

Effect of pH and Treatment Time on the Removal of Arsenic Species from Simulated Groundwater by Using Fe³⁺ and Ca²⁺ Impregnated Granular Activated Charcoals

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Abstract This paper deals with the removal of arsenic species from simulated groundwater containing arsenic (As(III):As(V): 1:1), Fe and Mn in concentrations of 0.188mg/l, 2.8mg/l and 0.6mg/l respectively, by surface modified granular activated charcoals produced by impregnating Fe³⁺ and Ca²⁺ on GAC surface. Effects of pH and treatment time on the removal of arsenic species by using these adsorbents have been compared. The phenomenon has been explained on the basis of individual p*H*_{zpc} of oxides and metal complexes present in the adsorbents. The present approach clearly explains the adsorption of negatively charged arsenic species at high pH (>11). Under optimum process conditions at neutral pH, Fe³⁺ impregnated granular activated charcoal (GAC-Fe) has been found more efficient for the treatment of contaminated groundwater than Ca²⁺ impregnated granular activated charcoal (GAC-Ca). Treatment time for equilibrium adsorption of arsenic species on GAC-Ca is found to be less than that of GAC-Fe.

Keywords: arsenic, GAC-Fe, GAC-Ca, p*H*_{zpc}, adsorption, surface modification

1. Introduction

Long term consumption of arsenic contaminated groundwater by common people has caused numerous health disorders around the world. However, most devastating form of arsenic poisoning has been observed in India and Bangladesh.

Amongst various arsenic removal techniques such as adsorption, ion-exchange, coagulation-precipitation, reverse osmosis etc., surface modified adsorbents are widely being investigated for the development of cheaper arsenic removal technique in recent years. Untreated granular activated carbon (GAC), widely used in water treatment facilities, occupies predominantly negatively charged surface at neutral pH and hence is not a good adsorbent for negatively charged / neutral arsenic. However, by impregnating positively charged ions on the surface of GAC, its arsenic removal capacity can be improved significantly [1]. It has been proved that the improvement in arsenic removal capacity of metal impregnated GAC depends on the charge of metal ions and its aqueous phase chemistry. Further, in an adsorption process, the effect of pH on the removal of adsorbate depends on the chemistry of both adsorbent surface and adsorbate in aqueous phase. In most of the recent literature adsorption of arsenic species on metal impregnated surface modified adsorbents has been explained on the basis of pH at zero charge potential of the adsorbent

surface [2,3,4,5,6]. However, this cannot explain the adsorption of negatively charged arsenic species above the p*H*_{zpc} of the adsorbents.

In the present paper the effects of pH and treatment time on the removal of arsenic species by using untreated GAC and Fe³⁺ and Ca²⁺ impregnated GACs have been compared. Mechanism of adsorption has been explained on the basis of individual p*H*_{zpc} of the metal oxides and metal complexes present on the adsorbent surface, which explains the arsenic removal at high pH > 11.

2. Materials and Methods

All the chemicals, purchased from *s.d. fine-chem* limited, India, were of reagent grade and solutions were prepared by Milli-Q water (Q-H₂O, Millipore Corp. with resistivity of 18.2 MΩ-cm). The stock solutions of 100mg/l As (V) and As(III) were prepared by dissolving Na₂HAsO₄·7H₂O and NaAsO₂ in Milli-Q water and filtered through 0.45 μm membrane.

2.1. Preparation of Surface Modified GACs

GAC of bulk density 40g/100ml, derived from wood, was procured from *s.d fine chemicals*, India and screened with standard sieves to separate the fractions having 2–4mm particle size. It was further pretreated by soxhlet extraction with acetone/n-heptane (50:50, v/v) and surface modification was done by using aqueous solutions of

FeCl₃ and CaCl₂ containing 2.5wt% of Fe³⁺ and Ca²⁺ respectively for the production of GAC-Fe and GAC-Ca through salt evaporation method. Bulk density of the adsorbents was measured by a picnometer. Surface area and micro pore volume of the samples were measured by N₂ adsorption isotherm using an ASAP 2010 Micromeritics instrument by Brunauer-Emmett-Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (77.15K). SEM photograph was taken by an electron microscope (LEO Electron Microscopy Ltd., England). Table 1 summarizes some characteristics of the adsorbents.

Table 1. Properties of GAC and surface modified GACs

Adsorbent	Particle size (mm)	BET Surface area (m ² /g)	Micropore volume (cm ³ /g)	Bulk density (g/l)	Metal content (%)
GAC	2-4	583.23	0.2044	605.02	-
GAC-Fe	2-4	488.24	0.1746	658.01	Fe: 4.78
GAC-Ca	2-4	532.25	0.1893	659.57	Ca: 1.89

2.2. Procedure

Each 50ml of the synthetic water sample containing 188 µg/l As (As(III) : As(V) = 1:1), 2.8mg/l Fe and 0.6mg/l Mn was added with calculated amount of adsorbents, as optimized elsewhere [7,8] in 100ml plastic bottle. The optimum adsorbent dose was fixed to get the arsenic concentration below 10 µg/l from an initial concentration of 188 µg/l. Temperature and agitation speed were maintained at 29 ± 1 °C and 180rpm respectively. To study the effect of pH, the initial pH of the solution was varied from 2 to 12 using the optimum treatment times. To study the effect of treatment time, shaking time was varied from 0.5 to 52h for each solution. pH was maintained at 7.1 ± 0.1. The pH of the solution was measured after every 2h interval and maintained at the desired value (initial pH) by the drop wise addition of N/10 HNO₃ when required. After each experiment, the solution was filtered through 0.45 µm membrane filter. The filtrate was analyzed for total arsenic by a Perkin Elmer ICP-MS (model ELAN-DRC-e). Arsenic speciation was done by modified Edward's ion exchange method using strong base anion resin AG 1 X8. All the experiments were repeated thrice and average results have been reported.

3. Results and Discussions

Effects of pH and treatment time on the removal of arsenic species using GAC, GAC-Fe and GAC-Ca are discussed below:

3.1. Effect of pH

The effects of pH on the % removal of As(V) and As(III) from the simulated water samples are shown in Figure 1(a) and 1(b) respectively.

From Figures 1a and 1b it is evident that the % removals of arsenic species for surface modified GACs are more than that of untreated GAC throughout the pH range investigated. The % removal of As(III) and As(V) for GAC-Fe and GAC-Ca are almost similar at higher pH.

However, the GAC-Fe has more arsenic removal capacity (0.036mg/g) than that of GAC-Ca (0.022mg/g) at neutral pH. Above pH11 the % removal of As(III) is more than As(V), which is reverse at pH lower than 11 for both of the surface modified GACs.

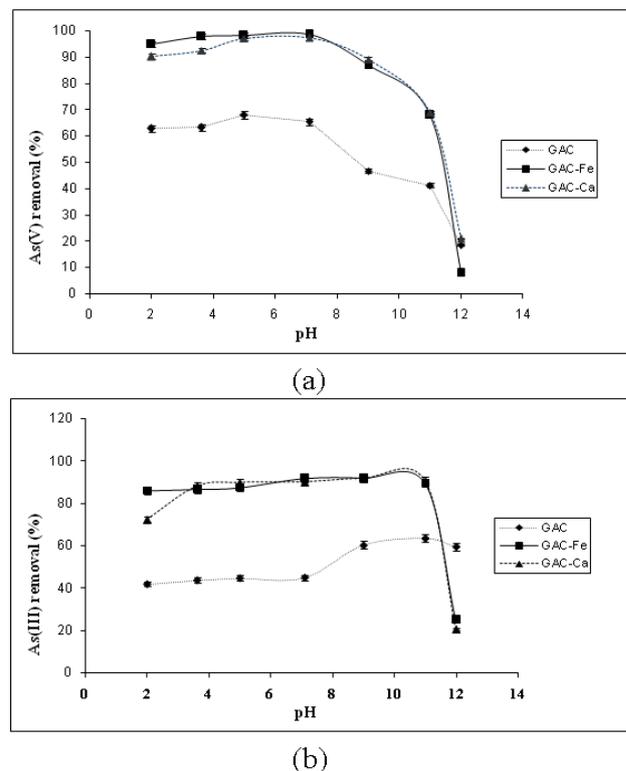


Figure 1. Effect of pH on the removal of arsenic species; (a) As(V), (b) As(III)

GAC used in the present work had 2.58% of ash, which contains oxides like 54% SiO₂, 12.5% CaO, 7.23% Al₂O₃, 3.25% MgO and 2.15% Fe₂O₃ etc. Different constituents present in rest of ash (~ 21% of total ash) are not known. It is logical to conclude that those oxide molecules, which are on the surface of GAC will only contribute towards surface charge on reaction with H⁺ or OH⁻ ions of the solution. Further, the present GAC does not contain any S and P as evident from the ultimate analysis shown in Table 1, which indicates the absence of sulphate and phosphates groups in untreated GAC. However, the carboxyl as well as phenolic groups are available on the surface of GAC, which also creates negative charges.

At pH below p_{HZPC} of an oxide, it produces substantially more positive charges than negative charges on the surface whereas, at pH above p_{HZPC} it produces more negative charges on the surface than positive charges. The value of p_{HZPC} for SiO₂, Al₂O₃, CaO, MgO and Fe₂O₃ are 2.2, 8.3, 11.0, 12.4 and 8.0 respectively [9]. Hence, the surface of GAC is predominantly negatively charged under the experimental pH. Thus, chemisorption of arsenic species is less which lowers removal of arsenic species. However due to impregnation of metal ions the positive charge density on surface modified GACs increases as consequently arsenic removal increases. Optimum adsorbent concentrations was considered for GAC, GAC-Fe and GAC-Ca as 16g/l, 5g/l and 8g/l respectively on the basis of earlier experiments as reported elsewhere [7,8]. Thus, the amount of GAC, GAC-Fe and GAC-Ca present in 50ml solution are 0.8g, 0.25g and 0.4g

respectively. From the analysis of metal contents in the adsorbents as reported in Table 1 as well as the ash composition of GAC as mentioned above, the numbers of gram moles of various oxides of ash and impregnated metal ions present in 0.8g of GAC, 0.25g GAC-Fe and 0.4g GAC-Ca are shown in Table 2. It also shows the pHzpc of individual oxides and the metal complexes.

Table 2. Number of gram moles of various oxides and metal complexes on the adsorbents

Components	pHzpc	No. in 0.8 g GAC	No. in 0.25 g GAC-Fe	No. in 0.4g GAC-Ca
SiO ₂	2.2	1.86×10 ⁻⁴	0.58×10 ⁻⁴	0.93×10 ⁻⁴
Fe ₂ O ₃	8	0.28×10 ⁻⁵	0.09×10 ⁻⁵	0.14×10 ⁻⁵
Al ₂ O ₃	8.3	0.15×10 ⁻⁴	0.47×10 ⁻⁵	0.75×10 ⁻⁵
CaO	11	0.47×10 ⁻⁴	0.15×10 ⁻⁴	0.23×10 ⁻⁴
MgO	12.4	0.17×10 ⁻⁴	0.05×10 ⁻⁴	0.08×10 ⁻⁴
M-O-Fe(OH) ₂ and (M-O) ₂ -Fe(OH)	7.5- 8.5	-	2.14×10 ⁻⁴	-
(C-X) ₂ -Fe(OH) ⁺² , (C-X)-Fe(OH) ₂ ⁺ , (C-X) ₂ -Fe(OH) ₃ ⁰	12.8	-		-
M-O-Ca(OH)	11	-	-	1.89×10 ⁻⁴
(C-X) ₂ -Ca(OH) ⁺ , (C-X) ₂ -Ca(OH) ₂ ⁰	>11.5	-	-	

These oxides and the metal complexes formed by impregnation of metal ions, produce positive as well as negative sites on the adsorbent surface depending on the pH of the solution and thus, change surface charge behavior of adsorbent with change in solution pH. Due to this phenomenon adsorption of arsenic species on adsorbent surface takes place through different mechanism depending on the pH value of the solution. Considering these facts and keeping a view on the relative concentration for various charged moieties on the adsorbent, as shown in Table 2, the likely mechanism for adsorption of arsenic species on the surface modified GACs at various pH can be summarized as shown in Table 3. From Table 3 it seems that based on the oxides present on the adsorbent surface as well as metal complexes formed, a certain adsorption mechanism becomes favourable under a given pH range. For example, in pH range 8 to 8.5 the oxides like SiO₂, Al₂O₃ and Fe₂O₃ create negative charges on GAC-Fe surface whereas other oxides such as CaO and MgO create positive charges on GAC-Fe surface due to their pHzpc values as provided in Table 2. Further, the metal complexes produced on GAC-Fe such as (M-O)-Fe(OH)₂, (M-O)₂-Fe(OH), (C-X)₂-Fe(OH)⁰ etc., also remain neutral in this pH range. Consequently, the surface of the GAC-Fe is predominantly neutral and hence adsorption takes place predominantly through exchange of hydroxyl ions in this pH range. The detail discussion on the creation of various surface charges on the surface modified GACs and likely route for the adsorption of arsenic species have been provided elsewhere [8].

From Table 3 it seems that at lower pH (<8) the surface of both GAC-Fe and GAC-Ca are predominantly positively charged due to the creation of positive sites by all oxides (except SiO₂) and the additionally impregnated metals and chemisorptions is the main mechanism of

adsorption. As the number of additionally impregnated metals in GAC-Ca is less than GAC-Fe the positive charge created on GAC-Fe is more than that of GAC-Ca. Formation of more impregnated metal complexes in GAC-Fe is also evident by comparing the SEM of GAC-Fe and GAC-Ca as shown in Figure 2.

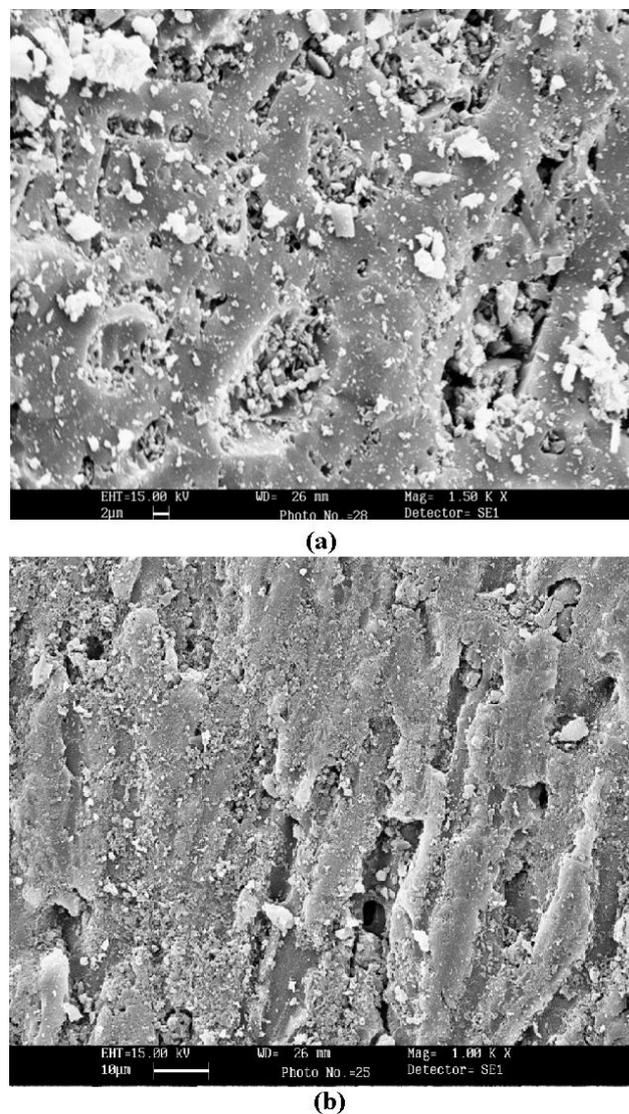


Figure 2. SEM of surface modified GACs with 1.5KX magnification; (a) GAC-Fe, (b) GAC-Ca

Further, arsenic exists as predominantly neutral or negatively charged species in the solution. Thus, GAC-Fe shows more removal of arsenic species. Within the pH range investigated, As(V) exists as negatively charged divalent and mono-valent species whereas As(III) exists mainly as neutral or negatively charged mono-valent species.

Within pH 8 to 11 the surface of GAC-Fe is either predominantly neutral or negatively charged and capture of arsenic species takes place through ion exchange mechanism. Whereas, within this range of pH, the GAC-Ca is predominantly or slightly positively charged having chemisorptions as main mechanism. Some ion exchange can also take place above pH 10. Chemisorptions create stronger bonding between active sites and arsenic species than that created by ion-exchange mechanism. Thus, less positive charge on GAC-Ca is compensated by the bonding nature of chemisorptions and it shows similar

removal capacity to GAC-Fe. At higher pH (> 11) the removal of some negatively charged arsenic species on the negatively charged adsorbent surface is possible due to the exchange of hydroxyl ion and the more negative character of As(V) than As(III) results less removal of As(V) than As(III). However, at lower pH the adsorbent surface is positively charged and As(V) removal is more than that of As(III). Although some literatures [3,5,10] describe the effect of pH on arsenic removal by using surface modified adsorbents, in these cases either As(III) or As(V) has been taken in solution. However, in the present study both

As(III) and As(V) has been considered along with Fe and Mn to simulate the real groundwater samples. Further, in those literatures the removal of arsenic species has been mainly explained on the basis of pH_{zpc} of the adsorbents and chemisorption has been considered as most probable route for adsorption. However, in the present study the pH_{zpc} of individual oxides and metal complexes has been considered which helps to explain the more removal of negatively charged As(III) species on negatively charged adsorbent surface at higher pH through exchange of hydroxyl ions.

Table 3. Contribution of various oxides and metal complexes towards the surface charge of adsorbent at various pH and possible mechanism of adsorption of arsenic species on adsorbent [3,5,8,10]

pH range	Charge present on the surface of adsorbents due to oxides as a function of pH				Metal complexes formed on surface of surface modified GACs as a function of pH		Predominant surface charge (PSC) on adsorbent surface and likely route (LR) for arsenic adsorption / attachment	
	GAC-Fe		GAC-Ca		GAC-Fe	FAC-Ca	GAC-Fe	GAC-Ca
	-ve	+ve	-ve	+ve				
<2.2	Nil	All oxides	Nil	All oxides	(M-O)-Fe(OH ₂ ⁺) ₂ (M-O) ₂ -Fe(OH ₂ ⁺) (C-X) ₂ -Fe(OH) ²⁺ (C-X)-Fe(OH) ₂ ⁺	(M-O)-Ca(OH ₂ ⁺) (C-X) ₂ -Ca(OH) ⁺	PSC: Highly positive; LR: Chemisorption	PSC: Highly positive LR: Chemisorption
2.2 - 8	SiO ₂	Al ₂ O ₃ , CaO, MgO, Fe ₂ O ₃	SiO ₂	Al ₂ O ₃ CaO MgO Fe ₂ O ₃	(M-O)-Fe(OH ₂ ⁺) ₂ (M-O) ₂ -Fe(OH ₂ ⁺) (C-X) ₂ -Fe(OH) ²⁺ (C-X)-Fe(OH) ₂ ⁺	(M-O)-Ca(OH ₂ ⁺) (C-X) ₂ -Ca(OH) ⁺	PSC: Positive LR: Chemisorption	PSC: Positive; LR: Chemisorption
8 - 8.5	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃	CaO, MgO	-	-	(M-O)-Fe(OH) ₂ (M-O) ₂ -Fe(OH) (C-X) ₂ -Fe(OH) ⁰	-	PSC: Neutral; LR: Exchange of hydroxyl ion	-
8.5 - 11	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃	CaO, MgO	-	-	(M-O)-Fe(O) ₂ (M-O) ₂ -Fe(O) (C-X) ₂ -Fe(OH) ⁰	-	PSC: Negative ; LR: Exchange of hydroxyl ion	-
8-10	-	-	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃	CaO MgO	-	(M-O)-Ca(OH ₂ ⁺) (C-X) ₂ -Ca(OH) ⁺	-	PSC: Positive; LR: Chemisorption
10-11	-	-	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃	CaO MgO	-	(M-O)-Ca(OH ₂ ⁺) (C-X) ₂ -Ca(OH) ₂ ⁰	-	PSC: Neutral or slightly positive; LR: Exchange of hydroxyl ion as well as chemisorption
11-11.5	-	-	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ O ₃ CaO	MgO	-	(M-O)-Ca(O) (C-X) ₂ -Ca(OH) ₂ ⁰	-	PSC: Negative; LR: Exchange of hydroxyl ion
>11.5	-	-	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO	MgO Upto pH 12.4	-	(M-O)-Ca(O) (C-X) ₂ -Ca(OH) ₂ ⁻	-	PSC: Highly Negative; LR: virtually does not favour arsenic adsorption above pH 12.4
11-12.4	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO	MgO	-	-	(M-O)-Fe(O) ₂ (M-O) ₂ -Fe(O) (C-X) ₂ -Fe(OH) ₃ ⁰	-	PSC: Negative ; LR: Exchange of hydroxyl ion	-
>12.4	All oxides	Nil	-	-	(M-O)-Fe(O) ₂ (M-O) ₂ -Fe(O) (C-X) ₂ -Fe(OH) ₃ ⁰ (C-X) ₂ -Fe(OH) ₄ ⁻	-	PSC: Highly negative; LR: Virtually does not favour arsenic adsorption above pH 12.8	-

3.2. Effect of Treatment Time

Effects of treatment time on the removal of total arsenic, As(T), using various adsorbents are shown in Figure 3.

From Figure 3 it is evident that for all the adsorbents investigated i.e., GAC, GAC-Fe and GAC-Ca the rate of increase in the percentage removal of arsenic species with increase in treatment time is appreciably fast at the initial stage. However, after a certain period (~ 12h, 10h and 8h for GAC, GAC-Fe and GAC-Ca respectively) of agitation, the rate of increase in percentage removal of arsenic species with increase in treatment time is less and equilibrium treatment time of these adsorbents are 48h, 42h and 24h respectively.

At the neutral pH, the surface of GAC is predominantly negatively charged whereas GAC-Fe and GAC-Ca surfaces are predominantly positively charged. Hence, under the same experimental conditions the rate of transportation of arsenic species from the bulk of the solution to the adsorbent surface is less for GAC than surface modified GACs. Due to this reason GAC takes more time to reach adsorption equilibrium than surface modified GACs.

Further, the rate of exchange of hydroxyl ions from the surface metal complexes (C-X)₂-M(OH)_n^m of GAC-Fe and GAC-Ca by negatively charged arsenic species may vary depending upon the properties of metal as well as the stability of the surface metal complexes. Where, M stands for Fe, and Ca. The values of m are 0, +1 or +2, whereas,

the values of n are 1, 2 or 3. It has been reported recently that the rate of exchange of H_2O ligand or OH^- ion from metal aqua-complexes decreases with the increase in the stability of the aqua complexes of metals [11]. The stability of aqua-complexes of Ca may be less than that of Fe because of the electron configuration of Ca^{2+} ion ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^0$). As a result the rate of exchange of H_2O ligand or OH^- ion from aqua-complexes of Fe is slower than that of Ca. Therefore, it may be possible that the rate of attachment of negatively charged arsenic species through exchange of hydroxyl ions of these surface complexes in the present case decreases in the following order: $GAC-Fe < GAC-Ca$. Hence, as an overall effect the treatment time required to reach equilibrium decreases as follows: $GAC > GAC-Fe > GAC-Ca$. The above observations can also be explained on the basis of the migration and diffusion rates of arsenic species on the surface modified GACs. As described elsewhere [7,12] the film diffusion coefficients of As(III) and As(V) for GAC-Fe are more than that of GAC-Ca whereas pore diffusion coefficients of As(III) and As(V) for GAC-Fe are less than that of GAC-Ca. The higher value of film diffusion coefficient for GAC-Fe may be due to the more positive charge on GAC-Fe and more pore diffusion coefficient of GAC-Ca may result lower equilibrium time for GAC-Ca than GAC-Fe.

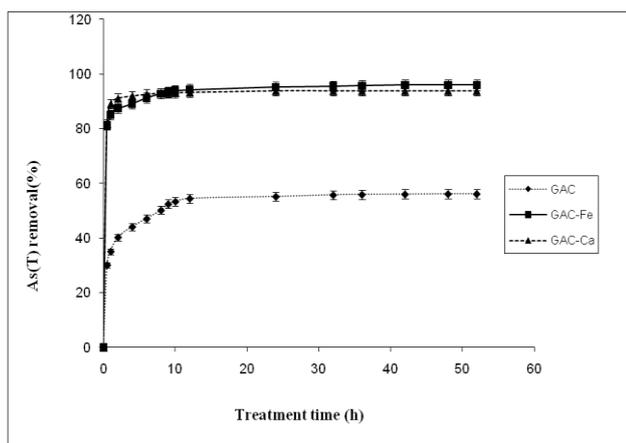


Figure 3. Effect of treatment time on the removal of total arsenic As(T)

4. Conclusions

From the above discussions the following conclusions are made:

- At higher pH (> 11), the removal of As(III) is more than that of As(V) for both the surface modified GACs.
- At higher pH, the attachment of negatively charged arsenic species on predominantly negatively charged

adsorbent surface takes place through the exchange of hydroxyl ions.

- At neutral pH the arsenic removal capacity of GAC-Fe is more than that of GAC-Ca. However, the treatment time of equilibrium adsorption for GAC-Ca is lower than GAC-Fe.

Statement of Competing Interests

The authors have no competing interests.

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