1 INTRODUCTION

1.1 General Introduction

Arsenic contamination of groundwater is a crucial worldwide water quality problem. Severe arsenic contamination of ground water was first reported in Bengal Delta (Bangladesh and west Bengal, India) in the early 90's [1]. In Nepal it is reported first in 1999 [2]. Arsenic get introduced into ground water through the dissolution of minerals and ores found in earth, industrial waste discharges, agricultural use of arsenical herbicides, and pesticides etc [2,3,4].

Exposure to high level of arsenic causes chronic and acute poisoning. It enters into human body through ingestion and inhalation or skin absorption of arsenic compound. Organic species of arsenic are predominantly found in foodstuffs such as shellfish and include in the form of monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA). Inorganic arsenic which is mainly present in drinking water is more toxic than the organic form and has been classified by international agency for research on cancer (IARC) as group 1 human carcinogen, showing prevalence of skin, lung and bladder cancer [5,6,7,8].

Apart from the elementary arsenic with oxidation state of 0 it is stable in the oxidation states of +5, +3, and -3 under different conditions in aqueous media, but the most prevalent species of dissolved arsenic in water are the anionic species of arsenite [As (III)] and arsenate [As (V)]. However, the predominant form between pH 3 to pH 7 is $H_2AsO_4^-$ between pH 7 and 11 it is $HAsO_4^{2-}$, are the most prevalent in well-oxidized waters, while under reducing environments it occurs as a neutral undissociated species H_3AsO_3, as in natural ground waters where reducing conditions prevails. In natural waters As (V) is the dominant species. The toxicity of arsenic depends on its chemical form. Arsenite [As (III)] is more toxic than arsenate [As (V)] and has been reported to be more mobile in the environment [9, 10].

Both species As (III) and As (V) have significant difference in chemical behavior. They form arsenious acid (H_3AsO_3) and arsenic acid (H_3AsO_4) respectively. They dissociate giving arsenite and arsenate anions respectively. The equilibrium constants for the dissociation of the two oxidation states of arsenic are quite different and are reported below [11, 12]:

Arsenious acid: H_3AsO_3

$$H_3AsO_3 = H^+ + H_2AsO_3^- \qquad pKa_1 = 9.22$$

$H_2AsO_3^{-} = H^{+} + HAsO_3^{2-}$ $\quad pKa_2 = 12.13$

$HAsO_3^{-2} = H^{+} + AsO_3^{3-}$ $\quad pKa_3 = 13.40$

Arsenic acid: H_3AsO_4

$H_3AsO_4 = H^{+} + H_2AsO_4^{-}$ $\quad pKa_1 = 2.20$

$H_2AsO_4^{-} = H^{+} + HAsO_4^{2-}$ $\quad pKa_2 = 6.97$

$HAsO_4^{-2} = H^{+} + AsO_4^{3-}$ $\quad pKa_3 = 11.53$

The WHO provisional guideline value for arsenic in drinking water is 10µg/l [2]. The provisional guideline value of arsenic in drinking water in Nepal is 50µg/l [13].

Various methods exist for the removal of heavy metal ions from wastewater which include chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption [14, 15]. Amongst all the treatment processes mentioned, adsorption using sorbents is one of the most popular and effective processes for the removal of heavy metals from wastewater. The adsorption process offers flexibility in design and operation and in many cases produces treated effluent suitable for re-use, free of colour and odour. In addition, because adsorption is sometimes reversible, the regeneration of the adsorbent with resultant economy of operation may be possibl**e** [16].

Activated carbon adsorbents are used widely in the removal of organic contaminants, to lesser extent heavy metal contaminants in product purification and pollution control. Carbon is converted to activated carbon by heating in the absence of air. The activation process results in the creation of a network of fine pores in the carbon particles. The vast areas (300–4000 m^2g^{-1}) of the walls within these pores account for the most of the total surface area of the carbon [17]. In spite of its prolific use, activated carbon remains an expensive material and the higher the quality of activated carbon, the higher its cost. Also, in practice activated carbon is employed more frequently for adsorption of organic compounds rather than heavy metal ions.

Characterisation of the adsorption process is often carried out using a number of isotherm models. These include the most common Langmuir (1918) and Freundlich (1926) isotherms and other related models [18, 19, and 20].

More recently lognocellulosic waste materials from forestry and agriculture find attention to separation science as cost effective bioadsorbents for the removal of toxic heavy metals from aqueous media. Cellulose the most abundant and renewable polymer resource available worldwide a polymer comprises of repeating β-D-glucopyranose units which are covalently linked through acetal functions between the OH group of the C4 and C1 carbon atoms (β-1, 4-glucan). Cellulose is a large, linear-chain polymer with a large number of hydroxyl groups (three per anhydroglucose (AGU) unit) and present in the preferred 4 C1 conformation. To accommodate the preferred bond angles, every second AGU unit is rotated 180° in the plane. The length of the polymeric cellulose chain depends on the number of constituent AGU units (degree of polymerisation, DP) and varies with the origin and treatment of the cellulose raw material. Cellulose has a ribbon shape which allows it to twist and bend in the direction out of the plane, so that the molecule is moderately flexible. There is a relatively strong interaction between neighbouring cellulose molecules in dry fibres due to the presence of the hydroxyl (–OH) groups, which stick out from the chain and form intermolecular hydrogen bonds. Regenerated fibres from cellulose contain 250–500 repeating units per chain [21]. This molecular structure gives cellulose its characteristic properties of hydrophilicity, chirality and degradability. Chemical reactivity is largely a function of the high donor reactivity of the OH groups [22].

Unmodified cellulose has a low heavy metal adsorption capacity as well as variable physical stability. Therefore, chemical modification of cellulose can be carried out to achieve adequate structural durability and efficient adsorption capacity for heavy metal ions [23].Chemical modification can be used to vary certain properties of cellulose such as its hydrophilic or hydrophobic character, elasticity, water sorbency, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance [24].

1.2 Adsorption Study

The phenomenon of accumulation of any substance on the surface of solid or liquid phase as compared to that present in the bulk of the material is called adsorption. The substance adsorbed is called adsorbate, while the surface to which it gets attached is called adsorbent. Adsorption is a surface phenomenon and at a given temperature and pressure depends on the surface area of the adsorbent [20]. The adsorption can be studied in batch adsorption and column adsorption modes.

In column adsorption method, an adsorbent column with fixed weight of adsorbent is made and effluent is allowed to percolate through the column at constant flow rate using flow controller. Effluent samples are collected at each interval of time and examined for residual adsorbate concentration to evaluate the efficiency of the column. The adsorbate concentration before and after adsorption are measured.

In batch study, the aliquot of sample is pipette out in the Erlenmeyer flask and a definite amount of adsorbent is added to the sample. The pH of sample solution is adjusted by suitable acid solution and base solution by hit and trial method as per requirement. The Erlenmeyer flask is shaken for prescribed length of time and the adsorbate concentration is determined by some appropriate technique. The adsorption of adsorbate onto the different adsorbents is affected by parameters such as contact time, pH, initial concentration and amount of adsorbent used. In order to understand the mechanism and effectiveness of adsorption one of the above parameter is changed by keeping other constant.

From the adsorbate concentration determined before and after adsorption (C_i and C_f) respectively and dry weight of adsorbent (w), the volume of sample (v), the amount of adsorbate adsorbed in mg/g at equilibrium is computed by the following formula.

$$\boxed{q = \frac{(C_i - C_e)\,v}{w}\ \text{mg/g} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{i})}$$

Where C_i and C_e are the initial and equilibrium or final concentrations of the adsorbate in mg/l respectively, v is volume of adsorbate solution taken in litre and w is weight of adsorbent in gram.

The adsorbate removal percentage is defined as the ratio of decrease in adsorbate ion concentration before and after adsorption to the initial concentration of metal in aqueous solution. Percentage removal or removal efficiency is given by

$$\boxed{\text{Removal \%} = \frac{C_i - C_e}{C_i} \times 100\ \% \ldots\ldots\ldots\ldots\ldots\ldots\ldots (\text{ii})}$$

The distribution ratio for the adsorption process at equilibrium is determined by following equation.

$$D = \frac{q}{C_e} \quad \text{......................................(iii)}$$

Where, D is the distribution factor for the adsorption in (l/g).

1.3 Technologies For The Removal Of Arsenic

The presence of arsenic in drinking water is one of the greatest threats to public health. In countries like Nepal, India, and Bangladesh any treatment method will be acceptable only when it is low cost, easy to operate, effective and socially acceptable. Many technologies have been established for the removal of arsenic from water. Most of the technological experiences have been with municipal treatment plant but some of them are applicable at community or household level. All of the established technologies for the removal of arsenic are based on the following chemical principles:

- Oxidation / reduction: - alter their chemical form thereby optimising other processes.
- Coagulation / co-precipitation: - forms the removable low- solubility solid mineral.
- Adsorption: - attracts the arsenic to surface sorption sites.
- Ion exchange: - reversibly displaces the adsorbed ion from surface by dissolved ion.
- Membrane processes: - act as molecular filters for the removal of dissolved arsenic.
- Biological removal processes: - catalyses the removal processes.

Majority of the established technologies for the removl of arsenic make use of these processes at once or in sequence [25].

Conventional treatment technologies for the removal of toxic heavy metals are not economic and further generate huge quantity of toxic chemical sludge. Biosorption is an emerging potential alternative to the existing conventional technology for the removal and recovery of metal ions from aqueous solutions. The major advantage of bio-sorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of bio-sorbents and possibility of metal recovery [26].

1.4 Adsorption Isotherms

A graphical representation of the amount of adsorbate adsorbed per unit mass of the adsorbent as a function of the amount of the adsorbate left in bulk solution at equilibrium at constant temperature is adsorption isotherm [27]. The experimental adsorption isotherms have wide applicability for describing adsorption capacity to monitor the feasibility of these processes for a given condition and application of adsorbent. The adsorption data obtained from the sorption behavior of adsorbate can be analyzed with the help of well- known models given by Langmuir and Freundlich.

In 1916, Langmuir established the first quantitative model of adsorption. This model has been successfully applied for the adsorption of solute from a liquid solution, which involves active adsorbent sites, homogenous surface for adsorption with the formation of monolayer coverage and adsorption is independent of the occupation of neighboring sites [20, 28]. The Langmuir adsorption isotherm is given by the following equation.

$$\frac{C}{X} = a + bC \text{ ....(iv)}$$

Where, C is the concentration of adsorbate, X is the amount of adsorbate adsorbed per gram of adsorbent, ‘a’ and ‘b’ are Langmuir constants. In order to establish the maximum adsorption capacity, the linear form of Langmuir adsorption isotherm is provided by the following equation.

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \text{ ....(v)}$$

On simplification, equation (v) gives the following equation.

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

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g), C_e is the equilibrium concentration of the adsorbate in mg/l, q_m is the maximum adsorption capacity (mg/g) and ‘b’ is the Langmuir adsorption equilibrium constant 1/mg.

A plot of C_e/q_e against C_e gives a straight line with slope $1/q_m$ and an intercept $1/q_mb$ from which ‘q_m’ and ‘b’ can be determined.

According to the Hall et al., (1966), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (K_L), which is given by the relationship.

$$K_L = \frac{1}{1 + bC_i} \quad \dots\dots (vii)$$

Where, C_i is the initial concentration of the adsorbate (mg/l) and K_L indicates the shape of isotherm and nature of the adsorption process, [$K_L > 1$, unfavorable, $K_L = 1$, linear, $0 < K_L < 1$ favourable, $K_L = 0$, irreversible]. The value of K_L between 0 and 1 indicates that adsorption is favorable.

The adsorption data obtained can also be analyzed with Freundlich adsorption model. In 1906, Freundlich established relationship that describes the adsorption phenomenon. The linear form of Freundlich isotherm is given by the equation.

$$q_e = KC_e^{1/n} \quad \dots\dots (viii)$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l); ‘K’ and ‘n’ are Freundlich equilibrium coefficient, which are considered to be the relative indicators of adsorption capacity and adsorption intensity. The logarithmic form of the Freundlich equation is given by

$$\log q_e = \log K + \frac{1}{n} \log C_e \ldots\ldots\ldots\ldots\ldots\ldots(\text{ix})$$

When log q_e is plotted against log C_e, a straight line is obtained with slope 1/n and intercept log K. From this plot, the value of 1/n and K can be determined. The value of 1/n between 0.1 and 1.0 indicates the favourable adsorption of adsorbate; heavy metal ions [27].

1.5 Adsorption Kinetics

The study of adsorption kinetics describes the adsorbate uptake rate and mechanism of the adsorption phenomenon and evidently this rate controls the residence time of adsorbate uptake at the solid- solution interface. Various sorption kinetic models are in practice to describe the uptake of metals by different adsorbents. The first order kinetic model is used for the reversible reaction with an equilibrium established between liquid and solid phase. The pseudo first order rate equation (Lagergren, 1898), the pseudo second order rate equation (Ho and McKay, 1999) and second order rate equation (Ho et al, 1996) has been used extensively for the description of adsorption kinetics.

This relationship between experimental data and the model predicted value is expressed by correlation coefficient. This helps in determining which reaction model better describes the adsorption of heavy metals onto the adsorbent. A relatively high value of correlation coefficient (R^2~1) indicates that the models successfully describes the kinetics of adsorption [29].

- Pseudo-first order kinetic model:

The pseudo first order kinetic model is employed for the reversible reaction with an equilibrium established between liquid and solid phase. The pseudo first order rate equation (Lagergren, 1898) is generally expressed as

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \ldots\ldots\ldots\ldots\ldots\ldots(\text{x})$$

where, q_e and q_t are the amount of lead (II) adsorbed per gram at equilibrium and at time ‘t’ in mg/g. K_1 is the rate constant of pseudo-first order adsorption (min^{-1}).

After integration and applying boundary conditions, the linear form of the equation (x), When t = 0 to t = t and $q_t = 0$ and $q_t = q_t$

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \text{ ....}(\text{xi})$$

The plot of log (q_e-q_t) versus‘t’ should give a linear relationship, from which k_1 and q_e can be determined from the slope and intercept of the plot respectively.

- Pseudo- second order kinetic model:

The pseudo-second order kinetic rate equation (Ho and McKay, 1999) is used to study the kinetics of adsorption of heavy metal which is generally expressed as,

$$\frac{dq_t}{dt} = K_2\,(q_e - q_t)^2 \text{ ....}(\text{xii})$$

Where, K_2 is the rate constant for pseudo-second order adsorption in (g mg^{-1} min^{-1}), q_e and q_t are the amount of metals adsorbed (mg/g) at any time‘t’ and at equilibrium time(e) respectively.

Integration of equation (xii) and applying boundary condition, $q_t = 0$ at $t = 0$, $q_t = q_t$ at $t = t$, gives following rearranged linear form as,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\,t \text{ ....}(\text{xiii})$$

If the initial adsorption rate is V_0 (mg/g min),

Then $V_0 = K_2 q_e^2$

The equation (xiii) can be written as

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_e}\,t \text{ ....}(\text{xiv})$$

Experimentally, the value of q_e and K_2 can be determined from the linear plot of t/q_t versus't' with the help of slope and intercept of the plot respectively.

- Second order kinetic model:

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_c} + K_2 t \text{..} (\text{xv})$$

where, q_e is the amount of metal ions adsorbed at equilibrium (mg/g), q_t is the amount of metal ions adsorbed at 't' (mg/g), t is contact time (min) and K'_2 is second order rate constant (g mg^{-1} min^{-1}). The plot of $1/(q_e-q_t)$ versus't' gives a linear plot, from which K'_2 and q_e can be determined from the slope and intercept respectively [30].

1.6 Methods For The Determination Of Arsenic

Several methods have been developed and reported in the literature, for the analysis of total arsenic in water. Among these some are expensive and time consuming while others are inexpensive, rapid and more effective. Many of these essentially use the same principles, but apply different reagents or concentration.

Following are the methods for the routine monitoring of arsenic in water samples: -

- Silver diethyldithiocarbamate spectrophotometric method (SDDC).
- Hydride generation atomic absorption spectrometry (HGAAS).
- Graphite furnace atomic absorption spectrometry (GFAAS).
- Inductively coupled plasma atomic emission spectrometry (ICP-AES).
- Inductively coupled plasma mass spectrometry (ICP- MS).
- Atomic fluorescence spectrometry (AFS).
- Polarographic techniques.
- Stripping voltammetry.
- Kit method.
- Molybdenum blue method.

Though ICP-MS and ICP-AES are the best methods, these are extremely expensive so it is not affordable for developing countries. AAS is also the sensitive and rapid technique among others; but the last method, i. e. molybdenum blue method mentioned above being simple in instrumentation, rapid and cost effective is still the choice in many laboratories [25, 31, and 32].

1.7 Literature Survey

An extensive study on the research related to the removal of arsenic from aqueous media shows that several techniques such as coagulation-flocculation, chemical precipitation, reverse osmosis, electrodialysis, ultrafiltration, adsorption ion-exchange, etc. can be used. Some of these methods are not wide in practice because of incomplete removal, high reagent doses, high energy requirements, and generation of toxic sludge which are difficult to manage [25, 33]. Amongs the technologies, adsorption, which makes use of adsorbents either in their natural or modified form, is considered one of the most promising being economical and easy in setup. The efficiency of the adsorbents depends upon the capacity, affinity and specificity including its physio-chemical nature. The adsorbents are employed either in their natural form or modified by some chemical(s) and thermal treatment for increasing their sorption capabilities.

Recently, biosorption, which makes use of biosorbents such as rice husk, orange waste, wooden ash, saw dust, etc., has emerged as a new and promising area of research for the removal of toxic metals from aqueous media, being cost effective, efficient for dilute solutions, minimal generation of chemical or biological sludge, high possibility of biosorbent regeneration and metal recovery [34, 35].

Robins et al., (1991) showed that arsenic (V) could be effectively removed from stream and wastewater by precipitation with excess of iron (III), which is attributed to the formation of basic ferric arsenates [25].

Jekel et al., (1994) had reported that arsenic can be removed from water by filtration through solid ferric hydroxide [25].

McNeill et al., (1996) studied the removal of arsenic during metal hydroxide precipitation. They found that arsenic could be removed with Fe coagulation at pH 6.5-8 [25].

Driehaus et al., (1998) used granular ferric hydroxide for As removal from natural water, and have shown high adsorption capacity [25].

Manju et al., (1998) studied the adsorption of As (III) onto copper impregnated activated carbon prepared by carbonising coconut husk with concentrated sulphuric acid (1:1.8, w/w) and demonstrated that maximum adsorption occurred at pH 12 [36].

Nasir et al., (1998) studied the adsorptive removal of arsenic from water by using rice husk as bioadsorbent and demonstrated that maximum adsorption occurred at 0.01 M of HNO_3, HCl, or H_2SO_4 for 5.97x 10^{-3} M. The adsorption was found to follow Freundlich model over the concentration range 8.69x10^{-3} M to 1.73x 10^{-3} M [37].

Karcher et al., (1999) reported that arsenic removal could be optimized by varying ferric chloride coagulant dose in the pH range 5.5-8 [25].

Altundogan et al., [2001] reported that red mud can used as an effective adsorbent for the removal of As (III), and As (V) at pH 9.5 and 3.2 respectively [25].

Ghimire et al., (2003) investigated the adsorptive separation of As (III), i.e. arsenite, and As (V), i.e. arsenate ions with iron (III)-loaded phosphorylated cellulose and orange waste from aqueous media and reported that arsenite removal was favoured at alkaline conditions for both gels whereas arsenate removal occurred at acidic conditions at pH 2-3 & 2-6 for the cellulose gel and orange waste gel respectively. They found that the loading capacity for the iron (III)-loaded phosphorylated orange gel and cellulose were 67.57 mg/g (1.21mol/kg) and 53.61 mg/g (0.96 mol/kg) respectively and demonstrated that iron (III)-loaded phosphorylated orange gel has higher arsenic removal efficiency due to high ligand exchange capacity [38].

Singh et al., (2004) investigated the adsorption of As (III) onto activated alumina and its iron oxide impregnated form and reported that the highly pH dependent adsorption followed both Freundlich and Langmuir models with higher adsorption capacity(12 mg/g) for the iron oxide impregnated form than activated form(7.6 mg/g) [39].

Islam et al., (2007) monitered the arsenic removal efficiency from drinking water by the bio-adsorbents such as jute stick, jute leaf, sugarcane, lily leaf, fish ayes, egg's skull, dheki (pteris) vegetable powder, fern (Dryopteris ramosa) plant powder and water hyacinth root powder in batchwise and columnwise manner and found that jute stick, jute leaf, dheki (pteris) vegetable powder and fern (Dryopteris ramosa) plant powder were suitable adsorbents for arsenic mitigation [40].

Mamisahebei et al., (2007) studied the removal of arsenic (V) from aqueous media by $FeCl_3$ treated waste tea fungal biomass and reported that the rapid sorption followed pseudo-second order & first order kinetic models and adsorption was in tune with Langmuir model. The optimum initial pH for the effective arsenic (V) removal was in the range 6-8 and the maximum monolayer sorption capacity was found to be 3.98x10^{-3} mmol/g [41].

Rahman et al., (2008) investigated the removal of arsenic by heat treated laterite and reported that laterite can be effectively used for the removal of arsenic from ground water [42].

Igwe et al., (2008) studied the adsorption kinetics of As (III) onto unmodified and thiolated coconut fiber and found that the kinetics of sorption followed the pseudo second-order rate equation (R^2 = 0.9999) with a rate constant value of 1.16 x 10^{-4} g/mg/min and the sorption process also followed the particle diffusion proces [43].

Jahan et al., (2008) investigated the arsenic removal efficiency of activated carbon prepared from jute stick using H_3PO_4 as activant in a batch and continuous system. The results showed that continuous system were better than batch system for the removal of both As (III) and As (V) species from water. The highest removal rate for As (III) and As (V) were about 80% and 100% from 0.15 ppm arsenic solution respectively. 100% separation was achieved when the solution was pretreated with $KMnO_4$ even when the higher concentration of 0.4 ppm was used [44].

Urik et al., (2009) studied the effectiveness of unmodified and urea or Fe (III) modified saw dust of spruce (Picea abies) for the removal of As (V) from aqueous solution. The results showed that effective biosorption occured with Fe (III) oxyhydroxide modified form and the adsorption was well described by both Langmuir and Freundlich isotherm models and followed pseudo second order kinetics. The maximum Langmuir adsorption capacity of the Fe (III) oxyhydroxide modified form was found to be 9.259 mg/g [45].

Dang et al., (2009) used 5% iron-modified rice husk carbon as an adsorbent for the removal of arsenic from simulated ground water using a mixture of 70% As (III) and 30% As (V) through batch technique. The influence of pH, contact time, and initial metal concentration were investigated. The experimental isotherm data were analyzed using the Langmuir, Freundlich equations. The highest removal rate was achieved at pH of 8-9, contact time 144 hours and initial concentration 4.62 mg/l. The monolayer adsorption capacity was 2.24 mg/g and the adsorption was found to follow the pseudo-second order kinetics [46].

Ghanizadeh et al., (2010) used iron-impregnated activated carbon as an adsorbent for the removal of arsenic (V) from water using 300 and 600 µg/l arsenate through batch technique. The adsorption of As (V) had a good compliance with Langmuir model (R^2 =

0.995) and the maximum adsorption capacity was 0.024 mg/g. The iron- impregnated activated carbon was effective for the removal of arsenic from water [47].

Kamsonlian et al., (2011) used powdered maize (Zea mays) leaves as a bioadsorbent for the removal of arsenic (III) from aqueous solution in batch technique. The results demonstrated that the sorption of As (III) had a good compliance with Freundlich model with the maximum uptake of As (III) at pH 8, contact time of 4 hours, temperature of 40 ^{0}C and the kinetics was suited to pseudo second-order model with linear correlation coefficient (R^2 = 0.997) [48].

Maheswari et al., (2011) studied the biosorption of As (III) onto the dry biomass of Aspergillus flavus from aqueous solution. The results demonstrated that the sorption of As (III) had a good compliance with Freundlich model with the maximum uptake of As (III) at pH 5, contact time of 240 min, temperature of 35 ^{0}C and the kinetics was better described by pseudo second-order model [49].

Kamsonlian et al., (2012) used palm bark biomass for the removal of As (V) from aqueous solution. The effects of pH, contact time, initial concentration were studied in batch experiments. The maximum uptake of As (V) was obtained at pH 4. Sorption equilibrium was established in 90 minutes. The adsorption of of As (V) increased as the initial concentration of As (V) increased in the medium. The maximum As (V) adsorbed was found to be 2.23 mg/g. The adsorption of As (V) was correlated well (R^2 = 0.990) with Freundlich equation as compared to Langmuir isotherm equation under the concentration range studied [50].

Considering the unsuitability of conventional methods at small-scale [51], bioadsorbents such as Eichhornia crassipes [52], wooden ash [53], Psidium guajava leaf [54], Moringa oleifera Lamarck seed powder [55], Orange waste gels [56], have currently been employed for the removal of arsenic from aqueous media.

After such an extensive literature survey, the research was done on arsenic removal by sawdust and its modified form. So it seems that it is interesting to investigate the efficiency of Dalbergia sissoo & Arundo donax sawdusts' chemically modified form towards the adsorptive removal of arsenic from aqueous solution. Therefore, an effort has been made through this dissertation work to study the sorption capacity of Dalbergia sissoo & Arundo donax sawdust as a biosorbent for removal of As (III) and As (V) from aqueous solution at laboratory condition.

1.8 Objectives Of The Present Study

- General objective:

The general objective of the present research work is to prepare low- cost biosorbent from Dalbergia sissoo & Arundo donax sawdusts'and to investigate their sorption capacities for the sorption of As (III) and As (V) from aqueous system.

- Specific objectives:

The specific objectives of the present research work are as follows:

I. To prepare, modify and to determine efficiency of the biosorbent for the adsorption of As (III) and As (V) from aqueous solution.

II. To investigate the effect of contact time, pH, initial concentration of adsorbate and adsorbent dose for the adsorptive removal of As (III) and As (V) from aqueous solution.

III. To study the nature of adsorption isotherm for the removal of As (III) and As (V) from aqueous solution.

IV. To study the kinetics of the sorption process.

V. To compare the sorption capacities of the modified Dalbergia sissoo & Arundo donax sawdusts'as biosorbent.

2 EXPERIMENTAL

All the experiments were performed in batch mode in duplicate using modified form of Dalbergia sissoo & Arundo donax sawdusts'as adsorbent for the adsorption of arsenic [As (III) and As (V)] from aqueous solution.

2.1 Instruments

- Weighing balance, Model GT210V, OHAUS, USA.
- Hot air oven, India.
- Laboratory mill (Grinder).
- Digital pH meter, India.
- Sieve no 212 mesh, India.
- WPAS104 Spectrophotometer, UK.
- Shaker, India.
- Magnetic stirrer hotplate, UK.

2.2 Chemical Reagents

- Arsenic trioxide; As_2O_3, M.W. =197.84, (purity 95%, L.R. grade, s.d. Fine- Chem., dried at 110°C for an hour).
- Sodium arsenate; $Na_2HAsO_4.7H_2O$, M.W. = 312.02, (purity 99%, s.d. fine chemical limited, Mumbai).
- Ammonium hepta molybdate; $(NH_4)_6Mo_7O_{24}.4H_2O$, (98%, L.R., Qualigens Fine Chemicals).
- Potassium permanganate; $KMnO_4$ (99%, L.R., Qualigens Fine Chemicals).
- Hydrazine hydrate solution; $NH_2NH_2.H_2O$ (99%, L.R., Qualigens Fine Chemicals).
- Sulphuric acid; H_2SO_4 (Qualigens Fine Chemicals).
- Hydrochloric acid; HCl (Qualigens Fine Chemicals).
- Sodium hydroxide; NaOH (Qualigens Fine Chemicals).
- Nitric Acid; HNO_3 (Qualigens Fine Chemicals).
- Orthophosphoric acid; H_3PO_4 (Qualigens Fine Chemicals).
- Dimethyl formamide, dmf; (Qualigens Fine Chemicals).
- Urea; NH_2CONH_2, (Qualigens Fine Chemicals).
- Paraffin oil heavy; (Qualigens Fine Chemicals).
- Propanol; (Qualigens Fine Chemicals).
- Ferric chloride anhydrous; $FeCl_3$ (96%, Qualigens Fine Chemicals).

- Ferric chroride hexahydrate; $FeCl_3.6H_2O$ (98%, HiMedia Laboratories Pvt. Ltd.).
- Buffer tablets of pH 4, 7, and 9.2, (Qualigens Fine Chemicals).

All the chemical reagents used for this dissertation work were of LR/AR grade and were used without any further purification.

2.3 Preparation Of Reagents

- Preparation of 1000 mg/l Stock As (III) Solution:

0.660 gm of arsenic trioxide (As_2O_3, dried at 110°C for an hour) was weighed out accurately and dissolved in 5ml of 10 M sodium hydroxide solution (Merck). After shaking well, final volume was made to 500ml in volumetric flask with distilled water.

1 ml of arsenic trioxide solution = 1000 μg of As (III).

- Working **As (III)** Solution:

Standard arsenic (III) solutions were prepared by appropriate dilution of stock arsenic (III) solution by adding 1 ml of concentrated nitric acid (Qualigens) in volumetric flasks with distilled water.

- Preparation of 1000 mg/l Stock As (V) Solution:

1.035 gm of sodium arsenate ($Na_2HAsO_4.7H_2O$) was weighed out accurately and dissolved in few ml of distilled water. After shaking well, final volume was made to 250 ml in volumetric flask with distilled water.

1 ml of sodium arsenate solution = 1000 μg of As (V).

- Working **As (V)** Solution:

Standard arsenic (V) solutions were prepared by appropriate dilution of stock sodium arsenate solution with distilled water in volumetric flasks.

- Preparation of Ammonium Molybdate Reagents:

i) Ammonium Molybdate Reagent (I) [2.5% w/v]

12.5g of ammonium hepta molybdate was dissolved in 87.5ml of distilled water in 500ml volumetric flask. Then 140ml of concentrared sulphuric acid was cautiously added to 200ml distilled water placed in 500ml beaker and the solution was allowed to cool. This cooled content was added to ammonium hepta molybdate solution and diluted upto the mark present in the neck of the volumetric flask to obtain 500ml of ammonium molybdate reagent (I).

ii) Ammonium Molybdate Reagent (II) [5% w/v]

20.05g of ammonium hepta molybdate was dissolved in 250ml of distilled water in 500ml volumetric flask, then 198ml of ammonium molybdate reagent (I) was slowly added to the 500ml volumetric flask and the solution was allowed to cool. This cooled content was diluted with distilled water upto the mark present in the neck of the volumetric flask to obtain 500ml of ammonium molybdate reagent (II) which was approximately 5% (w/v).

iii) Working Ammonium Molybdate Reagent [0.5% w/v]

Exactly 10ml of ammonium molybdate reagent (II) was diluted in 100ml volumetric flask by using distilled water as solvent which was approximately 0.5% (w/v).

- Preparation of 0.1 N Potassium permanganate; $KMnO_4$ solution:

0.1 N potassium permanganate solution was prepared by dissolving 0.790g of $KMnO_4$ with distilled water in 250 ml volumetric flask. The solution was stored in dark.

- Preparation of 0.5M Hydrazine hydrate solution; $NH_2NH_2.H_2O$:

2.5ml of concentrated hyhrazine hydrate was diluted in 100ml volumetric flask.

- Preparation of Hydrochloric acid; HCl solutions**:**

The solutions of required strength were prepared by the appropriate dilutions of concentrated hydrochloric acid.

- Preparation of Sodium hydroxide; NaOH solutions:

The solutions of required strength were prepared by dissolving the appropriate amount of sodium hydroxide pellets in definite volume of distilled water.

- Preparation of 1.5N Sulphuric acid; H_2SO_4 solution:

It was prepared by diluting requisite volume of concentrated sulphuric acid with distilled water in 250ml volumetric flask.

- Buffer solutions:

Buffer solutions of pH 4, 7, and 9.2 were prepared dy dissolving the respective buffer tablet in 100ml distilled water using 100ml volumetric flasks.

2.4 Preparation Of Adsorbents From Sawdust's

- **Iron (III) – Loaded Phosphorylated Dalbergia sissoo Sawdust**:

Dalbergia sissoo sawdust was collected from local saw mill Baneshwor, Kathmandu. It was exposed to sunlight for 6 hours to make it dry. The dried sawdust was sieved by 212 micron mesh to obtain definite particle size. It was stored in clean and dry polyethylene bottle. This sawdust powder was considered as raw Dalbergia sissoo sawdust [RDSD].

20.000g of Raw Dalbergia sissoo sawdust [RDSD] was soaked in 250ml concentrated dimethyl formamide [dmf] in a 500ml three necked flask which was equipped with magnetic stirrer and was stirred for 1 hour, and left overnight. Then 30g urea was added in the content of three necked flask followed by the dropwise addition of 30ml 85% orthophosphoric with constant stirring. The whole content was stirred for 1 hour at room temperature, and then it was refluxed for 2 hours at 150^0C with continuous stirring in paraffin oil bath. After cooling to room temperature, the content was washed with 70% propanol till the clear supernatant was obtained, followed by water washing upto litmus neutrality. Then the neutral mass so obtained was activated by soaking with frequent stirring at intervals in 250ml of 0.1N hydrochloric acid for 1 hour in 500ml beaker. After the activation was complete, the supernatant was rejected and the residue left was washed with distilled water several times till neutrality with litmus was achieved. The solid mass so obtained was sun dried for 12 hours followed by drying in covection oven for 12 hours at 60-70^0C. It was termed as phosphorylated Dalbergia sissoo sawdust [PDSD] [38].

4.000g of phosphorylated Dalbergia sissoo sawdust [PDSD] was brought in contact with 400ml of 0.2M aqueous solution of anhydrous Ferric chloride in 500ml beaker, and stirred in a magnetic stirrer for 6 hours, and was kept in contact for 24 hours. Then the upper supernatant was carefully poured and the residue left was washed with distilled water in portion several times till litmus neutrality was achieved. The so obtained solid product was dried in a convection oven for 12 hours at 80^0C. The so obtained dry solid product was termed as iron (III) - loaded phosphorylated Dalbergia sissoo sawdust [FePDSD]. It was stored in clean and dry polyethylene bottle and was considered as potential sorbent for the adsorptive removal of As (III) and As (V) from aqueous system.

- **Iron (III) – Loaded Phosphorylated Arundo donax Sawdust**:

Arundo donax sawdust was prepared and was exposed to sunlight for 24 hours to make it dry. The dried sawdust was sieved by 212 micron mesh to obtain definite particle size. It was stored in clean and dry polyethylene bottle. This sawdust powder was considered as raw Arundo donax sawdust [RASD].

20.000g of Raw Arundo donax sawdust [RASD] was soaked in 250ml concentrated dimethyl formamide [dmf] in a 500ml three necked flask which was equipped with magnetic stirrer and was stirred for 1 hour, and left overnight. Then 30g urea was added in the content of three necked flask followed by the dropwise addition of 30ml 85% orthophosphoric with constant stirring. The whole content was stirred for 1 hour at room temperature, and then it was refluxed for 2 hours at 150^0C with continuous stirring in paraffin oil bath. After cooling to room temperature, the content was washed with 70% propanol till the clear supernatant was obtained, followed by water washing upto litmus neutrality. Then the neutral mass so obtained was activated by soaking with frequent stirring at intervals in 250ml of 0.1N hydrochloric acid for 1 hour in 500ml beaker. After the activation was complete, the supernatant was rejected and the residue left was washed with distilled water several times till neutrality with litmus was achieved. The wet solid mass so obtained was termed as phosphorylated Arundo donax sawdust [PASD] [38].

The whole phosphorylated Arundo donax sawdust [PASD] was brought in contact with 0.2M aqueous solution of Ferric chloride hexahydrate maintained at pH 3 in a 500ml beaker and stirred in a magnetic stirrer for 6 hours, and was kept in contact for 24 hours. Then the upper supernatant was carefully poured and the residue left was washed with distilled water in portion several times till litmus neutrality was achieved. The so obtained solid product was dried in a convection oven for 12 hours at 80^0C. The so obtained dry solid product was termed as iron (III) - loaded phosphorylated Arundo donax sawdust [FePASD]. It was stored in clean and dry polyethylene bottle and was considered as potential sorbent for the adsorptive removal of As (III) and As (V) from aqueous system.

2.5 Adsorption Study

- Batch Adsorption Studies:

Batch adsorption experiments were carried out with synthetic working solutions of As (III) and As (V) of predetermined concentration and adsorbents iron (III) - loaded phosphorylated Dalbergia sissoo sawdust [FePDSD] and iron (III) - loaded phosphorylated Arundo donax sawdust [FePASD]. The working solutions of various required concentration were prepared by diluting 10 mg/l, and 15 mg/l of As (III) and As (V) solutions.

Firstly, pH of the 100ml As (III) and As (V) solutions were adjusted by using HCl and NaOH solutions in 250ml beaker. Then 50 ml of the pH adjusted working solution was kept in 100 ml stoppered reagent bottle with the help of burette and 50 mg or as per requirement of iron (III) - loaded phosphorylated Dalbergia sissoo sawdust [FePDSD] and iron (III) - loaded phosphorylated Arundo donax sawdust [FePASD] was added to the corresponding stoppered reagent bottles. The stoppered reagent bottles were shaken for definite length of time in a mechanical shaker to attain equilibrium. The equilibrated solutions were filtered using ordinary filter paper and the filtrates were analyzed for the residual concentrations of As (III) and As (V). The As (III) and As (V) concentrations before and after adsorptions were determined by the molybdenum blue method by using WPAS104 Spectrophotometer. All experiments were performed in duplicate and average values were reported.

- Batch Equilibrium Contact Time Studies:

50 ml of corresponding optimum pH adjusted As (III) and As (V) solutions of about 1 mg/l concentration were taken in 100 ml stoppered reagent bottles and 50 mg of corresponding adsorbents were added and shaken in a mechanical shaker for different length of time. Then the sample solutions were filtered through filter papers. The analyte concentrations in the filtrates were determined spectrophotometrically.

- Batch pH Studies:

Batch pH studies were performed by shaking 50 ml of pH adjusted 1 mg/l As (III) and As (V) solutions with 50 mg of adsorbent for 5hours followed by 19 hours contact to attain equilibrium over a wide range of initial pH values 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 by using 0.1M, 1M, 3M HCl and 0.1M, 1M, 3M NaOH solutions as per requirements in 100 ml stoppered reagent bottles. The equilibrated solutions were filtered through ordinary filter paper. The filtrates were used for determining final concentrations by the molybdenum blue method by using WPAS104 Spectrophotometer.

- Effect of Initial Concentration of As (III) and As (V):

Adsorption isotherm studies were conducted by varying initial concentrations of As (III) and As (V). 50 ml of corresponding optimum pH adjusted solutions of different concentrations were used and were shaken in a mechanical shaker for 5 hours followed by 19 hours contact with 50 mg of adsorbent doses. The residual concentrations of As (III) and As (V) in the filtrates were determined spectrophotometrically. The experimental data were employed to determine maximum adsorption capacity.

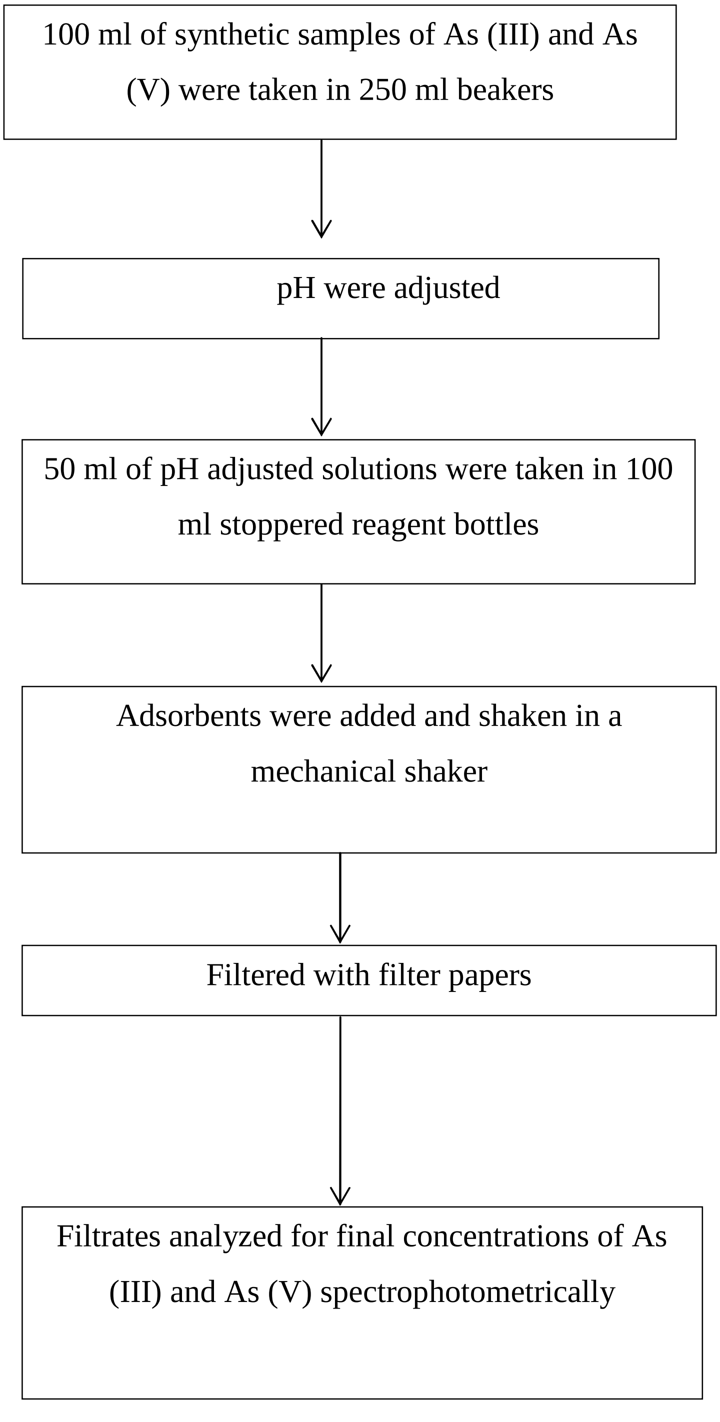
- Effect of Adsorbent Dose:

The effect of adsorbent dose was studied by taking 50 ml of corresponding optimum pH adjusted 1 mg/l As (III) and As (V) solutions in 100 ml stoppered reagent bottles and then the amount of corresponding adsorbents were varied on mg basis (were added to different sample). The contents were then shaken in a mechanical shaker for 5 hours followed by 19 hours contact and the equilibrated solutions were filtered through filter paper. The filtrates were analysed for the residual concentrations of As (III) and As (V) by using WPAS104 Spectrophotometer.

- Batch Kinetic Studies:

The adsorption kinetic experiments were performed at corresponding optimum pH for As (III) and As (V) by equilibrating 50 ml of 1mg/l in 100 ml stoppered reagent bottles with 50 mg of corresponding adsorbents. The bottles were shaken for different length of time in a mechanical shaker at constant speed. The kinetics was investigated by taking out reagent bottles after desired period of contact time and immediately filtered through filter papers to obtain filtrates and concentrations in the filtrates were determined spectrophotometrically. The data obtained was tested with pseudo-first order (Lagergren, 1898), pseudo-second order (Ho, 1999 and Ho & McKay, 2000) and second order kinetic models (Ho et al., 1996).

Adsorption Tests of As (III) and As (V) onto [FePDSD] and [FePASD]



2.6 Preparation Of Calibration Curve For The Spectrophotometric Determination Of Arsenic

Arsenic solutions of concentrations 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ppb were prepared in 25ml volumetric flasks by following the procedure mentioned below.

Firstly, to each flask was added successively 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 ml of 5000ppb arsenic solution. Then to each flask was added 4.5ml 1.5N H_2SO_4, 3 drops (from 1ml pipette) of 0.1N KMnO4, 3ml of 0.5% ammonium molybdate reagent, and 3ml 0.5M hyazine hydrate solution. Then the volume was made upto the the mark with distilled water, and shaked well and kept aside for 20 minutes for maximum color development. Finally, the blue colored solution was poured into a clean and dry spectrophotometric cell and the absorbance at 840 nm (experimentally determined) was measured with respect to the reagent blank using WPA S-104 spectrophotometer. A plot of absorbance versus concentration of arsenic in μg/l (ppb) is shown in figure 2.

3 RESULTS AND DISCUSSION

The sorption of As (III) and As (V) in aqueous solution was examined by optimizing various physicochemical parameters such as contact time, initial pH, initial adsorbate concentration and adsorbent dose.

3.1 Spectrophotometric Determination Of Arsenic By Molybdenum Blue Method

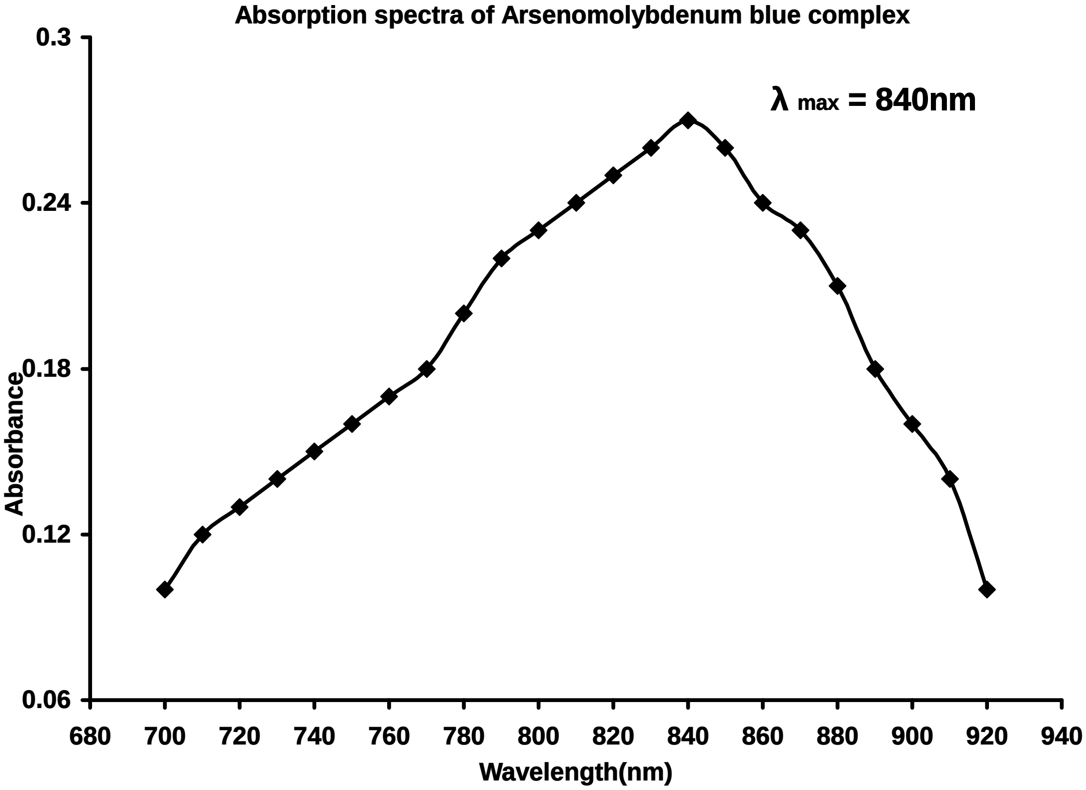


Figure 1: A plot of absorbance versus wavelength for arsenic at 900 ppb.

The absorption spectra of arsenomolybdenum blue complex showed the maximum absorbance at 840 nm as shown in figure 1, which was in tune with literature value [32].

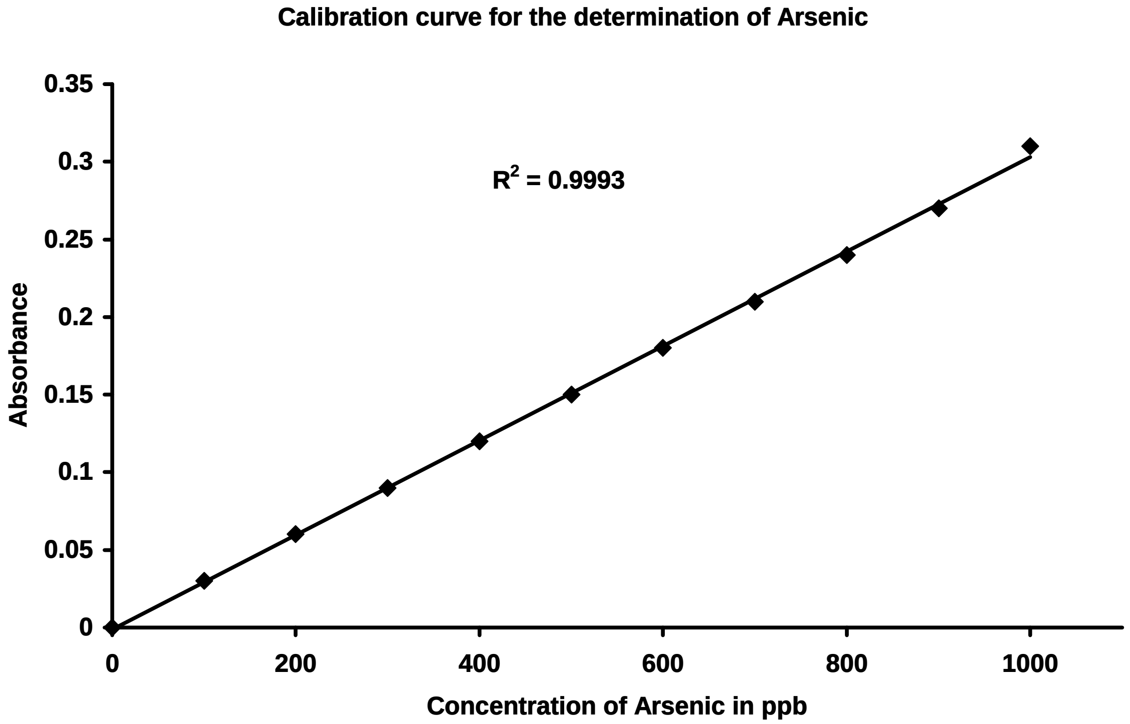


Figure 2: A plot of absorbance versus concentration of arsenic in ppb.

The calibration curve prepared for the determination of arsenic by molybdenum blue method is shown in figure 2 which shows that the plot is linear and obeys Beer's law up to 1000 ppp. The applicable range of the method is 100 to 1000 pppb. The amount of arsenic below and above this range can be determined by method of standard addition and dilution to bring the concentration of arsenic in the directly measurable range [32].

3.2 Effect Of pH

The pH of solution is the most important parameter governing adsorption of ionic species because H^+ ions themselves are strong competing ions and partly pH influences the chemical speciation of the adsorbate and functional groups available on the adsorbent surface.

To evaluate the influence of pH on the sorption process, experiments were carried out at different initial pH. The effect of pH on the sorption efficiencies of As (III) and As (V) on the bioadsorbents prepared are shown in figures $3A^1$, $3A^2$, $3B^1$, and $3B^2$ and table 3 which showed that:

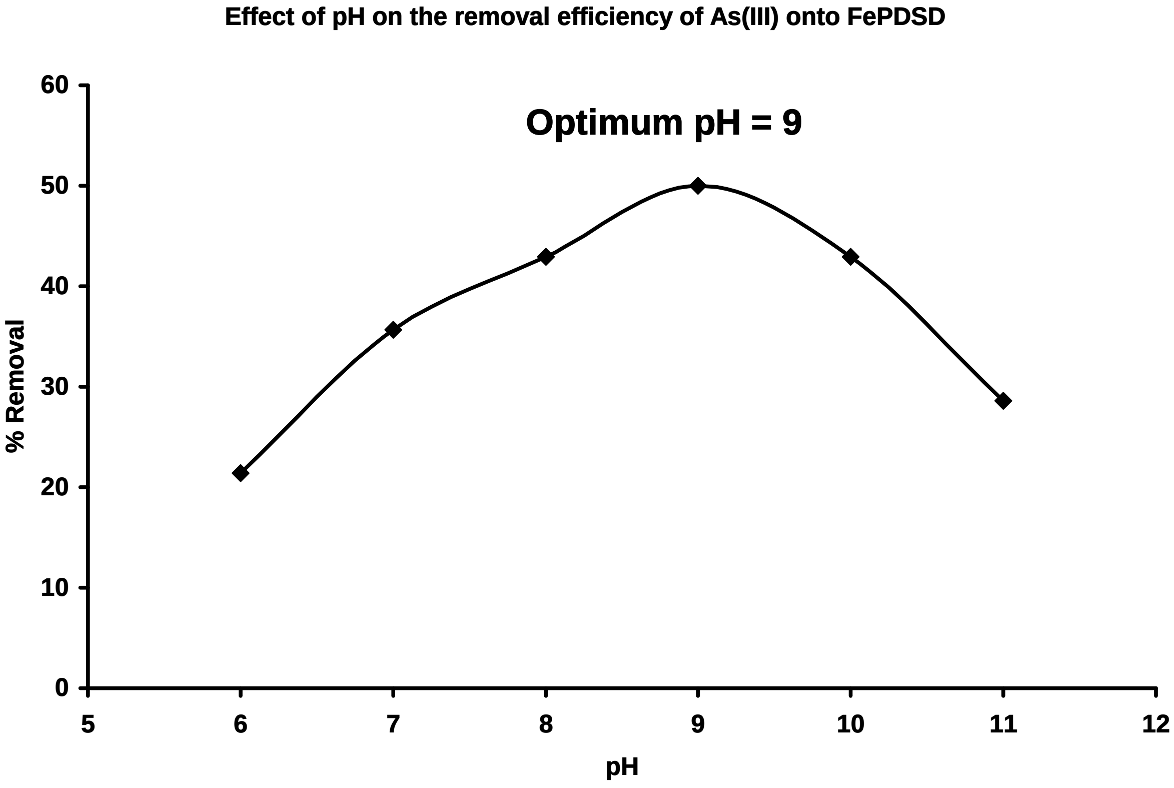


Figure 3A^1: Effect of pH on the adsorption of As (III) onto FePDSD.

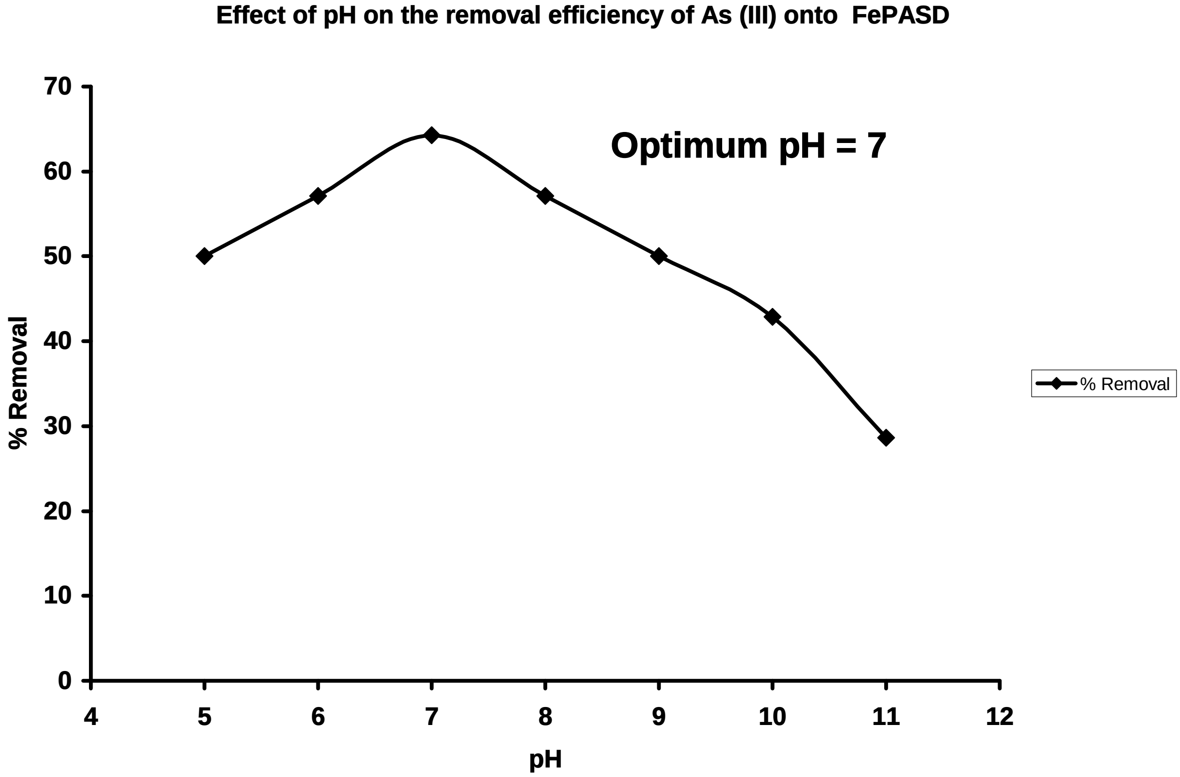


Figure 3A^2: Effect of pH on the adsorption of As (III) onto FePASD.

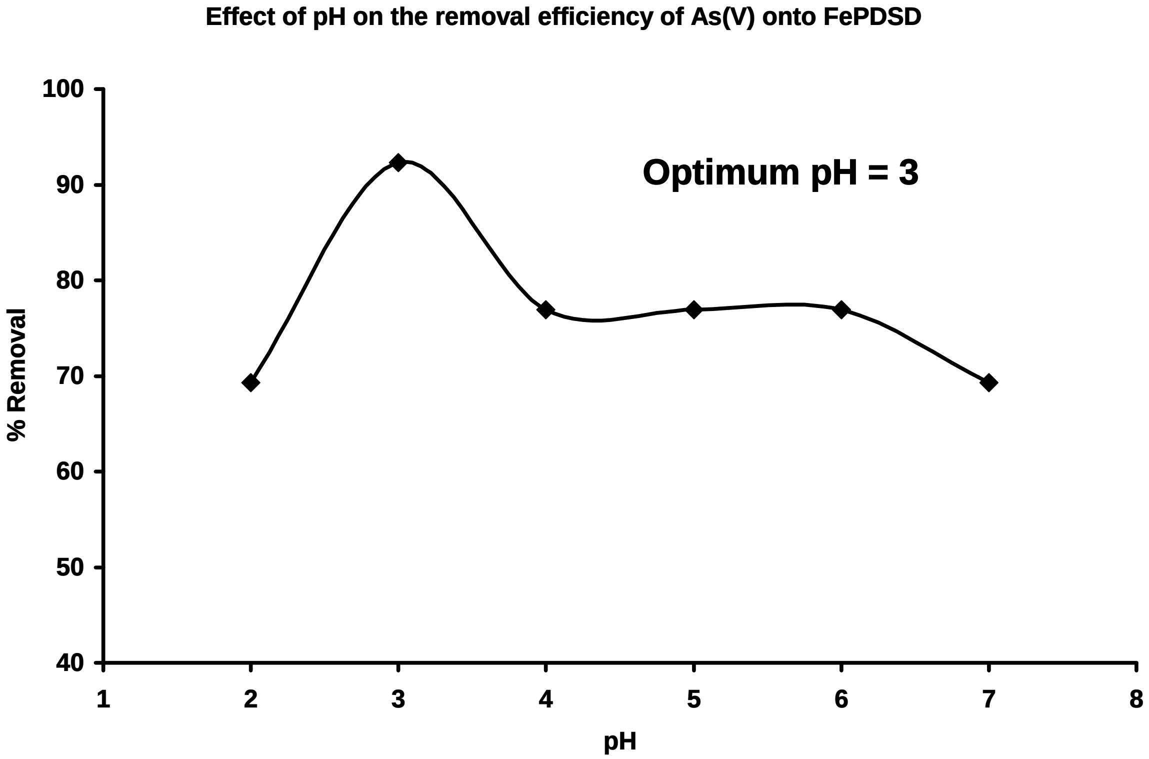


Figure 3B^1: Effect of pH on the adsorption of As (V) onto FePDSD.

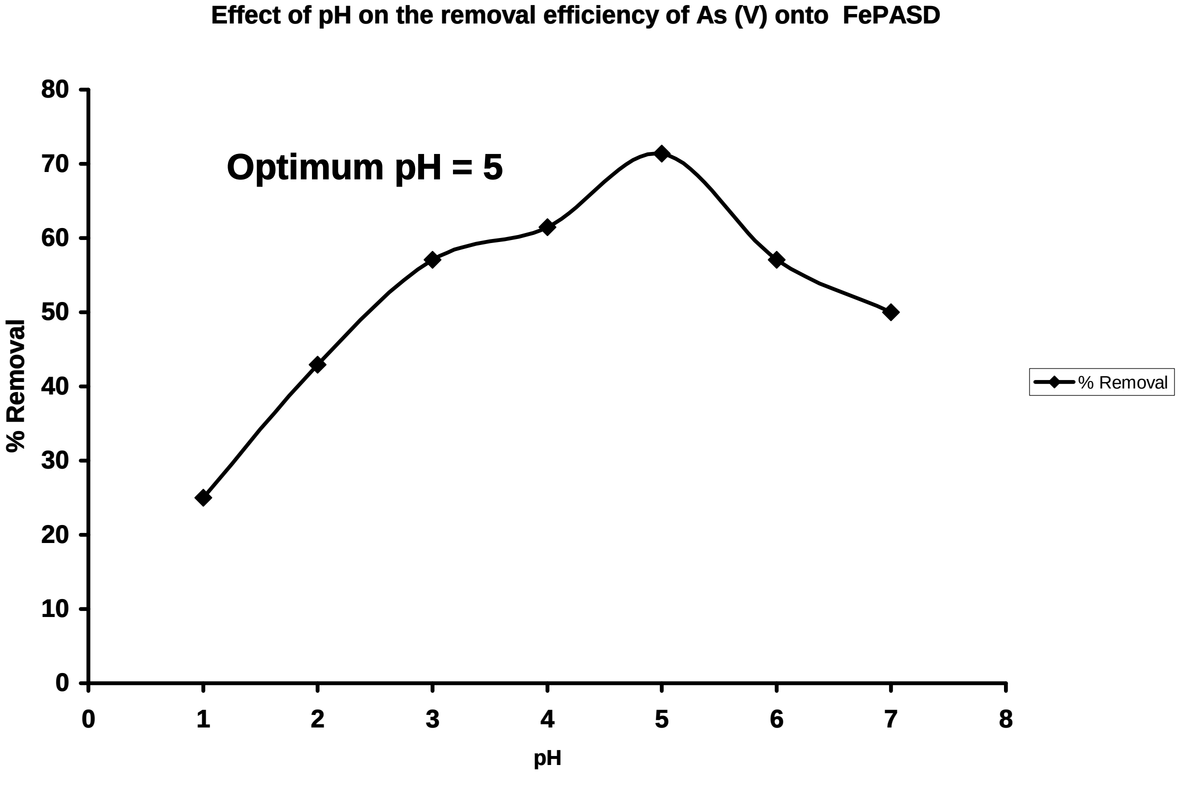


Figure 3B^2: Effect of pH on the adsorption of As (V) onto FePASD.

i) Removal of arsenic (III) increased with the increase in pH and maximum removal value was reached at pH 9 and 7 for FePDSD and FePASD respectively. The low degree of adsorption at low pH can be explained by the fact that at low pH, H^+ ions concentration is high and As(III) exists as neutral H_3AsO_3 in the pH range 0-9 [11,25, 57], therefore protons (H^+ ions) can compete with neutral H_3AsO_3 in forming a bond with the surface active sites. These bonded active sites become saturated with H^+ and was inaccessible to H_3AsO_3. In addition when pH increases, there is decrease in positive surface charge because of the deprotonation of the adsorbent functional groups which results in lower electrostatics repulsion between the H_3AsO_3 and the surface of FePDSD and FePASD favoring adsorption i.e. with increase in pH of the solution, charges on the surface of FePDSD and FePASD becomes negative. Thereby leading to attractive forces between H_3AsO_3 and, FePDSD and FePASD, enhancing adsorption of As (III). Hence maximum adsorption of As (III) from solution. At high pH, i.e., > 9, the negatively charged $H_2AsO_3^-$ [11, 25, and 57] become predominant where as the bioadsorbents surfaces become more negatively charged; thus electrostatic repulsion results in decreased adsorption. Similar results were reported by Nagarnaik et al. (pH = 7) [58] and Kamsonlian et al. (pH = 8) [48] for adsorption of As (III) onto saw dust carbon and powdered maize leaves biomass respectively.

ii) Removal of As (V) occurred at acidic pH and maximum adsorption was achieved at pH of 3 and 5 for FePDSD and FePASD respectively. This can be explained by the fact that in the pH range 3-6, As (V) predominantly exists as the oxyanion $H_2AsO_4^-$ [11,25, 57] where as the the bioadsorbents surface become positively charged; so the adsorption of anionic As (V) may be a result of electrostatic attractions between $H_2AsO_4^-$ and the positively charged bioadsorbent surface. Similar results were reported by Kamsonlian et al. (pH = 4) for adsorption of As (V) onto palm bark biomass [50].

3.3 Effect Of Adsorbent Dose

The effect of variation of adsorbent amount on the adsorption efficiency of As (III) and As (V) by FePDSD and FePASD are shown in figures 4A^{1,} 4A^{2,} 4B^{1,} & 4B^{2} given below and table 4.

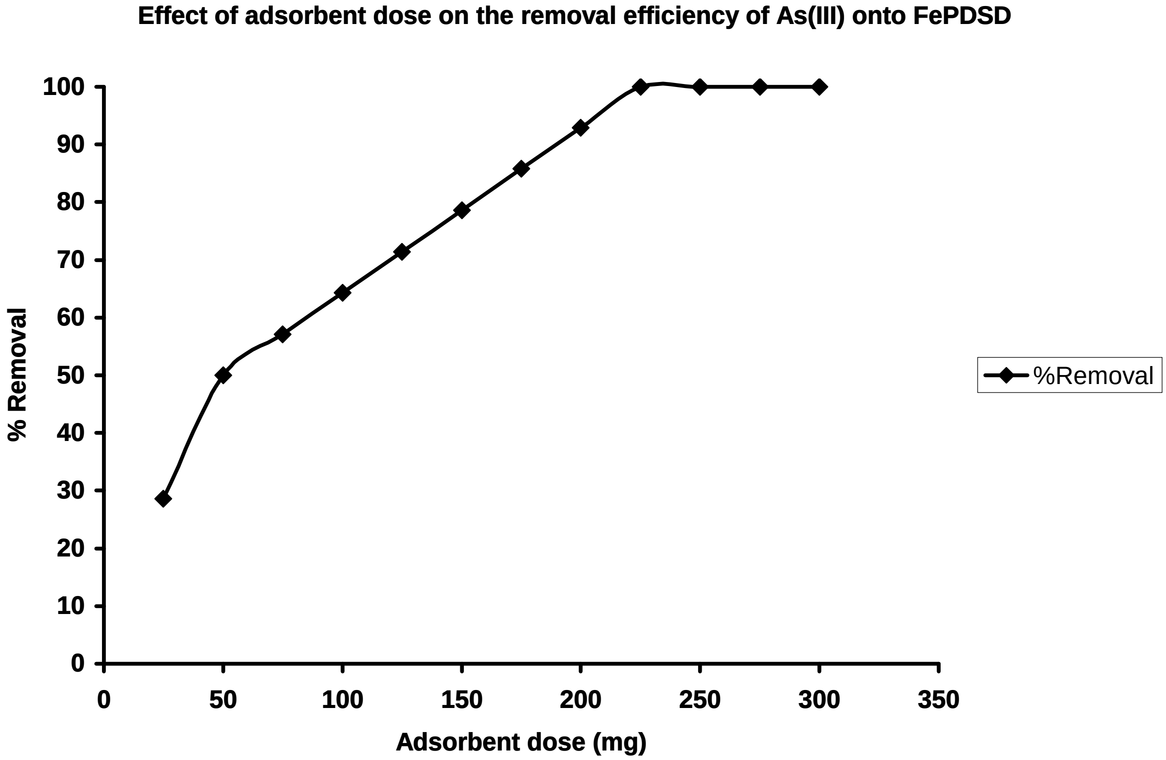


Figure 4A^{1}: Effect of adsorbent dose on the adsorption of As (III) onto FePDSD.

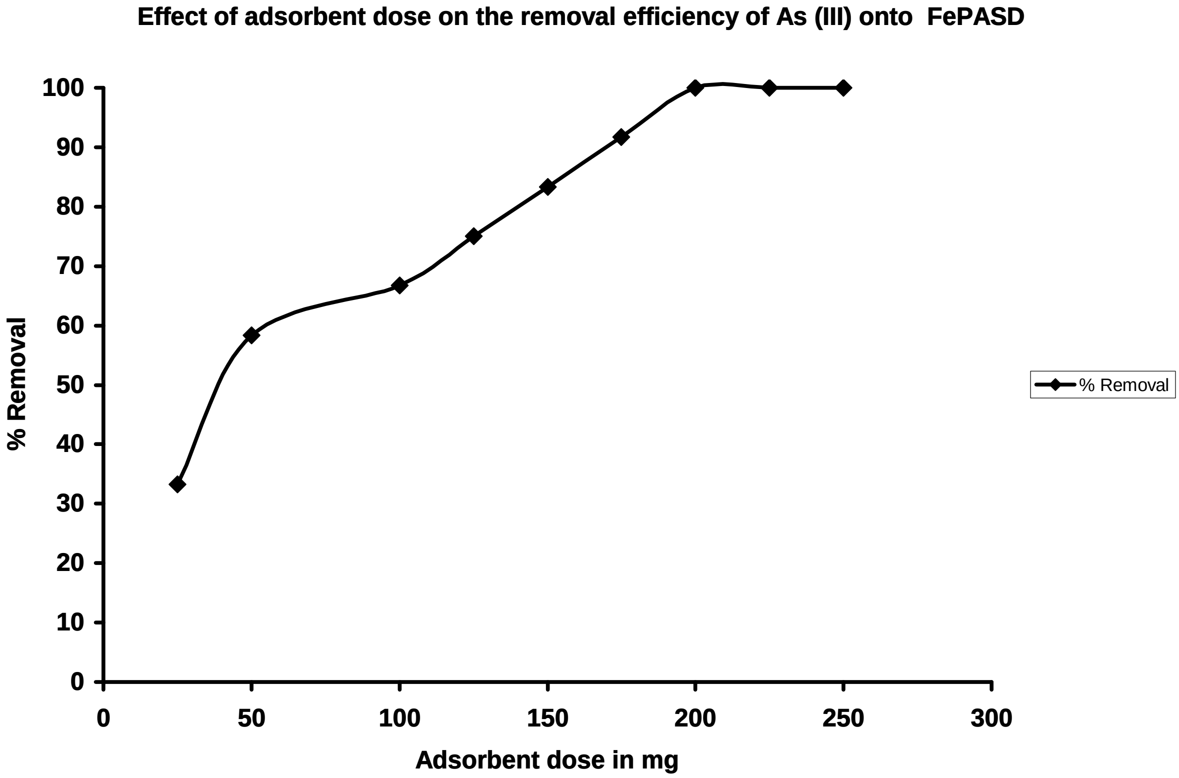


Figure 4A[2]: Effect of adsorbent dose on the adsorption of As (III) onto FePASD.

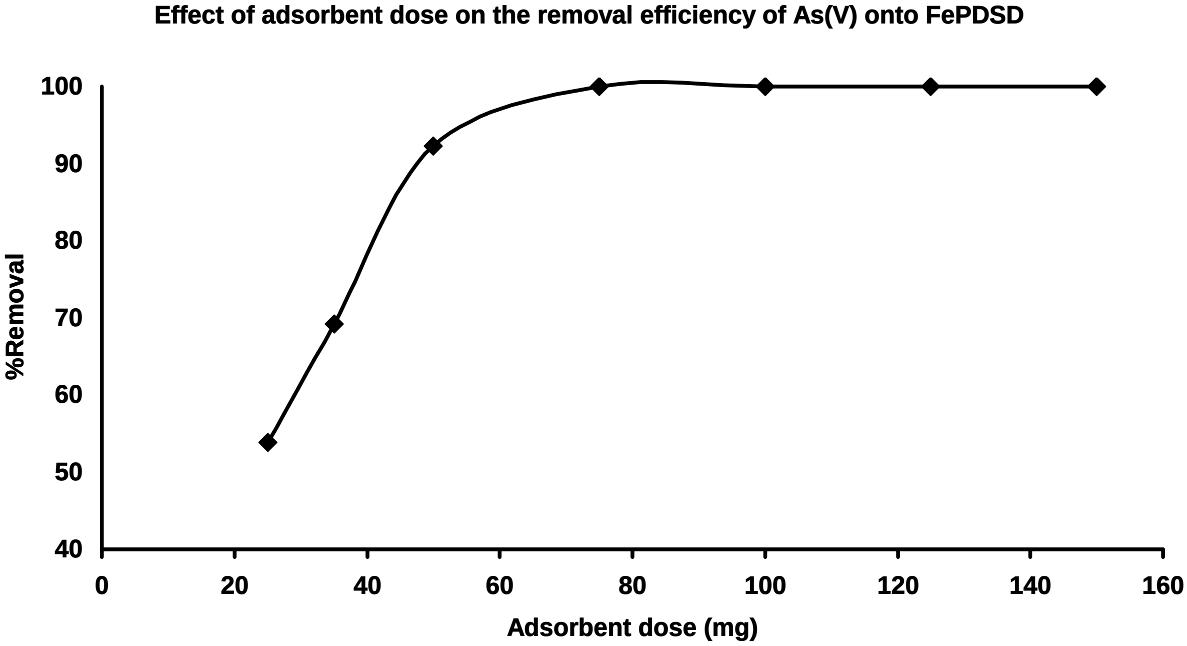


Figure 4B[1]: Effect of adsorbent dose on the adsorption of As (V) onto FePDSD.

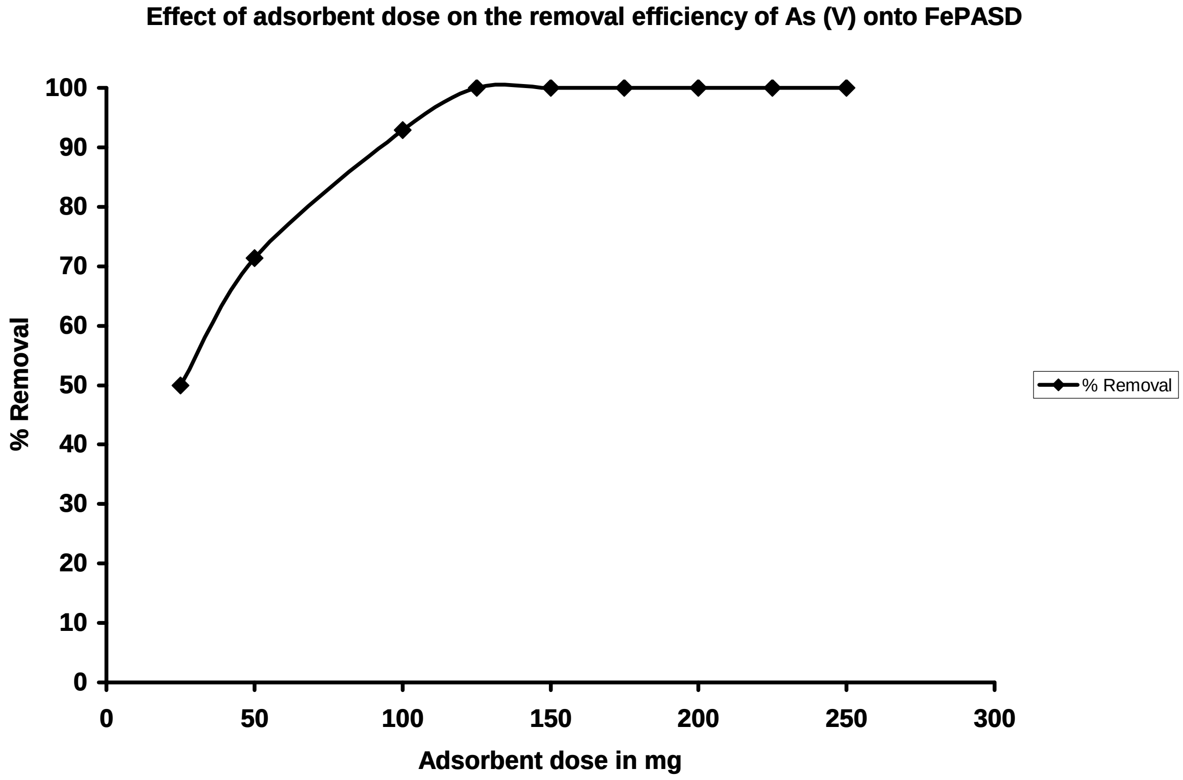


Figure 4B^2: Effect of adsorbent dose on the adsorption of As (V) onto FePASD.

The removal of As (III) and As (V) was found to increase with an increase in adsorbent doses. The removal remains almost unchanged after adsorbent dose of 225 mg for As (III), 200 mg for As (III), 75 mg for As (V), 125 mg for As (V), for FePDSD and FePASD respectively. Increase in adsorption with increase in adsorbent doses attributed to the availability of large surface area and more adsorption sites. At low adsorbent dose, the adsorbent surface becomes saturated with As (III) and As (V) and the corresponding residual As (III) and As (V) ion concentration in the solutions are large.

3.4 Effect Of Contact Time

The rate of adsorption is the most important for performing the batch adsorption experiment. The experimental study measuring the effect of contact time on the batch adsorption of 1 mg/l As (III) and As (V) with 50 mg of adsorbent FePDSD and FePASD are shown in figures 5A^{1,} 5A^{2,} 5B^{1,} & 5B^{2} and table 5.

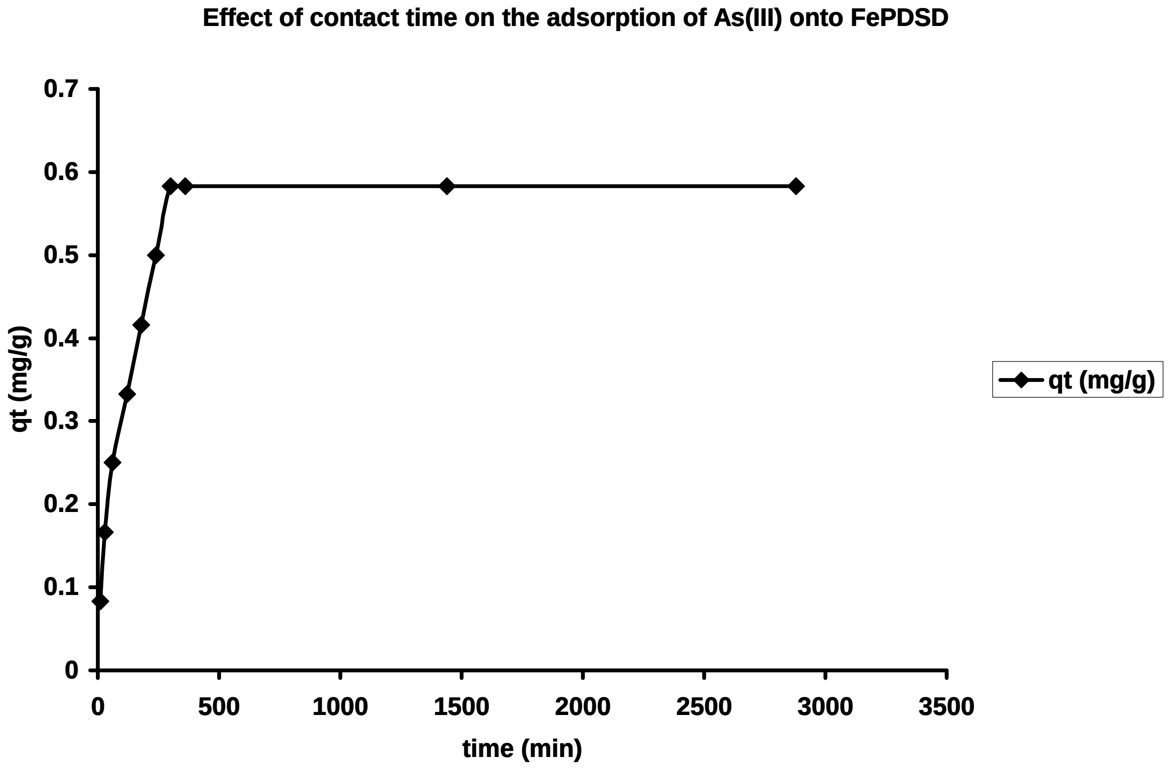


Figure 5A^1: Effect of contact time on the adsorption of As (III) onto FePDSD.

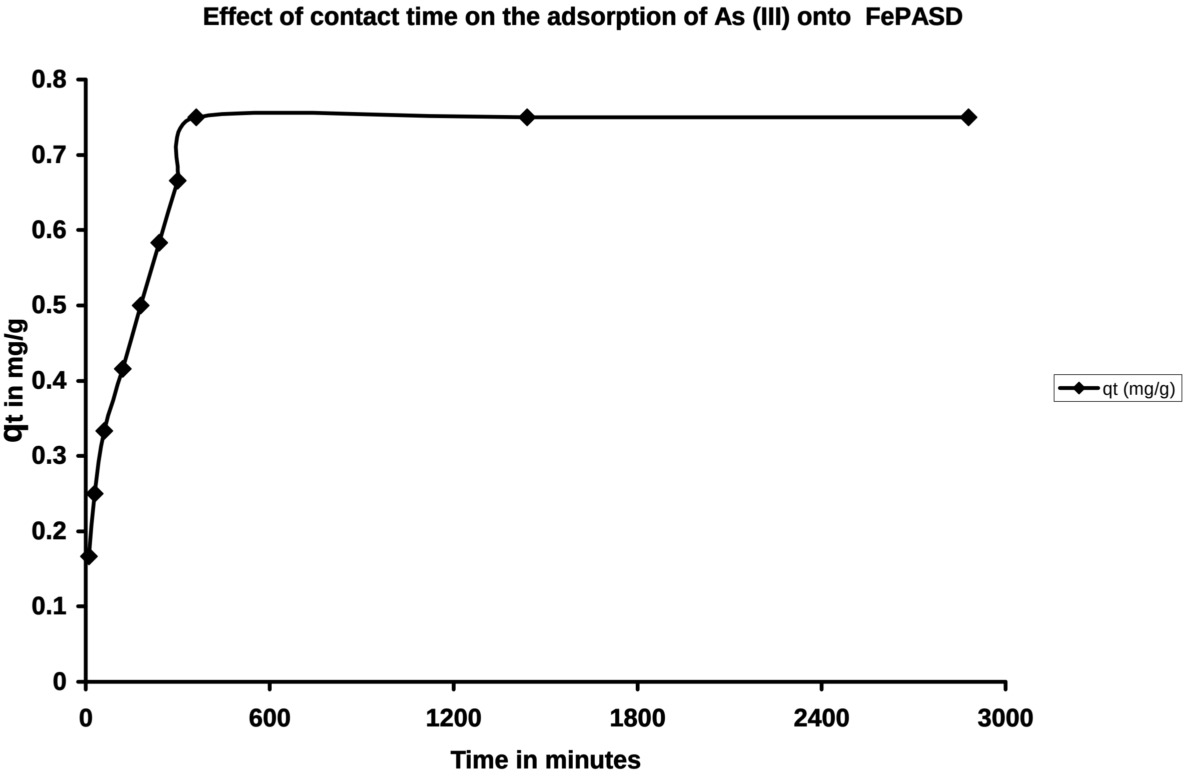


Figure 5A[2]: Effect of contact time on the adsorption of As (III) onto FePASD.

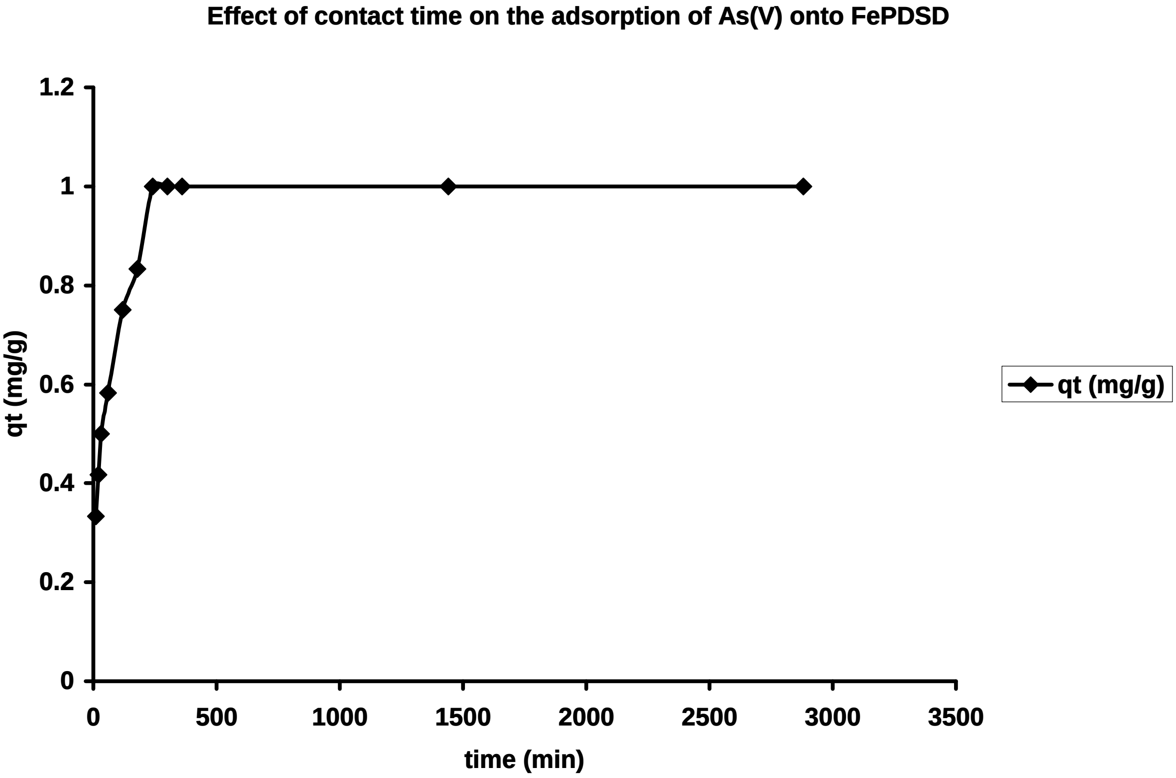


Figure 5B[1]: Effect of contact time on the adsorption of As (V) onto FePDSD.

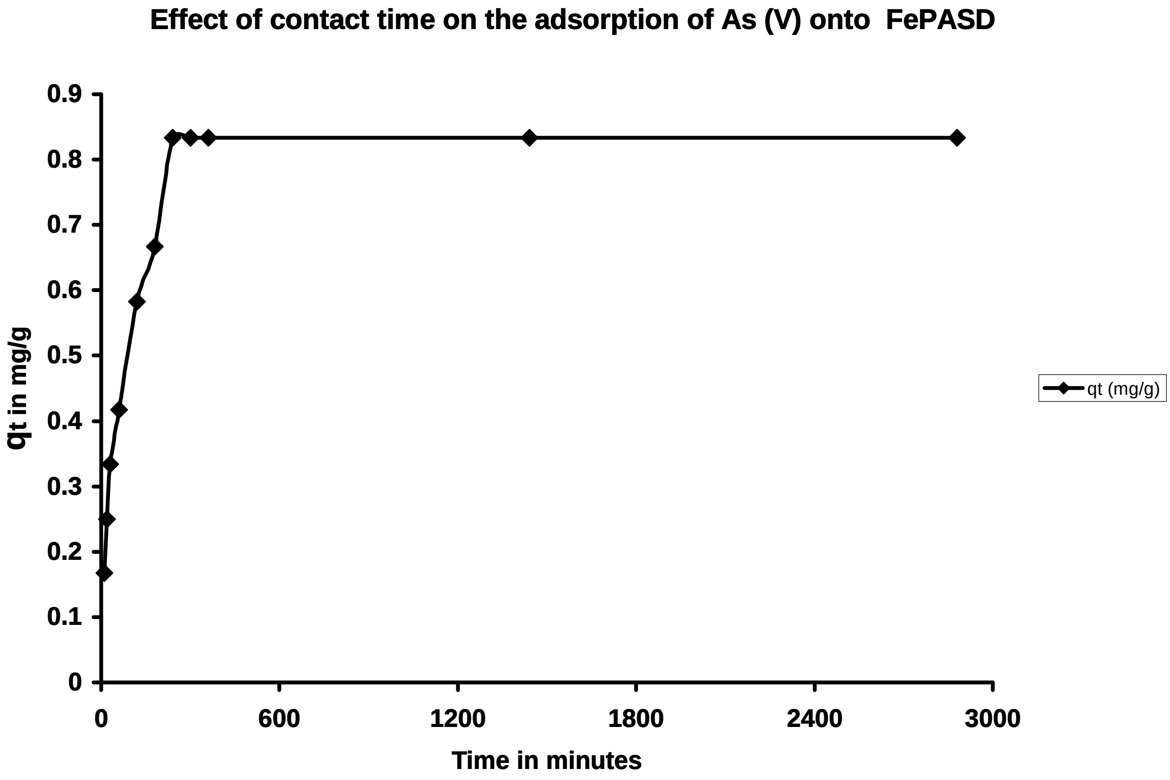


Figure 5B^2: Effect of contact time on the adsorption of As (V) onto FePASD.

The figures and table showed that the equilibrium contact times for adsorption of As (III) and As (V) on to FePDSD and FePASD reached within the first 300 minutes, & 240 minutes, and 360 minutes, & 240 minutes for FePDSD and FePASD respectively and beyond that saturation level reached. From the data, it was found that the adsorption rate was rapid at first because of the presence of large number of adsorption sites or complexation sites so that large amount of As (III) and As (V) ions attached selectively to the adsorbent sites initially. The rate slowed down gradually till it attained equilibrium at specific time for both FePDSD and FePASD beyond which there was no significant increase in adsorption rate due to decrease in active sorption sites in the adsorbent and after reaching the saturation point adsorption becomes constant. Higher adsorption efficiency of FePDSD and FePASD towards As (V) as compared to could be attributed to the higher availability of different oxyanion ion selective surface functional groups obtained by chemical modification.

3.5 Effect Of Initial Concentration

The effect of As (III) and As (V) concentrations are shown in the figures given below.

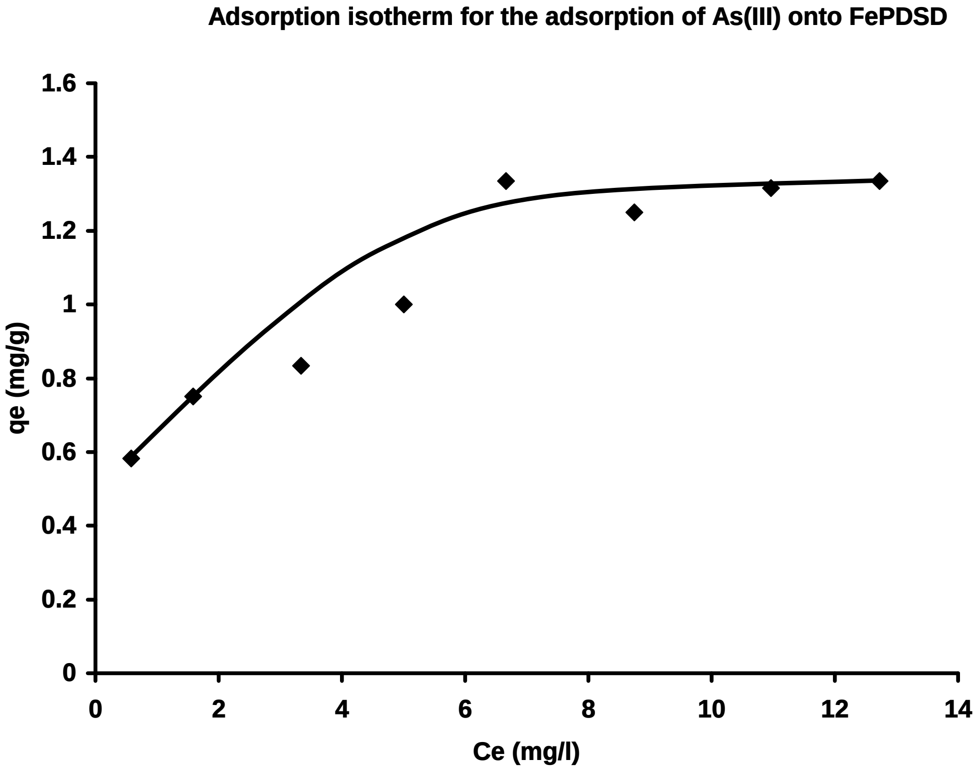


Figure 6A[1]: Effect of initial concentration on the adsorption of As (III) onto FePDSD.

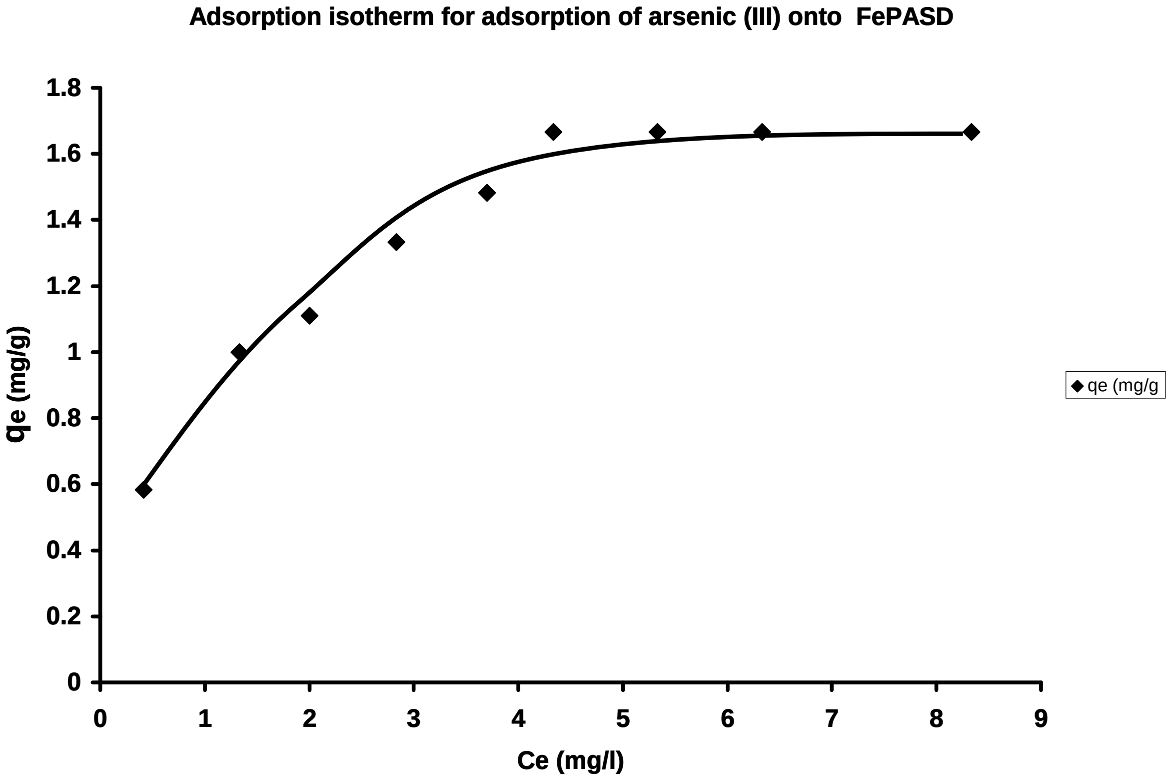


Figure 6A^2: Effect of initial concentration on the adsorption of As (III) onto FePASD.

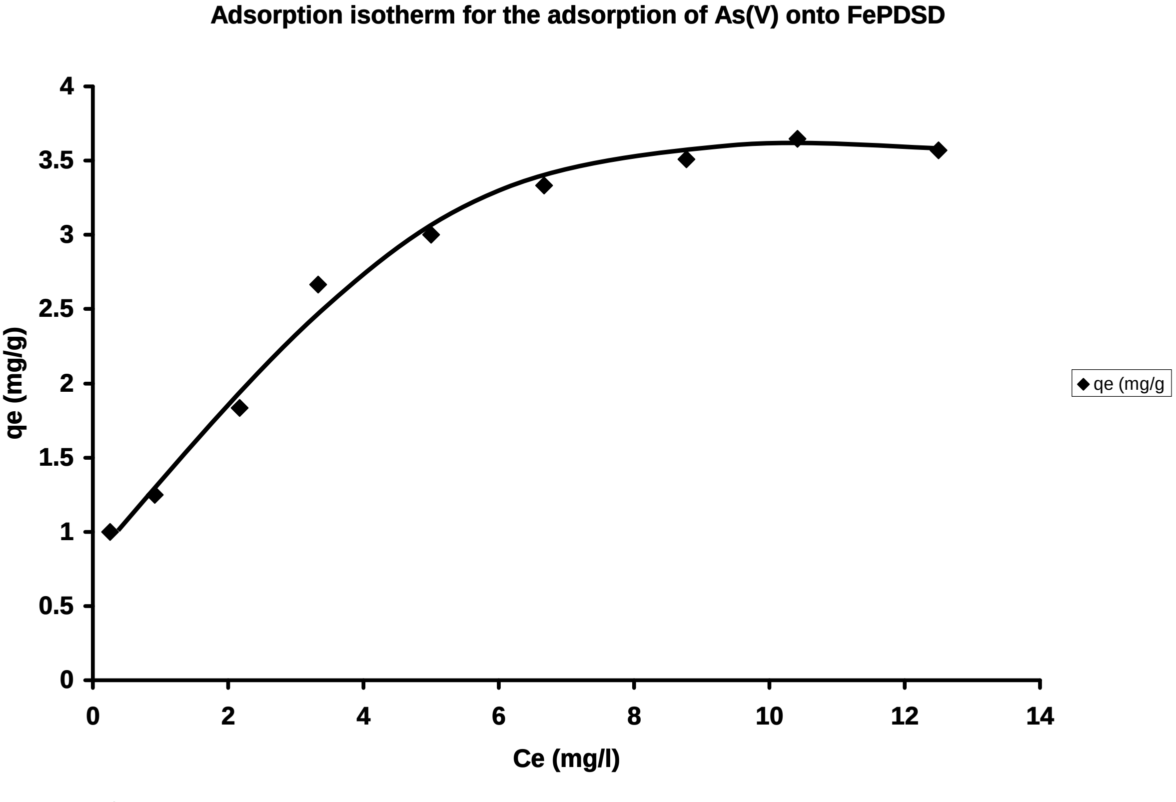


Figure 6B^1: Effect of initial concentration on the adsorption of As (V) onto FePDSD.

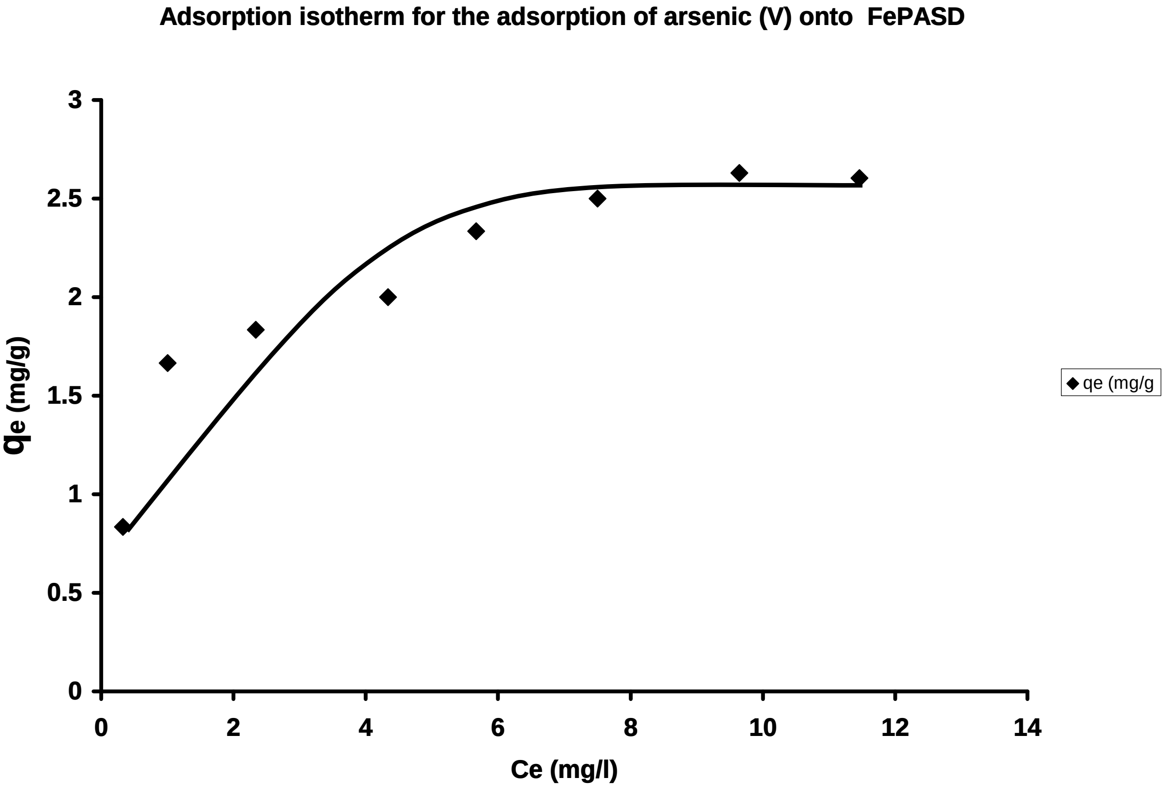


Figure 6B^2: Effect of initial concentration on the adsorption of As (V) onto FePASD.

The effect of As (III) and As (V) concentrations for both FePDSD and FePASD are shown in figures 6A^{1,} 6A^{2,} 6B^1, & 6B^2 and tables 6, 8, 7, & 9 which showed that adsorption of As (III) and As (V) on both adsorbents increases with increase in initial concentration of As (III) and As (V) solutions and attain equilibrium which is attributed to the availability of limited sorption sites. The increase in concentration of As (III) and As (V) increases the mass transfer driving force and therefore increases the rate at which As (III) and As (V) ions pass from the bulk solution to the particle surface that would results in higher adsorption.

From the results, it was found that on changing the initial concentration of As (III) and As (V) from k mg/l to p mg/l (which are tabulated below) the amount adsorbed increased from q_k mg/g to q_p mg/g at corresponding optimum pH for FePDSD and FePASD signifying that both the bioadsorbents prepared were found to more efficient for the adsorptive removal of As (V) as compared to As (III).

Species	Species conc. k mg/l	Species conc. p mg/l	Amount adsorbed q_k mg/g	Amount adsorbed q_p mg/g	Bioadsorbent at optimum pH
As (III)	1.166	14.062	0.583	1.334	FePDSD
As (V)	1.083	16.071	1.000	3.571	FePDSD
As (III)	1.000	10.000	0.584	1.667	FePASD
As (V)	1.166	14.062	0.833	2.604	FePASD

3.6 Batch Isotherm Studies

Adsorption of As (III) and As (V) onto FePDSD and FePASD gives the linear relationship with Langmuir and Freundlich isotherm which are shown in figures $7A^{1L}$, $7A^{1F}$, $7A^{2L}$, $7A^{2F}$, $7B^{1L}$, $7B^{1F}$, $7B^{2L}$, & $7B^{2F}$ and tables 6, 8, 7, & 9.

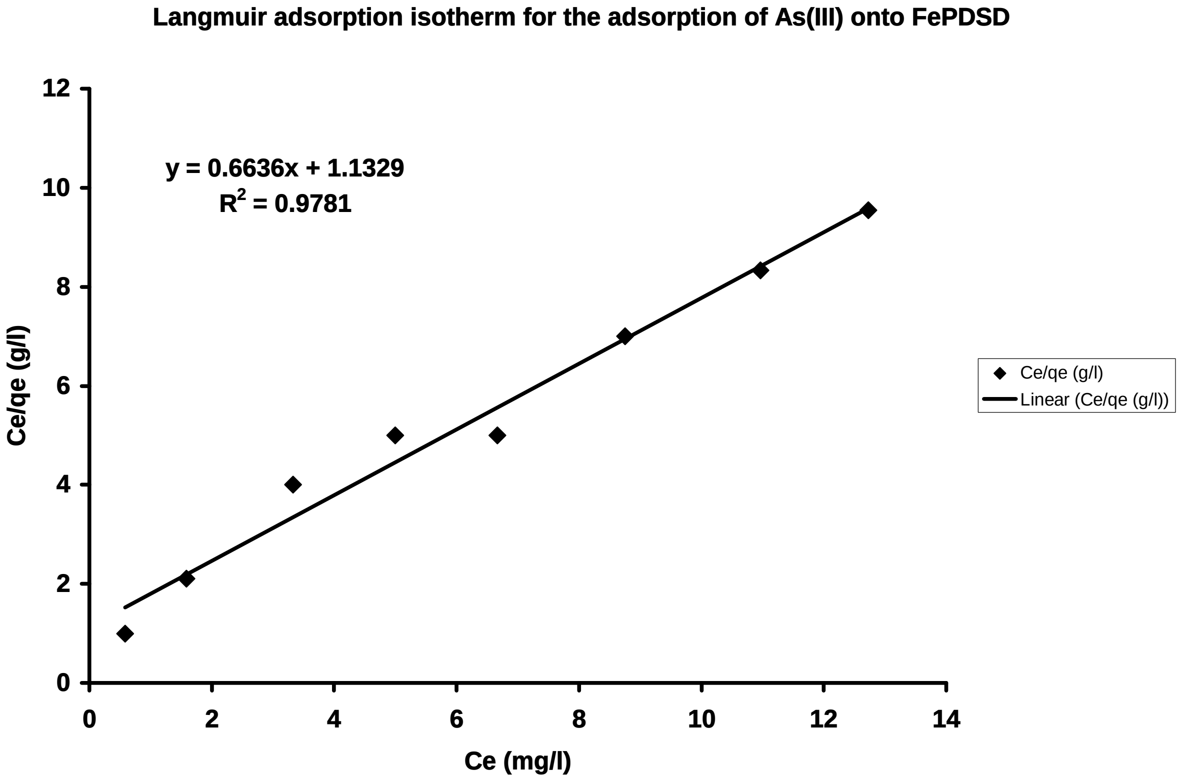


Figure $7A^{1L}$: Langmuir Adsorption Isotherm for the Adsorption of As(III) onto FePDSD.

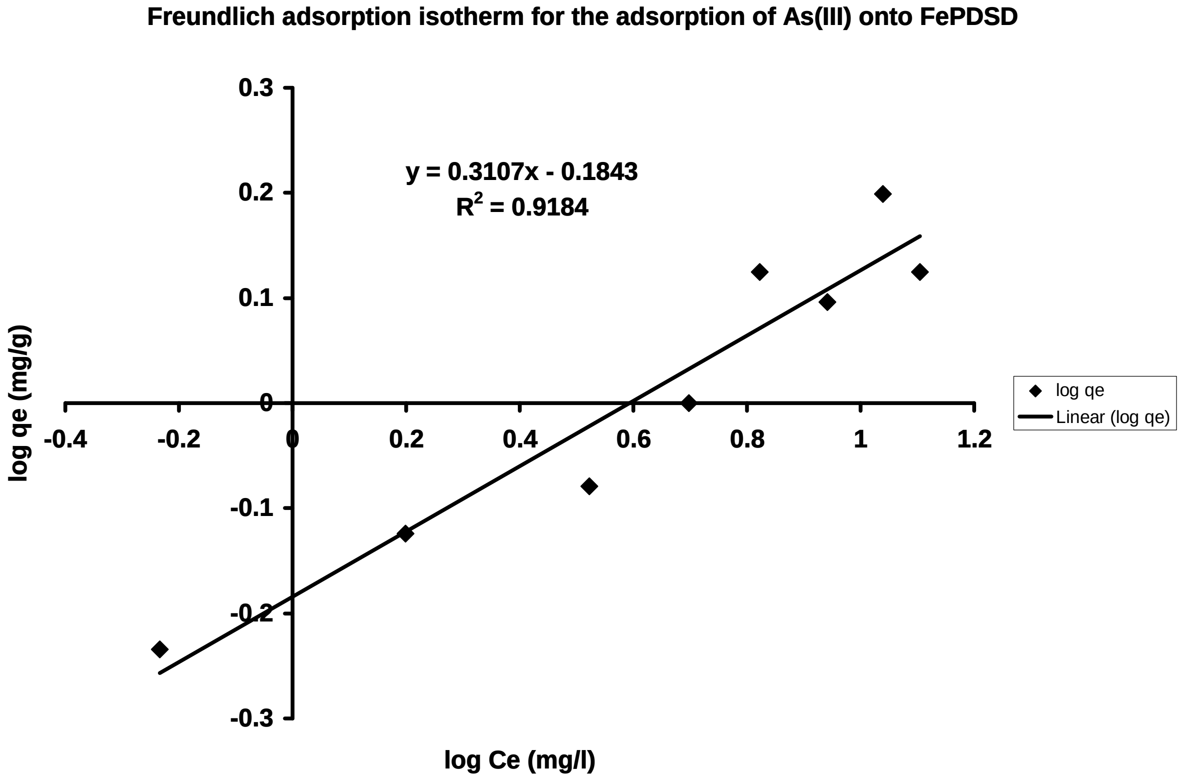


Figure 7A^{1F}: Freundlich Adsorption Isotherm for the Adsorption of As (III) onto FePDSD.

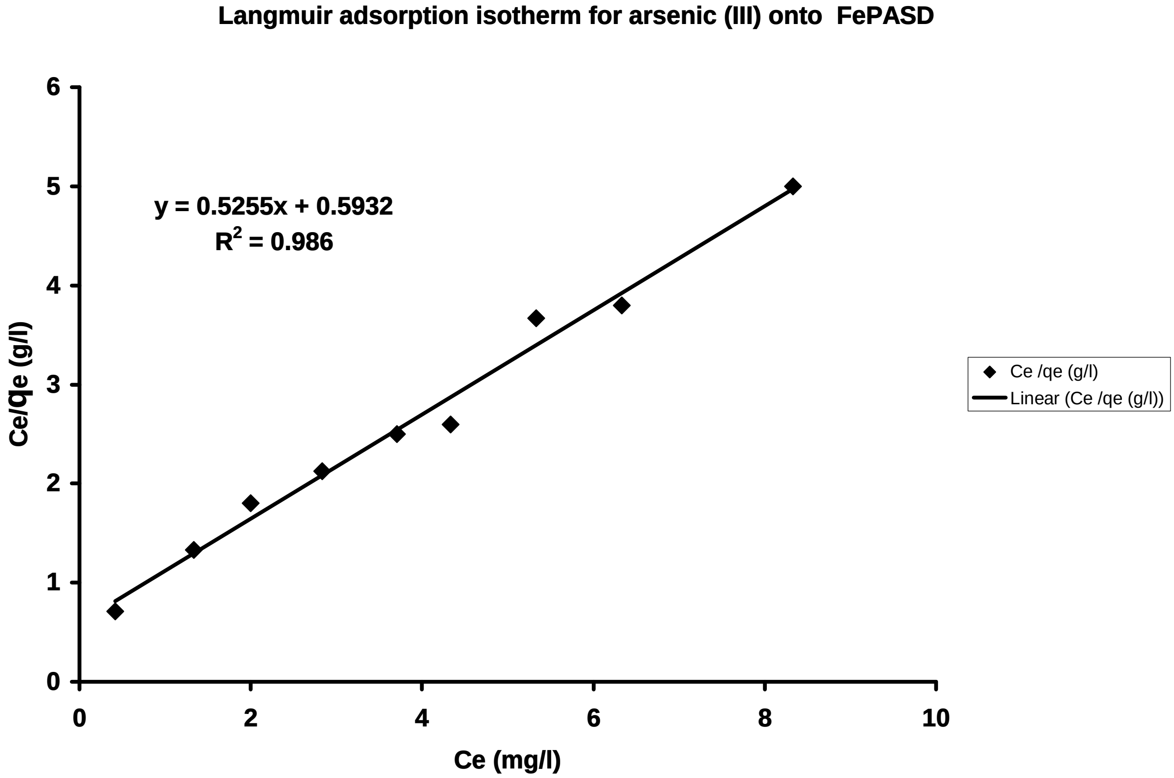


Figure 7A^{2L}: Langmuir Adsorption Isotherm for the Adsorption of As (III) onto FePASD.

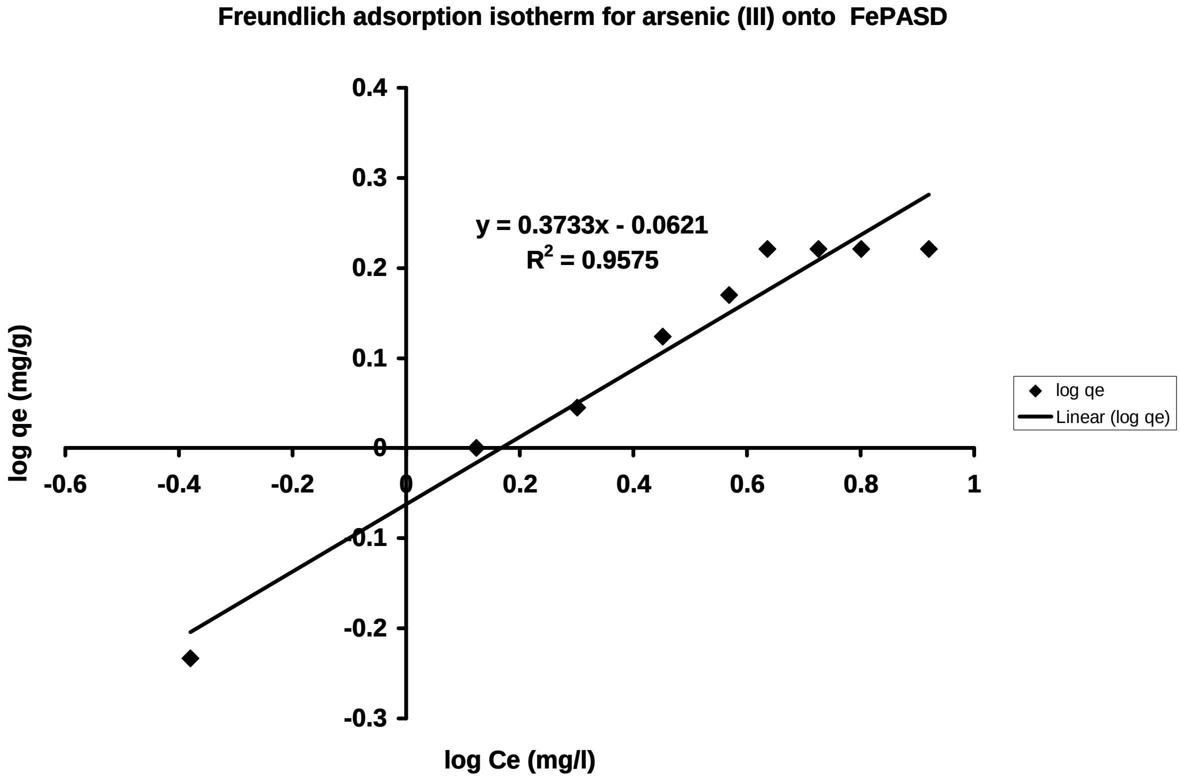


Figure 7A^{2F}: Freundlich Adsorption Isotherm for the Adsorption of As (III) onto FePASD.

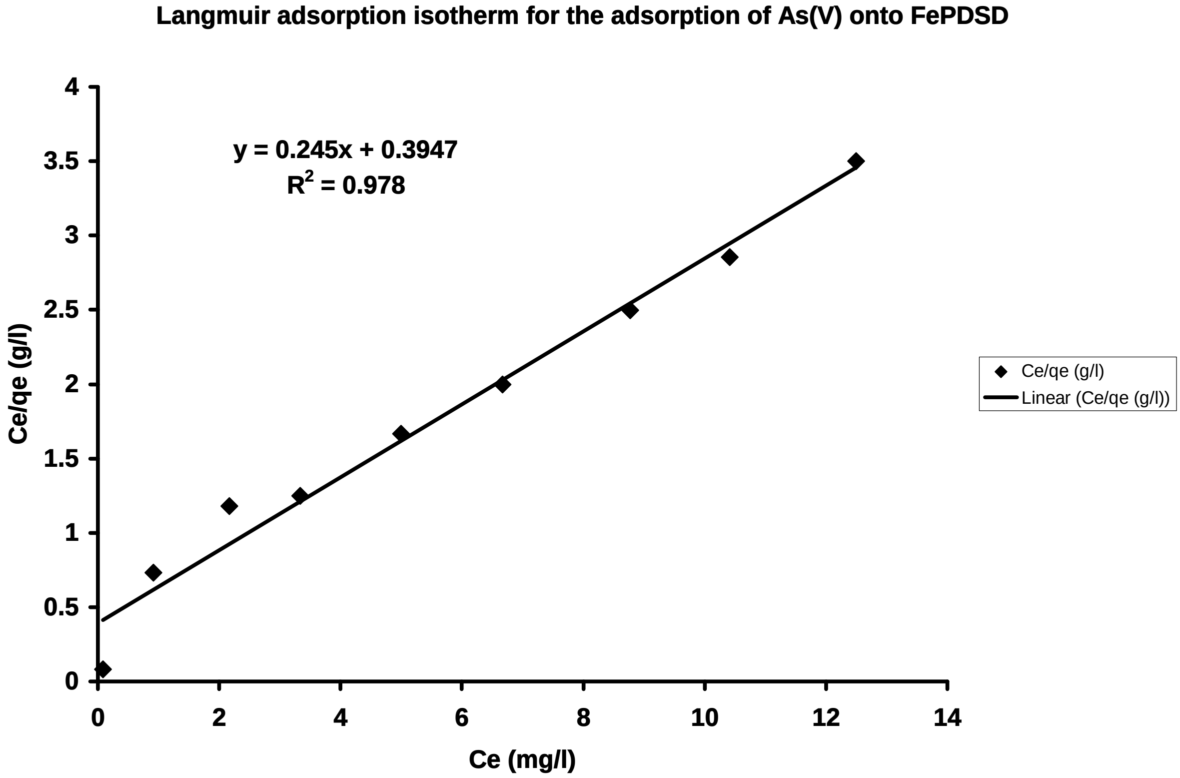


Figure 7B^{1L}: Langmuir Adsorption Isotherm for the Adsorption of As (V) onto FePDSD.

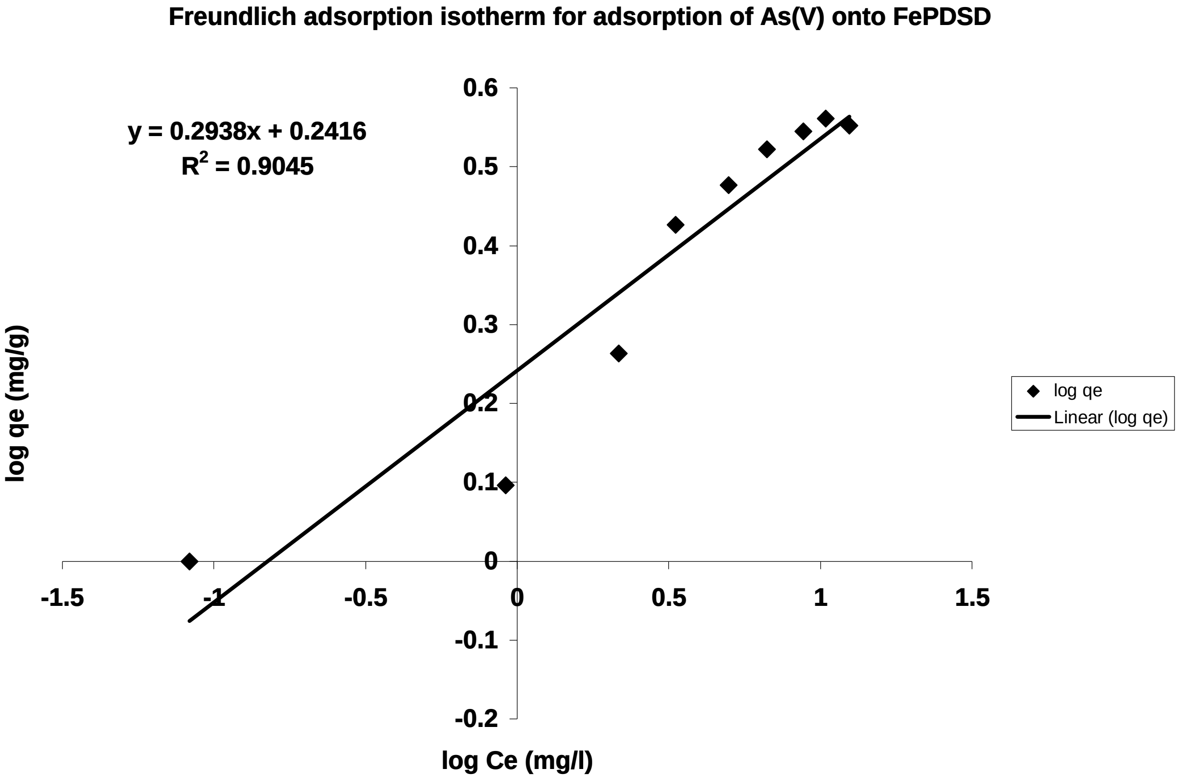


Figure 7B^{1F}: Freundlich Adsorption Isotherm for the Adsorption of As (V) onto FePDSD.

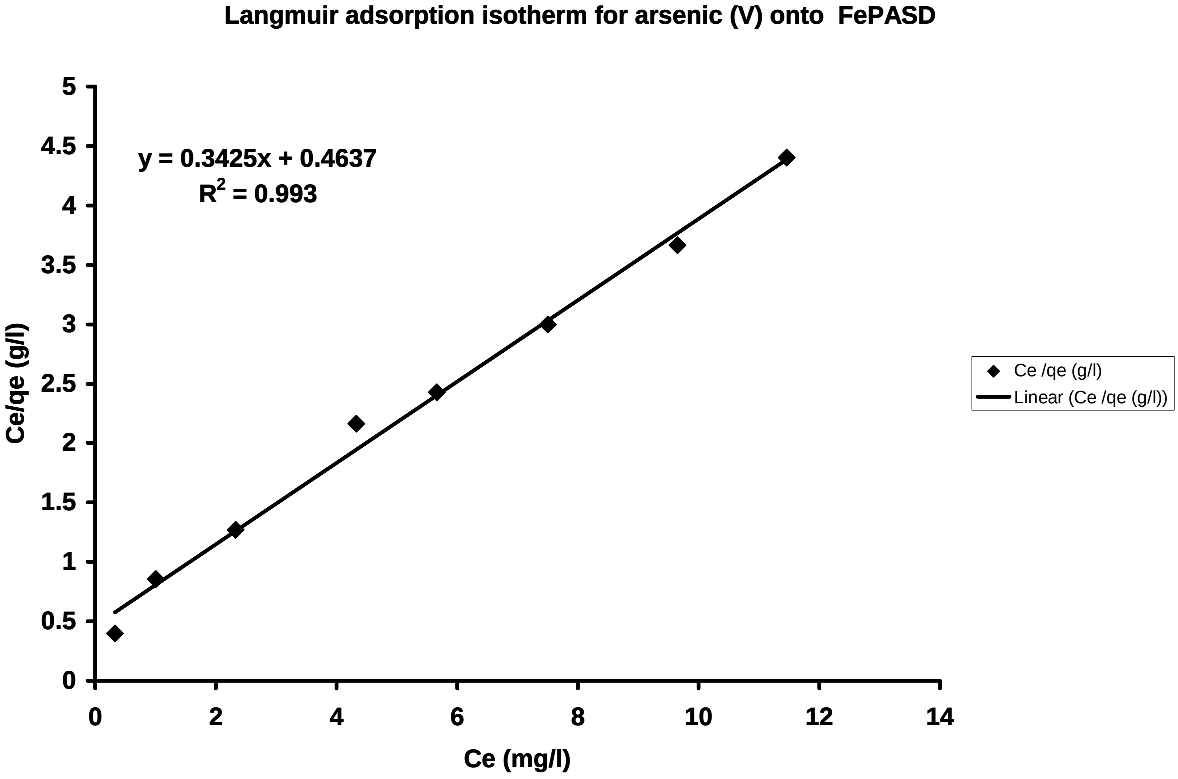


Figure 7B^{2L}: Langmuir Adsorption Isotherm for the Adsorption of As (V) onto FePASD.

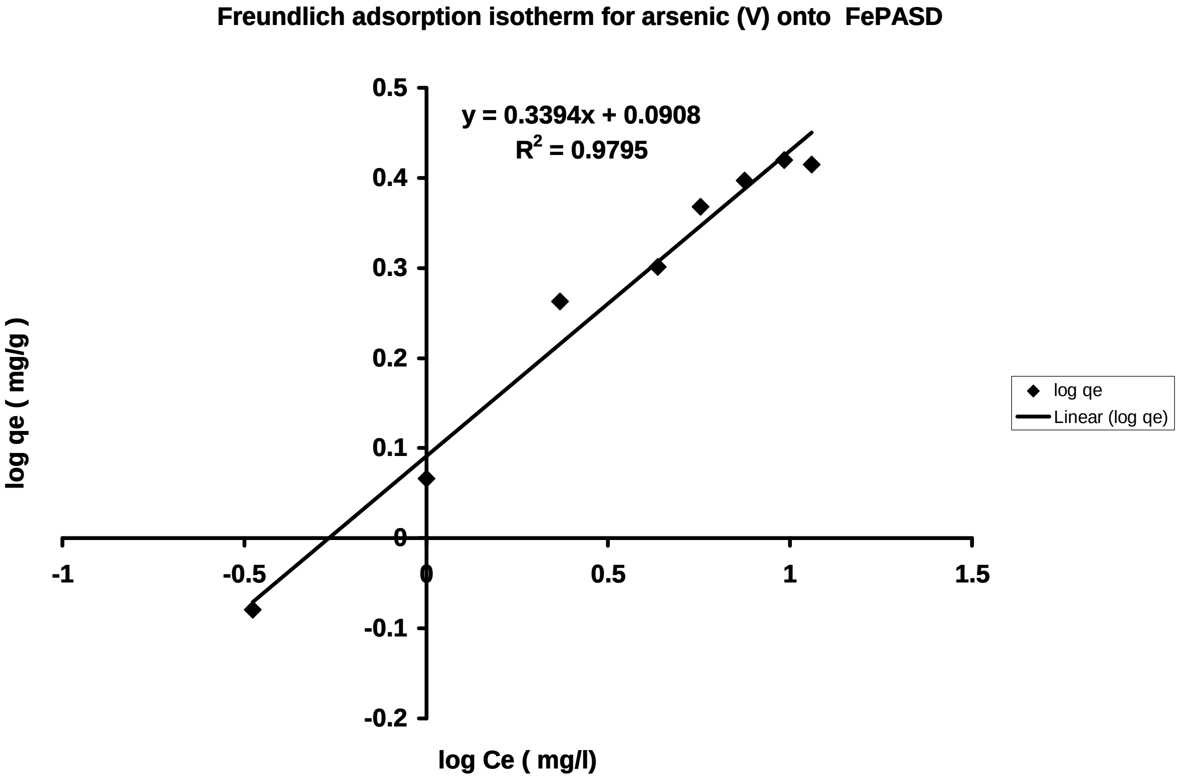


Figure 7B^{2F}: Freundlich Adsorption Isotherm for the Adsorption of As (V) onto FePASD.

Langmuir and Freundlich parameters shown in table 14 were determined from the slope and intercept of their respective plots. The values of Langmuir equilibrium parameters which in table lied between 0 and 1 indicated that equilibrium data fits well with Langmuir adsorption isotherm. The values of 1/n lied between 0 and 1 indicated that adsorption process was favourable.

However, the correlation coefficient values for Langmuir isotherms were found to be greater than that of Freundlich isotherms indicating that the adsorption process is better defined by the Langmuir adsorption isotherm model than by the Freundlich, which indicated the homogeneous distribution of active sites on the surface of adsorbents. The monolayer sorption capacities of FePDSD and FePASD for As (III) and As (V) were found to be 1.506 mg/g, & 4.081 mg/g and 1.902 mg/g, & 2.919 mg/g respectively.

3.7 Batch Kinetic Studies

Kinetic studies for the adsorption of As (III) and As (V) onto FePDSD and FePASD were studied using pseudo-first order (Langergren, 1898), Pseudo-second order (Ho, et al.1995 and Ho and Mckay, et al. 2000) and second order (Langergren, 1898) models. The kinetic study of As (III) and As (V) adsorption by FePDSD and FePASD are shown in figures $8A^{1p2}$, $8A^{1p1}$, $8A^{12}$, $8A^{2p2}$, $8A^{2p1}$, $8A^{22}$, $8B^{1p2}$, $1B^{1p1}$, $8B^{12}$, $8B^{2p2}$, $8B^{2p1}$, $8B^{22}$ and tables 10, 12, 11, &, 13.

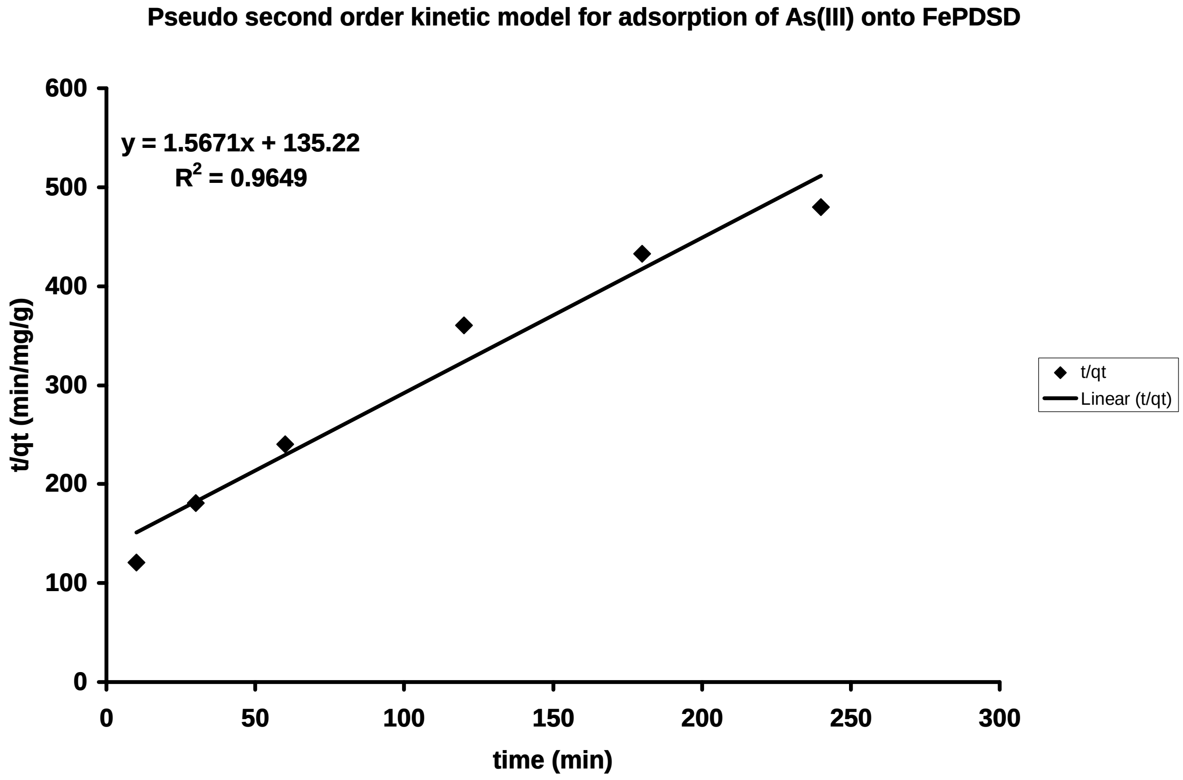


Figure $8A^{1p2}$: Pseudo Second Order Kinetic Model for Adsorption of As (III) onto FePDSD.

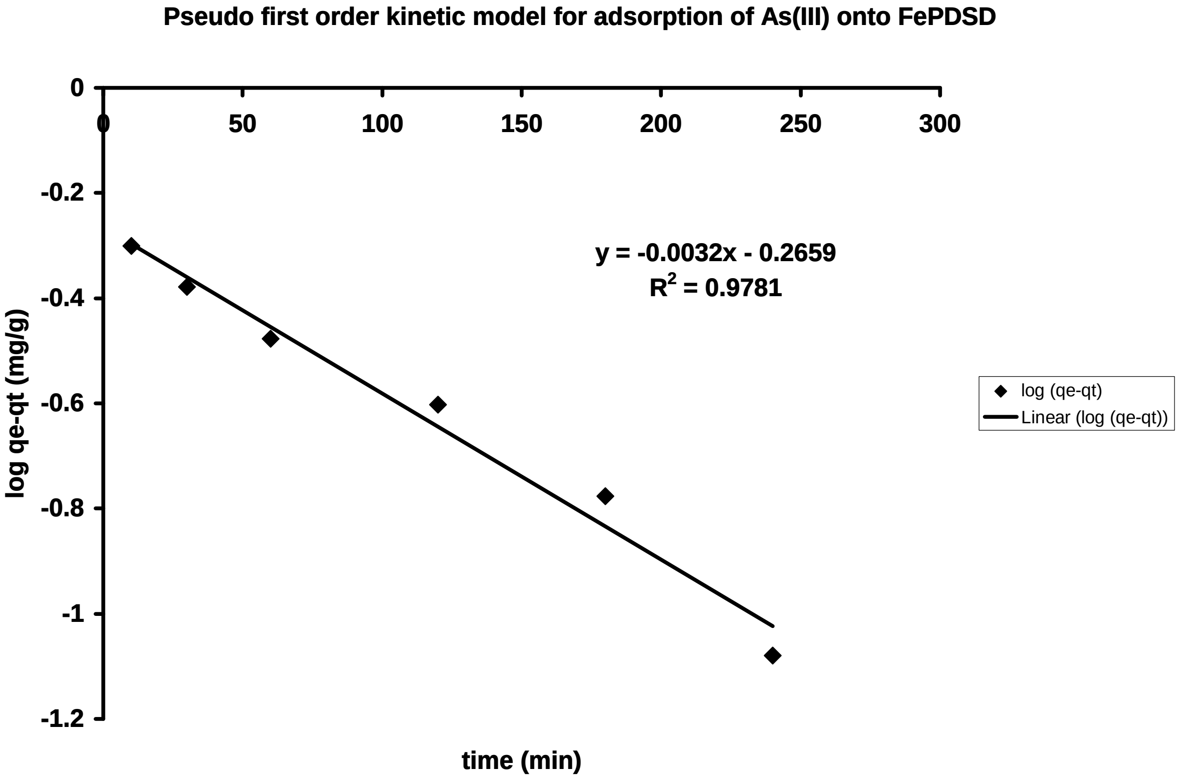


Figure 8A^{1p1}**: Pseudo First Order Kinetic Model for Adsorption of As (III) onto FePDSD.**

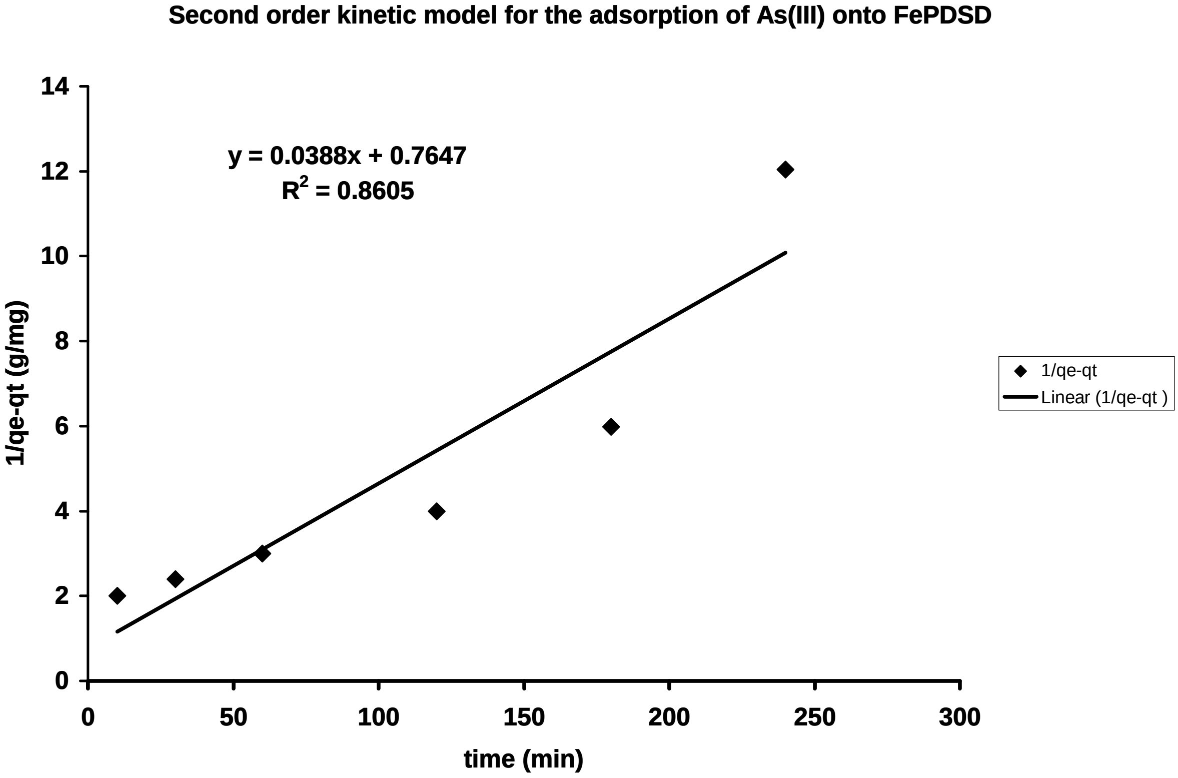


Figure 8A^{12}**: Second Order Kinetic Model for Adsorption of As (III) onto FePDSD.**

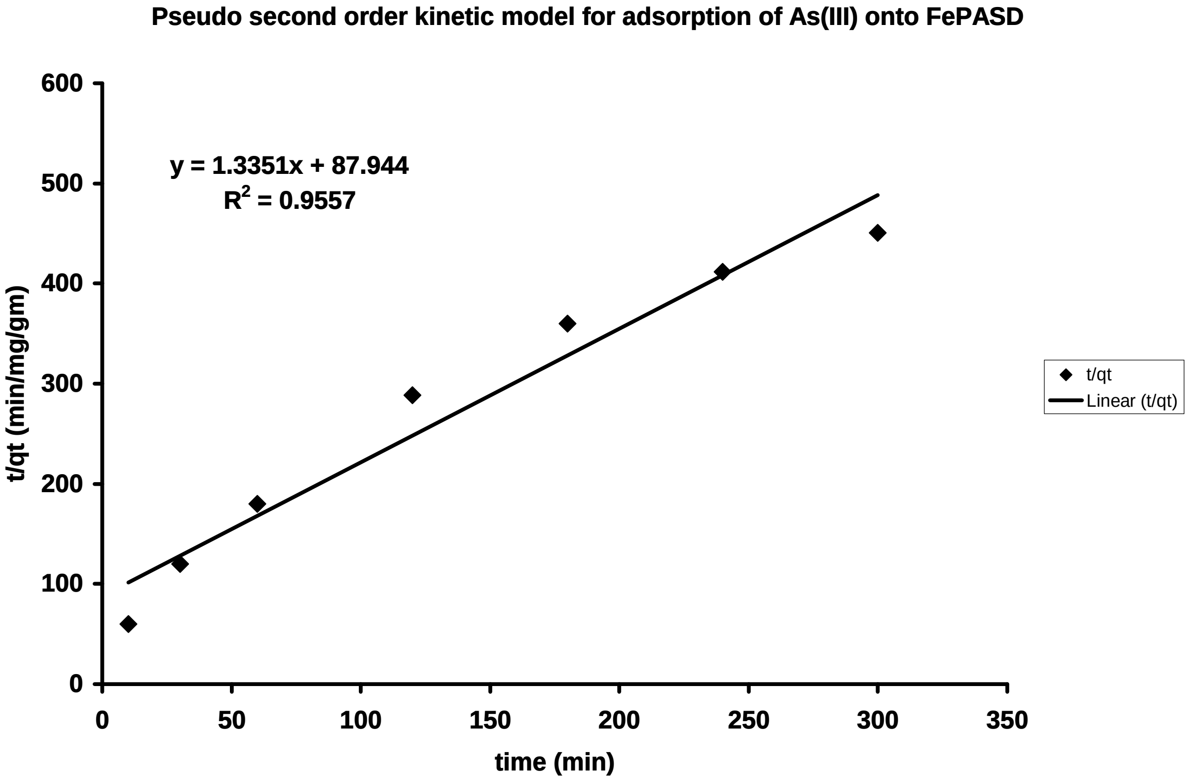


Figure 8A^{2p2}: Pseudo Second Order Kinetic Model for Adsorption of As(III) onto FePASD.

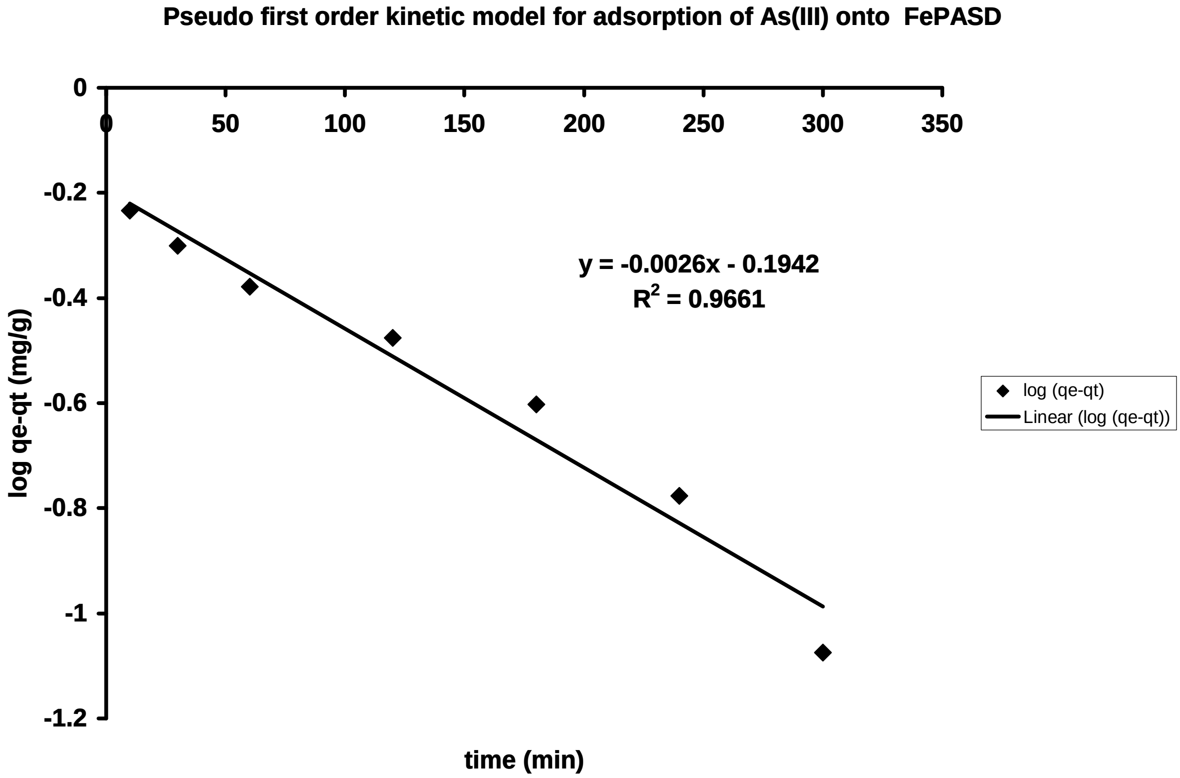


Figure 8A^{2p1}: Pseudo First Order Kinetic Model for Adsorption of As (III) onto FePASD.

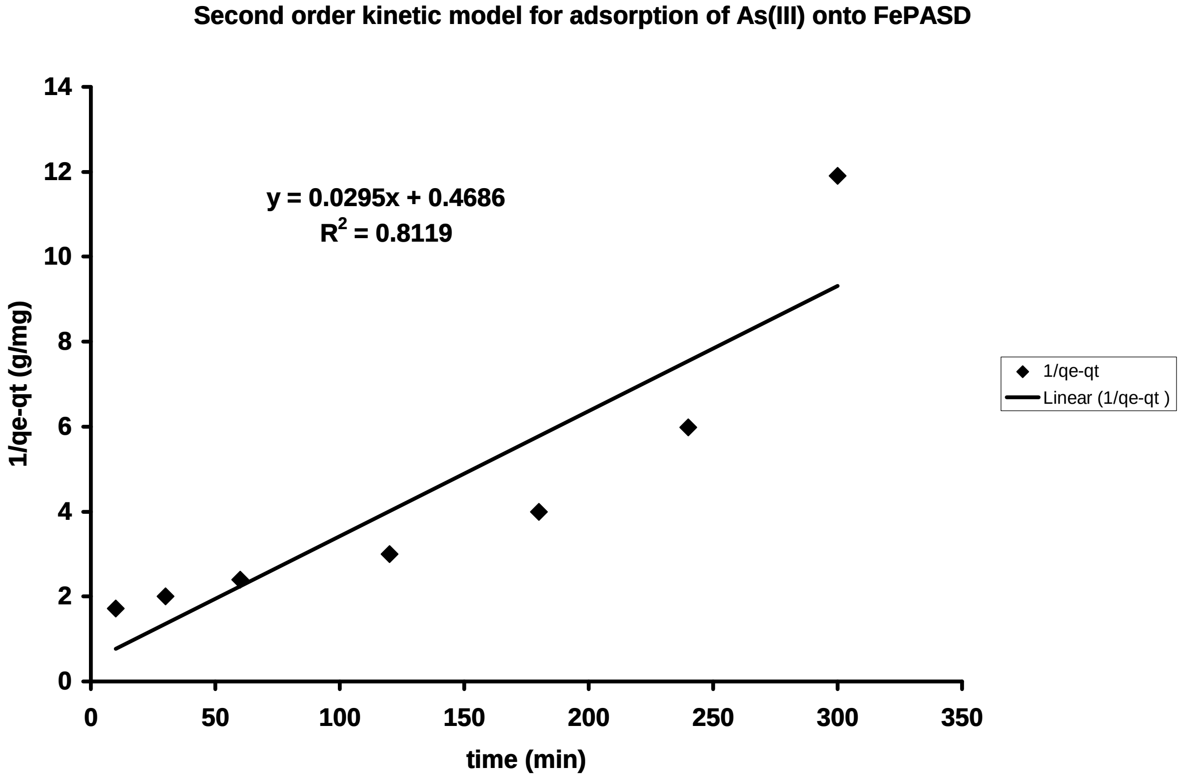


Figure 8A^{22}: Second Order Kinetic Model for Adsorption of As (III) onto FePASD.

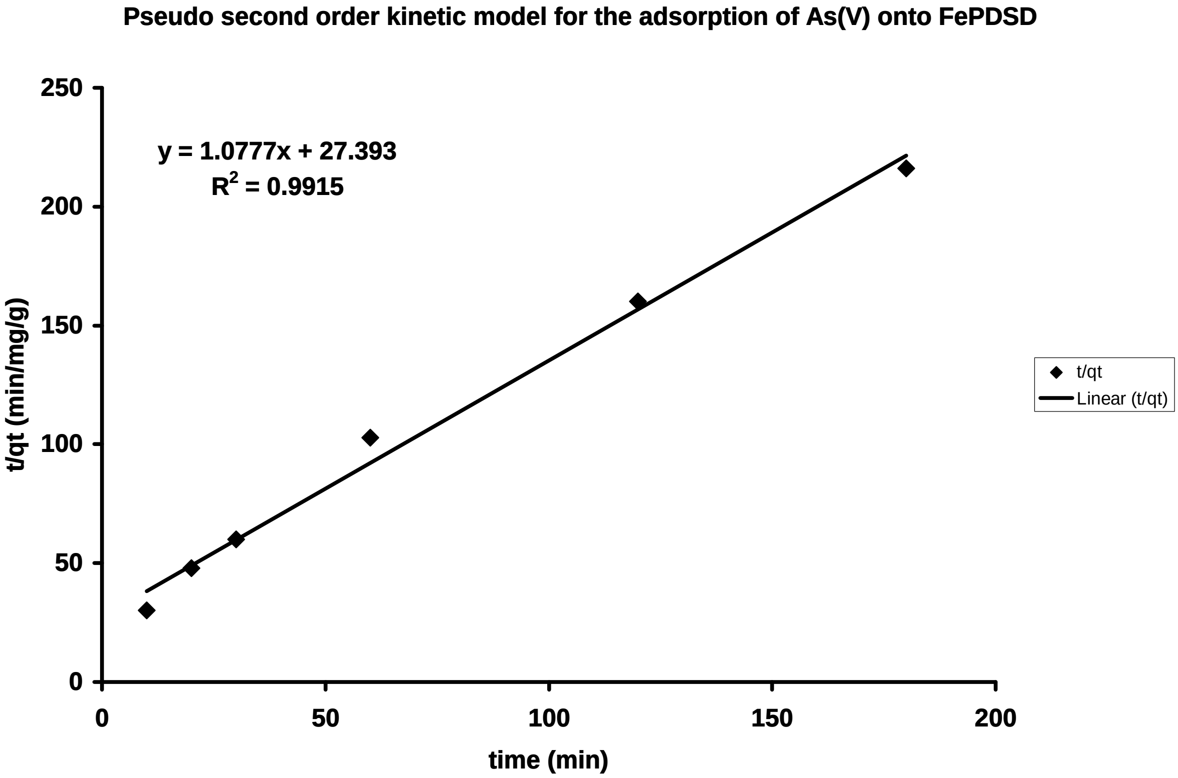


Figure 8B^{1p2}: Pseudo Second Order Kinetic Model for Adsorption of As (V) onto FePDSD.

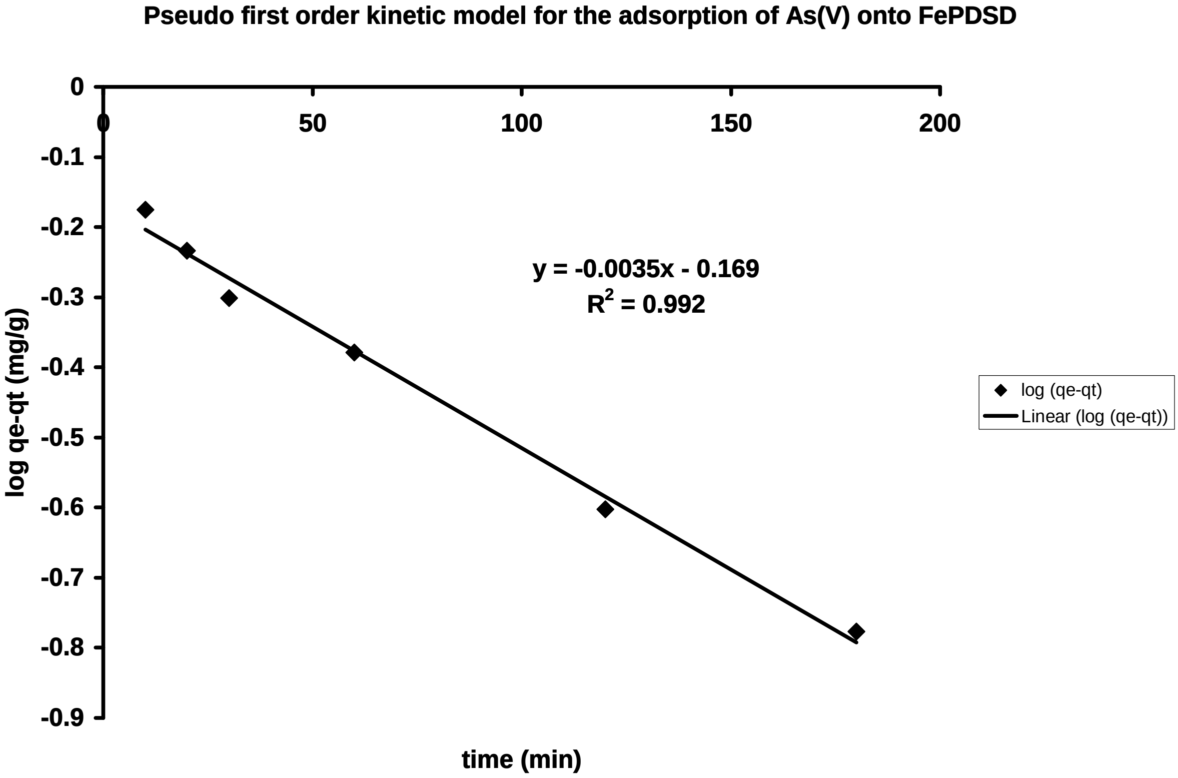


Figure 8B^{1p1}: Pseudo First Order Kinetic Model for Adsorption of As (V) onto FePDSD.

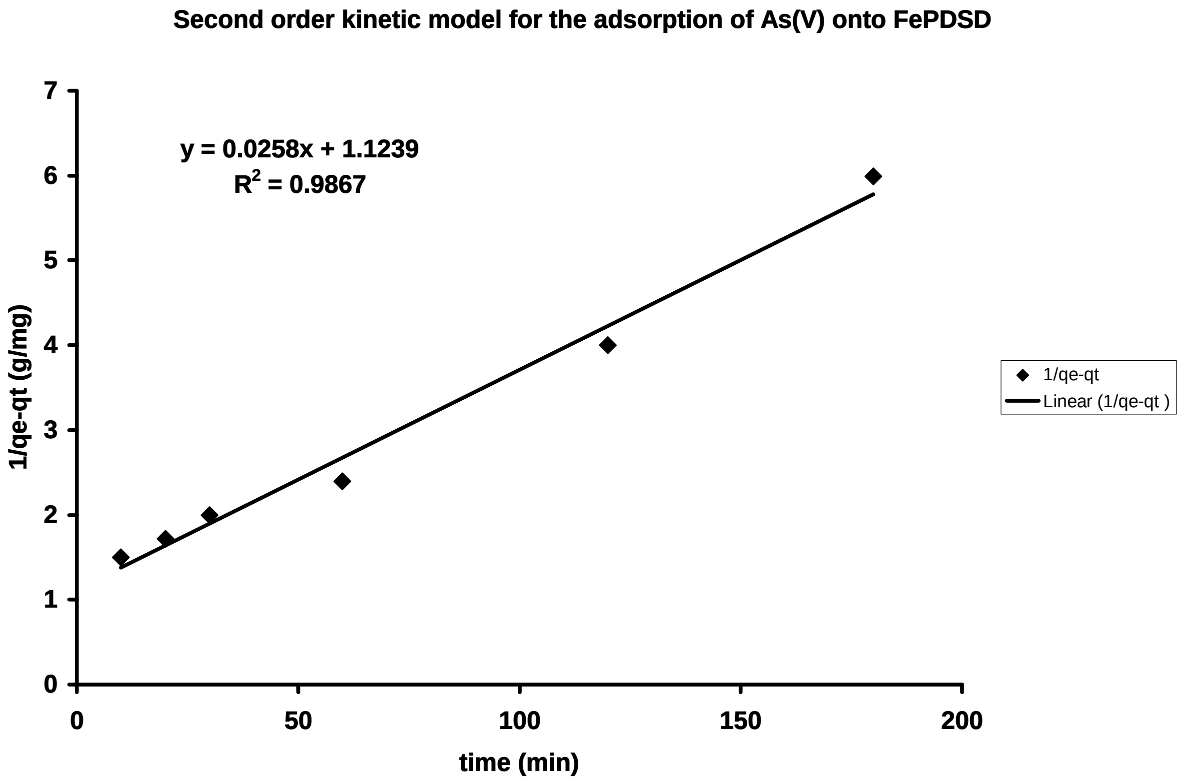


Figure 8B[12]: Second Order Kinetic Model for Adsorption of As (V) onto FePDSD.

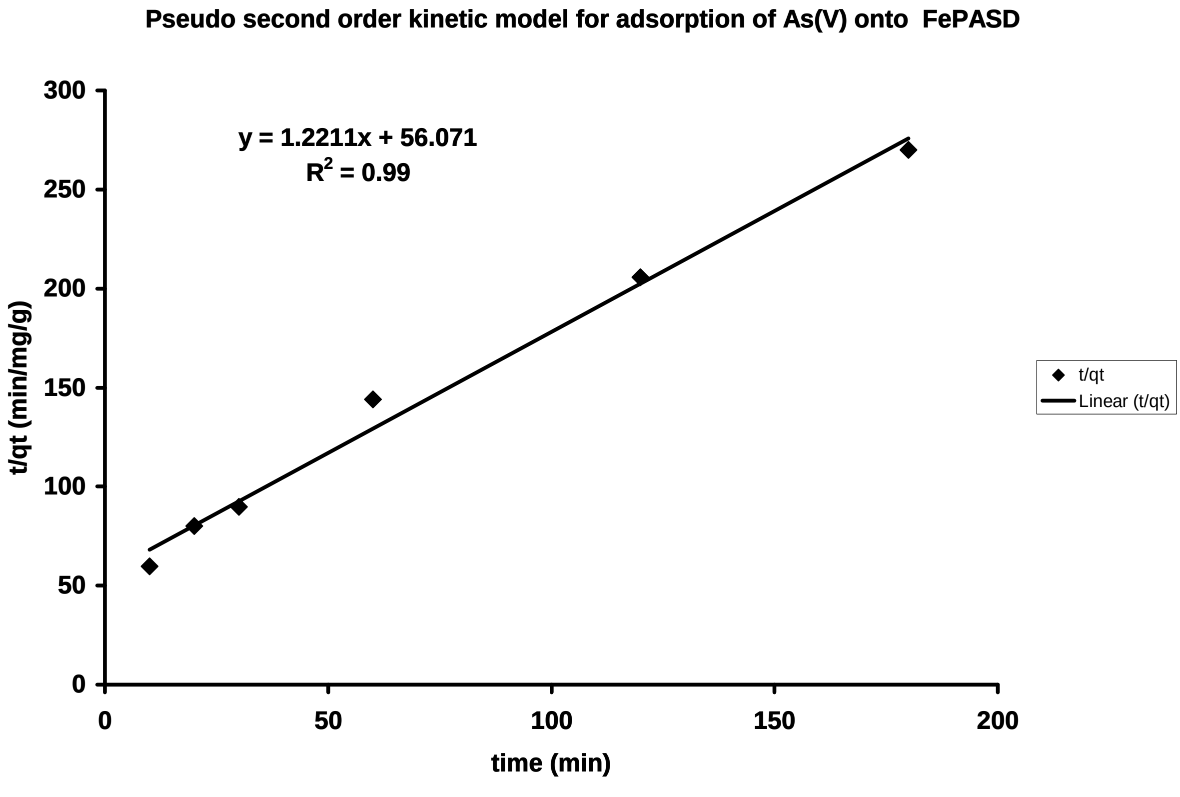


Figure 8B[2p2]: Pseudo Second Order Kinetic Model for Adsorption of As (V) onto FePASD.

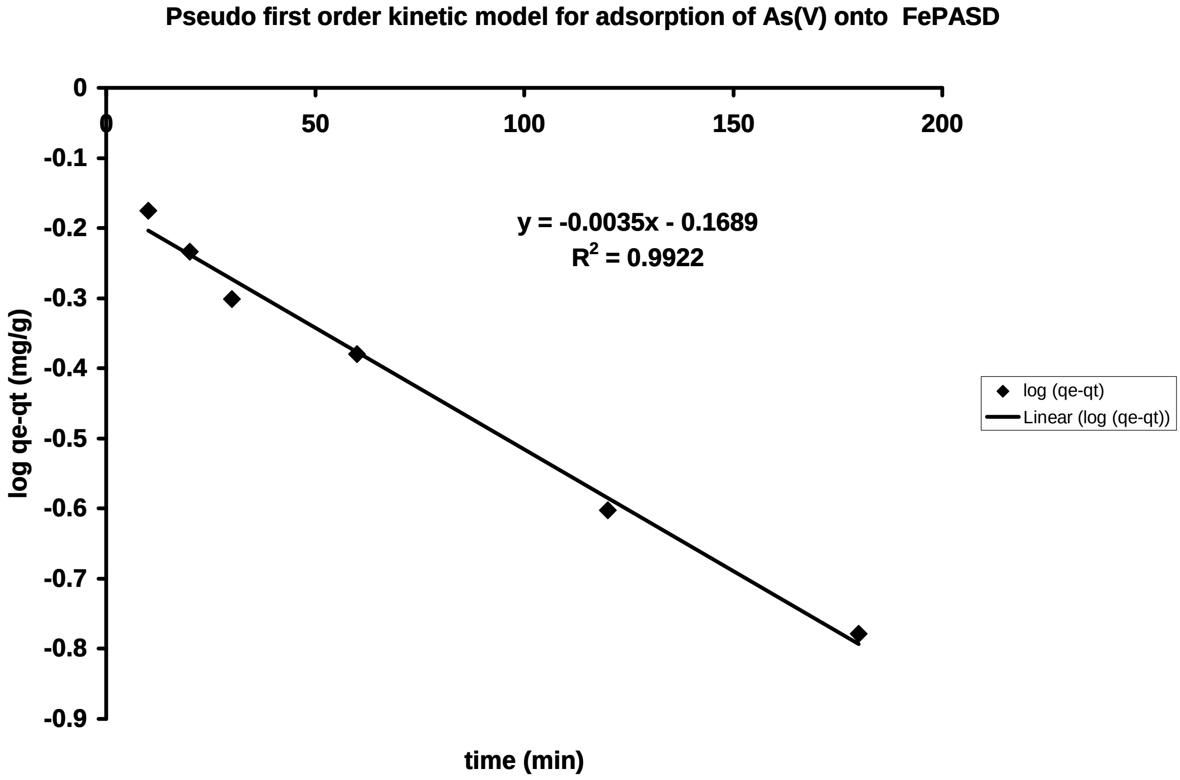


Figure 8B^{2p1}: Pseudo First Order Kinetic Model for Adsorption of As (V) onto FePASD.

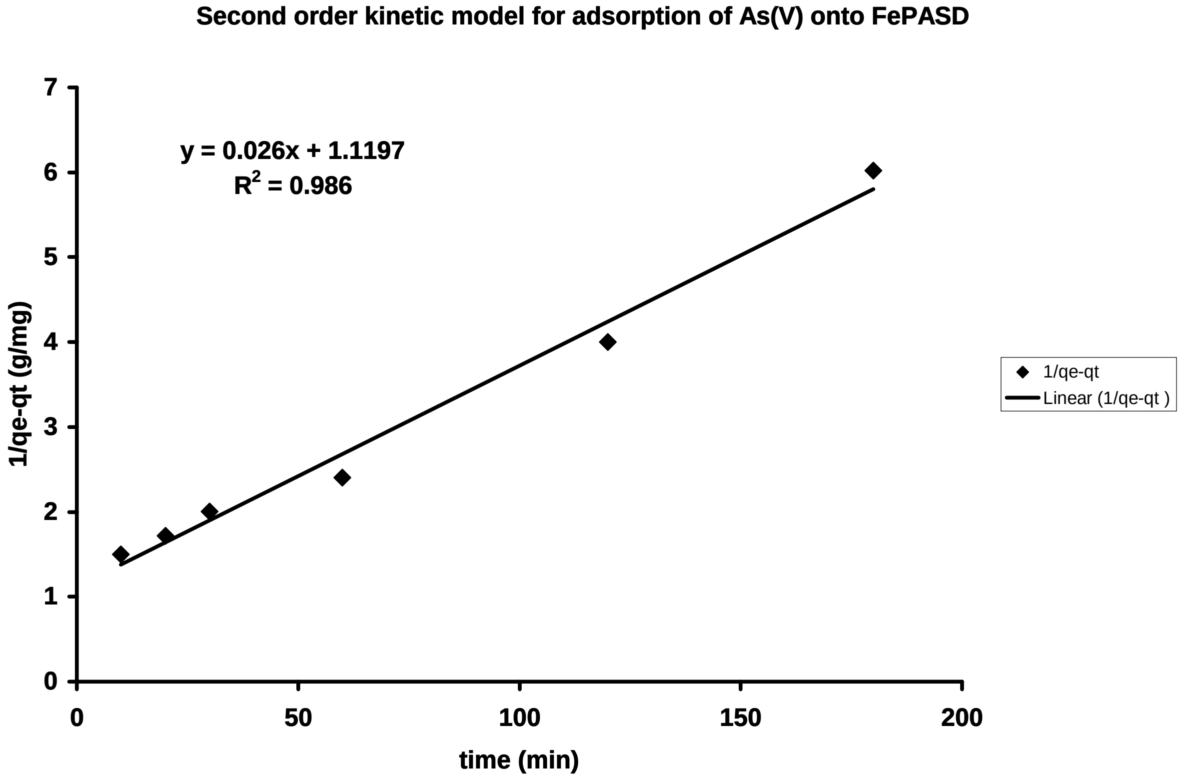


Figure 8B^{22}: Second Order Kinetic Model for Adsorption of As (V) onto FePASD.

From the kinetic plots of As (III) and As (V) for both the adsorbents and table 15, it can be observed that the correlation coefficients (R^2) for pseudo first order were found to be higher than that of pseudo-second order and second order kinetics for both adsorbents FePDSD and FePASD.

According to pseudo first order model, the plot of log q_e-q_t versus‘t’ gives a straight line with negative slope value. Therefore, the adsorption of As (III) and As (V) onto FePDSD and FePASD follows the pseudo-first order kinetic model.

3.8 Comparison Of The Maximum Adsorption Capacity(q_{max})

Comparison of the maximum adsorption capacity (q_{max}) of the FePDSD and FePASD with earlier investigated adsorbents are tabulated below. The results reveal that the prepared saw dusts posses higher potentiality towards the adsorptive removal of As (III) and As (V) from aqueous solution.

S.N.	Adsorbent and Species	q_{max} (mg/g)	Source
1	Palm bark towards As (V)	2.23	[50]
2	Iron oxide coated sand towards As (III)	0.029	[59]
3	Iron impregnated activated carbon towards As (V)	0.024	[47]
4	Activated carbon towards As (V)	1.05	[60]
5	Iron oxide coated cement towards As (III)	0.69	[61]
6	FePDSD towards As (III)	1.334	[This work]
7	FePASD towards As (III)	1.667	[This work]
8	FePDSD towards As (V)	3.646	[This work]
9	FePASD towards As (V)	2.631	[This work]

4 CONCLUSIONS

In the present work, the removal of As (III) and As (V) from easily available, low cost adsorbents, Dalbergia sissoo & Arundo donax sawdusts'chemically modified form were investigated and their efficiencies for removal of As (III) and As (V) were compared. Basic adsorption experiments indicated that the adsorption of As (III) and As (V) by FePDSD and FePASD was an adsorbate, adsorbent dependent process and the optimum adsorption capacity for the FePDSD and FePASD were achieved at pH 9, & 7 for As (III) and at pH 3, & 5 for As (V) respectively at an initial concentration of 1 mg/l. The equilibrium contact times for the sorption of As (III) onto FePDSD and FePASD were found to be 300 minutes and 360 minutes where as for As (V) were 240 minutes and 240 minutes respectively. The optimum doses of FePDSD and FePASD for As (III) & As (V) were 225 mg, & 200 mg and 75 mg, & 125 mg respectively. The maximum adsorption capacities were found to be 1.334 mg/g & 1.667 mg/g for As (III), 3.646 mg/g & 2.631 mg/g for As (V) with FePDSD and FePASD respectively, signifying that both the bioadsorbents prepared were found to more efficient for the adsorptive removal of As (V) as compared to As (III) and results revealed that Langmuir adsorption isotherm model was found to be more applicable than Freundlich adsorption isotherm model for the better description of the adsorption behavior of both the As (III) and As (V) ion onto FePDSD and FePASD, signifying the surface homogenity with respect to active sites. The kinetic data was analyzed by pseudo-first order, pseudo-second order and second order kinetic models and it was found that the obtained data were best fitted by the pseudo-first order kinetic model.

Comparisons of the maximum adsorption capacity of the FePDSD and FePASD with earlier investigated adsorbents have shown that both bioadsorbents posses higher potentiality towards the adsorptive removal of As (III) and As (V) from aqueous media.

Hence it can be concluded that Dalbergia sissoo & Arundo donax sawdusts'and can be used as an efficient and economical material for the adsorptive removal of As (III) and As (V) from aqueous system.

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ANNEX

Table 1: Determination of λ_{max} for the Arsenomolybdenum blue complex

S. N.	Wavelength ;λ, in nm	Absorbance; A
1	800	0.23
2	810	0.24
3	820	0.25
4	830	0.26
5	840	0.27
6	850	0.26
7	860	0.24
8	870	0.23
9	880	0.21
10	890	0.18
11	900	0.16

Table 2: Calibration curve for the determination of total arsenic

S. N.	Concentration of As in ppb	Absorbance; A
1	0	0
2	100	0.03
3	200	0.06
4	300	0.09
5	400	0.12
6	500	0.15
7	600	0.18
8	700	0.21
9	800	0.24
10	900	0.27
11	1000	0.31

Table 3: Effect of pH on the adsorption of As (III) and As (V) onto FePDSD and FePASD

Initial arsenic concentration = 1 mg/l
Total volume of sample =50 ml
Amount of adsorbent =50 mg
Shaking time = 5 hours
contact time=24 hours

FePDSD		FePDSD		FePASD		FePASD	
As (III)		As (V)		As (III)		As (V)	
pH	% R	pH	% R	pH	% R	pH	% R
6	21.4	2	69.3	5	50	1	25
7	35.7	3	92.3	6	57.1	2	42.9
8	42.9	4	76.9	7	64.3	3	57.1
9	50	5	76.9	8	57.1	4	61.5
10	42.9	6	76.9	9	50	5	71.4
11	28.6	7	69.3	10	42.9	6	57.1
6	21.4			11	28.6	7	50

Table 4: Effect of adsorbent dose on the adsorption of As (III) and As (V) onto FePDSD and FePASD

Initial arsenic concentration = 1 mg/l
Total volume of sample = 50 ml
pH adjusted at optimum
Shaking time = 5 hours
Contact time= 24 hours

FePDSD		FePDSD		FePASD		FePASD	
As (III)		As (V)		As (III)		As (V)	
Dose (mg)	% R	Dose (mg)	% R	Dose (mg)	% R	Dose (mg)	% R
25	28.6	25	53.84	25	33.3	25	50
50	50	35	69.23	50	58.3	50	71.4
75	57.1	50	92.3	100	66.7	100	92.9
100	64.3	75	100	125	75	125	100
125	71.4	100	100	150	83.3	150	100
150	78.6	125	100	175	91.7	175	100
175	85.8	150	100	200	100	200	100
200	92.9			225	100	225	100
225	100			250	100	250	100
250	100						
275	100						
300	100						

Table 5: Effect of contact time on the adsorption of As (III) and As (V) onto FePDSD and FePASD

Initial arsenic concentration = 1 mg/l

Total volume of sample = 50 ml

pH adjusted at optimum

Adsorbent dose = 50 mg

FePDSD		FePDSD		FePASD		FePASD	
As (III)		As (V)		As (III)		As (V)	
Time (min)	q_t (mg/g)	Time (min)	q_t (mg/g)	Time (min)	q_t (mg/g)	Time (min)	q_t (mg/g)
10	0.083	10	0.333	10	0.167	10	0.167
30	0.166	20	0.417	30	0.25	20	0.25
60	0.25	30	0.5	60	0.333	30	0.334
120	0.333	60	0.583	120	0.416	60	0.417
180	0.416	120	0.75	180	0.5	120	0.583
240	0.5	180	0.833	240	0.583	180	0.667
300	0.583	240	1	300	0.666	240	0.833
360	0.583	300	1	360	0.75	300	0.833
1440	0.583	360	1	1440	0.75	360	0.833
2880	0.583	1440	1	2880	0.75	1440	0.833
		2880	1			2880	0.833

Table 6: Adsorption isotherm for the adsorption of As (III) onto FePDSD

Volume of sample = 50 ml
Amount of adsorbent =50 mg
Shaking time = 5 hours
pH = 9
Contact time = 24 hours

S.N.	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	C_e/q_e (g/l)	log C_e	log q_e
1	1.166	0.583	0.583	1	-0.234	-0.234
2	2.333	1.583	0.75	2.11	0.199	-0.124
3	4.166	3.333	0.833	4	0.522	-0.079
4	6	5	1	5	0.698	0
5	8	6.666	1.334	4.997	0.823	0.125
6	10	8.75	1.25	7	0.942	0.096
7	12.28	10.964	1.316	8.331	1.039	0.199
8	14.062	12.728	1.334	9.541	1.104	0.125

Table 7: Adsorption isotherm for the adsorption of As (V) onto FePDSD

Volume of sample = 50 ml

Amount of adsorbent =50 mg

Shaking time = 5 hours

pH = 3

Contact time = 24 hours

S.N.	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	C_e/q_e (g/l)	log C_e	log q_e
1	1.083	0.083	1	0.083	-1.08	0
2	2.166	0.916	1.25	0.732	-0.038	0.096
3	4	2.166	1.834	1.181	0.335	0.263
4	6	3.333	2.667	1.249	0.522	0.426
5	8	5	3	1.666	0.698	0.477
6	10	6.666	3.334	1.999	0.823	0.522
7	12.28	8.771	3.509	2.499	0.943	0.545
8	14.062	10.416	3.646	2.856	1.017	0.561
9	16.071	12.5	3.571	3.5	1.096	0.552

Table 8: Adsorption isotherm for the adsorption of As (III) onto FePASD

Volume of sample = 50 ml

Amount of adsorbent =50 mg

Shaking time = 5 hours

pH = 7

Contact time = 24 hours

S.N.	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	C_e /q_e (g/l)	log C_e	log q_e
1	1	0.416	0.584	0.712	-0.38	-0.233
2	2.333	1.333	1	1.333	0.124	0
3	3.111	2	1.111	1.8	0.301	0.045
4	4.166	2.833	1.333	2.125	0.452	0.124
5	5.185	3.703	1.482	2.498	0.568	0.17
6	6	4.333	1.667	2.599	0.636	0.221
7	7	5.333	1.667	3.666	0.726	0.221
8	8	6.333	1.667	3.799	0.801	0.221
9	10	8.333	1.667	4.998	0.92	0.221

Table 9: Adsorption isotherm for the adsorption of As (V) onto FePASD

Volume of sample = 50 ml

Amount of adsorbent =50 mg

Shaking time = 5 hours

pH = 5

Contact time = 24 hours

S.N.	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	C_e /q_e (g/l)	log C_e	log q_e
1	1.166	0.333	0.833	0.399	-0.477	-0.079
2	2.166	1	1.666	0.857	0	0.066
3	4.166	2.333	1.833	1.272	0.367	0.263
4	6.333	4.333	2	2.166	0.636	0.301
5	8	5.666	2.334	2.427	0.753	0.368
6	10	7.5	2.5	3	0.875	0.397
7	12.28	9.649	2.631	3.667	0.984	0.42
8	14.062	11.458	2.604	4.4	1.059	0.415

Table 10: Kinetic data for the adsorption of As (III) onto FePDSD

Volume of sample = 50 ml

Amount of adsorbent= 50 mg

Initial concentration taken = 1 mg/l

pH = 9

Time; t(min.)	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	t/q_t (min/mg/g)	1/qe-qt (g/mg)	Log qe-qt (mg/g)
10	1.166	1.083	0.083	120.48	2	-0.301
30	1.166	1.000	0.166	180.72	2.398	-0.379
60	1.166	0.916	0.250	240	3.003	-0.477
120	1.166	0.833	0.333	360.36	4	-0.602
180	1.166	0.750	0.416	432.692	5.988	-0.777
240	1.166	0.666	0.500	480	12.048	-1.08
300	1.166	0.583	0.583	514.579		
360	1.166	0.583	0.583	617.495		
1440	1.166	0.583	0.583	2469.98		

Table 11: Kinetic data for the adsorption of As (V) onto FePDSD

Volume of sample = 50 ml

Amount of adsorbent= 50 mg

Initial concentration taken = 1 mg/l

pH = 3

Time; t(min.)	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	t/q_t (min/mg/g)	1/qe-qt (g/mg)	Log qe-qt (mg/g)
10	1.083	0.750	0.333	30.03	1.499	-0.175
20	1.083	0.666	0.417	47.961	1.715	-0.234
30	1.083	0.583	0.500	60	2	-0.301
60	1.083	0.500	0.583	102.915	2.398	-0.379
120	1.083	0.333	0.750	160	4	-0.602
180	1.083	0.250	0.833	216.086	5.988	-0.777
240	1.083	0.083	1.000	240		
300	1.083	0.083	1.000	300		
360	1.083	0.083	1.000	360		
1440	1.083	0.083	1.000	1440		

Table 12: Kinetic data for the adsorption of As (III) onto FePASD

Volume of sample = 50 ml

Amount of adsorbent= 50 mg

Initial concentration taken = 1 mg/l

pH =7

Time; t(min.)	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	t/q_t (min/mg/g)	qe-qt (mg/g)	1/qe-qt (g/mg)	Log qe-qt (mg/g)
10	1.083	0.916	0.167	59.88	0.583	1.715	-0.234
30	1.083	0.833	0.25	120	0.5	2	-0.301
60	1.083	0.75	0.333	180.18	0.417	2.398	-0.379
120	1.166	0.75	0.416	288.46	0.334	2.994	-0.476
180	1.166	0.666	0.5	360	0.25	4	-0.602
240	1.166	0.583	0.583	411.66	0.167	5.988	-0.777
300	1.166	0.5	0.666	450.45	0.084	11.904	-1.075
360	1.166	0.416	0.75	480	0		
1440	1.166	0.416	0.75	1920	0		

Table 13: Kinetic data for the adsorption of As (V) onto FePASD

Volume of sample = 50 ml

Amount of adsorbent= 50 mg

Initial concentration taken = 1 mg/l

pH = 5

Time; t(min.)	Initial concentration; C_i (mg/l)	Equilibrium concentration; C_e (mg/l)	Amount adsorbed; q_e (mg/g)	t/q_t (min/mg/g)	qe-qt (mg/g)	1/qe-qt (g/mg)	Log qe-qt (mg/g)
10	1	0.833	0.167	59.88	0.667	1.499	-0.175
20	1	0.75	0.25	80	0.583	1.715	-0.234
30	1	0.666	0.334	89.82	0.499	2.004	-0.301
60	1	0.583	0.417	143.884	0.416	2.403	-0.38
120	1.083	0.5	0.583	205.831	0.25	4	-0.602
180	1.083	0.416	0.667	269.865	0.166	6.024	-0.779
240	1.166	0.333	0.833	288.115	0		
300	1.166	0.333	0.833	360.144	0		
360	1.166	0.333	0.833	432.172	0		
1440	1.166	0.333	0.833	1728.69	0		

Table 14: Langmuir and Freundlich Parameters for the Adsorption of As (III) and As (V) onto FePDSD and FePASD

Species	Adsorbents	q_m(mg/g)	Langmuir isotherm			Freundlich isotherm		
		Exptl. Maxima	q_m(mg/g)	b(L/mg)	R^2	K(mg/g)	1/n	R^2
As (III)	FePDSD	1.334	1.506	0.586	0.978	0.654	0.310	0.918
As (III)	FePASD	1.667	1.902	0.886	0.986	0.886	0.373	0.957
As (V)	FePDSD	3.646	4.081	0.620	0.978	1.744	0.293	0.904
As (V)	FePASD	2.631	2.919	0.738	0.993	1.232	0.339	0.979

Table 15: Pseudo First Order Reaction Rate Constants and Correlation Coefficients for the Adsorption of As (III) and As (V) onto FEPDSD and FePASD

Species	Adsorbent	Pseudo First Order	
		K_1 min^{-1}	R^2
As (III)	FePDSD	7.369☒ 10^{-3}	0.978
As (III)	FePASD	5.987☒ 10^{-3}	0.966
As (V)	FePDSD	8.060☒ 10^{-3}	0.992
As (V)	FePASD	8.060☒ 10^{-3}	0.992