REMOVAL OF ARSENIC FROM SYNTHETIC WASTEWATER

A DISSERTATION

Submitted in partial fulfilment of the
Requirements for the award of the degree
of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

by

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CANDIDATE's DECLARATION

I hereby declare that the report, entitled "**REMOVAL OF ARSENIC FROM SYNTHETIC WASTEWATER**" in partial fulfilment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in **Industrial Pollution Abatement (IPA)** and submitted in the **Department of Chemical Engineering of Indian Institute of Technology Roorkee, India,** is an authentic record of my own work carried out during the period from JUNE 2012 to JUNE 2013, under the supervision of **Dr. C. Balomajumder**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, India.

The matter embodied in this report has not been submitted by me for the award of any other degree of this or any other Institute / University.

Date: SMITA MONDAL

Place:

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Arsenic contamination in wastewater, even in drinking water has been recognized as a worldwide problem. It affects human health severely if the limit of toxicity is crossed. There are several treatment methods capable of this level of performance - membranes, coagulation, anion exchange, disposable iron media, softening, adsorption etc. But adsorption is the cheaper and easier as well as efficient method compared to other methods for removal of metal ions. The present study has been carried out using two different raw bioadsorbents like rice husk and maize leaves. Several work has been done on these bio-adsorbents and it has been already reported that rice husk and maize leaves are one of the cheap and effective bioadsorbents for removal of arsenic from industrial wastewater. But the removal efficiency has been increased when adsorbents are impregnated by zirconium and zinc. Different analysis such as FESEM, EDAX, TGA, DTA, FTIR has been done to characterize the adsorbent. FESEM can be able to capture the images of the adsorbents with high resolution. EDAX determines metals and elements presence on the rice husk.DTA/TGA shows the loss of the moisture with respect to temperature. SDDC method was applied for analysis of arsenic. Batch experiments were conducted by varying various process parameters such as pH, contact time and temperature. At optimum treatment conditions (pH 8, contact time of 5 hrs and temperature of 35°C, adsorbent dose 10 g/l) 89.5% As was removed from aqueous solution. Langmuir and Freundlich isotherms were used for equilibrium studies. Freundlich isotherm was better fitted with experimental data. As well as adsorption biological methods are promising field due to cost-effectiveness and in this method possibility of sludge production is nil. In this study immobilization of *P. putida* MTCC 1194 on zirconium impregnated rice husk has been done in order to increase arsenic removal capacity.

TABLE OF CONTENTS PAGE NO

FIGURE LIST OF FIGURES PAGE NO

PAGE

TABLE LIST OF TABLES NO

CHAPTER 1

INTRODUCTION

1.1 General

Arsenic, one of the toxic heavy metals causes severe damage in human beings and also to plants. The fact which is responsible for presence of arsenic in water is leaching from arsenic containing rocks. The occurrence of arsenic is due to earth's crust. It can be found most commonly in the form of FeAsS or Iron Arsenide Sulfide. The other source of arsenic emitting into the air is coal-power plants, burning of dry vegetation, combustion of fossil fuels, mining activities, use of arsenic pesticides (Khan et al.,2011).There are many different compounds of both inorganic and organic arsenic (Saha et al.,1999).Arsenic can be found in water in following oxidation states e.g., As(V), As(III), As(0) and As (-III) (Berg et al.,2001). Since arsenic is not biodegradable, it comprises severe health hazards. Bangladesh, West Bengal (India), and regions of China, Vietnam (Berg et al.,2001) are badly affected by toxicity of arsenic. Primary drinking water standard for arsenic has been reduced from 50 µg/l to 10 µg/l by United States Environmental Protection Agency for the sake of human health.

Efficiency of activated carbon in adsorption process for heavy metals removal is worldwide known. But due to its high cost research on low cost adsorbing materials have been conducting till now. Rice husk and maize leaves are cheap and easily available bio-adsorbents for removal of arsenic from wastewater. To increase the efficiency of raw rice husk iron,copper,manganese,$CaCl_2$ impregnation on to raw rice husk has been already reported (Goel et al., 2004), (Gu et al.,2005), (Jubinka et al.,1992),(Mondal et al.,2007).In this study surface modification has been done by zirconium oxychloride, zinc chloride. Previously zirconium loaded phosphoric chelate resin and zirconium loaded activated carbon has been used and efficiency for the case of arsenic removal was quite high.(Daus et al.,2004).So from this result it can be expected that zirconium impregnated rice husk can be quite effective for arsenic removal due to modified surface of raw rice husk.

As well as adsorption biological methods are promising field due to cost-effectiveness and since the possibility of sludge production is nil so this method has increased its popularity continuously. In the present study SAB (simultaneous adsorption and bioaccumulation) has been studied by immobilized *p.putida* MTCC 1194 on the zirconium impregnated rice husk.

1.2 Toxicity limit

Drinking water: US EPA 10 µg/l (ppb)

1.3 Sources of arsenic

The occurance of arsenic is due to earth's crust. It can be found most commonly in the form of FeAsS, or Iron Arsenide Sulfide. It can also be found in the form of arsenic trioxide dusts, a by-product of industrial smelting operations. The major sources of arsenic are of natural origin such

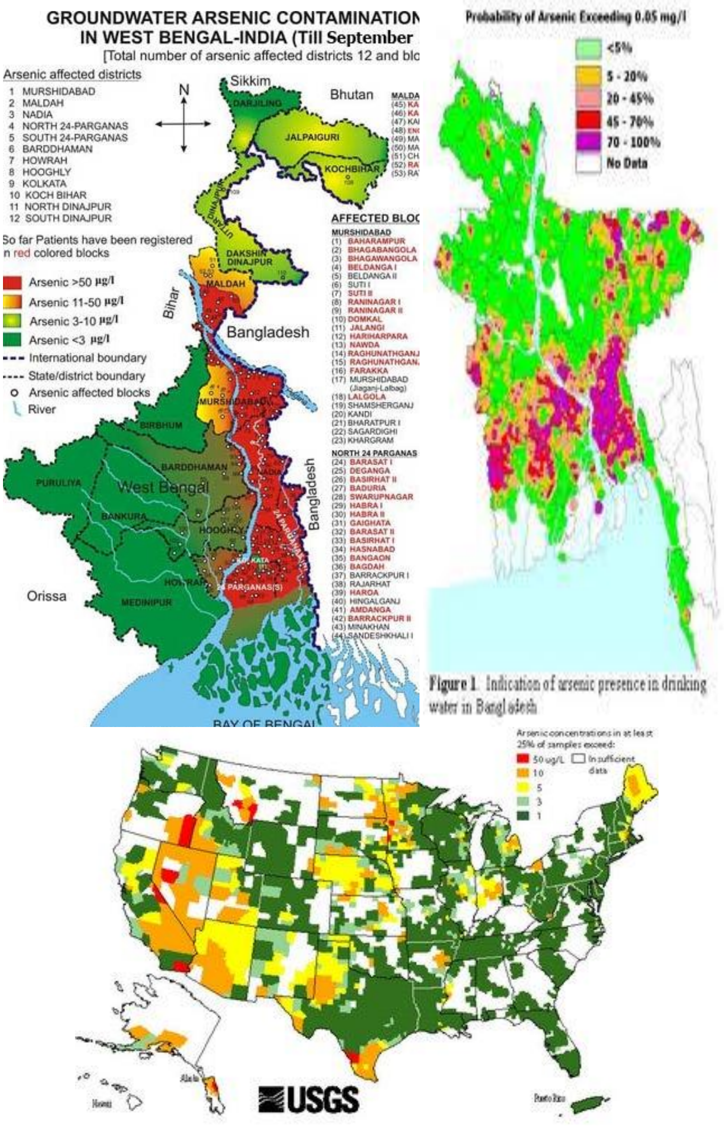


Fig:1.1 Arsenic affected area in West Bengal, Bangladesh and USA

as volcanic action, low temperature volatilization, geothermal activity etc. Anthropogenic sources of arsenic are processing of ores, wool and cotton processing, from glass and semi conductor industry etc (Environmental protection agency,2002).Surface water is less contaminated of arsenic than groundwater. But surface water (ex: river water) when mixed with industrial effluents, then contamination of arsenic in surface water increases (Vasireddy, 2005).

1.4 Arsenic occurrence in the environment

Arsenic is present in all over the atmosphere, rocks, soils, water and air. Arsenic occurrence in environment is through earth crust. Rocks containing arsenopyrite (FeAsS) which is natural source of arsenic. As concentration in this material is almost 20000 ppm which is highly responsible for occurrence of As in environment. Arsenic contamination in water occurs due to leaching of arsenic from arsenic contaminated rocks and soils. Contamination of arsenic in water is dependent on different factors, Type of water,(ground water is more affected than surface water), degree of biological activity by which inorganic arsenic is converted to methylated arsenic acids, sources of anthropogenic activity etc. In gold mining water, As remains 1g/l in seawater whether groundwater level of As is 15 ppb only. Ground water is generally primary source of drinking water. As contamination in drinking water is a great thread to human beings. The regions of ground water affected badly due to arsenic contamination are Bangladesh, West Bengal (India),China, Argentina, USA, Australia, Mexico, Chile, Taiwan and Viet Nam. As concentration level of groundwater of these region are 200- 1000 ppb. Volcanic emission, weathering reactions are responsible for As contamination in air. Anthropogenic activities are mining, fossil fuel, metal refining, use of pesticides, cotton desiccants, defoliants, and soil sterilants. It has been reported that 24000 tonnes of arsenic per year are discharged to the atmosphere due to anthropogenic activity (WHO 2000, 2001).

Arsenic is found in nature in two forms: organic and inorganic. As (III) and As (V) are inorganic arsenic mostly found in environment. Biological activity is the source of organic arsenic. Organic arsenic is found in foodstuffs, shellfish in form of monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and arseno-sugars etc. Biological activity is also a source of organic arsenic. However, using of agricultural pesticides has been banned in 2009 by USEPA. But a weed herbicide containing monosodium methanearsonate (MSMA), is till continuing for use in cotton fields. Some organic arsenic compounds are used as additives for poultry for gaining weight and also used for treatment.(EPA 2000,EPA 2006,FDA 2008a, b).

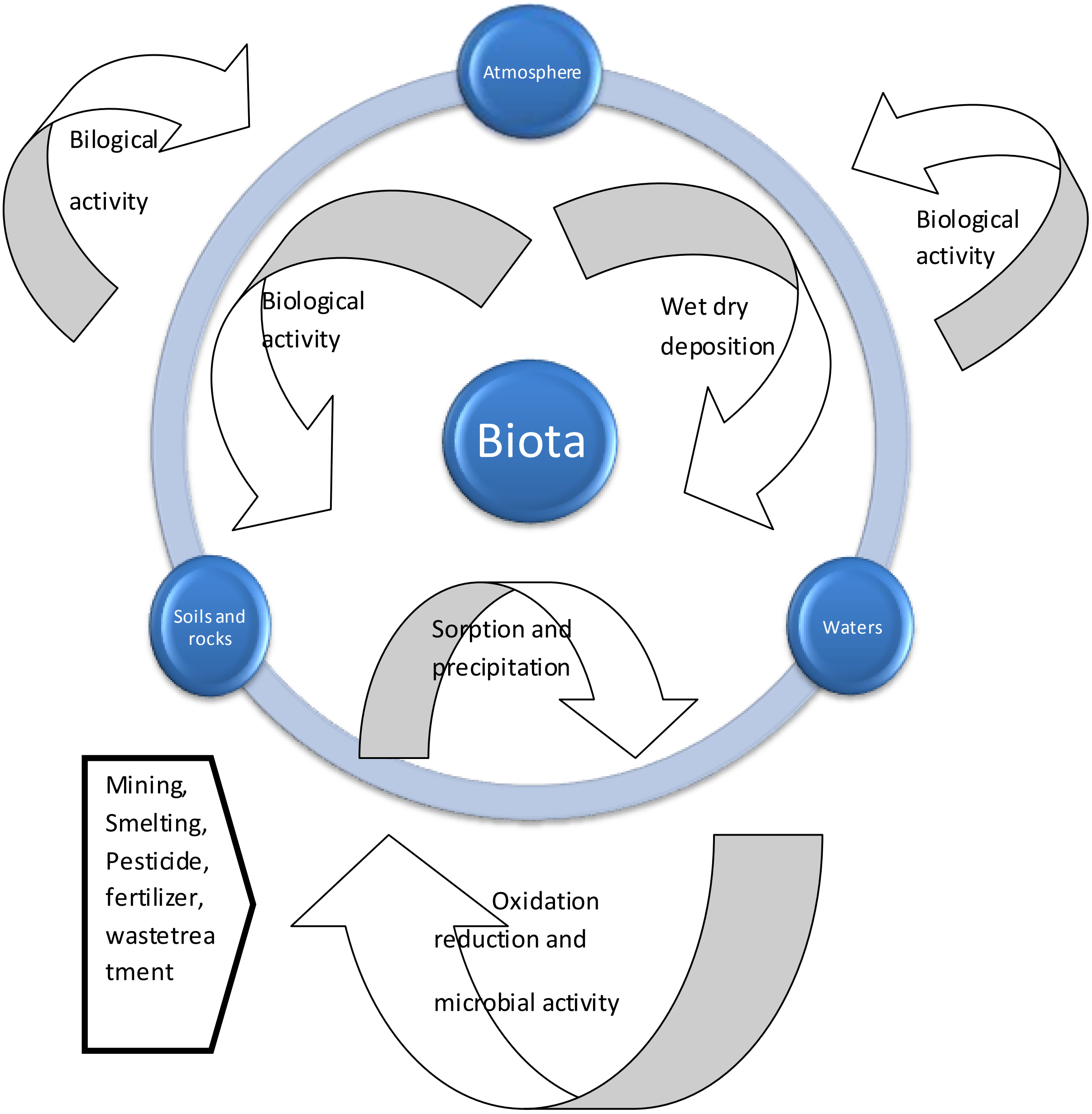


Fig:1.2 Arsenic cycle in environment

1.5 Chemistry of arsenic

Arsenite-As(III)	$H_4AsO_3^+$	H_3AsO_3	H_2AsO_{3-}	$HAsO_3^{2-}$	AsO_3^{3-}
Arsenate-As(V)	H_3AsO_4	H_2AsO4-	$HAsO_4^{2-}$	ASO_4^{3-}	

Elemental arsenic is a grey-coloured crystalline metallic solid. It has atomic no 33 and atomic mass 74.92 and it exists in group 15 in periodic table. Though it is considered as a metal but it behaves as an intermediate of metal and non-metal. It exhibits the behaviour of semi-metal and it has low conductivity. Inorganic arsenic remains stable in four oxidation states (-3, 0,+3, +5). Arsenite (+3) and arsenate (+5) are the more common form available in nature. Though As (III) and As (V) are positive but arsenic remains as an anion in aqueous media. As (III) is only available in ground water but As (V) exists in both surface water as well as groundwater. pKa values expressed as const of dissociation are as follows:

For arsenate, H_3AsO_4 $pK_1 = 2.19$, $pK_2 = 6.94$, $pK_3 = 11.5$.

For arsenite, H_3AsO_3 $pK_1 = 9.20$, $pK_2 = 14.22$, $pK_3 = 19.22$ respectively. (Bard et al., 1985)

This means trivalent As(III) is stable at 0-9 pH since pKa value of As (III) is 9.20 and pentavalent As(V) remains as oxi-anions because pKa values of As(V) are 6.94 and 11.5 for $H_2AsO_4^-$ and $H_2AsO_4^{\ 2-}$ respectively (Bard et al., 1985).From the diagram it is seen that at low pH (< 2) arsenic acid is only predominant compound. During the range of (2-11) H_2AsO_4 and $HAsO_4$ also predominates. With increases of pH H_2AsO_3 appears and after 12 pH $HAsO_3$ prevails. As (III) reacts with sulphur and sulphuric compound but As (V) can not react with sulphuric compound. As (V) reacts with amine groups but As (III) does not react with these groups. [Environmental engineers,(2003)].

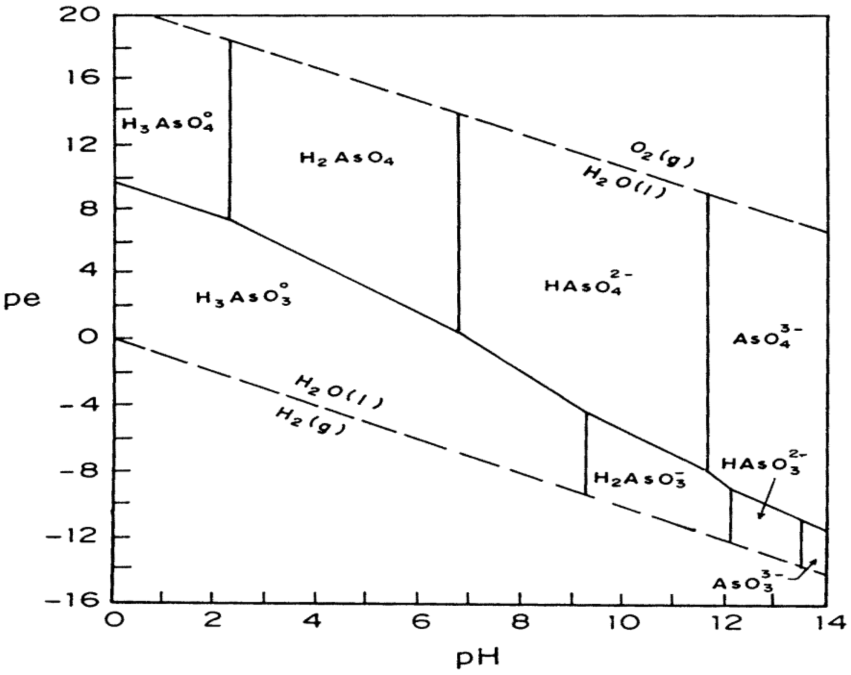


Fig: 1.3 The Eh-pH diagram for arsenic at 25°C and 1 atm, with total arsenic 10^{-5} mol/l (Shih,2005

1.6 Arsenic toxicity

Chronic effects of inorganic As exposure via drinking water include skin lesions, hyperpigmentation neurological effects etc. Arsenic interrupts ATP production cycle which causes multi-organ failure and leads to death ultimately. Intrinsic or extrinsic factors of As metabolites are As dose, age, individual genetic variant, sex etc (Anawar et al., 2002; NRC, 2001).The most affected human organs by As are cardiovascular, gastrointestinal and urinary. Chronic exposure to arsenic have severe (both cancer and non-cancer) effects on human beings. Ingestion of inorganic As is also responsible for bladder and lung cancer (Kumaresan et al.,2001).Repression of cell metabolic activity, respiratory effects, irritation of mucous membranes, fever, anorexia, headache, weakness, hepatomegaly, melanosis, cardiac arrhythmia etc are the non-cancerous effects of arsenic toxicity (NRC, 2001). Chronic exposure of arsenic causes neurotoxicity in nervous system of cell. (Goyer and Clarkson, 2011).

Fig.1.4 : Adverse effects on human health

CHAPTER 2

LITERATURE REVIEW

2.1 Methods for arsenic removal:

i) Chemical oxidation

ii) Membrane process

iii) Coagulation/ electrocoagulation/ coprecipitation

iv) Adsorption

v) Ion-exchange techniques

2.2 Brief Description of different methods

2.2.1 Chemical oxidation

Oxidation is very simple and rapid process. As (III) is neutral and As (V) is ionic in nature at normal pH. So removal of As (V) from drinking water is easier and also effective than As (III).Because of its neutral nature As (III) are not readily removed. Most of the technologies used so far is greatly effective for As (V) and there is a requirement of pre-oxidation of As(III) to As(V) to remove effectively As(T) from water (Ahmed,2001).Oxidation process involves simply addition of oxidants to arsenite so that it converts to arsenate by losing of electron. Here, arsenite reacts with iron oxide and produced a precipitated of $FeAsO_4$ removed by filtration. Optimum pH for the process is less than 7.5 and proportion of iron to arsenic is 20:1 (selecky et al., 2003). Different oxidants are oxygen(air), free chlorine, permanganate, hydrogen peroxide etc. Advantage of this process is production of minimal residual mass.

2.2.2 Coagulation/ Co-precipitation:

Coagulation/co-precipitation is one of the most effective process for removal of arsenic. Transformation of dissolved contaminants into insoluble solids or formation of insoluble solids onto which contaminants are adsorbed**.** Coagulants provide opposite charge onto the colloids so that it collide and produce larger particles. Cataionic coagulants induce positive electric charge onto the colloids and reduce negative charges (to achieve zeta potential) by neutralizing the force. Then by filtration precipitated solid is removed. As (V) contains negative charge so removal of As (V) ion is easier than As (III). So initially oxidation of As (III) to As (V) are required and then coagulants are added in the solution.

Advantages

- Low capital cost
- Quite simple in operation
- A wider range of pH is effective for coagulation

Disadvantages

- Forms toxic sludges
- Pre-oxidation may be required

2.2.3 Ion-exchange Techniques

Ion exchange is a process where similar charges of ions are exchanged. Ions held on the surface of solid phase are called ion exchange resin and they exchange similar charge of ions to be removed. In this process no permanent change of structure of solid occurs. For As removal solid is to be anion exchange resin such as chloride ions (Cl^-). In water treatment method, presence of other anions like sulphate, selenium, fluoride ions reduce the effectiveness of removal of arsenic because then a competition has been taken place between anions. Usually As contaminated water is passed through chloride ion exchange resin and in effluent arsenic ions are quite less compared to water entering in to the vessel.

Advantages

- No regeneration is required
- As(III) and As(V) both can be removed through this technique.
- pH independent

Disadvantages

- High cost medium
- High-tech operation and maintenance
- Produces toxic solid waste

- Regeneration creates a sludge disposal problem

2.2.4. Membrane Techniques

Membranes are permeable to particular dissolved compound among all other dissolved compounds in the solution. Compounds are separated on the basis of selective permeability of membrane for dissolved compounds. Membrane separation process depends on two process parameters: Flux and Selectivity. Flux is defined by resistance of membrane material (volumetric rate of fluid per unit area of membrane).Selectivity is the intrinsic nature of particular membrane and it is defined by permeability of the membrane for specific substance.

Advantages

- No toxic sludge is produced
- High-removal efficiency

Disadvantages

- High-capital and running cost
- pre-conditioning;
- high water rejection
- High tech operation and maintenance

2.2.5 Adsorption

Adsorption is a physical, chemical or biological phenomena where separation of substances from fluid and concentration of substances on to the adsorbent happens. Activated carbon, charcoal, metal hydrides, rice husk are used as an adsorbent. Adsorption is taken place generally into two different phases. Physical adsorption is taken place due to van der waals force of attraction and electrostatic forces between adsorbate and adsorbent surface. Optimum parameters for adsorption are pH, temperature, initial concentration, adsorbent dose, contact time.

2.2.6 Bio-sorption

Bio-sorption process is characterized by metal binding capacity of different biological materials. Efficacy of accumulation of toxic metals from wastewater is quite high. Accumulation of heavy metals is taken place through physico-chemical pathways of uptake or metabolically (Fourest and Roux, 1992). The advantages of biosorption compared to other treatment methods are discussed below.

- Very cheap;
- High efficiency;
- No additional nutrient requirement;
- Biosorbent can be regenerated;

Biosorption process is related to two phase. Solid phase and liquid phase. Solid phase is referred to sorbent material to which sorbate species containing in a liquid phase are adsorbed due to high affinity. Process establishes an equilibrium relation between the amount of sorbate species attached in the sorbent and the amount remaining in the solution.

Biosorption mechanisms can be divided into two steps:

1. Metabolism dependent
2. Non -metabolism dependent.[Kapaj et al.,(2006)]

Biosorption process refers following steps:

1. In the first step, metal ions are attached to surroundings of the biosorbent.
2. After that metal ions are transported to the surface of the biosorbent.
3. Then it goes from the surface to the intraparticular active sites of the biosorbent.

2.2.6.1 Factors affecting biosorption

The factors affected the biosorption process are following:

1. Temperature: Removal efficiency increases with increase in temperature upto 30^0C. Biosorption performances in the range of 30-35°C remain stable (Aksu et al. 1992).
2. pH of the solution is an important parameter and it affects biosorption process highly.
3. Bio-adsorbent dose: increase of biomass concentration tends to increase in uptake capacity of heavy metals but after a certain concentration specific uptake decreases with increase in biomass. Because increase in biomass causes interference between the active sites of the bio-adsorbent (Gadd et al.,1988).

2.3 Brief review on work done with different adsorbent

Adsorbent	pH	Initial concentration(mg/l)	Surface area (m^2/g)	Temp (^{o}C)	Capacity (mg/g)		Removal Efficiency	Reference
					As(III)	As(V)		
Manganese- loaded Fly ash cenospheres		500µg/l As(V)		35		162 µg/g	95.5%	Li et al., (2012)
Pine leaves	4	10 mg/l As(V)		25		3.27		Shafique et al.,(2012)
Tea waste biomass	7.5 ±0.2	200 mg/l		40			84.5% As (III)	Kamsonlian et al.(2011)
Aluminum-Coated Pumice	**7**	250 µg/l of As(V)					98% of As (V)	Heidari et al.,(2011)
Iron oxide Coated natural rock	7.5	40µg/l		25		0.36		Maji et al.,(2011)
Modified native cellulose fibres	9 for As (III) and 2 for As(V)	0.05-8.9 mg/l			0.06-7.8	0.05-8.7		Tial et al.,(2011)
Fe coated mosoporous carbon		5	401.0	-	5.96	5.15		Zhimang and Baolin, (2007)
Magnetite	6.5	75	90.0	-	20.9	25.6		Javier et al.,(2007)
Chitosan coated Biosorbent	4	100 ppm	-	-			100%	Boddu et al.,(2008)

Iron coated composite	7	500 µg/l	-	-	<10µg/l			Gupta et al., (2009)
Composite of ppy with PVA	7	25* 10^-3g/l	-	-	17.56* 10^-3	-		Eisazodeh H., (2008)
Iron oxide coated sand	11	163-184(III) 149-165(IV)	-	-	-	-	94-99%	Joshi A and Chowdhury M (1996)
Coconut shell carbon with 3% ash	5	0-200 mg/l	1150-1250	25		2.4		Lorengen et al., (1995)
Oxisol	5.5	10-1000 mg/l	35.7	25	2.60	3.20		Ladeira A.C.Q and Ciminelli V.S.T (2004)
Gibbsite	5.5	10-1000 mg/l	13.5	25	3.30	4.60		Ladeira A.C.Q and Ciminelli V.S.T (2004)

Activated carbon	-	300 mg/l	1000	25	-	2860		P.Navarro and F.J.Alguasil (2002)
Silica containing iron (III) oxide	6-8	-	186	-	-	-	89%	Le Zeng et al.,(2003)
Mycan	3.0	1-300 mg/l	-	25	-	24.52		M.X Loukidou and K.A.Matis (2003)
Mesoporous alumina	5	20mM	307		47	121	24%(III), 72%(V)	Youngghun kim and Changmook kim (2004)
Manganese oxide coated sand		1mg/l	-	-	-	-	85%-98%	Bajpai and Chaudhuri (1999)
Basic yttrium carbonate	9.8-10.As (III) 7.5-9 As(V)	5.0–0.20 mmol/l for As(III) and 10–60 mmol/l for As(V)	28.6	20,30,40	305.8, 356.8, 428.1	352.6, 428.1, 483.4	-	S.A. Wasay et al., (1996)
Rice husk	6.5-6	100µg/l	-	-	-	-	71-96%	Amin et al.,(2006)
GAC	6-7		583.23	29±1	-	-	86%	Mondal et al.,(2007)
Maize leaves	8	-	-	40			84.9%	Kamsonlian et al., (2011)

Sulphate reducing bacterial culture	6.9	2g/l	-	25	0.20	1.76	77 As(V) 55% As(III)	Teclu et al.,(2008)
Iron coated sand	7.6		-	22±2	.04	.04	-	Thirunavuk karasu et al., (2003)
TiO_2	4			22	3.45	4.65	-	Lenoble et al., (2002
Tea fungal biomass	7.2			30	1.11	4.95	-	Murugesan et al., (2006)
Iron hydroxide coated alumina	6.6–6.7 for As(III); 7.1–7.2 for As(V)			25	7.64	36.64		Hlavay and Polyak (2005)
Manganese ore	6.3 for As (III); 6.5 for As (V)				0.53	15.38		Chakravarty et al., (2002)
Fe3+ Impregnated activated carbon							92.4% As(III) 97.6% As(V)	Mondal et al.,(2007)

Tea waste biomass	7.5			25- 40			84.5	Kamsonlian et al., (2011)
Orange juice residue	7–11 for As (III) and 2–6 for As(V)	-	-	30	70.43	67.43	-	Ghimire et al., (2002)
Zr(IV)-loaded phosphoric acid chelating resin (RGP)	1.14	2.5 mmol/l	-	29.2	-	49.0	-	Zhu et al., (2001)
Titanium di oxide(TiO2)	7	-	-	-	32.4	41.4		Sunbaek et al., (2005)
Immobilized biomass	6-8	100 mg/l	-	30	-	-	90-100 As(III)	Kamala et el., (2005)
Quaternized rice husk	7.5			28±2	-	18.98		Lee et al., (1998)
Char carbon	7	1 mg/l		20	4.5	-	-	Pattanayak, et al.,(2000)

Calcium chloride impregnated rice husk		10000 ppb			(18.2 ± 0.05 μg/g)	-	-	Mondal et al.,(2007)
Reused sanding wastes	8	10mg/l As(III)						Lim et al.,(2009)
Inonotus hispidus	2-6	10-500 mg/l		20	51.9 at pH 6	59.6 at pH 2		Ahmet Sari and Mustafa Tuzen., (2009)
Momordica charantia	9	1.5 mg/l of As (III)					88%	Pandey et al., (2009)
Waste materials such as Atlantic Cod fish scale, chicken fat	4	200–1000 μg/l						Rahaman et al.,(2008)
Green algae(*Ulothrix cylindricum*)	2-8	10 - 400 mg/l			67.2			Mustafa et al., (1995)
Iron doped activated carbons prepared by impregnation with Fe(III) and Fe(II)	2-13	300 ppb			0.036			Muniz et al.,(2009)

Ralstonia eutropha MTCC 2487 and GAC	6-7							P.Mondal et al.,(2007)
Fe^{3+} impregnated GAC	7.1						As(T),As(III), As(V) are ~95%,92.4% and 97.6% respectively	P.Mondal and C.B.Majumder (2007)
Natural siderite	7	1 mg/l As(III)		20	1.04			Guo et al., (2007)
Activated alumina	7.6	1 mg/l As(V)		25		0.81		Singh and pant (2004)
Bone char	9-13	Initial As concentration – 0.5, 1.0 and 1.5 mg/l						Chen et al., (2007)
Pretreated waste tea fungal biomass	7.20			30			100% of As(III) after 30 min and 77% of As(V) after 90 min	Murugesan et al.,(2006)

Activated alumina grains	5-7	Initial As conc.= 11.5 mg/l for As (V) and 4.90 mg/l for As(III)		25	3.8	15.9		Lin Wu et al.,(2001)
Activated bauxsol	4.5	Initial As(V) conc. – 2272 mg/l		23		1.081		Genc Fuhrman et al., (2004)
Red mud	3.5	Initial As (III) conc. – 28.4 mg/l		25	0.663 mg/g	0.514		Altundogan et al., (2003)
Kaolinite	5.5	10-1000	8.5	25	-	<0.23		Ladeira et al., (2004)
Zeolitic tuff ZH	4	0.1 – 4	-	22	.002	.006		Elizalde-Gonzalez et al.,(2001)

Geothite	9	0-60	39	22	22	4		Lenoble et al., (2002)
Hematite	4.2	133.5 µmol/l	14.4	30	-	.2		Singh et al., (1996)
Activated alumina grain			118	25	3.5(7)	15.9(5.2)		Lin and Wu.,(2001)

Table : 2.1 Review on work done with different adsorbent

2.3.1 Granular activated carbon

Gu et al., (2005)

In this study Iron-containing granular activated carbon adsorbents (As-GAC) was used for arsenic removal from drinking water. Impregnation has been done by ferrous chloride ($FeCl_2$) followed by NaClO chemical oxidation. X-ray diffraction patterns were same for both untreated and treated carbon. Removal of arsenic was most efficient when iron content was 6%. Further increases in iron decreased arsenic adsorption. Arsenate adsorption decreased at $pH > 9.0$. The maximum adsorption capacities of untreated GAC, GAC-Fe (0.05 M),GAC-Fe-O_2 (0.05 M),GAC-Fe-H_2O_2 (0.05 M),GAC Fe-NaClO (0.05 M) were 3.78×10, 2.96×10^3, 1.92×10^3,3.94×10^3, 6.57×10^3 µg As/g of adsorbent, respectively. So GAC-Fe is the most efficient adsorbent compared to other impregnated GAC.

Chuang et al., (2005)

This study involves with adsorption of As (V) by activated carbon (AC) derived from oat hulls. Adsorption process was most effective at low pH (5).But with increase in pH of the process, adsorption capacity decreased up to 1.57 from 3.09 mg/g. A modified linear model coupled with the Langmuir isotherm explained the kinetic process. Due to porous structure of the adsorbent, pore diffusion mechanism was dominant throughout the process.

2.3.2 Titanium di oxide

Pena et al.,(2005)

This study describes the capacity of nanocrystalline titanium dioxide (TiO_2) for removal of [As (V)] and [As(III)]. Photocatalytic oxidation was done for oxidizing As (III) to As (V). Batch adsorption and oxidation experiments were conducted with TiO_2 suspensions prepared in a 0.04 M NaCl solution. The time required for reaching equilibrium condition for removal of As (V) and As (III) was 4h and a pseudo-second-order equation was used to describe the kinetics. Maximum removal for As (III) was at 7.5 pH. At 0.6mM arsenic concentration maximum uptake capacity of As (T) was 0.5 mmol/g. Photocatalytic oxidation has been taken place through which As (III) was converted to As(V) . This study has been shown that nanocrystalline TiO_2 is an efficacious adsorbent as well as a effective photocatalyst for arsenic removal.

2.3.3 Iron Oxide impregnated Activated Alumina

Tony Sarvinder Singh and Kamal K. Pant ,(2006)

A comparative study was carried out between activated alumina and iron oxide impregnated activated alumina. The maximum removals of As (III) and As (V) were 96.8% and 98.4% where as for activated alumina these values were 94.2% and 96.1% respectively. Equilibrium was attained at 12 h. Reaction kinetics followed pseudo-second order rate equation for As(III) adsorption over iron oxide impregnated activated alumina and first-order Lagergren for As adsorption over activated alumina. Initially surface diffusion has developed but with time pore diffusion controlled the adsorption process.

2.3.4 Char carbon

Pattanayak, et al., (2000)

In order to compare effectiveness between char carbon(CC) ,commercially available Darco activated carbon (DC) and a carbon produced by arcing of graphite rods for As(III) and As(V) removal this study has been carried out. CC and AC both removed almost same amounts of As(V) but for As(III) CC removed more than AC. DC was the least effective adsorbent compared to other. Factors affected in adsorption were pH, initial metal concentration and temperature. Zeta potential measurements explained the adsorption mechanism of adsorbents. Study revealed that CC was the best adsorbent and also feasible for industrial cases also.

Chen et al., (2008)

Bone char was used for removal of As (V) in this study. pH, dosage of adsorbent, and contact time were varied for conducting batch studies. Uptake capacity rate for 30 min were very high and reaction followed a first order kinetic equation. Fourier transform infrared spectra revealed that Ca–OH functional group involved for As (V) adsorption process.

2.3.5 Rice husk

Amin et al., (2006)

This paper presents the comparative study for As removal with four types of adsorbent namely rice husk, rice straw, tea leaves, and newspaper. The removal efficiencies of rice straw were 65% and 75 %, for tea leaves were 57% and 58%, for newspaper were 18% and 55% for As(III) and As(V) respectively. So, from this it is clearly noted that rice husk was best adsorbent among other three adsorbents for removal of total arsenic. In this paper raw rice husk was used. The conditions in which the complete removal of both As(III) and As(V) have occurred : initial As concentration 100 g/l; rice husk amount 6 g; average particle size 780 and 510 μm; treatment flow rate 6.7 and 1.7 ml/min; and pH 6.5 to 6.0. It has been also shown that the desorption efficiency was up to 96% after treating arsenic contaminated adsorbent with 1 M of KOH.

Lee et al., (2006)

In this paper quaternized rice husk was used as a adsorbent for removal of As(V). quaternized rice husk was prepared by treating with Na_2CO_3 and N-(3-chloro-2-hydroxypropyl)-trymethyl ammoniumchloride at temp 60 -70^{O}C . Here both batch and column studies were carried out. Langmuir Isotherm have been fitted with sorption capacity 18.98 mg/g, pH 7.5 and temp 28±2 ^{O}C.It is also reported that anions such that $SO_4{}^{2-}$, $CrO_4{}^{2-}$ interfere with the uptake of As(V).

2.3.6 Impregnated riice husk

Mondal et al., (2007)

In this paper arsenic removal was done by $CaCl_2$ impregnated rice husk carbon. The optimum concentration of Ca^{2+} ions were 2% for impregnation. At initial concentration 1000 ppb the maximum specific uptake capacity (18.2± 0.05) μg/g has taken place. Polynomial isotherm was best fitted and Freundlich isotherm gave better result compared to Langmuir isotherm.

2.3.7 Maize leaves

Kamsonlian et al., (2011)

This study shows that maize leaves biomass is an effective adsorbent for removal of As (III). Maximum As (III) removal was 84.9% at pH 8, contact time of 4 hrs and 40^{O}C of temperature. Freundlich isotherm (R^2 = 0.997) has been shown better result than Langmuir isotherm. Negative value of G° referred to the spontaneous nature of the adsorbent and positive value of S° and H° represented the feasibility of this bio-adsorbent.

2.4 Biological methods for removal of Arsenic

Despite of conventional technologies for removal of arsenic biological methods are promising field now-a-days because of its cost-effectiveness. It has been reported that different types of bacteria named *A. faecalis, B. subtilis,* bacteria *NT26, C. glutamicum, Leptothrix ocracia,Pseudomonas putida, Pseudomonas arsenitoxidans, Ralstonia picketti, Thiomonas Ynys1, Thiobacillus ferroxidans[5,7,9,10,11,12,13,14]* has been used for removal of arsenic. These bacteria are several types such as arsenic oxidizing, iron oxidizing, sulphate reducing or arsenic resistant type. These different types of bacteria produce different types of gene.

Microbial species	Operating condition	Percentage removal or uptake capacity of Arsenic by microbes	References
Marinomonas communis	Initial As = 0.07 mg/l	45%	Takeuchi (2007)
Lactobacillus casei	As(V) 100 mg/l, pH =7	38.1± 9% removal of As(V)	Halttunen et al.,(2005)
Fresh GAC & immobilized *R. eutropha MTCC 2487* (SABA)	Initial As = 5–47 mg/l pH 6–7,	2.78 mg/g	Mondal et al.,(2008)
L. nigrescens	50–60 ppm As pH 2.5	45.2 mg/g	Hansen et al.,(2006)
A. facealis strain O1201	As (III) 10–500 ppm pH 4–9		Mondal et al.,(2006)

Table 2.2: Review on work done with different bioadsorbent

2.5 Conclusion of literature review

Activated carbon is most effective and widely known adsorbent among of all adsorbents used till now in the adsorption process. But due to its high price, a limitation in use of activated carbon in industrial field has been noticed. To find out low cost adsorbents various researches have been carried out. Rice husk, banana leaves, maize leaves, coconut husk carbon, pine needles, tea leaves, saw dust, cactus leaves, orange juice residue, kaolin, goethite, hematite have been found as an alternative of activated carbon and also as low cost adsorbents. Adsorption capacity depends on various parameters: pH, initial arsenic concentration, temperature, adsorbent dose. Maximum adsorbent capacity has been found by optimizing these parameters. Uptake capacity of different adsorbents differs due to difference in pore structure, surface area, functional groups (Ozsoy and Kumbur, 2006).Removal capacity of microbes is quite high. Different types of bacterial strain have been used so far. Bioaccumulation and simultaneous bioaccumulation adsorption (SAB) both have been used for removal of arsenic.

2.6 Objective of the work

[1] Selection of adsorbent material and preparation of adsorbent rice husk and maize leaves. Rice husk and maize leaves are cheap and easily available bio-adsorbents for removal of arsenic from wastewater. So from that respect the method is economically viable.

[2] Characterization of prepared adsorbent

i) Scanning electron microscopy
ii) Thermogravimetric analysis
iii) XRD analysis
iv) FTIR analysis for functional group detection

[3] To determine maximum efficiency another study has been carried out with impregnated bioadsorbents. Impregnation has been done with positive ions such as Zn^{+2}, Zr^{+4}.

[4] To determine the optimum condition at which the efficiency of removal is highest batch study was carried out. Study of optimum condition for following parameter.

i) pH
ii) Adsorbent dose
iii) Initial concentration
iv) Temperature
v) Contact time

[5] To develop mathematical model for adsorption of arsenic species kinetic, equilibrium and thermodynamic studies should be carried out and to investigate feasibility of the new work for implementation in the industry.

[6]Growth study on suitable micro-organism capable of arsenic remediation .

[7]Immobilization of microbes onto best adsorbent.

[8]Removal of Arsenic in SAB reactor.

CHAPTER 3

MATERIALS AND METHODS

3.1Preparation of rice husk and maize leaves adsorbent

Rice husk and maize leaves were collected from Uttaranchal, Roorkee. Then these were washed with distilled water several times and kept in an oven for drying at 60°C for 24 hours. The dried rice husk and maize leaves were grinded and sieved and to determine the characterization of the adsorbent SEM, EDAX, FTIR ,TGA analysis has been done.

Fig: 3.1 raw rice husk powder

Fig: 3.2 raw maize leaves powder

3.2 Preparation of $ZnCl_2$, $ZrOCl_2$ loaded rice husk

$ZnCl_2$ and $ZrOCl_2$ solution of 2.5% Zn^{+2} and Zr^{+4} ions (w/w) were prepared by dissolving a calculated amount of $ZnCl_2$ and $ZrOCl_2$ into distilled water. The pH of the solution was maintained at 7. In 1 L of each solution ($ZnCl_2$ and $ZrOCl_2,8H_2O$), 5 g of rice husk was added and heated at 70 °C until the excess water had evaporated from the beaker containing $ZnCl_2$ and $ZrOCl_2,8H_2O$ solution for impregnation of the Zn^{+2} and Zr^{+4} on to rice husk. The adsorbents were then dried in an oven at 70 °C for 24 h.

Fig:3.3 Rice husk with $ZnCl_2$

Fig:3.4 Rice husk with $ZrOCl_2,8H_2O$

3.3 Preparation of stock solution of Arsenic:

To prepare stock solution of total arsenic salt of As(III) ($NaAsO_2$) and As(V) (Na_2HAsO4 , $7H_2O$) were mixed in the ratio of 1:1 respectively.

Fig:3.5 Stock solution of Arsenic

3.4 Batch Experiments:

Firstly a definite amount of rice husk (1g/l) was added to 100 ml containing arsenic solution. pH of the solution was maintained at 7. To maintain the pH of the solution 1N NaOH and 1N HCl were added using a pH meter. Then the solution mixture was kept in the shaker for 24 h at 120 rpm. The solution was filtered and filtrate was preserved for further analysis.

3.5 Analysis Method:

Spectrophotometrically arsenic was determined by Silver diethyl diethocarbamate (SDDC) method(IS 3025: 1988 and ASTM D 2972: 2008).The range of arsenic which can be determined through this method is 5 µg/l to 250 µg/l (ASTM D 2972: 2008). The solution used for SDDC method was prepared by following method.

KI solution : 15gm KI was mixed with 100 ml H_2O

$SnCl_2$ solution:40 gm $SnCl_2$ +100 ml HCl

Lead acetate solution: 10 gm LA+100 ml H_2O

SDDC solution: 1gm SDDC +200 ml pyridine

In this method 8 ml HCl solution, 4 ml KI solution,1 ml $SnCl_2$ solution were added into the conical flask containing Arsenic solution and 3 ml yellow coloured SDDC solution was poured into the arsenic generator tube(Fig:3.6).After that 3 gm zinc dust was added into solution and persistently arsine gas(AsH_3) was formed by which the colour of the SDDC solution became into reddish. The absorbance at 540 nm wavelength was measured by spectrophotometer. Percentage removal of arsenic was calculated from the following equation

Percentage removal = $(C_i – C_f) *100/C_i$

where C_i = initial concentration of arsenic, C_f = final concentration of arsenic.

Fig: 3.6 Chemicals used in SDDC method

Fig:3.7 Arsenic solution after adsorption

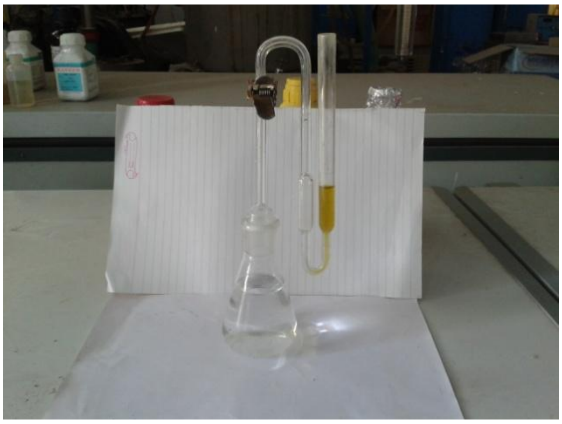


Fig: 3.8 SDDC solution before generation of arsine gas

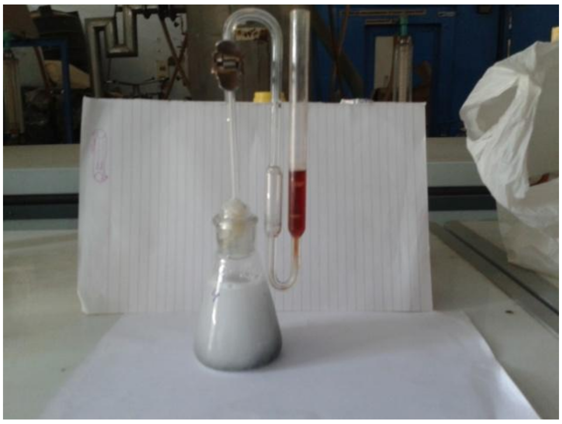


Fig: 3.9SDDC solution after generation of arsine gas

3.6 Zirconium oxychloride impregnated rice husk immobilized by *Pseudomonas putida*

3.6.1 Sterilization

All the equipments such as conical flasks, petridishes, serum bottles, test tubes were washed with distilled water thrice and dried in an oven at 110^{o} C temperature. These glasswares along with liquid nutrient cultured medium were autoclaved at 15 psi and 120^{o}C for 20 min. The medium were allowed to cool at room temperature.

Fig:3.10 Bacterial strain of *P.putida*

3.6.2 Growth of bacteria

Microbial strain *Pseudomonas Putida* (MTCC 1194) was purchased from MTCC, Chandigarh, India. The microorganism was initially cultured in nutrient broth and then plated nutrient agar and preserved. Nutrient Broth and Nutrient agar was obtained from HiMedia Laboratories Pvt. l.t.d. Mumbai.

3.6.3 Plating of bacteria

Plating of the microorganism was done in the following manner.

1. 1 g of nutrient agar was added in 30 ml of distilled water to prepare 25 ml of nutrient agar solution. The solution was autoclaved at 121 ° C for 20 min.
2. The solution was allowed to cool for some time. Cooling is required to avoid condensation of vapour on petridish. Then the medium was poured in dish slowly. The petridish was kept to solidify overnight at room temperature.
3. Wire loop has been flamed on a spirit lamp and it was allowed to cool for a second. The micro-organism was taken from the nutrient broth by sterilized wire loop and spread onto the solidified media in the culture plate. The whole process was done in laminar hood to avoid contamination.
4. Plates were incubated for 24 hr at 30 °C.
5. After incubation, It is observed that colonies of microorganisms were grown on the plates. These plates were preserved at 4 ^{o}C for further use in future work.

3.6.4 Preparation of minimal media

For preparation of minimal media following reagents are added in 800 ml solution. The pH of the solution was 7.(Liu et al.1992)

Chemicals	Amount(g/l)
Na_2HPO_4	8.8
KH_2PO_4	1.2
NaCl	5
NH_4Cl	1
$MgSO_4$, 7 H_2O	0.25
Glucose(w/v) %	2

Table 3.1 Chemicals used to prepare minimal medium

- After preparing the media, it was autoclaved at 120^o C. The medium was allowed to cool at room temperature.
- Medium was divided into four flasks and zirconium impregnated rice husk was poured into each flask (10g/l)
- The microbial strain was inoculated into each flask in laminar hood.
- Subsequently, the bottles were incubated at the shaker for 48 h at 180 rpm.

CHAPTER 4

RESULTS AND DISCUSSIONS

Rice husk and maize leaves are cheap and easily available bio-adsorbent for removal of arsenic from wastewater. In this study surface modification has been done by zirconium oxychloride, zinc chloride.

4.1Characterization of the adsorbent

Scanning electron microscopy (SEM) and EDAX analysis were carried out for understanding the morphology of the adsorbent and elementary analysis respectively(QUANTA, Model 200 FEG, Netherland).To know the functional group present in the adsorbent an analysis has been done using FTIR spectrometer (Thermo Nicolet, NEXUS, USA).To know the loss of the moisture with respect to temperature Thermogravimetric analysis (TGA) was carried out using a DuPont Hi-Res TGA 2950, USA) under the following condition: heating rate 10 K/min, in the presence of nitrogen atmosphere, Heated up to 1000°C temperature.

4.2 Scanning electron microscopy (SEM)

To understand the morphological behaviour of the raw rice husk, maize leaves and impregnated rice husk SEM analysis has been done. From these figures it has been concluded that the adsorbent has irregular shapes and porous structures. From the fig 4.1, 4.2, 4.3, 4.4 and 4.5 it can be reported that the impregnated rice husk has more porous structures than the raw rice husk that means the surface area is more for impregnated rice husk.

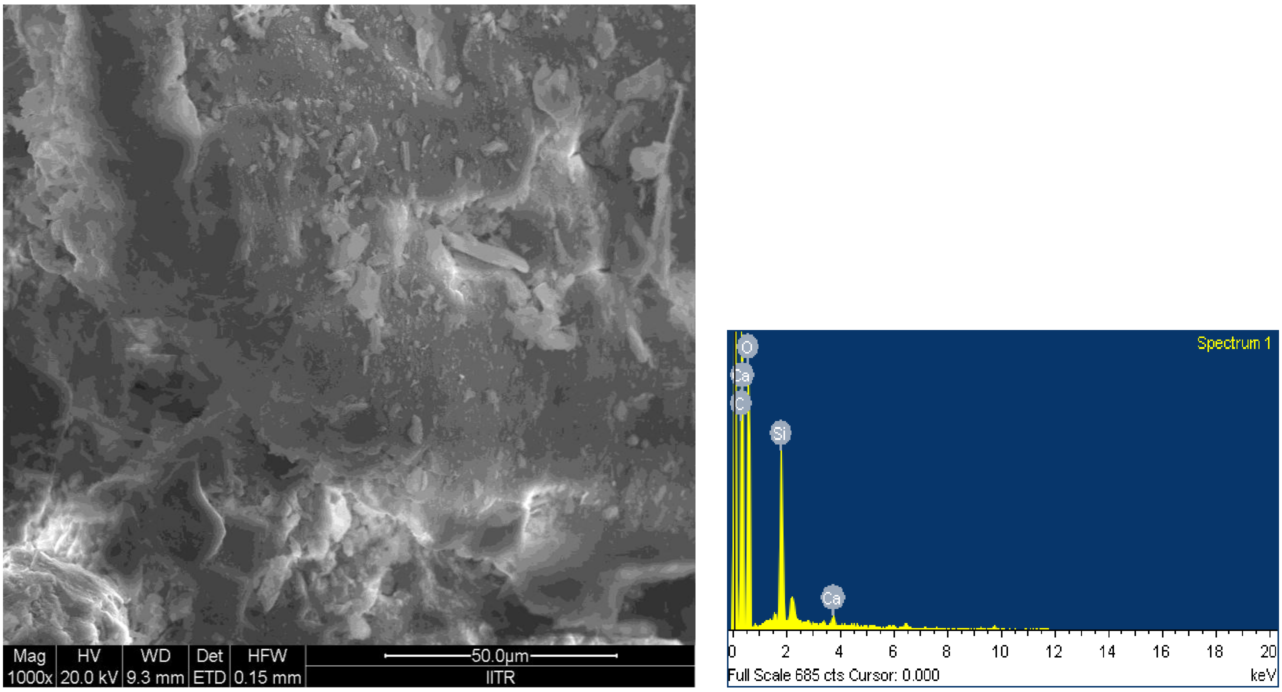


Fig:4.1 SEM and EDAX analysis of rice husk

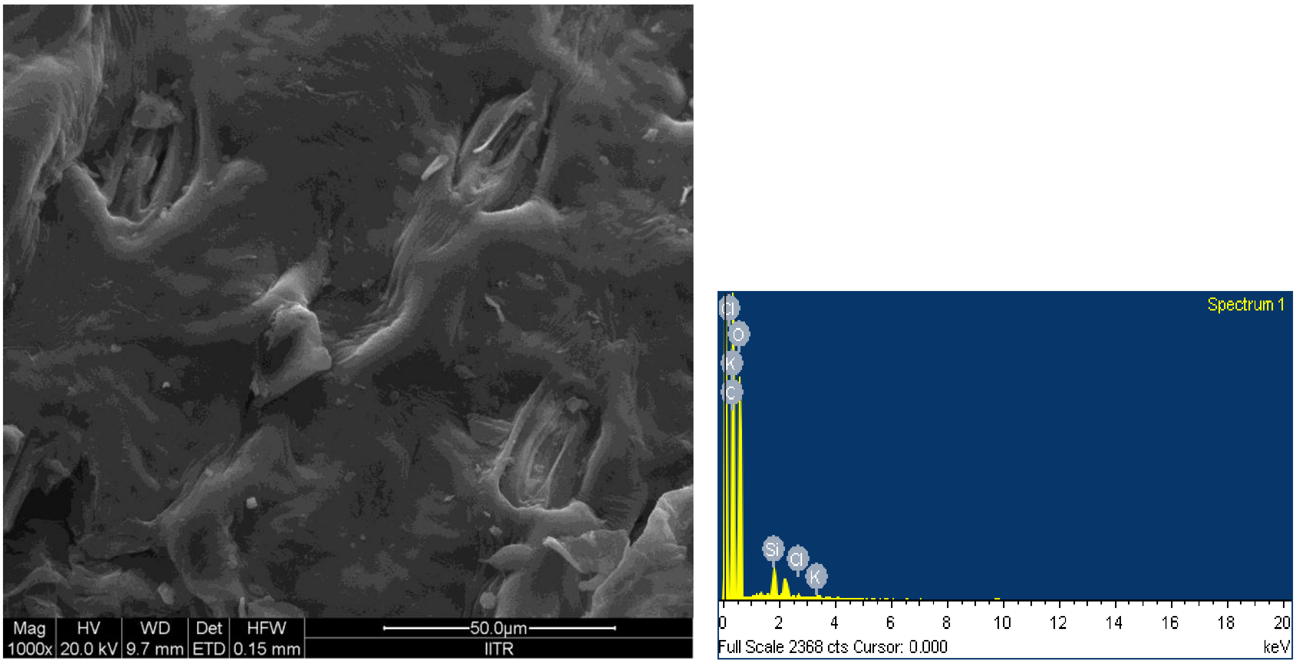


Fig:4.2 SEM and EDAX analysis of maize leaves

From EDAX analysis of raw rice husk and maize leaves the elements present are Silica, Carbon,Oxygen and very low amount of calcium and potassium.

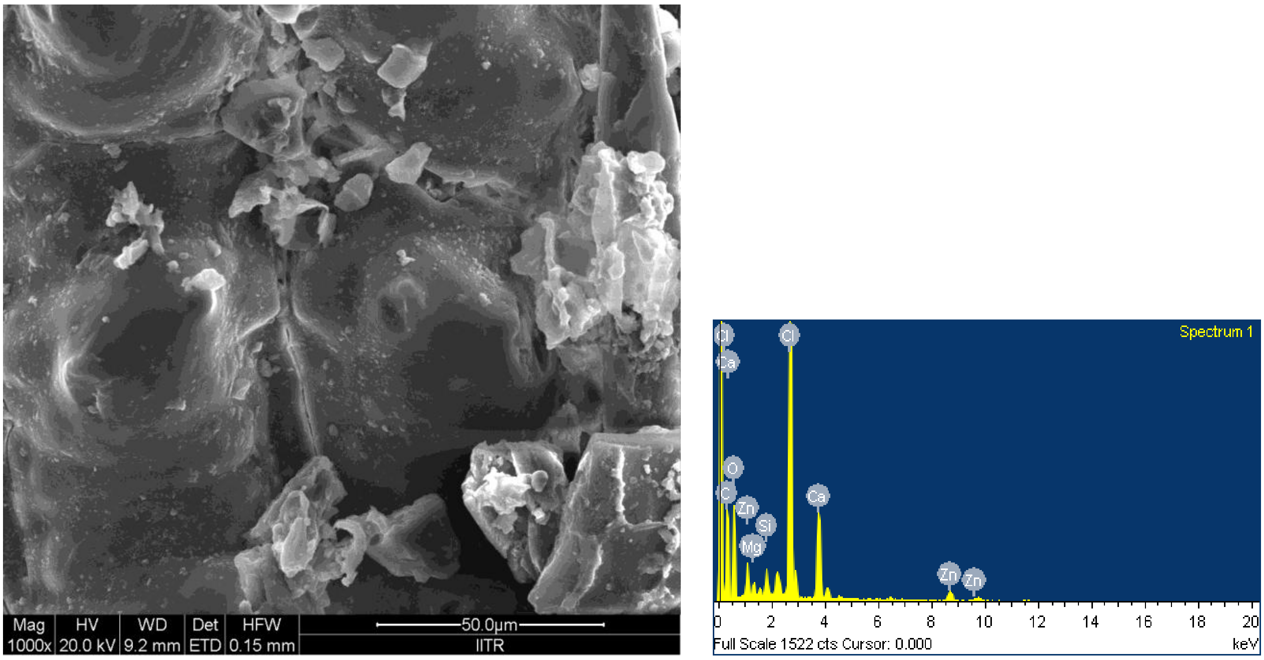


Fig:4.3 SEM and EDAX analysis of rice husk with $ZnCl_2$ loaded

From the SEM analysis it is seen that Zn impregnated rice husk is more porous than the raw rice husk or maize leaves. EDAX analysis shows the presence of Zn, Cl as well as C,O,Si,Ca.

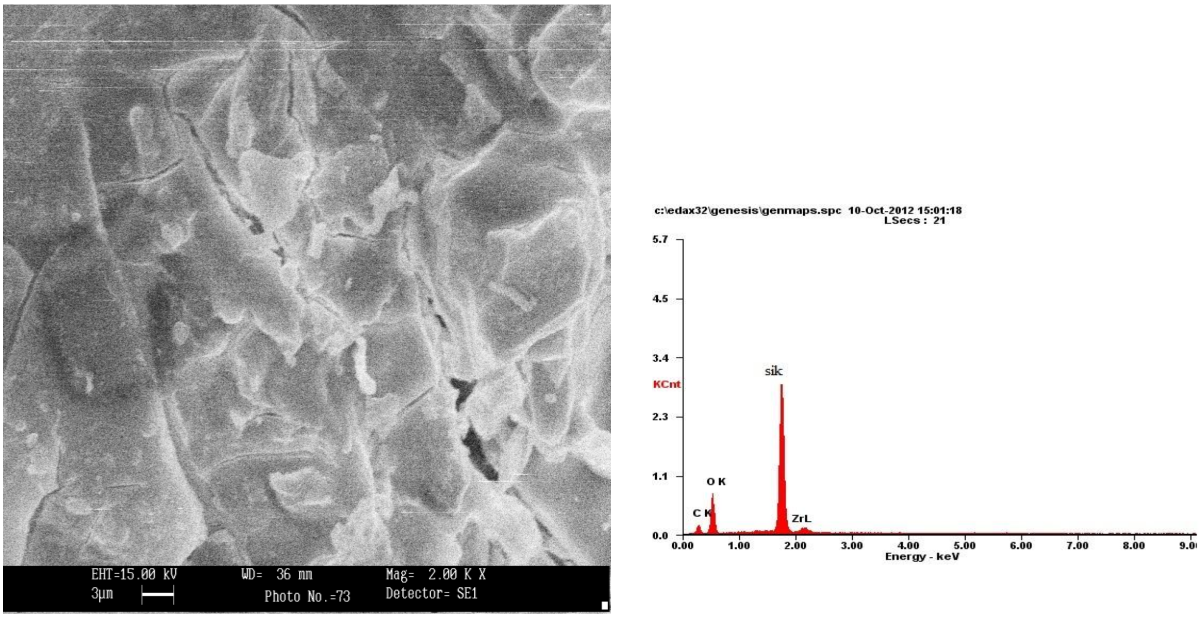


Fig:4.4 SEM and EDAX analysis of rice husk with Zr loaded before adsorption

Fig 4.4 and 4.5 are SEM analysis of Zr loaded rice husk before and after adsorption respectively. Zr impregnation creates an amorphous layer on the raw rice husk. The EDAX analysis shows the presence of C, O, Si, Zr in the adsorbents. Fig 4.5 shows the irregular and porous shape of adsorbents and it supports the adsorption of arsenic onto the active side of Zr impregnated rice husk.

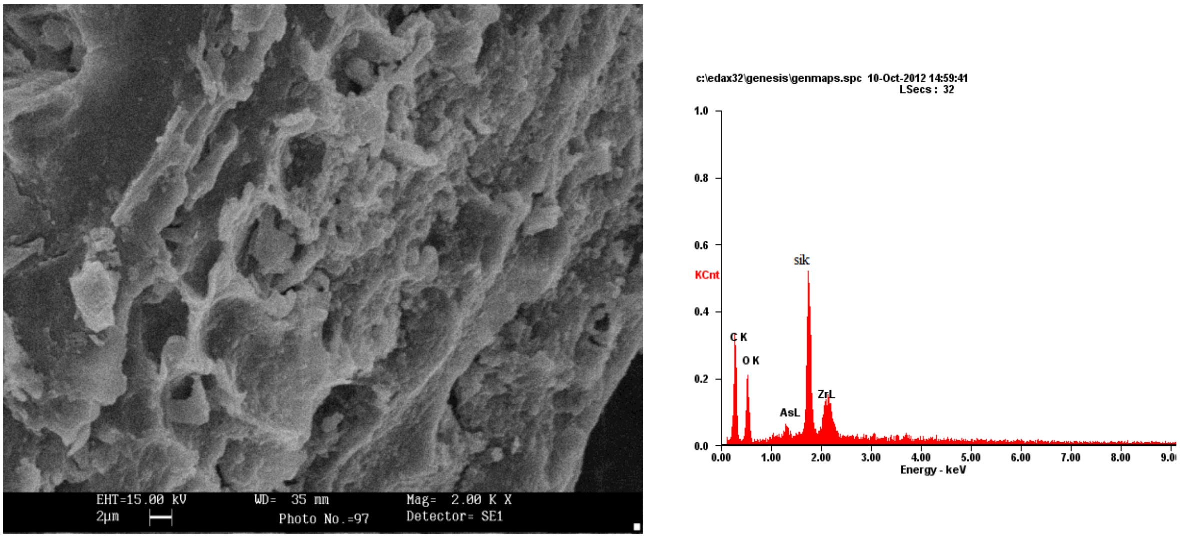


Fig:4.5 SEM and EDAX analysis of rice husk with Zr loaded after adsorption

4.3 Fourier transformation infrared (FTIR) spectra:

FTIR spectra are used to determine the functional group present in the adsorbent. The following groups are present in the raw rice husk. A stretching in the regions of 1546.8-1652.88 cm^{-1} is due to C=C stretching of alkene. The peak between 470-790 cm^{-1} shows the presence of SiO_2. Peak at 3935.66 cm^{-1} is attributed the presence of OH and SiOH.

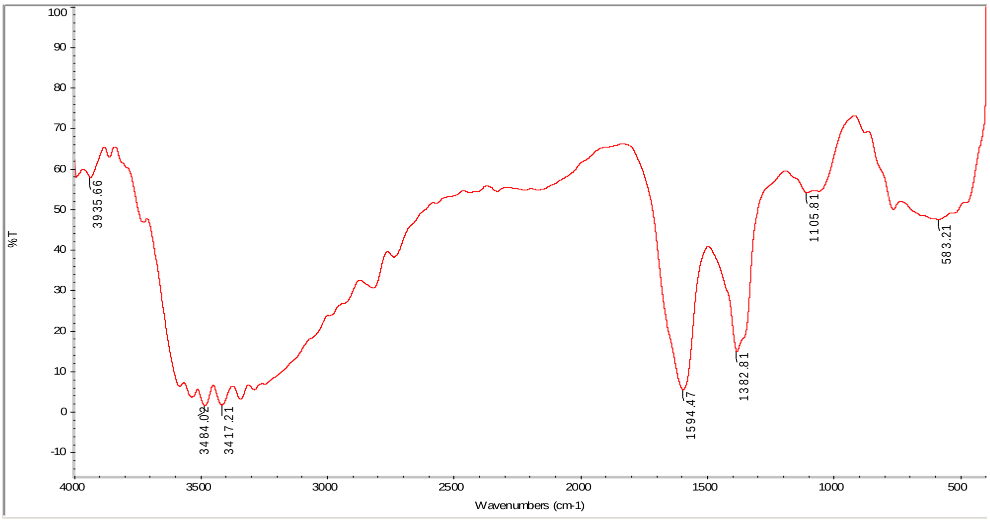


Fig:4.6 FTIR of Rice husk

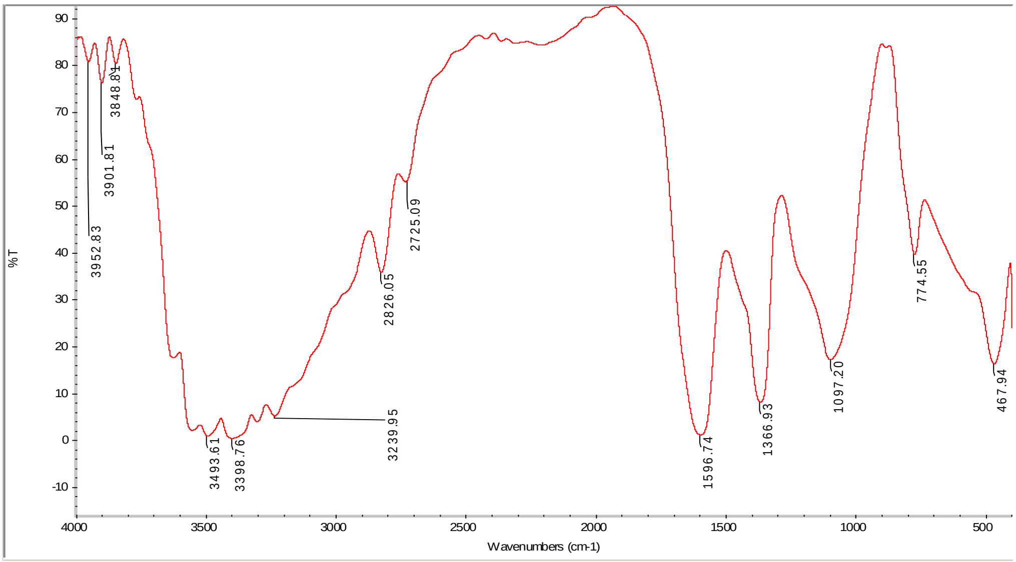


Fig:4.7 FTIR of Rice husk with Zr

For Zr loaded rice husk a peak at1366.93 cm^{-1} has been appeared which is due to presence of aromatic CH and carbonyl carbon. A band between 1091-1097 cm^{-1} indicates O-Si-O stretching vibration . The peak between 470-790 cm^{-1} shows the presence of SiO_2. Peak at 3935.66 cm^{-1} is attributed the presence of OH and SiOH.

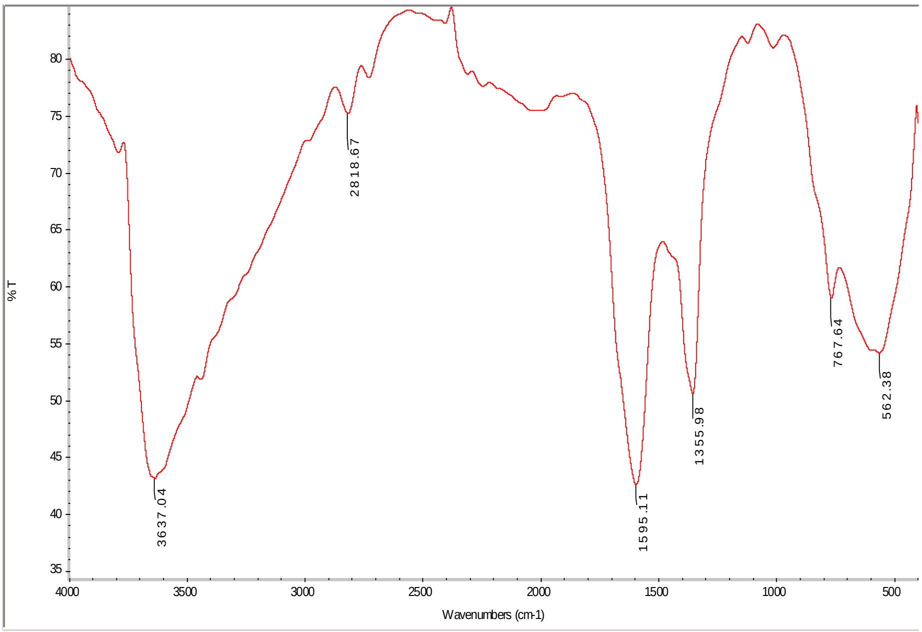


Fig: 4.8 Rice husk $ZnCl_2$

From the Fig 5.8, a peak at 1366.93 cm^{-1} indicates the presence of aromatic CH and carbonyl carbon.Peak between 470-790 cm^{-1}suggests the possibility of presence of SiO_2.

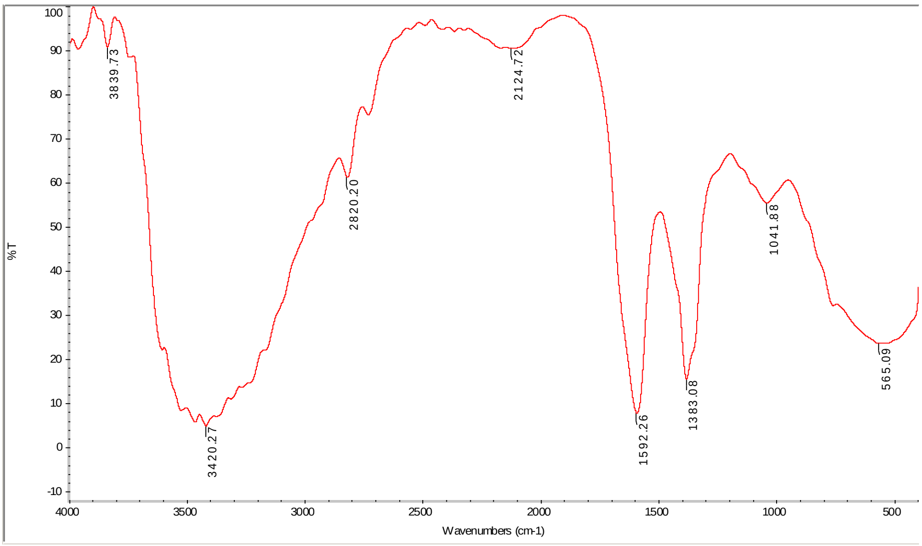


Fig: 4.9 Maize leaves

A band between 3853.21 – 3430.97cm^{-1} indicates vibration of OH or -NH. Peak at 2922.65 cm^{-1} shows C=H stretching vibration. A band between 1734.05 – 1047.60 cm^{-1} suggests -CN and C-C stretching. A peak at 565.09 cm^{-1} is attributed stretching of C-O band.

4.4 Thermogravimetric analysis :

Thermogravimetric analysis was done to determine the weight loss with respect to temperature.DTA and TGA graph are shown for raw rice husk, Zn impregnated rice husk, zirconium impregnated rice husk and maize leaves respectively. There is 6.42% and 9.84% ,10% and 12% weight loss for rice husk, zirconium impregnated rice husk, Zn impregnated RH and maize leaves respectively upto 200°C.So upto 200°C weight loss was due to loss of moisture. After 200°C a great weight loss occur due to phase change or formation of crystalline structure. After 600°C weight loss is quite stable due to almost complete combustion of carbon species of the bio-adsorbents. The TGA/DTA graphs are shown below.

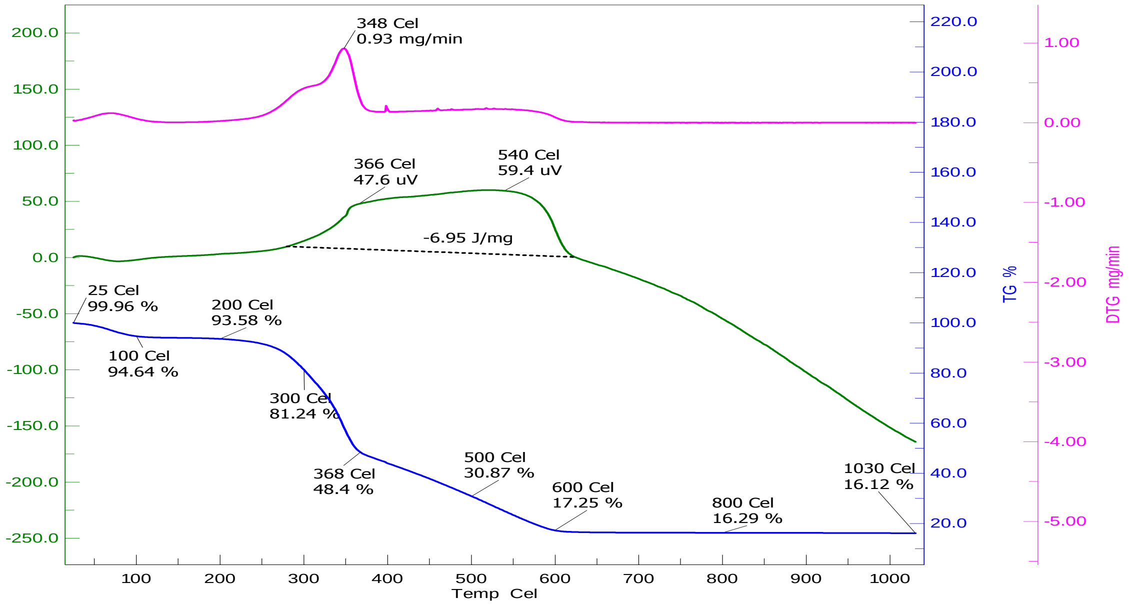


Fig:4.10 DTA curve for raw Rice husk

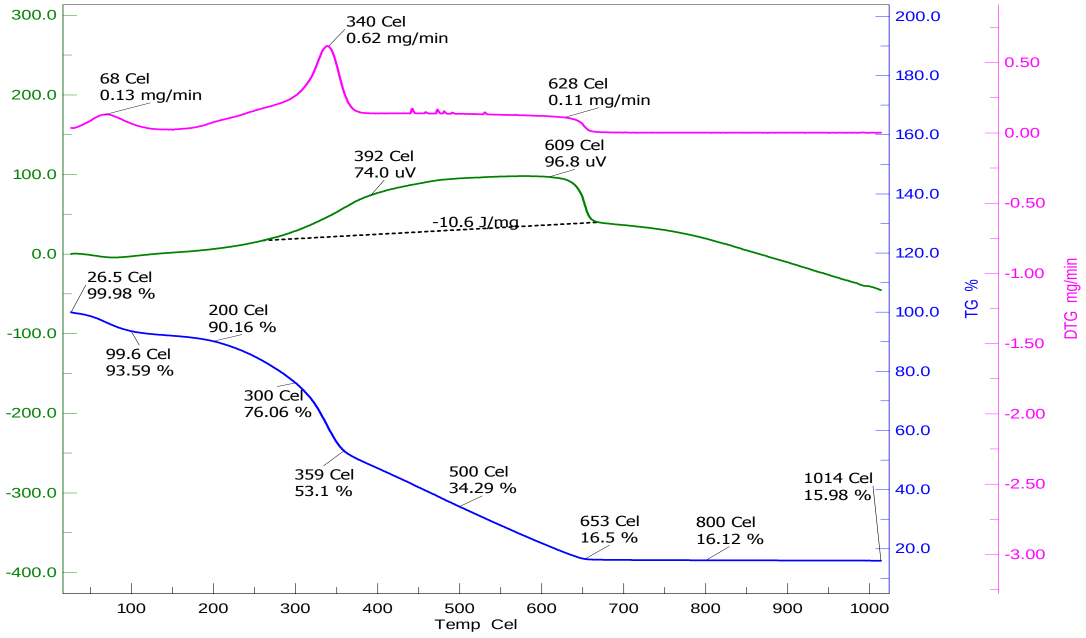


Fig:4.11 DTA curve for Rice husk with Zr

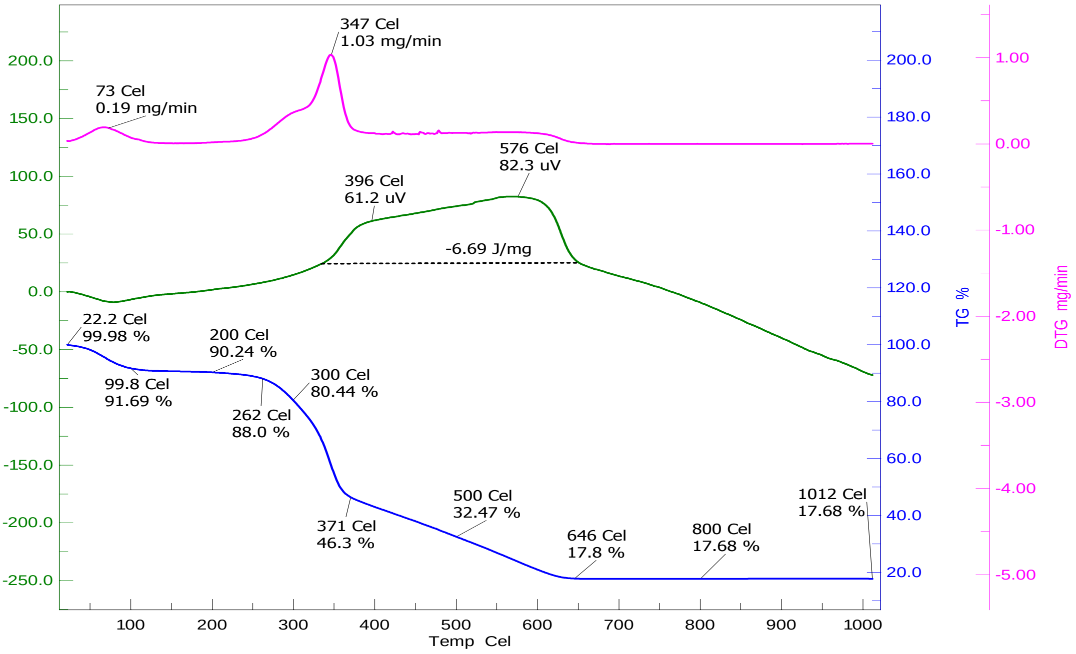


Fig:4.12 TGA/DTA curve for Rice husk with $ZnCl_2$

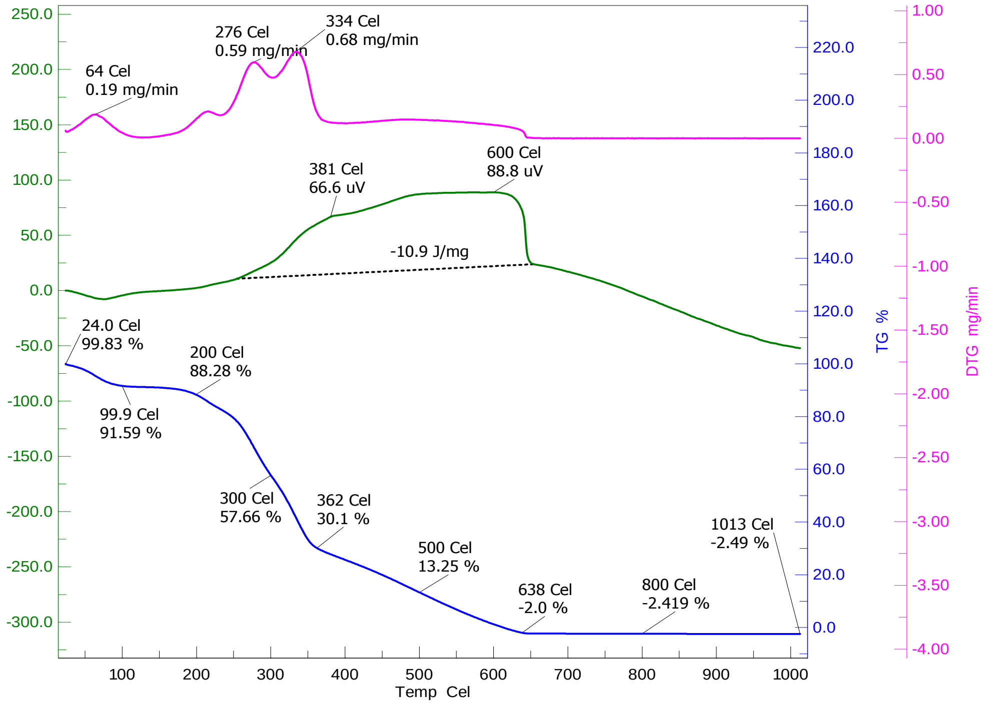


Fig:4.13 TGA/DTA curve for Maize leaves

4.5 XRD :

XRD pattern for each adsorbents have been shown below. Generally XRD shows the crystalline structure of the adsorbents. At 12° there has been shown a sharp peak which is for the presence of

Silica. From the figure given below it is suggested that the structure of adsorbent is not crystalline rather it is amorphous.

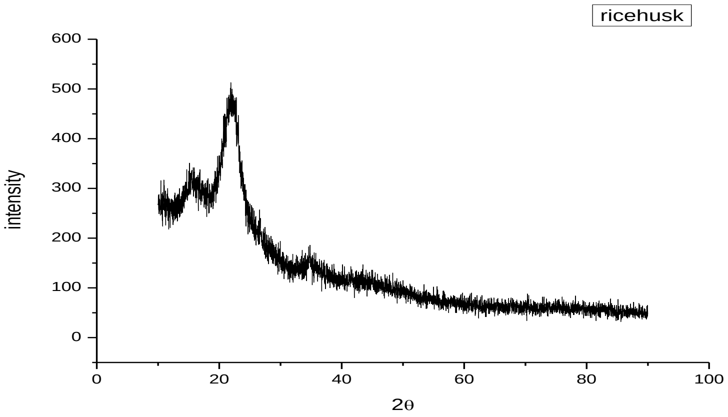


Fig:4.14 XRD pattern for rice husk

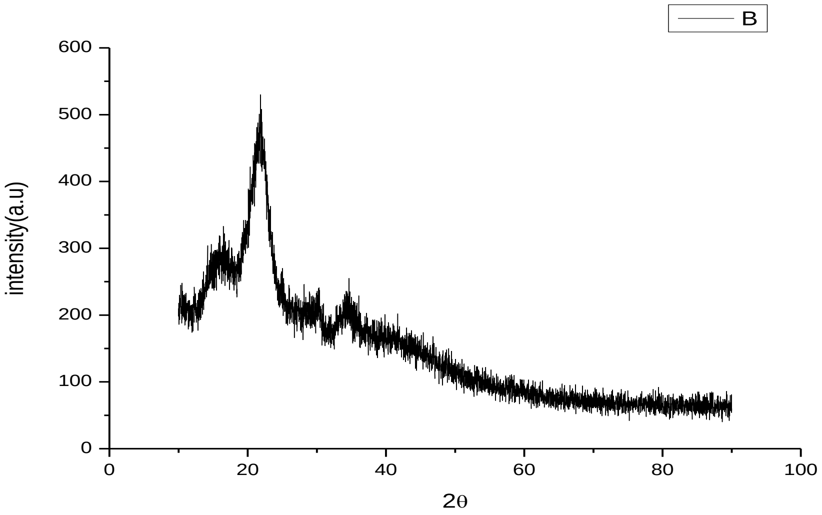


Fig:4.15 XRD pattern for maize leaves

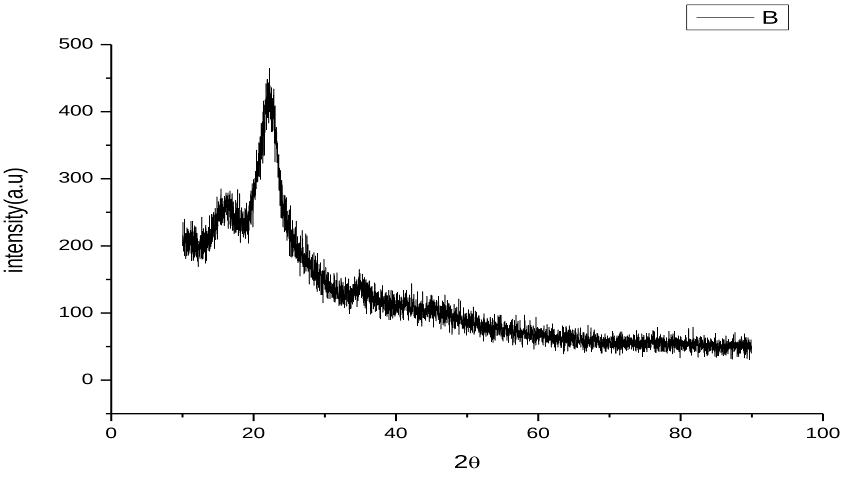


Fig: 4.16 XRD pattern rice husk zr loaded

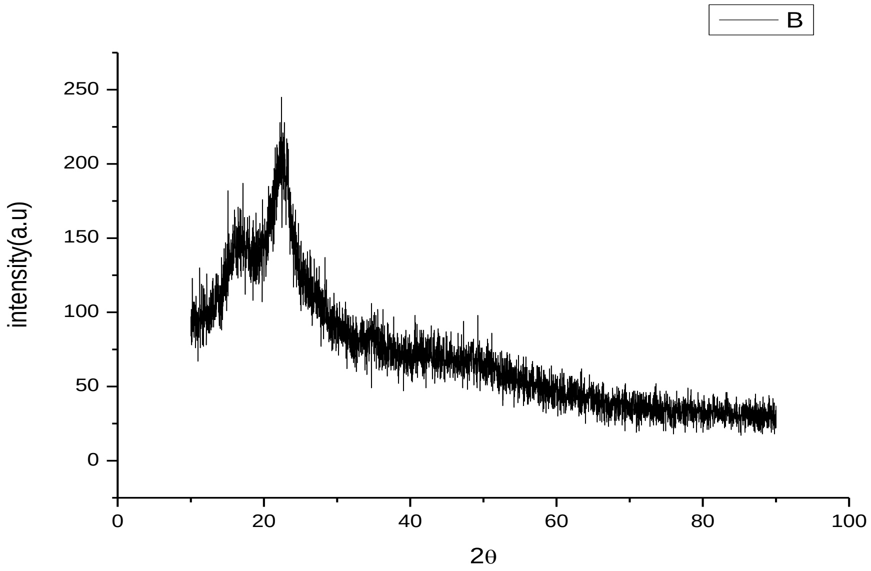


Fig:4.17 XRD pattern rice husk $ZnCl_2$ loaded

4.6 Calibration Curve

First of all calibration curve was plotted using known concentration of arsenic sample. Different concentration of arsenic 50 µg/l, 100µg/l, 150 µg/l and 200 µg/l were used for preparing calibration curve and the absorbance was measured by UV-spectrophotometer at 540 nm wavelength. The R^2 value for the calibration curve was 0.997. 1 g of each adsorbent was added to arsenic solution where pH was 7, initial concentration (C_i) 20 mg/l, contact time 24 h and temperature 30°C.After determining the most efficient adsorbent for removal of arsenic then the optimization for that adsorbent was evaluated.

Using the calibration curve (shown in Appendix) the concentration of arsenic after adsorption of rice husk and maize leaves was determined and the removal efficiency was also determined. To compare between the efficiency of rice husk and maize leaves 1g of each adsorbent was added to arsenic containing solution. The parameters of pH of the solution was 7, initial concentration (Ci) 20 mg/l, contact time 24 h and temperature 30°C.The removal efficiency of rice husk was higher than maize leaves. So rice husk was sorted out for further study. To compare the best adsorbent between zirconium impregnated rice husk and zinc impregnated rice husk a further study has been carried out under previously mentioned condition. Zirconium impregnated rice husk has achieved the highest removal efficiency. Removal efficiency of maize leaves, rice husk, $ZnCl_2$ impregnated rice husk and zirconium impregnated rice husk were 62%, 67%, 76%, 79% respectively (fig:4.18).

The exact mechanism of the whole process may be a complex combination of the different processes. All of the components in the adsorbent system used may participate in arsenic removal. The carbon in the Zn or Zr impregnated rice husk adsorbent does not only act as a support material for Zn or Zr attachment but also as an adsorbent where arsenic ions can be adsorbed by their affinity to the pores of carbon particles in the rice husk. Also, depending on the activation process used to prepare the adsorbent, carbon can be positively charged causing arsenic adsorption by electrostatic or coulombic attraction. With the existence of more than 50% of silica/silicate in the rice husk, it may play a role as a support material for more uniform distribution of Zn or Zirconium on the surface where Zn or Zr active sites are more widely spread. Since Zirconium impregnated rice husk was the best adsorbent among of all the adsorbents, optimization of all parameters for this particular adsorbent has been studied.

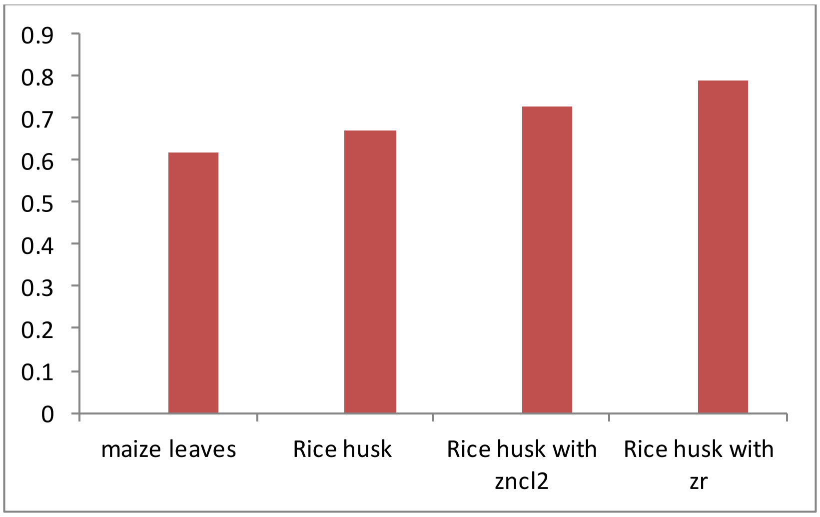


Fig:4.18 Removal efficiency for different adsorbents

4.7 Optimization of different parameters for zirconium impregnated rice husk

For pH optimization it was varied from 7 to 12.To determine the adsorbent dosage, it was varied from 1 to 15 g/l. In order to determine agitation period contact time was varied from 2 h to 24 h keeping fixed the other parameters. Initial concentration was varied from 20 mg/l to 50 mg/l, temperature was varied from 20° C to 50°C to optimize concentration and temperature. For each of the case the solution was filtered and the arsenic presents in the filtrate after adsorption was analysed by spectrophotometrically (Sauntak et al.,2006).

4.7.1Effect of pH for As adsorption:

The effect of arsenic removal efficiency was studied with change of pH from 6 to 11, initial concentration (Ci) 20 mg/l, contact time 24 h and temperature 30°C, adsorbent dose was 1g/l. The pH of the medium was adjusted by 1M NaOH and 1M HCl. With the increase of pH the electrostatic force was increased, so the arsenic removal efficiency increased upto 8 pH and the value was 85%.It is seen from the fig 4.19 that there was a sharp increase in removal efficiency from 6 to 8 and values are 67.2% to 85.2% respectively. It is also reported that after pH 8 the value decreased gradually and reaches to 84.5% at pH 11.Since after that in spite of increase in pH there was no positive effect on arsenic removal due to limitation in metal ion mobility (Sauntak et al.,2011), the optimum pH for this study was 8.

Surface charge results from protonation, dissociation or surface complexation reactions of reactive surface hydroxyl groups at solid surfaces. It is known to us that As (III) remains generally as a neutral species and As(V) remains as a negatively charged in the solution. So As(V) can be removed from solution at a neutral pH and for removal of As(III),the pH of the solution should be higher.(14-16) because at higher pH it is converted to a negatively charged moiety. Negative charge on molecule means dissociation occurs in the solution and pKa values which is expressed as const of dissociation are as follows:

For arsenate, H_3AsO_4 $pK_1 = 2.19$, $pK_2 = 6.94$, $pK_3 = 11.5$.

For arsenite, H_3AsO_3 $pK_1 = 9.20$, $pK_2 = 14.22$, $pK_3 = 19.22$ respectively. (Bard et al.,1985)

This means trivalent As(III) is stable at 0-9 pH since pKa value of As (III) is 9.20 and pentavalent As(V) remains as oxi-anions because pKa values of As(V) are 6.94 and 11.5 for $H_2AsO_4^-$ and $H_2AsO_4^{2-}$ respectively (Bard et al., 1985).For the lower pH(5-9) of the solution since As(V) exits as negatively charged anion, so the adsorption of As(V) occurs due to electrostatic attraction between negatively charged arsenic and positively charged Zn^{2+} or Zr^{4+} on the surface of the rice husk. (Mondal et al.,2007).So As(III) and As(V) can be removed in the pH range(5-9).

At higher pH (9-12) As(III) converts from neutral H_3AsO_3 to $H_2AsO_3^-$ and As(V) already exists as a negative anion. Hence, both forms of arsenic (As(III) and As(V)) are removed in the pH range study.(pH 5-9).Though As(III) exists in the solution as a neutral compound (H_3AsO_3), it may also be removed by chemical reaction at the lower range of pH (pH 5-9). The negatively-charged arsenic ions and positively-charged adsorbent surface favour the arsenic adsorption by electrostatic attraction.

4.7.2 Effect of initial concentration

The effect of initial concentration of the total arsenic was studied from 20 mg/l to 50 mg/l(fig:4.20).When the arsenic concentration was 20 mg/l the removal efficiency was 88.2% but when the conc. was 50 mg/l the efficiency was decreased to 69.2%. Hence with the increase in concentration of As in the solution the efficiency was decreased.

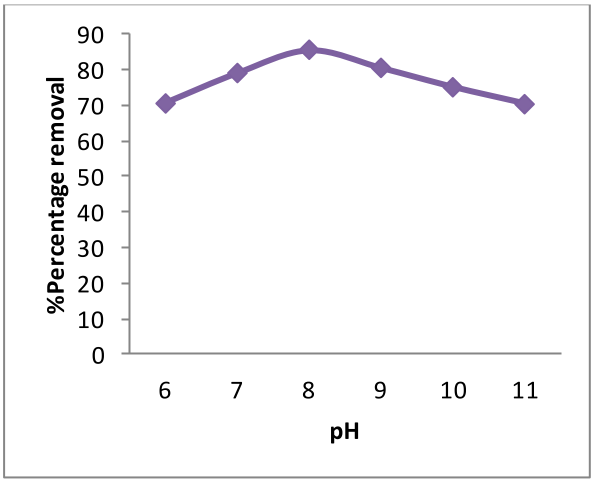


Fig:4.19 Effect of pH (initial concentration (Ci) 20 mg/l, contact time 24 hr, temperature 30°C, adsorbent dose was 5 g/l)

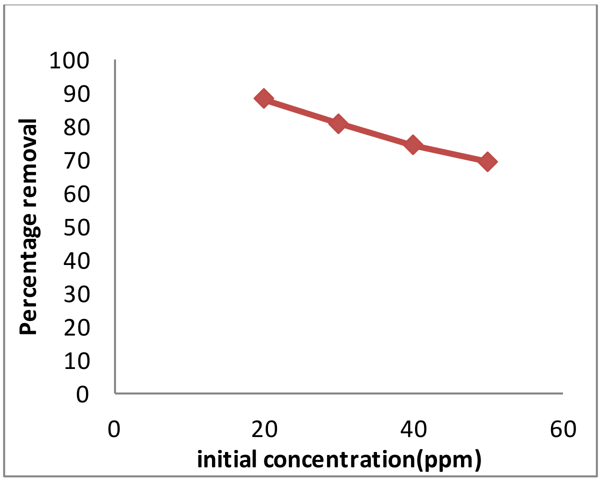


Fig: 4.20 Effect of initial concentration (pH 8, contact time 24 h and temperature 30°C, adsorbent dose was 5 g/l)

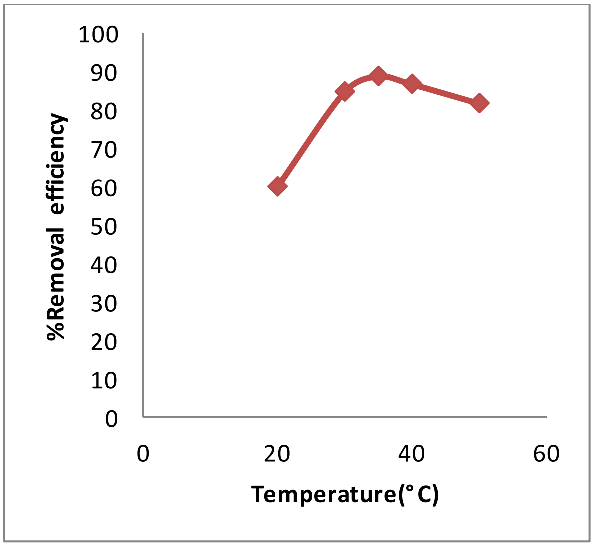


Fig: 4.21 Effect of temperature (pH 8,initial concentration (Ci) 20 mg/l, contact time 24 h and adsorbent dose was 5 g/l)

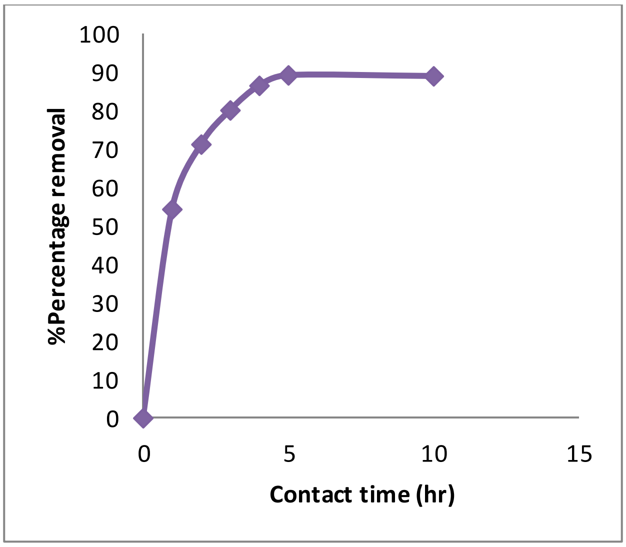


Fig:4.22 Effect of contact time (initial concentration C_i 20 mg/l, pH 8 and temperature 35°C, adsorbent dose was 5 g/l)

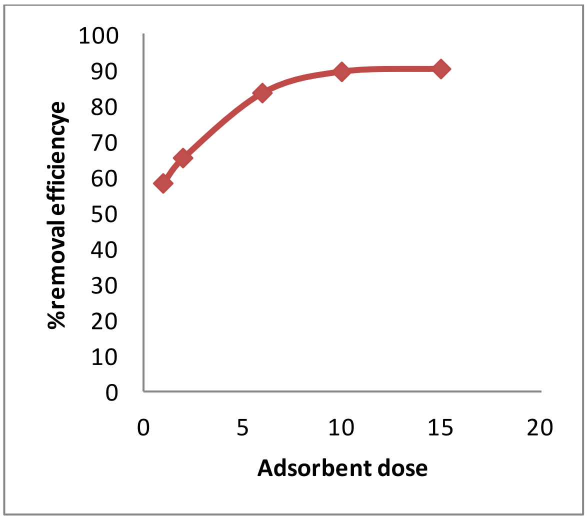


Fig:4.23 Effect of adsorbent dose (initial concentration (Ci) 20 mg/l, contact time 5 h and temperature 35°C,pH 8)

4.7.3 Effect of temperature

Temperature has a great impact on adsorption process. With increase in temperature uptake capacity increases. Initially it increases sharply, after that it increases gradually. At 20° C the efficiency was only 60.3% but the value reached to 89% at 35°C. The optimum temperature was 35°C at which removal of As was 89 % (fig 4.21).Generally adsorption process is an exothermic process but when the process is diffusion controlled, then endothermic nature can be seen that means uptake of metal ions increase with increase in temperature. Process involves with increase in mobility of arsenic ions and retarding forces acting on metal ions decreases. Increase in adsorption capacity with temperature indicates that the process involves chemisorption.

4.7.3 Effect of contact time on As adsorption:

The effect of agitation time for the removal of arsenic was studied from 1 h to 10 h where the pH value of the solution was 8, initial concentration of As was 20 mg/l , temperature was 35°C and adsorbent dose was 1g/l respectively. Initially removal of As increases with time and reaches equilibrium at 5 h. At contact time of 5 h 89.2% removal of arsenic was achieved (fig: 4.22). After 5 h there was a slight decrease in arsenic removal. So the optimized condition for contact time was 5 h for this experimental study.

4.7.4 Effect of adsorbent dose

The adsorbent dose was varied from 1-15 g/l where the pH value of the solution, initial concentration of As, temperature and contact time was 8, 20 mg/l, 35°C and 5 h respectively. The experiment result reveals that removal efficiency of arsenic was 58.2% at 1 g/l adsorbent dose where as at 10 g/l the value was 89.5%. Fig 4.23 indicates that after 10 g/l increase or decrease in removal of Arsenic is almost negligible. So an adsorbent dose of 10g/l was taken for further experiment. Increase in adsorbent in the solution increases the surface of adsorption, for that reason removal efficiency increases with increase in adsorbent up to 10g/l.

4.8 Equilibrium Isotherm Models

Separation of sorbate species from solution and attachment onto the bio-sorbent maintains an equilibrium relation. At equilibrium the adsorbed amount of solute onto the adsorbent and desorbed amount of solute into the solution is same and also the concentration of the solution remains constant. Solid phase concentration versus liquid phase concentration was plotted to describe the equilibrium isotherm. Several isotherm Langmuir, Freundlich are used for understanding the exact mechanism followed by adsorbent. Separation of the solute causes on the basis of affinity towards the adsorbent and active sites of the adsorbent. These can be determined from constant parameters of the isotherm equation.

These equilibrium isotherm models represent a linear relation between adsorption of the metal ion on the adsorbent and the metal presents in the liquid solution after adsorption. Adsorption capacity versus equilibrium concentration is plotted generally. Langmuir, Freundlich isotherm model have been used to determine the isotherm relation.

Langmuir isotherm model

Langmuir isotherm describes homogeneous and monolayer adsorption because this model suggests that all active sides of adsorbents are symmetrical. Langmuir Isotherm is represented by

$q_e = (K_L * C_e)/(1 + b * C_e)$……………………………………………………………(5.1)

The linearized form of this equation is

$\frac{1}{q_e} = \frac{1}{b\, q_m C_e} + 1/q_m$……………………………………………………………………...(5.2)

where qe is the adsorption of adsorbate to the adsorbent (mg/g) and Ce is the equilibrium solute concentration (g/l) and q_m is the maximum uptake capacity of the adsorbent. K_L is the solute adsorptivity. The value obtained from the figure 4.24 are given in the table 4.1.

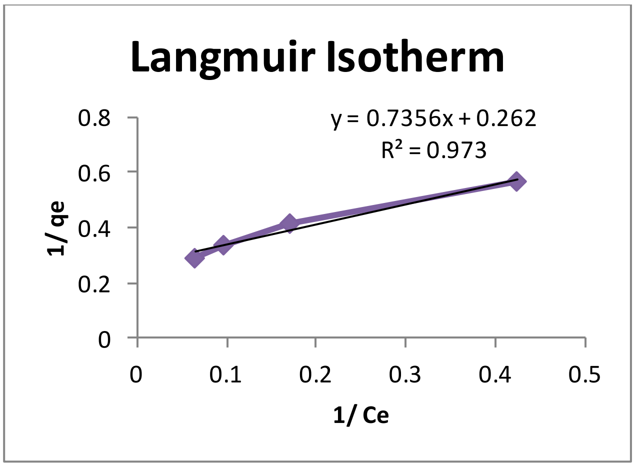


Fig:4.24 Langmuir model

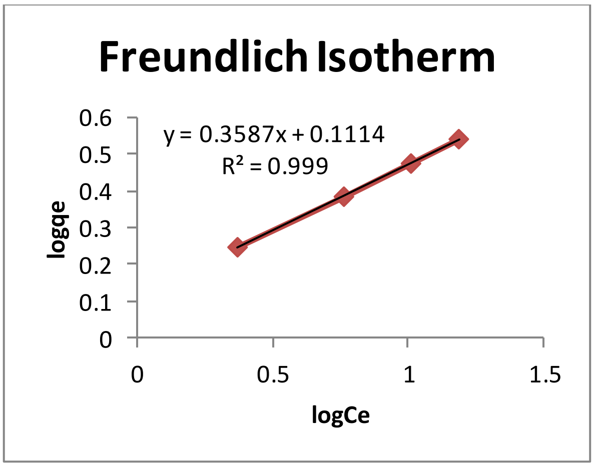


Fig: 4.25 Freundlich Model

Freundlich Isotherm Model (H.M. Freundlich,1906**)**

The Freundlich isotherm model describes the heterogeneity of the surface and multilayer adsorption. The equation which describes this isotherm is

$qe = K_F\ C_e^{1/n}$…………………………………………………………………......(4.3)

where K_F is the equilibrium constant indicates adsorption capacity (l/g). Adsorption capacity increases with increase in $K_{F.}$ 'n' is the adsorption equilibrium constant. 1/n is called heterogeneity factor and its range is from 0 to 1. The value of 1/*n* near to zero indicates heterogeneity of surface. The value of 1/n also represents whether adsorption process constant throughout the process (1/n = ≠1) or decreases with increase of concentration of metal ion (1/n).The linearized form of this model is $\log q_{e} = \log K_{F} + \left(\frac{1}{n}\right) \log C_{e}$…………………………………………………………….(4.4)

Langmuir Isotherm	**Freundlich Isotherm**
q_m = 3.816 mg/g	K_F =1.292
B = 0.0356	n = 2.786
R^2 = 0.973	R^2 = 0.999
MPSD = 6.59	MPSD = 0.5578

Table: 4.1 Constant parameters of isotherm model for adsorption

The data obtained from the experiments were plotted in the Langmuir and Freundlich isotherm model (figure: 4.24) and (figure: 4.25). From the correlation coefficient (R^2) it is concluded that Freundlich model gives a better prediction of adsorptive capacity of As ion onto the zirconium impregnated rice husk with linear correlation coefficients (R^2 = 0.999). Constant parameters of the Langmuir and Freundlich equation were evaluated from isotherms (table 4.1) In Langmuir isotherm R^2 value for Langmuir model was 0.973.Constant b in Langmuir isotherm model represents affinity of the adsorbent towards the toxic metals. Increasing the value of b, increases the energy of adsorption. q_{max} depicts the maximum active binding sites present in the adsorbent. q represents binding sites already attached by adsorbent at the concentration $C_{f.}$ MPSD value of Freundlich model is lower than Langmuir model. So from that respect Freundlich model also represents better prediction than Langmuir model.

4.8.2 Kinetic Models

Kinetic study presents the rate of equation and also helps us to find out rate limiting step. Pseudo 1st order model and pseudo 2nd order model were used to find out the rate limiting step for this study (Salemah et al.,2010).

Lagergren Model [Lagergren et al.(1898)]

Lagergren showed that the rate of adsorption of pollutants on the adsorbent followed a pseudo-first order equation:

$$dqt/dt = k_1(qe - qt) \ldots\ldots\ldots\ldots\ldots (4.5)$$

where qe and q_t are the sorption capacity (mg/g) of the adsorbent at equilibrium and at time t (h), respectively and k_1 is the pseudo-first order sorption rate constant (h^{-1}).Integrating and applying the boundary conditions t=0 to t = t and q_t =0 to q_t

$$qt = qe[1 - exp(-k_1t) \ldots\ldots\ldots\ldots\ldots\ldots (4.6)$$

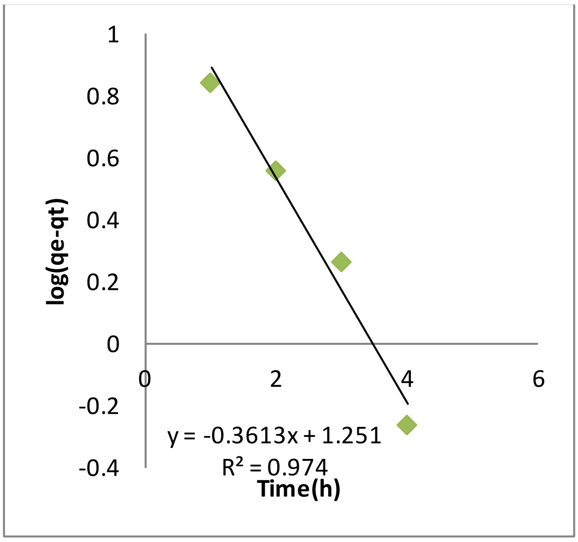


Fig: 4.26 Pseudo 1st order Model

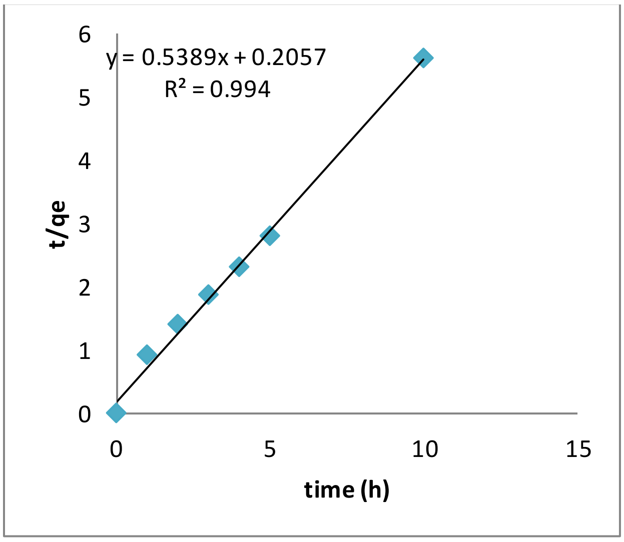


Fig:4.27 Pseudo 2nd order model

The values of K_1 (min-1) and q_e (mg/g) have been calculated from the intercept and slope of the plots of log ($q_e - q_t$) versus t. Results of pseudo first order model are shown in table 4.2

Pseudo 2nd order Model

Ho and McKay proposed that the kinetics of the sorption process was best described by a pseudo-second order equation:

$$\frac{dqt}{dt} = k_2(qe - qt)^2 \ldots\ldots (4.7)$$

Integrating and applying the boundary conditions t=0 to t and qt =0 to qt and rearranging:

$$\frac{1}{qe-qt} = \frac{1}{qe} - k_2t \ldots\ldots\ldots (4.8)$$

where k_2 is the pseudo-second order sorption rate constant.

Pseudo 1^{st} order model	**Pseudo 2^{nd} order model**
$q_e = 17.82$ mg/g	$q_e = 18.55$mg/g
$K_1 = 0.8328$ /min	$K_2 = 0.141$ g/mg.min
$R^2 = 0.974$	$R^2 = 0.994$

Table 4.2: Constant parameter of kinetic models

K_2 and q_e as intercept and slope of the curve has been calculated respectively. The graph of pseudo second order model has been represented in figure 4.27 and the Results of pseudo 2^{nd} order model has been shown in table 4.2 Pseudo second order model gives better prediction of uptake capacity rate and the linear correlation coefficients was $R^2 = 0.994$.

4.9 Identification of growth of bacteria in the presence of Arsenic

After inoculation of both bacteria into minimal media in the presence of arsenic the growth of bacteria was observed through increasing the turbidity of the culture medium.

Fig:4:28 Medium with different concentration of arsenic after 2 days of inoculation of *p.putida* in presence of arsenic

4.10 Effect of simultaneous adsorption bioaccumulation (SAB) on As removal

Pseudomonas putida (MTCC 1194) is arsenic resistant type bacteria which removes arsenic in two steps. It contains ars-R and ars-C genes and produces ars-R protein in presence of arsenic ions. Ars-R protein reduces As(V) to As(III) by reductase enzyme and after reducing it accumulates As(III).

4.10.1Mechanism of SAB reactor

The basic mechanism for SAB reactor is
1) formation of bio-layer onto the adsorbent
2) accumulation of arsenic (III) by Ars-R protein (Mergeay et al., 2003).
Here adsorbent is used as a solid support. Formation of bio-layer on to the active sides of the adsorbent basically reduces the porosity of the adsorbent so that capacity of arsenic adsorption by adsorbent is reduced in SAB reactor (Terada et al.,2005). But the overall capacity after bio-adsorption is increased compared to only adsorption.

4.10.2 Effect of initial concentration

Effect of initial concentration on SABA reactor is quite different compared to only adsorption process. Initially when initial concentration of arsenic <20 ppm, percent removal of arsenic increases with increasing in concentration. When initial concentration of arsenic >20 ppm there is a trend to decrease in percentage removal. This is because at lower concentration of arsenic *P.putida* absorb very less amount of arsenic and also release Ars-R protein and reductase enzyme quite less. With increase in arsenic, percentage removal of arsenic increases because *P.putida* produces more amount of Ars-R protein and as well as reductase enzyme. This enzyme reduces As (V) to As (III) and after that it accumulates As(III) .So initially microbes can grow with the help of arsenic but at a higher value of arsenic(>20 ppm) it has an opposite effect. At higher value of arsenic death phase of the microbes begin to start because at higher concentration the maximum segregation capacity of *p.putida* is crossed and then As acts as a substrate inhibitor.

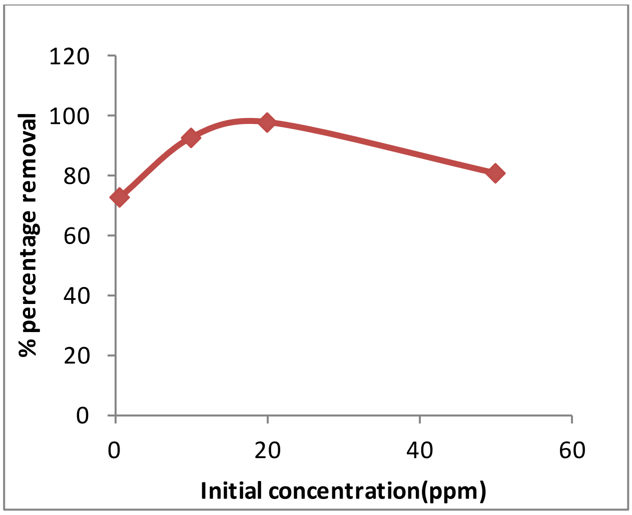


Fig:4.29 Effect of initial concentration on SAB

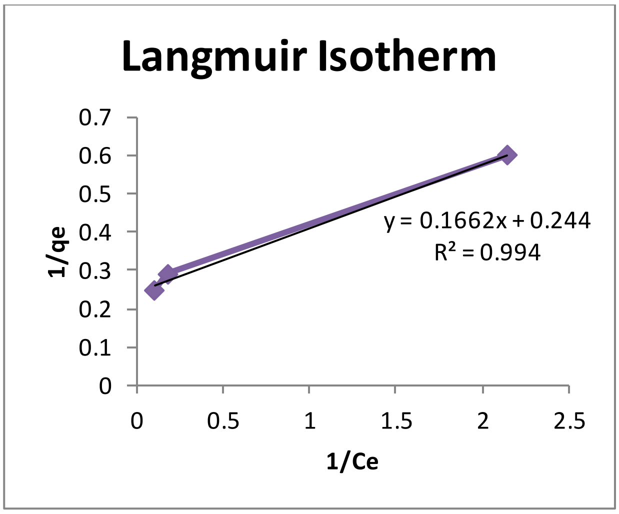


Fig:4.30 Langmuir model for SAB

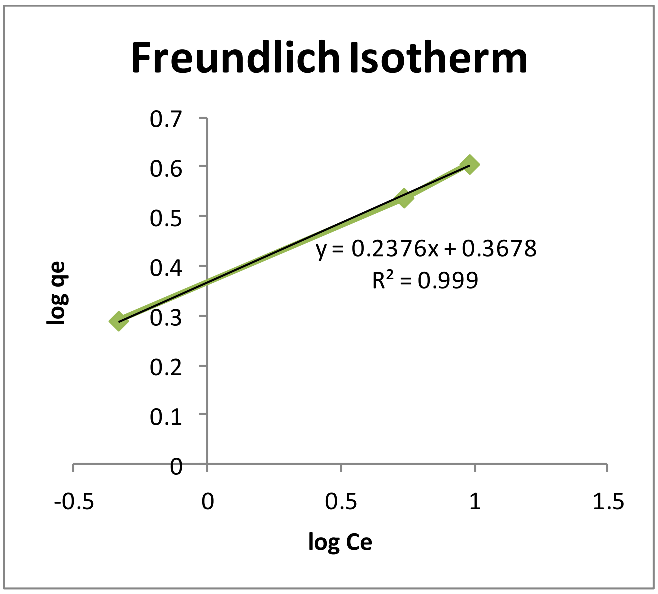


Fig:4.31 Freundlich model

Langmuir Isotherm	**Freundlich Isotherm**
q_m = 4.09 mg/g	K_F =1.728
b= 1.46	n = 4.2
R^2 = 0.994	R^2 = 0.999

Table : 4.3 Constant parameters of isotherm model for bioadsorption

The experimental data were fitted with the Langmuir and Freundlich isotherm model. Figure 4.30 and 4.31 represents the isotherm plot for sorption of As ion onto the biosorbent. Constant parameters and correlation coefficient values of each model obtained are given above. From the correlation coefficient (R^2) obtaining from Langmuir and Freundlich isotherm equations, Freundlich model provides a better understanding of As ion biosorption with linear correlation coefficients(R^2 = 0.999). However, Langmuir model was not fitted well. R^2 value for Langmuir model was 0.994.

CHAPTER 5

CONCLUSION

[1] Zirconium impregnated rice husk gives highest removal efficiency of arsenic (As (III) and As(V)) among all of other adsorbents(rice husk, maize leaves and $ZnCl_2$ impregnated rice husk).

[2] Maximum percentage removal of total As for Zr impregnated RH was 89.5% at temperature of 35°C, initial conc. 20 mg/l, contact time 5 hrs, adsorbent dose of 10 g/l, pH 8 respectively.

[3] Characterization of adsorbents have been done by FE-SEM, XRD, DTA/TGA, FTIR. Functional groups presented on the surface of adsorbents due to impregnation of positive ions significantly affect the adsorption process.

[4] For equilibrium studies, Freundlich isotherm was better fitted than to Langmuir model. The regression coefficient was 0.999.The uptake of As ions onto solid surface of maize leaves was studied by using kinetic models. The pseudo second-order kinetic model gives better result with linear regression co-efficient $R^2 = 0.994$.

[5] In SAB process removal percentage of arsenic increases with increase in concentration of initial concentration. Almost 96% removal of arsenic in SAB process represents that immobilization of *P.putida* on zirconium oxychloride impregnated rice husk is a highly effective adsorbent for adsorption process.

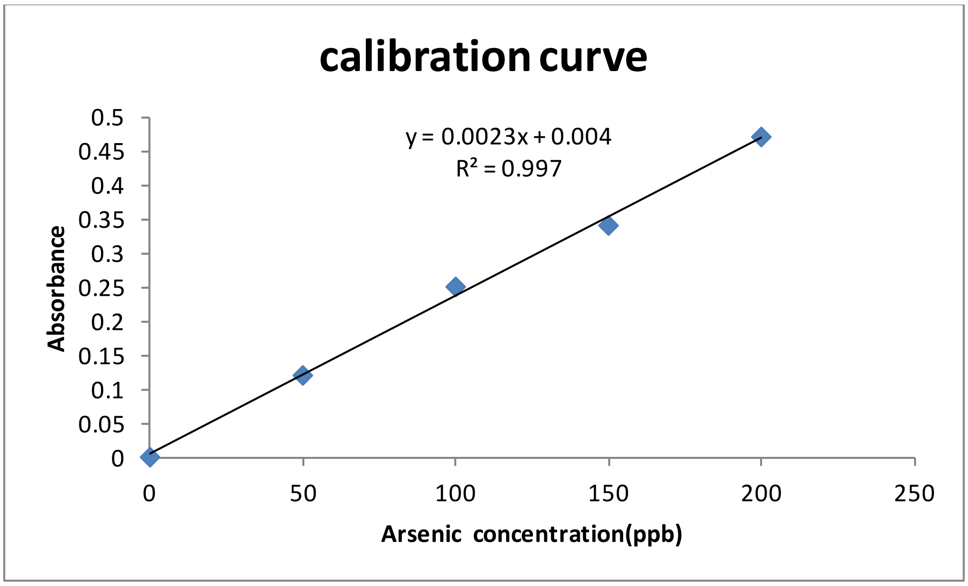
This study contributes a novel adsorbent which is cheap and also efficient for removal of arsenic from arsenic contaminated water.

FUTURE RECOMMENDATION

Though in this study it has been seen that both zirconium loaded rice husk and immobilized zirconium loaded rice husk are novel and effective adsorbents for removal of total arsenic, but removal of arsenic on real wastewater has not been examined. So feasibility of these adsorbents for real wastewater can be studied in future.

APPENDIX

Calibration Curve



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