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As(III) removal from aqueous medium in fixed bed using iron oxide-coated cement (IOCC): Experimental and modeling studies

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Abstract

Continuous fixed bed studies were undertaken to evaluate the efficiency of iron oxide-coated cement (IOCC) as an adsorbent for the removal of As(III) from aqueous solution under the effect of various process parameters like bed depth (10–20 cm), flow rate (4.3–12 ml min^{-1}) and initial As(III) concentrations (0.5–2.7 mg l^{-1}). The results showed that the total As(III) uptake decreased with increasing flow rate and increased with increasing initial As(III) concentration. Also, the total As(III) removal percentage increased with the increase in bed depth. The dynamics of the adsorption process was modeled by bed depth service time (BDST), mass transfer, Thomas and Yoon–Nelson models. The BDST model fitted well with the experimental data in the initial region of the breakthrough curve but showed slight deviations above break points. Though the experimental data points and the data points predicted using the mass transfer model followed a similar trend, they slightly deviated from each other. The Thomas and Yoon–Nelson model predictions were in very good agreement with the experimental results at all the process parameters studied indicating that they were very suitable for IOCC column design. The apparent mechanism of As(III) removal in the IOCC column were ion exchange and physisorption on the adsorbent surface.

Keywords: Adsorption; Arsenic; Breakthrough curve; BDST model; Mass transfer model; Thomas model; Yoon–Nelson model

1. Introduction

Arsenic is a ubiquitous element in the natural environment that has long affected human life in two contradictory ways as an essential as well as a toxic element. It has been used in humanity's favour as medicine, insecticides, and herbicides and also as a poison since humans first became interested in chemistry [1]. The pesticide sprays began contaminating human foods and environment with arsenic, resulting in serious health risks to humans. However, in recent years, arsenic threatens the drinking water resources in many parts of the world by lurking underground, and the consumption of this tainted water over the years have resulted in unprecedented sufferings of millions of people worldwide.

In natural waters, usually inorganic arsenic in the form of As(III) and/or As(V) is found to be prevalent. Arsenite [As(III)] is much more toxic [2,3] and more soluble and mobile [4] than arsenate [As(V)]. In the pH range of most natural waters (6.5–7.5), As(III) predominantly exists as an uncharged ($H_3AsO_3{}^0$) specie due to which this form of arsenic is very difficult to be removed by the conventionally applied physico-chemical treatment methods [5] than As(V) [6]. In addition to this, excessive use of chemicals, bulky sludge, and high cost limits their use in small-scale treatment systems. For such systems, fixed-bed treatment processes, such as adsorption, are receiving increasing attention for arsenic removal because of their simplicity, ease of operation and handling, regeneration capacity, and sludge-free operation.

Most of the available literature on arsenic removal by adsorption deal with As(V) removal and very few studies have been reported on As(III) removal in fixed bed [7–10]. Different adsorbents have been developed by researchers for the removal of As(III) from water with various degrees of success. Removal of As(III) from water by adsorption on coconut husk carbon [11], MnO_2 coated sand [12], basic yttrium carbonate [13], activated alumina [14], carbon from fly ash [15], granular titanium dioxide [16], and hybrid polymeric sorbent [17] have been tried. Considering the affinity of arsenic toward iron, various types of iron ores [18], iron oxides [19], iron oxide coated materials [20–24] and also zerovalent iron [25–27] have been effectively used as

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adsorbents for the removal of both As(III) and As(V) from the aqueous environment. However, most of the reported studies for arsenic removal have been conducted in batch operation and each adsorbent has its merits and demerits in terms of regeneration, adsorbent strength, adsorption capacities of the sorbents, pressure loss during column runs, etc. Batch reactors are very easy to use in the laboratory study, but less convenient for field applications. Moreover, accurate scale-up data for fixed bed systems cannot be obtained from the adsorption isotherms of batch results, so the practical applicability of the adsorbent should be ascertained in column operations. Adsorption on fixed bed columns presents numerous advantages. It is simple to operate, gives high yields and can be easily scaled up from a laboratory process.

Considering the affinity of arsenic towards aluminium and iron, a Ca–Al–Si–Fe–O containing complex substance (iron oxide-coated cement (IOCC)), was used as adsorbent to evaluate its column performance for As(III) removal under continuous flow conditions in a fixed bed mode after promising results were obtained in the batch tests [28]. Breakthrough studies were carried out to evaluate the effect of process parameters, such as the flow rate, bed depth, and influent concentration, on the shape of the breakthrough curve. The dynamics of the adsorption process were modeled by various kinetic models as bed depth service time (BDST) model, mass transfer model, Thomas model and Yoon–Nelson model.

2. Analysis of column data

2.1. Mathematical analysis

The loading behaviour of As(III) to be removed from solution in a fixed bed containing the IOCC media are shown by breakthrough curves that are expressed in terms of normalized concentration defined as the ratio of effluent As(III) concentration to inlet As(III) concentration (C_t/C_0) as a function of time (t) or volume of effluent (V_{eff}) for a given bed height (h). The volume of the effluent (V_{eff}) can be calculated from the following equation:

$$V_{\text{eff}} = Qt_{\text{tot}} \tag{1}$$

where Q is the volumetric flow rate (ml min^{-1}) and t_{tot} is the total time of flow till exhaust (min), respectively. The total adsorbed As(III) quantity (q_{tot}; mg) in the column for a given feed concentration (C_0) and flow rate (Q) can be found by calculating the area under the breakthrough curve (A) which is obtained by integrating the adsorbed As(III) concentration (C_{ads} (mg l^{-1}) = inlet As(III) concentration (C_0) − effluent As(III) concentration (C_t)) versus time t (min) plot (Eq. (2))

$$q_{\text{tot}} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=\text{tot}} C_{\text{ads}}\,\mathrm{d}t \tag{2}$$

The total amount of As(III) fed to the column (X; mg) is calculated from the following equation:

$$X = \frac{C_0 Q t_{\text{tot}}}{1000} \tag{3}$$

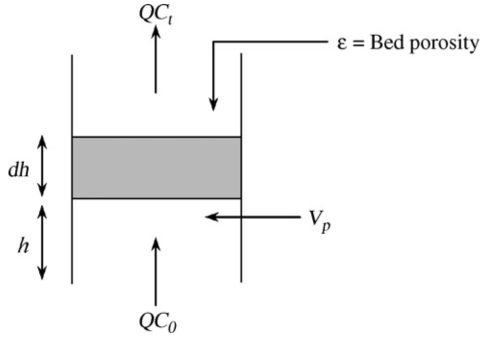

Fig. 1. Scheme of bed depth [29].

The total percent removal of As(III) by the column, i.e. the column performance by IOCC can be calculated from the following equation:

$$\text{total As(III) removal (\%)} = \frac{q_{\text{tot}}}{X} \times 100 \tag{4}$$

2.2. Modeling of breakthrough curves

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 as the feed moves through the bed. The fundamental transport equations for a fixed bed are those of material balance between the solid and fluid. Fig. 1 illustrates the variation of this balance during the reaction. The equation of mass balance material can be stated as: input flow = output flow + flow inside pore + matter adsorbed onto the bed.

The mass balance material equation for this system can be expressed mathematically as

$$\frac{QC_0}{1000} = \frac{QC_t}{1000} + V_{\text{p}}\frac{\mathrm{d}C}{\mathrm{d}t} + m\frac{\mathrm{d}q}{\mathrm{d}t} \tag{5}$$

where QC_0 is the inlet flow of As(III) in the column (mg min^{-1}), QC_t the outlet flow of As(III) leaving the column (mg min^{-1}), V_{p} the porous volume (l) ($V_{\text{p}} = (1/(1-\varepsilon))V$ where V is the bulk volume (l) and ε is the void fraction in the bed), $V_{\text{p}}(\mathrm{d}C/\mathrm{d}t)$ the flow rate through the column bed depth (mg min^{-1}) and $m(\mathrm{d}q/\mathrm{d}t)$ the amount of As(III) adsorbed onto IOCC (mg min^{-1}) where m is the mass of IOCC (g) and $\mathrm{d}q/\mathrm{d}t$ is the adsorption rate (mg g^{-1} min^{-1}).

From the above relation (Eq. (5)), it is evident that the linear flow rate ($u = Q/S_{\text{c}}$, where S_{c} is the column section, m^2), the initial solute concentration, the adsorption potential and the porous volume are the determining factors of the balance for a given column bed depth. Therefore, it is necessary to examine these parameters and to estimate their influence in order to optimize the fixed bed column adsorption process. However, these equations derived to model the fixed bed adsorption system with theoretical vigor are differential in nature and usually require complex numerical methods to solve them. Because of