Arsenate removal from aqueous media on iron-oxide-coated natural rock (IOCNR): a comprehensive batch study

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ABSTRACT

Iron-oxide-coated natural rock (IOCNR) was used as an adsorbent of arsenate, As(V), from aqueous solution. Batch adsorption studies were performed at $25 \pm 2°C$ and pH 5.7 ± 0.2 with agitation at 200 rpm. Based on a batch study, 0.148 mm particles were adopted in this investigation. A $5\,g\,L^{-1}$ dose of adsorbent removed $\sim99.6\%$ As(V) from the aqueous media within a shaking time of 4 h when the initial As(V) concentration was $3\,mg\,L^{-1}$. The adsorption process followed the pseudo-second-order kinetic model. The maximum adsorptive capacity of IOCNR was calculated from the Langmuir isotherm $16.92\,mg\,g^{-1}$. The D–R isotherm revealed the nature of the adsorption process. The dimensionless parameter (R_L) and Gibbs free energy changes (ΔG^o) suggest that the process is favorable and spontaneous. The study was performed in the presence of different coexisting ions, including organic contaminants, at various pH values of the medium, to determine their effects on the removal of As(V). Film diffusion controlled of the process was evidenced from the D_f value and multiple interruption tests. The As(V) removal efficiency (%) was compared with that of the patented adsorbent LEWATIT FO36. Finally, the IOCNR has been applied to remove arsenic from real arsenic-bearing sample.

Keywords: As(V); Batch adsorption; Natural rock; Kinetic study; Isotherm; pH

1. Introduction

The pollution of groundwater by arsenic is a serious global problem. In Asia, about 100 million people are affected by arsenic-related diseases [1]. In many parts of the world including various parts of Taiwan, large amounts of arsenic-contaminated groundwater are consumed [2–4]. The leaching of arsenic into groundwater is still not clearly understood, but the literature includes a number of hypotheses. Arsenic that is sorbed and sequestered on

Fe/Mn oxides is considered to be one of the most common sources of arsenic in some sedimentary basins. Arsenic-enriched Fe(III) hydroxides are a likely source of arsenic, which is released by reductive dissolution upon changes in pH or redox conditions [5,6]. The biochemical cycles of Fe, S, and As are closely linked to each other [4,7]. Arsenic can also leach into groundwater by the oxidation of pyrite or arsenopyrite [8,9]. Groundwater pollution can be caused by inorganic and organic arsenic compounds. However, organic arsenicals are of little importance as they are detoxified via biotransformations. The pollution of

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water by inorganic arsenicals is mostly due to arsenite, As(III), and arsenate, As(V). Arsenic speciation depends on the redox conditions. As(III) is usually present in reducing groundwater, and As(V) is normally present in oxidizing groundwater [4]. In oxidizing environments, As(V) is generally present in the form of $HAsO_4^{2-}$ at high pH and $H_2AsO_4^{-}$ under acidic conditions. As(III) typically exists as $As(OH)_4^{-}$ at high pH and $As(OH)_3$ over most acidic and neutral pH values. The adsorption of As(V) is higher at lower pH values and that of As(III) is higher at higher pH values [10]. As(V) adsorption is highest at a pH of 4.0 whereas that of As(III) is highest at pH of 7.0 [11].

The people who live in the mountainous area of the Lanyang Plain (Northeastern Taiwan) consume much arsenic-contaminated groundwater ($As_{tot} = 0.60\,mg\,L^{-1}$) and use it for household chores. The level of contamination is much higher than the limit, $0.01\,mg\,L^{-1}$, that is recommended by the World Health Organization (WHO). High arsenic concentrations of 4.32 and $4.60\,mg\,L^{-1}$ in groundwater have been found in the hot spring areas of Beitou and the volcanic areas of Tatun, Taiwan, and this groundwater is used in the homes of the population [12–14]. The toxicity of arsenic is well documented and As(III) is assumed to be more toxic than As(V), because it readily attacks the sulfhydryl radicals that are in our bodies and denature the proteins and enzymes [1]. Long-term exposure to highly arsenic-contaminated water can cause dermal problems, headaches, vomiting, cancers in different organs, and finally death. Although WHO recommends a maximum contaminant level (MCL) of $0.01\,mg\,L^{-1}$, different countries have their own guidelines [13].

The effectiveness of a number of approaches in removing arsenic from drinking water has been investigated [15–19]. They efficiently remove arsenic from drinking water, but they require toxic and expensive chemicals and generate a large amount of exhaust sludge, which is sometimes not regenerable. Secondly, the pH of the aqueous media must sometimes be adjusted to improve efficiency, requiring post-treatment of the effluents. However, adsorption is a very efficient method for removing contaminants from aqueous media.

Numerous adsorbents have been developed and used to remove arsenic from drinking water and these have been extensively reviewed [20,21]. Iron, aluminum, and copper are believed to have greater affinity toward arsenic, as they form different adsorbed compounds with it [22,23]. Hence, different natural adsorbents have been developed where sometimes a high adsorbent dose is required with low removal efficiency [23–29]. Therefore, synthetic adsorbents have been developed to remove arsenic from aqueous media and are found to be effective [22,30–38].

This investigation considers the efficiency of the removal As(V) from an aqueous medium by a newly developed adsorbent iron-oxide-coated natural rock (IOCNR). The removal efficiency of the developed adsorbent was compared with those in previous studies and with that of a commercially available patented adsorbent. The granulated natural rock (NR) that is used in this study is granite. Granite is an igneous rock and is formed from magma. Granitic magma has many potential origins but it always intrudes upon other rocks. Most granite intrusions are at depths of between 1.5 km and 50 km in the thickest part of the continental crust. Although the elemental composition of granite rock depends on its source, it has some common constituents [39]. The granulated NR rock in this study was crushed and loaded with Fe(III).

2. Materials and methods

2.1. Reagents

All of the chemicals that were used herein were of analytical reagent grade and used without further purification. All of the aqueous solutions were prepared in Milli Pore (MP) water. The MP water was tested to determine its arsenic concentration, if any. It contained no arsenic to within the limits of detection ($<5\,\mu g\,L^{-1}$). As(V) stock solution with an arsenic concentration of $20\,mg\,L^{-1}$ was prepared using $Na_2HAsO_4.7H_2O$ (Alfa Aesar). It was diluted as required. An average result of three replicates was considered in each case.

Concentrated HCl, NaOH, $Fe(NO_3)_3.9H_2O$, $NaNO_3$, Na_2HPO_4, $Na_2SiO_3.9H_2O$, $Na_2EDTA.2H_2O$, $CaCl_2$, NaCl, $FeCl_3.6H_2O$, NH_4OH, NH_4Cl, $MgCl_2.6H_2O$, Erichrome black T, and 2-methoxy methanol were purchased from J. T. Baker. Sodium sulfate, Na_2SO_4 was purchased from Fluka. The sodium salt of humic acid was obtained from Aldrich and 2,4-dychlorophenoxiacetic acid (2,4-D) was obtained from Sigma. Endosulfan (soluble in warm water) was purchased from Chem. Service. The chemicals were used as received. Appropriately diluted solutions were made as and when required.

2.2. Apparatus and instruments

All of the apparatus used were soaked in concentrated HNO_3 (J. T. Baker) for 12 h and then washed in MP water followed by tap water, before being dried in a hot-air oven. A Perkin Elmer AAnalyst 200, atomic absorption spectrophotometer was connected to a high-performance liquid chromatography (HPLC, PerkinElmer, series 200) to quantify arsenic. A JEOL JSM-7000F (Japan) field scanning electron microscope

was used to perform SEM and EDX. An electrical balance was used for weighing. A mechanical orbital shaker was used to shake all of the solutions. Gilson micropipettes with disposable tips were used to add samples. A digital pH meter was used to measure all pH values. The total amount of iron in aqueous media before and after treatment with IOCNR was measured by the ferrozine method using a spectrophotometer (Thermo, Genesys 10 vis, Japan).

2.3. Preparation and characterization of adsorbent IOCNR

Commercially available granulated NR was purchased and used as the raw material for the arsenic adsorption. After washing in tap water and drying in the sun for 2–3 days, it was manually crushed and sieved to obtain the adsorbent of appropriate geometric mean size 0.148 mm. This was thoroughly washed in large volumes of tap water to remove the unwanted dust, sand, and small particles. Finally, it was washed in MP water and dried in a hot-air oven overnight at 140–150°C. At room temperature, 100 g of this adsorbent was soaked in Fe(III) nitrate solution (50 g in 150 mL MP water). This solution was then homogeneously mixed with a magnetic stirrer for 30 min. The solution was evaporated in a hot-air oven overnight at 140–150°C. This process enabled Fe(III) to be coated as an oxide onto adsorbent surface [40]. At room temperature, the Fe(III) oxide-coated-dried-adsorbent was repeatedly washed in MP water to remove excess Fe(III) oxide from the adsorbent surface until the supernatant water (iron concentration $< 0.2\,\mathrm{mg\,L^{-1}}$) was removed. The adsorbent was dried a third time in a hot-air oven overnight at 140–150°C and called IOCNR. The constituent elements and surface morphology of the adsorbent before and after loading with Fe(III) oxide were characterized using SEM and EDX (Table 1). Only surface morphology of the adsorbent can be revealed from SEM. No clear differences were observed between the two images, but the elemental compositions of the adsorbent were obtained from EDX. The technique did not detect any iron in the raw NR, but revealed the presence of a significant amount of iron (11.78% by weight) on the adsorbent after the treatment with Fe(NO$_3$)$_3$.9H$_2$O. No arsenic was detected in raw NR or IOCNR but after As(V) adsorption, adsorbed arsenic was detected on IOCNR by EDX (Table 1) (Fig. 1). The surface area and the pore volume of the adsorbent, determined using BET analysis (Micrometry TriStar 300), were 15.3120 m^2/g and 0.01347 cm^3/g, respectively. The smaller the size of the particle the larger the surface area, but this helps to clog the column during the operation.

During EDX study, the JEOL JSM-7000F field scanning electron microscope was operated under the probe current of 8 nA and in the operation voltage of 15 kV. The software, Inca-4.09 was used to run the instrument. The total sample area on the sample probe was $1 \times 0.5\,\mathrm{cm^2}$. Prior to the analysis, to make the sample conductive, C-sputtering (SPI module carbon coater) was done on the sample for 100 s. This may cause the presence of carbon in the adsorbent. The particle magnification was between 40–100 μm and the processing option was oxygen by stoichiometry (normalized). During EDX, the X-ray penetrates 2 μm thickness of the particle. The total of 8 standards were (C as CaCO$_3$, Na as albite, Mg as MgO, Al as Al$_2$O$_3$, Si as CaSiO$_3$, Ca as CaSiO$_3$, Fe as Fe$_2$O$_3$, and As as InAs) followed during the analysis. Fig. 1 shows the EDX spectra of the adsorbent before and after loading of Fe(III) and As(V).

2.4. Batch adsorption study

Batch experiments were carried out at 25 ± 2°C using 50 mL synthetic As(V) samples of arsenic in a mechanical shaker at an agitation speed of 200 rpm. The samples were put in 100 mL polyethylene bottles. The experiments were carried out to determine the dose and size of the adsorbent that were effective for As(V) removal. To evaluate the optimal adsorbent dose, experiments were carried out using adsorbent doses of 0–6 g L^{-1}. The pH of the medium was 5.7 ± 0.2 and the As(V) concentration was 3 mg L^{-1}. The optimal adsorbent dose, 5 g L^{-1}, effectively reduced the concentration of As(V) to the MCL of 0.01 mg L^{-1}, so this dose was selected in the subsequent studies.

An equilibrium study of the contact time of an As(V)-contaminated sample with the adsorbent was also conducted using an arsenic concentration of 3 mg L^{-1}. The pH of the medium was 5.7 ± 0.2. The shaking time varied from 0–7 h. The equilibrium time was found to be 4 h, and this was used for further studies. To determine the optimal As(V) concentration, experiments were conducted with various initial As(V) concentrations from 3 to 6 mg L^{-1} under the same experimental conditions. An initial As(V) concentration of 3 mg L^{-1} declined to 0.01 mg L^{-1} and was selected in all subsequent studies. Studies were then carried out to assess the As(V) removal efficiency onto IOCNR at different pH values of the medium and to determine the optimum pH range for removal. In each case, the adsorbent dose was 5 g L^{-1} and the agitation speed was 200 rpm. The pH of the medium was adjusted by adding HCl or NaOH. Water may contain various common cations and anions, but the present

Table 1
Characteristics and composition of IOCNR before and after treatment with Fe(III) and loading with As(V)

Properties	Quantitative values (EDX)		
	Before Fe(III) loaded	After Fe(III) loaded	After As(V) loaded
Geometric mean size (mm)	0.148	—	—
Bulk density (g cm^{-3})	3.3	—	—
Surface area (m^2 g^{-1})	15.3120	—	—
Pore volume (cm^3 g^{-1})	0.01347	—	—
Al (%)	3.14/1.88 (*w/a)	2.72/1.76 (w/a)	2.39/1.53 (w/a)
Fe (%)	—	11.78/3.69 (w/a)	10.53/3.26 (w/a)
Si (%)	9.93/5.70 (w/a)	9.29/5.78 (w/a)	7.48/4.6 (w/a)
C (%)	18.56/24.92 (w/a)	15.75/22.94 (w/a)	17.09/24.59 (w/a)
Na (%)	1.42/0.99 (w/a)	0.97/0.74 (w/a)	0.82/0.62 (w/a)
Mg (%)	0.63/0.42 (w/a)	0.80/0.58 (w/a)	—
Ca (%)	1.51/0.61 (w/a)	—	—
As (%)	−0.21/−0.04 (w/a)	−0.40/−0.09 (w/a)	0.47/0.11 (w/a)
O (%)	65.01/65.52 (w/a)	59.08/64.60 (w/a)	59.91/64.71 (w/a)
pH$_{ZPC}$	5.8	—	—
Cation exchange capacity	8.6 mequiv/100 g	—	—

Notes: ^{*w} = weight %, ^{a} = atomic %.

study is concerned with the effects of some of them on As(V) removal. The ions of interest were Cl^- (0–1,000 mg L^{-1}), NO_3^- (0–1,000 mg L^{-1}), SO_4^{2-} (0–1,000 mg L^{-1}), HPO_4^{2-} (0–100 mg L^{-1}), SiO_3^{2-} (0–10 mg L^{-1}), Ca^{2+} (0–1,000 mg L^{-1}), Fe^{3+} (0–5 mg L^{-1}), and ethylenediaminetetraacetic acid (0–10 mg L^{-1}), as well as those of common organic contaminants, such as humic acid (10 mg L^{-1}), endosulfan (10 mg L^{-1}), and 2,4-dichlorophenoxyacetic acid (2,4-D; 10 mg L^{-1}). High concentrations of some ions were considered as these are frequently present in industrial discharge. In each instance, the term "0" represents the blank condition. All of the interference studies were carried out at pH 5.7 ± 0.2. Adsorption isotherm experiments were also conducted to understand the equilibrium distribution of As(V) onto IOCNR. In all experiments, the samples were allowed to stand for 5 min after shaking and were then filtered through Advantec 5C filter paper; the remaining concentration of As(V) in the filtrate was then analyzed.
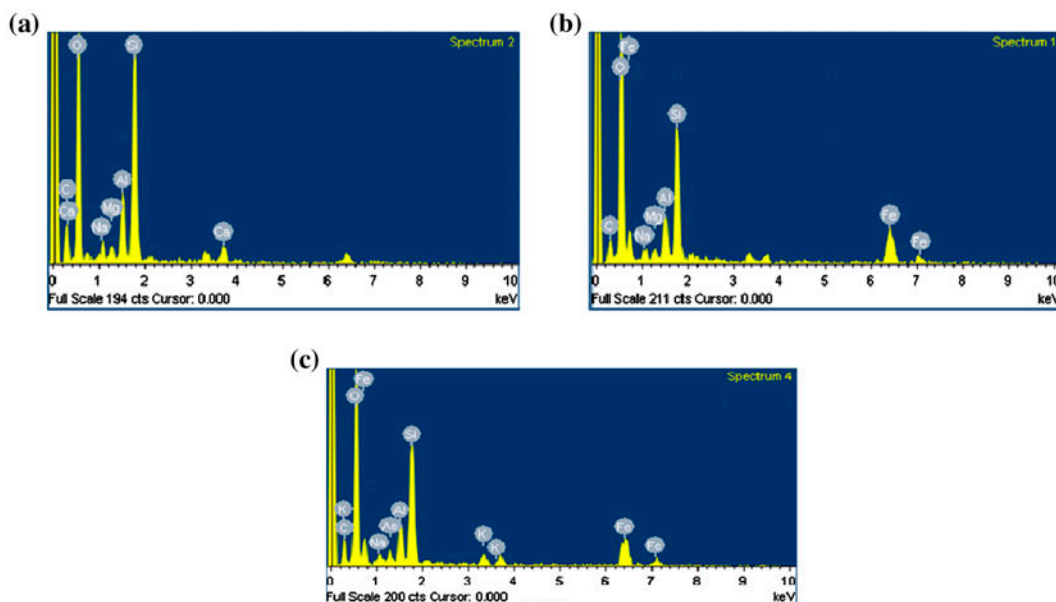

Fig. 1. EDX spectra (a) before loading Fe(III), (b) after loading Fe(III), and (c) after loading As(V) on IOCNR.

2.5. Procedure for interruption test

It is important to determine the rate-limiting step (the slowest step) of the adsorption process in batch study. To conduct this study, a series of 10 plastic bottles (100 mL capacity) were taken for As(V). In each bottle, 50 mL arsenic solution of $3 \, mg \, L^{-1}$ concentration was taken with the addition of $5 \, g \, L^{-1}$ dose of IOCNR as an adsorbent. Out of 10 such bottles, only 5 bottles were used for interruption tests and 5 for uninterrupted tests. The bottles were agitated in a mechanical shaker at 200 rpm speed. In the interruption tests after 15 min of shaking, the first sample bottle was withdrawn and interrupted for a period of 30 min. With the completion of 30 min of interruption, the sample bottle was reintroduced into the shaker and shaken for 15 min, and the same sample bottle was finally withdrawn. Therefore, the first sample was agitated for 30 min (15 + 15 min) with an interruption of 30 min. Similarly, the second sample bottle was withdrawn after 30 min of shaking and interrupted for 30 min and finally agitated for another 30 min and withdrawn completely. Therefore, the second bottle was agitated for 1 h with an interruption of 30 min. Similarly, 3rd, 4th, and 5th sample bottles were withdrawn for an interruption of 30 min after an initial agitation of 45, 60, and 75 min, respectively, and reintroduced for another period of 45, 60, and 75 min. Thus, all the bottles were interrupted for 30 min and had a total agitation of 30, 60, 90, 120, and 150 min sequentially from first to fifth bottle. For the uninterrupted test, five bottles on the shaker were withdrawn completely after 30, 60, 90, 120, and 150 min of shaking without any interruption. The samples were collected from all the 10 bottles and remaining concentrations of arsenic were analyzed.

3. Results and discussions

3.1. Batch adsorption of As(V) on IOCNR

3.1.1. Effect of contact time on adsorption

In the batch experiments, the equilibrium time (optimal contact time between adsorbate and adsorbent) for the uptake of arsenic by IOCNR had to be determined. These experiments were conducted at 25 ± 2°C. The initial As(V) concentration was set to $3 \, mg \, L^{-1}$; the adsorbent dose was $5 \, g \, L^{-1}$, and the size of the adsorbent particles was 0.148 mm. The pH of the medium was 5.7 ± 0.2. The shaking time was varied from 0 to 7 h and the agitation speed was 200 rpm. Within 1 h of shaking, ~78% As(V) was adsorbed on IOCNR. Shaking for another 3 h removed ~99.6% As(V) from the aqueous medium. Fig. 2

shows the equilibrium kinetic profile of the uptake of As(V) by IOCNR over time. A contact time of 4 h was chosen to ensure that equilibrium was reached in the removal of As(V). Notably, only ~25% As(V) was removed using an adsorbent dose of $20 \, g \, L^{-1}$ adsorbent without Fe(III) loading, when the initial As(V) concentration was $0.5 \, mg \, L^{-1}$ and the contact time was 5 h, keeping all other experimental conditions fixed.

3.1.2. Effect of initial As(V) concentration

Batch studies were performed using various As(V) concentrations (3, 4, 5, and $6 \, mg \, L^{-1}$) to determine the optimal As(V) concentration for IOCNR. The adsorbent dose was $5 \, g \, L^{-1}$. All other experimental conditions, pH of medium, temperature, adsorbent size, shaking speed, and shaking time (4 h, equilibrium time) were kept constant. Then, the filtered samples were analyzed to determine the concentration of As(V) in the solution. The removal efficiency, which depended on the As(V) concentration, varied from ~99.6 to ~85.2%. The number of adsorbent sites is assumed to be the same in all cases, explaining the decrease in removal efficiency with increasing As(V) concentration [41]. Fig. 3 plots the As(V) removal efficiencies at various concentrations.

3.1.3. Effect of adsorbent dose

Batch adsorption studies were conducted using various adsorbent doses. The initial As(V) concentration was $3 \, mg \, L^{-1}$. All other experimental conditions were kept constant as they were used in determining the effect of contact time on the adsorption process (Section 3.1.1.). The adsorbent dose was varied from 0
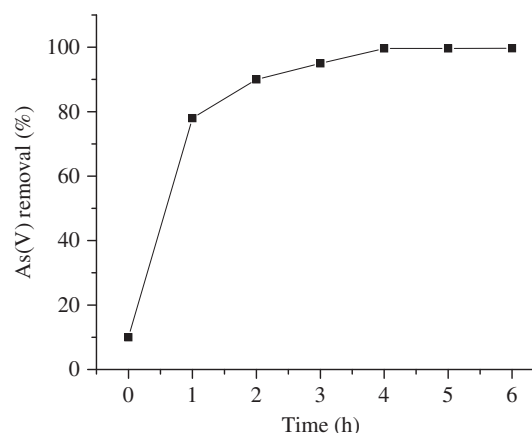

Fig. 2. Equilibrium kinetic profile over time (h) [conditions: As(V) = $3 \, mg \, L^{-1}$, pH = 5.7 ± 0.2, temperature = 25 ± 2°C, dose = $5 \, g \, L^{-1}$, shaking speed = 200 rpm].

to $6\,g\,L^{-1}$. Approximately 99.6% As(V) was removed at an adsorbent dose of $5\,g\,L^{-1}$, which was selected in all subsequent studies. Fig. 4 shows the results.

3.1.4. Effect of particle size and kinetic study

Adsorbent particles of two sizes, 0.148 mm (surface area $15.3120\,m^2\,g^{-1}$ and pore volume $0.013476\,cm^3\,g^{-1}$) and 0.178 mm (surface area $11.1602\,m^2\,g^{-1}$ and pore volume $0.009204\,cm^3\,g^{-1}$), were prepared and their capacity to adsorb As(V) from the aqueous media was investigated. The experiment was performed under the optimized conditions. About 99.6 and ∼85.2% As (V) were removed after 4 h (equilibrium time) of shaking time, using particles of sizes 0.148 and 0.178 mm, respectively. The smaller particles had a larger surface area and therefore a higher adsorption rate [42]. Thus, particles of size 0.148 mm were used as the adsorbent throughout the study.

In batch experiments, kinetic studies determined the contact time of the adsorbent with adsorbate and evaluate reaction coefficients. In order to investigate the mechanism of arsenic adsorption onto IOCNR, four kinetic models were analyzed: first-order reaction model [43], based on the solution concentration, pseudo-first-order equation of Lagergren et al. [44], based on the solid capacity, second-order reaction model, based on the solution concentration, and pseudo-second-order reaction model of Ho and Mckay [45], based on the solid phase sorption. The best-fit sorption mechanisms were also compared.

3.1.4.1. First-order reaction model.
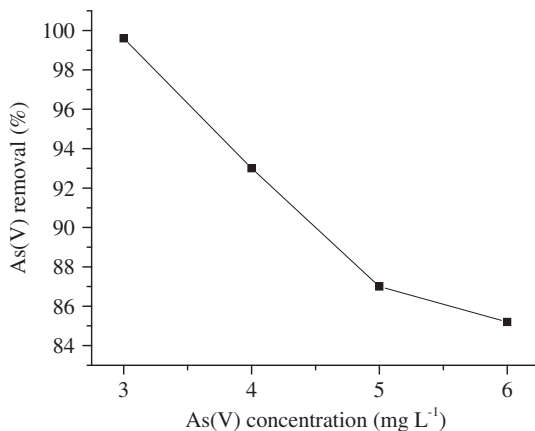The integrated form of first-order rate equation based on the solution concentration can be represented as:

Fig. 3. Effect of initial As(V) concentration on removal [conditions: As(V) = 3 mg L^{-1}, pH = 5.7 ± 0.2, temperature = 25 ± 2°C, dose = 5 g L^{-1}, shaking speed = 200 rpm].
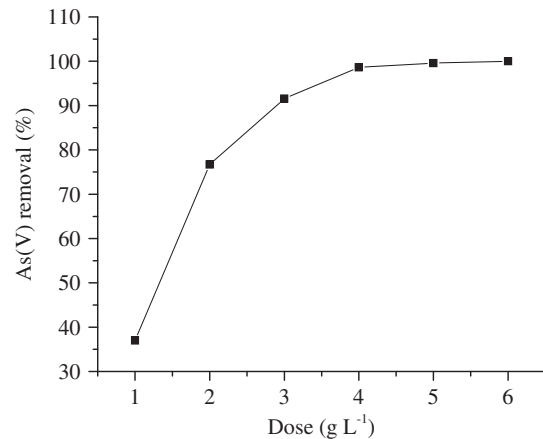

Fig. 4. Effect of adsorbent dose on As(V) removal) [conditions: As(V) = 3 mg L^{-1}, pH = 5.7 ± 0.2, temperature = 25 ± 2°C, shaking speed = 200 rpm].

$$\ln C_t = \ln C_0 - k_1 t \qquad (1)$$

Eq. (1) dictates that a plot of $\ln C_t$ vs. time (t) indicates the linear plot of the first-order equation (Fig. 5 (a)). Best-fit line is drawn and the coefficient of the determinant of (R^2) value was 0.950, which indicates that the adsorption process followed the first-order reaction model in a little better way.

3.1.4.2. Pseudo-first-order reaction model.
The integrated form of pseudo-first-order kinetic model based on the solid capacity for sorption analysis is of the form:

$$\ln(q_1 - q_t) = \ln q_1 - ks_1 t \qquad (2)$$

Therefore, Eq. (2) infers that a linear plot of $\ln(q_1-q_t)$ vs. time (t), indicates a pseudo-first-order as shown in Fig. 5(b). The linear fit correlation coefficient of the determinant of (R^2) value was 0.950 indicates that the adsorption process also followed pseudo-first-order reaction model in a little better way.

3.1.4.3. Second-order reaction model.
Integrated form of second-order rate equation is widely used for adsorption process and can be mathematically represented as:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \qquad (3)$$

Eq. (3) dictates that a linear plot of $1/C_t$ vs. time (t) indicates that the reaction rate is of second order. Fig. 5(c) displays a plot of $1/C_t$ vs. time (t) for the process. The poor linear correlation coefficient of the determinant value ($R^2 = 0.920$) indicates that the adsorption did not follow the second-order reaction model.
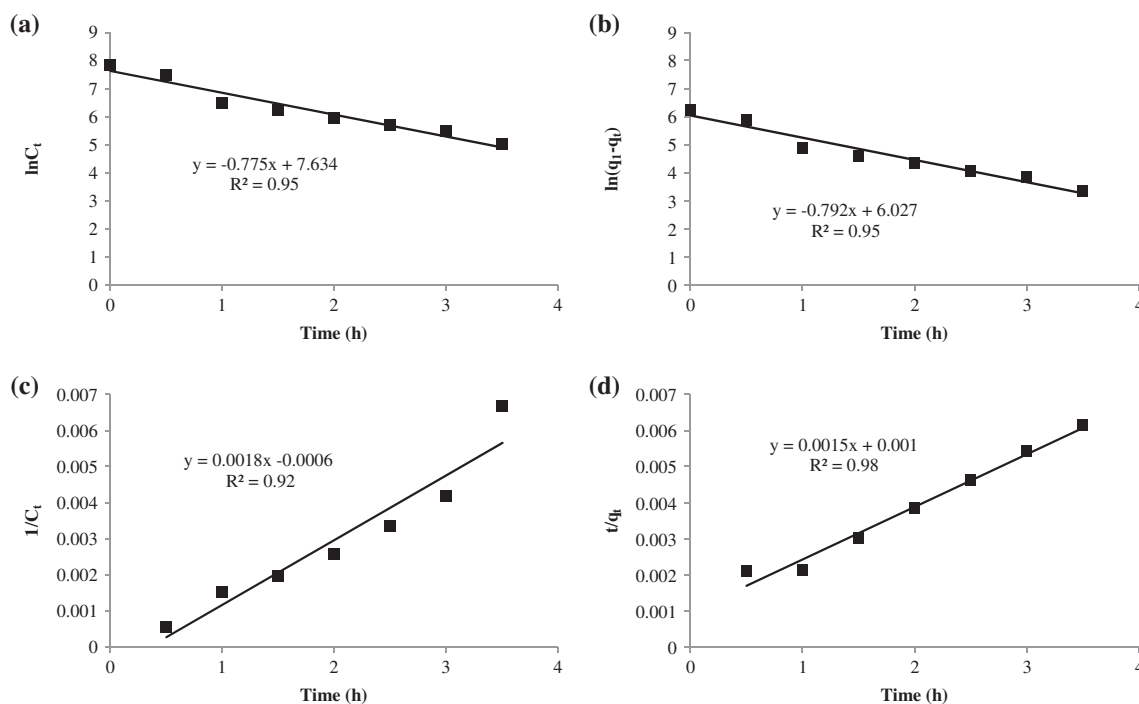
Fig. 5. Different linear kinetic models (a) first-order reaction model, (b) pseudo-first-order reaction model, (c) second-order reaction model, and (d) pseudo-second-order reaction model [conditions: As(V) = 3 mg L^{-1}, pH = 5.7 ± 0.2, temperature = 25 ± 2°C, shaking speed = 200 rpm, dose 5 g L^{-1}].

3.1.4.4. Pseudo-second-order reaction model. An integrated form of pseudo-second-order expression based on the adsorption equilibrium capacity may be expressed as:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{4}$$

This is the integrated rate law for a pseudo-second-order reaction.

Rearranging Eq. (4) obtains:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{5}$$

where $h = k \, q_e^2$

Eq. (5) indicates that a linear plot of t/q_t vs. time (t) confirms that the reaction rate followed pseudo-second-order kinetics (Fig. 5(d)). The correlation coefficient of the determinant of (R^2) value was 0.980. Based on the coefficient of the determinant of values, the adsorption processes followed the pseudo-second-order reaction kinetic model better than the other three kinetic models. Table 2 presents the equations for all reaction kinetic models with their correlation coefficient (R^2) values.

3.1.5. Adsorption isotherm study

An isotherm study was carried out to determine the amount of adsorbate adsorbed per unit mass of adsorbent at a particular temperature. Such a study can be performed in two ways: varying the adsorbate concentration with a fixed adsorbent dose or vice versa. In this investigation, the latter method is used, fixing the adsorbate concentration, and varying the adsorbent dose, since in a real sample, the arsenic concentration is fixed [42]. The disfavoring of the solvent (lyophobic) by the adsorbate and the van der Waals forces drive the adsorption process. Electrostatic forces and the exchange of ions also cause the sorption of adsorbate onto the adsorbent. If the uptake of arsenic (both As(III) and As(V)) by the adsorbent (in this case, IOCNR) is assumed to involve physical attraction or chemical coordination between the arsenic and the chemical moiety on the adsorbent, then the maximum number of adsorption sites must be finite. When the adsorbent and adsorbate come into contact with each other, a dynamic equilibrium is established between the adsorbate concentrations in the two phases. This state is dynamic, as the amount of adsorbate that returns into the adsorbent is balanced by the amount of adsorbate that migrates back into the solution. The relationship between the

Table 2
Equation for each reaction kinetic models

Model	Equation of linear fit line	R^2
First-order reaction model	$\ln C_t = 7.634 - 0.775t$	0.950
Pseudo-first-order reaction model	$\ln (q_1 - q_t) = 6.027 - 0.792t$	0.950
Second-order reaction model	$1/C_t - 0.0018t = 0.0006$	0.920
Pseudo-second-order reaction model	$t/q_t = 0.001 + 0.0015t$	0.980

amount of adsorbate that is adsorbed by the adsorbent and the equilibrium concentration of the adsorbate at a constant temperature can be expressed by the linearized Langmuir adsorption isotherm as [46],

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}}\left(\frac{1}{C_e}\right) \tag{6}$$

and the Freundlich isotherm as [47],

$$\ln q_e = \ln k_f + \frac{1}{n}(\ln C_e) \tag{7}$$

where q_e is the amount of the adsorbate (in mg) that is adsorbed per unit mass (g) of adsorbent; Q_{max} is the maximum adsorption capacity; b is the energy of adsorption (L mg^{-1}); and n and k_f are constants that depend upon the nature of the adsorbate and adsorbent, where n represents the adsorption intensity and k_f represents the adsorption capacity (mg g^{-1}). Table 3 represents the obtained values of the constants of studied adsorption isotherms.

Different adsorption isotherms are drawn to establish the model of adsorption with which they are consistent. Fig. 6(a) plots the Langmuir isotherm for As(V). The equilibrium time was 4 h; the initial arsenic concentration was 3 mg L^{-1}, and the adsorbent dose was varied from 0.5 to 5 g L^{-1}. All other experimental conditions were remained constant. The equation obtained for the Langmuir isotherm is $1/q_e = 0.0003$ (1/C_e, in mg L^{-1}) + 0.0591, yielding the coefficient of the determinant of (R^2) 0.970. The maximum adsorption capacity (Q_{max}) was 16.92 mg As(V)/g IOCNR, which agrees closely with values obtained in earlier studies (Table 4).

The Freundlich isotherm for the adsorption was also drawn for As(V) (Fig. 6(b)) by plotting ln q_e vs. lnC_e. The equation for the Freundlich isotherm is ln$q_e = 0.0898$ (lnC_e, in mg L^{-1}) + 2.9389, producing the coefficient of the determinant of (R^2) 0.910. The high value of n (>1) indicates the high adsorption of As(V)

by IOCNR. Based on the coefficient of the determinant values, the adsorption process followed the Langmuir isotherm model more closely than the Freundlich isotherm (Table 3).

A high As(V) removal rate (~78%) was observed within the first hour of shaking; it gradually increased to ~99.6% with further shaking. This high adsorption rate reveals that, in this case, the process is predominantly film diffusion controlled, because of the large difference between the concentration in the bulk solution and that in the solid phase [48]. The adsorption followed the Langmuir isotherm, further implying that the process involves monolayer chemisorption. Hence, the overall adsorption process was complex.

To understand whether the adsorption mechanism was physisorption or ion exchange, Dubinin–Radushkevich (D–R) isotherm (Eq. (8)) was drawn, using the equilibrium data [24,31,32,49] under the same experimental conditions.

$$\ln Q = \ln Q_m - k\varepsilon^2 \tag{8}$$

where ε (Polanyi potential) = $[RT \ln (1 + (1/C_e)]$; Q is the amount of arsenic adsorbed per unit weight of adsorbent (mg g^{-1}); Q_m is the adsorption capacity (mg g^{-1}); k is a constant that is related to the adsorption energy; R is the universal gas constant, and T is the absolute temperature (K). Fig. 6(c) plots ln$Q$ vs. ε^2 and the values of the constants were (Q and k) calculated from the slope and the intercept. The mean free energy of adsorption (E), defined as the change in free energy when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the k-value using the equation:

$$E = -(2k)^{-0.5} \tag{9}$$

Table 3
Constant values of different adsorption isotherms

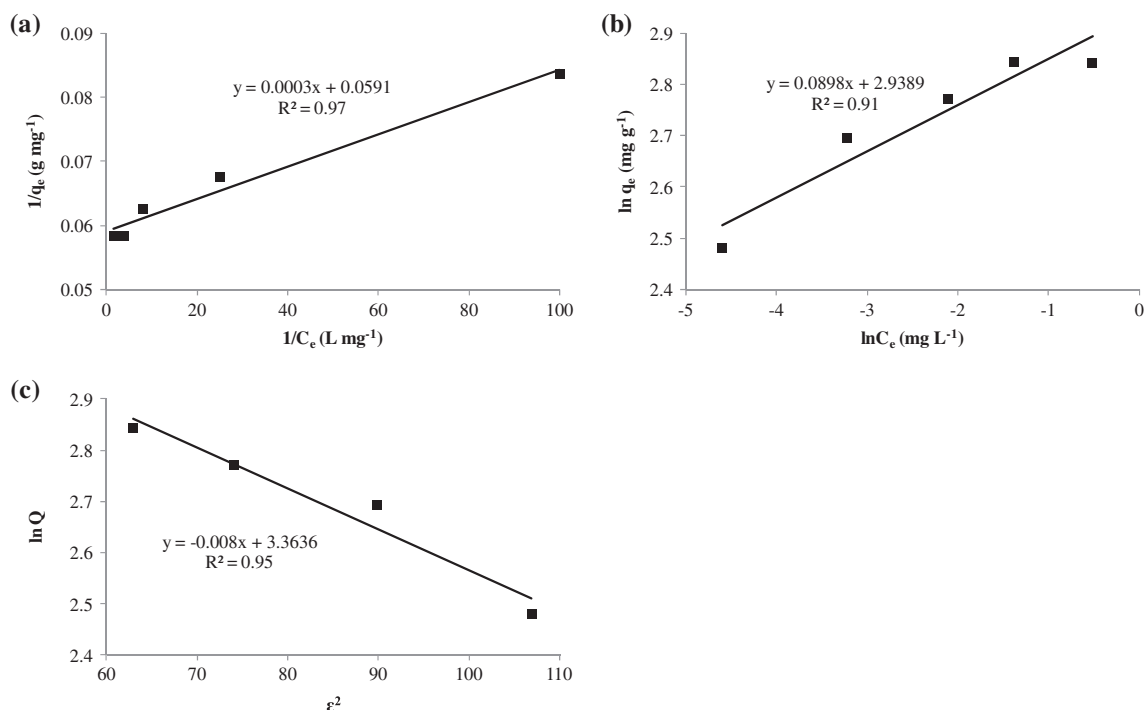| Arsenic Temperature (K)		As(V) 298 ± 2	Real sample 298 ± 2
Langmuir isotherm	Q_{max} (mg g^{-1})	16.92	0.09
	b (L mg^{-1})	197	11.40
	R^2	0.970	0.969
	k_f (mg g^{-1})	18.90	0.13
	n	25.64	5.11
Freundlich isotherm	R^2	0.910	0.983
D–R isotherm	E (kJ mol^{-1})	8.01	4.03
	Q_m (mg g^{-1})	28.90	0.47
	R^2	0.950	0.986
R_L		0.002	0.305

Fig. 6. Different isotherm models (a) Langmuir adsorption isotherm, (b) Freundlich adsorption isotherm, and (c) D–R adsorption isotherm) [conditions: As(V) = 3 mg L^{-1}, pH = 5.7 ± 0.2, temperature = 25 ± 2°C, shaking speed = 200 rpm].

Table 4
As(V) removal efficiencies of different adsorbents

Adsorbent	Adsorbent dose (g L^{-1})	Initial As(V) (mg L^{-1})	Removal (mg g^{-1})	References
Red mud	20	10	0.51	[25]
Ferralite	10	[As]$_{tot}$ = 0.185	0.01683	[29]
Laterite soil	20	0.5	0.04	[42]
Natural and modified attapulgite	125	1	12.40	[64]
Ce(IV)-doped iron oxide	0.06	1	16 .00	[65]
Char-carbon	5	157	3.04	[66]
Titanium dioxide	5	0.3	41.40	[67]
Granular ferric hydroxide	25	0.01	32.50	[68]
Surface sediments	100	10	0.092	[69]
Natural Fe and Mn enriched sample	100	0.1	8.50	[70]
IOCNR	5	3	16.92	Present study

The calculated E value was 8.01 kJ mol^{-1} (Table 3). The magnitude of E can be used to estimate the type of adsorption: if it is between 8 and 16 kJ mol^{-1}, then the adsorption proceeds by ion exchange and if <8 kJ mol^{-1}, it proceeds by physisorption [24,31,32,49]. In the present study, the obtained E value is within the range of ion exchange energies ($E > 8$ kJ mol^{-1}), because on the experimental time scale, As(V) exists in anionic form and the surfaces of the adsorbent are positively charged.

To predict the adsorption efficiency of the process and to determine whether Langmuir adsorption is favored or disfavored, the shape of the isotherm is specified by a term, R_L, which is the dimensionless equilibrium parameter that is determined using the following Equation:

$$R_L = \frac{1}{(1 + bC_0)} \tag{10}$$

where C_0 is the initial As(V) concentration (mg L^{-1}) and b is the Langmuir isotherm constant. $R_L < 1$ indicates that the adsorption is favorable whereas $R_L > 1$ means that adsorption is unfavorable [24,31]. The R_L value for an initial As(V) concentration of 3 mg L^{-1} in this study was found to be 0.002, indicating that the adsorption is highly favorable. The changes in the standard Gibbs free energy (ΔG^o) for the adsorption process can be calculated using the following equation:

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^o}{RT} \qquad (11)$$

where b (Table 3) is the Langmuir isotherm constant; R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), and T is the absolute temperature. The calculated negative ΔG^o value (-13.09 kJ mol^{-1}) indicates that adsorption of As(V) on IOCNR is a spontaneous process [24,40].

3.1.6. Effect of pH

The chemical characteristics of both adsorbent and adsorbate may vary with pH. Different As(V) oxyanions are present in aqueous media of various pH values. Hence, the adsorption study must be carried out in the media with various pH values: pH strongly influences the arsenic uptake capacity of the adsorption of As(V) by IOCNR. Prior to the addition of adsorbent into the arsenic containing solution in the bottle, the pH was adjusted to the medium. After the addition of adsorbent and during the shaking time (4 h) further pH was not adjusted, looking for the real arsenic-bearing sample, where the pH is fixed. In the batch study, the pH of the medium was varied from 2.06 to 9.68, with all other experimental conditions fixed. Table 5 presents the As(V) removal efficiency at various pH values of the medium with the final (after equilibrium) pH variation of ± 0.4. The zero point charge (Z_{PC}) of the IOCNR was determined to be 5.8 [50]. At low pH (<7), the adsorption of As(V) was effective, but the removal efficiency sharply decreased as the pH of the aqueous solution increased above seven.

As(V) oxyanions, such as $H_2AsO_4^-$ and $HAsO_4^{2-}$, exist (in this study also) in slightly acidic to basic solution. Thus, the adsorption of negatively charged As(V) species is assumed to have increased with up to the Z_{PC} of the IOCNR, because the surfaces of the adsorbent are positively charged. However, the removal efficiency was greater in the medium with a pH of 6.92. The As(V) removal efficiency sharply decreased as the pH increased above 7.0. Hence, As(V) adsorption is assumed to have occurred via ion

exchange/ion attraction, and the adsorption was reduced perhaps because of the repulsion between the As(V) oxyanions and the negatively charged surfaces of the adsorbent [11,25,35,42,51]. It is worth to mention here that at low pH, there is a chance to dissolve the coated Fe(III) from the adsorbent surface attributing the lower removal efficiency. However, in the present study, the removal efficiency at low pH was not much affected and this may be the cause of low contact time of adsorbent with solution, 4 h only.

This above phenomenon can be further explained by postulating a simple reaction mechanism that is involved in the adsorption of As(V) on Fe(III) oxide-coated adsorbent. In a water medium (acting as an oxidant), the surfaces of the Fe(III) oxide-coated adsorbent are oxidized to =FeOOH, which has a more active surface than do simple iron oxides. Dynamic electrochemical studies have shown that water is the primary oxidant for iron. Infrared spectroscopy and extended X-ray absorption fine structure have shown that As(V) and As(III) form bidentate, bimolecular surface complexes with =FeOH (or =FeOOH or hydrous ferric oxide, HFO), as the predominant species, tightly immobilized on the iron surface. The As(V) oxyanions (chemical moiety) that are present in aqueous media are attracted to the iron-oxide-coated surfaces and bound with the active sites (–OH groups), through weak intermolecular H-bonds; finally, they are bound with the surfaces eliminating water molecules [38,52,53]. Hence, adsorption is inferred to proceed via a complicated ion exchange/ion attraction.

3.2. Effect of coexisting ions

3.2.1. Effect of cations

A batch adsorption study was conducted in the presence of cations to determine their effects on the efficiency of removal of As(V) by IOCNR. It was carried out in the presence (0–1,000 mg L^{-1}) of Ca^{2+} and (0–5 mg L^{-1}) Fe^{3+}. The adsorbent dose and the initial

Table 5
As(V) removal efficiencies in media of various pH values

pH	As(V) removal efficiency (%)
2.06	99
4.35	100
5.64	99.6
6.92	99.6
8.20	95
9.68	90

As(V) concentration were $5\,g\,L^{-1}$ and $3\,mg\,L^{-1}$, respectively. The contact time was 4 h. The As(V) removal efficiency (~99%) was not much affected by the presence of Ca^{2+}. The As(V) removal efficiency was also not affected (~98.8%) by the presence of Fe^{3+}.

3.2.2. Effect of anions

An experiment was conducted to determine whether the presence of common anions in the aqueous medium had any effects on As(V) removal. Under constant experimental conditions, various concentrations of anions were added. The common anions Cl^-, NO_3^-, and SO_4^{2-} were separately added to concentrations of $0–1,000\,mg\,L^{-1}$. As(V) adsorption efficiency was not affected (~98.8%) by the presence of chloride or nitrate ions, but adding sulfate ions reduced the adsorption efficiency (from ~99 to 83%) of As(V). Similar results have been obtained in previous studies [52,54,55]. At low pH (<7, and specifically 5.7 ± 0.2, in the present study), sulfate ions were assumed to compete with arsenic removal as they formed an outer-sphere complex on the surfaces of the adsorbent [56]. The presence of HPO_4^{2-} strongly affected the As(V) removal efficiency. In the presence of only $20\,mg\,L^{-1}$ HPO_4^{2}, the As(V) removal efficiency was suppressed to ~66%. It was further reduced to ~53, ~50, ~47, and ~40% in the presence of 40, 60, 80, and $100\,mg\,L^{-1}$ of HPO_4^{2-} in the medium, because As(V) is removed mostly by exchange of the oxyanions of As(V); in this study, HPO_4^{2-} was also competitively adsorbed [11,42,57]. A similar result (~94.8%) was obtained for SiO_3^{2-} at concentrations of $4–10\,mg\,L^{-1}$ [52,58].

Ethylenediaminetetraacetate (EDTA) is a common compound, rarely present in drinking water. It may be present in industrial wastewater and infiltrate to groundwater. Thus, an experiment was conducted to determine whether the presence of EDTA has any effect on As(V) removal, using various concentrations $(0–10\,mg\,L^{-1})$ of EDTA. The obtained results suggest that EDTA did not affect As(V) removal efficiency.

3.2.3. Interference by organic contaminants

Drinking water sometimes becomes contaminated with organic compounds such as humic acid and some pesticides, which leach from agricultural land. Therefore, an experiment was conducted to determine the effects of 2,4-D (a common herbicide), humic acid (natural organic matter, NOM), and endosulfan (a common insecticide) at a concentration of $10\,mg\,L^{-1}$. The experimental results suggested that neither 2,4-D

nor humic acid affected As(V) removal efficiency. Endosulfan $(10\,mg\,L^{-1})$ has significant effect on As(V) removal, reducing the removal efficiency to ~50%, because this molecule may be rather insoluble in water and is adsorbed onto the IOCNR, reducing its removal efficiency [42].

3.3. Determination of rate-limiting step

In adsorption process, the rate of reaction is of prime importance and an understanding of the rate-limiting step greatly aids in the selection of adsorber configuration [60]. To interpret the experimental data properly, it is necessary to determine the initial step in the adsorption process, which governs the overall removal rate. The detailed explanations have been extensively discussed in the earlier study [59].

In the present study, we considered two ways to determine the rate-limiting step like (i) using first-order kinetics data [60] and (ii) using the data of interruption study [61].

3.3.1. Using first-order kinetic data

The rate-limiting step of the adsorption processes can be calculated using the first-order kinetic data and was widely used [59,62], instead of the followed pseudo-second-order kinetic data. It is because of the direct relation of diffusion coefficient values with the first-order kinetic data (rate constant) according to Michelson et al. [60] and Asher and Pankow [63]. Assuming the spherical geometry of the adsorbents, the first-order rate constant, k_1 obtained from first-order kinetic profile can be correlated to the pore diffusion (12) and film diffusion coefficients (13) as:

$$t_{\frac{1}{2}} = 0.030\frac{r^2}{D_p} \tag{12}$$

$$t_{\frac{1}{2}} = 0.23\frac{r\delta}{D_f}\times\frac{C_s}{C_e} \tag{13}$$

where $t_{1/2}$ is called the half-time equations, r is the mean geometric radius of the adsorbent particle (cm). D_p and D_f are the pore diffusion and film diffusion coefficients $(cm^2\,s^{-1})$, respectively. C_s and C_e are the concentrations of adsorbate on the adsorbent and in the solution at equilibrium $(mg\,L^{-1})$, and δ is the film thickness 0.001 cm.

The relationship between $t_{1/2}$ and k_1 (overall reaction rate constant) to obtain $t_{1/2}$ values can be expressed as [63]:

$$t_{\frac{1}{2}} = -\frac{\ln(0.5)}{k_1} \tag{14}$$

$t_{1/2}$ values can be calculated from Eq. (14) and by substituting $t_{1/2}$ values in Eqs. (12) and (13), the D_p and D_f values can be calculated for initial As(V) concentration of $3\,\mathrm{mg\,L^{-1}}$ assuming $\delta = 0.001\,\mathrm{cm}$. The values obtained are presented in Table 6. According to Michelson et al. [60], for the film diffusion to be the rate-limiting step, the value of film diffusion coefficient (D_f) should be in the range of 10^{-6}–$10^{-8}\,\mathrm{cm^2\,s^{-1}}$, and for the pore diffusion to be the rate-limiting, the pore diffusion coefficient (D_p) should be in the range of 10^{-11}–$10^{-13}\,\mathrm{cm^2\,s^{-1}}$. In the present case, film diffusion appears to be the rate-limiting step as is evidenced from Table 6.

3.3.2. Using multiple interruption tests

In an interruption test, the adsorbent is periodically separated from the adsorbate solution for a brief period of time and then recontacted when the concentration gradient of the adsorbate exists on the adsorbent due to the differential rates of film and pore diffusion. This pause introduced by interruption is expected to give an opportunity for the concentration gradient to level off. When pore diffusion is the rate-limiting step, the rate of adsorbate removal will increase immediately after the re-immersion, compared to an uninterrupted sample. However, if film diffusion is the rate-limiting process, no change in the kinetic profile will be observed upon re-immersion of the adsorbate. The curve for the interruption test is shown in Fig. 7. It is observed that there was no significant enhancement in the uptake of arsenic before and after the interruption, and the two curves are almost parallel to each other. In fact, there is a slight drop in removal efficiency. Hence, film diffusion appears to be the rate-limiting step for the present study. From the above theoretical and practical test, we can conclude that arsenic adsorption on to the adsorbent IOCNR occurs via film diffusion mechanism and hence an introduction of a pause will

Table 6
Pore and film diffusion constant values

Initial As(V) concentration ($\mathrm{mg\,L^{-1}}$)	3.0
C_e ($\mathrm{mg\,L^{-1}}$)	~0.01
k_1 ($\mathrm{s^{-1}}$)	2.15×10^{-4}
$t_{1/2}$ (s)	3.22×10^3
r (cm)	7.4×10^{-3}
D_f ($\mathrm{cm^2\,s^{-1}}$)	1.6×10^{-7}
D_p ($\mathrm{cm^2\,s^{-1}}$)	5×10^{-10}

not help in increasing the adsorption capacity of the adsorbent [59].

3.4. Batch desorption and re-adsorption

Approximately 5 g of exhausted and hot-air oven-dried IOCNR (from the batch study) was soaked in 50 mL of 1 M aqueous NaOH (in a plastic bottle) and shaken for 4 h at 200 rpm and room temperature 25 ± 2°C. The IOCNR was then separated from the suspension by filtration. The eluent was examined for the desorbed arsenic that originated from the IOCNR. Approximately 98% of the adsorbed arsenic (~99.6%) was recovered. The regenerated IOCNR was repeatedly washed in MP water to achieve a pH of ~7.0, and subsequently, dried overnight in a hot-air oven at 140–150°C. A 50 mL synthetic As(V) sample ($3\,\mathrm{mg\,L^{-1}}$) was then added to the regenerated IOCNR, keeping all other experimental conditions constant. The treated water was collected and tested to determine the remaining As(V) concentration. The result revealed that the arsenic removal efficiency of the regenerated IOCNR decreased in the second cycle to ~25% (from ~99.6% in the first-cycle). Alkaline treatment of the exhausted IOCNR by washing with NaOH washed the Fe(III) coating as Fe(III) hydroxide from the adsorbent surfaces, potentially reducing the efficiency of removal of arsenic by IOCNR [40].

3.5. Comparison of IOCNR with patented material

The commercially available patented adsorbent, LEWATIT FO36, lot No. CHK2004 (Lanxess), was purchased. Its As(V) removal efficiency was evaluated and compared with that of the developed adsorbent IOCNR. A batch experiment was conducted under the experimental conditions described above. The adsorbent dose was $5\,\mathrm{g\,L^{-1}}$, the initial As(V) concentration
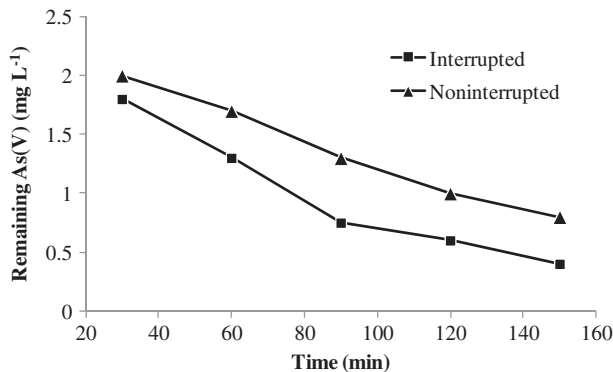

Fig. 7. Interruption test for As(V) adsorption [conditions: As(V) = $3\,\mathrm{mg\,L^{-1}}$, pH = 5.7 ± 0.2, temperature = 25 ± 2°C, shaking speed = 200 rpm].

was $3\,\mathrm{mg\,L^{-1}}$, and the contact time was 4 h. The patented adsorbent was as good as IOCNR and the As(V) removal was found to be ~100%. The effluent water quality (IOCNR-treated water) was also tested to identify the leaching of any components present in the adsorbent. No significant leaching of components was observed. The pH of the effluent water did not change much (±0.3) and iron leaching was <0.2 mg L^{-1}. The hardness of the effluent was $14\,\mathrm{mg\,L^{-1}}$.

3.6. Application to real arsenic-bearing sample

IOCNR has been used to remove arsenic from real arsenic-bearing groundwater [40]. To assess its efficiency, real arsenic-bearing groundwater was collected from the Lizen area of Lanyang Plain, East Taiwan, Taiwan. Table 7 presents the characteristics of the groundwater (before and after treatment), supplied by the Agricultural Engineering Research Centre, Tao-Yuan, Taiwan. The As$_{(tot)}$ concentration was $0.2\,\mathrm{mg\,L^{-1}}$ and the pH was 8.7. The batch study was conducted under the same experimental and operational conditions as described above. A high adsorbent dose of $38\,\mathrm{g\,L^{-1}}$ and a contact time of 7 h were required to reach the equilibrium (optimal conditions) to remove ~95% As$_{(tot)}$ from the water medium (declined to ~0.01 mg L^{-1}). The combined high concentrations of total organic carbon (TOC), phosphate, bicarbonate, and sulfate in groundwater (Table 7) may have caused the slow adsorption rate [40,49]. Hence, the Langmuir isotherm yielded a lower efficiency of adsorption by IONCR, $0.09\,\mathrm{mg\,g^{-1}}$ (dose variation studied, 5–38 g L^{-1}). The adsorption followed the Freundlich isotherm more closely than it did the Langmuir isotherm (Table 3). The adsorption process is always governed in the presence of different coexisting ions (cations/anions/organics) in the medium. However, in the present study, in great difference, values of k_f and n for the real arsenic-bearing sample with respect to As(V) synthetic sample are therefore may be the presence of both As(III) and As(V) and some undetermined ions (cations/anions/ organics). The similar result has also been reported earlier [24]. The calculated R_L value and negative ΔG^o value ($-6.029\,\mathrm{kJ\,mol^{-1}}$) suggested the favorability and spontaneity of the process. The mean free energy of adsorption (E) $(4.03\,\mathrm{kJ\,mol^{-1}})$ that was calculated from the D–R isotherm suggests physisorption, perhaps because of the presence of the naturally occurring predominant As(III) species in the experimental range of pH [10]. The quality of tested effluent water suggested that the treated water from which arsenic has been removed could be used for household purposes.

Table 7
Characteristics of real arsenic-bearing groundwater sample (before and after treatment)

Parameter	Before treatment	After treatment (filtered)
pH	8.7	8.3
Turbidity (NTU)	100	5
Hardness (mg L^{-1})	200	195
SO$_4^{2-}$ (mg L^{-1})	2.3	1.7
TOC (mg L^{-1})	43	42
Fe$_{(tot)}$ (mg L^{-1})	4.13	<0.4
HCO$_3^-$ (mg L^{-1})	1,100	1,085
PO$_4^{3-}$ (mg L^{-1})	14.00	13.82
As$_{(tot)}$ (mg L^{-1})	0.20	~0.01
Cl$^-$ (mg L^{-1})	10.0	9.6
Mg (mg L^{-1})	20.13	20.08
Ca (mg L^{-1})	28.28	28.20
Mn (mg L^{-1})	0.066	0.062

4. Conclusions

The efficiency of removal of As(V) from aqueous media using a newly developed adsorbent IOCNR was tested. A batch study was conducted at 25 ± 2°C. Experimental results suggest that a contact time of 4 h sufficed to reduce the initial As(V) concentration $(3\,\mathrm{mg\,L^{-1}})$ to the MCL 0.01 mg L^{-1} (~99.6%), which is the maximum recommended by WHO, at an adsorbent dose of $5\,\mathrm{g\,L^{-1}}$. The adsorption process followed the Langmuir isotherm model more closely than it followed the Freundlich isotherm model. The maximum adsorptive capacity of IOCNR was determined from the Langmuir isotherm model to be 16.92 mg As(V)/g IOCNR. The favorability and spontaneity of the process were estimated from the dimensionless parameter (R_L) and the Gibbs free energy changes (ΔG^o). Batch experiments were performed in the presence of different coexisting ions to determine whether they had any effects on the adsorption of As(V). Silicate, sulfate, and hydrogen phosphate adversely effected the removal of As(V). The same experiments were also performed in the presence of organic contaminants. D–R isotherm and pH studies revealed that the adsorption of As(V) on IOCNR involved ion exchange/ion attraction-type chemisorption. The adsorption process followed the pseudo-second-order reaction model more closely than other three kinetic models. Both the results using first-order kinetic data and multiple interruption tests suggested for the film diffusion of the process, the rate-limiting step. The As(V) uptake efficiency (%) of the developed adsorbent IOCNR was compared with that of the commercially available patented adsorbent. The IOCNR also

successfully removed arsenic from a real arsenic-bearing sample and the treated water could be used for domestic purposes.

Acknowledgements

List of symbols

n	—	adsorption intensity
q_e	—	amount of adsorbate adsorb at equilibrium $(mg\,g^{-1})$
q_t	—	amount of adsorbate adsorb at time $(mg\,g^{-1})$
C_s	—	adsorbate concentration on solid
C_t	—	concentration at time $(mg\,L^{-1})$
R_L	—	dimensionless equilibrium parameter
Q_m	—	D–R adsorption capacity
C_e	—	equilibrium concentration $(mg\,L^{-1})$
D_f	—	film diffusion coefficient
δ	—	film thickness
k_1	—	first-order rate constant
k_f	—	Freundlich adsorption capacity
ΔG^o	—	Gibbs free energy
$t_{1/2}$	—	half-time
C_0	—	initial concentration $(mg\,L^{-1})$
IOCNR	—	iron-oxide-coated natural rock
Q_{max}	—	Langmuir adsorption capacity
b	—	Langmuir isotherm constant
E	—	mean free energy of adsorption
r	—	mean geometric radius of the adsorbent particle
ε	—	polanyi potential
D_p	—	pore diffusion coefficient
ks_1	—	pseudo-first-order rate constant
k	—	pseudo-second-order rate constant
k_2	—	second-order rate constant
h	—	sorption rate constant
t	—	time

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