir isotherm for Cr(VI) adsorption onto nutshell(contact time 2 hrs, initial Cr concentration 200 μg/L, pH 5, temp 25^0 C, amount of nutshell 5g, volume 100 mL)

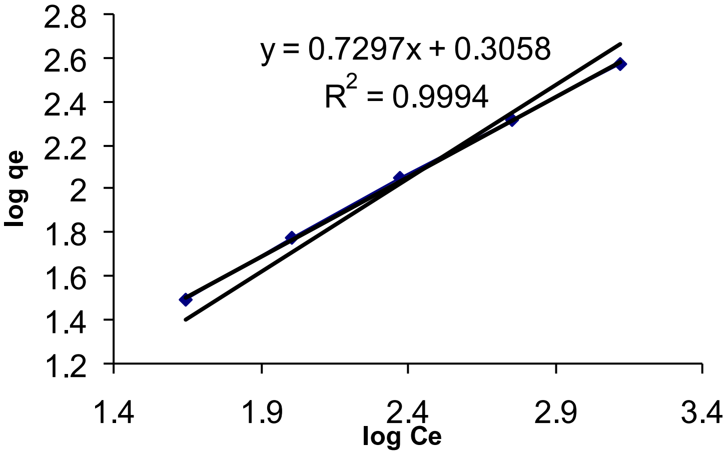


Fig 7: Freundlich isotherm for Cr(VI) adsorption onto nutshell(contact time 2 hrs, initial Cr concentration 200 μg/L, pH 5, temp 25^0 C, amount of nutshell 5g, volume 100 mL)

The isotherms for nutshell at 25±1°C are given in Fig. 6 and Fig 7. The results indicate that the Langmuir and Freundlich adsorption isotherms were best fitted models for the Cr (VI) adsorption on nutshell with R^2 values of 0.9945 and 0.9994 respectively. The essential features of Langmuir and Freundlich adsorption isotherms can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (*R*L), which is defined by the following relationship (Hall *et al.,* 1966; Malik, 2004):

$$R_L = \frac{1}{1+bC_0} \ldots\ldots\ldots\ldots(2)$$

Where, *C*o is the initial Cr (VI) concentration (µg/L). The *R*L value indicates the shape of the isotherm to be irreversible (*R*L = 0), favorable (0 <*R*L <1), linear (*R*L = 0) or unfavorable (*R*L >1) (Mckay *et el.,* 1982; Malik, 2004). Through the above-mentioned equation, *R*L value for investigated Cr-adsorbent system is found to be 0.71. From the value of *R*L, it is confirmed that nutshell is desirable for adsorption of Cr (VI) from wastewater under the conditions used in this study. For Freundlich isotherm, n is equal to 1.37. The situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that cause a decrease in adsorbent-adsorbate interaction with increasing surface density (Reed and Matsumoto, 1993).

Adsorption kinetics

In order to define the adsorption kinetics of heavy metal ions, the kinetics parameters for the adsorption process were studied for contact times ranging from 30 to 240 min by monitoring the removal percentage of the Cr (VI). The data were then regressed against the Lagergren equation (Eq. 3), which represents a first order kinetics equation (Namasivayam and Yamuna, 1995).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \ldots\ldots\ldots\ldots\ldots (3)$$

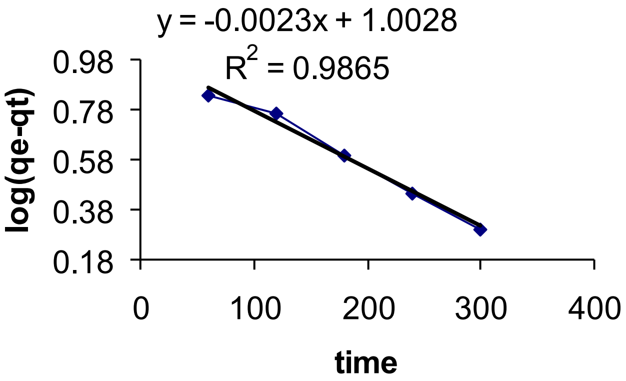


Fig 8: First-order kinetics plot for adsorption of chromium on nutshell

where, q_t is the Cr (VI) uptake per unit weight of adsorbent (µg/g) at time t, q_e is the metal uptake per unit weight of adsorbent (µg /g) at equilibrium, and k_1 (min^{-1}) is the rate constant of the first-order (Argun *et al.,* 2006). The slopes and intercepts of these curves were used to determine the values of K_1, as well as the equilibrium capacity (q_e).

The first-order kinetic constants for adsorption of chromium on are rate constant (K=0.0053 (1/ min) and correlation factor (R^2 = 0.9865). The results indicated that the adsorption process follows first-order model. The plot of log (q_e-q_t) versus t gives a straight line as shown in Fig. 8.

Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorbs chromium (VI) from the nutshell surface with various eluents, such as hydrochloric, sulfuric and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. The results are presented in Table 1. Although the achievement of arsenic eluting using strong acidic or alkaline solution has been reported in the literature (Lorenzen *et el.,* 1995), the present work showed that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was useful for the desorption of chromium from the surface of nutshell and the desorption efficiencies with 1M KOH was 87%.

Table1: Influence of the Eluent on the desorption of Cr (VI) (shaking time-2 hours)

Desorption agent	Desorption (%)
NaOH (1M)	60.0 ± 0.03
KOH(1M)	87.0 ± 0.04
HCl(1M)	7.8 ± 0.01
H_2SO_4(1M)	5 ± 0.04
HNO3(1M)	12.8 ± 0.01

Adsorption process: Initial Cr concentration, 200 μg/L, nutshell 5gm, volume of desorption agent, 100mL, RPM 60.

2.5.4 Application of the Developed Treatment System

Tanning industries are one of the main economic activities in Bangladesh. It has been well documented that waste water discharged from tanneries without appropriate treatment results in detrimental effects on the ecosystem. No ecotoxicity evaluation of any aquatic environment in Bangladesh has been conducted so far. In this study Chromium analysis were carried out from water samples obtained from two sampling points: Kalo Nagar,Hazaribug (S1),where different effluents of tanneries are flowing and effluent discharging site on River Buriganga (S2), in the Hazaribagh tannery area of Dhaka City, Bangladesh. The concentrations of chromium in the samples were 3.1 mg/L and 1.46 mg/L respectively. The treatment results are presented in Table 18. Although 25g of adsorbent was applied in the treatment, the concentrations of chromium in the treated sample water could be lower to 121μg/L and 50 μg/L respectively. The desorption efficiencies with 100mL of 0.5M KOH were 100%. From the present results, the chromium was successfully removed from practical chromium contaminated water and adsorbed chromium could be recovered from the surface of nutshell.

Fig -9: Tannery Effluent in Kalonagar, Hagaribag, Dhaka, Bangladesh flowing to the river Buriganga

Table 2: Removal and Desorption of Chromium from the contaminated water of Bangladesh

	Sample1	Sample2
pH	7.5	8
initial Cr conc(µg/L)	3100 ± 2.0	1460 ± 1.0
final Cr conc(µg/L)	121 ± 0.06	50 ± 0.02
removal[a] (%)	96.10 ± 0.04	96.57 ± 0.04
desorption[b] (%)	100 ± 0.05	100 ± 0.05

2.5.5 Conclusion

The present research showed that nutshell can be effectively used as an excellent alternative for the removal of Cr (VI) from aqueous solutions. The adsorption of Cr (VI) was found to depend on pH, particle size, contact time, adsorbent dosage and initial metal concentration. Both Langmuir and Freundlich isotherms show very good fit with the experimental adsorption equilibrium data. The kinetics analysis of the study showed that the adsorption of Cr (VI) ions onto Nutshell could be well described with the first-order kinetics model. It can be concluded that the developed method can be effectively applied for the removal of chromium from chromium containing water and effluent.

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2.6 Removal of chromium (III) from aqueous solution using *Linum usitatissimum* (Flax)

2.6.1 Introduction

Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents. Industrial pollution continues to be a potential threat affecting the water. The discharge of non-biodegradable heavy metals into water stream is hazardous because the consumption of polluted water causes various health problems. Waste streams containing heavy metals such as Cu, Zn, Ni, Pb, Cd, and Cr are often encountered in various chemical industries.

(Venkateswarlu et al. 2007) Among these, Chromium is one of the main toxic heavy metals in the environment. In the recent years, a large quantity of wastes containing chromium has been directly discharged into the environment without treatment (Wang et al. 2011). Chromium (III) is an essential microelement that can be toxic in large doses (Khawaja, 1998). Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive under normal conditions. However, all forms of chromium can be toxic at high levels. Chromium has been considered as one of the top 16th. toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern (Torresdey et al. 2000). Chromium can be released to the environment through a large number of industrial operations, including tannery industry, metal finishing industry, iron and steel industries and inorganic chemicals production (Gao et al. 2007). Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (EPA, 2007). Adsorption process is considered very effective in textile and tannery waste water treatment (Idris et al. 2012). There are various methods to remove Cr (III) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis (Verma et al. 2006). These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost (Li et al. 2007). For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using natural adsorbents which are economically viable such as agricultural wastes including sunflower stalks (Sun and Shi, 1998), Eucalyptus bark (Sarin and Pant, 2006), maize bran (Singh et al. 2006), coconut shell, waste tea, rice straw and tree leaves. In this study, Flax has been used for Cr (III) removal from aqueous solution. However, the adsorption behavior of Cr (III) on flax without any treatment has not been extensively studied. The present study is intended to use of this locally available as a conventional cheap material as a chromium adsorbent.

2.6.2 Materials and Methods

Preparation of adsorbent

All the reagents and chemicals used were of A.R grade (Merck, Germany). The solutions were prepared in double-distilled water. The Flax was ground and its particle sizes between 0.063 and 0.841mm were obtained by passing the milled material through standard steel sieves. Then, these particular flaxes were used for experiments without any physical or chemical treatments as adsorbents. The chemical composition of flax has been reported as 65 wt % cellulose, 16 wt % hemicellulose, 3 wt % pectin, 2.5 lignin, 3 wt % proteins, 1.5 wt % fats and waxes, 1 wt % ash(minerals) , 8 wt % water (Bismarch et al. 2002)

Batch sorption experiments

The sorption studies were carried out at 25±1 °C. Solution pH was adjusted with H_2SO_4 or NaOH. A known amount of adsorbent was added to samples and was agitated by a shaker (Labtech, Korea) at 60 rpm agitation speed, allowing sufficient time for adsorption equilibrium. Then, the mixtures were filtered through filter paper, and the Cr (III) ions concentration was determined in the filtrate using Atomic Absorption Spectrophotometer (Varian AA240 FS). Batch adsorption studies were carried out under varying experimental conditions of contact time, initial chromium concentration, adsorbent dose, pH and particle size. The chromium removal efficiency at any instant of time was determined by the following equation:

$$\text{Chromium removal efficiency} = \frac{Co - Ct}{Co} \times 100$$

Where, Co and Ct are the concentration of Cr (III) in the sample solution before and after the treatment. Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 10 g per 100 mL while maintaining the initial chromium concentration at 200 µg/L.

2.6.3 Result Discussion

Effect of adsorbent dose on chromium (III) adsorption by flax

At this stage, the experiments were done under the conditions with pH of 1.5 and variable adsorbent doses (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/100 mL). The effect of adsorbent doses on the adsorption of chromium by flax was presented in Fig.17. As illustrated in Fig.17, The increase in percentage adsorption with the increase in adsorbent dose might be due to the increased number of free surface available, which caused increased number of adsorbate molecules to adsorb. The decrease in uptake might be due to the larger surface area at higher dose which remained free for adsorption at equilibrium.

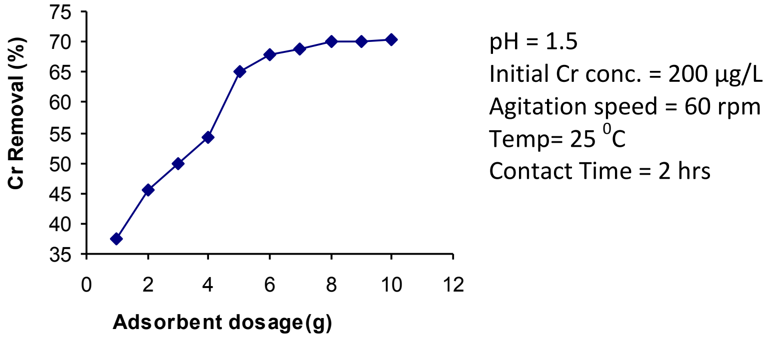

Fig 1: Effect of adsobents dosage on Cr(III) adsorption (contact time 120 min, initial concentration 200 µg/L; initial pH 1.5 of Cr (111) solution in the case of Flax

Effect of contact time on Chromium (III) adsorption by flax

In order to find out the equilibrium contact time, experiments were carried out for 8 h. From the experimental data it was observed that percentage adsorption increased with increase in contact time up to 7 h and after that it attained a stationary phase. From Fig.18, it is observed that initially the adsorption rate was fast followed by a slower rate. Further, the plots between times vs. percentage adsorption were smooth and continuous suggesting the possible monolayer adsorption of Cr (III) on the surface of adsorbent. As optimum adsorption was achieved in 2 h, rest of the experiments were carried out for 2 h time

In this stage, all of the parameters except contact time, including temperature (25 °C), adsorbent dose (5 g/100 mL), pH (1.5), initial chromium concentration (200 µg/L) and agitation speed (60 rpm), were kept constant. There was no significant change in equilibrium concentration after 420min up to 480 min and after 420min, the adsorption phase reached to equilibrium. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Besides, the metal ions are adsorbed into the meso-pores that get almost saturated during the initial stage of adsorption. Thus the driving force for the mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to traverse farther and deeper into the pores encountering much larger resistance (Srivastava, V. C., 2006). This results in the slowing down of the adsorption during the later phase.

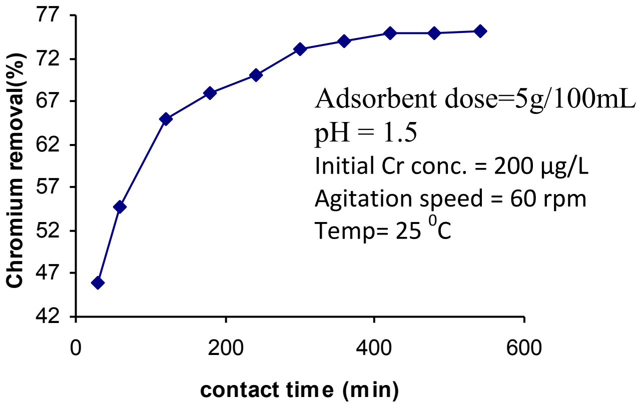

Fig 2: Effect of contact time on Cr III) adsorption (initial concentration 200 µg/L; initial pH 1.5; adsorbent dose 5g/100ml; rotation speed 60 rpm)

Effect of pH on Chromium (III) adsorption by flax

Adsorption experiments were performed at different pH values (1.5, 2.0, 4.0, 6.0, 7.0, 8.0, 10.0, 12.0). From Fig.18, it is observed that the percentage of adsorption increased from 65.2 to 70 percent at a pH from 1.5 to 2 then decrease the percent adsorption with the increase of pH up to 12. The increase in percentage adsorption as well as uptake at lower pH could be well explained by protonation properties of the adsorbent. At low pH values, i.e., higher hydrogen ion concentration, the negative charge at the surface of internal pore were neutralized and some more new adsorption sites were developed which provided a positive charge for anionic Cr(III) complex to get adsorbed on the surface. Again it is observed that the final pH of the solution was always greater than the initial pH of the solution, which confirmed the neutralization of H^+ ions with the negative charge at the surface and envelopment of more H^+ ions in formation of positively charged surface. As a result, the concentration of H^+ ions decreased in the solution and hence the pH of the solution increased. Many authors also reported similar results [Yu, L. J., 2003]. From the adsorption uptake at both higher and lower pH (12 and 1.5) it is concluded that the adsorbent can be used for the treatment of Cr (III) contaminated mining water at higher pH and Cr (III) contaminated industrial water at lower pH.

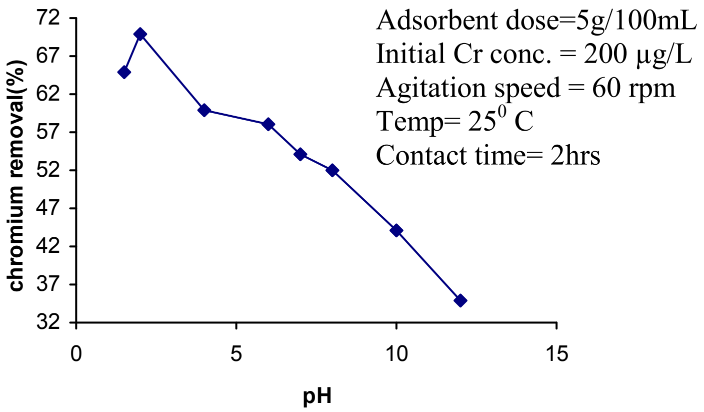

Fig 3: Effect of pH on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg/L; adsorbent dose 5g/100ml)

Effect of initial chromium concentration on Cr (III) adsorption by flax

The percentage adsorption with different adsorbate concentrations was studied by varying Cr(III) concentration from 200 ppb to 3200 ppb keeping adsorbent dose at (5 g/100 mL), stirring speed (60 rpm), pH (1.5), and temperature (25 ^{0} C) constant. Fig.19 shows the effect of initial adsobate concentration. It is observed that the percentage of adsorption decreased with the increase of adsorbate concentration. This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ions remained unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increased. Thus, the loading was faster with higher initial concentrations of adsorbate.

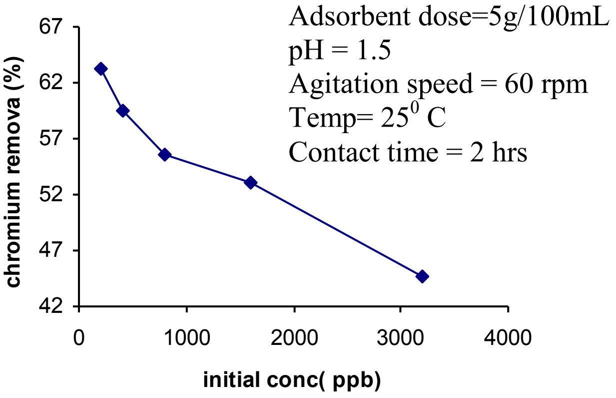

Fig 4: Effect of initial chromium concentration on adsorption (contact time 120 min, initial pH 1.5, adsorbent dose 5g/100ml, rotation speed 60rpm)

Effect of particle size on Cr (III) adsorption by flax

Batch adsorption experiments were carried out for the removal of chromium from aqueous solution using six different particle sizes (0.063,0.074, 0.125, 0.177, 0.42, 0.841 mm). The results are shown in Figure 21. With decresing particle size, the removal incresed from 65.6 to 90.5%.Munaf and Zein reported that, when the size of the adsorbents particles increased, the adsorption of metal ions decreased. Similar trends have been reported by Wong et al. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites compare to larger particles.

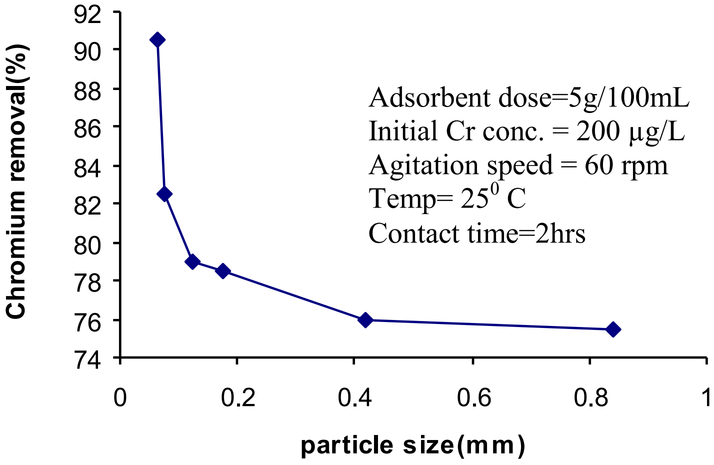

Fig 5: Effect of particle size on Cr(III) adsorption (contact time 120 min, initial concentration 200 µg/L adsorbent dose 5g/100ml, pH 1.5)

2.6.4 FTIR Analysis for Flax

Apart from electrostatic force of attraction, the adsorption might be due to formation of complex in the ligands available in the adsorbents. The adsorbent as such showed peaks at 3421, 2926, 1577, 1261 and 1045 cm-1 which correspond to bonded OH group, aliphatic C-H group, NH_2 scissoring, C-O stretching and C-C stretching respectively. The Cr (III) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups. Therefore

FTIR studies showed the vital role played due to chelation. Chelation is favoured at lower pH and so the adsorption efficiency was more. The results are shown in Table1.

Table 1: FTIR peaks and group assignment (flax)

Peak wavelength cm^{-1}	Assign to
1045	C-C stretching
1261	O-C (sometimes 2-peaks)
1355	a-CH_3 bending
1413	a-CH_2 bending
1577	NH_2 scissoring
2926	CH_3, CH_2 & CH 2 or 3 bands
3421	O-H (H-bonded), usually broad

Adsorption isotherms

At a fixed initial concentration of the adsorbate (200 µg/L), the adsorbent dose was varied. Different adsorption isotherms were tested for the adsorption process. It was found that the data fitted well into the linearized Freundlich adsorption isotherm, whose mathematical expression is $\text{Log } q_e = \log k + \frac{1}{n} \log c$. The plot of log qe vs. log (Ce). Fig -22 shows a linear curve and hence the adsorption obeys the Freundlich adsorption isotherm. Freundlich constant ‘1/n’ from the ‘Y’ intercept and ‘K’ from the slope of the curve was found to be 0.7754 and 0.923 respectively. The Langmuir adsorption isotherm whose mathematical expression is given in above equation was applied for the equilibrium adsorption data and was plotted in Fig. 23. The linear plot of 1/qe vs. ‘1/Ce’ shows that the adsorption obeys the Langmuir adsorption isotherm also.‘Qo’ (µg/g) and ‘b’ (L/µg) are determined from the slope and intercept of the curve and found to be 303.03 and 0.00122 respectively.

Table 2: Isotherm equations (Bulut and Baysal, 2006; Argun *et al*., 2006)

Isotherm name	Isotherm equation	Parameters
Langmuir	$q_e = \frac{\theta . b . C_e}{1 + b . C_e}$	C_e: the equilibrium concentration (mg/L) q_e: the amount adsorbed per amount of adsorbent at the equilibrium (mg/g) θ : (mg/g) and b(L/mg): the Langmuir constant related to the maximum sorption capacity and energy of adsorption, respectively.
Freundlich	$q_e = KC_e^{1/n}$	K(mg/g): an indicator of the adsorption capacity $\frac{1}{n}(mg/L)$:adsorption intensity K: constant related to the adsorption energy (mol^2/KJ^2)

Freundlich isotherm:

Freundlich isothermal equation is

Log q_e= logk +$\frac{1}{n}$logc . . . . (2)

where 'qe' is equilibrium adsorption capacity (mg/g), 'Ce' is the equilibrium concentration of the adsorbate in solution, 'K', and 'n' are constants related to the adsorption process such as adsorption capacity and intensity respectively

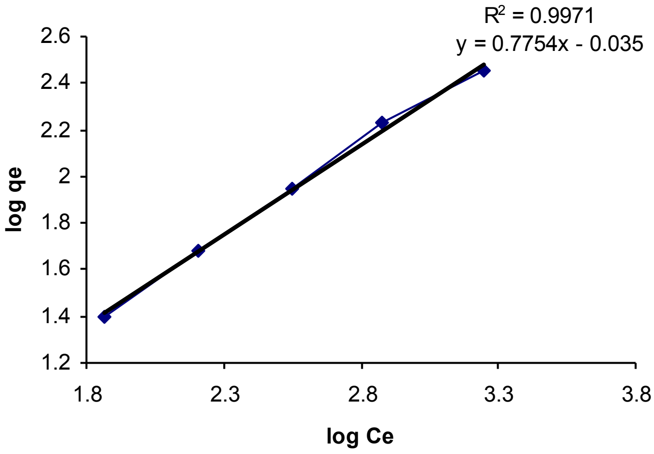

Fig 6: Freundlich isotherm for Cr(III) adsorption onto flax(contact time 2hrs, initial Cr concentration 200 µg/L; pH 1.5; temp 25^0 C; amount of flax 5g; volume 100mL)

Table 3:Freundlich Isotherm variables in case of flax

log Ce	Log (qe)
1.866	1.4
2.209	1.678
2.551	1.948
2.876	2.229
3.248	2.456

Langmuirm isotherm:

The Langmuir isothermal equation is

$$\frac{Ce}{qe}=\frac{1}{Qeb}+\frac{Ce}{Qe}\text{ . . . . (3)}$$

Where 'Ce' is the equilibrium concentration and 'qe' is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g); 'Q_0' and 'b' are Langmuir constants related to the sorption capacity and intensity respectively

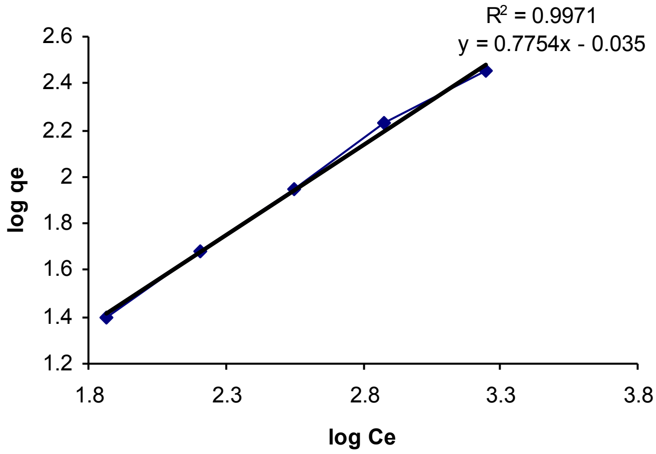

Fig 7: Langmuir isotherm for Cr(III) adsorption onto flax(contact time 2hrs, initial Cr concentration 200 μg/L, pH 1.5, temp 25^0 C, amount of flax 5g, volume 100mL)

Table 4: Langmuirm isotherm variables in case of flax

1/Ce	1/qe
0.00057	0.00486
0.00133	0.0059
0.00281	0.01126
0.00617	0.021
0.0136	0.0395

Adsorption kinetic

In order to find the adsorption kinetic of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging from 30 to 480 min by monitoring the removal percentage of the Cr(III). The data were then regressed against the Lagergren equation (Eq. 6), which represents a first order kinetics equation (Namasivayam and Yamuna, 1995).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \ldots\ldots\ldots\ldots\ldots (6)$$

The correlation coefficient and rate constants were calculated and are given in Table.28. From the table it is observed that the correlation coefficients are in good agreement with the pseudo first order kinetic.

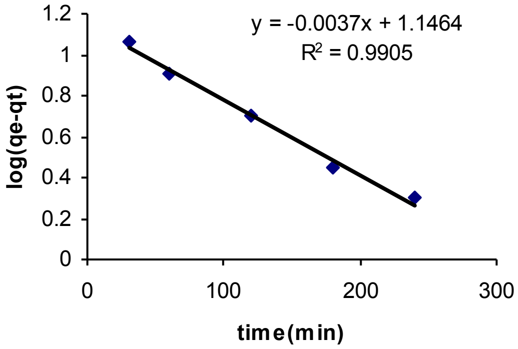

Fig 8: First-order kinetics plot for adsorption of chromium on flax

Table 5: Kinetic variables in case of flax

t (min)	log (qe - qt)
30	1.0645
60	0.911
120	0.6021
180	0.4472
240	0.301

where, qt is the metal uptake per unit weight of adsorbent (µg/g) at time t, qe is the metal uptake per unit weight of adsorbent (µg /g) at equilibrium, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order (Argun *et al.,* 2006). The slopes and intercepts of these curves were used to determine the values of K_1, as well as the equilibrium capacity (qe).

Table 6: Different constants in kinetics in case of flax:

log (qe)	k	R2
1.1239	0.00829	0.9684

Table 7: Different constants in Freundlich isotherm in case of flax:

log k	k	1/n	R2
-0.035	0.923	0.7754	0.9971

Table 8: Different constants in Langmuir isotherm:

Q°(µg/g)	b(L/µg)	R2
303.03	0.00122	0.997

Mechanism of adsorption

pH is an important parameter to determine the efficiency of adsorption. A number of experiments were carried out by varying the initial pH from 1.5 to 12 and the results are shown in Fig 3. It was observed that in all cases, the equilibrium pH was higher than initial pH, which indicated acid neutralization effect and proton adsorption of hydroxylated mineral surface, popularly known as ligand exchange mechanism. It is widely believed that the mechanism for the adsorption of anions onto adsorbent surface involved surface complexation. There are two types of surface complexation such as inner and outer complexation. Formation of these types of complexation depends on the degree of surface protonation or dissociation as shown below:

$$\equiv SOH(s) + H^+ \equiv SOH^+_2(s) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$\equiv SOH(s) \equiv SO^-(s) + H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

where ≡ SOH(s) is surface of the adsorbent.

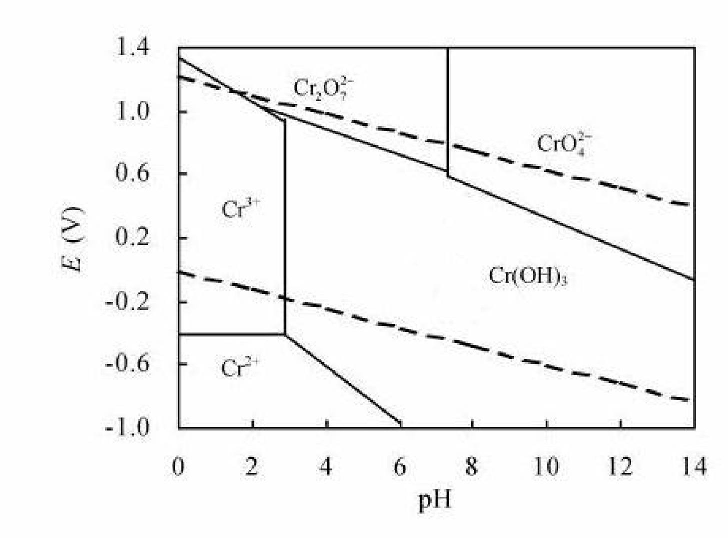

Figure -9; Stability diagram E_h-pH for chromium compounds

If the numbers of protonated surface groups are more than that of dissociated groups, the surface would be positively charged, thus facilitating the anion adsorption. On the other hand, if the amounts of both the species were equal, then the net charge would be zero. Thus the complex formation reaction can be shown as:

Outer sphere complex

$\equiv SOH^+_2(s) + A^{-n} \equiv SOH^+_2(s)\ A^{-n}$ . . . .(10)

Inner sphere complex

$\equiv SOH^+_2(s) + A^{-n} \equiv SA^{(n-1)}(s) + H_2O$ . . . .(11)

where, A is the anion and Cr(III) in the present case. The most dominant species in the aqueous solution are $HCrO_4^-$, CrO_4^{-2} and $Cr_2O_7^{-2}$, whereas the dominant species in pH range 1.7-4.5 (as in case of the present studies) are Cr^{+3} and $HCrO_4^-$. Increase in the initial pH would convert $HCrO_4^-$ to CrO_4^{-2} . It was observed that the lower initial pH facilitated the adsorption of Cr(VI) but not Cr^{+3}.This is because, Cr^{+3} ion under goes competition with the protonation .But at pH-2 , Cr^{+3} ion get sufficient sites to be adsorbed on the $SO^-(s)$ sites. Though the percentage of adsorption increased slightly when the initial pH increased from 1.5to 2.0; on further increase, the adsorption efficiency decreased sharply. This is because, at higher pH the most dominant species is Cr $(OH)_3$ which under goes competition with OH group to adsorb on the surface of adsorbent. Again, the adsorption might be due to formation of complex with the chelating agent present in the adsorbent. Evidence of complex formation was obtained from Fourier Transform Infrared spectroscopy. The adsorbent as such showed peaks at 3421, 2926, 1577, 1261 and 1045 cm-1 which correspond to bonded OH group, aliphatic C-H group, NH_2 scissoring, C-O stretching and C-C stretching respectively. The Cr (III) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional groups. Therefore FTIR studies showed the vital role played due to chelation. Chelation is favoured at lower pH and so the adsorption efficiency was more.

Desorption

Desorption: Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorbs chromium (III) from the flax surface with various eluents, such as hydrochloric, sulfuric and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. The results are presented in Table 1. Although the achievement of arsenic eluting using strong acidic or alkaline solution has been reported in the literature (Lorenzen *et el.,* 1995), the present work showed that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was useful for the desorption of chromium from the surface of flax and the desorption efficiencies with 0.5M KOH was 90%.

Table 9: Influence of the Eluent on the desorption of Cr (III) (shaking time-2 hours)

Desorption agent	Desorption (%)
NaOH (0.5M)	72.0 ± 0.03
KOH(0.5M)	90.0 ± 0.05
HCl(0.5M)	17.0 ± 0.01
H_2SO_4(0.5M)	28.0 ± 0.02
HNO3(0.5M)	29.5 ± 0.02

Adsorption process: Initial Cr concentration, 200 μg/L, flax 5gm, volume of desorption agent, 100mL, RPM 60.

2.6.5 Application of the Developed Treatment System

Tanning industries are one of the main economic activities in Bangladesh. It has been well documented that waste water discharged from tanneries without appropriate treatment results in detrimental effects on the ecosystem. No ecotoxicity evaluation of any aquatic environment in Bangladesh has been conducted so far. In this study Chromium analysis were carried out from water samples obtained from two sampling points: Kalo Nagar,Hazaribug (S1),where different effluents of tanneries are flowing and effluent discharging site on the river Buriganga (S2), in the Hazaribagh tannery area of Dhaka City, Bangladesh. The concentrations of chromium in the samples were 3.1 mg/L and 1.46 mg/L. The treatment results are presented in Table 32. Although 25g of adsorbent was applied in the treatment, the concentrations of chromium in the treated sample water could be lower to 322μg/L and 174 μg/L. The desorption efficiencies with 100mL of 0.5M KOH were 100%. From the present results, the chromium was successfully removed from practical chromium contaminated water and adsorbed chromium could be recovered from the surface of flax.

Fig 10: Tannery Effluent flowing to the river Buriganga from Hazaribag, Dhaka, Bangladesh

Fig 11: The polluted Buriganga (the water is deeply black in color and bad odor)

Table 10: Removal and Desorption of Chromium from the contaminated water of Bangladesh

	Sample1	Sample2
pH	7.5	8
initial Cr conc(μg/L)	3100 ± 2.0	1460 ± 1.0
final Cr conc(μg/L)	322 ± 0.5	174 ± 0.3
removal^a (%)	89.61 ± 0.1	88.0 ± 0.1
desorption^b (%)	100 ± 0.9	100 ± 0.5

2.6.6 Conclusion

The present research showed that flax can be effectively used as an excellent alternative for the removal of Cr (III) from aqueous solutions. The adsorption of Cr

(III) was found to depend on pH, particle size, contact time, adsorbent dosage and initial metal concentration. Both Langmuir and Freundlich isotherms show very good fit with the experimental adsorption equilibrium data. The kinetics analysis of the study showed that the adsorption of Cr (III) ions onto flax could be well described with the first-order kinetics model. It can be concluded that the developed method can be effectively applied for the removal of chromium from chromium containing water and effluent.

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2.7 Accumulation and Histopathological Effects of Arsenic in Tissues of Shingi Fish (Stinging Catfish) *Heteropneustes Fossilis* (Bloch, 1794)

2.7.1 Introduction

Study of toxicology pertaining to aquatic animals has become important in water pollution studies. Heavy metal contaminants in aquatic ecosystems pose a serious environmental hazard because of their persistence and toxicity. Among the heavy metal pollutants, arsenic (As) receives a special attention due to its potential health hazard to aquatic fauna and human life in particular. The recent research has suggested that As acts as an endocrine disruptor at extremely low concentrations (Stoica *et al.* 2000). The presence of As in industrial wastes and its high toxicity along with considerable bioaccumulation in freshwater fishes make it a toxicant that should be given due consideration in aquatic toxicology. The term bioaccumulation refers to the wastes which have been reconcentrated in organisms often having undergone initial dilution in environment producing toxic effects in fishes (Dallinger *et al.* 1987). Availability of heavy metals in the aquatic ecosystem and its impact on the flora and fauna had been reported by many investigators (Nayak 1999 and Shrinivas and Balaparameswara 1999). The accumulation of heavy metals in different tissues of fish may cause various physiological defects and mortality (Torres *et al.* 1987). Heavy metals accumulated in the tissues of aquatic animals may become toxic when accumulation reaches a substantially high level (Kalay and Canli 2000). The pattern of accumulation of metals in animals differs from metal to metal and organ to organ during their functional status. Most of the investigations pertaining to heavy metals contaminants in aquatic systems are dealt either with toxicity or with accumulation (Rushforth *et al.* 1981 and Khadiga *et al.* 2002).Heavy metals have been shown to be concentrated in the liver of various fishes (Sorensen1991 and Rao *et al.* 1998). The highest concentrations of As was recorded in the liver, while the lowest one was in the muscle. Mormede and Davies (2001) suggested that the liver was the target organ, showing the detoxification and accumulation role of the liver. Muscle is generally considered to have a weak accumulating potential (Erdoğrul and Erbilir 2007, Uysal *et al.* 2009 and Bervoets and Blust 2003). Histological changes associated with heavy metals in fish have been studied by many authors (Thophon *et al.* 2003, Mohamed and Gad 2005, Athikesavan *et al.* 2006, Giari *et al.* 2007, Jiraungkoorskul *et al.* 2007 and Van Dyk *et al.* 2007). Hence, the present study was aimed to investigate the accumulation of As in *Heteropneustes fossilis* (Bloch) and the associated histopathological changes in three organs (muscle, liver and intestine) at laboratory condition.

2.7.2 Materials and Methods

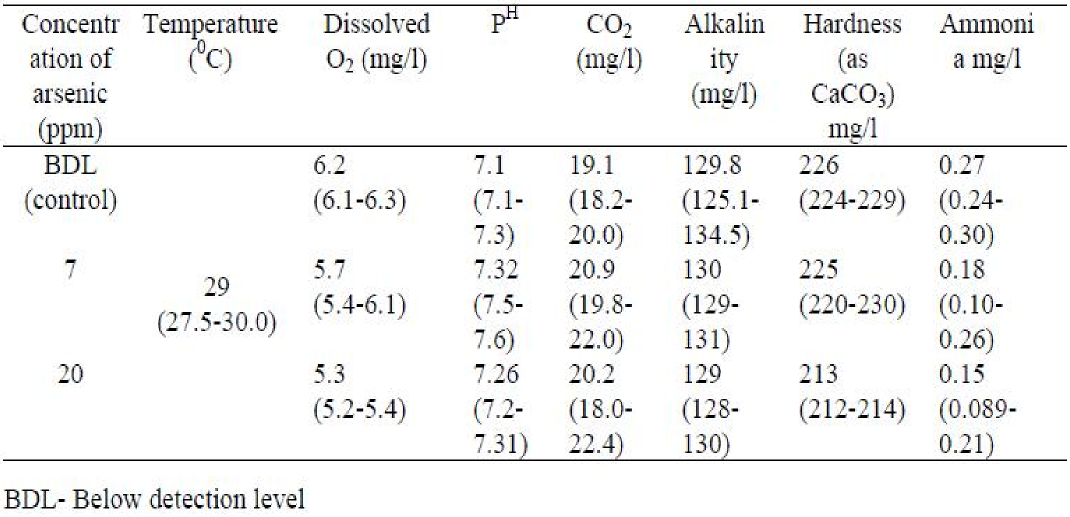
Special care was taken to make sure that the fish were approximately of similar size and weight. Fishes with almost similar length (8.15±0.51 cm) and weight (6.25±0.75 g) were collected from local market and were acclimatized under laboratory conditions (29.0±1 ^{0}C). Fishes were transported to the laboratory in large buckets with proper covering and frequent agitation. On arrival at the laboratory, these were immediately released into three big tanks containing tap water and then maintained there for about 6-7 days in a static condition. Fishes were fed on artificial feed twice daily. Any debris or unwanted particles were removed from the tank after feeding. The water medium was changed at 24 hours interval to remove the metabolic-pollutants. Air compressor with air stones was used for oxygenation of water. The water quality parameters of the acclimation tank were studied at times. However, after acclimation, only healthy fishes were used for experiment. Arsenic trioxide (As_2O_3) was collected from the BDH laboratory (England) in original package form. By mixing with tap water two different concentrations of As_2O_3 was used as stock solution. The fishes were exposed to two concentrations for a period of 1, 15 and 60 days in glass aquaria containing 10-20 L water. Tap water stored in the tank for two months confirming the settlement of iron, were used for the experiment. The water was aerated for one day before starting the experiment. Stone aerators connected to a compressed air supply were used to maintain an adequate level of dissolved oxygen in each aquarium. The liver, intestine and muscle tissues of control and treated fishes were isolated and dried in an oven at 105 ^{0}C for 24 hours. The known amounts of dried tissues Accumulation and histopathological were digested with nitric acid and perchloric acid. After the accomplishment of complete digestion, the digested samples were made-up to 25 ml with metal free double distilled water and arsenic measurements were made using atomic absorption spectrophotometer (Begum *et al.* 2005). Values were expressed as µg/g, dry weight.

At the end of the exposure period, muscle, intestine and liver were collected from the *H. fossilis* and preserved in small plastic vials with 10% buffered neutral formalin (Begum *et al.* 1996). The number at section of samples was prepared using a microtome, stained and studied under a photomicroscope (Olympus, CH4O, Japan). Photomicrographs were taken after the examination of histological condition of each of the tissue slides.

2.7.3 Results and Discussion

The physico-chemical properties (temperature, dissolved oxygen, pH, carbon dioxide, alkalinity, total hardness and ammonia concentration) of the tap water were monitored during the acclimation period and trial with fishes exposed to As_2O_3 (Table 1). It is evident from the data that (Table 1), the water quality parameters did not fluctuate greatly among the different treatment aquariums as well as between different experimental trials. Moreover, the water quality was always within the normal ranges.

Table 1. Physico-chemical parameters of aquarium water with different treatments of arsenic (As).

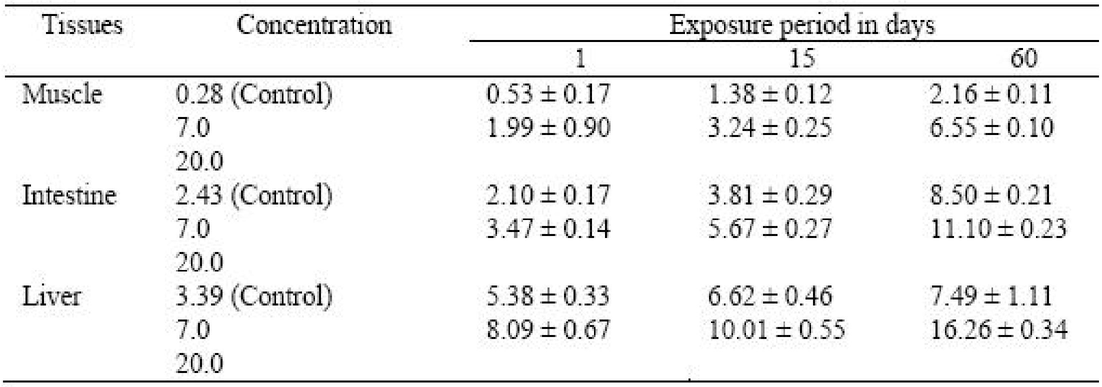


Concentration of arsenic (ppm)	Temperature (^{0}C)	Dissolved O_2 (mg/l)	P^H	CO_2 (mg/l)	Alkalinity (mg/l)	Hardness (as $CaCO_3$) mg/l	Ammonia mg/l
BDL (control)	29 (27.5-30.0)	6.2 (6.1-6.3)	7.1 (7.1-7.3)	19.1 (18.2-20.0)	129.8 (125.1-134.5)	226 (224-229)	0.27 (0.24-0.30)
7		5.7 (5.4-6.1)	7.32 (7.5-7.6)	20.9 (19.8-22.0)	130 (129-131)	225 (220-230)	0.18 (0.10-0.26)
20		5.3 (5.2-5.4)	7.26 (7.2-7.31)	20.2 (18.0-22.4)	129 (128-130)	213 (212-214)	0.15 (0.089-0.21)

BDL- Below detection level

The levels of arsenic (As) accumulation in the liver, intestine and muscle tissues of *H. fossilis,* during exposed to control, 7 and 20 ppm of concentration for 1, 15 and 60 days are presented in Table 2. In the present investigation, the highest level of As accumulation (10.01 ± 0.55) and (16.26 ± 0.34) was found in the liver and lowest level (3.24 ± 0.25) and (6.55 ± 0.10) in muscle to 15 and 60 days of exposure periods, respectively. Similar pattern of accumulation of As in the liver tissues of *Mugil cephalus* has been reported by Maher et al. (1999) and found significantly higher than in any other tissues. Pazhanisamy et al. (2007) investigated the accumulation of As in Labeo rohita after exposed in two sub lethal concentration of As trioxide. They found that the maximum level of accumulation of As was in the liver whereas, the lowest level in the muscle tissue at the end of 28 days of exposure. Similarly, the distribution and accumulation pattern of heavy metals in the liver of various teleosts fishes have been studied by Noel-Lambot et al. (1978) and Thiruvalluvan et al. (1997). In the present study, the rate of accumulation was found to increase gradually with the As concentration and the exposure time. The findings are identical with the report of Karuppasamy (1999) while, described the bioaccumulation as dose and time dependent in phenyl mercuric acetate exposed fish *Channa punctatus*.

Table 2. Accumulation of arsenic (µg/g, dry weight) in tissues of *H. fossilis* exposed to different concentration and exposure periods (days).



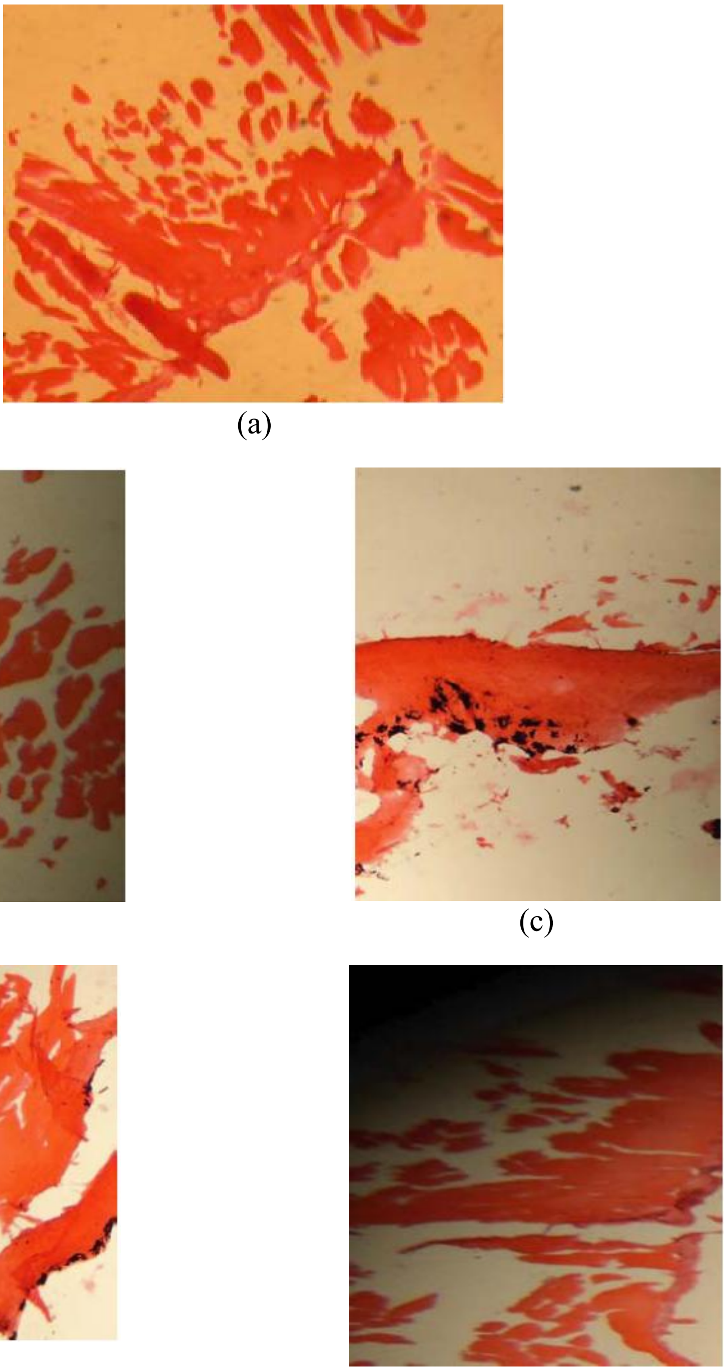
Tissues	Concentration	Exposure period in days		
		1	15	60
Muscle	0.28 (Control)	0.53 ± 0.17	1.38 ± 0.12	2.16 ± 0.11
	7.0	1.99 ± 0.90	3.24 ± 0.25	6.55 ± 0.10
	20.0			
Intestine	2.43 (Control)	2.10 ± 0.17	3.81 ± 0.29	8.50 ± 0.21
	7.0	3.47 ± 0.14	5.67 ± 0.27	11.10 ± 0.23
	20.0			
Liver	3.39 (Control)	5.38 ± 0.33	6.62 ± 0.46	7.49 ± 1.11
	7.0	8.09 ± 0.67	10.01 ± 0.55	16.26 ± 0.34
	20.0			

Then, with the rate of accumulation of As and days of exposure, the histopathological study also showed drastic changes in muscle, intestine and liver tissues of the exposed fish. These findings suggested that the observed changes were undoubtedly as a result of various toxicological impact of As exposure. Even, these changes were directly related with the concentration of 7 and 20 ppm of Arsenic along the 1, 15 and 60 days of exposure (Plate 1a). However, at 7 ppm exposed to As, the muscle tissue exhibited dystrophic changes with marked thickening and separation of muscle bundles after 15 days of exposure (Plate 1b), but, such a change after 60 days of exposure, the vacuolar degeneration in muscle bundles with aggregations of inflammatory cells between them and focal areas of necrosis were observed (Plate 1c). Again, at 20 ppm of Arsenic concentration, the muscle tissues exhibited dystrophic changes with marked thickening and vacuolar degeneration of muscle bundles along with severe intramuscular edema after 15 days of exposure (Plate 1d) while, atrophy and edema of muscle bundles as well as splitting of muscle fibers were seen in 60 days of As exposure of fish (Plate 1e). It is true that like gills, muscle tissue also come into close contact with pollutants dissolved in water. Therefore, the muscles of *H. fossilis* showed degeneration in muscle bundles accompanied with focal areas of necrosis as well as atrophy and vacuolar degeneration. Similar findings had been observed in Nilotica fish by Mohamed (2008).

In the case of intestine (Plate 2a), the histopathological changes so obtained in 7 ppm of As concentration and 15 days of exposed included partial intactness of serosa but, more or less organized mucosa and disorganized villi (Plate 2b). The same organ, even at same concentration after 60 days of exposure exhibited partially damage of muscles, but disorganized, slightly swollen and shorten of villi (Plate 2c). This in 20 ppm concentration of As and after 15 days of exposure showed damaged serosa disorganized and consequent fussion of mucosa, degeneration and edema between the intestinal submucosa and lamina propria (Plate 2d). Further, these damages were characterized by the increases in number of goblet (mucosal) cells, width of the lamina propria and degeneration of villi after 60 days of As exposure (Plate 2e). The findings suggest that however, uptake of As and other metals occur mainly through gills but may also occur *via* intestinal epithelium. Therefore, the histopathological alterations so far observed in the intestine tissues of studied fish may be a result of uptake of toxic As. The present results are in agreement with those observed by many investigators about the effects of metals on fish intestine (Giari *et al.* 2007 and Hanna *et al.* 2005).

Observations on the fish liver (Plate 3a) revealed that in 7 ppm of As concentration, and 15 days of exposure primary degeneration occurred in the hepatocytes (Plate 3b), which at the end of 60 days showed further changes like focal areas of necrosis, haemorrhage and haemolysis between the hepatocytes (Plate 3c). On the other hand, fish exposed to As concentration of 20 ppm, the hepatocytes became more irregular and lose their polygonal shape, areas of hepatocytes with eosinophilic cytoplasm (Plate 3d). Moreover, haemosiderin was seen around central veins and hepatoportal blood vessels. In some cases, dilation and intravascular haemolysis in hepatoportal blood vessels were noticed at 60 days of exposure (Plate 3e). Sorensen (1991) stated that the liver is a critical target organ for As toxicity in fish due to the role it plays in metabolism and detoxification. Such a statement is supported by the results of our present study, as livers of shingi fish exposed to different concentrations of As showed significant changes in architectural and structural arrangements, as well as areas of inflammation and focal necrosis. Similar alterations have been observed in fish liver being exposed to As in both the laboratory and field conditions (Gilderhus 1966 and Joshi and Sahu 2007).

Thus, comparing the entire findings it is clear that the highest/maximum level of As accumulation obtained in the liver and intestine, whereas, the lowest in the muscle tissues at the end of exposure periods. At the same time, it indicates about the intensity of histological alterations are also dose (As concentration) and time dependent. In conjugation of these two facts, the As trioxide affects severely on the tissues of internal organs of *H. fossilis* leading to life threat and poor reproductive performance. Moreover, the present study suggests further detailed investigation on the possible As pollution sources as well as the rate of accumulation in different fish tissues and possible histological changes.



(a)

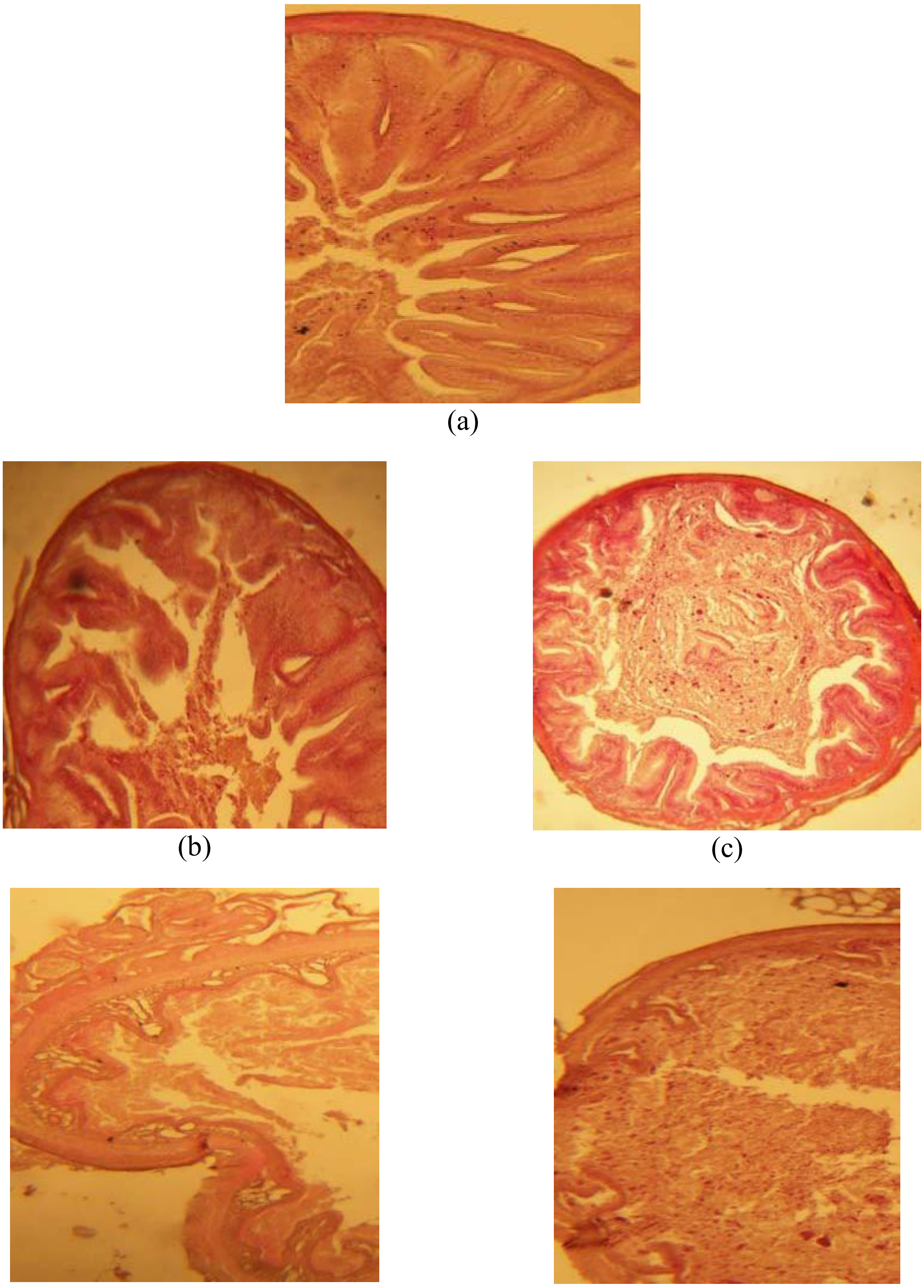
(b)

(c)

(d)

(e)

Plate 1. (a) Muscles of fish showing the normal, (b) separation in muscle bundles, (c) focal area of necrosis, (d) intramuscular edema and (e) splitting of muscle fibers and atrophy of muscle bundles.



(a)

(b)

(c)

(d)

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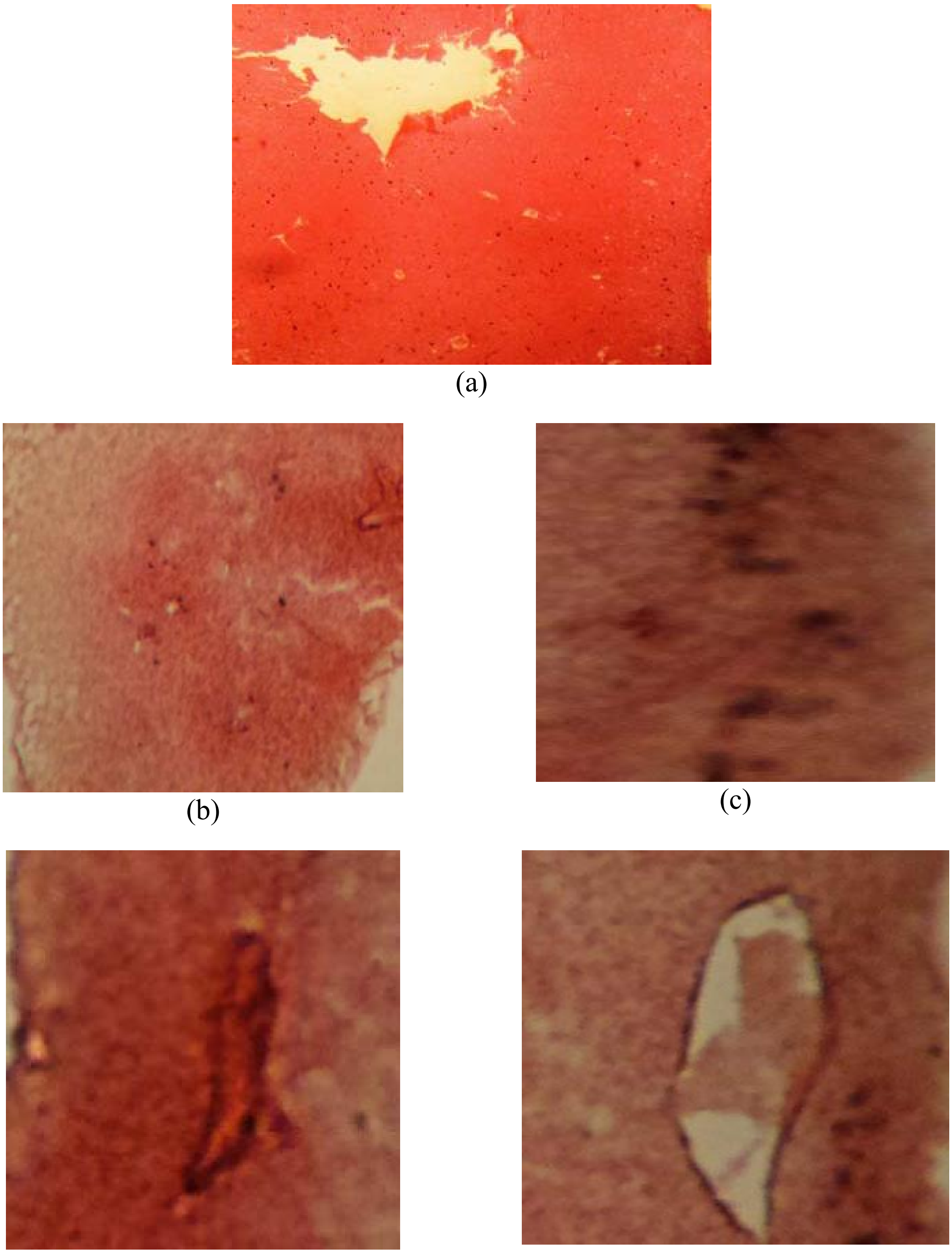
Plate 2. (a) Intestine of fish showing the normal, (b) serosa showed partial intacness and disorganized villi, (c) severe damage in muscularis and villi slightly swollen and shortened, (d) degeneration and edema between the intestinal submucosa and lamina propria and (e) increase in the width of lamina propria and villi degenerated.



(a)

(b)

(c)

(d)

(e)

Plate 3. (a) Liver of fish showing the normal, (b) vacuolar degeneration, (c) focal areas of necrosis, (d) haemorrhage and haemolysis between the hepatocytes, intravascular haemolysis in blood vessels and (e) intravascular haemolysis in hepatoportal blood vessels.

2.7.4 References

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CHAPTER THREE: CONCLUSIVE REMARKS

The experimental results show that duckweed (*Lemna minor)* and neembark (*Azadirachta indica)* are excellent alternatives for the removal of As (III) from aqueous solutions. The adsorption of As (III) was dependent on pH, particle sizes, contact time, adsorbent dose and initial metal concentration. It was observed that the optimum efficiency of adsorption of As (III) by duck weed is at a condition of pH 5.5, flow rate 1.67 ml/min, adsorbent amount 3g/100ml whereas for neembark the optimum efficiency was at pH 7, flow rate 1.67 ml/min, adsorbent amount 5g/100ml of 100 ppb As (III) solution. Moreover, the desorption experiments show that the metals can be desorbed after adsorption and arsenic (III) can be recovered as well as used for various purposes.

The proposed treatment coulumn systems are suitable and apporapriate for homemade approaches to arsenic removal in rural and local areas, beacuse of their easy operation, simplicity and handling. The present method is effective for a wide range of As (III) concentrations (i.e., 50-500 µg/L), which were quite similar to those observed in contaminated Bangladeshi groundwater. No secondary- pollution problem will occur, because desorption of the arsenic is possible. Direct removal of arsenic (III) can be achieved without first oxidizing arsenate to arsenite, whereas the traditional methods require the oxidation process. Based on the results of this research, duck weed and neem bark can be considered as low cost, effective, available and natural adsorbent for removing arsenic from ground water.

In case of chromium removal, the experimental results show that ground nutshell and flax are excellent alternatives for the removal of chromium from aqueous solutions. The adsorption of Cr (III) and Cr (VI) were dependent on pH, particle sizes, contact time, adsorbent dose and initial metal concentration. It was observed that the optimum efficiency of adsorption of Cr (III) by nutshell is pH 7, adsorption time 2 hours, adsorbent amount 5g/100ml solution of 200 ppb Cr (III) solution and that for flax is pH 2, adsorption time 2 hours, adsorbent amount 5g/100ml solution of 200 ppb Cr (III) solution. Also for the removal of Cr (VI) with nutshell, the optimum pH of the solution was observed at pH 2. Both Langmuir and Freundlich isotherms were followed by the adsorption of Cr (III) and Cr (VI). The kinetic analysis of the study showed that the adsorption of Cr (III) ions onto ground nutshell could be well described with the first-order kinetics model on the other hand, the flax could be pseudo-first order kinetics model and the rate constant for the process was found to be 0.01min^{-1} at 25 °C for nutshell and flax. Moreover, the desorption experiments show that the metal can be desorbed after adsorption and chromium can be recovered. Based on the results of this research, ground nutshell and flax can be considered as cost effective, available and natural adsorbent for removing chromium from aqueous solutions.

A 60-day experiment was conducted to compare the accumulation and toxicological effects of arsenic (muscle, intestine and liver) of shingi fish, *H. fossilis* (Bloch) after exposure to two concentrations (7.0 and 20.0 ppm) of arsenic trioxide at different time intervals. It is observed that accumulation of arsenic in the liver gradually increasing with time of exposure whereas the lowest level of arsenic was found to accumulate in the muscle tissues at the end of exposure period. It is apparent from the study that the damage of the liver of test fish due to 15 days exposed period was less compared to the damage caused by 60 days exposure periods. The intensity of histological alterations was observed to increase gradually with the arsenic concentration and the exposure time. Moreover, the present study suggests further detailed investigation on the possible arsenic pollution sources as well as the rate of its accumulation in different fish tissues and possible histological changes.

Based on the results of this research, duckweed and neembark can be considered as low cost, effective, available and natural adsorbents for removal of arsenic (III) and ground nutshell, flax can be effectively applied for the removal of chromium (III) and chromium (VI) from waste water.

LIST OF PUBLICATIONS BASED ON THE PRESENT WORK

1. “Adsorption, Desorption and kinetic study on hexavalent Chromium removal from aqueous solution using ground nut shell**”, Tasrina R. Choudhury**, M. N. Amin, S.B Quraishi, A.I.Mustafa, Research Journal in Engineering and Applied Sciences, 3(1), pp. 1-6, 2014.
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