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Dynamic column adsorption of As on iron-oxide-coated natural rock (IOCNR) and sludge management

Sanjoy K. Maji, Yu-Hsuan Kao, Yeuh-Bin Wang, Chen-Wuing Liu*

Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei 106, Taiwan, ROC, Tel. +886 2 3366 3473; Fax: +886 2 2363 9557; emails: maji.sanjoy@gmail.com (S.K. Maji), d97622004@ntu.edu.tw (Y.-H. Kao), ybwang@epa.gov.tw (Y.-B. Wang), cwliu@ntu.edu.tw (C.-W. Liu)

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ABSTRACT

An extended column adsorption study on arsenic (As(III)/As(V)) was conducted using the developed adsorbent iron-oxide-coated natural rock. We considered a column with a diameter of 2 cm and varying bed depths, including 10 , 15 , and 20 . The breakthrough ($C/C_0 = 0.016$) times were 31.0, 49.0, and 63.0 h and the exhaust ($C/C_0 = 0.90$) times were 60.0, 90.0, and 110.0 h, respectively for As(III). For As(V), those were found to be (breakthrough times corresponding to $C/C_0 = 0.0033$) 5.0, 11.0, and 18.0 h and 20.0, 27.0, and 36.0 h, respectively. The up-flow rate was maintained at 8 mL min^{-1}. The As(III) and As(V) concentrations were 0.6 and 3 mg L^{-1}. Bohart and Adams sorption model was employed to determine the important column design parameters. The column was designed by the bed-depth-service-time model. The adsorption capacity (N_0) and the adsorption rate constant (K) calculated were 295.30 mg L^{-1} and 20.41 L mg^{-1} h^{-1}, respectively, for As(III) and 599.82 mg L^{-1} and 0.233 L mg^{-1} h^{-1}, respectively, for As(V). The effects on the variation of initial concentrations and flow rates were also investigated. The 10-cm exhaust bed (As(III)) was regenerated with 1 M NaOH, and its performance was evaluated. An attempt has been made to minimize the As adsorbed exhausted sludge mixing with Portland cement and the prepared blocks were used for leaching tests in different inorganic mediums for 90 d; immobility was accounted from D_e values.

Keywords: Arsenic; Column adsorption; Natural rock; BDST model; Sludge management

1. Introduction

Issues of arsenic (As) pollution in surface water/groundwater and its toxicity are one of the serious problems in the world though its leaching into groundwater is still remained unclear [1]. Oxidation of As-rich iron pyrites may be one possible mechanism [2,3]. The biochemical cycles of iron (Fe), sulfur (S), and As are closely linked to each other [4,5]. As-enriched Fe(III) hydroxides are a likely source of As, and are released by reductive dissolution following changes in pH or redox conditions in the presence of particular chemical reductants, such as H_2S, and various organic compounds such as ascorbate and humic acids [6]. People from different parts of the world consume high As-contaminated water for their daily use over the maximum permissible concentration recommended by the World Health Organization (WHO), 0.01 mg L^{-1}, the maximum contaminant level

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*Corresponding author.

[7]. Recently, Taiwan, especially northeastern Taiwan, has gained attention due to As groundwater pollution. The Lanyang Plain, which is located in Yilan County in northeastern Taiwan, is the alluvial fan of the Lanyang River. The triangular of the area is bordered by the Pacific Ocean next to the east, Snow Mountains located to the northwest, and Central Mountains located to the southwest. The river through the middle of the area flows from west to east. The area is approximately 400 km^2 with each side of triangular region about 30 km long. Well, the groundwater also in this area flows from west to east. This area is highly As-contaminated (0.60 mg L^{-1}) as well as high As concentrations of 4.32 and 4.60 mg L^{-1} in groundwater have also 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 [8,9]. Consumption of high As-contaminant water causes dermatological problems, headaches, vomiting as well as cancer in different organs, and finally death [10,11]. Among the various forms of As, generally arsenite (As(III)) and arsenate (As(V)) are responsible for water contamination where, As(III) is more toxic and more mobile than the latter. Hence, it is important and urgent to remove this toxic contaminant from the aquatic environment with developing an As-adsorbed suitable adsorbent and tried.

In respect of other developed technologies, adsorption is found to be effective to remove contaminants from the aqueous media because of its simplicity, ease of operation and handling, sludge-free operation, and regeneration capacity and hence, developed numbers of adsorbents and tried [12–14]. Considering the affinity of As toward iron, various iron-based media have been developed and used effectively as adsorbents for removing both As(III) and As(V) from water. However, the fine powdery form of iron oxides hinder their separation from the aqueous solution following the adsorption activity, and limits their use in column operations. Furthermore, the lack of extensive study, low-sorbent adsorption capacity, high-pressure loss during column runs, and regeneration difficulty are additional disadvantages that limit their use [15]. Few reports on the removal of As in fixed-bed media have been published [14,16–20]. Observation of fixed-bed columns is vital for predicting the column breakthrough or shape of the wave front, which determine the operation life span of the bed and the regeneration time. Additionally, the observation of continuous flow systems is also important for obtaining basic engineering data. Batch studies of adsorption capacities may not provide accurate scale-up information regarding the column operation system [21] because of several undetermined factors. To develop an alternative, this study evaluates the removal of As by a continuous flow fixed-bed column system with different bed depths, flow rates, and varying initial concentrations using the developed adsorbent iron-oxide-coated natural rock (IOCNR), and including the regeneration and re-adsorption. Column study intended for the characterization of packing of adsorbent and the behavior of adsorption during flow through the packed adsorbent. Column tests are normally performed for providing more realistic laboratory results, since it has a greater resemblance to the flux conditions in full-scale constructed filters than short-term stirred batch experiments, which can result in over estimation of sorption capacities. The dynamics of adsorption process were modeled using bed-depth-service-time (BDST) approach.

Disposing off the As-sorbed exhausted sludge in the environment (open place) causes, once again leaching of As into the surface water as well as infiltrates to the groundwater. Burning the same produces highly toxic arsenious oxides or arsine and pollutes the atmosphere. Hence, it is very important to find out the suitable alternative to minimize the exhausted sludge and tried. Cement-based solidification/stabilization technology currently has been found the most promising solution for the disposal of As-wastes [22] and is clearly described by [23]. However, in short, mixing the fly ash and $Ca(OH)_2$ with cement (as a binder), As-waste can be solidified as the formed calcite seals the pores of the solidified sample and precipitated the calcium arsenite (C-As) [24–27]. Three important immobilization mechanisms have been proposed namely, sorption of As onto C–S–H (calcium–silica–hydrate) surface, replacing SO_4^{2-} of ettringite, and reaction with cement components to form C–As compounds are supposed to chemically fix the As-waste into cementations environment [28]. Consequently, early hydration of cement is inhibited by the formed insoluble $Ca_3(AsO_4)_2$ on the surface of hydrating cement particles in the presence of AsO_4^{3-} which helps to immobilize the waste due to its high strength [29]. Therefore, highly stable solidified As-laden or other heavy metal-laden solid waste with cement should be a suitable technique to reduce leachability of those metals [22–25].

The granulated natural rock (NR) that is used in this study is granite. Granite is an igneous rock formed from magma. Granitic magma has numerous possible origins, but it always intrudes other rocks. Most granite intrusions are typically at a depth of between 1.5 and 50 km in the thickest part of the continental crust. Although the elemental composition of granite is dependent on its source, all types of granite share common elemental constituents [30]. The granulated NR rock used in this study was crushed and loaded with Fe(III).

2. Materials and methods

2.1. Reagents

All the chemicals used without further purification and were of analytical reagent grade. All aqueous solutions were prepared in using deionized (DI) water. The DI water was tested to determine its As-concentration, if any. It contained no As within the limits of detection (<5 μg L^{-1}). As(III) and As(V) stock solution with an As concentration of 20 mg L^{-1} was prepared using $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich) and diluted as required.

Concentrated HCl, NaOH, $Fe(NO_3)_3 \cdot 9H_2O$, $Na_2EDTA \cdot 2H_2O$, NH_4OH, NH_4Cl, $MgCl_2 \cdot 6H_2O$, $NaBH_4$, Erichrome black T, 2-methoxy methanol, NaCl, $NaNO_3$, Na_2HPO_4, and $CaCl_2$ were purchased from J.T. Baker. Sodium sulfate (Na_2SO_4) was purchased from Fluka. The all chemicals were used as received. Appropriately diluted solutions were prepared as and when required.

2.2. Instrumentation

The all apparatus used were soaked in concentrated HNO_3 (J.T. Baker) for 12 h and then washed in DI water followed by tap water, before being dried in a hot-air oven. To quantify As, a Perkin-Elmer AAnalyst 200, atomic absorption spectrophotometer was coupled with high-performance liquid chromatography equipment (HPLC, Perkin Elmer, series 200). A JEOL JSM-7000F field scanning electron microscope (Japan) was used to perform SEM and EDX. An electrical balance (A&D Company Limited, Fx-200i, Japan) was used for weighing. Mechanical orbital shaker, Deng Yng, D600 (Taiwan) was used to shake all solutions. Gilson micropipettes with disposable tips were used to add samples. A digital pH meter (Suntex pH meter, sp-2300, Taiwan) was used to measure all pH values. An electrically operated flow rate controlled peristaltic pump (Chrom Tech, Taiwan) was used to charge samples into the column. 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. Adsorbent preparation and characterization

The IOCNR adsorbent used in this study was prepared by heating a mixture of 100 g NR (0.148 mm) in a solution of $Fe(NO_3)_3 \cdot 9H_2O$, prepared by dissolving 50 g $Fe(NO_3)_3 \cdot 9H_2O$ in 150 mL DI water. The IOCNR has been used to remove As from the real-As bearing sample and the detailed procedures for the preparation and characterization of the IOCNR and the removal mechanism have been discussed in our previous studies [31]. Table 1 shows the elemental compositions of the adsorbent obtained form EDX.

2.4. Fixed-bed column studies

Borosilicate glass column of 2 cm internal diameter and 55 cm length was used to conduct the fixed-bed column study. In the column, the adsorbent IOCNR was packed between the two supporting layers of glass wool (~3 cm; Fig. 1) to prevent the floating of adsorbent from the outlet. The bed depths were taken as 10 , 15 , and 20 for the experimental purposes where the corresponding beds were loaded with ~48, ~73, and ~97 g of IOCNR, respectively. The column was charged with As-bearing synthetic sample in the up-flow mode with a volumetric flow rate of 8 mL min^{-1} (~1.538 $m^3 m^{-2} h^{-1}$). The initial As(III) and As(V) concentrations were 0.6 and 3 mg L^{-1}, respectively, and the pH was 5.7 ± 0.2. The remaining As-concentrations in the effluent were analyzed collecting the samples after certain time intervals.

2.5. Preparation of As-laden cement block

The As (As(III) and As(V)) exhausted sludge was collected after the exhaustion of 20-cm bed-depth column. The column was treated with an initial As concentration of 0.6 and 3 mg L^{-1}, respectively, for As(III) and As(V), with an up-flow rate of 8 mL min^{-1}. The exhaustion time and the corresponding treated contaminated water were 110.0 h and 52.80 L, respectively, with the total adsorbed As(III) of 31.68 mg whereas those values for As(V) were 36.0 h, 17.28 L, and 51.84 mg, respectively. The exhausted sludge was then homogeneously mixed with Portland cement (Taiwan Company) separately in the ratio of 1:1 (w/w, with 20 mL DI water, to make slurry) and prepared blocks of the dimension of $3 \times 2 \times 0.5\ cm^3$. The blocks were then dried in the room temperature at least 20 d moistening with water (three times per day), to give the strength and for the complete hydrolysis of both As-laden cement blocks. After the scheduled time of curing, the blocks were then immersed in 250 mL of different solutions. Every 10 d intervals, an aliquot of each solution was collected and tested the leaching of As(III)/As(V) for about three months considering the duration of rainy season, as these blocks (solidified As-laden cement blocks) are wanted to use for building construction purposes.

Table 1
Physical and chemical properties of IOCNR from EDX

	Quantitative value (from batch study during optimum conditions)			
Properties	Before Fe(III) loaded	After Fe(III) loaded	After As(V) loaded	After As(III) 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)	1.67/1.01 (w/a)
Fe (%)	–	11.78/3.69 (w/a)	10.53/3.26 (w/a)	7.67/2.25 (w/a)
Si (%)	9.93/5.70 (w/a)	9.29/5.78 (w/a)	7.48/4.6 (w/a)	5.57/3.25 (w/a)
C (%)	18.56/24.92 (w/a)	15.75/22.94 (w/a)	17.09/24.59 (w/a)	20.02/27.29 (w/a)
Na (%)	1.42/0.99 (w/a)	0.97/.74 (w/a)	0.82/0.62 (w/a)	0.70/10.50 (w/a)
Mg (%)	0.63/0.42 (w/a)	0.80/0.58 (w/a)	–	0.45/0.30 (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)	0.02/0.00 (w/a)
O (%)	65.01/65.52 (w/a)	59.08/64.60 (w/a)	59.91/64.71 (w/a)	63.90/65.40 (w/a)
pH_{zpc}	5.8	–	–	–
Cation exchange capacity (CEC)	8.6 mequiv/100 g	–	–	–

Note: w = weight %, a = atomic %.

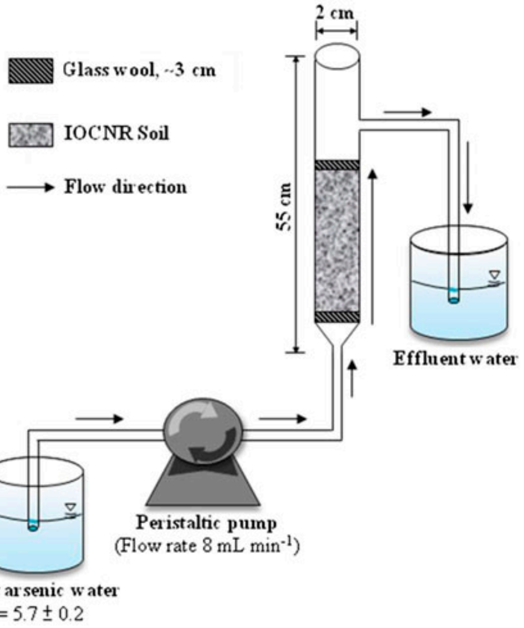

Fig. 1. Schematic diagram of small scale laboratory based column for fixed-bed study.

3. Results and discussion

3.1. Column studies for As(III)

3.1.1. Column behavior on adsorption

The plot of exit concentrations of the adsorbate (As in the present case) as a function of lapse times or volumes of water treated is the breakthrough curve. The point on the breakthrough curve at which As-concentration reaches its maximum allowable value of 0.01 $mg\,L^{-1}$ (corresponding to $C/C_0 = 0.016$) was taken as "breakthrough point" and that corresponding to 90% of the influent concentration as "point of exhaustion." Three different bed depths, 10 , 15 , and 20 were selected for the column studies. The DI water-spiked As(III) solution was charged through the columns with an up-flow mode and volumetric flow rate of 8 $mL\,min^{-1}$ (~1.538 $m^3\,m^{-2}\,h^{-1}$). The marginal flow rate was chosen to have an adequate amount of effluent water after a period of time for practical purpose and is common for column design [16,18,32]. The up-flow mode was considered to avoid unnecessary column logging. The As(III) concentration was 0.6 $mg\,L^{-1}$, optimized from batch studies (~98.5% removed within 6 h of contact time, at the dose of 13 $g\,L^{-1}$, shaking at 180 rpm). The breakthrough times (Fig. 2(a)) were found to be 31.0, 49.0, and 63.0 h for the columns of bed depths of 10 , 15 , and 20 , respectively, and the exhaust times were found to be 60.0, 90.0, and 110.0 h, respectively. The volumes of the contaminated water treated at breakthrough points were 14.88, 23.52, and 30.24 L, respectively, for the corresponding bed depths. On the other hand, the volumes of the contaminated water treated at exhaust points were 28.80, 43.20, and 52.80 L, respectively.

To calculate some important column design parameters the following mathematical equations have been used.

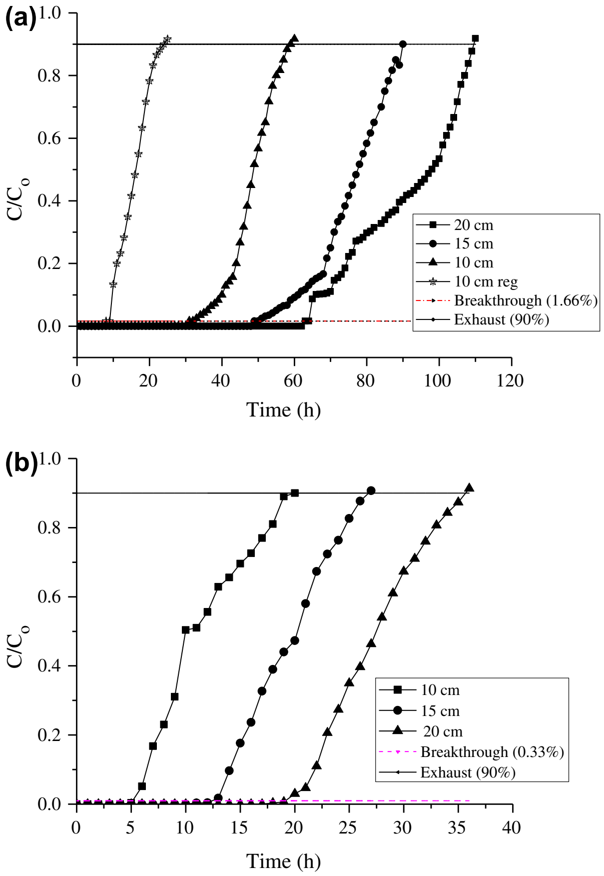

Fig. 2. Breakthrough curves at different bed depths (a) As(III), (b) As(V).

The time required for the exchange zone to move the length of its own height up/down the column once it has become established is:

$$t_z = \frac{V_E - V_B}{Q_w} \tag{1}$$

where V_E is the total volume of wastewater treated to the point of exhaustion (L), V_B is total volume of wastewater treated to the point of breakthrough (L), and Q_w is the wastewater flow rate (L h^{-1}).

Rate at which the exchange zone is moving up or down through the bed is:

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \tag{2}$$

where h_z is the height of exchange zone (cm), h is the total bed depth (cm), t_f is the time required for the exchange zone to initially form (h), and $t_E = V_E/Q_w$.

The value of t_f can be calculated as follows:

$$t_f = (1 - F)t_z \tag{3}$$

where C_0 is the initial solute concentration (mg L^{-1}) and $F = \frac{\int_{V_B}^{V_E}(C_o - C)\mathrm{d}V}{C_o(V_E - V_B)}$.

The percentage of the total column saturated at breakthrough is:

$$\%\,\text{saturation} = \frac{h + (F-1)h_z}{h} \times 100 \tag{4}$$

The above equations were used to determine the different parameters for the column studies such as, time required for the exchange zone to move its own height (t_z), height of exchange zone (h_z), exchange zone moving up rate (U_z), bed saturation (%), and empty bed contact time (EBCT) using the obtained above data [33] and are shown in Table 2.

3.1.2. Determination of column design parameters

A number of mathematical models have been developed to design the column using the full-scale column adsorption data during column study. Among the various developed models, Bohrat and Adams [34] is widely used [16–18,32]. The equation, which is based on surface reaction rate theory, can be represented as follows:

$$\ln\left(\frac{C_0}{C_B} - 1\right) = \ln\left(e^{KN_0\frac{x}{V}} - 1\right) - KC_0t \tag{5}$$

where C_0 is the initial concentration (mg/L), C_B is the desired concentration of solute at breakthrough (mg L^{-1}), K is the adsorption rate constant (L mg^{-1} h^{-1}), N_0 is the adsorption capacity (mg L^{-1}), x is the bed depth of column (cm), V is the linear flow velocity of feed to bed (cm h^{-1}), and t is the service time of column under above conditions (h).

Eq. (5) can be rearranged to yield an expression for service time, t as,

Realizing that $e^{KN_0\frac{x}{V}} \gg 1$, the equation simplifies to:

$$\ln\left(\frac{C_0}{C_B} - 1\right) = \ln\, e^{KN_0\frac{x}{V}} - KC_0t \tag{6}$$

Solving the above equation for t:

$$t = \frac{N_0}{C_0V}x - \frac{1}{C_0K}\ln\left(\frac{C_0}{C_B} - 1\right) \tag{7}$$

Table 2
Column behavior parameters

		Bed depth			
Arsenic	Parameters	10 cm	15 cm	20 cm	Average
As(III)	h_z (cm)	5.52	5.01	4.81	5.12
	U_z (cm h^{-1})	0.19	0.12	0.10	0.14
	EBCT (min)	4.10	6.20	8.25	
	Bed saturation (%)	92.86	95.03	93.76	
	t_z (h)	29	41	47	
As(V)	h_z (cm)	13.90	8.02	6.47	9.46
	U_z (cm h^{-1})	0.87	0.50	0.34	0.57
	Bed saturation (%)	26.26	64.59	70.70	
	t_z (h)	16	16	18	

The Eq. (7) is called the Bohart–Adams equation and can be used to evaluate the service time, t, for a column of bed depth, x, given the values of N_0, C_0, and K which must be determined for laboratory columns operated over a range of velocity values, V.

Setting $t = 0$ and solving Eq. (7) for x yields,

$$x_0 = \frac{V}{KN_0} \ln\left(\frac{C_0}{C_B} - 1\right) \tag{8}$$

where x_0 is the minimum column height necessary to produce an effluent concentration C_B.

Nine individual column data are required to follow the Bohart–Adams approach and is a time consuming task, but according to Hutchins [35], requires only three column tests to collect the necessary data to design the column, called the BDST approach. The Bohart–Adams equation can be expressed as:

$$t = ax + b \tag{9}$$

where,

$$a = \text{slope} = \frac{N_0}{C_0 V} \tag{10}$$

$$b = \text{intercept} = \frac{1}{KC_0} \ln\left(\frac{C_0}{C_B} - 1\right) \tag{11}$$

The breakthrough times (corresponding to $C/C_0 = 0.016$) were found to be 31.0, 49.0, and 63.0 h for the of bed depths of 10 , 15 , and 20 and the exhaust times (corresponding to $C/C_0 = 0.9$) were found to be 60.0, 90.0, and 110.0 h, respectively, and is mentioned earlier. Fig. 3(a) shows the plot of depth

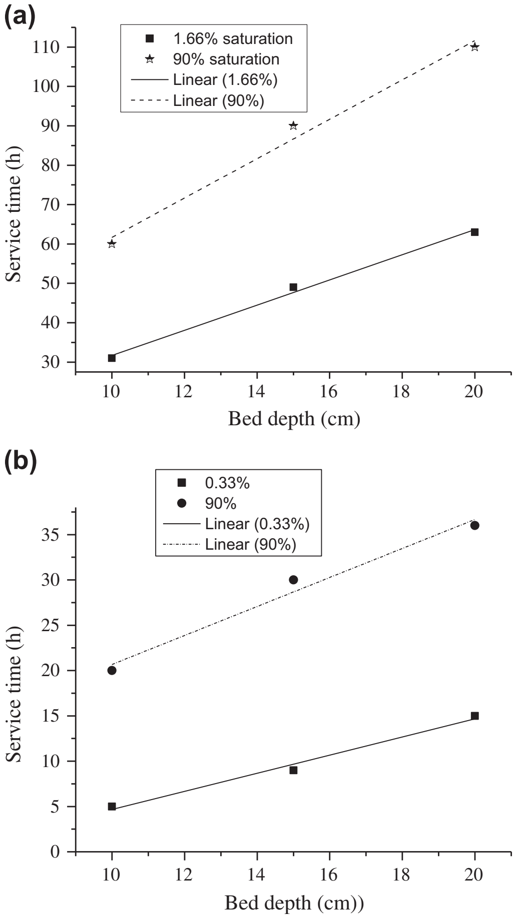

Fig. 3. (a) Bed depth vs. service time at 1.66 and 90% saturation for As(III), (b) Bed depth vs. service time at 0.33 and 90% saturation for As(V).

vs. service time for 1.66 and 90% saturation of column. The obtained equations of these lines were as follows:

For 90% saturation,

$$t = 5x + 11.66 \tag{12}$$

For 1.66% saturation,

$$t = 3.2x - 0.333 \tag{13}$$

From the slope and intercept of the 1.66% saturation line, design parameters N_0 and K were evaluated as (Eqs. (10) and (11)) 295.30 mg $L^{-1}$and 20.41 L mg^{-1} h^{-1}, respectively, for the minimum bed depth of 0.104 cm (x_0) (Eq. (8)).

3.1.3. Design of adsorption column

The obtained column design parameters could be used for the design of adsorption column for practical purpose. According to BDST approach, if the value is determined for one flow rate, values for the other flow rates can be calculated by multiplying the original slope a by the ratio of the original and the new flow rates. Not necessary to adjust b value, since it is assumed to be insignificantly affected by changing flow rates.

It is proposed that the data collected for one influent solute concentration can be adjusted by the BDST technique and can be used to design systems for treating other influent solute concentrations. If a laboratory experiment is conducted at solute concentration C_1, yielding an equation of the form:

$$t = a_1 x + b_1 \tag{14}$$

Then it is possible to predict the equation for concentration C_2 as follows:

$$a_2 = a_1 \frac{C_1}{C_2} \tag{15}$$

$$b_2 = b_1 \left(\frac{C_1}{C_2}\right) \frac{\ln\left(\frac{C_2}{C_F} - 1\right)}{\ln\left(\frac{C_1}{C_B} - 1\right)} \tag{16}$$

where a_1 is the slope at concentration C_1, a_2 is the slope at concentration C_2, b_1 is the intercept at concentration C_1, b_2 is the intercept at concentration C_2, C_F is the effluent concentration at influent concentration C_2, and C_B is the effluent concentration at influent concentration C_1.

3.1.3.1. Design of adsorption column for different flow rates. Column (10 cm height and 2 cm diameter) study was conducted with two different flow rates of 5 and 10 mL min^{-1}, whereas original flow rate was 8 mL min^{-1}. The initial As(III) concentration was kept constant at 0.6 mg L^{-1}. The breakthrough times (corresponding to 0.01 mg L^{-1} effluent concentration) were found to be 55.0 and 22.0 h, respectively, for the two different corresponding flow rates. The revised values of a were calculated from flow rates ratio and the values were found to be 5.12 and 2.56, respectively. From these values of a and b, the service times (breakthrough time) for 10-cm column were found to be 50.867 and 25.267 h for the two different flow rates with the intercept value of −0.333. These values were found to be comparable with experimental values.

3.1.3.2. Design of adsorption column for different initial concentrations. Column (10 cm height and 2 cm diameter) was study with two different initial As(III) concentrations of 0.3 and 1.0 mg L^{-1}, whereas original As (III) concentration was 0.6 mg L^{-1}. The flow rate was kept at 8 mL min^{-1}. The breakthrough (corresponding to 0.01 mg L^{-1} effluent concentration) times were found to be 65.0 and 20.0 h, respectively, for the two different initial As(III) concentrations. The values of a_2 and b_2 calculated from Eqs. (15) and (16) are 6.40 and 0.5499, respectively, for the concentration of 0.3 mg L^{-1}, whereas for the concentration of 1.0 mg L^{-1}, these values are 1.92 and 0.225, respectively. From these values of a and b, the service times (breakthrough time) for 10 cm column were calculated and these were 63.451 and 18.975 h, respectively. These values were comparable with the experimental values. It is important to mention here that the breakthrough curves become steeper with the increase of flow rate and concentration. This is possibly due to the low-contact time between the adsorbate and the adsorbent, causes reduction on the diffusion of As(III) into the pores of the adsorbent. Hence, a quick saturation (breakthrough and exhaustion) of the bed was observed.

The As(III)-exhausted (after 60 h) 10-cm bed-depth column was regenerated using 1 M NaOH. In the same experimental conditions, the column re-adsorption study was also conducted using the same As(III) concentration of 0.6 mg L^{-1}. The detailed study and obtained results have been reported earlier [36]. However, low-removal efficiency in the second cycle of operation (Fig. 2(a)) is attributing the removal of Fe(III) hydroxide from the IOCNR surfaces during the treatment with concentrated NaOH. Understanding the above result, we did not consider the column regeneration and re-adsorption study for As(V).

3.2. Colum study for As(V)

The same experimental conditions were followed to conduct the column study of As(V) on IOCNR. The As(V) concentration was 3 mg L^{-1}, optimized from batch studies (~99.6% removed within 4 h of contact time, at the dose of 5 g L^{-1}) [31]. The breakthrough times (corresponding to $C/C_0 = 0.0033$; Fig. 2(b)) were found to be 5.0, 11.0, and 18.0 h for the columns of bed depths of 10 , 15 , and 20 , respectively, and the exhaust times were found to be 20.0, 27.0, and 36.0 h, respectively. The volumes of the contaminated water treated at breakthrough points were 2.4, 5.28, and 8.64 L, respectively, for the corresponding bed depths. On the other hand, the volumes of the contaminated water treated at exhaust points were 9.60, 12.96, and 17.28 L, respectively. Different parameters for the column studies are shown in Table 2. Fig. 3(b) shows the plot of depth vs. service time for 0.33 and 90% saturation of column and the equations of these lines were as follows:

For 90% saturation,

$$t = 1.6x + 3.666 \tag{17}$$

For 0.33% saturation,

$$t = 1.3x - 8.166 \tag{18}$$

From the slope and intercept of the 0.33% saturation line, design parameters N_0 and K were calculated as (Eqs. (10) and (11)) 599.82 mg L^{-1} and 0.233 L mg^{-1} h^{-1}, respectively, for the minimum bed depth of 6.27 cm (x_0) (Eq. (8)). It is worthy to mention here that the average height of exchange zone is found to be 9.46 cm (Table 2). The height of exchange zone is found to be 13.90 cm, which is more than the lowest column depth i.e. 10 cm. This may be the cause of high-As(V) concentration, low-contact time, and low diffusion on IOCNR attributing the quick saturation.

Column (10 cm height and 2 cm diameter) study was conducted with different flow rate of 4 mL min^{-1}, whereas original flow rate was 8 mL min^{-1}. The initial As(V) concentration was kept constant at 3 mg L^{-1}. The breakthrough time (corresponding to 0.01 mg L^{-1} effluent concentration) was found to be 14.0 h. The revised value of a was calculated from flow rate ratio and the value was found to be 2.60. From this value of a and b, the service time (breakthrough time) for 10-cm column was found to be 17.83 h with intercept value of −8.166. This value was found to be comparable with experimental value.

Column (10 cm height and 2 cm diameter) study was conducted with different initial As(V) concentration of 1 mg L^{-1}, whereas original As(V) concentration was 3 mg L^{-1}. The flow rate was kept at 8 mL min^{-1}. The breakthrough (corresponding to 0.01 mg L^{-1} effluent concentration) time was found to be 15.0 h. The values of a_2 and b_2 calculated from Eqs. (15) and (16) are 3.90 and 27.10, respectively, for the concentration of 1 mg L^{-1}. From these values of a and b, the service time (breakthrough time) for 10-cm column was calculated and this was 12.0 h. This value was comparable with the experimental value.

It is worth to mention here that during column study, till exhaustion point, the pH did not change (within ±0.5), iron leaching was < 0.1 mg L^{-1}, the hardness was ~20–22 mg L^{-1}, and no significant leaching of silica and other components was observed.

3.3. Leaching of As from the cement block

Because to minimize the As-removed exhausted sludge, the sludge instead of sand, was mixed with Portland cement and prepared blocks were used for leaching tests as these blocks are wanted to use as one of the building materials for the construction purposes. Hence, the leaching test is very important in concern of environmental protection. The leaching tests were performed immersing the blocks in 250 mL of different solutions at least 3 months. The leaching tests were conducted in presence of different inorganic ions such as SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}, and Ca^{2+} (each of 200 mg L^{-1}). The tests were also conducted immersing the blocks in rain water (pH 4.01), tap water (pH 7.0), DI water (pH 7.0), and an aqueous (prepared in DI water) solution of pH 9.8. The properties of the rain water and tap water are shown in Table 3. The cumulative leaching of As(III) and As(V) is summarized in Tables 4(a) and 4(b), respectively. The obtained results suggested that after 90 d, the cumulative concentrations of leaching As(III)/As(V) were below than that

Table 3
Properties of tap water and rain water

Parameters	Tap water	Rain water
pH	7.0	4.01
F^- (mg L^{-1})	0.18	0.19
Cl^- (mg L^{-1})	6.67	1.29
NO_3^- (mg L^{-1})	2.19	6.52
SO_4^{2-} (mg L^{-1})	12.55	7.04
Mg^{2+} (mg L^{-1})	3.12	0.45
Ca^{2+} (mg L^{-1})	8.52	1.48

of the WHO recommended, $0.01\,\mathrm{mg\,L^{-1}}$. It is possibly due to the formation of $CaHAsO_4$, $CaHAsO_3$, and $Ca_3(AsO_4)_2$ [23,27–29] by the reaction of As and the hydrated products ($Ca(OH)_2$, calcium–silica–hydrate gel) of Portland cement as well as the encapsulation of As within the micropores of the amorphous gel structure of calcium–silica–hydrate (C–S–H) [28].

3.3.1. The mathematical calculation

Different transport processes such as diffusion, dissolution, ion exchange, corrosion, and surface effects may occur during the leaching of As from the As-laden cement blocks containing As-removed exhausted sludge to the liquid medium and is believed to have mostly a diffusion-controlled process [37]. The diffusion equation depends on the initial and boundary conditions and the cement-based waste is assumed to be a semi-infinite medium, which implies that the mass of the constituents removed from the waste is negligible in comparison of the total mass in waste. It is assumed that the contaminants are uniformly distributed in the solidified waste having a zero surface concentration in the surrounding medium once leaching begins. The relation of constant diffusion co-efficient, the diffusion flux (J) across the solid/solution interface can be expressed [22] as:

$$J = \frac{\mathrm{d}M_t}{\mathrm{d}S\mathrm{d}t} = \sqrt{(D_e C_o/\pi t)} \tag{19}$$

where C_0 is the initial concentration of the leaching substance in the waste specimen ($\mathrm{mg\,cm^{-3}}$), D_e is the effective diffusion co-efficient ($\mathrm{cm^2\,s^{-1}}$), and t is the leach time (s).

The total amount of leaching substance that has diffused out of the medium surface at time t, M_t, can be derived from Eq. (19) by integration over time and surface area as follows:

$$\int \mathrm{d}M_t = \int_0^t \int_0^S [\sqrt{(D_e/\pi t)}] C_0 \mathrm{d}S\mathrm{d}t \text{ or } M_t = 2M\frac{S}{v} = \sqrt{(D_e t/\pi)} \tag{20}$$

where M is the total initial amount of leaching substance in the waste specimen (mg), S is the surface area of the specimen ($\mathrm{cm^2}$), and v is the volume of the specimen ($\mathrm{cm^3}$).

The cumulative fraction of leaching substance that has been released from solidified waste at time t (CFR) is defined as the ratio of M_t and M and is given by:

$$\mathrm{CFR} = \frac{M_t}{M} = \frac{2}{\sqrt{\pi}}\frac{S}{v}\sqrt{D_e t} \tag{21}$$

The linear plot of $\sqrt{t}$ vs. CFR was drawn for the leachate sample collected from the DI water (pH 7.0) (Fig. 4). D_e values generally range from $10^{-5}\,\mathrm{cm^2\,s^{-1}}$ (very mobile) to $10^{-15}\,\mathrm{cm^2\,s^{-1}}$ (immobile), but in the present study, the value of D_e (Fig. 4) has been found out as $0.266\times10^{-16}\,\mathrm{cm^2\,s^{-1}}$, and as $0.612\times10^{-16}\,\mathrm{cm^2\,s^{-1}}$, respectively, for As(III) and As(V). The very low value of D_e in the order of 10^{-16} (in each condition, figure not shown) indicates that the As(III)/As(V) is highly immobilized after incorporating in the cement and hence can be used as the construction material, which controls the environmental pollution [23].

Table 4(a)
Cumulative leaching of As(III)

Medium	Cumulative [As(III) (in $\mu g\,L^{-1}$)], d								
	10	20	30	40	50	60	70	80	90
SO_4^{2-}	1.32	2.14	2.55	2.76	3.75	3.25	3.24	3.58	3.86
NO_3^-	2.94	3.20	3.35	3.33	3.53	3.36	3.47	3.58	3.86
Cl^-	1.21	1.21	2.20	2.65	2.87	2.97	3.31	3.65	3.94
PO_4^{3-}	5.62	5.68	6.91	6.76	6.13	4.65	5.48	6.2	7.12
Ca^{2+}	0	0	0	0	0	0	0	0	0
Rain water (pH 4.01)	2.33	2.4	2.6	2.7	3.27	3.8	3.8	4.0	4.0
Tap water (pH 7.0)	0.38	0.49	0.71	1.31	1.5	1.61	1.75	2.3	2.4
pH (DI = 7.0)	1.21	1.68	2.08	2.25	2.66	2.7	2.7	2.8	2.9
pH 9.80	2.32	2.32	2.5	2.7	2.4	2.5	2.5	2.7	2.7

Table 4(b)
Cumulative leaching of As(V)

	Cumulative [As(V) μg L^{-1}], d								
Medium	10	20	30	40	50	60	70	80	90
SO_4^{2-}	0	0	0	0	0	2.58	2.75	2.92	3.01
NO_3^-	1.02	2.22	2.58	3.13	3.88	5.04	6.22	7.99	9.21
Cl^-	0	2.21	2.65	2.66	2.85	3.30	3.91	3.97	4.11
PO_4^{3-}	1.03	1.54	1.78	2.07	2.85	6.54	7.91	8.88	9.81
Ca^{2+}	0	0	0	0	0	0	0	2.45	3.73
Rain water(pH 4.01)	0	1.21	1.32	2.54	3.13	3.48	3.50	3.53	3.84
Tap water (pH 7.0)	0	0	0	0	0	0	0	1.85	5.32
pH (DI = 7.0)	0	1.26	1.71	1.81	2.11	2.88	3.76	4.46	5.04
pH 9.80	1.26	1.71	1.81	2.11	2.89	3.58	3.99	4.78	5.87

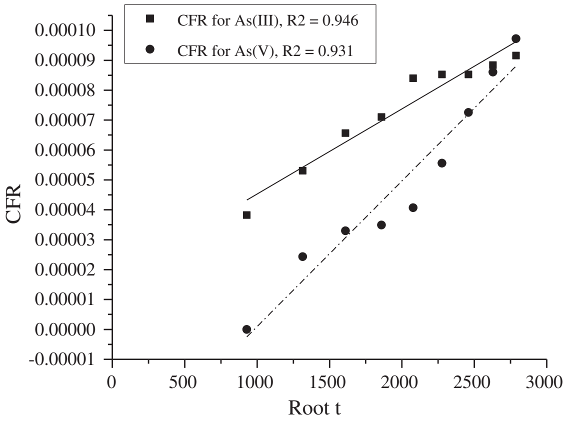

Fig. 4. Curve of root *t* vs. CFR for As(III) and As(V).

4. Conclusions

Fixed-bed column adsorption study was conducted to find out the effectiveness of the developed adsorbent IOCNR on As (As(III)/As(V)) removal from the aqueous media with an up-flow rate of 8 mL min^{-1}. The study was conducted with three different bed depths column of 10, 15, and 20, respectively, at room temperature, when the initial As(III) and As(V) concentrations were 0.6 and 3 mg L^{-1}. The column was designed by the BDST model. The adsorption capacity and adsorption rate constant were found to be 295.30 mg L^{-1} and 20.410 L mg^{-1} h^{-1} for As(III), whereas 599.82 mg L^{-1} and 0.233 L mg^{-1} h^{-1} for As(V). Effectiveness of the column was also tested with different concentrations and flow rates. No significant components leaching into the effluent from the IOCNR was observed. The 10-cm exhaust bed (As(III)) was regenerated with 1 M NaOH, and its performance was evaluated. An attempt has been made to minimize the As adsorbed exhausted sludge mixing with Portland cement and the prepared blocks were used for leaching tests in different inorganic solutions. As immobility from cement blocks was accounted from D_e values. The very low value of D_e assures that the sludge mixed Portland cement is an environmental friendly material and can be used for building construction purpose.

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List of symbols

K — adsorption rate constant (L mg^{-1} h^{-1})
N_0 — adsorption capacity (mg L^{-1})
M_t — amount of leaching material leaching out at time
V_B — breakthrough volume (L)
C_B — breakthrough concentration
x — bed depth of column (cm)
J — diffusion flux
U_z — exchange zone moving up rate
D_e — effective diffusion co-efficient (cm^2 s^{-1})
h_z — height of exchange zone (cm)
C_0 — initial solute concentration
IOCNR — iron-oxide-coated-natural rock
V — linear flow velocity of feed to bed (cm h^{-1})
x_0 — minimum height for C_B
t — service time
S — surface area of the specimen (cm^2)
V_E — treated wastewater volume (L)
t_z — time for exchange zone moving
h — total bed depth (cm)

M — total initial amount of leaching substance
M — total initial amount of leaching substance
v — volume of the specimen (cm^3)
Q_w — wastewater flow rate ($L\,h^{-1}$)

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