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Preparation of Metal Immobilized Orange Waste Gel for Arsenic(V) Removal From Water

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Abstract - The toxicity of arsenic is known to be a risk to aquatic flora and fauna and to human health even in relatively low concentration. In this research an adsorption gel was prepared from agricultural waste material (orange waste) through simple chemical modification in the view to remove arsenic (V) from water. Orange waste was crushed into small particles and saponified with $Ca(OH)_2$ to prepare saponified orange waste, which was further modified by immobilizing gadolinium(III) to obtain desired adsorption material (Gd(III)-immobilized SOW gel). The effective pH range for arsenic adsorption was found to be 7.5 – 8.5. Adsorption capacity of the gel was evaluated to be 0.45 mol-arsenic (V)/kg. Dynamic adsorption of arsenic (V) in column-mode was conducted and a dynamic capacity was found to be 0.39 mol/kg. Elution of arsenate was tested after complete saturation of the column packed with gadolinium-immobilized orange waste adsorption gel. A complete elution of arsenate was achieved with the help of 1 M HCl and 28 times pre-concentration factor was attained. This study showed that a cheap and abundant agro-industrial waste material could be successfully employed for the remediation of arsenic pollution in aquatic environment.

Keywords: Arsenic; Orange waste; Gadolinium(III); Adsorption; Elution.

Introduction

Arsenic, the twentieth most abundant element in the earth's crust, is known for centuries to be a poison. It is broadly distributed in the environment; particularly as arsenopyrite or as metal arsenates (Lenoble *et al.*, 2004). Introduction of arsenic into water is reported to occur via natural as well as anthropogenic sources. In some parts of India, Bangladesh and Nepal, the arsenic contamination of water is recognized to be a very serious problem. The excessive presence of naturally occurred arsenic in aquifers has been found because of rock-water interactions and geophysical as well as geo-chemical interaction (Smedley and Kinniburgh, 2002). The inorganic form of arsenic (trivalent arsenite present in groundwater or pentavalent arsenate present in oxygenated water) is naturally occurred in aquatic media and poses a huge threat in terms of toxicity. Organic arsenic, on the other hand, is less toxic although the use of organic arsenicals is phased out. An acceptable level of maximum arsenic contamination in drinking water was defined to be 10 μ g/l by the World Health Organization (WHO) in 1993. But many countries such as Bangladesh, China and India have been using the earlier WHO guideline of 50 μ g/l (Mohan *et al.*, 2007). So considering the global threat of arsenic contamination, cost-effective arsenic removal processes are very much required.

A wide range of treatment technologies have been so far developed and employed for high concentration of arsenic removal, which includes but not limited to co-precipitation, liquid-liquid extraction, ion exchange, ultra filtration, adsorption. Co-precipitation-coagulation with metal (ferric) salts and lime followed by adsorption onto the resulting insoluble metal (ferric) hydroxide is often considered to be a common approach for arsenic removal from water. However, safe separation and handling of the contaminated sludge are the two major problems with this technology. Anion exchange, a physical-chemical ion exchange between solid and liquid phase, process is also commonly used but it delivers low selectivity in the presence of other coexisting anions (Tsuji, 2002). Adsorption, on the other hand, has been evolved to be an effective arsenic removal technique even from a low concentration, which cannot be usually removed by other techniques. As adsorption with commercial resins is expensive, low-cost and environmentally benign adsorbents with high adsorption capacity are immensely needed to cope with the current problem of arsenic removal. At this point, adsorbents, derived from biomass and natural products, have emerged as very good alternatives for building up of eco-friendly water treatment processes. Even though a number of materials have been investigated for the removal of toxic ions over the last two decades, only a limited number of studies have been performed on the use of adsorbents obtained from biological sources e.g., bio-char (Mohan et al., 2007), methylated yeast biomass (Seki et al., 2005), fungal biomass (Say et al., 2003), chicken feathers (Teixeira and Ciminelli, 2005) for the removal of arsenic.

Orange waste, an agro-industrial waste material, was investigated to find out its suitability for making an efficient adsorption gel in this study. It contains approximately 10% pectin that exists in its cell wall as intercellular cementing material (Biswas *et al.*, 2008a). Saponifying with alkali (e.g. Ca(OH)₂), pectin can be easily converted into pectic acid. However, in our previous study, we found that pectic acid functions as a natural chelating material to selectively adsorb cationic metal ions and, in addition, by immobilizing some high-valence cationic metal ions, it works as an anionexchange material selectively adsorbing some toxic anionic species like arsenic (Dhakal *et al.*, 2005). Recently, lanthanide elements, which show specific affinity for anions (phosphate, arsenate, selenite, fluoride etc.), have been reported to be effective for the removal of such hazardous anions from water (Wasay *et al.*, 1996; Zhang *et al.*, 2003). Gadolinium, one of the lanthanides, combines with arsenic, selenium, phosphorus and many other elements to form Gd(III) derivatives. Similar to most lanthanide ions, it forms chelated complexes with high coordination numbers. Therefore, the objective of this study was to prepare an adsorbent by immobilizing gadolinium(III) onto orange waste and to investigate the adsorption characteristics for arsenic(V) through batch and columnmode sorption techniques.

Materials and Methods Materials

All chemicals and reagents used in this study were of analytical grade and used without further purification. Arsenate dibasic heptahydrate (Na₂HAsO₄·7H₂O) was dissolved in deionized water to prepare arsenate stock solution (13.33 mmol/l), which was further diluted to prepare working solutions of any desired concentrations. Aqueous gadolinium solution was prepared by dissolving analytical grade gadolinium chloride hexahydrate (GdCl₃·6H₂O) in 0.1 M HCl. If required, 0.1 M HEPES, a buffering agent, was used to adjust the pH of test solutions.

Preparation of adsorption gel from orange waste

The saponified orange waste (SOW) gel was prepared in light of our previous article (Biswas *et al.*, 2008b). Eight gram (8 g) of $Ca(OH)_2$ was taken along with 100 g of orange waste in a juice mixer and crushed into small particles. The produced suspension was transferred into a beaker where a substantial amount of deionized water was added and the suspension was stirred at 200 rpm at room temperature for 24 h in order to facilitate saponification. Sodium hydroxide was added to the suspension to maintain pH at 12.5. After stirring for 24 h, the suspension was successively washed (with deionized water) and decanted until neutral pH is attained. The

suspension was finally filtered to obtain a wet gel, which was dried in a convection oven for 48 hours at 70°C to produce the dry SOW gel.

The SOW gel was further modified by immobilizing with Gd(III) to facilitate ligand exchange adsorption of arsenic(V). Approximately 4 g of SOW gel was equilibrated with 500 ml of 5.6 mM gadolinium chloride hexahydrate solution at pH 6.5 for 24 h. The suspension was then washed with deionized water and filtered naturally. The wet solid was dried in vacuo until constant weight and finally sieved to produce a particle size fraction of between 75 and 150 μ m for carrying out adsorption tests. The amount of Gd(III) ion immobilized in the SOW gel was calculated from the difference in the metal concentration in the solution before and after immobilization. However, the maximum immobilization of Gd(III) onto SOW gel was estimated to be 0.54 mol/kg.

Batch adsorption tests for arsenic(V) removal

Batch-wise adsorption tests were performed to examine the adsorption behavior of arsenic(V) onto Gd(III)-immobilized SOW gel. The adsorption tests were carried out individually for arsenate in the concentration range 0.013-10.0 mmol/l at an optimum pH value. However, to determine the optimum pH value, adsorption of arsenic(V) at varying pH was first examined where the initial arsenic concentration was maintained constant (15 ppm). Here, pH was adjusted by adding small amounts of sodium hydroxide or hydrochloric acid solution. For carrying out batch adsorption experiments, 50 ml stoppered conical flasks were taken in each of which 25 mg gel was added together with 15 ml of arsenic solution of specific concentration. The samples were then shaken in a thermostated shaker (THOMAS thermostatic shaking incubator AT24R) at 30°C and 138 rpm for about 24 h to attain equilibrium. After 24 h, the samples were filtered by using 1-µm filter paper (ADVANTEC) and their equilibrium concentrations were measured. The amounts of adsorbed arsenic were calculated from the decrease in the arsenic concentrations. The adsorption isotherms for As(V) measured at its optimum pH value, which was 7.5.

Column studies: adsorption followed by elution

Column adsorption tests of As(V) onto a Gd(III)-immobilized SOW gel were performed in a transparent glass column at 30°C. The column was 20 cm high and has an inner diameter of 0.8 cm. It was fitted with a glass filter at the bottom so that the packed materials were retained. The entire column was equipped with a jacket surrounding the column to keep the temperature constant. One hundred fifty milligram (150 mg) of Gd(III)-immobilized SOW gel was taken in a 50 ml beaker and adequate amount of deionized water was added to it so that the gel is sufficiently soaked. Finally the gel was carefully packed into the column. The column was then conditioned by passing water at a certain pH (here 7.5) for 24 h. The test solution, containing 0.2 mmol/l of arsenic (≈15 ppm), was fed through the column using a micro tube pump (EYELA model MP-3N) at a flow rate of 8 ml/h. The pH of the feed solution was maintained at 7.5. BIORAD (Model 2110) fraction collector was used to collect the fractions of effluent at definite time intervals in 8 ml plastic test tubes. After achieving a complete saturation of the gel, elution tests for As(V) were carried out by using 1 M hydrochloric acid keeping the flow rate same as before. It was mandatory that, prior to the elution tests, the column was washed with de-ionized water so that unbound arsenic was driven out from the column. Arsenic concentrations were measured by using Shimadzu ICPS-8100 ICP/AES spectrometer. However, reproducibility of all data (both batch and column-mode experiments) was confirmed by carrying out same test in triplicate and the average value was taken.

Results and Discussion

Effect of pH on adsorption of arsenic species

The effect of equilibrium pH on arsenic (V) removal over a broad pH range (pH 1 – 13) by using Gd(III)-immobilized SOW gel is depicted in Figure 1. It is evident from this figure that the pH of the aqueous solution is an important parameter, which plays a significant role in the adsorption process. Figure 1 shows that As(V) can be effectively adsorbed by using the Gd(III)-immobilized SOW gel over a pH range from 6.5 to 9.5. However, pH 7.5 was selected as an

optimum value for carrying out further batch adsorption tests. It is reported that arsenic(V) can exist as different ionic species depending on the pH of the aqueous solution (Ghimire *et al.*, 2002). In the above mentioned pH range the dominant species of arsenate are $H_2AsO_4^-$ and $HAsO_4^{-2}$, which can be adsorbed on the gel through substitution of negatively charged hydroxyl ions (OH) from the coordination sphere of the immobilized gadolinium ions. Since gadolinium tends to be hydrolyzed in aqueous environment, a lot of hydroxyl ions are therefore available for such ligand exchange with arsenic anions (Cotton *et al.*, 1999).



Figure 1. As(V) removal as a function of equilibrium pH by using Gd(III)-immobilized SOW gel (Condition: Solid-to-liquid ratio = 1.67 mg/ml, Shaking time = 24 h, Temperature = 30°C).

Arsenate is inferred to be adsorbed onto the Gd(III)-loaded gel according to surface complexation method where ligand exchange reaction takes place (Figure 2). Ligands involved in such exchange processes may be hydroxyl ions existing in the gadolinium coordination spheres. The inferred mechanisms have been further supported by the fact that the pH of the solution had increased after arsenic adsorption under the stated experimental conditions. Similar mechanisms have also been reported for the adsorption of arsenate on aluminum-loaded Shirasu-zeolite (Xu *et al.*, 2002), arsenate and arsenite on Fe(III)-loaded cross-linked seaweed (Ghimire *et al.*, 2008). Figure 1 also shows that arsenic removal decreases with a further increase in pH (>9.5). This phenomenon can be explained by the fact that hydroxyl ions, predominant at higher pH, competes with anionic arsenic species for the adsorption sites.



Figure 2. Inferred mechanism of surface complexation and ligand exchange for arsenic(V) adsorption onto the Gd(III)-immobilized SOW gel (M = Gadolinium).

Adsorption isotherm

Adsorption isotherm for As(V) with Gd(III)-immobilized SOW gel was measured at optimum condition as shown in Figure 3. It is evident that at low concentration the adsorption of arsenate increases with increasing arsenic concentration and reaches a plateau region. This suggests that the adsorption takes place according to the Langmuir mechanism. However, the adsorption isotherm of the gel fitted very well with the linear plot of Langmuir monolayer adsorption equation. From this linear plot, binding constant was evaluated to be 7.16 l/mmol. A high value of

correlation coefficient (>0.99) for the linear plot signifies a homogeneous distribution of active adsorption sites on the gel surface (McKay *et al.*, 1985). During the study we confirmed that there was no leakage of gadolinium from the gel under the stated experimental conditions.



Figure 3. Adsorption isotherm for As(V) removal by using Gd(III)-immobilized SOW gel (Condition: Solid-to-liquid ratio = 1.67 mg/ml, Shaking time = 24 h, pH = 7.5, Temperature = 30° C).

The maximum adsorption capacity of the Gd(III)-immobilized gel was evaluated to be 0.45 mol As(V)/kg (33.71 mg/g). The ratio of adsorbed arsenic to that of immobilized gadolinium onto the gel suggests that the binding ratio of arsenic with gadolinium is approximately 1:1. Even though it is difficult to directly compare the Gd(III)-immobilized SOW gel with other adsorbents because of their different experimental conditions, it was found that the adsorption capacity of the prepared gel is considerably higher than that of other adsorbents e.g. 1.05 mg As(V)/g for activated carbon (Gupta and Chen, 1978), 12.88 mg As(V)/g for La(III)-impregnated alumina (Wasay *et al.*, 1996), 16.0 mg As(V)/g for Ce(IV)-doped iron oxide (Zhang *et al.*, 2003), 0.74 mg As(V)/g for polymetallic sea nodules (Maity *et al.*, 2005), 28.2 mg As(V)/g for *Lessonia nigrescens*, an algae (Hansen *et al.*, 2006), 27.62 mg As(V)/g for PAEA microfibers (Vu *et al.*, 2013). So it is elucidated that high adsorption capacity of the present gel for arsenic(V) can be achieved by simple modification of agro-industrial waste material (orange waste) by immobilizing Gd(III).

Column adsorption and elution tests

The performance of the Gd(III)-immobilized SOW gel was studied in a column through which arsenate solution of specific concentration was continuously percolated at a certain flow rate. Figure 4 shows the breakthrough profile of As(V) at pH 6.5 from which it is evident that the breakthrough for As(V) started at 125 bed volumes (BV) and a complete saturation of the column was achieved at 1400 BV. Such result implied that arsenate could be entirely retained on the present gel up to 125 BV and no arsenate would be adsorbed behind 1400 BV. Here, bed volume represents the ratio of the volume of solution passed through the column to that of the packed gel. The effective dynamic adsorption capacity was determined to be 0.39 mol-As(V)/kg, which was 86% of its corresponding equilibrium sorption capacity may be explained by various phenomena such as channeling where effective phase contact was poor, and too short contact time between the gel and the arsenic solution which resulted impediment to attaining equilibrium in the column. Similar results on arsenic removal have also been documented by Lenoble *et al.* (2004) and Zouboulis and Katsoyiannis (2002) who studied MnO₂-loaded resin and iron oxide loaded alginate beads, respectively.

After complete saturation of the column, elution test was carried out by using 1 M hydrochloric acid and the result is depicted in Figure 5. This figure shows that more than 28 fold

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pre-concentration of arsenate was attained during the column operation. Such a high preconcentration factor is a very good characteristic parameter for elucidating the sensitivity of the column. These results are in agreement with our previous studies where La(III)- and Ce(III)loaded orange waste gels were employed for arsenic removal (Biswas *et al.*, 2008b). A complete elution of As(V) was found to be achieved within less than 4 h by using just about 30 ml of eluent. However, such a complete elution indicated that the gel could be reused for adsorption purpose.



Figure 4. Column-mode adsorption of As(V) on Gd(III)-immobilized SOW gel (Condition: Weight of gel = 150 mg, As(V) concentration = 15 ppm, pH = 7.5, Flow rate = 8 ml/h).



Figure 5. Elution profile for As(V) from Gd(III)-immobilized SOW gel by using 1 M HCl (Condition: Flow rate = 8 ml/h).

Analyses of IR Spectra of the gel before and after As(V) adsorption

IR spectra analysis permits spectrophotometric observation of the adsorbent in the range of $400 \sim 3900$ cm⁻¹ and serves as direct means for the identification of main functional groups on the surface. It is reported that FTIR spectra analyses of any adsorbent, before and after adsorption reaction, not only provides information regarding the surface functional groups that might have participated in the adsorption reaction but also indicates the surface sites on which adsorption has taken place (Namasivayam and Kavitha, 2006). However, FT-IR spectra of the gel, before and after arsenate adsorption, were recorded on a JASCO model 410 Fourier Transform Infrared spectrometer using powder-pressed KBr pellet at room temperature (as shown in Figure 6) in order to understand the structural change as well as the involvement of main functional groups in arsenic adsorption.

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It is obvious from the figure that at 3400 cm^{-1} , both spectra show the O-H stretching. A new band at 825 cm⁻¹ corresponds to the As-O stretching vibration band, which confirms arsenic adsorption onto the metal-immobilized SOW gel. Mondal *et al.*, (2007) reported a similar phenomenon for arsenic adsorption on activated carbon. Carboxyl group is considered to be the main characteristic group of pectic acid, which is the key compound in orange waste to make adsorption gel. It is also observed from Figure 6 that the asymmetrical C=O stretching band for carboxyl group at 1583 cm⁻¹ observed for the adsorption gel has shifted to 1637 cm⁻¹ after arsenic adsorption with a different magnitude. These band changes indicate that carboxyl groups involve in arsenic adsorption, through chelation or complexation (Kamala *et al.*, 2005).



Figure 6. FT-IR spectra of metal-immobilized gel taken before and after As(V) adsorption.

Conclusions

In this study Gd(III)-immobilized SOW gel, a novel adsorption material was used for removal of arsenic(V) from synthetic water. The FTIR analysis confirmed the arsenic adsorption. The maximum removal efficiency of arsenic(V) under the observed conditions (pH 7.5, temperature 30°C, adsorbent dose 1.67 g/l) was found to be 98%. From the batch adsorption studies it is obvious that the equilibrium data are best supported to Langmuir isotherm model with a correlation coefficient of >0.99. The process yielded a maximum adsorption capacity of 0.45 mol As(V)/kg. The dynamic adsorption capacity in continuous mode was 0.39 mol/kg, which was little less than the Langmuir adsorption capacity. A complete elution of arsenic was found to occur by using 1 M HCl solution in continuous-mode. From the above study it can be concluded that a cheap and locally-available agro-industrial waste material (orange waste) can be chemically modified through some simple steps to make adsorption material, which can be successfully used for removal of arsenic from water.

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