

# 1. Introduction

## 1.1 General Introduction

Waste water containing heavy metal pollutants cause direct toxicity, both to human and other living organism due to their presence beyond specific limits. Being one of the toxic heavy metal arsenic has been gaining public and scientific concern pertaining to its high toxicity and increased appearance in the biosphere [1]. In view of this regard, the World Health Organization has set the standard for arsenic in drinking water as 0.01mg/L (WHO, 1993). Recently As contamination of ground water has become a major problem on global scale and potentially impacts millions of people, since more and more groundwater withdrawal is taking place due to human usage and agricultural irrigation (Smith *et al.*, 1998) [2].

Arsenic (Inorganic and Organic) occurs in several oxidation states as 0, +5, +3, and -3 under different conditions in aqueous media. Organic species of arsenic include in the form of monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA) and are predominantly found in food stuffs such as shellfish. Inorganic arsenic exists in As(III) and As(V) state. In ground water As usually exist as oxyanion compound namely arsenite (trivalent arsenic, As(III)) and arsenate (pentavalent arsenic, As(V)), where As(III) is predominant species which is more toxic and more difficult to remove than As(V). The As contamination of ground water is not only caused by the physical geographic change as volcanic emission, weathering reactions, anthropogenic activities but also human activities, such as the use of arsenical preservatives in the wood industry, arsenical pesticides in agriculture, As mine drenching have also elevated As concentrations in groundwater in recent years (Chakraborti *et al.*, 2002; Matschullat, 2000) [3, 4, 6].

Exposure to high level of As causes acute and chronic poisoning. Human exposure of As takes place through ingestion, inhalation or skin absorption. Inorganic As is readily absorbed from the gastro intestinal tract and becomes distributed through out the body, tissues and fluids. Long term exposure to As causes various kinds of effects. Effects range from acute lethality to chronic effects such as arsenial dermatosis, skin, lung, kidney cancer, pigmentation etc [3, 13].

There are several techniques for the removal of As from water including physiochemical, biological treatment and membrane filtration. However these techniques are sophisticated and expensive cannot be practiced in rural areas in developing and poor countries [2]. A promising method that can be considered efficient and low cost for wide-scale application is adsorption using appropriate readily available cheap adsorbent [2]. The activated carbon is widely used as adsorbent for As removal. Despite its widespread use question remains concerning the economic feasibility of AC and determining suitable carbons for specific contaminants often requires extensive experimentation, time, cost [3, 5].

Hence there is a need to come up with a low cost adsorbent and at least as effective as AC. In such case the biological method (biosorption) proves to be effective due to their high efficiency, low operating cost and simplicity [3]. In this method the biological wastes are utilized to facilitate the removal of metal ions (As) from aqueous solution. The biological waste include agricultural and natural wastes such as nutshells, rice husk, coconut shells, saw dust, orange residue, wood coal, sugarcane begasse etc which are readily available [3, 12]. The bioadsorbent are chemically modified which increases the surface area of adsorbent resulting the increased adsorption capacity. The adsorbent gets chemically modified due to the formation of different functional groups.

Further the adsorbent coated with metals like Fe(III) markedly increases the arsenic removal. The adsorption takes place by either anion exchange or ligand exchange mechanism.

The use of agricultural and natural wastes as bioadsorbent thus not only would provide a less costly sorbent to AC, but also offers a potential alternative to conventional method for As removal [7]. On account of such possibility the present study is based on the development and characterization of the adsorbent prepared from sugarcane waste for adsorption of As(III) ions. Sugarcane plant is readily available as it is harvested in different parts of the country for the production of sugar. The sugarcane wastes can be easily obtained from juice vending center. The residue generated as a waste can be utilized for adsorption. Thus it is economical and environment friendly bioadsorbent used for the removal of As(III) from aqueous solution.

## **1.2 Arsenic Removal Techniques**

Several treatment technologies have been adopted to remove arsenic from drinking water under both laboratory and field conditions. The major mode of removing arsenic from water is by physical-chemical treatment. Technologies for removing arsenic from drinking water include:

- ) Precipitation processes, including coagulation/filtration, direct filtration, coagulation assisted microfiltration, enhanced coagulation, lime softening, and enhanced lime softening
- ) Adsorptive processes, including adsorption onto activated alumina, activated carbon and iron/manganese oxide based or coated filter media
- ) Ion exchange processes, specifically anion exchange

- ) Membrane filtrations, including nano-filtration, reverse osmosis and electro dialysis reversal.
- ) Alternative treatment processes, especially greensand filtration
- ) In situ (sub-surface) arsenic removal (Jacks *et al.* 2001; Appelo and de Vet, 2003)
- ) Biological arsenic removal (Katsoyiannis and Zouboulis, 2004)

Some of these treatment technologies, such as co-precipitation, adsorption, ion exchange, and membrane process have been demonstrated to be effective in removing arsenic from contaminated groundwater (Cheremisinoff, 1998). However, questions remain regarding these technologies, particularly concerning economical viability and social acceptability. The technique, adsorption seems to be promising for As removal primarily due to its low cost and environmentally benign nature. Different kinds of agricultural and natural wastes can be used as adsorbent in this process which are readily available from house hold activities. Common adsorbent include AC, Activated Alumina, Metal oxide etc and the adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength [12, 29].

### **1.3 Adsorption study**

Adsorption is defined as the concentration of a substance at an interface or a surface. This process can occur at an interface between any two phases, such as liquid liquid, liquid solid etc. The substance which gets adsorb is called adsorbate and on which adsorption takes place is called adsorbent. The adsorption process addressed here is the concentration of arsenic from aqueous solution to the surface of iron-loaded activated

carbon. The adsorption phenomenon can be studied by column and batch experiments.

In column experiment, a glass column of particular length and internal diameter is filled with known amount of adsorbent. With the help of porous sheet at the bottom of the column, the adsorbent bed is supported inside. This also provides the uniform inlet flow and good liquid distribution. The top of the bed is generally closed by a layer of glass bed (1mm in diameter) which avoids the loss of biomass and also ensures a closely packed arrangement. A known concentration of the metal solution is now fed through the bed in up flow mode at the desired flow rate with a peristaltic pump connected at the bottom of the column. Samples are collected periodically and filtered through cellulose nitrate filter paper. The filtrate is then analyzed for the remaining metal ion concentration. Operation of the column is stopped when the effluent concentration reached a constant value [8].

In the batch adsorption study a definite volume of the metal solution having known concentration is taken in the stopper bottle. A distinct mass of the adsorbent is added to it and the stopper bottle is vigorously shaken in a mechanical shaker at the room temperature for 24 hrs to ensure the adsorption equilibrium. The initial and the final concentrations of the metal ions are determined by using either AAS or spectrophotometer. Heavy metal adsorption onto different adsorbent is affected by different parameters such as initial concentration of metal ions (mg/L), contact time (sec) amount of the adsorbent used (g/L), temperature and pH of the solutions. To understand the mechanism and effectiveness of adsorption, one of the above parameter is changed by keeping other constant. From the measurement of the metal concentration before and after the adsorption, weight of the dry adsorption gel and from the volume of

aqueous solution, the amount of adsorbed metal is calculated according to following equation [8].

$$q_t = \frac{(C_i - C_e) V}{W} \quad (I)$$

Where,  $C_i$  and  $C_e$  are the metal ion concentration in mg/L initially and at the equilibrium respectively.  $V$  is a metal solution in litre and  $W$  is the weight of adsorbent in gram.

The distribution ratio ( $D$ ) is defined as the ratio of the amount of adsorption to the metal ion concentration in aqueous solution at equilibrium and is calculated according to equation III,

$$D = q_e / C_e \quad (II)$$

Where,  $q_e$  is the equilibrium amount of the adsorption of metal ion per unit mass of the adsorbent,  $C_e$  is the equilibrium concentration in mg/L.

Percentage adsorption of metal is defined as the ratio of the decrease in metal ion concentration after adsorption to the initial concentration of the metal in aqueous solution.

Percentage adsorption is determined by the following expressions.

$$A\% = \frac{(C_i - C_t) 100}{C_i} \quad (III)$$

Where,  $C_i$  and  $C_t$  are the concentration of metal ion in (mg/L) initially and at time 't' respectively.

#### **1.4 Adsorption Isotherm**

Adsorption usually described through isotherms gives the extent of adsorption at equilibrium. It is defined as the amount of solute adsorbed per unit weight of the adsorbent 'q' as a function of the residual

equilibrium concentration  $C_o$ , of the solute remaining in solution. Several models have been developed to describe adsorption behaviour. But Langmuir and Freundlich adsorption isotherms equations are most widely used to represent the data of sorption from the aqueous solution [9].

#### 1.4.1 Langmuir isotherm

The maximum adsorption capacity of the adsorbent is determined by Langmuir adsorption isotherm model. The Langmuir sorption is the best known of all isotherms describing adsorption and it has been successfully applied to many adsorptions processes. Langmuir isotherm is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by the following expressions [10].

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (IV)$$

Where,  $q_e$  is the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g),  $q_m$  is the maximum uptake capacity of the sorbent or the number of moles of solute adsorbed per unit mass of the adsorbent in forming a complete monolayer on the surface be constant and temperature independent (mg/g), it is determined solely by the nature of the adsorbent,  $b$  is adsorption constant (L/mg) related to the energy of adsorption.

The rearranged and linear form of langmuir isotherm equation is given as,

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + C_e / q_m \quad (V)$$

From the experimental  $C_e$  and  $q_e$  data, the linear plot of  $C_e / q_e$  against  $C_e$  can be drawn to evaluate the langmuir constant  $q_m$  and  $b$ , from the slope and intercept respectively for all metals. The values obtained from the

langmuir model ( $q_m$  and  $b$ ) can provide information in the screening of the adsorbent. It means that potentially a good adsorbent can be comparatively evaluated from the values of  $q_{max}$  and  $b$ . However, the langmuir gives no mechanistic aspects of sorption [11].

#### **1.4.2 Freundlich adsorption isotherm**

The Freundlich model named after Freundlich (1926) is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$q_e = K_F C_e^{1/n} \quad \text{(VI)}$$

Where,  $q_e$  = the adsorption density (mg of metal ion adsorbed/g biomass),  $C_e$  = concentration of metal ion in solution at equilibrium (mg/L),  $K_F$  and  $n$  are the Freundlich constants which determines the curvature and steepness of the isotherm (Akgerman and Zardkoohi, 1996). Also, the value of  $n$  indicates the affinity of the adsorbate towards the biomass. The above equation is conveniently used in linear form as:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad \text{(VII)}$$

A plot of  $\ln C_e$  against  $\ln q_e$  yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The constants  $1/n$  and  $\ln K_F$  can be determined from the slope and intercept respectively [10].

#### **1.5 Study of adsorption kinetics**

Adsorption kinetics deals with the study of the rate and mechanism of the adsorption phenomenon. The kinetics of arsenic adsorption can be studied using mostly pseudo first-order, second-order and pseudo-second order reaction models.



### 1.5.1 Pseudo first-order model

The pseudo first-order is given by (Lagergren, 1989):

$$dq/dt = K_1 (q_e - q_t) \quad (\text{VIII})$$

Where,  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at time  $t$ , respectively (mg/g),  $K_1$  is the rate constant of pseudo first-order adsorption (L/min). After integration and applying boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of Equation (VIII) becomes:

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (\text{IX})$$

A plot of  $\log (q_e - q_t)$  against  $t$  gives a straight line.  $K_1$  and  $q_e$  can be determined from the slope and intercept respectively.

### 1.5.2 The Pseudo second-order model

The pseudo second-order reaction kinetic is expressed as (Ho *et al.*, 2000):

$$dq/dt = K_2 (q_e - q_t)^2 \quad (\text{X})$$

Where,  $K_2$  is the rate constant of pseudo second-order adsorption (g/mg min). For the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of equation (XI) becomes:

$$1/(q_e - q_t) = 1/q_e + K_2 t \quad (\text{XI})$$

This is the integrated rate law for a pseudo second-order reaction. Equation (XI) can be rearranged to obtain equation (XII), which has a linear form:

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \quad (\text{XII})$$

If the initial adsorption rate  $q_0$  (mg/g min) is:

$$q_0 = k_2 q_e^2 \quad (\text{XIII})$$

Then, equation (XII) and (XIII) becomes:

$$t/q_t = 1/q_0 + t/q_e \quad (\text{XIV})$$

The plot of  $(t/q_t)$  against  $t$  using equation (XIV) should give a linear relationship from which  $q_e$  and  $K_2$  can be determined from the slope and intercept respectively [10].

### 1.5.3 The second-order model

The second-order rate equation (Lagergren, 1898) is generally expressed as,

$$dq/dt = k'_2(q_e - q_t)^2 \quad (\text{XV})$$

Where,  $k'_2$  is the second-order rate constant for adsorption (g/mg min).

On integration using boundary condition, as  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the equation becomes,

$$1/q_e - q_t = 1/q_e - k'_2 t \quad (\text{XVI})$$

The plot of  $1/q_e - q_t$  against  $t$  gives a linear plot, from which  $k'_2$  and  $q_e$  can be calculated from the slope and intercept respectively.

The validity of the kinetic model can be investigated by studying the kinetics at different time intervals with different initial metal concentration.

## 2. Literature Review

The presence of arsenic in the environment is of major concern because of its toxicity, bio accumulating tendency and threat to human life and the environment [1]. In recent years many low cost adsorbents such as algae, fungi, bacteria and lignocellulosic agricultural by product have been investigated for their biosorption capacity towards arsenic. Though a number of removal techniques such as oxidation, precipitation, coagulation, membrane separation are available adsorptive removal of arsenic from aqueous solution is evolving as a front line defense and is usually achieved by using activated carbon or activated alumina (Faust and Aly, 1987) [3, 12]. Much work has been done on arsenic removal through adsorption in different parts of the world, because the system can be simple to operate and cost effective. Also this method detects trace concentration of arsenic left after the detection by other methods (precipitation, coagulation etc) which are more reliable at higher concentration. All the studies indicate that only As(V) can be separated from the aqueous phase effectively and the removal of As(III) which is about four times toxic than As(V) is very difficult.

Raven *et al.*, [15] compared the adsorption behavior of arsenite and arsenate on ferrihydrite  $[(\text{Fe}^{3+}\text{O}_3\text{O}.5(\text{H}_2\text{O}))]$ . At relatively high As concentrations, adsorption was almost complete in a few hours and arsenite reacted faster than arsenate with the ferrihydrite. However, arsenate adsorption was faster at low As concentration and low pH. Adsorption maxima at pH 4.6 (pH 9.2 in parentheses) of 0.60 (0.58) and 0.25 (0.16) molAs/molFe were achieved for arsenite and arsenate, respectively. Overall arsenite and arsenate have strong affinities for

ferrihydrate, and arsenite retained in much larger amounts than arsenate at high pH (approximately >7.5) or at high As concentrations in solution.

Ranjan *et al.*, [16] synthesized hydrous ferric oxide, for arsenic sorption. As(V) sorption strongly depended on the system's concentration and pH, while As(III) sorption was pH insensitive. As(III) required less contact time to attain equilibrium.  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{HCO}_3^-$  competed poorly with As(III) sorption, anions (chloride, nitrate, sulfate, and phosphate).

Eguez and Cho [17] studied adsorption of As(III) and As(V) on activated charcoal versus pH and temperature. The capacity of As(III) on carbon was constant at pH 0.16-3.5. However As(V) exhibited a maximum adsorption at pH 2.35 over the pH range of 0.86-6.33.

Guo and Chen [18] utilized iron oxyhydroxide-loaded cellulose beads for arsenate and arsenite removal from water. The Langmuir adsorption capacities for arsenite and arsenate were 99.6 and 33.2 mg/g at pH 7.0 for beads with a Fe content of 220 mg/mL.

Sulfate addition had no effect on arsenic adsorption, whereas phosphate greatly retarded arsenite and arsenate elimination.

Pierce and Moore, (1982) [19] found that arsenate adsorption on amorphous Fe-hydroxide increased at low pH, exhibited maxima in the pH range 3 to 7 and decreased at high pH, somewhat similar behaviour was found for arsenite adsorption where adsorption increased at low pH exhibited a peak in the pH range 7 to 8.

Singh and Pant, (2004) [20] removed arsenites from water with activated alumina (AA) and iron oxide impregnated activated alumina. The effect of adsorbent dose, pH and contact time were investigated. As(III)

removal was strongly pH dependent. Both Freundlich and Langmuir isotherm were fit by the experimental data. As(III) adsorption on AA was exothermic while it is endothermic with impregnated activated alumina. Adsorption kinetics was governed by pseudo first order rate equation in both the cases.

Mandal *et al.*, [23] removed arsenic from a simulated contaminated ground water by adsorption on to Fe<sup>3+</sup> impregnated granular activated carbon (GAC-Fe) in the presence of Fe<sup>2+</sup>, Fe<sup>3+</sup>, and Mn<sup>2+</sup>. The effect of shaking time, pH and temperature on the percentage of As removal of As(III), As(V), Fe<sup>2+</sup>, Fe<sup>3+</sup> and Mn has been reported. The shaking time for optimum arsenic removal was 8 hrs for GAC-Fe and 12 hrs for GAC respectively. Maximum As(V) and As(III) removal was in pH range of 5 to 7 and 9 to 11 respectively for both the adsorbents. Gupta and Chen (Gupta *et al.*, 1978) investigated the adsorption of arsenic by activated alumina, activated bauxite and activated carbon. Activated carbon was much less effective than others. Activated alumina obtained consistently higher adsorption capacities and faster adsorption rates.

Ghimire *et al.*, (2003) [25] has also phosphorolated both cellulose and orange wastes. The chemically modified adsorbents were then loaded with iron(III) in order to create a medium for arsenate and arsenite chelation. Arsenite removal was favored under alkaline conditions for both gels. The orange waste gel showed some removal capacity even at pH 7. Conversely, arsenate removal took place under acidic conditions at pH 2-3 and 2-6 for the cellulose gel and orange waste gel led to greater arsenic removal. Arsenite or arsenates are adsorbed by liquid exchange on the immobilized Fe(III) centers of the Fe(III)-loaded phosphorolated cellulose and phosphorolated orange wastes. The ligand involved in such an exchange process may be hydroxyl ions or neutral water molecules

present in the Fe(III) co-ordination sphere. The loading capacity for Fe(III) on phosphorylated orange gel was 67.57mg/g (1.21 mol/kg) higher than on the gel prepared from cellulose 53.61mg/g (0.96 mol/kg) and found that arsenic removal efficiency was higher on the phosphorylated orange gel due to higher uptake capacity of gel on Fe(III) which in turn have more ligand exchange capacity.

Nasir *et al.*, (1998) [26] used the rice husk as bioadsorbent for arsenic from water and reported that maximum adsorption occurred at 0.01mol/L of HNO<sub>3</sub>, HCl or H<sub>2</sub>SO<sub>4</sub> using 1g of adsorbent for 5.97x10<sup>-3</sup> mol/L of arsenic for 5 minute. The Freundlich isotherm was followed over concentration range from 8.69x10<sup>-3</sup> mol/L to 1.73x10<sup>-3</sup> mol/L of arsenic. The uptake of arsenic increases with increasing temperature.

Altundogan *et al.*, (2000) [27] studied the adsorption of As(III) and As(V) on red mud at alkaline and acidic medium and concluded that an alkaline aqueous medium (pH 9.5) favored As(III) removal, where as the acidic pH range (1.1-3.2) was effective for As(V) removal. The capacities were 4.31 μmolg<sup>-1</sup> at the pH of 9.5 for As (III) and 5.07 μmolg<sup>-1</sup> at the pH of 3.2 for As(V).

Nowadays, much attentions have been focused on arsenic removal by adsorption utilizing low cost bioadsorbent readily available from agricultural wastes especially sugarcane begasse. The process is simple and effective and many researchers are has taken this as a subject of interest.

### **3. Objective of the present study**

Adsorption process seems more effective and reliable than other convectional removal techniques for As(III) removal. The efficiency of the bio-adsorbent used depends upon the source and chemical treatments. The study mainly focuses on the development and characterization of the low cost adsorbent prepared from agricultural wastes ie sugarcane begasse and also to test the viability and cost effectiveness of the adsorbent addressed for As(III) removal.

#### **3.1 Specific Objectives**

**The specific objectives of the present work are:**

- ❖ To develop and characterize the friendly low cost bioadsorbent for As(III) removal from aqueous solution.
- ❖ To find out the nature of adsorption isotherm for the adsorption of As(III)
- ❖ To study the effect of pH, contact time during the adsorption process under fixed concentration.

## **4. Experimental**

### **4.1 Preparation of the reagents**

#### **4.1.1 Arsenic stock solution**

1.3200 gm of arsenic trioxide ( $\text{As}_2\text{O}_3$  dried at 110 C for an hour) was weighed out accurately and dissolved in 5ml of 10m sodium hydroxide solution. After shaking well, final volume was made to 100ml in volumetric flask with distilled water.

1ml of arsenic trioxide solution = 1000 $\mu\text{g}$  of As

#### **4.1.2 5% Ammonium molybdate Reagent**

5% Ammonium molybdate reagent  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$  was prepared by dissolving 25.00 gm of ammonium molybdate in 500ml volumetric flask with distilled water and the final volume was maintained up to the mark.

#### **4.1.3 0.5 M Hydrazine Hydrate solution (Approx.)**

0.5M Hydrazine Hydrate solution  $[\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}]$  was prepared by dissolving 2.44ml of concentrated hydrazine hydrate in 100ml of volumetric flask with distilled water.

#### **4.1.4 1.5M Sulphuric acid solution (Approx.)**

1.5M Sulphuric acid solution was prepared by dissolving 10.41 ml of concentrated acid in 250 ml volumetric flask with distilled water.



#### **4.1.5 0.5% of Ammonium Molybdate solution (Approx.)**

0.5% of ammonium molybdate was prepared by dissolving 100ml 5% ammonium molybdate reagent in 1000 ml volumetric flask with distilled water.

#### **4.1.6 5M Hydrochloric Acid (Approx.)**

11.3ml of conc. hydrochloric acid (HCl) was taken in 25mL volumetric flask and volume was maintained up to the mark.

#### **4.1.7 5M Sodium Hydroxide Solution (Approx.)**

5M of sodium hydroxide solution was prepared by dissolving 20 gm of sodium hydroxide pellets in 100ml volumetric flask with distilled water.

#### **4.1.8 Buffer solution of pH 4, 7, 9.2**

Buffer solution of pH 4, 7, 9.2 was prepared by dissolving buffer tablet of pH 4, 7, 9.2 in 100 ml volumetric flasks with distilled water.

### **4.2 Analysis**

The following laboratory based methods are well described for As determination,

- ❖ Silver Diethyldithiocarbamate spectrophotometric method (SDDC)
- ❖ Atomic fluorescence spectrometry (AFS)
- ❖ Hydride generation atomic absorption spectrometry (HGAAS)
- ❖ Graphite furnace atomic absorption spectrometry (GFAAS)

## **Molybdenum Blue Method**

All the techniques mentioned above are expensive and socially unacceptable and also require trained manpower generally experienced in dealing with trace elements and hazardous chemicals. However, the Molybdenum Blue Method mentioned above is the choice among other techniques in most of the laboratories.

### **4.2.1 Spectrophotometric determination of arsenic by Molybdenum Blue Method**

The cheap and significant method for the determination of arsenic at trace or higher amount is the Molybdenum Blue method. It is more sensitive and accurate among other methods. In this method, arsenic(III) is oxidized to arsenic(V) by  $\text{KMnO}_4$  in acidic medium. The resultant arsenate is treated with ammonium molybdate to form arsenomolybdate which on reduction with hydrazine hydrate forms a soluble complex of blue color "molybdenum blue". A spectrophotometric measurement of the blue complex determines the amount of reduced arsenomolybdate and arsenic is determined with reference to an analytical curve prepared from the standards. The working range is from 0.1 mg/L to 1 mg/L. Samples of higher concentration need to be diluted.

## **4.3 Preparation of adsorbent**

### **4.3.1 Preparation of unmodified sugarcane bagasse**

Sugarcane bagasse was collected from a local juice vending center. It was washed with water and dried in the sunlight. The dried sugarcane bagasse was cut into small pieces and was grinded into powder form. It was sieved to a particle size of 250 to 450  $\mu\text{m}$ .

### **4.3.2 Preparation of iron-loaded modified sugarcane begasse**

The sugarcane begasse powder was weighed and acidified with concentrated sulphuric acid in the ratio of 2:1(W/V). This was allowed to soak for 24 hrs at room temperature. The sample was then washed with distilled water till neutrality was maintained.

Then 5gm of modified sugarcane begasse was mixed with 500ml of  $1.5 \times 10^{-2}$ M anhydrous Fe(III) chloride solution maintained at pH 3 and stirred in rotatory shaker at room temperature for 24 hrs. This then was washed with distilled water till neutrality and was dried.

## **4.4 Characterization of adsorbent**

### **4.4.1 Determination of surface area**

The extent of adsorption depends on the surface area of the adsorbent. Higher the surface area of the adsorbent higher is the adsorption. The surface area can be determined by the following relation,

$$S = 1/b \times N \times 21 \times 10^{-20} \text{ m}^2/\text{g}$$

Where, N is the Avogadro's number, S is the specific area and b is the Langmuir constant.

### **4.4.2 Boehm's titration (surface chemistry)**

The surface chemistry of the AC is determined by the acidic and basic character of the surface. The acidic behaviour is associated with oxygen functional groups such as carboxyl, lactones and phenol. Boehm in 1996 used the titration method to determine the number of oxygenated surface groups. The free carboxylic group, lactones and phenolic group are neutralized by sodium carbonate, sodium hydroxide neutralizes carboxyl

and lactones, sodium bicarbonate neutralize only carboxyl groups. Thus by selective neutralization using bases of the surface acidic group in carbon can be determined. The basic properties can be derived from the basic groups and the  $\pi$ -electron system of carbon basal planes. The volume of sodium hydroxide required to neutralize the sample is equivalent to the total titrable surface functional groups.

#### **4.5 Determination of calibration curve**

1, 2, 3, 4, 5, 6, 7, 8, 9, 10 ml of 2.5mg/L arsenic solution (prepared from stock solution) were taken in 25 ml volumetric flask and were acidified with 4.5 ml of 1.5N sulphuric acid. To each flask was added 0.1N potassium permanganate which gives faint pink colour in order to oxidize As(III) to As(V). Then 3ml of 0.5% AM was added and shaken well, finally 3ml of 0.5 M hydrazine hydrate was added as a reducing agent. Then the volume was made up to the mark with distilled water. Each solution was allowed to stand for 20 minutes for the maximum color development. Blue coloured complex was formed whose absorbance was measured at 840 nm (which corresponds to  $\lambda_{\text{max}}$  for arsenic determination) with reference to blank solution using WPA-104 spectrophotometer and the calibration curve was drawn.

A plot of absorbance against concentration of arsenic in mg/L is shown in figure 2.

#### **4.6 Batch adsorption studies**

Batch adsorption studies were carried out with Fe(III)-loaded modified sugarcane bagasse to determine the adsorption behaviour of As(III). The effect of pH of the solution, effect of initial concentration of metal ion and the effect of contact time of the adsorption process was investigated.

The pH of the solution was maintained by using HNO<sub>3</sub> acid solution and NaOH solution of concentration 1M to 5M. For the batch adsorption 25 ml of the metal solutions were taken in 125 ml stopper bottles and 25mg of the adsorbent were added to each of them. The bottles were shaken in a mechanical shaker for 24 hours at room temperature. Then the solutions were filtered and filtrates were analyzed for the determination of equilibrium concentration. Concentration before and after the adsorption were determined by using WPA-104 spectrophotometer.

#### **4.6.1 pH study**

pH is an important parameter for adsorption of metal ions from aqueous solution because it effects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction or it in fact determines the chemistry and speciation of metal ions and also the effect the surface charge of the adsorbent. To examine the effect of the pH on the As(III) removal efficiency the pH were varied from 6 to 12. The pH studies were conducted by shaking 25 ml of metal solution with 25mg of adsorbent.

After shaking for 24 hr in mechanical shaker each solution were filtered and equilibrium pH of the filtrate was noted. The filtrates were then analyzed for the equilibrium concentration. From, the value of equilibrium concentration and initial concentration, the % adsorption at each pH were calculated by which optimum pH of the adsorption was evaluated.

#### **4.6.2 Isotherm study**

The effect of As(III) concentration on the adsorption was studied under optimized pH. The study was carried out with different initial concentration of metal ion ranging from 50mg/L to 500mg/L with 25gm of the adsorbent. The solutions were shaken in a mechanical shaker and metal concentration before and after the adsorption were analyzed by using spectrophotometer.

Freundlich and Langmuir isotherm model are widely used for fitting the data obtained. To get equilibrium data, initial As(III) concentration were varied while the adsorbent mass in each sample was kept constant.

#### **4.6.3 Equilibrium time study**

After determining the optimum pH, the equilibrium time for the adsorption of As(III) was studied at optimum pH values at room temperature. For the experiment, 25 ml of the solutions were agitated with 25mg of the adsorbent in 125ml reagent bottle respectively. The solutions were equilibrated in a mechanical shaker for 10 min, 20 min, 30min, 40 min, 50, 60 , 70, 80 , 90 , 100, 110 , 120 min, 24 hr and for infinite time respectively. The change in concentration before and after adsorption was analyzed by using spectrophotometer.

#### **4.6.4 Kinetics study**

Batch kinetics studies were performed at optimum pH. The experiments were carried out by shaking 25mg of the adsorbent with 25ml of metal solution in 125ml reagent bottle. The bottles were shaken for the times ranging from 20 min to 140 min. The data obtained were then analyzed for pseudo first-order (Lagergren, 1898), pseudo second-order (Ho and Mckay *et al.*, 2000) and second order (Lagergren, 1898) kinetics model.

## **5. Result and Discussion**

### **5.1 Spectrophotometric determination of Arsenic by Molybdenum**

#### **Blue method:**

Arsenic is mostly determined by the formation of a molybdoarsenic heteropoly acid with the help of spectrophotometer. In this method an acidified As(III) solution is oxidized to As(V) with the help of potassium permanganate. The arsenate in the acid solution reacted with molybdenum to give a colourless heteropoly acid, which is then reduced to arsenomolybdenum blue colour complex by hydrazine hydrate. The blue form of the molybdoarsenic heteropoly acid exhibits absorption maxima at 840 nm.

The absorption spectra of arsenomolybdenum blue complex shows the maximum absorbance at a wavelength of 840 nm, which is the  $\lambda_{\max}$  for arsenomolybdenum blue complex as shown in figure 1. The result is in agreement with the reported value.

The Lambert-Beer's plot for arseno molybdenum complex was drawn at 840 nm. A linear correlation was found between the absorbance of As(III) arseno molybdenum complex and the concentration of arsenic which is shown in the figure 2.

### **5.2 Characterization of charcoal**

#### **5.2.1 Surface Area Determination**

The surface area the activated sugarcane begasse charcoal was found to be  $113.10\text{m}^2/\text{g}$ .

### **5.2.2 Boehm's titration**

The surface functional group of sugarcane charcoal was found to be 372.67 mg/g.

### **5.3 Effect of pH studies**

Study of the effect of pH shows the adsorption of arsenic from aqueous solution using activated carbon was found to be a highly pH dependent process. In this experiment, the adsorption behaviour of As(III) was studied at different pH values ie from 6 to 12. Optimum As(III) removal occurs at pH 10 and declining at lower pH. Fig 1 shows the percentage adsorption of As(III) as the function of equilibrium pH. The removal of As(III) by adsorption on iron-loaded modified sugarcane bagasse was found to increase when the pH was increased from 6 to 10 and thereafter a slight decline in removal was observed with increase in pH. The metal ions are adsorbed according to ligand exchange mechanism and are adsorbed at alkaline condition. The adsorption increase rapidly near the optimum range at higher pH. The uptake of metal ions from aqueous solution by modified SB is usually accompanied by a reduction in the pH of the metal ion solution. This is generally believed due to the exchange of the  $H^+$  ion in the substrate by the metal ions. The increase or decrease of sorption capacity with pH may be attributed on the basis of the surface functional charge of the adsorbent, the degree of ionization and the speciation of the surface functional groups.

### **5.4 Effect of concentration: Adsorption isotherm**

The effect of As(III) concentration on the adsorption was studied under optimized pH. Figure 2 shows the plot of adsorption isotherm for As(III) on iron-loaded sugarcane bagasse. Decrease in adsorption percentage at



higher concentrations might be due to the relatively smaller numbers of active sites available at higher arsenic concentrations. With increasing of the initial concentration of arsenic total amount of arsenic removal (X/m) is increased.

### 5.5 Adsorption isotherm model

Figure 3 and 4 represent the plot of Langmuir and Freundlich isotherm respectively. The result obtained is shown in table 1. The adsorption data for arsenic were also further analyzed by means of the Langmuir and Freundlich isotherm models. Langmuir and Freundlich parameters are determined from the slope and intercept respectively. The analysis of the data obtained for As(III) sorption showed that they fit better with the linearized form of Langmuir equation due to comparatively high value of correlation coefficient for Langmuir adsorption as compared to Freundlich adsorption. The langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The adsorption capacity of the media will increase As(III) concentration, until some maximum adsorption capacity is attained, which is consistent with the data presented in this study. The data shows that the maximum adsorption amount ( $q_{max}$ ) of arsenite. The maximum adsorption capacity of As(III) was determined from the slope which is found to be 59.17mg/g.

**Table: 1 Langmuir and Freundlich adsorption isotherm and correlation coefficient with experimental  $q_{max}$  for As(III)**

Langmuir isotherm			Experimental $q_{max}$ (mg/g)	Freundlich isotherm		
$q_{max}$ (mg/g)	b(L/mg)	$R^2$		$K_F$ (L/g)	1/n	$R^2$
59.17	0.0174	0.995	54.64	2.922	0.348	0.952

## 5.6 Effect of contact time of adsorption

The effect of contact time on As(III) adsorption was studied using pseudo first-order, pseudo second-order, and second-order kinetics model. The time dependence curve of As(III) removal is shown in figure 5. It was found that uptake of As(III) increases with lapse of time. However, the adsorption rate of As(III) was rapid in the first hour, after which rate slowed down as the equilibrium approached. The results obtained from the experiments were used to study the rate limiting step in the adsorption process. The adsorption of arsenite was found to be constant after 2 hrs. Kinetics study revealed that uptake of As(III) ion by rapid and equilibrium time was independent of initial As(III) concentration and the adsorption process followed a pseudo second-order kinetics equation. The different parameters for the three kinetics plots are shown as following:

**Table: 2 Kinetic parameter for As(III) adsorption with correlation coefficient**

Metal	$q_{\text{exp}}$ mg/g	Pseudo first-order			Pseudo second-order			Second-order		
		$k_1 \times 10^{-3}$ g/mg min	$q_e$ mg/g	$R^2$	$k_2 \times 10^{-3}$ g/mg min	$q_e$ mg/g	$R^2$	$k'_2 \times 10^{-3}$ g/mg min	$q_e$ mg/g	$R^2$
As(III)	15.0	1.82	8.5	0.902	7.5	14.92	0.985	1.03	7.6	0.595

## 6. Chemical modification

It is known that sugarcane bagasse consists of cellulose, lignocellulose lignin and poly phenolic compounds. In presence of conc. sulphuric acid the polymeric moiety contained in sugarcane bagasse may change into following types.

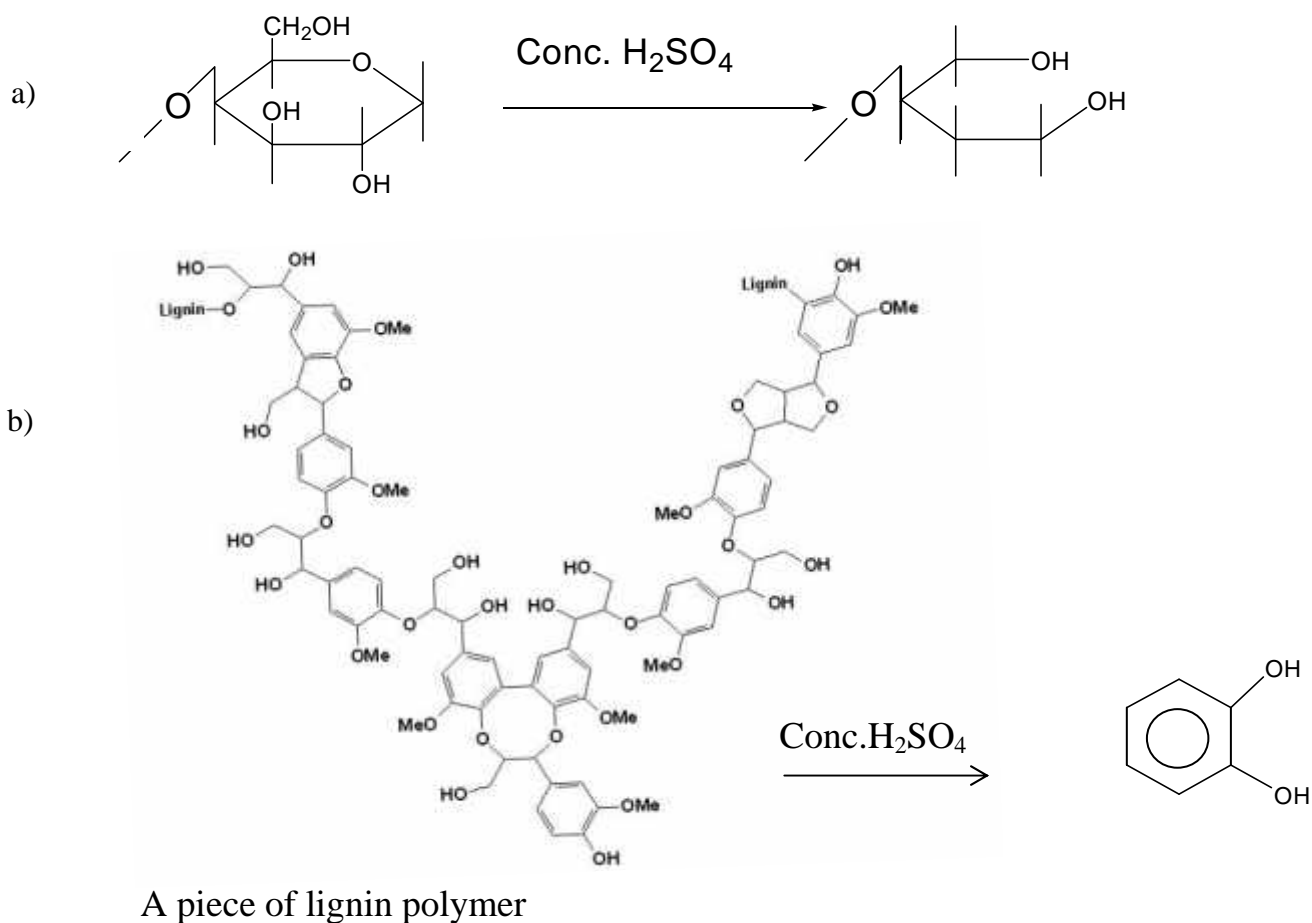
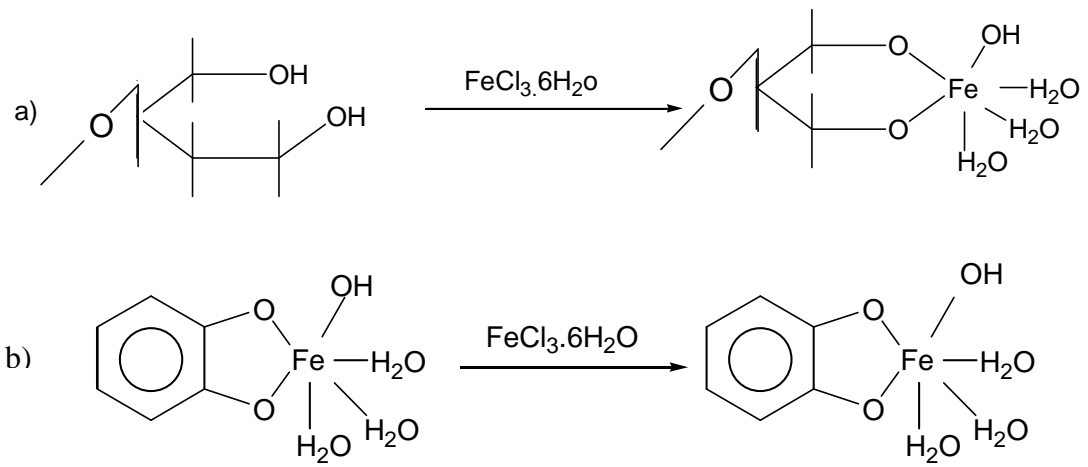
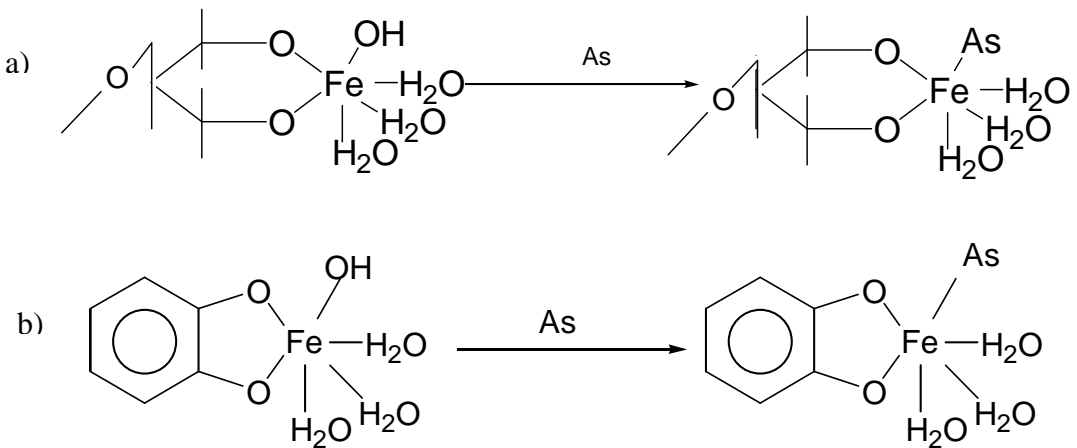


Figure: Polyethoxy and polyphenolic moiety contained in sugarcane bagasse.

## 6.1 Iron-loading mechanism



## 6.2 Arsenic Adsorption via ligand exchange process



## 7. Conclusion

Of the techniques available, adsorption processes offered the potential for arsenic removal from drinking water. Adsorption facilities usually involve low capital costs and minimal space and energy requirements. The process is flexible in its application, simple to operate (no skilled supervision), and produces low residual concentrations. The sugarcane bagasse, the well known friendly adsorbent is utilized to study the adsorption behaviour of arsenic in aqueous medium.

The adsorption of arsenic was found to be strongly dependent on pH of the solution, initial concentration of the metal ion, adsorbent dose, and contact time respectively. The adsorption of arsenic As(III) occurs in the alkaline medium. The optimum pH value for removal of As(III) from aqueous solutions using Fe(III) modified sugarcane bagasse was found 10. A maximum of 56.79% As(III) removal of 5mg/L could be achieved at optimum pH ie 10. Langmuir and Freundlich isotherm were tested to describe the adsorption behaviour of As(III). The analysis of the data revealed from isotherm studies shows that the data best fit the Langmuir equation as compared to Freundlich. The kinetic study for the adsorption of As(III) was studied. The required equilibrium time for the adsorption was attained after 2 hrs. Analysis of the kinetic data shows that the adsorption process follows pseudo second-order kinetics.

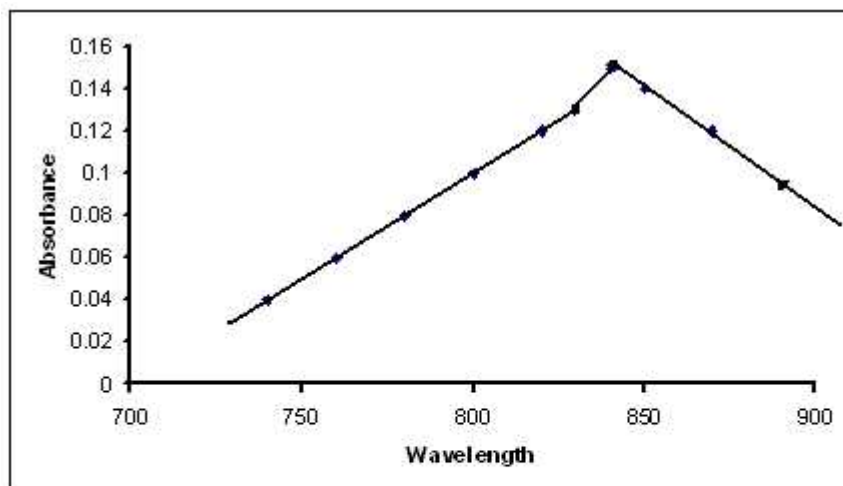
Hence by the use of adsorption technique the toxic and carcinogenic metal As(III) can be removed to some extent to achieve water quality goals in diverse application scenarios.

## **8. Limitations of the study**

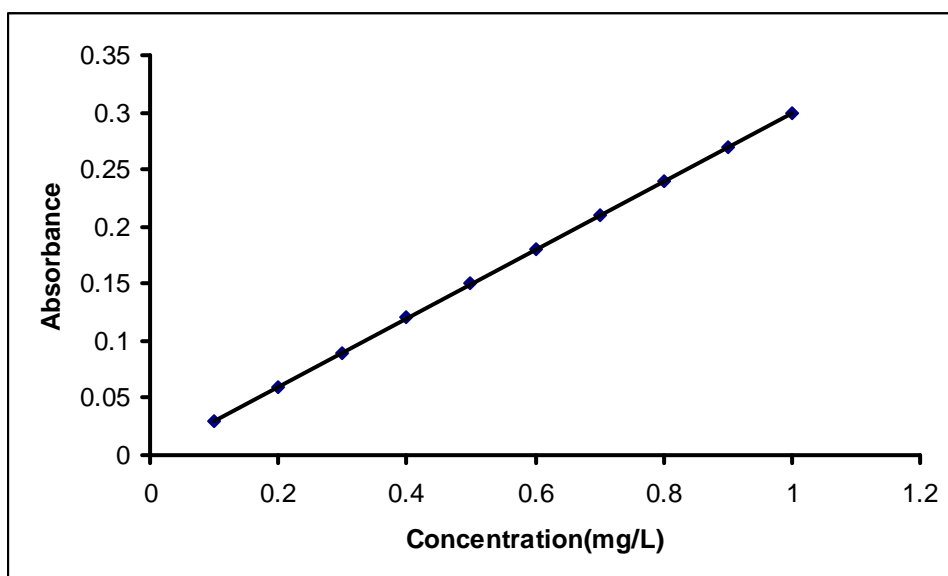
- ❖ Characterization of the adsorbents was done only by determining surface area and Boehm's titration.
- ❖ The metal concentration was measured by spectrophotometer which is less sensitive than AAS.
- ❖ Kinetic study was performed at lab temperature and change in adsorption behavior with the change in lab temperature was not considered.
- ❖ Due to unavailability of certified standard metal ion samples, chemicals available in the laboratory were used directly for their respective concentration evaluation with careful attention as mention in the standard text.

# **APPENDICES**

## FIGURES

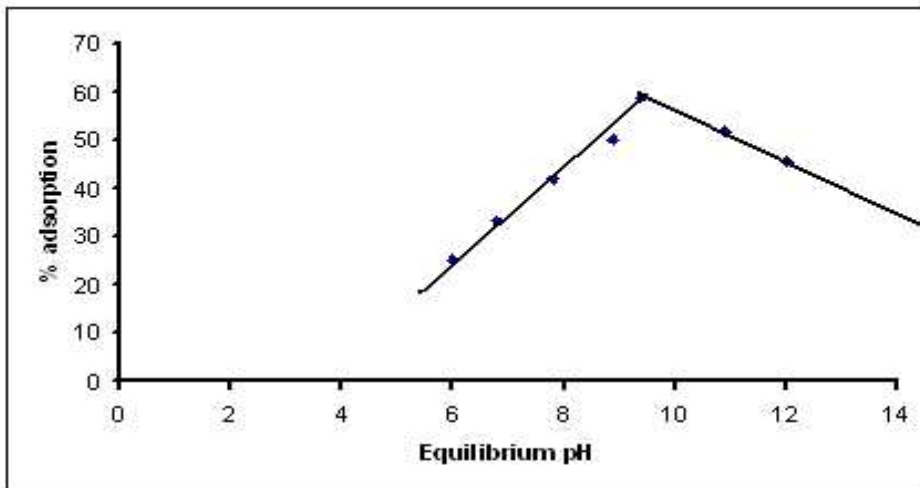


**Fig. 1 Determination of  $\lambda_{\max}$  of As(III) of 0.5mg/L**

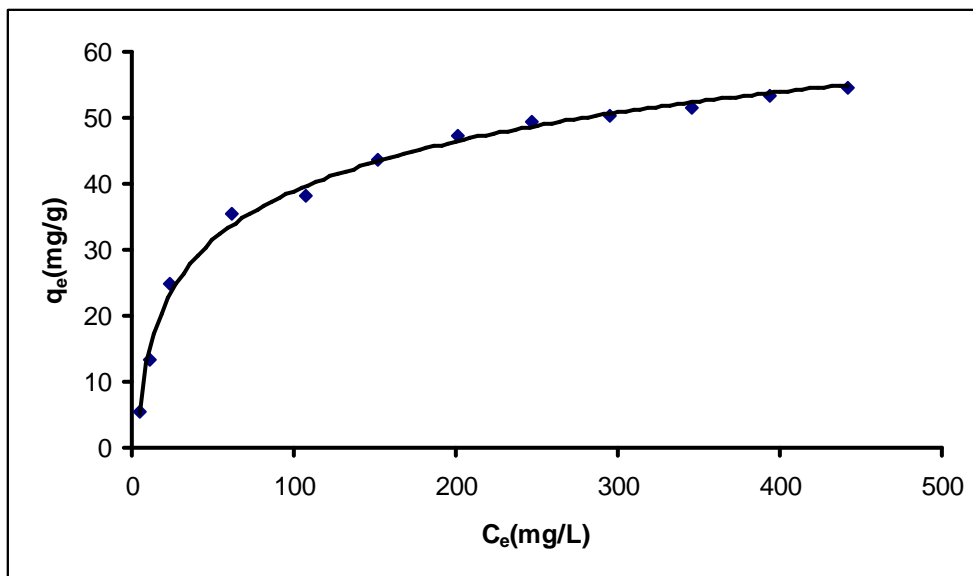


**Fig. 2 Calibration Curve for the determination of As(III)**

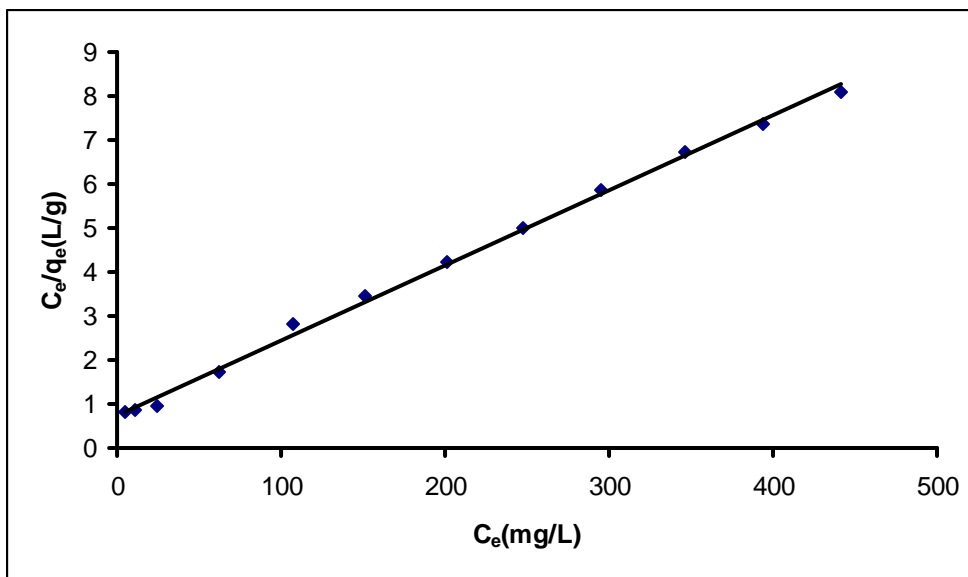




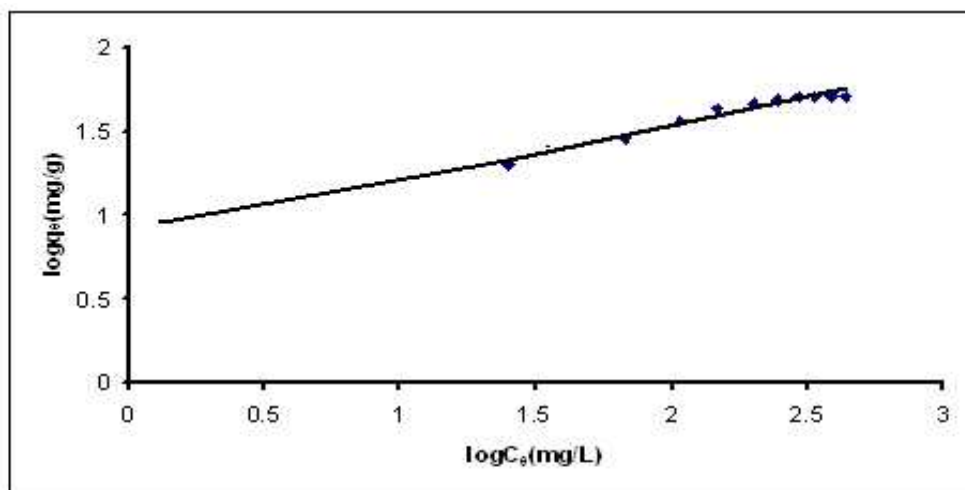
**Fig. 3 Effect of adsorption as a function of Equilibrium pH**



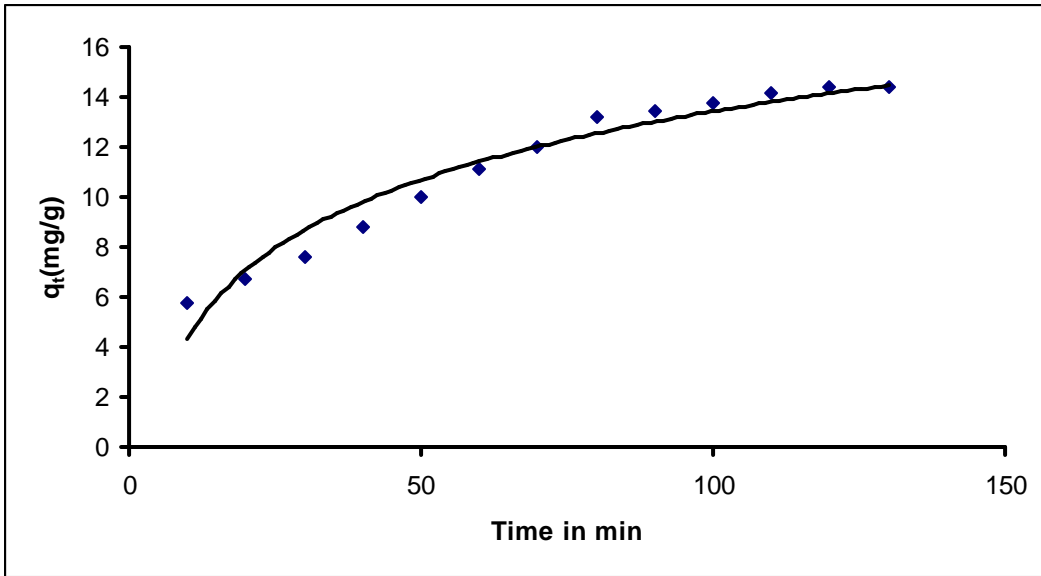
**Fig. 4 Adsorption isotherm for the determination of As(III) on Fe(III)-loaded BS**



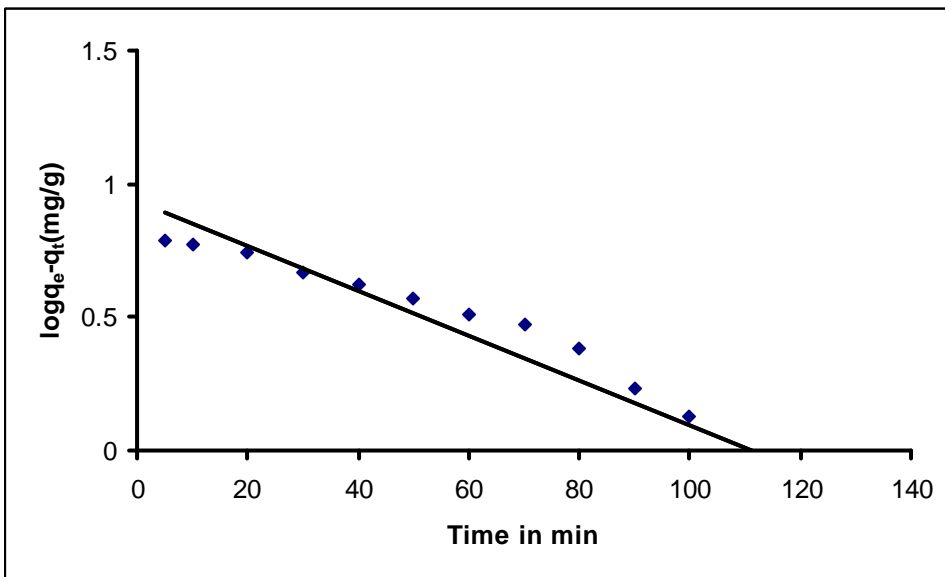
**Fig. 5 Langmuir isotherm for the adsorption of As(III) on Fe(III)-loaded SB**



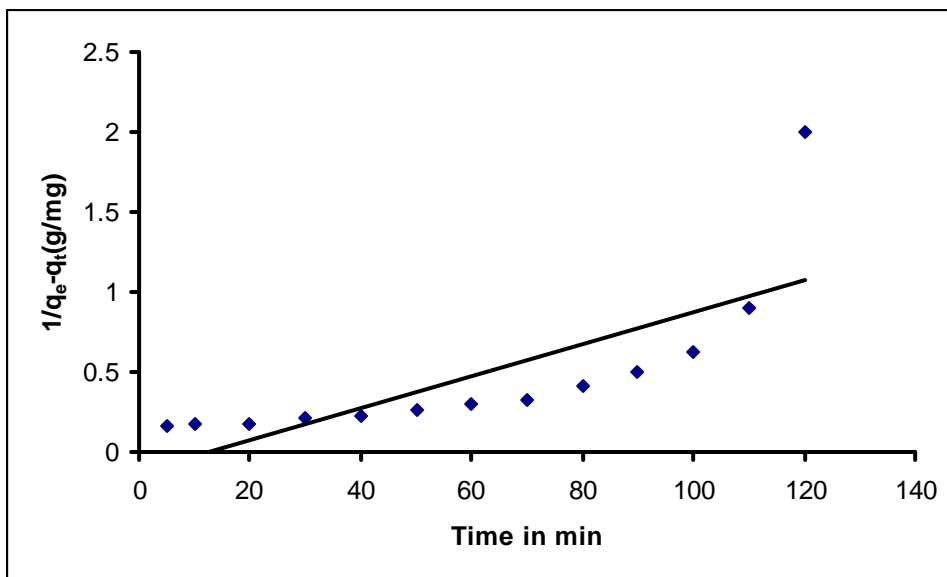
**Fig. 6 Freundlich isotherm for the adsorption of As(III) on Fe(III)-loaded SB**



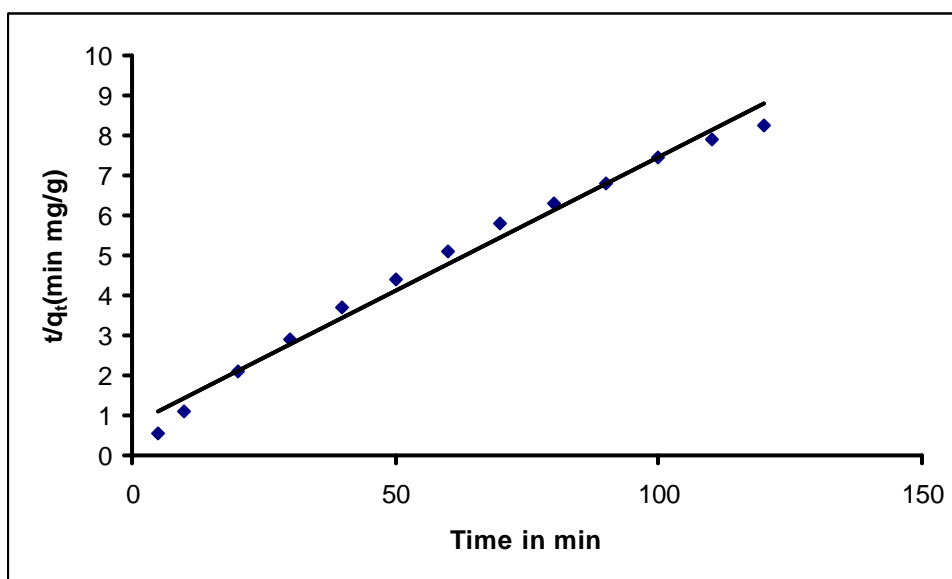
**Fig. 7 Effect of contact time for the adsorption of As(III) on Fe(III)-loaded SB**



**Fig. 8 Pseudo first-order Kinetic plot for the adsorption of As(III) on Fe(III)-loaded SB**



**Fig. 9 Second-order Kinetic plot for the adsorption of As(III) on Fe(III)-loaded SB**



**Fig. 10 Pseudo Second-order Kinetic plot for the adsorption of As(III) on Fe(III)-loaded SB**

## Tables

**Table1: Spectrophotometric determination of  $\lambda_{\text{max}}$  of As(III)**

S.N	Wavelength(nm)	Absorption(O.D)
1	740	0.04
2	760	0.06
3	780	0.08
4	800	0.10
5	820	0.12
6	830	0.13
7	840	0.15
8	850	0.14
9	870	0.12
10	890	0.11

**Table 2: Calibration Curve for the determination of arsenic metal concentration**

Concentration(mg/L)	Absorbance(O.D)
0.1	0.03
0.2	0.06
0.3	0.09
0.4	0.12
0.5	0.15
0.6	0.18
0.7	0.21
0.8	0.24
0.9	0.27
1.0	0.30

**Table 3: Effect of pH for adsorption of As(III) on Fe (III)-loaded SB**

Total volume = 25 ml

Amount of adsorbent = 25mg

S.N	Initial pH	Equilibrium pH	Initial concentration $C_i$ (mg/L)	Equilibrium concentration $C_e$ (mg/L)	% adsorption
1	6	6.0	20.25	15.15	25.18
2	7	6.8	20.25	13.5	33.33
3	8	7.8	20.25	11.75	41.97
4	9	8.9	20.25	10.12	50.02
5	10	9.4	20.25	8.75	56.79
6	11	10.9	20.25	9.75	51.85
7	12	12.0	20.25	11.0	45.67

**Table 4: Adsorption isotherm for adsorption of As(III) onto Fe(III)-loaded SB**

Total volume = 25ml

Amount of adsorbent = 25mg

pH = 10

S.N	Initial Concentration $C_i$ (mg/L)	Equilibrium Concentration $C_e$ (mg/L)	Amount of As(III) adsorbed $q_e$ (mg/g)	$C_e/q_e$ (L/g)	Log $C_e$ (mg/L)	Log $q_e$ (mg/g)	% adsorbed
1	10	4.55	5.45	0.83	0.65	0.74	54.5
2	25	11.8	13.20	0.89	1.07	1.12	52.8
3	48.75	24.0	24.75	0.96	1.38	1.39	49.74
4	97.27	61.80	35.45	1.74	1.79	1.54	36.44
5	146.25	107.87	38.13	2.82	2.03	1.58	26.07
6	195.00	151.25	43.75	3.45	2.17	1.64	22.0
7	248.375	201.125	47.25	4.25	2.30	1.67	19.02
8	296.50	247	49.5	4.98	2.39	1.69	16.69
9	345.75	295.3	50.45	5.85	2.47	1.71	14.59
10	397.68	346.23	51.45	6.72	2.53	1.71	12.93
11	446.79	393.34	53.45	7.35	2.53	1.71	11.73
12	496.00	441.36	54.64	8.07	2.64	1.73	11.01

**Table: 5 Effect of contact time for the adsorption As(III) on Fe(III)-loaded SB**

Total volume = 25ml

Amount of the adsorbent = 25mg

Initial concentration  $C_i = 20.25\text{mg/L}$

pH =10

S.N	Time (min)	Equilibrium Concentration $C_e(\text{mg/L})$	$q_t(\text{mg/g})$	$t/q_t$ (min mg/g)	$q_e - q_t$ (mg/g)	$1/q_e - q_t$ (g/mg)	$\text{Log}(q_e - q_t)$ (mg/g)
1	5	11.45	8.80	0.56	6.20	0.16	0.795
2	10	11.25	9.00	1.11	6.00	0.17	0.77
3	20	10.75	9.50	2.10	5.50	0.18	0.74
4	30	10.25	10.25	2.92	4.75	0.21	0.67
5	40	9.50	10.75	3.72	4.25	0.23	0.62
6	50	9.00	11.25	4.40	3.75	0.26	0.57
7	60	8.50	11.75	5.10	3.25	0.30	0.51
8	70	8.21	12.04	5.81	2.96	0.33	0.47
9	80	7.65	12.60	6.34	2.40	0.41	0.38
10	90	7.23	13.02	6.80	1.98	0.50	0.29
11	100	6.82	13.43	7.44	1.57	0.63	0.19
12	110	6.35	13.90	7.91	1.1	0.91	0.04
13	120	5.74	14.51	8.27	0.49	2.04	-0.30
	Infinite	5.25	15.00	-	-	-	-



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