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Adsorption Isotherm, Thermodynamic and Kinetic Study of Arsenic (III) on Iron Oxide Coated Granular Activated Charcoal

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Abstract

In this paper, adsorption of arsenic (As) (III) as arsenite on iron oxide coated granular activated charcoal (FeOGAC) has been studied. Percentage adsorption of As (III) on FeOGAC was determined with respect to pH, contact time and adsorbent dose. The study revealed that the removal of As (III) was best achieved at pH range from 7.5 to 9.5. The initial As (III) concentration (100 µg/L) came down to less than 10 µg/L at contact time 90 min with adsorbent dose of 7.5g/50mL. The adsorption was studied for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The Langmuir isotherm model was found to be fitted well. During the study the thermodynamic parameters like enthalpy change (ΔH°), free energy change (ΔG°), entropy change (ΔS°) and activation energy (E_a) were determined for the better understanding of the adsorption process. The adsorption was found to be kinetically pseudo-second order controlled process.

Keywords: Arsenic, iron oxide, granular activated charcoal, adsorption, kinetic.

Introduction

Water is one of the most essential requirements for all life on earth and it is considered as very important resource for human civilization. Safe source for pure and affordable water is certainly one of the basic humanitarian goals, and is identified as a major global challenge for the 21st century. Water contamination is a most important critical issue facing the world due to an increase in population growth and has become a serious threat to environmental and human health. Therefore, decontamination of polluted water is become one of the most important environmental matter in the recent decade.

The availability of arsenic in groundwater specially in drinking water, is causing a major environmental and health issue[1,2] in several developing regions[3-5]. The minimum lethal dose for adult humans for various compounds has been reported to be 100 to 200 mg[6]. Various effects like carcinogenic, cardiovascular, respiratory, dermal, gastrointestinal, mutagenic etc. may be occurred due to short-term exposure to arsenic and also it may disturb the immune system of our body. Cancer of the skin, kidney, bladder, lungs, nasal passages, liver and prostate may be resulted due to long-term exposure to arsenic. All these health problems occur mainly due to the consumption of drinking waters containing high dose of arsenic.

Arsenic pollution has been reported recently in USA, China, Chile, Bangladesh, Taiwan, Mexico, Romania, United Kingdom, Argentina, Poland, Canada, Hungary, New Zealand, Vietnam, Japan and India[7]. In India, NE states along with Jharkhand, Bihar, West Bengal, Madhya Pradesh, Uttar Pradesh, etc. are badly affected by groundwater contaminated with arsenic [8-11]. Thus, the World Health Organization (WHO, 2006) the United States Environmental Protection Agency (USEPA, 2009) and also Turkish Standards Institute (TSE-266, 2005) have applied the maximum allowable level of arsenic in drinking water as 10 µg/L (10 ppb).

Arsenic contamination of water systems is mainly occurs from natural and anthropogenic sources[12,13]. Beside these, another primary contamination source of arsenic is the industrial wastewater. Arsenic in aqueous systems exists in both organic and inorganic forms; inorganic arsenic is mostly found in natural water systems. In general inorganic arsenic is more poisonous to loving systems than organic arsenic[14]. Generally, in natural aqueous systems inorganic arsenic has two different oxidation states, i.e. trivalent (+3) and pentavalent (+5)[15,16]. The mobility of arsenical forms in waters is very dependent on pH, Eh conditions and presence of different chemical species[12] Pentavalent arsenic [As (V), arsenate] is stable in oxidative condition and exists as a monovalent ($H_2AsO_4^-$) or divalent ($HAsO_4^{2-}$) anion, while trivalent arsenic [As (III), arsenite] is stable in reductive conditions [17] and exists as an uncharged ($H_3AsO_3^0$) or anionic species ($H_2AsO_3^-$). Inorganic As(III) is approximately ten times more toxic than As(V) [18]. Recent report [19] reveals that the toxicity order of arsenic is as follows: inorganic As^{3+}>organic As^{3+}>organic As^{5+}> inorganic As^{5+} [20,21].

In the last two decades huge attention has gained for the development of cost effective technologies to remove arsenic along with other heavy metals from drinking water. During this period several physiochemical techniques such as adsorption, ion-exchange or chelation, lime softening, reverse osmosis (membrane techniques), coagulation and precipitation have been applied to remove arsenic as well as other heavy metals from aqueous systems[22-34]. But these techniques have several drawbacks like incomplete metal removal, high capital and operational cost or the disposal of the residual metal sludge, and sometimes are not suitable for small-scale industries. Among these technologies, adsorption processes are effective techniques and they have long been used in the water and wastewater industries to remove inorganic and organic pollution for its ease of handling, minimal sludge production, cost effectiveness and its regeneration capability[1,35]. The technique is also popular because of the availability of a wide range of adsorbents such as activated alumina, activated carbon, fly ash, ferric hydroxide, chitosan-coated biosorbent, oxides, clay minerals and zero valent iron[26-40]. Among all types of conventional and non-conventional adsorbents, granular or powdered activated carbon is the most widely used adsorbent for arsenic removal[37] because of their high surface area, micro/mesoporous structure and significant adsorption capacity. Activated carbon modified with iron has been used for the removal of various contaminants from water [41-43]. However, some of these processes are not economic or require the control of pH and/or other parameters to achieve the optimum arsenic removal; therefore, a more effective and economical technique would be highly desirable.

Arsenic removal from drinking water using iron compounds has been reported by several authors[44-46]. Elementary iron[40-42], granular iron hydroxides and ferrihydrites[50-53] have been proposed for the arsenic decontamination of water. Most of the adsorption processes investigated so far was reported in the review of Mohan and Pittman[28].

In the present study experiments were carried out to evaluate the performance of iron oxide coated granular activated charcoal (FeOGAC) for As (III) removal. The process parameters such as effect of adsorbent dose, pH, initial arsenic concentration and contact time were studied. Four isotherms like Langmuir, Freundlich Temkin and Dubinin-Radushkevich models were studied. Various thermodynamic parameters were also calculated for the process to complete the investigation for efficacy of FeOGAC in adsorption of arsenic from contaminated water. The process was also analysed for kinetic models like pseudo first order, pseudo second order, Elovich and Intra-particle diffusion models at different experimental conditions.

Material and Methods

Materials: The granular activated carbon (GAC) used in this study was obtained from Clariant Chemicals. The GAC, prior to use in this study was backed in an oven at 200°C for 24 hrs and washed several times with deionised water. After washing the GAC was completely dried in oven at 110°C, cooled in desiccators, and stored at room temperature in a covered glass container until further use. The As_2O_3, $FeCl_3$, HCl and NaOH etc. used were LR grade from Merck and used as such. Stalk solution of 1000 µg/L arsenic solution was prepared by dissolving 0.00132 g of As_2O_3 in 1000 ml of deionised water with a pallet of NaOH. All the instruments used during the experiments were calibrated as per standard procedure. The initial pH of the arsenic solutions was adjusted using NaOH (0.1 M) and/or HCl (0.1M) solutions as and when necessary and analysed by Cyberscan pH 510 (Eutech) instrument. The determination of concentration of arsenic (III) was done using AA 7000 Atomic Absorption Spectrophotometer (Labindia) having detection limit 5µg/L.

Adsorbent Preparation: Iron oxide coated GAC (FeOGAC) was prepared by mixing 200 g of GAC with 100 ml of 2M $FeCl_3$ solution and gradually adding 5M NaOH solution (nearly 180 ml) under slow agitation until the pH of the final mixture was attained at around 11.0. The mixture was then allowed to settle for few hours so air trapped in pores could escape. After that the mixture was completely dried in an oven at 95°C, allowed to cool to room temperature, and washed several times with deionised water to remove excess Fe-oxide. The FeOGAC thus obtained was then dried in an oven at 100°C and stored at room temperature in air tight glass container until use.

Adsorption Experiments: The experiments were carried out by batch process to obtain rate and equilibrium data. Two parallel experiments were conducted using control granular activated charcoal (GAC) and FeOGAC (figure-1) separately to compare few parameters. The reaction mixture consisting of 50 mL known concentration of As (III) solution and known quantity of adsorbent was shaken in a temperature controlled orbital shaker with shaken speed of 175 rpm at three different temperatures of 298 K, 303 K and 308 K. The effect of adsorbent dose was studied by varying the adsorbent dose from 2.5 to 10g/50 ml and maintaining pH of the solution at 7.5 with a constant contact time of 90 min. In this study the spiked water arsenic concentration was fixed at 100 µg/L. The study of the effect of initial pH of the solutions on arsenic adsorption by the FeOGAC was done by using 100 µg/L of the adsorbent at varying pH of the solutions. The effect of contact time was studied with varying contact time from 30 to 180 minutes keeping pH of the solutions and dose of the adsorbent constant. The effect of initial arsenic concentration in feed water was studied with various adsorbent doses with varying initial arsenic concentration from 50 to 250 µg/L. The adsorption isotherm was also performed by using 7.5g of FeOGAC with 50 mL spiked water at different initial concentrations of arsenic. The kinetics and thermodynamic parameters for arsenic adsorption on FeOGAC were established by conducting the experiments at different contact times and at three different temperatures respectively.

Figure-1
Image of FeOFAC

Desorption experiments: To determine the reusability of the FeOGAC samples the adsorption/desorption cycles were carried out. The saturated FeOGAC was prepared by treating 30 g of FeOGAC with 200 ml of 250 µg/L arsenic solution under agitation for about 3 hours at shaken speed of 175 rpm. Then filtered the arsenic saturated FeOGAC and dried in oven 100°C. The arsenic saturated FeOGAC (7.5 g) was agitated for about 3 hours at shaken speed of 175 rpm with 100 mL of NaOH solution (0.1, 0.3 and 0.5 M solution were used separately). The aqueous phases were then separated and concentrations of arsenic in that phase were determined.

Results and Discussion

Effect of adsorbent dose: The effect on arsenic (III) removal at fixed initial arsenic (III) concentration 100 µg/L by adsorbent dose is shown in figure-2. It shows that the adsorption efficiency of arsenic (III) from the solution increases rapidly with increase in adsorbent dose from 2.5-7.5g/50 mL; a marginal increase is observed on further increase in the adsorbent dose for both GAC and FeOGAC. The increase in the removal efficiency of arsenic (III) may be attributed to the fact that with the increase in adsorbent dose, available surface for adsorption increases for the solute to be adsorbed[54,55].

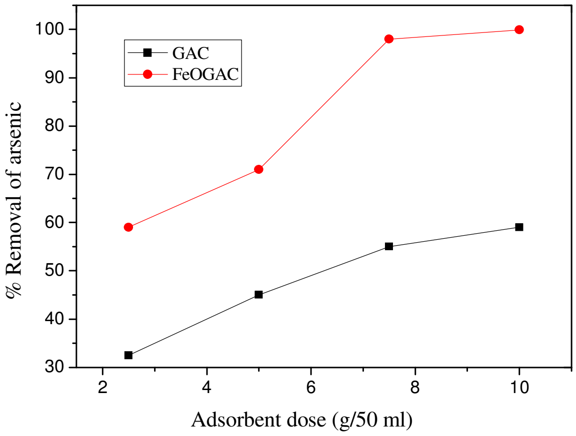


Figure-2
Plots of percent removals of arsenic versus adsorbent dose

Effect of pH: The effect of pH on the adsorption of arsenic (III) onto FeOGAC and GAC were studied in the pH range of 5.5 to 11.5. Different pH solutions were prepared by adding dilute NaOH or HNO_3 solutions drop wise to achieve pH values. The figure-3 reveals that the efficiency of arsenic (III) removal increases with increasing pH from 5.5 to 7.5 after that the marginal increase was observed. In the study highest arsenic removal was achieved at pH range from 7.5 to 9.5. The results suggested that the removal efficiency of FeOGAC and GAC were found to decrease both at lower and higher than pH 9.5. This may be due to the fact that highly and extreme low protonated surface of FeOGAC and GAC are not favourable for arsenic (III) adsorption [56]. The variation of adsorption with respect to the initial solution pH can be understood from the zero point charge (pHzpc) of the adsorbent. pHPZC is the point of pH, at which the solid surface of the adsorbent has the net zero charge. The pHzpc of the FeOGAC is determined by plotting initial pH of the working solution versus the final pH of the solution. The pHzpc is the pH corresponds to the point at which the curve crosses the straight line of plot Initial pH=Final pH (figure-4). The pHzpc was found to be at pH 8.2. At pH >pHzpc the surface of FeOGAC become negatively charged and the As(III) is positively charged. In this situation the electrostatic attraction between the metal ions and the adsorbent surface increases resulting in increased adsorption of As(III) on to the FeOGAC surface is observed. But in the case, at pH<pHzpc the surface of FeOGAC become positively charged leading to a decreased adsorption of the As(III) due to the higher concentration of the H^+ ions in the solution that will compete with the positively charged As(III) ions for the active sites.

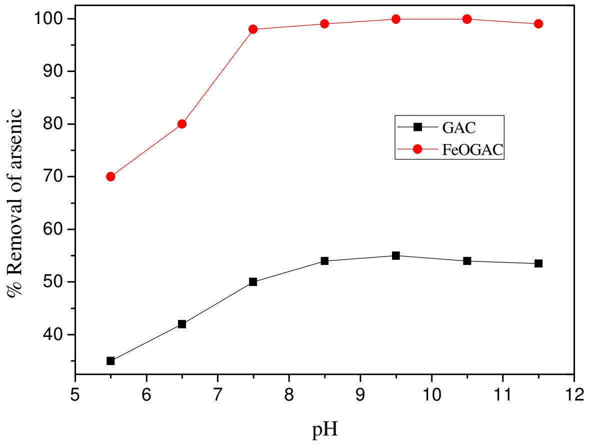


Figure-3
Plots of percentage removal of arsenic versus pH

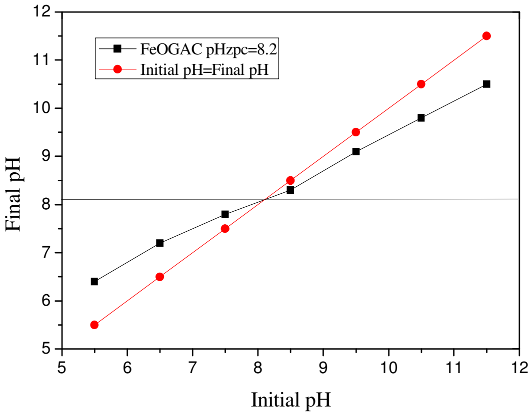


Figure-4
Determination of point zero charge (pHpzc) of FeOGAC

Effect of contact time: Effect of duration of agitation time was studied with various adsorbent doses by varying the agitation time using feed water containing 100 µg/L of arsenic. From the figure-5 it is clear that adsorption efficiency increases with increasing the contact time, reaching nearly maximum removal at contact time of 90 minutes; thereafter removal becomes nearly constant for both the cases of FeOGAC and GAC. The reason may be due to the fact that, initially all adsorbent sites were empty and the arsenic concentration was high. Afterward, the arsenic (III) adsorption capacity of the adsorbent was decreased significantly due to the decrease in available adsorption sites as well as arsenic concentration [57]. It was also observed that the removal efficiency increases with increasing the adsorbent dose. The fact has already been discussed during the discussion of effect of adsorbent dose.

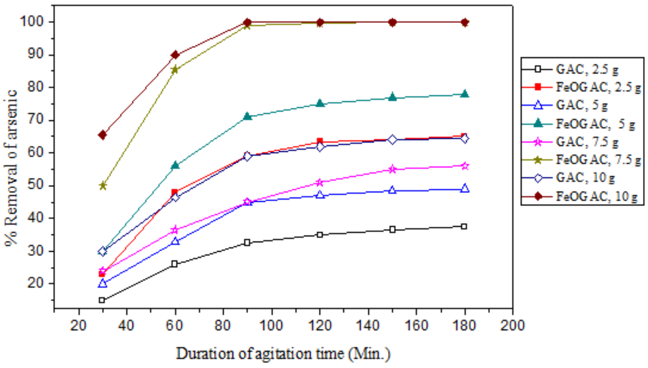


Figure-5

Effect of duration of agitation time on the adsorption of As (III) onto FeOGAC using various adsorbent doses

Effect of initial arsenic concentration: The influence of initial arsenic concentration in feed water was studied using various adsorbent doses by varying initial arsenic (III) concentration. Figure-6 reveals that adsorption efficiency is higher at lower initial arsenic concentration (50 µg/L) and a slow decrease in arsenic (III) adsorption by FeOGAC as well as GAC were observed with increasing initial arsenic (III) concentration. The reason for the decrease in As (III) removal efficiency at higher initial concentration may be due to saturation of the active sites of the adsorbent by the arsenic (III) and hence, further increasing the arsenic (III) concentration not leading to the increase in absorption significantly [58]. From the result it is revealed that for 50 ml feed water containing maximum 100 µg/L arsenic the minimum effective adsorbent dose to reduce the arsenic content to less than 10 µg/L (WHO limit) is 7.5 g.

Desorption Study: The experimental results (table-1) from the desorption study revealed that trend of desorption percentage at different concentration of NaOH is in the 0.1M < 0.3M < 0.5M. The maximum desorption of arsenic was found to be 71.4 % with 0.5 M NaOH solution. From the study it is revealed that the used FeOGAC can be regenerated satisfactorily and reused for further arsenic (III) removal due to which the process is seems to be cost effective and suitable for the application in the rural areas.

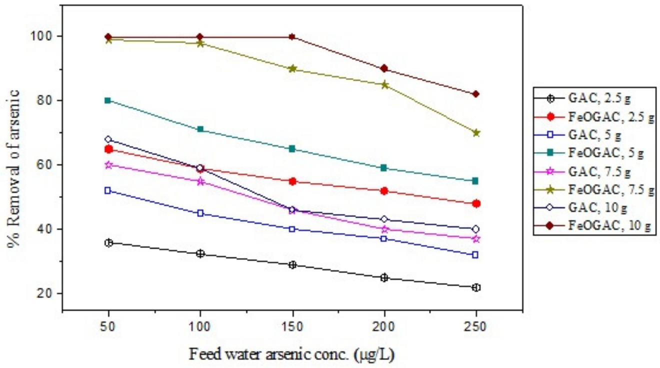


Figure-6

Effect of initial arsenic concentration on the percentage removal of As (III) using various adsorbent doses

Table-1

Desorption Study of FeOGAC

Adsorbet adsorbed by adsorbent at saturated point (µg/g)	Eluent used	Conc. of eluent (M)	Adsorbet eluted from adsorbent (µg/g)	Regeneracy of adsorbent (%)
1.4	NaOH	0.1	0.42	30
1.4	NaOH	0.3	0.59	42
1.4	NaOH	0.5	1.0	71.4

Adsorption Isotherms Study: Langmuir isotherm: The main assumptions of the Langmuir adsorption isotherm are; i. The adsorption is mainly due to saturated monolayer adsorption of adsorbate molecules on the adsorbent surface, ii. the energy of adsorption is constant and iii. in the plane of adsorbent surface, no transmigration of adsorbate molecules.

The Langmuir adsorption isotherm[59] can be expressed by the equation given below:

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

Or $$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$$

Where; q_e (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent, C_e (µg/L) = the unabsorbed adsorbrent concentration in solution at equilibrium condition, q_m (µg/g) = the maximum amount of adsorbate adsorbed per unit mass of adsorbent to form a complete monolayer on the surface b (L/µg)= Langmuir constant.

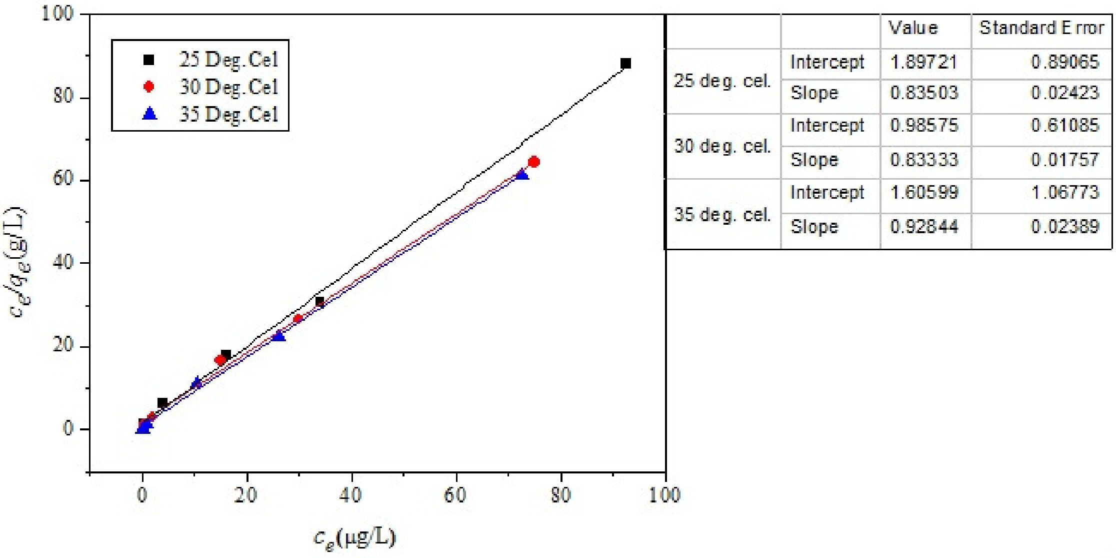
The Langmuir adsorption model was adopted for the determination of maximum arsenic uptake (q_m) at different arsenic (III) concentration (50 µg/L- 250 µg/L). The linear plot of C_e/q_e versus C_e (figure-7) with greater correlation coefficient (R^2) value indicates the monolayer adsorption on FeOGAC. The values of q_m and b were calculated from the slope and intercept respectively are presented in table-2. From the results it was observed that the maximum arsenic uptake (q_m) and the value of Langmuir constant (b), related to the affinity of the binding sites were increased with the increase of temperature.

Freundlich isotherm: Both the monolayer (chemisorption) and multilayer adsorption (physisorption) can be studied by the Freundlich adsorption isotherm. The isotherm considered the adsorption of the adsorbate onto the heterogeneous surface of an adsorbent[60]. The Freundlich isotherm[61] can be expressed by a linear equation as:

$$q_e = K_f C_e^{1/n}$$

Or $\log q_e = \log K_f + \frac{1}{n} \log C_e$

Where q_e (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent, K_f [µg/g (L/µg)$^{1/n}$] = a constant, sorption capacity of the adsorbent, n = favourability of the adsorption process, constant related to energy of intensity of adsorption.



		Value	Standard Error
25 deg. cel.	Intercept	1.89721	0.89065
	Slope	0.83503	0.02423
30 deg. cel.	Intercept	0.98575	0.61085
	Slope	0.83333	0.01757
35 deg. cel.	Intercept	1.60599	1.06773
	Slope	0.92844	0.02389

Figure-7
Langmuir isotherms of FeOGAC for arsenic adsorption at different temperatures

Table-2
Adsorption isotherms

		298°K	**303°K**	**308°K**
Adsorption isotherm	**Adsorption parameters**	**Values**		
Langmuir	q_m (µg/g)	1.0771	1.1773	1.2000
	b (L/µg)	0.5781	0.7696	0.8454
	R^2	0.9980	0.9968	0.9967
Freundlich	n	4.2141	4.1982	5.5835
	K_f [µg/g (L/µg)$^{1/n}$]	0.4272	0.4687	0.6058
	R^2	0.9350	0.9413	0.9774
Temkin	B	0.3534	0.3753	0.2816
	A (L/g)	18.7893	22.0525	269.841
	b (kJ/mol)	7.0107	6.7123	8.9458
	R^2	0.9434	0.977	0.9823
Dubinin-Radushkevich	q_D (µg/g)	0.9162	0.975	0.9772
	B_D (mol^2/kJ^2)	3x10^{-7}	3x10^{-7}	4x10^{-8}
	E_D (kJ/mol)	1.291	1.291	3.5355
	R^2	0.843	0.868	0.837

The value of K_f and n (table-2) were obtained from the linear plot (figure-8) of log q_e versus log C_e. The values of n lying between 1 and 10 indicating chemisorptions[62]. Isotherms with n >1 are known as L-type isotherms indicating a high affinity between the adsorbate and the adsorbent and is denotes the chemisorption[63]. The Freundlich isotherm constant, K_f, which is associated with the adsorption capacity of the adsorbent, increased with temperature, reflecting the endothermic adsorption process. The relatively high value of correlation coefficient (R^2) value indicates the satisfactory fitness of the data with the Freundlich isotherm model.

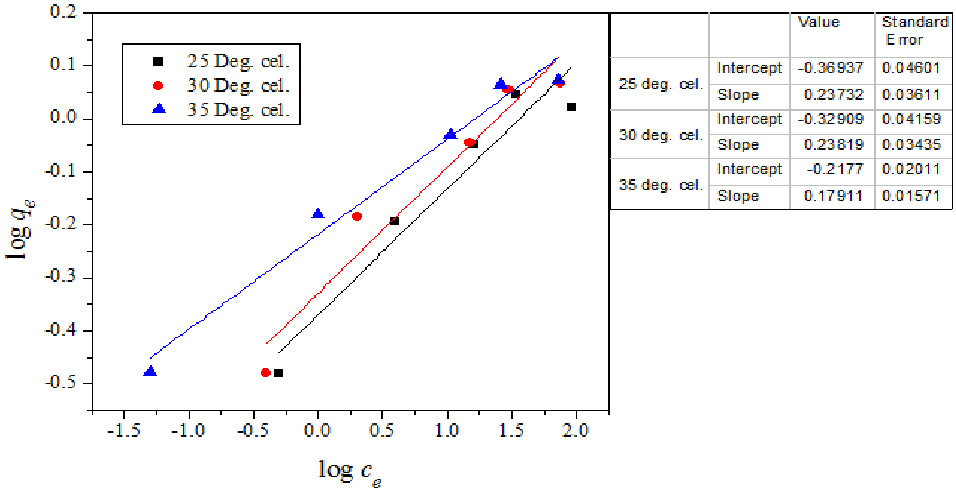
Temkin Isotherm: The Temkin isotherm model is based on the assumptions that the adsorption energy decreases linearly with the surface coverage, which is due to the adsorbent-adsorbate interactions. The Temkin isotherm model[64] is expressed by the linear equation as;

$$q_e = (\frac{RT}{b})\log(AC_e)$$

Or $q_e = B\log A + B\log C_e$

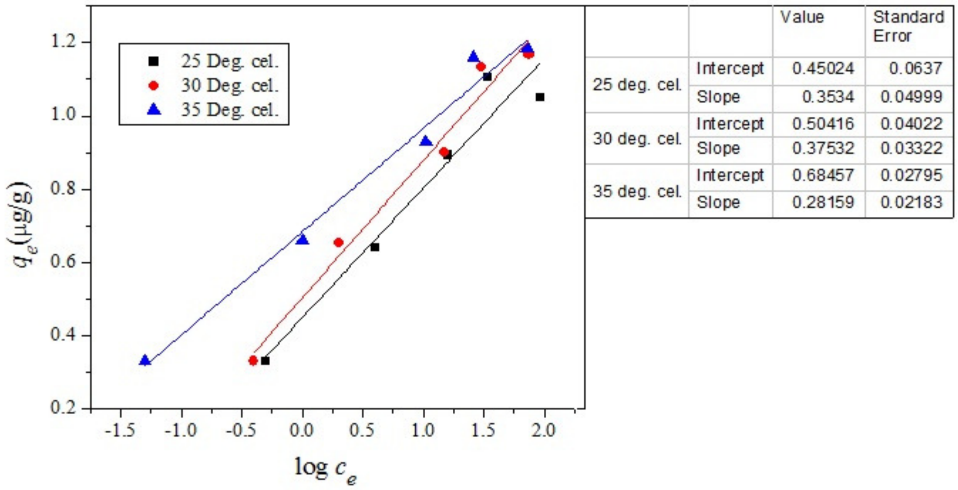
Where: $B = \frac{RT}{b}$, b (J/mol) = Temkin constant, related to heat of sorption, A (L/g) = Temkin isotherm constant also, called equilibrium binding constant, R = gas constant (8.314 J/mol.k), T (k) = absolute temperature.

The linear plot (figure-9) of q_e versus logC_e at different temperatures for Temkin adsorption isotherm, which consider the chemisorptions of an adsorbate onto the adsorbent[65], fitted satisfactorily with correlation coefficients (R^2) >0.94 (table-2). This supports the findings that the adsorption of arsenic onto FeOGAC is a chemisorption process[66].



		Value	Standard Error
25 deg. cel.	Intercept	-0.36937	0.04601
	Slope	0.23732	0.03611
30 deg. cel.	Intercept	-0.32909	0.04159
	Slope	0.23819	0.03435
35 deg. cel.	Intercept	-0.2177	0.02011
	Slope	0.17911	0.01571

Figure-8
Freundlich isotherms of FeOGAC for arsenic adsorption at different temperatures



		Value	Standard Error
25 deg. cel.	Intercept	0.45024	0.0637
	Slope	0.3534	0.04999
30 deg. cel.	Intercept	0.50416	0.04022
	Slope	0.37532	0.03322
35 deg. cel.	Intercept	0.68457	0.02795
	Slope	0.28159	0.02183

Figure-9
Temkin Isotherms of FeOGAC for arsenic adsorption at different temperatures

Dubinin Radushkevich (D-R) Isotherm: Dubinin–Radushkevich (D-R) isotherm model predicts that the adsorption process follows a pore filling mechanism and is expressed by a semi-empirical equation. The assumptions of the model are that the adsorption has a multilayer character, involves van der Waals forces and is applicable for physical adsorption processes[67]. The D-R isotherm model is presented linearly by the equation as given below;

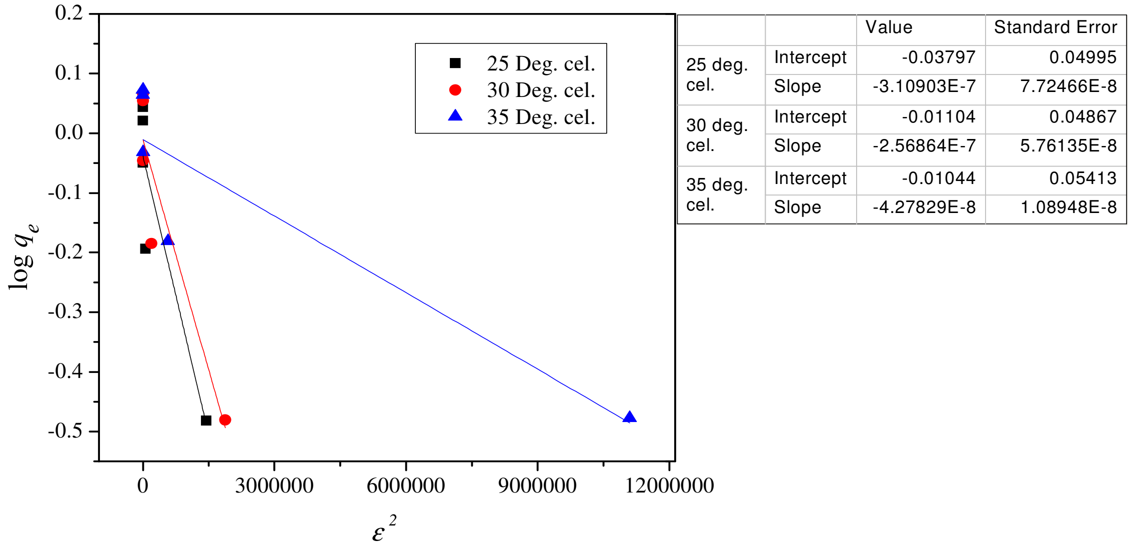
$$\log q_e = \log q_D - B_D \varepsilon^2$$

Where; $\varepsilon = RT\log(1+\frac{1}{C_e})$ q_D (µg/g) = theoretical saturation capacity, B_D (mol^2/kJ^2) = constant related to adsorption energy, R = gas constant (8.314 J/mol.K), T (k) = absolute temperature, $E_D = \frac{1}{\sqrt{2B_D}}$, E_D (kJmol^{-1}) = the mean energy of sorption , The magnitude of E_D furnishes the information on the nature of adsorption process i.e. physical/ chemical., From the plot (figure-10) log q_e versus ε^2 at different temperatures, it is revealed that the q_D values are not complying with the previously determined Langmuir isotherm q_m values. The correlation coefficients for the D-R isotherm are the lowest compared to those values of the other three isotherm models (table-2) suggest that the arsenic (III) adsorption onto FeOGAC is not a physical process[66].

Dimensionless equilibrium parameter (R_L): Dimensionless equilibrium parameter or Langmuir isotherm constant parameter (R_L), the essential characteristics of the Langmuir isotherm provides the valuable information on the adsorption efficiency of the isotherms process. The R_L can be related with Langmuir isotherm constant by the following equation[68];

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

Where b is the Langmuir isotherm constant and C_o is the initial arsenic concentration (µg/L). The shape of the isotherms can be predicted by the R_L value. The Langmuir isotherm is favourable if the value is $0 < R_L < 1$, if $R_L = 0$ then it is irreversible, if $R_L = 1$ it is linear and if $R_L > 1$ the isotherm is unfavourable. R_L values at different temperatures studied were calculated (table-3) and the values are ranges from 0.0047 to 0.0334, which implies that the Langmuir isotherm is favourable.



		Value	Standard Error
25 deg. cel.	Intercept	-0.03797	0.04995
	Slope	-3.10903E-7	7.72466E-8
30 deg. cel.	Intercept	-0.01104	0.04867
	Slope	-2.56864E-7	5.76135E-8
35 deg. cel.	Intercept	-0.01044	0.05413
	Slope	-4.27829E-8	1.08948E-8

Figure-10
Dubinin–Radushkevich (D-R) isotherms of FeOGAC for arsenic adsorption at different temperatures

Table-3
The R_L and χ^2values of arsenic adsorption onto FeOGAC

Temp	R_L values					χ^2 values for Adsorption kinetics	
(°K)	50 µg/L	100 µg/L	150 µg/L	200 µg/L	250 µg/L	Pseudo first order	Pseudo second order
298	0.0334	0.0170	0.0114	0.0086	0.0069	9.9459	0.7027
303	0.0253	0.0128	0.0086	0.0065	0.0052		
308	0.0231	0.0117	0.0078	0.0059	0.0047		

χ^2 (Chi square) analysis: The difference between the experimental and various models data can be measures with the help of Chi-square test analysis. Mathematically it can be expressed as:

$$\chi^2 = \sum \left[\frac{\left(q_{e.\exp} - q_{e.cal}\right)^2}{q_{e.cal}} \right]$$

Where, $q_{e,exp}$ is experimental equilibrium capacity data and $q_{e,cal}$ is the equilibrium capacity from a model. If data from the model are similar to experimental data, χ^2 value will be small and if they differ, χ^2 will be large[69].

The χ^2 values were calculated (table-3) for Pseudo first and Pseudo second order kinetic models. The lower χ^2 value (i.e. 0.7027) with respect to the pseudo-second order model revealed that arsenic (III) adsorption onto FeOGAC obeyed the pseudo-second order kinetics. The pseudo-first order model provided higher χ^2 values (i.e 9.9459) suggesting poor pseudo-first order fit to the data for arsenic (III) adsorption onto the FeOGAC.

Thermodynamic investigations: The thermodynamic parameters like enthalpy change (ΔH°), free energy change (ΔG°), entropy change (ΔS°) and activation energy (E_a) are the parameters, which determine the spontaneity of a process. A process will be spontaneous if there is a decrease in ΔG° value with increasing temperature [70]. The temperatures used in the thermodynamic study were 298, 303 and 308 K. The thermodynamic parameters were calculated based on the following equations:

$$\log b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} = -\frac{\Delta G^\circ}{RT}$$

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

Where: b is the equilibrium constant, R is the universal gas constant (8.314 J/mol K), and T is the temperature (K). The calculated values of the thermodynamic parameters are listed in the table-4. The positive enthalpy change, ΔH° (+ 12.629 kJ/mol), implies the endothermic nature of the adsorption process, due to which the adsorption efficiency increases with the increase of temperature. The positive entropy change, ΔS° (+ 0.0404 J/mol K), reveals that the randomness increases at the solid/liquid interface during the adsorption onto the FeOGAC. The positive and weak values of free energy change, ΔG° which is decreasing with increasing temperature, indicates that the process is favourable but non spontaneous.

The sticking probability, $S^*$of an adsorbate on adsorbent can be expressed by a modified Arrhenius-type equation related to the surface coverage (θ). The S^* is a function of the adsorbate/adsorbent system and it is the measure of the ability of an adsorbate to remain on the adsorbent indefinitely, [71] and it is expressed as;

$$S^* = (1-\theta)\exp-(\frac{E_a}{RT})$$

Or

$$\log(1-\theta) = \log S^* + \frac{E_a}{RT}$$

Where, θ is surface coverage, E_a is activation energy.

$$\theta = (1 - \frac{C_e}{C_o})$$

Where, C_o and C_e are the initial and equilibrium arsenic concentrations respectively.

From the plot of $\log(1-\theta)$ versus $\frac{1}{T}$ with intercept of $\log S^*$ and slope of $\frac{E_a}{R}$, the value of S^* and E_a were calculated (table-4). The value of S^* was found to be 1.17×10^{-20} which is very close to zero indicates that adsorption mechanism follows chemisorptions [72] whereas the determined activation energy (E_a) for the process was 45.934 kJ/mol.

Adsorption kinetics: The adsorption mechanism of arsenic (III) onto FeOGAC was investigated by studying the pseudo first order, pseudo second order, Elovich and Intra-particle diffusion kinetic models at various experimental conditions.

Pseudo first order kinetic model: The linear form of pseudo-first-order kinetic model[73] is expressed as:

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

Where;K_1 (1/min)= rate constant, q_e (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent at equilibrium, q_t (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent at time t, t (min) = time.

Table-4
Thermodynamic parameter

	Thermodynamic parameters				
Temp. (K)	ΔG^o (KJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ /mol K)	E_a (kJ/mol)	S*
298	0.56	12.629	0.0405	45.934	1.17×10^{-20}
303	0.3575				
308	0.155				

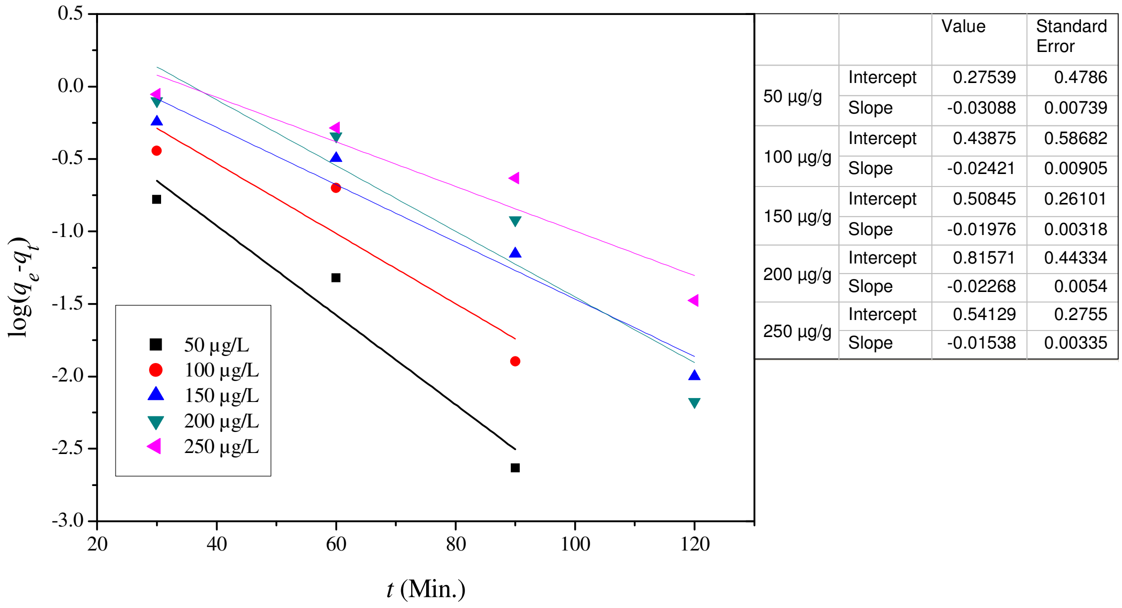
The Lagergren plots of $\log(q_e - q_t)$ versus *t* for various initial arsenic concentration viz. 50, 100, 150, 200 and 250 µgL^{-1} at 303 K are given in figure-11. The values of K_1 at five different initial arsenic concentrations were calculated from slopes of the respective linear plots and also the correlation coefficient (R^2) was computed and the values are given in table-5.

Pseudo second order model: The most popular pseudo second order kinetic model [74], linear form of equation is expressed as;

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

Where: K_2 (g/µg min.) = rate constant, q_e (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent at equilibrium, q_t (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent at time t

t (min) = time.



		Value	Standard Error
50 µg/g	Intercept	0.27539	0.4786
	Slope	-0.03088	0.00739
100 µg/g	Intercept	0.43875	0.58682
	Slope	-0.02421	0.00905
150 µg/g	Intercept	0.50845	0.26101
	Slope	-0.01976	0.00318
200 µg/g	Intercept	0.81571	0.44334
	Slope	-0.02268	0.0054
250 µg/g	Intercept	0.54129	0.2755
	Slope	-0.01538	0.00335

Figure-11
Lagergren plots of $\log(q_e - q_t)$ versus *t* for various initial arsenic concentrations

Table-5
Kinetic parameters for the adsorption of arsenic (III) on FeOGAC

C_o (µg/L)	q_e (µg/g	Pseudo first order kinetic model			Pseudo second order kinetic model			Elovich kinetic model			Intra-particle diffusion kinetic model		
		K_1 (1/min)	q_e (µg/g)	R^2	K_2 [g/(µg min)]	q_e (µg/g)	R^2	α [µg/(g min)]	B (g/µg)	R^2	K_{id} [µg/(g min$^{1/2}$)]	I (µg/g)	R^2
50	0.333	0.0712	1.885	0.9459	0.0830	0.4021	0.9767	1.3362	0.2115	0.8361	0.0193	0.1061	0.7292
100	0.666	0.0557	2.746	0.8773	0.0240	0.879	0.9659	0.3141	0.4976	0.8944	0.0465	0.1108	0.8187
150	0.970	0.0456	3.224	0.9508	0.0116	1.3729	0.9617	0.1502	0.7877	0.9327	0.0742	0.0747	0.8665
200	1.253	0.0523	6.542	0.8983	0.0063	1.9342	0.9377	0.0860	1.1019	0.9397	0.104	-0.0044	0.8774
250	1.4	0.0355	3.478	0.9132	0.0053	2.1838	0.9632	0.0752	1.2238	0.9693	0.1167	-0.032	0.9233

From the plot of $\frac{t}{q_t}$ versus *t* for arsenic adsorption on FeOGAC at different initial arsenic concentration viz. 50, 100, 150, 200 and 250 µgL^{-1} at 303 K, the experimental value of q_e and K_2 of the pseudo second order equation were obtained. The plot (figure-12) gives a straight line with higher correlation coefficient, R^2 values, which was higher than that of the observed pseudo-first-order model indicating the better fitness of the pseudo second order model. The values of q_e, K_2 and R^2 are shown in table-5. The value of q_e increases with the increase in initial arsenic concentration; this is due to the higher availability of arsenic to adsorb at higher initial arsenic concentration. The values of rate constant, K_2 decreases with increase with initial arsenic concentration which indicates the saturation of the FeOGAC with arsenic at higher initial arsenic concentration.

Elovich model: The equation of Elovich model is expressed [75] as below;

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t)$$

Where; α (µg/(g min) = Elovich coefficients represents initial adsorption rate, β (g/µg) = the adsorption coefficient, Assuming

$\alpha\beta_t >> 1$, $q_t = 0$, $t = 0$ and $q_t = q_t$ at $t = t$

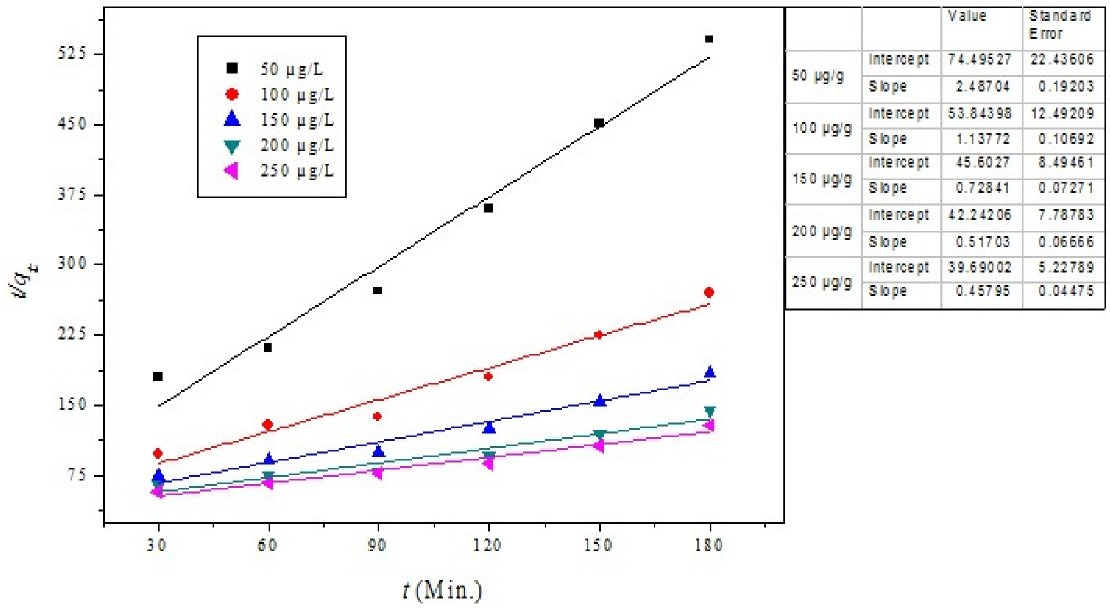
$$q_t = \beta \log(\alpha\beta) + \beta \log t$$

The figure-13 shows a plot of q_t versus log t, a linearization form of Elovich model at all concentrations studied. From the slope and intercept of the plot the constant β and the initial adsorption rate α were calculated. The results with the correlation coefficients are shown in Table-5. The comparatively low correlation coefficients for the Elovich kinetic model suggest that this adsorption system is not an acceptable for this system.

Intraparticle diffusion model: The intraparticle diffusion model is based on the assumptions that the adsorbate species are transported through intraparticle diffusion from the bulk of the solution into the solid phase and is often considered as the rate controlling step in many biosorption processes. The intraparticle diffusion model is expressed as[76,77],

$$q_t = K_{id} t^{1/2} + I$$

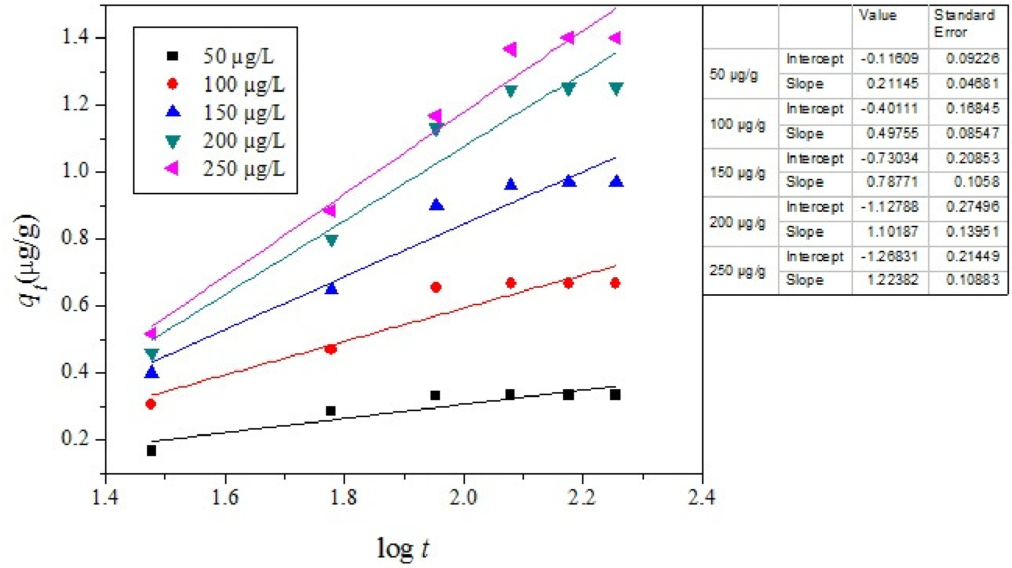
Where: q_t (µg/g) = the amount of adsorbed adsorbate per unit mass of adsorbent at time *t*, K_{id} (µg/(g min$^{1/2}$)= rate constant of Inter Particle Diffusion Model, t (min) = time, I = constant associated with the boundary layer thickness. According to this model, if we plot q_t versus $t^{1/2}$ it will give a straight line, and then the biosorption process is controlled by intraparticle diffusion. The larger values of intercept the greater is the boundary layer effect. Figure-14 show a plot of q_t versus $t^{1/2}$ at all concentrations studied. From the plot it was observed that the external surface adsorption was completed before 90 minute, and then the intraparticle diffusion control stage was attained and continues from 90 minute to 150 minute. Finally, final equilibrium adsorption started after 150 minute. The arsenic (III) was slowly transported via intraparticle diffusion into the particles and was finally retained in the micropores. The rate parameters along with the correlation coefficients are presented in table-5.



		Value	Standard Error
50 µg/g	Intercept	74.49527	22.43606
	Slope	2.48704	0.19203
100 µg/g	Intercept	53.84398	12.49209
	Slope	1.13772	0.10692
150 µg/g	Intercept	45.6027	8.49461
	Slope	0.72841	0.07271
200 µg/g	Intercept	42.24206	7.78783
	Slope	0.51703	0.06666
250 µg/g	Intercept	39.69002	5.22789
	Slope	0.45795	0.04475

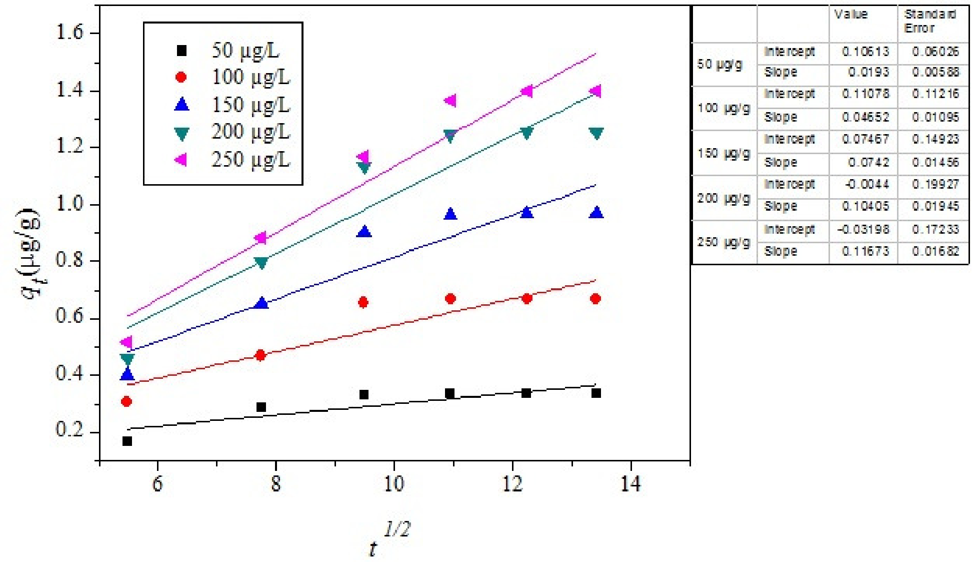
Figure-12

Plots of $\frac{t}{q_t}$ versus *t* for various initial arsenic concentrations



		Value	Standard Error
50 µg/g	Intercept	-0.11609	0.09226
	Slope	0.21145	0.04681
100 µg/g	Intercept	-0.40111	0.16845
	Slope	0.49755	0.08547
150 µg/g	Intercept	-0.73034	0.20853
	Slope	0.78771	0.1058
200 µg/g	Intercept	-1.12788	0.27496
	Slope	1.10187	0.13951
250 µg/g	Intercept	-1.26831	0.21449
	Slope	1.22382	0.10883

Figure-13
Plots of q_t versus log *t* for various initial arsenic concentrations



		Value	Standard Error
50 µg/g	Intercept	0.10613	0.06026
	Slope	0.0193	0.00588
100 µg/g	Intercept	0.11078	0.11216
	Slope	0.04652	0.01095
150 µg/g	Intercept	0.07467	0.14923
	Slope	0.0742	0.01456
200 µg/g	Intercept	-0.0044	0.19927
	Slope	0.10405	0.01945
250 µg/g	Intercept	-0.03198	0.17233
	Slope	0.11673	0.01682

Figure-14
Plots of q_t versus $t^{1/2}$ for various initial arsenic concentrations

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References

1. Ranjan D., Talat M., Hasan S.H., Rice polish: an alternative to conventional adsorbents for treating arsenic bearing water by upflow column method. *Ind Eng Chem Res*, **48**, 10180-10185 **(2009)**.
2. Biterna M., Antonoglou L., Lazou E., Voutsa D., Arsenite removal from waters by zero valent iron: batch and column tests, *Chemosphere*, **78**, 7-12 **(2010)**
3. Haque N., Morrison G.M., Perrusquia G., Gutierrez M., Aguilera A.F., Aguilera I.C., Gardea-Torresdey J. L., Characteristics of arsenic adsorption to sorghum biomass, *J Hazard Mater,* **145**, 30-35 **(2007)**
4. Yadav Gaurav, Pandey Devendra N. and Patel Dharmendra Kumar, Assessment of Ground Water Quality and its Impact on Health of people around Rewa City, MP, India, *Int. Res. J. Environment Sci.,* **3(7)**, 70-72 **(2014)**

5. Choudhury Moharana, Paul Chinmoy and Kamboj Nitin, Potable Water is a Serious Environmental Issue: A Special Study on Umiamm Area, of Ri-Bhoi District, Meghalaya, India, *Int. Res. J. Environment Sci.,* **3(9)**, 37-42 **(2014)**

6. Schweitzer G.K., Pesterfield L.L., The Aqueous Chemistry of Elements, Oxford University Press, (**2010)**

7. Budinova T., Savova D., Tsyntsarski B., Ania C.O. , Cabal B. , Parra J.B. , Petrov N., Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions, *Appl. Surf. Sci.*, **255 (8)**, 4650-4657 **(2009)**

8. Chakrabarti D., Singh E.J., Das B., Shah B.A., Hossain M.A., Nayak B., Ahamed S., Singh N.R., Groundwater arsenic contamination in Manipur, one of the seven North-Eastern Hill states of India: a future danger, *Environ Geol*, **56**, 381-390 **(2008)**

9. Chakraborti D., Sengupta M.K., Rahman M.M., Ahamed S., Chowdhury U.K., Hossain M.A., Mukherjee S.C., Pati S., Saha K.C., Dutta R.N., Quamruzzaman Q., Groundwater arsenic contamination and its health effects in the Ganga–Meghna–Brahmaputra plain, *J Environ Monit*, **6**, 74-83 **(2004)**

10. Banerjee S., Das B., Umlong I.M., Devi R.R., Kalita H., Saikia L.B., Borah K., Raul P.K., Singh L., Heavy metal contaminants of underground water in Indo Bangla Border Districts of Tripura, India, *Int J ChemTech Res*, **3**, 516-522 **(2011)**

11. Tasneem G.K., Muhammad B.A., Jameel A.B., Muhammad K.J., Hassan I.A., Nusrat J., Raja A.S., Abdul Q.S., Abdul N., The correlation of arsenic levels in drinking water with the biological samples of skin disorders, *Sci. Total Environ.*, **407 (3)**, 1019-1026 **(2009)**

12. Smedley P.L., Kinniburgh D.G., A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* **17 (5)**, 517-568 **(2002)**

13. Kim M.J., Nriagu J., Haack S., Arsenic species and chemistry in groundwater of southeast Michigan, *Environ. Pollut*. **120 (2)**, 379-390 **(2002)**

14. Schaeffer R., Soeroes C., Ipolyi I., Fodor P., NikolaosS.T.,. Determination of arsenic species in seafood samples from the Aegean Sea by liquid chromatography-(photo-oxidation)-hydride generationatomic fluorescence spectrometry. *Anal. Chim. Acta*, **547 (1)**, 109-118 **(2005)**

15. Elizalde-Gonzalez M.P., Mattusch J., Einicke W.D., Wennrich R., Sorption on natural solids for arsenic removal, *Chem. Eng. J.*, **81**, 187-195 **(2001)**

16. Chutia P., Kato S., Kojima T., Satokawa S., Arsenic adsorption from aqueous solution on synthetic zeolites, *J. Hazard. Mater.*, **162**, 440-447 **(2009)**

17. Grossl P.R., Eick M., Sparks D.L., Goldberg S., Ainsworth C.C., Arsenate and chromate retention mechanisms on Goethite, Kinetic evaluation using a pressure-jump relaxation technique, *Environ. Sci. Technol.*, **31**, 321-326 **(1997)**

18. Pontius F.W., Brown K.G., Chen C.J., Health implications of arsenic in drinking water, *J. Am. Water Work Assoc.*, **86 (9)**, 52-63 **(1994)**

19. Vega L., Styblo M., Patterson R., Cullen W., Wang C. Q, Germolec D., Differential Effects of Trivalent and Pentavalent Arsenicals on Cell Proliferation and Cytokine Secretion in Normal Human Epidermal Keratinocytes, *Toxicology and Applied Pharmacology*, **172 (3)**, 225-232 **(2001)**

20. Arain M.B., Kazi T.G., Baig J.A., Jamali M.K., Afridi H.I., Shah A.Q., Jalbani N., Sarfraz R.A., Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: estimation of daily dietary intake, *Food Chem. Toxicol,* **l47**, 242-248 **(2009)**

21. Michon J., Deluchat V., Shukry R.A., Dagot C., Bollinger J., Optimization of a GFAAS method for determination of total inorganic arsenic in drinking water, *Talanta*, **71**, 479-485 **(2007)**

22. Nguyen V.T., Vigneswaran S., Ngo H.H., Shon H.K., Kandasamy J., Arsenic removal by a membrane hybrid filtration system, *Desalination*, **236**, 363-369 **(2009)**

23. Choong T.S.Y., Chuah T.G., Robiah Y., Gregory K.F.L., Azni I., Arsenic toxicity, health hazards and removal techniques from water: An overview. *Desalination*, **217**, 139-166 **(2007)**

24. Fierro V., Muniz G., Gonzalez-Sánchez G., Ballinas M.L., Celza A. Arsenic removal by iron-doped activated carbons prepared by ferric chloride forced hydrolysis, *J. Hazard. Mater.*, **168**, 430-437 **(2009)**

25. (Eid I. Brima and Parvez I. Haris, Arsenic Removal from Drinking Water using Different Biomaterials and Evaluation of a Phytotechnology Based Filter, *Int. Res. J. Environment Sci.,* **3(7)**, 39-44 **(2014)**)

26. Talukdar M.I. and Hasnine M.T., Application of Chitosan-Based Filtration Technique for Removal of Heavy Metals from Surface Water, *Int. Res. J. Environment Sci.,* **3(3)**, 5-10 **(2014)**

27. Hossain M.F. Arsenic contamination in Bangladesh: An overview. *Agriculture, Ecosyst. Environ.*, **113**, 1-16 **(2006)**

28. Mohan D., Jr. Pittman C.U., Arsenic removal from water/wastewater using adsorbents -A critical review, *J. Hazard. Mater.*, **142**, 1-53 **(2007)**

29. Singh Dhanesh, Mishra M., Mishra A.K. and Singh Anjali, Removal of Lead from Waste Water Using Low Cost Adsorbent, *Int. Res. J. Environment Sci.,* **2(9)**, 23-

26 **(2013)**

30. Bhat Irshad Ul Haq, Elias Nursafura B and Khanam Zakia, Adsorption Studies of Cr (VI) and Fe (II) Aqua Solutions Using Rubber Tree Leaves as an Adsorbent, *Int. Res. J. Environment Sci.,* **2(12)**, 52-56 **(2013)**

31. Atkinson S. Filtration technology verified to remove arsenic from drinking water, *Membr. Technol.*, **3**, 8-9 **(2006)**

32. Mondal P., Majumder C.B., Mohanty B., Laboratory, Based approaches for arsenic remediation from contaminated water: Recent developments, *J. Hazard. Mater.*, **137**, 464-479 **(2006)**

33. Sun H., Wang L., Zhang R., Sui J., Xu G., Treatment of ground water polluted by arsenic compounds by zero valent iron, *J. Hazard. Mater.*, **129**, 297-303 **(2006)**

34. Shobana R., Arockia Sahayaraj P., Dharmalingam V. and Soruba R., Adsorption Study on Zinc (II) ions from Aqueous solution using Chemically Activated Fruit of *Kigelia Pinnata* (JACQ) DC carbon, *Int. Res. J. Environment Sci.,* **3(9)**, 65-69 **(2014)**

35. Srivastava S., Raj K.R., Kardam A., Efficient arsenic depollution in water using modified maize powder, *Environ Chem Lett*., **11(1)**, 47-53 **(2013)**

36. Chen W., Parette R., Zoau J., Cannon F.S., Dempsey B.A., Arsenic removal by iron-modified activated carbon, *Water Res.*, **41**, 1851-1858 **(2007)**

37. Boddu V.M., Abburi K., Talbott J.L., Smith E.D., Haasch R., Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent., *Water Res.,* **42(3)**, 633-642 **(2008)**

38. Jeon C.S., Baek K., Park J.K., Oh Y.K., Lee S.D., Adsorption characteristics of As(V) on iron-coated zeolite, *J Hazard Mater*, **163**, 804-808 **(2009)**

39. Twindell L.G., Robins R.G., Hohn J.W., The removal of arsenic from aqueous solution by coprecipitation with iron (III), In: Reddy RG, Ramachandran V (Eds) Arsenic metallurgy: Fundamentals and Applications, *TMS (The Minerals, Metals & Materials Society),* 3-24 **(2005)**

40. Ladeira A.C.Q., Ciminelli V.S.T., Duarte H.A., Alves M.C.M., Ramos A.Y., Mechanism of anion retention from EXAFS and density functional calculations: arsenic (V) adsorbed on gibbsite, *Geochim Cosmochim Acta*, **65,** 1211-1217 **(2001)**

41. Hatam G., Ghodratolah S.K., Seyed H.M., The Application of Iron-Coated Activated Carbon in Humic Acid Removal From Water, 2011 2nd International Conference on Environmental Science and Technology IPCBEE, IACSIT Press, *Singapore*, 6 **(2011)**

42. Huan J. F.., Tachung W., Anderson P.R., Removal of Cu II by iron oxide coated granular activated carbon, *J. Chinese Inst. Environ. Engg.*, **10 (3)**, 193-199 **(2000)**

43. Kelly B.P., Tarek M. A.-F.., Adsorption of Arsenate and Arsenite by Iron-Treated Activated Carbon and Zeolites: Effects of pH, Temperature, and Ionic Strength, *J. Environ. Sci. and Health*, **40**, 723-749 **(2005)**

44. Manning B.A., Goldberg S., Adsorption and stability of arsenic (III) at the clay mineral water interface, *Environ. Sci. Technol*., **31**, 2005-2011 **(1997)**

45. Manning B.A., Fendorf S.E., Goldberg S., Surface structures and stability of arsenic (III) on goethite: spectroscopic evidence for inner-sphere complexes, *Environ. Sci. Technol.*, **32**, 2383-2388 **(1998)**

46. Wilkie J.A., Hering J.G., Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes, Colloids Surf. A: Physicochem, *Eng. Aspects*., **107**, 97-110 **(1996)**

47. Lackovic J.A., Nikolaidis N.P., Dobbs G.M., Inorganic arsenic removal by zerovalent iron, *Environ. Eng. Sci.*, **17**, 29-39 **(2000)**

48. Su C., Puls R.W., Arsenate and arsenite removal by zero valent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.*, **35**, 1487-1492 **(2001)**

49. Su C., Puls R.W., Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride, *Environ. Sci. Technol.*, **35**, 2568–4562 **(2001)**

50. Driehaus W., Jekel M., J. Hildebrandt, Granular ferric hydroxide-a new adsorbant, for the removal of arsenic from natural water, *J. Water Supply Res. Technol. Aqua*, **47**, 30-35 **(1998)**

51. Thirunavukkarasu O.S., Viraraghavan T., Subramanian K.S., Removal of arsenic in drinkingwater by iron oxide-coated sand and ferrihydrite-batch studies, *Water Qual. Res. J. Can*., **36**, 55-70 **(2001)**

52. Raven K.P., Jain A., Loeppert R.H., Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.*, **32**, 344-349 **(1998)**

53. Badruzzaman M., Westerhoff P., Knappe D.R.U., Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH), *Water Res.,* **38**, 4002-4012 **(2004)**

54. Das B. and Mondal N.K., Calcareous soil as a new adsorbent to remove lead from aqueous solution: equilibrium, kinetic and thermodynamic study, *Universal J. Environ Res. Technol.*, **1**, 515-530 **(2011)**

55. Lewinsky A.A., Hazardous materials and wastewater: treatment, removal and analysis, *Nova Science*, New

York, pp.375 **(2007)**

56. Roy P. and Mondal N.K., Bhattacharya S., Das B., Das K., Removal of arsenic (III) and arsenic (V) on chemically modified low-cost adsorbent: batch and column operations, *Appl. Water. Sci.*, **3**, 293-309 **(2013)**

57. Islam M. and Patel R.K., Evaluation of removal efficiency of fluoride from aqueous solution using quick lime, *J. Hazard. Mater.*, **143**, 303-310 **(2007)**

58. Lalvani S.B. and Wiltowski T., Hubner A., Weston A., Mandich N., Removal of hexavalent chromium and metals cations by a novel carbon adsorbent, *Carbon*, **36 (7-8)**, 1219-1269 **(1998)**

59. Chowdhury S. and Saha P., Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies, *Chem. Eng. J.*, **164**, 168-177 **(2010)**

60. Yang C.H., Statistical mechanical study on the Freundlich isotherm equation, *J. Colloid Interface Sci.*, **208**, 379-387 **(1998)**

61. Meenakshi S. and Sundaram C.S., Sukumar R., Enhanced fluoride sorption by mechanochemically activated Kaolinites. *J. of Hazard. Mater.*, **153**, 164-172 **(2008)**

62. Jiang J.Q., Cooper C. and Ouki S., Comparison of modified montmorillonite adsorbents-part I: preparation, characterization and phenol adsorption, *Chemosphere,* **47**, 711-716 **(2002)**

63. Taha M.R., Ahmad K., Aziz A.A. and Chik Z., Geo environmental aspects of tropical residual soils, in: Huat B.B.K., Sew G.S., Ali F.H. (Eds.), Tropical Residual Soils Engineering, A.A. Balkema Publishers, London, UK, pp. 377-403 **(2009)**

64. Wang X.S. and Qin Y., Equilibrium sorption isotherms for of Cu^{2+} on rice bran, *Process Biochem*, **40**, 677-680 **(2005)**

65. Biswas K., Saha S.K. and Ghosh U.C., Adsorption of fluoride from aqueous solution by a synthetic iron(III)-aluminum (III) mixed oxide, *Ind. Eng. Chem. Res.*, **46**, 5346-5356 **(2007)**

66. Hardiljeet K.B., Meera J. and O'Carroll D.M., Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. of Hazard. Mater.*, **186**, 458-465 **(2011)**

67. Hutson N.D. and Yang R.T., Theoretical basis for the Dubinin-Radushkevitch (D-R) adsorption isotherm equation, *Adsorption*, **3**, 189-195 **(1997)**

68. Samarghandi M.R., Hadi M., Moayedi S. and Askari F.B.,. Two-parameter isotherms of methyl orange sorption by pinecone derived activated carbon. *Iran J. Environ. Health Sci. Engg.*, **6**, 285-294 **(2009)**

69. Rajiv G.M., Kalaivani G. and Meenakshi S., Sorption of chromate and fluoride onto duolite a 171 anion exchange resin- a comparative study, *Elixir Pollution*, **32**, 2034-2040 **(2011)**

70. Ngah W.S.W. and Hanafiah M.A.K.M., Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies, *Biochem. Eng. J.*, **39**, 521-530 **(2008)**

71. Sairam S.C., Viswanathan N. and Meenakshi S., Defluoridation chemistry of synthetic hydroxyapatite at nano scale: Equilibrium and studies, *J. of Hazard. Mater.*, **155**, 206-215 **(2008)**

72. Horsfall M. and Spiff A. L., Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by caladium bicolour (Wild Cocoyam) biomass, *Electron J. Biotechnol.*, **8**, 162-169 **(2005)**

73. Lagergren S., Zur theorie der sogenannten adsorption gelöster stoffe. *K. Sven Vetenskapsakad. Handlingar*, **24 (4)**, 1-39 **(1898)**

74. Ho Y.S., Second-order kinetic for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, *Water Research*, **40**, 119-125 **(2006)**

75. Chien S.H. and Clayton W.R., Application of Elovich Equation to The Kinetics of Phosphate Release and Sorption on Soils, *Soil Sci. Soc. Am. J.*, **44 (2)**, 265-268 **(1980)**

76. Weber W.J. and Morris J.C, Kinetics of Adsorption on Carbon from Solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, **89 (2)**, 31-60 **(1963)**

77. Demirbas E., Kobya M., Oncel S. and Sencan S., Removal of Ni(II) from Aqueous Solution by Adsorption onto Hazelnut Shell Activated Carbon: Equilibrium Studies, *Bioresour. Technol.*, **84 (3)**, 291-293 **(2002)**