



Removal of Arsenite from Water by Iron Modified Activated Carbon Fibre

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Trivalent arsenic is a highly toxic pollutant with carcinogenicity and it is typically detected in ground water. It is most essential to remove As(III) effectively and efficiently before water distribution. In this study, activated carbon fibre was modified with iron salt (FeCl_3) by wet impregnation method and used for As(III) removal by adsorption. The morphology of iron modified activated carbon fibre was not altered significantly by SEM measurement. By EDX analysis, the molar ratio of C, Fe and O on iron modified activated carbon fibre was observed to be 92.2, 0.70 and 7.1 %, respectively. The kinetics of adsorption experiment indicated that most of the uptake of As(III) occurred in the first 60 min. Pseudo-second-order model well fitted the kinetics data. The increase of solution pH caused an increase of As(III) adsorption capacity. Ionic strength test indicated that the adsorption process formed inner-sphere complexes. The presence of sulfate, carbonate and nitrate had insignificant influence on As(III) adsorption, while phosphate and silicate hindered the adsorption obviously. The Freundlich equation well described the adsorption isotherm. External electric field was proved to have improved the As(III) adsorption onto the sorbent and helped the desorption of As(III) as well.

Key Words: Arsenite, Adsorption, Impregnation, Activated carbon fibre, Water purification.

INTRODUCTION

Ground water is an indispensable drinking water source especially in the rural areas of developing countries. However, elevated concentrations of arsenic in ground water are found in many countries such as Bangladesh, India, Vietnam, Chile, China and Argentina¹⁻³. Chronic intake of arsenic is proved to be responsible for the increased risks of cancers, diabetes, developmental and reproductive problems and cardiovascular disease^{4,5}. A lethal dose effect on acute arsenic poisoning can lead to muscular weakness, loss of appetite, nausea and it has direct effect towards the skin. Excess exposure to arsenic may cause lung and kidney cancer⁶⁻⁹. Between As(III) and As(V), As(III) has an especially high affinity towards tissue proteins by strong binding to mercaptan groups existing in biomolecules such as amino acids, peptides and proteins, which is associated with its higher toxicity and metabolism of arsenic in mammals¹⁰. Millions of people are actually at a risk of developing cancer due to chronic arsenic poisoning. As such, the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) implemented the reduction of arsenic maximum contaminant level (MCL) in drinking water from 50 to 10 $\mu\text{g/L}$ as early as in 2006. This regulation has enhanced the development of water treatment technologies and improved the water quality around the world.

A number of water treatment technologies such as coagulation/precipitation, ion exchange, lime softening, membrane separation and adsorption, are effective for As(V) removal, but much less for As(III). In anoxic groundwater, As(III) is present predominantly and more mobile. Meanwhile, it is a hydrophilic and neutral species below pH 9 and the major removal process such as adsorption and anion exchange are not so effective as expected¹¹⁻¹⁴. However, adsorption is still considered as one of the cost-effective and practical methods for arsenic removal. Adsorption has its advantages such as ease of operation and high efficiency. A large variety of adsorbents such as titania¹⁵, zero-valent iron¹⁶ and zirconium nanoparticles¹⁷ are proved to be capable of removing arsenic effectively from water.

In this study, activated carbon fibre was modified with iron salt (FeCl_3) by wet impregnation method in order to improve its adsorption performance for As(III) removal. A series of batch adsorption experiments, including kinetics and isotherm studies, pH and co-existing anions effects, were carried out to understand the adsorption behavior of iron modified activated carbon fibre. The electrochemically assisted adsorption of As(III) was examined under external electric field. The possibility for the regeneration of iron modified activated carbon fibre was also checked by reversing the polarity of the electric field applied.

EXPERIMENTAL

Sodium arsenite (NaAsO_2) was supplied by Fluka (Switzerland). Other chemicals such as sodium sulphate, sodium nitrate, sodium phosphate, sodium bicarbonate and sodium silicate were purchased from Chinese Chemical Company of Beijing. Other materials used in the test were of analytical purity. Deionized and doubly distilled water was used throughout the study.

Preparation of iron modified activated carbon fibre:

The activated carbon fibre was provided by Liaoning Anshan Senxin Activated Carbon Environmental Materials Co., Ltd, China. Its thickness is 2 mm and the average surface area is $1500 \text{ m}^2/\text{g}$. Before use, the activated carbon fibre was immersed in HCl for 24 h, then washed with distilled water to neutral pH and dried at 353 K. The pretreated activated carbon fibre was impregnated in concentrated FeCl_3 solution for 24 h and dried in an oven at 80°C overnight. The above procedures were repeated for 6 times and the iron modified activated carbon fibre was prepared.

The morphologies of activated carbon fibre and iron modified activated carbon fibre were recorded on a Philips Quanta-2000 scanning microscope coupled with an energy dispersive X-ray (EDX) spectrometer. Their X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-3B X-diffractometer.

Adsorption of arsenite on iron modified activated carbon fibre: A stock solution of 1000 mg/L in As(III) was prepared by dissolving a certain amount of sodium As(III) into deionized water. An aliquot of the stock solution was mixed with a certain volume of water so that As(III) solutions were prepared at the desired experimental concentration.

The reaction was carried out in a series of conical flasks and 100 mL of the As(III) solution with a concentration of 50 mg/L was used under otherwise stated. A desired amount of raw activated carbon fibre or iron modified activated carbon fibre was added into the solution. The solution pH was adjusted with 0.1 M HCl or NaOH. The mixtures were shaken on an orbit shaker at 200 rpm for 24 h at $24 \pm 1^\circ\text{C}$. The samples were collected at a desired time interval and used for determination.

Electrochemically assisted adsorption and desorption of arsenite: Electrochemically assisted adsorption and desorption of arsenite was conducted in 150 mL vessel in which 100 mL of arsenite solution (50 mg/L) under vigorous electromagnetic stirring. The anode employed is iron modified activated carbon fibre with a size of $20 \text{ mm} \times 40 \text{ mm}$. Titanium mesh with the same sizes was used as the cathode. The distance between the anode and cathode is 10 mm. The stable voltage of 1.2 V was supplied by a DH1715A-3 potentiostat (Beijing Dahua Radio Instrument Factory).

Analyses: Samples were collected and filtered through a $0.45 \mu\text{m}$ membrane before As(III) analyzing. Hydride generation atomic fluorescence spectrometry (HG-AFS) (AFS-8220, Beijing Jitian Analytical Instrument Company) was used for As(III) concentration measurement.

RESULTS AND DISCUSSION

Fig. 1 shows the SEM images of raw activated carbon fibre and iron modified activated carbon fibre after adsorption.

Iron modified activated carbon fibre has the identical morphology with the raw activated carbon fibre and only the image of raw activated carbon fibre is presented here. It can be observed that both the raw activated carbon fibre and unmodified activated carbon fibre are smooth and even. Compared with the raw activated carbon fibre, a large number of granules are obviously observed on the iron modified activated carbon fibre after adsorption. They can be deduced to be iron oxide because only FeCl_3 was added when modifying the activated carbon fibre. By EDX analysis (Fig. 2), the molar ratio of C, Fe and O on iron modified activated carbon fibre after adsorption is 92.2, 0.70 and 7.1 %, respectively. There was no Fe detected on the raw activated carbon fibre. In addition, the weak existence of iron oxide only partly modified the appearance of activated carbon fibre and it is still not clear to what extent the properties of activated carbon fibre can be changed.

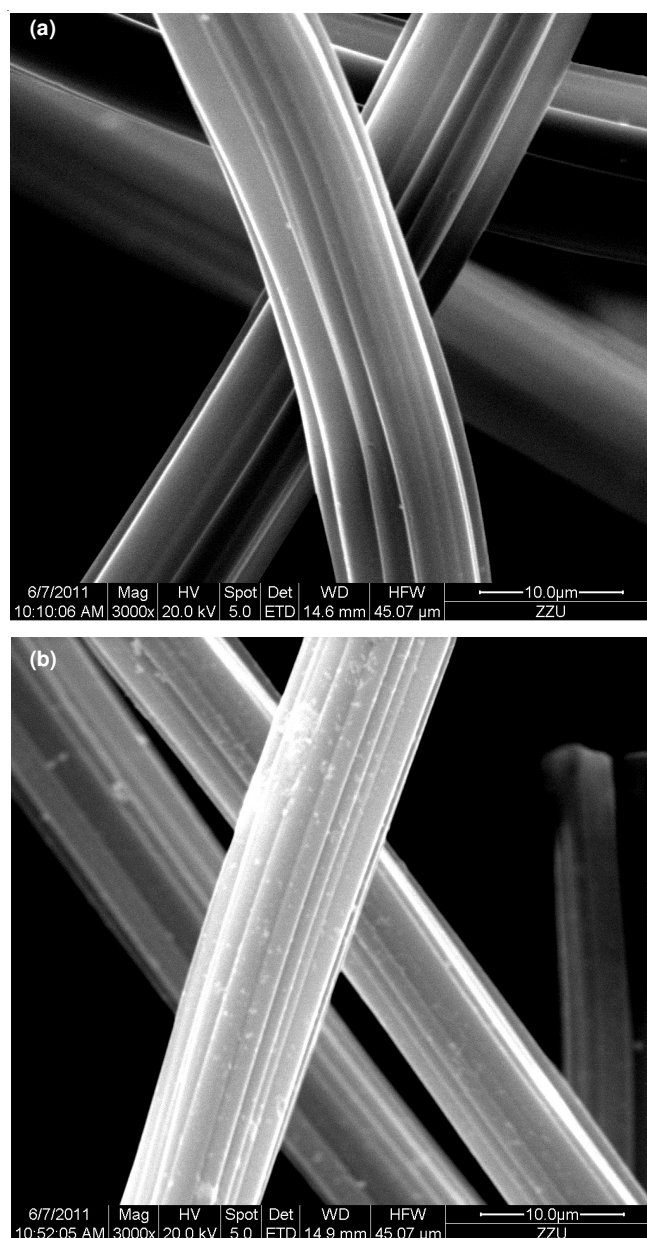


Fig. 1. SEM images of raw activated carbon fibre (a) and iron modified activated carbon fibre after adsorption (b)

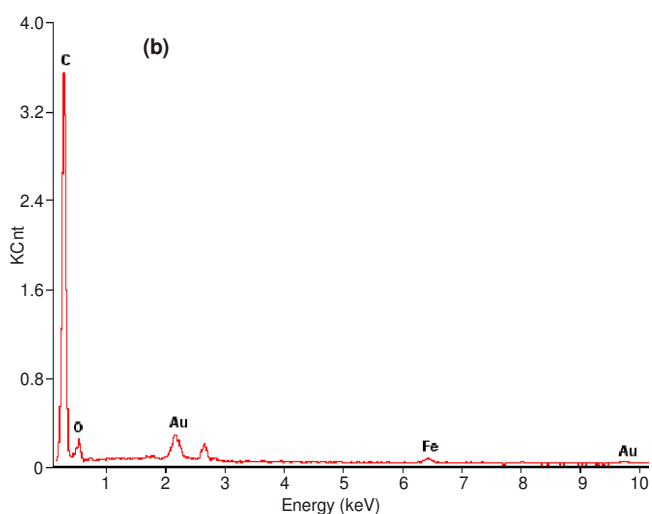
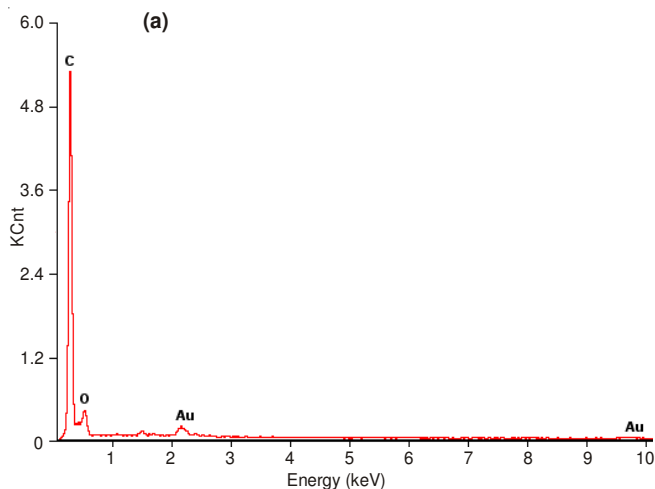


Fig. 2. EDX analysis of raw activated carbon fibre (a) and iron modified activated carbon fibre (b)

Fig. 3 shows the XRD patterns of the iron modified activated carbon fibre and raw activated carbon fibre. The broad diffraction peaks of iron modified activated carbon fibre and raw activated carbon fibre indicate a disorder amorphous material. The raw activated carbon fibre has two weak peaks at 2θ of 25.8° and 41.3° , corresponding to the (0 0 2) and (1 0 0) planes of graphite, which is consistent with other study¹⁸. The XRD patterns of the iron modified activated carbon fibre were an integration of FeCl_3 and raw activated carbon fibre. However, it has an almost identical XRD patterns with those of raw activated carbon fibre, which may be due to the negligible amount of FeCl_3 immobilized on activated carbon fibre.

Adsorption kinetics: The adsorption kinetics of As(III) on activated carbon fibre and iron modified activated carbon fibre is illustrated in Fig. 4. As other study reported¹⁹, the adsorption process could be divided into two steps in terms of kinetics. A quick step in the beginning and a subsequent slow one were observed while adsorption occurred. In our test, 61 % of the adsorption capacity was achieved for activated carbon fibre and 89.3 % for iron modified activated carbon fibre within 60 min due to the immediate electrostatic interaction between the adsorbents and As(III). The adsorption processes resulted

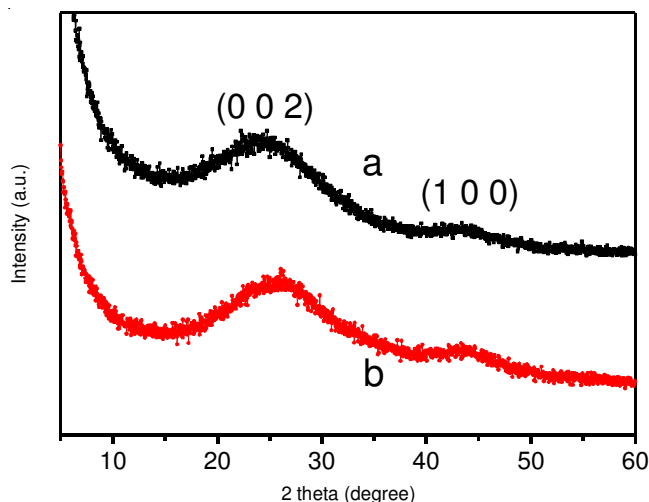


Fig. 3. XRD patterns for the iron modified activated carbon fibre (a) and raw activated carbon fibre (b)

from electrostatic attraction alone is usually in the order of seconds²⁰. After 180 min, 93.6 % of the maximum adsorption for activated carbon fibre and 96.0 % for iron modified activated carbon fibre was realized, which also indicated the slow step occurred before the final equilibrium. The above might indicate that a specific adsorption occurring between As(III) and iron modified activated carbon fibre.

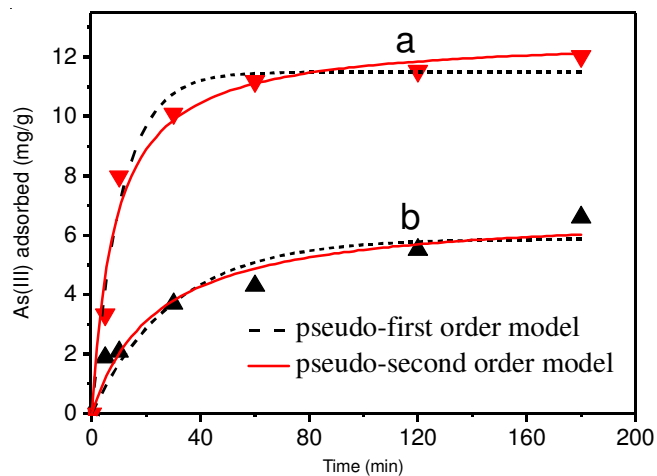


Fig. 4. Adsorption kinetics of As(III) (50 mg/L) on iron modified activated carbon fibre (a) and raw activated carbon fibre (b) in a 600 mg/L suspension at pH 7

Kinetics data for As(III) adsorption onto the iron modified activated carbon fibre was also studied with pseudo-first-order model and pseudo-second-order model^{21,22}. The mathematical representations of the models are given in

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium at any time t (min), respectively; and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

As a comparison, the intraparticle diffusion model is given as the following equation:

$$q_t = K_i t^{1/2} + C \quad (3)$$

where K_i (g/mg min^{1/2}) is the intraparticle diffusion rate constant and C is the intercept.

The rate constants obtained from the pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model are summarized in Table-1. It is obvious that pseudo-second-order model well fitted the kinetics data and K_2 value for raw activated carbon fibre and iron modified activated carbon fibre achieved 0.00531 and 0.00870 g mg/min, respectively.

Effect of solution pH: Fig. 5 shows the effect of initial solution pH on the amount of As(III) adsorbed at equilibrium conditions. The As(III) adsorbed at pH 9 on activated carbon fibre and iron modified activated carbon fibre achieved 9.3 and 15.5 mg/g, respectively. At pH 4, the values were 0.15 and 4.2 mg/g for activated carbon fibre and iron modified activated carbon fibre. It is apparent that the immobilization of iron oxide on activated carbon fibre could significantly improve the As(III) uptake by 67.8 % at pH 9. Furthermore, it is observed that the As(III) adsorbed increased with an increase of pH on both activated carbon fibre and iron modified activated carbon fibre. The pK_{a1} , pK_{a2} and pK_{a3} of H_3AsO_3 is 9.23, 12.10 and 13.41, respectively. This implies that H_3AsO_3 could not dissociated in acidic conditions, while deprotonation only occurs under highly alkaline conditions. On the other hand, the iron modified activated carbon fibre is positively charged in acidic conditions while more negatively charged in neutral and alkaline conditions.

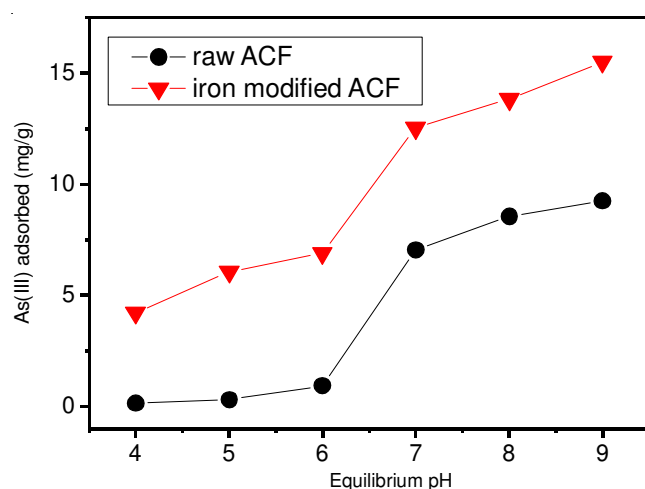


Fig. 5. Effect of solution pH on As(III) adsorption on iron modified activated carbon fibre and raw activated carbon fibre. Initial As(III) concentration was 50 mg/L and adsorbent content was a 600 mg/L

H_3AsO_3 is the predominant species for As(III) at neutral pH conditions as well as in the acidic ranges²³, which led to a weak uptake of As(III) on both adsorbents in this pH range due to a comparatively weak chemical adsorption. With the initial pH increasing from 6 to 9, As(III) removal was found to be not so significant when using activated carbon fibre alone. Once the iron oxide was immobilized on activated carbon fibre, the As(III) uptake was improved furthermore. This is mainly attributed to the effect of iron oxide immobilized on activated carbon fibre and the following reactions are expected to occur in neutral and alkaline conditions^{24,25}:



The $H_2AsO_3^-$ anions coordinated with the Fe(III) on the modified activated carbon fibre, producing more stable complexes such as Fe-O-As(OH)-O-Fe.

Effect of ionic strength: The effect of ionic strength on the adsorption process of As(III) by activated carbon fibre and iron modified activated carbon fibre at pH 7 is shown in Fig. 6. Sodium chloride was adopted as electrolyte in this investigation. It was found that the increase in NaCl concentration from 0 to 4 % enhanced the adsorption of As(III) dramatically for both adsorbents. It was reported that anions that adsorb by outer-sphere association are strongly sensitive to ionic strength²⁶. Due to the build-up of outer-sphere complexes through electrostatic forces, the adsorption of these anions is suppressed by competition with weakly adsorbing anions such as Cl^- and NO_3^- . By contrast, anions that adsorb by inner-sphere association either show little sensitivity to ionic strength or respond to higher ionic strength with greater adsorption²⁷. Consequently, the As(III) anions are expected to form inner-sphere

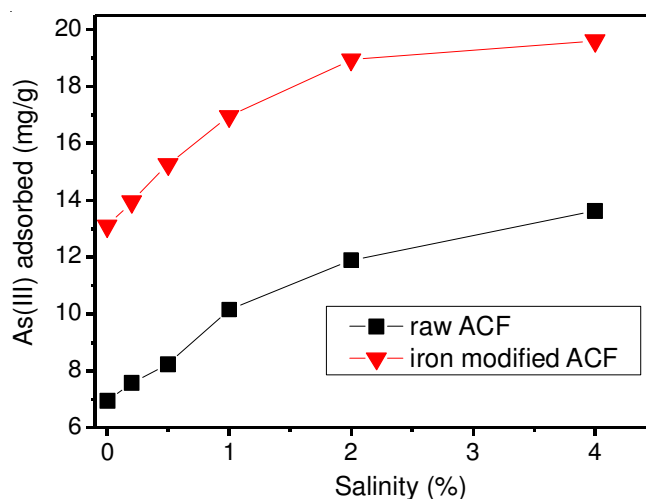


Fig. 6. Effect of ionic strength on As(III) adsorption on iron modified activated carbon fibre and raw activated carbon fibre. Initial As(III) concentration = 50 mg/L; adsorbent dose 600 mg/L; at pH 7

TABLE-1
ADSORPTION RATE CONSTANT OBTAINED FROM PSEUDO-FIRST-ORDER MODEL, PSEUDO-SECOND-ORDER MODEL AND INTRAPARTICLE DIFFUSION MODEL FOR RAW ACTIVATED CARBON FIBRE AND IRON MODIFIED ACTIVATED CARBON FIBRE

Adsorbent	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
	k_1	q_e (mg/g)	R^2	k_2 (g mg/min)	q_e (mg/g)	R^2	K_i (g/mg min ^{1/2})	C	R^2
ACF	1.88	5.77	0.965	0.00531	7.16	0.972	0.464	0.59	0.710
M- ACF	2.08	6.59	0.804	0.00870	12.66	0.998	0.834	2.91	0.968

surface complexes at the water/oxide interface. Some researchers also believed that with the increasing concentration of NaCl, more Na^+ could react with negative charges, reduce the electrostatic repulsion between anions and adsorbents and enhance the adsorption²⁸.

Effect of co-existing ions: Arsenic(III) is usually observed in contaminated underground water. Coexisting anions such as sulfate, nitrate and carbonate are generally present in the source water, which may interfere the adsorption of As(III) by competitive adsorption. The influences of coexisting anions, sulfate, phosphate, silicate, carbonate and nitrate on As(III) adsorption on iron modified activated carbon fibre are shown in Fig. 7. It should be mentioned that the concentrations of these coexisting anions are referred to their actual environmental levels. It is obvious that there is no significant influence on As(III) adsorption caused by the presence of sulfate, carbonate and nitrate. By contrast, the presence of phosphate and silicate have hindered the uptake of As(III) significantly. The similar adverse effects of phosphate and silicate on arsenic adsorption were reported by other researchers^{17,29}. The sharp decrease in the adsorption capacity resulted from phosphate and silicate may be due to their high affinity towards the iron modified activated carbon fibre.

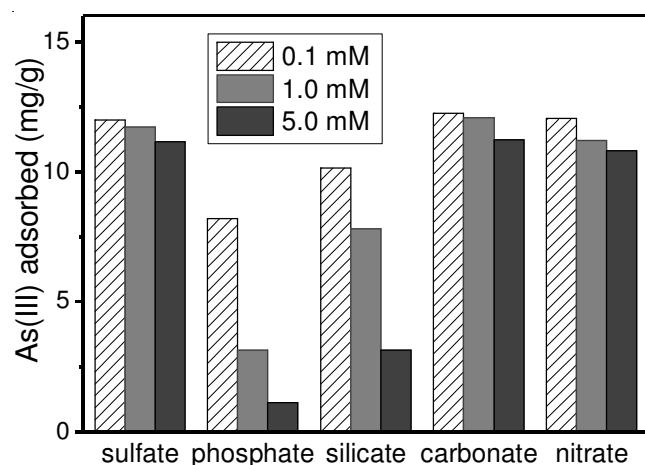


Fig. 7. Effect of co-existing ions on As(III) adsorption on iron modified activated carbon fibre. Initial As(III) concentration = 50 mg/L; adsorbent dose 600 mg/L; at pH 7

Adsorption isotherms: Both Langmuir and Freundlich models^{30,31} were employed to describe the adsorption isotherms obtained in the figure. The Langmuir equation is represented as:

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \quad (5)$$

where q_e is the amount of As(III) adsorbed onto iron modified activated carbon fibre (mg/g), C_e is the equilibrium concentration, q_{\max} is the maximum adsorption capacity of the sorbent and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

Freundlich model is applicable to adsorbents with heterogeneous surfaces and it can be expressed by the following equation:

$$q_e = k_f C_e^n \quad (6)$$

where k_f is roughly an indicator of the adsorption capacity and n is the heterogeneity factor, which has a lower value for more heterogeneous surfaces.

It was found that the Freundlich model fits the experimental data better than Langmuir model. The adsorption constants obtained from the Freundlich model are listed in Table-2. The Freundlich equation describes adsorption in which the adsorbent has a heterogeneous surface and adsorption sites have different adsorption energies. From this point of view, it can be deduced that the iron modified activated carbon fibre has a heterogeneous surface instead of a homogeneous one.

Adsorbents	n	lnk _f	R ²
ACF	0.846	-0.477	0.991
Iron modified ACF	0.538	0.287	0.986

Electrochemically assisted adsorption and desorption

of arsenite: The effect of external electric field on As(III) adsorption by iron modified activated carbon fibre were examined. It was observed that the adsorptive removal efficiency achieved 8.2 % after 60 min of adsorption. Once the electric field of 1.2 V was applied across the anode and cathode, the removal efficiency of 20.1 % was obtained. This indicates that the external electric field can help to improve the removal of As(III) by 145.1 %.

In order to examine the regeneration and reusability of iron modified activated carbon fibre for electrosorption, desorption experiment was conducted by reversing the polarity of the electric field and the results were presented in Fig. 8. It is noted that after 180 min of electrosorption, the 1.2 V electric field was reversed and desorption continued for 120 min. The desorption ability reached 76.8 % compared with the adsorption capacity at 180 min.

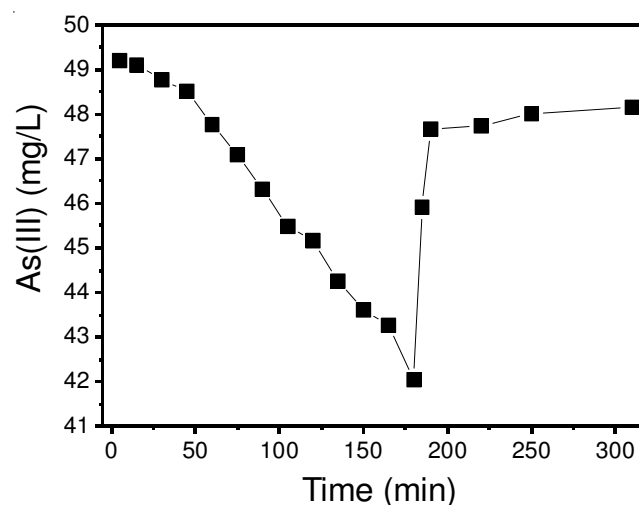


Fig. 8. Adsorptive kinetics curve by external electric field at 1.2 V and desorption of As(III) by reversing the polarity of the electric field on iron modified activated carbon fibre. As(III) solution (50 mg/L) 100 mL, at pH 7

Conclusion

Iron modified activated carbon fibre was prepared by wet impregnation method and used for the adsorptive removal of As(III). The kinetics adsorption experiment indicates that most of the uptake of As(III) occurred in the first 60 min. Pseudo-second-order model fitted the kinetics data better. Ionic strength test indicates that the adsorption process formed inner-sphere complexes. The presence of sulfate, carbonate and nitrate had insignificant influence on As(III) adsorption, while phosphate and silicate hindered the adsorption obviously. The increase of solution pH enhanced the adsorption capacity. The Freundlich equation well described the adsorption isotherm. External electric field was proved to have improved the As(III) adsorption onto the sorbent and helped the desorption of As(III) as well.

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