

Experimental and Modelling Studies on As(III) Removal from Aqueous Medium on Fixed Bed Column

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Abstract: A continuous adsorption study in a fixed-bed column was carried out by using IS:sand mixture as an adsorbent for the removal of As(III) from aqueous solution. The column experiments were conducted to study the effect of important parameters such as flow rate and bed depth on breakthrough curve and adsorption capacity. The Bed Depth Service Time model (BDST) was applied to the experimental data to represent the breakthrough curve and determine the characteristic design parameters of the column. The calculated adsorption capacity (N_0) and the rate constant (K) were $55.2 \mu\text{g}/\text{cm}^3$ and $12.2 \text{ cm}^3/\mu\text{g}/\text{h}$, respectively. It can be noticed that the IS:sand mixture can be used with good performances as adsorbent material in the removal process of As(III) on column studies.

Keywords: As(III) removal, column study, BDST model

1. Introduction

Source contamination of drinking water with arsenic represents a worldwide concern. Arsenic has been associated with various cancerous and non-cancerous health effects [1-6]. Thus, choosing a technology for the removal of arsenic from drinking water often represents a challenge.

A variety of treatment processes have been studied for arsenic removal from water. The major techniques include precipitation-coagulation, membrane separation, ion exchange and adsorption [1, 2, 7, 8, 9-17]. Simplicity and cost are the two major factors that should influence the selection of a treatment system for arsenic removal in small communities dependent on groundwater for drinking supply. For such systems, adsorption in fixed-bed treatment processes, are receiving increasing attention for arsenic removal because of their simplicity and ease of operation and handling.

Generally, an arsenic adsorbent should meet several requirements: low cost; granular type; high capacity, selectivity, and rate of adsorption; high physical strength (not disintegrating) in water and able to be regenerated if required [18]. In order to accomplish the first requirement we chose as adsorbent an iron containing waste sludge (IS) resulted from the hot-dip galvanizing process.

Before testing the performance of an adsorbent in fixed-bed column, equilibrium isotherm studies should be conducted to measure the maximum adsorption capacity of that adsorbent. In previous studies the authors have reported that IS has a high adsorption capacity for As(III) removal from aqueous medium [4]. Since the adsorbent is a powder, in order to avoid the clogging of the column we mixed the adsorbent with quartz sand. From previous studies we concluded the best IS:sand ratio is 1:1, when the highest adsorption capacity was reached [19]. Due to very small size of particles, IS penetrated between the grains of sand, and thus a high contact surface was created, the adsorption process occurred in good conditions. For a

larger amount of IS the column was clogged after a short time. For a larger amount of sand, the mixture contains a too small amount of IS active phase responsible for arsenic adsorption, and consequently the adsorption capacity lowers.

The objective of this study was to obtain the basic information for the design of the process of arsenic adsorption onto IS:sand mixture in fixed bed system in order to test the practical applicability for real underground waters. Effects of operating parameters (bed depth and flow rate) were studied and the obtained breakthrough curves were analyzed using the BDST model.

2. Experimental

Fixed bed adsorption studies were conducted in a 1.5 cm i.d., 20 cm length vertical down flow glass column packed with IS:sand adsorbent (in the ratio 1:1) for different bed height (5, 7.5 and 10 cm). The experiments were conducted with a $100 \mu\text{g}/\text{L}$ As(III) solution.

The column was charged with arsenic solution in the down-flow mode with various influent flow rates (2, 5, 10 mL/min), which was supplied and maintained throughout the experiments by the use of variable flow peristaltic pump (Heidolph 6201). The samples were collected at certain time intervals and were analysed for the remaining arsenic concentrations. The arsenic residual concentration in the resulting solutions was determined by means of atomic absorption spectrometry with hydride generation. This method uses the As(III) selective reduction to arsine H_3As with sodium boron hydride NaBH_4 (Merck-Schuchardt; 0.6% w/v) solution in NaOH buffer (Chemapol-Praha-Czechoslovakia; 0.5% w/v). The arsine gas was carried over the flame of atomic absorption spectrometer and the absorbance value measured at 193.7 nm was compared with the calibration curve registered using arsenic solutions of various known concentrations,

prepared from the stock solution. For the flow injection system, the carrier solution was prepared from HCl (37%, Corozin-Romania; 1:3). To determine As(III) concentrations, a VARIAN SpectrAA 110 atomic absorption spectrometer with a VARIAN VGA 77 hydride generation system was used.

All chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

3. Theoretical background

The shape of the breakthrough curve and the time for the breakthrough appearance are the predominant factors for determining the operation and the dynamic response of an adsorption column. Effects of adsorbent bed height (5-10 cm) and inlet feed flow rate 0.033-0.16 cm³/s) were investigated on the performance of breakthrough for the adsorption of As(III) by the IS:sand mixture.

Prediction of the breakthrough curve for the effluent is the predominant factor for the successful design of a column adsorption process. It is innately difficult to develop a model which accurately describes the dynamic behaviour of adsorption in a fixed bed system. The process does not operate in a steady state as the concentration of the adsorbate changes in the feed moves through bed. Figure 1 depicts a typical breakthrough curve where the column capacity is fully utilized. The concentration at breakthrough point is chosen arbitrarily at some low value, C_b . When the effluent concentration C_x is approaching to 90% of C_0 (inlet adsorbate concentration) then the adsorbent is considered to be essentially exhausted [20, 21].

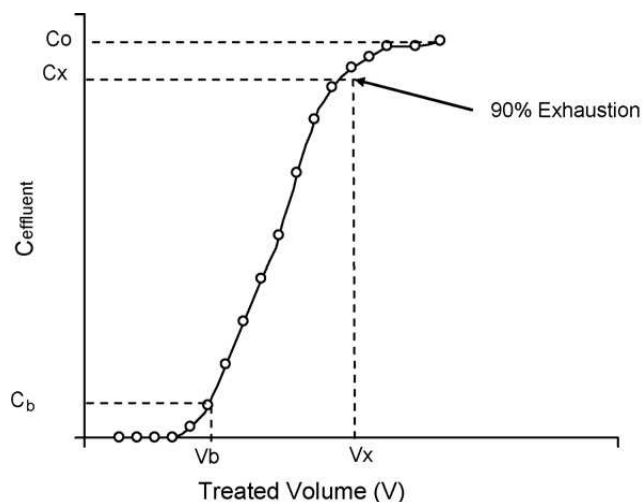


Figure 1. Ideal breakthrough curve [20, 21]

3.1. Bed-depth service time model (BDST)

It is generally accepted that the BDST model offers the simplest approach and rapid prediction of adsorber design and performance [21, 22]. The BDST is a model for predicting the relationship between bed depths, X and service time t . This BDST model was focused on the estimation of characteristic parameters such as the

maximum adsorption capacity (N_0) and kinetic constant (K). This model assumes that the adsorption rate is proportional to residual capacity of the sorbent and the concentration of the sorbing species. The service time was related to process conditions and operating parameters as:

$$\ln\left(\frac{C_0}{C_b} - 1\right) = \ln\left(\exp\left(\frac{KXN_0}{v}\right) - 1\right) - KC_0t \quad (1)$$

A linear relationship between bed-depth and service time may be given by Eq. (2) [21,22]:

$$t = \frac{N_0}{vC_0} X - \frac{1}{KC_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (2)$$

where C_0 is the initial concentration of solute ($\mu\text{g/L}$), C_b the desired concentration of solute at breakthrough ($\mu\text{g/L}$), K the adsorption rate constant ($\text{L}/\mu\text{g/h}$), N_0 the adsorption capacity (mg/L), X the bed depth of column (cm), v the linear flow velocity of feed to bed (cm/h), t is the service time of column under above conditions (hrs). Eq. (2) can be rewritten in the form of a straight line.

$$t = aX - b \quad (3)$$

Where a is slope of BDST line ($a = \frac{N_0}{vC_0}$) and the intercept of this equation represents as Eq. (4):

$$b = \frac{1}{KC_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (4)$$

Thus, N_0 and K can be evaluated from slope (a) and the intercept (b) of the plot of t versus X , respectively.

3.2. Empty bed contact time

Empty bed contact time is a critical parameter that determines the residence time during which the solution being treated is in contact with the adsorbent. Hence, EBCT may strongly affect adsorption, especially if the adsorption mainly depends on the contact time between the adsorbent and adsorbate [23]. The corresponding EBCT in the bed was in the range 55-535 s.

4. Results and discussions

4.1. Effect of flow rate

The effect of flow rate on As(III) adsorption by IS:sand was investigated by varying the flow rate from 2 to 10 mL/min and keeping the initial As(III) concentration (100 $\mu\text{g/L}$), bed depth (10 cm) and column diameter (1.5

cm) constant. Breakthrough plots between C_t/C_0 versus time at different flow rate are given in figure 2.

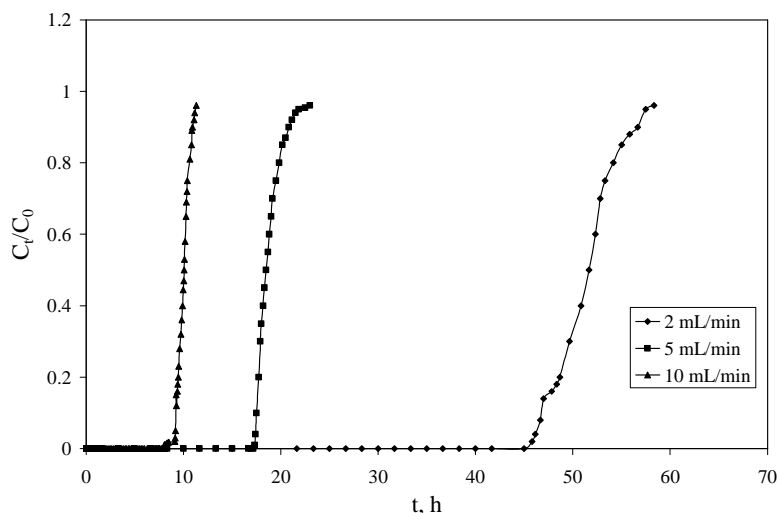


Figure 2. Effect of flow rate on breakthrough curves for As(III) adsorption onto IS:sand $C_0=100\mu\text{g/L}$, $h=10$ cm, $\text{pH}=6.8$

At low flow rate, relatively high volume was observed whilst much sharper breakthrough was obtained at higher flow rates. The time required to reach the breakthrough decreased with an increased flow rate (table 1). This is certainly because of the reduced contact time causes a poor distribution of the liquid inside the column, which leads to a lower diffusivity of the solute through the adsorbent particles. As seen from the results presented in table 1, an increased flow rate reduces the volume treated efficiently until breakthrough and thereby decreases the service time of the bed. This is due to the decrease in the residence time of the As(III) ions within the bed at higher flow rates.

4.2. Effect of bed depth

The breakthrough curves obtained for As(III) adsorption onto IS:sand at different bed depth, at a constant linear flow rate of 10 cm³/min are shown in figure 3.

Sorbent bed height strongly affects the volume of the solution treated or throughput volume. The curves followed characteristic S-shape profile, which is associated with adsorbate of smaller molecular diameter and more simple structure. As it is evident from figure 2, an increase in column depth increased the treated volume due to high contact time. The exhaust time (corresponding to an effluent concentration = 0.9C₀) increased with increasing

bed height, as more binding sites were available for sorption. The increase in adsorption with bed depth was due to the increase in adsorbent doses in larger beds which provided greater adsorption sites for As(III). The breakthrough time also increased with increasing bed depth, suggesting that it is the determining parameter of the process (table 1). The larger the breakthrough time, better is the intra-particulate phenomena.

One may notice that the best performance of the IS:sand mixture in the removal process of As(III) on column studies occurs under the process parameters of 10 cm bed depth and 2 mL/min flow rate.

4.3. Modelling of breakthrough curve

A plot of t versus bed depth (X) at a flow rate of 10 mL/min is shown in figure 4.

The equation of the linear relationship was obtained with R² above 0.99. This indicated the validity of the BDST model for present column system. The calculated adsorption capacity (N_0) and the rate constant (K) are 55.2 $\mu\text{g/cm}^3$ and 12.2 $\text{cm}^3/\mu\text{g/h}$, respectively. The advantage of the BDST model is that any experimental test can be reliably scaled up to other flow rates without further experimental runs.

TABLE 1. Adsorption data for fixed bed IS:sand column for As(III) adsorption at different process parameters.

Process parameters	Breakthrough time, h	Exhaust time, h	Volume of arsenic solution treated, L
Flow rate, Q(mL/min)			
2	45.8	58.3	5.5/7
5	17.3	23	5.2/6.9
10	8.03	11.3	4.82/6.8
Bed depth, h (cm)			
5	3.34	6.18	2/3.71
7.5	6.27	8.5	3.76/5.1
10	8.03	11.3	4.82/6.8

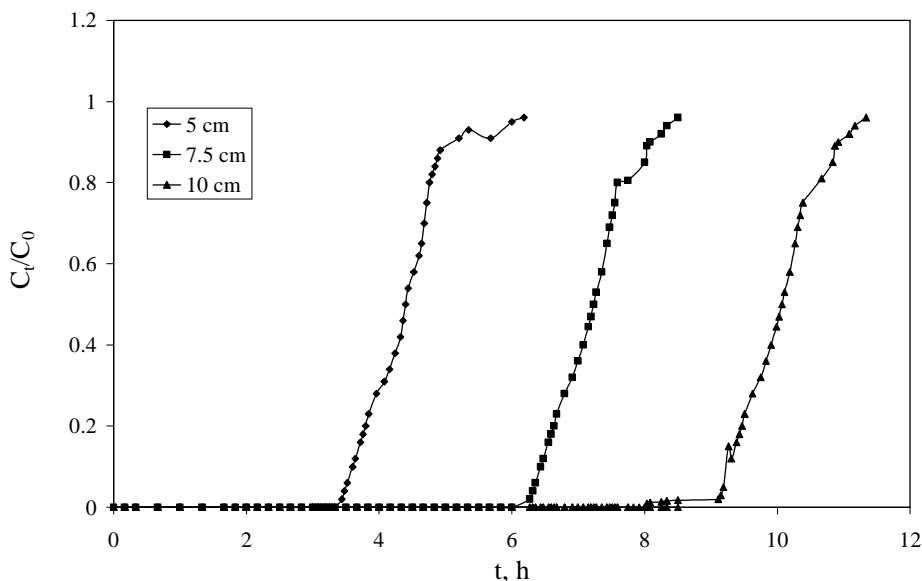


Figure 3. Effect of bed height on breakthrough curves for As(III) adsorption onto IS:sand
 $C_0=100\mu\text{g/L}$, flow rate=10 mL/min, pH=6.8

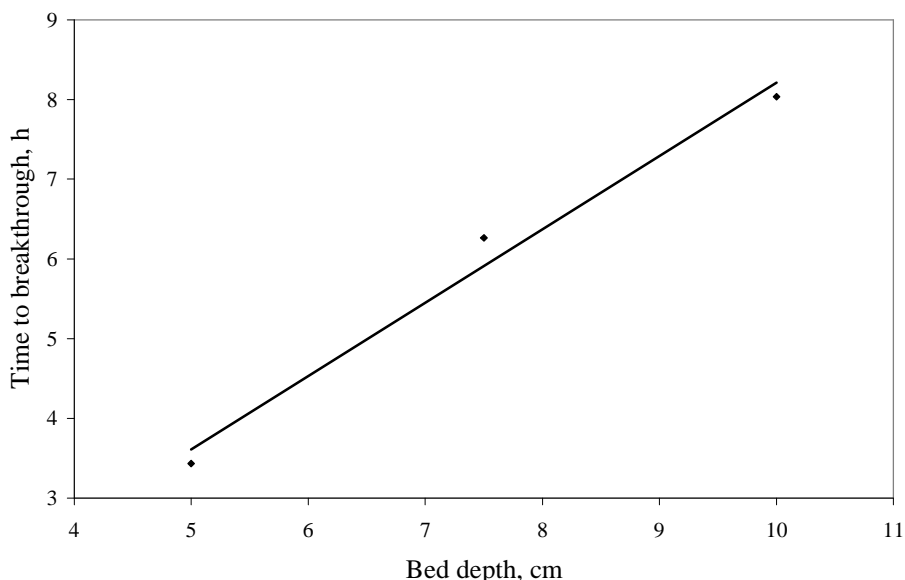


Figure 4. BDST model at breakthrough curve in fixed-bed column for As(III) adsorption by IS:sand

5. Conclusions

The results of this work indicate a good removal of As(III) by fixed bed IS:sand column. By studying the effect of important parameters such as flow rate and bed depth on breakthrough curve and adsorption capacity can be noticed that the best performance of the IS:sand mixture in the removal process of As(III) on column studies occurs under the process parameters of 10 cm bed depth and 2 mL/min flow rate. In these conditions a service time of 11.3 h (1t 90% exhaustion) was reported. The calculated adsorption capacity (NO) and the rate constant (K) were $55.2 \mu\text{g/cm}^3$ and $12.2 \text{ cm}^3/\mu\text{g/h}$, respectively. It can be noticed that the

IS:sand mixture can be used with good performances as adsorbent material in the removal process of As(III) on column studies.

ACKNOWLEDGEMENT

This work was supported by CNCISIS- UEFISCDI, project number PN II-IDEI 927/2008, "Integrated Concept about Depollution of Waters with Arsenic Content, through Adsorption on Oxide Materials, followed by Immobilization of the Resulted Waste in Crystalline Matrices".

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Received: 18 February 2011

Accepted: 10 May 2011