



A laboratory scale study on arsenic(V) removal from aqueous medium using calcined bauxite ore

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Abstract

The present work deals with the As(V) removal from an aqueous medium by calcined refractory grade bauxite (CRB) as a function of solution pH, time, As(V) concentration and temperature. The residual As(V) was lowered from 2 mg/L to below 0.01 mg/L in the optimum pH range 4.0–7.0 using a 5 g/L CRB within 3 h contact time. The adsorption data fits well with Langmuir isotherm and yielded Langmuir monolayer capacity of 1.78 mg As(V)/g of CRB at pH 7.0. Presence of anions such as silicate and phosphate decreased As(V) adsorption efficiency. An increase temperature resulted a decrease in the amount of As(V) adsorbed by 6%. The continuous fixed bed column study showed that at the adsorbent bed depth of 30 cm and residence time of 168 min, the CRB was capable of treating 340 bed volumes of As(V) spiked water ($C_0 = 2$ mg/L) before breakthrough ($C_e = 0.01$ mg/L). This solid adsorbent, although not reusable, can be considered for design of adsorption columns as an efficiency arsenic adsorption media.

Key words: adsorption; As(V); calcination; adsorption isotherm; column study

Introduction

The presence of arsenic in ground water due to natural and anthropogenic reasons is a major problem in several parts of the world. While, Bangladesh has been identified as the worst affected region, serious problems also exist in adjacent regions of India and parts of China. Long term exposure to arsenic in drinking water has been linked to a variety of health diseases, including several types of cancer, cardiovascular disease, diabetes and neurological damage (Abernathy *et al.*, 2003). Consequently, to protect people, the World Health Organization (WHO, 1993, 2001) has set a provisional guideline concentration for drinking water of 0.01 mg/L. It follows that for some water in Bangladesh a greater than 99% removal of arsenic is required to meet the WHO guidelines. However, many countries, including India and Bangladesh, still operate by the previous 0.05 mg/L standard.

Many technologies exist for removing arsenic from aqueous medium, but most of them suffer from one or more drawbacks, limitations and scope of application (USEPA, 2000). Adsorption and coagulation are two of the cheapest arsenic removal techniques, employed to date. Although coagulation with iron and aluminium salts is more effective, the requirement of skilled operator limits its application in small community and household levels. Moreover, in some coagulation treatments a large amount of salt must be added which introduces contaminants such

as sulfate ions into the water that requires subsequent treatment. In addition, the cost of the chemical reagents used in such treatments can limit their commercial applicability. In comparison, solid adsorbents are easy to handle and are appropriate for use in country side of India and Bangladesh where the largest number of people affected by arsenic contamination. Recently, the use of solid adsorbents particularly natural minerals has shown some promising results in removal of arsenic from contaminated ground water. Among these, manganese wad (Mohapatra *et al.*, 2006), oxisol (high surface area mixed Fe/Al oxide) and its constituents (Ladeira and Ciminelli, 2004), alumina (Halter and Pfeifer, 2001), modified calcined bauxite (Bhakat *et al.*, 2006), activated red mud (Altundogan *et al.*, 2002), natural iron ores (Zhang *et al.*, 2004), and hematite (Redman *et al.*, 2002) are the most often mentioned. Other advantages of using the solid adsorbent are the elimination of filtration and the ability to reuse the adsorbent after regeneration with NaOH solution (Yuan *et al.*, 2002).

If the logic for using Al(III) and Fe(III) flocculants is extended to solid natural adsorbents, bauxite would be the most potential candidate for the adsorption of arsenic. Bauxite is abundantly available, easy and safe to handle and probable to be reutilized in alumina production after arsenic adsorption. Our research group has studied the As(V) adsorption capacity of different grades of bauxite available in Eastern part of India (Mohapatra *et al.*, 2007). We found As(V) adsorption capacity varies between 1.26 and 1.49 mg/g of bauxite depending upon its chemical com-

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position, particularly iron and aluminium. Other natural minerals reported to have good As(V) adsorption capacity are manganese wad, 2.15 mg/g (Mohapatra *et al.*, 2006); natural iron ore, 0.4 mg/g (Zhang *et al.*, 2004); modified calcined bauxite, 1.57 mg/g (Bhakat *et al.*, 2006); gibbsite, 4.6 mg/g; goethite, 12.4 mg/g; oxisol, 3.2 mg/g (Ladeira and Ciminelli, 2004). In present study, to improve the adsorption capacity, we have activated the refractory grade bauxite (RB) at 500°C. In the earlier studies, adsorbents were subjected to activation to improve their adsorption ability by enhancing their reactivity and specific surface area (Altundogan *et al.*, 2002; Bhakat *et al.*, 2006). Also, it is well known that materials containing hydrated mineral phases can be activated by heating, which increases the porosity due to structural modifications.

In the present study, the results obtained from the As(V) adsorption experiments on the calcined RB (CRB) are reported. The effects of various parameters such as pH, temperature, co-existing anions, particularly phosphate and silicate which are commonly found in high concentrations in the study area ground water, on As(V) adsorption capacity have been studied. Finally, a column is also applied for the removal of As(V) from wastewater. The As(V) concentration selected in this study is based on the average arsenic found in the contaminated areas of India and Bangladesh.

1 Materials and methods

1.1 Material preparation and characterization

The refractory grade bauxite was collected from the Panchapatmali bauxite deposit, Orissa, Eastern India. The collected bauxite was powdered and sieved to the fraction size of about 75 µm, washed by deionized water (DW) by mixing at 1:5 solid/liquid ratio for 15 min and then filtered and dried at room temperature. Preliminary experiments show a minor improvement in As(V) adsorption capacity after a calcination temperature of 500°C. For the calcination, a 100-g portion of RB sample was placed in a porcelain dish and then heated in a muffle furnace at 500°C for 4 h. After heating, the calcined refractory grade bauxite (CRB) sample was cooled in a desiccator, and preserved in closed vessels for further study. The surface area measurement was carried out using a Micromeritics Tristar (v 5.02, Italy) instrument. Approximately 100–200 mg of dried, degassed sample was used for each analysis. The sample tube and its contents were loaded into the degassing port of the apparatus. A heating mantle was then applied to the sample tube and the contents heated under vacuum at 150°C for 24 h. The sample was then immersed in liquid nitrogen at 77 K before the sorption measurements were taken. Brunauer-Emmett-Teller (BET) equation was applied to determine the specific surface area. The mineralogical compositions of the sample were determined by X-ray diffraction analysis (Model-RH 200, Rigaku Corp., Japan,) over a range of 15°–80° with CuK α radiation at a scan speed of 2°/min. Silica content was determined by weight loss after treatment with a mix-

ture of HCl and HF (Vogel, 1989). Iron was determined by titration with potassium permanganate (Vogel, 1989). Density was measured by an analytical balance fitted with a density measurement kit (Precisa Instrument A. G., Model XT 202A, France). The point of zero charge (PZC) was determined by method adopted by Balistrieri and Murray (1981), using three different concentrations of sodium nitrate (NaNO₃) as an indifferent electrolyte. Other metal analysis was measured using ICP-MS (4500 series, Hewlett-Packard Co., USA) after acid digestion.

1.2 Adsorption study

A 1,000 mg/L As(V) stock solution was prepared from Na₂HAsO₄·7H₂O salt (Merck, Germany), which was subsequently used to prepare experimental solutions at specified concentrations. Adsorption studies were carried out in 250 ml glass conical flasks. Adjustment of pH was done before the addition of adsorbent by adding either 1 mol/L HCl or NaOH solution. Unless otherwise mentioned, all experiments were carried out at room temperature 25±1°C. After introducing the arsenic bearing solution of required strength and the CRB sample, the flasks were capped tightly and immersed into a temperature controlled water bath and then shaken for required time at the rate of 150±10 cycles/min with a mechanical shaker (SW-20C, JULABO, Germany). After the required time, the suspension was centrifuged, filtered through a 0.2-µm PVDF syringe filter (Advantec, Japan). The arsenic concentrations in aqueous solutions were determined using ICP-MS (4500 series, Hewlett-Packard Co., USA). To study the effect of interfering species (silicate and phosphate) on As(V) adsorption, different concentrations of these ions were added simultaneously with As(V). From the preliminary experiments it is found that a 3-h contact time is required to achieve equilibrium. Therefore, all further adsorption experiments were carried out for 3 h.

1.3 Column study

A column of 30 cm depth and 6 cm internal diameter filled with CRB (75 µm) was used as a fixed-bed downflow reactor at ambient temperature. The As(V) spiked water was pumped through the CRB packed column with a peristaltic pump. At beginning, tap water (without arsenic) was passed through the column for 6 h to minimize the pressure gradients and potential for channeling and fouling of the adsorbent. Initial As(V) concentration of 2 mg/L with flow rates of 50 and 200 ml/h were used to study the effect of the inflow rate on As(V) removal, and these flow rates yielded empty bed contact times (EBCT) of 168 and 43 min, respectively. The effluent samples were collected at different volume intervals and analyzed for residual As(V) concentration as mentioned earlier. Breakthrough or exhaustion curves were developed from the column data by plotting the ratio of C_e/C_0 with the volume of water passed. Where, C_e was the effluent concentration (mg/L). C_0 was the influent concentration (mg/L) of As(V). The volume after which the As(V) concentration in the effluent reached the maximum permissible value (0.01 mg/L) was referred to as the breakthrough volume. The volume after

which the effluent As(V) concentration reached 100% of the influent concentration (2 mg/L) was called the bed exhaustion volume.

The experimental data obtained from column experiments were analyzed using the Thomas expression, which is used in the design of fixed bed adsorption systems, is shown as Eq.(1) (Reynolds and Richards, 1996):

$$C_e/C_0 = \frac{1}{1 + \exp(k/F(Q_m - C_0V))} \quad (1)$$

where, C_e (mg/L) is the effluent concentration, C_0 (mg/L) is the influent concentration, k (mg/h) is the Thomas rate constant, F (L/h) is the flow rate, Q (mg/g) is the maximum adsorption capacity, V (L) is the bed volume and m (g) is the mass of adsorbent. Here the first step involves the calculation of the k value by plotting C_e/C_0 versus V , as the slope = kC_0/F . Each breakthrough curve is compared with the model estimate.

2 Results and discussion

2.1 Characterization of the sample

The RB and activated RB were characterized for their physico-chemical compositions as shown in Table 1. X-ray diffractogram (XRD) was carried out using $\text{CuK}\alpha$ radiation source at 35 kV and 25 mA using a diffractometer (Model-RH 200, Rigaku Corp., Japan) (Fig.1). The XRD analysis reveals the presence of compounds including a

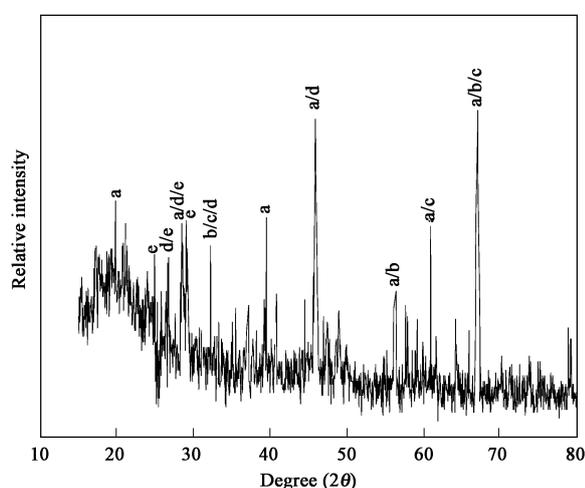


Fig. 1 X-ray diffractogram of calcined refractory grade bauxite (CRB). (a) aluminium oxide; (b) iron oxide; (c) aluminium iron oxide; (d) calcium magnesium aluminium oxide silicate; (e) silicon oxide.

luminum oxide, iron oxide, aluminum iron oxide, calcium magnesium aluminum oxide silicate, and silicon oxide in the CRB. Out of these compounds, calcium magnesium aluminum oxide silicate phase was not detected in the RB sample. The development of this phase may be due to the structural transformation taken place during activation. As shown in Table 1, after activation the surface area and porosity of the CRB increased from 24.1 to 32.2 m^2/g and 21.7% to 30.5%, respectively. Whereas, the pH_{pzc} (the pH value at which surface charge is zero) value of CRB (7.54), decreased slightly compared to 7.76 of RB.

2.2 Effect of pH

The pH of a solution often determines the extent of adsorption. Particularly, oxide and hydroxide mineral surfaces in contact with water, are electrically charged because of the ionization of the MOH functional group (M represents a metal ion at the solid surface). The magnitude and sign of the surface charge vary with the solution pH. Generally, low pH is favorable for uptake of anions due to protonated surfaces, while, cations found in a large degree of adsorption at a higher pH range due to deprotonated surfaces. Adsorption of As(V) on natural minerals is strongly pH dependent, as has been commonly observed for As(V) adsorption on oxide surfaces (Sadiq, 1997). Fig.2 shows the effect of initial pH values (4.0–10.0) on the efficiency of As(V) adsorption when the initial As(V) concentration of 2 mg/L and CRB dosages of 5 g/L. As shown in Fig.2, maximum adsorption was found in a broad pH range of 4.0–7.0 and decreased steadily afterwards. In this pH range the residual As(V) concentration was below the detectable limit (0.01 mg/L). As pH increased to 10.0, the residual As(V) concentration increased to 0.36 mg/L. This corresponds to more than 99% adsorption in the pH range 4.0–7.0 and 82% adsorption at pH 10.0. The RB showed

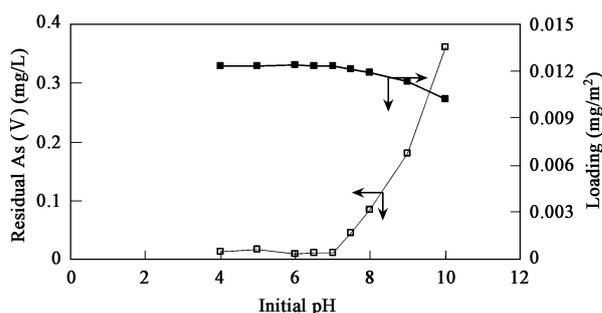


Fig. 2 pH dependence for As(V) adsorption. Conditions: As(V) 2 mg/L; adsorbent 5 g/L; contact time 3 h.

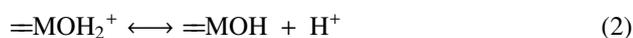
Table 1 Comparison of physico/chemical composition of refractory grade bauxite (RB) and calcined refractory grade bauxite (CRB)

| Chemical constituents (wt.%) | RB | CRB | Physical property | RB | CRB |
|--|-------|------|---|-------|------|
| Al_2O_3 | 78.6 | 81.3 | Bulk density (g/cm^3) | 2.56 | 2.61 |
| Fe_2O_3 | 1.52 | 1.86 | Porosity (%) | 21.7 | 30.5 |
| SiO_2 | 8.5 | 10.3 | Surface area (m^2/g) | 24.13 | 32.2 |
| CaO + MgO | 0.32 | 0.47 | pH_{pzc}^* | 7.76 | 7.54 |
| $\text{K}_2\text{O} + \text{Na}_2\text{O}$ | 0.19 | 0.59 | Bulk density (g/cm^3) | 2.56 | 2.61 |
| TiO_2 | 0.74 | 1.45 | Porosity (%) | 21.7 | 30.5 |
| Loss on ignition (LOI) at 1,100°C | 10.13 | – | | | |

* pH value at which surface charge was zero.

similar type of pH effect but at a cost of higher dosage of adsorbent. If specific surface area is taken into account, the adsorption sites per unit surface area decreased from 0.012 to 0.010 mg/m², when pH increased from 4.0 to 10.0. There was a significant difference between the initial pH and equilibrium pH values of the mixture, as shown in Fig.3. For example, when initial pH levels were 6.5 to 7.5, the equilibrium pH values showed a little change; however, when the initial pH was acidic or basic, the equilibrium pH values approached neutral. This pH change may be due to the buffering nature of the CRB sample. The adsorption of As(V) on to hydroxylated mineral surface can be described by a ligand exchange reaction mechanism, that involves the exchange of an aqueous ligand for a surface hydroxyl group resulting in the formation of an inner sphere complex, which causes an increase in solution pH.

This “buffering” nature can be explained by the amphoteric nature of the CRB as shown in Eqs.(2) and (3).



where, M represents metals like Fe, Al, and Mn. In low pH media the equilibriums in Eqs.(2) and (3) shift towards left, resulting in an increase in the bulk solution pH. In high pH media, the acid dissociation dominates causing a decrease in bulk solution pH (Zhang *et al.*, 2004).

The As(V) adsorption can also be explained on the basis of non-specific adsorption. Non-specific adsorption involves the coulombic interaction, and is mainly limited to pH dependent sites below pH_{pzc} of the adsorbent (Hingston *et al.*, 1967). As the present material contains different oxides/hydroxides, adsorption sites are supposed to be different in nature. It has been reported that Fe/Al/Mn-oxide/hydroxide surfaces may develop electrical charge due to hydration, specific adsorption (ligand exchange), changes in cation coordination, isomorphous replacement, and crystallinity (Sadiq, 1997). Therefore, adsorption of As(V) on these oxide and hydroxide surfaces can also be explained on the basis of the type of charges. Higher pH favors a negative net charge and lower pH enhances a positive net charge on these surfaces. Since the pH_{pzc} of CRB is 7.54, an increase in pH above this value make the adsorbent surfaces more negatively charged resulting in electrostatic repulsion, indicated by a decrease in adsorption as observed in our study. Therefore,

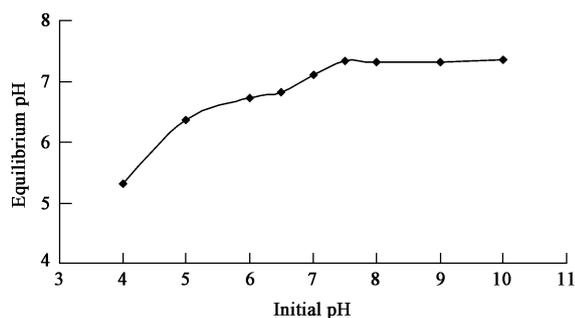


Fig. 3 Relationship between initial and final pH during As(V) adsorption. Conditions: As(V) 2 mg/L; adsorbent 5 g/L; contact time 3 h.

it is assumed that ligand exchange mechanism along with coulombic interaction plays an important role in the adsorption process.

2.3 Adsorption isotherms

The Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of compounds from a liquid phase onto a solid phase. The Langmuir model assumes monolayer adsorption onto homogeneous surface with a finite number of identical sites, while the Freundlich model is empirical in nature. The experimental data obtained were applied to linear forms of the Langmuir (Eq.(4)) and Freundlich (Eq.(5)) isotherms.

$$C_e/Q_e = 1/(bQ) + C_e/Q \quad (4)$$

$$\ln q_e = \ln K + 1/n \ln C_e \quad (5)$$

where, C_e (mmol/L) is the equilibrium concentration of adsorbate in the solution, Q denotes the number of moles of solute adsorbed per unit weight of adsorbent in forming a monolayer on the adsorbent surface, b is the Langmuir constant related to binding energy, q_e (mmol/g) is quantity of As(V) adsorbed at equilibrium, K is a constant which is a measure of sorption capacity, and $1/n$ is a measure of adsorption density. Table 2 summarizes the results of the adsorption isotherm parameters. The results indicated that, the Langmuir isotherm model (correlation coefficient $R^2 \geq 0.99$) can describe the isotherm better than the Freundlich isotherm model ($R^2 = 0.89$), which is mostly applicable to non-specific adsorption on heterogeneous solid surfaces. As shown in Table 2, the Langmuir isotherm for As(V) was characterized by a strong adsorption bond energy as indicated by the constant “ b ”, typical characteristics of a monolayer adsorption. This was further supported by a low Q value which signifies the adsorption process to be monolayer.

Figure 4 shows a plot of C_e versus C_e/q_e for CRB at pH 7.0. From the slope of the best fit, the maximum adsorption capacity (Q) was calculated to be 1.78 mg

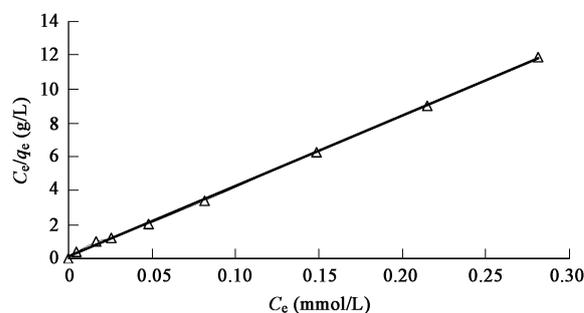


Fig. 4 Langmuir isotherm plots for As(V) adsorption on calcined refractory grade bauxite (CRB) at pH 7.0.

Table 2 Langmuir and Freundlich isotherm constants for CRB

| Adsorbent | Langmuir constant | | | Freundlich constant | | |
|-----------|-------------------|-------|-------|---------------------|-------|-------|
| | Q | b | R^2 | n | K | R^2 |
| CRB | 0.023 | 38.63 | 0.995 | 1.38 | 0.036 | 0.89 |

Conditions: adsorbent 5 g/L; pH 7.0; contact time 3 h.

As(V)/g CRB. The experimental loading data was found to be consistent with the model and according to the criterion of normalized standard deviation ($\pm 5\%$). This loading capacity of CRB (1.78 mg As(V)/g adsorbent) is around 20% higher compared to the As(V) loading capacity of RB (1.49 mg/g). Previous studies (Altundogan *et al.*, 2002; Altundogan and Tumen, 2003) revealed that thermal treatment of hydrous metal oxides strongly influenced the adsorption of metal ions. The higher As(V) adsorption capacity shown by CRB compared to RB can be explained by the physico-chemical properties of the two materials. As shown in Table 1, the specific surface area and porosity of the CRB increased due to the structural transformation and surface modification. Also, the content of iron and aluminum oxide/oxyhydroxide has been increased in CRB due to loss of structural water molecules. The above factors are supposed to be the contributing factor for better loading capacity of CRB.

2.4 Effect of silicate

The effect of silica concentration on As(V) adsorption is presented in Fig.5. The adsorption efficiency is found to show a significant decreasing trend in relation to silica concentrations. When 1 mg/L silica was applied, there was no significant adverse effect on As(V) adsorption. On the other hand, the adsorption of As(V) decreased significantly with the increasing silica concentrations from 2 to 20 mg/L. For example, the residual As(V) concentration increased from 0.012 to 0.34 mg/L when silica concentration increased from 1 to 20 mg/L. This corresponds to decrease in adsorption efficiency from above 99% to 83%. We assume that the decrease in As(V) adsorption resulted from the strong association of silica with CRB, which reduced the surface sites available for As(V) and increased electrostatic repulsion between As(V) and the negatively charged surface sites. Our result is consistent with several reports regarding the effect of silica or silicate on arsenic removal (Meng *et al.*, 2002; Singh *et al.*, 2005). At lower silica concentrations, the minimal effect on As(V) adsorption can be explained by the much lower binding constant of silicate (800 times less) compared to As(V) (Meng *et al.*, 2002). Considering the average silica concentration of 14 mg/L (Singh *et al.*, 2005) in surface and ground water of the study area, silica is expected to play a major role in As(V) adsorption using CRB.

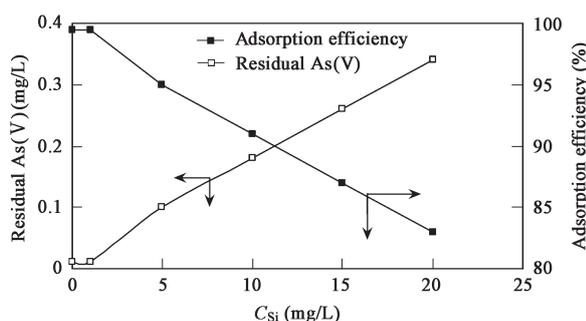


Fig. 5 Effect of silicate concentration on As(V) adsorption. Conditions: As(V) 2 mg/L; adsorbent 5 g/L; contact time 3 h.

2.5 Effect of phosphate

Depending on the pH value, phosphate can have any of the following forms in dilute aqueous solution: phosphate ion (PO_4^{3-}), hydrogen phosphate ion (HPO_4^{2-}), dihydrogen phosphate ion ($H_2PO_4^-$), or phosphoric acid (H_3PO_4). PO_4^{3-} is more prevalent in strongly basic conditions, and HPO_4^{2-} ions are more common in weakly basic conditions. Whereas, $H_2PO_4^-$ ions and aqueous H_3PO_4 are predominate in weakly and strongly acidic conditions, respectively (Altundogan and Tumen, 2001).

Several researchers have reported the adverse effect of phosphate on As(V) adsorption on different material surfaces due to their structural similarity (Manning and Goldberg, 1996; Meng *et al.*, 2002; Zhang *et al.*, 2004). The effect of phosphate on As(V) adsorption on CRB are presented in Fig.6. With increasing concentrations of P(V), the As(V) adsorption efficiency decreased significantly. For example, when P(V) concentration increased from 1 to 10 mg/L, As(V) adsorption efficiency decreased from >99% to 84.5%. It is evident that when P(V) is present along with As(V), the two ions compete for adsorption sites on the CRB. The ability of PO_4^{3-} to compete with As(V) for mineral surface sites is well documented since PO_4^{3-} , like arsenate, is adsorbed as an inner-sphere complex via a ligand-exchange mechanism (Altundogan *et al.*, 2002).

2.6 Effect of temperature

The effect of temperature on adsorption of As(V) by CRB was monitored at four different temperatures of 25, 40, 55, and 70°C (pH 7.0, adsorbent 5 g/L, time 3 h). The corresponding residual As(V) and adsorption efficiency percentage of CRB towards As(V) are presented in Fig.7. With increasing temperature from 25 to 70°C the adsorption efficiency decreased by 6%, although the trend was not consistent for different temperature zones. In general, an increase in the temperature resulted in a decrease of As(V) adsorbed, which shows the interactions to be exothermic. At high temperature, the adsorbate-adsorbent complex becomes unstable, as a result As(V) ions escape from the solid phase to the bulk solution. It is also likely that the instability of the complex may be accompanied by the damage to the adsorption sites in the CRB at higher temperatures, thereby decreased As(V) adsorption.

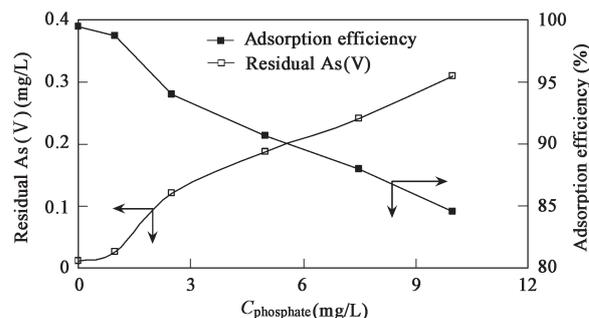


Fig. 6 Effect of phosphate concentration on As(V) adsorption. Conditions: As(V) 2 mg/L; adsorbent 5 g/L; contact time 3 h.

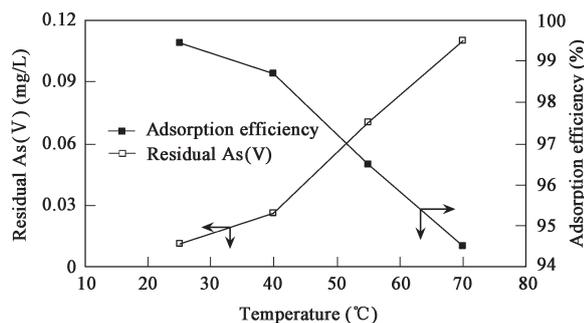


Fig. 7 Effect of temperature on As(V) adsorption. Conditions: As(V) 2 mg/L; adsorbent 5 g/L; contact time 3 h.

2.7 Column adsorption test

For a practical application of CRB to the continuous removal of arsenic from contaminated water and to compare the measured adsorption capacity for the batch and column systems, the column adsorption test was conducted. The results of the column tests were analyzed using the Thomas model, and the estimated modeled values of C_e/C_0 were compared with the observed values (Fig.8). The results of the column studies are summarized in Table 3. In general, the breakthrough volume and bed capacity decreased drastically as EBCT decreased from 168 to 43 min. When EBCT was 168 min, the breakthrough and bed exhaustion volumes were 340 and 1,300 L, respectively. The corresponding values for an EBCT of 43 min were 200 and 750 L, respectively. As shown in Fig.8, when EBCT

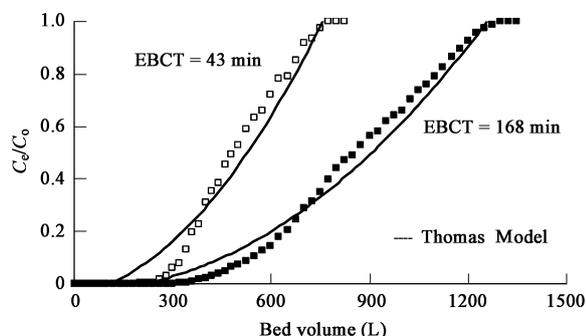


Fig. 8 Comparison of the breakthrough curves at 50 and 200 ml/h flow rates for As(V) adsorption onto CRB. Initial As(V) concentration: 2 mg/L.

Table 3 Summary of the column study

| Parameter | EBCT | |
|--|---------|--------|
| | 168 min | 43 min |
| Filter media | CRB | CRB |
| Particle size (μm) | 75 | 75 |
| Bed depth (cm) | 30 | 30 |
| Bed diameter (cm) | 6 | 6 |
| Average influent pH | 6.3 | 6.3 |
| Average effluent pH | 6.62 | 6.48 |
| Influent concentration (C_0) (mg/L) | 2 | 2 |
| Flow rate (ml/h) | 50 | 200 |
| Breakthrough bed volume (L) ($C_e = 0.01$ mg/L) | 340 | 200 |
| Exhaustion volume (L) ($C_0 = C_e$) | 1,300 | 750 |
| Adsorption capacity (Q) from column study (mg/g) | 1.71 | 0.92 |
| Q from Thomas Model (mg/g) | 1.65 | 1.02 |

EBCT: empty bed contact time.

was less, the data were scattered, suggesting that with less residence time homogenous distribution and effective diffusion of the inflow were not achieved. The As(V) adsorption capacity by CRB in column study was found to be 1.71 mg As(V)/g of CRB, which was very close to the results of the batch test (1.78 mg As(V)/g). On the other hand, the adsorption capacity decreased drastically to 0.92 mg As(V)/g CRB, when EBCT decreased to 43 min. The maximum adsorption capacity estimated from the Thomas model are 1.65 and 1.02 mg/g for EBCT 168 and 43 min, respectively, which are very close to the experimental results. The metals like Fe, Al, Ca, and Mg in the effluent and influent were also analyzed and found to be almost similar even after a breakthrough volume. This concluded that none of the metals were leached from the CRB to the solution. The results for the continuous fixed bed column showed that the application of CRB in removing As(V) was a feasible method and could be used for design of adsorption columns. However, a complete understanding of these findings requires a further study.

2.8 Regeneration of adsorbent

From the economical and environmental point of view, reuse of adsorbent is essential. So, in the present case a simple test was performed to study the possible reuse of CRB by the standard procedure (Vagliasindi and Benjamin, 1997; Yuan *et al.*, 2002). The saturated CRB was regenerated by passing 10 L of 0.1 mol/L NaOH with a flow rate of 200 ml/h through the bed. The process was discontinued when no arsenic was detected in the effluent. The As(V) eluted was calculated by subtracting As(V) removed from As(V) adsorbed on the bed. The percentage of As(V) recovered after this treatment was around 63% of the total adsorbed As(V) in the CRB. The remarkably low As(V) recovery suggested that the chemical bonds between As(V) and CRB adsorbent are strong and the adsorption sites on CRB are not easily accessible. The regeneration capability of the exhausted column with diluted NaOH suggests covalent bonding of As(V) to the active sites of adsorbent surface accompanied by hydroxide ion release into solution during the adsorption process (Fuhrman *et al.*, 2005). The adsorption capacity of reused CRB is subsequently reduced as a result of irreversibly adsorbed arsenic on surface. However, the adsorbents are not expensive. There may be little or no merit in attempting to regenerate the CRB particularly if the CRB loses some adsorption capacity after regeneration. It may be more cost effective to replace the CRB. The arsenic contaminated material can possibly be disposed in secured landfills with cementitious solidification.

3 Conclusions

The potential of CRB as adsorbent for removal of As(V) from aqueous media has been examined under various experimental conditions. The adsorption was strongly pH dependent, with maximum adsorption between pH 4.0 and 7.0. The increase in temperature and the presence of silicate and phosphate in the reaction medium have

adverse effect on As(V) adsorption. Adsorption capacity calculated from the Langmuir isotherm model was 1.78 mg As(V)/g of adsorbent. Whereas, in the fixed bed column study using CRB as adsorbent, the adsorption efficiency decreased marginally to 1.71 mg As(V)/g. With a bed height of 30 cm and a residence time of 168 min, it effectively treated 340 L of As(V) spiked water from an initial concentration of 2 mg/L to the permissible limits (< 0.01 mg/L). As a conclusion, CRB can be considered for design of adsorption columns as arsenic adsorption capacity is reasonably good. However, this medium cannot be regenerated.

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