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ORIGINAL ARTICLE

As (V) adsorption by unmodified and iron modified pozzolane

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Abstract As (V) adsorption from aqueous solutions was studied on a natural pozzolanic tuff. Results were compared from iron modified pozzolanic tuffs in two different fractions. The As (V) adsorption on natural pozzolane and iron modified pozzolane fractions was evaluated as a function of pH in batch experiments. Pozzolane samples were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). It was found that As (V) was adsorbed in all cases. However, As(V) adsorption improved in the iron modified samples. Finally, the results suggest that the As (V) adsorption depends on the iron content in the natural and Fe-modified pozzolane, the contact time between the pozzolanic material and the As(V) solutions, and the pH of these solutions.

Keywords Arsenic · Pozzolane · Adsorption · Iron

Introduction

Arsenic is a metalloid and a well-known toxic element that can harm humans through many means of exposure: by drinking contaminated water, by inhaling volatile arsenic compounds, by ingesting contaminated food, etc. Arsenic exposure can lead to hyperpigmentation of skin and liver cancer, as well as circulatory disorders. Arsenic can react to form both inorganic and organic compounds, with the trivalent species (arsenites) being more toxic [1, 2] than the pentavalent species (arsenates). Arsenic can be found in water contaminated by industrial and agrochemical wastes or in ground water obtained from wells drilled into arsenic-rich ground strata. The World Health Organization recommends a maximum contaminant level of 10 μg L^{-1}; however, arsenic concentrations in drinking water from wells can be far above that value. Thus, a topic of particular interest is the removal of arsenic from contaminated water.

Various separation methods have been studied for removing arsenic from water, such as nanofiltration [3] and arsenic adsorption on manganese oxides [4] and manganese dioxide-coated sand [5]. Similarly, to survey the removal of trace amounts of As from water, other authors have studied the elimination of arsenites and arsenates from polluted groundwater by using layered double hydroxide exchangers [6, 7]. Iron oxides [8] and Fe-modified solid materials, such as activated carbon [9] and zeolites [10] have also been reported as adsorbents that remove arsenite and arsenate anions from aqueous media. This removal has been attributed to either ion exchange, specific adsorption to surface hydroxyl groups, or coprecipitation [11]. Some factors that influence the adsorption of arsenic species dissolved in aqueous solutions are the amount of iron present in the adsorbent, the surface area, and the pH. However, other less-expensive, naturally-abundant materials, such as pozzolane [12], can be used. In this study, pozzolane and Fe-modified pozzolane were used in batch experiments to investigate their potential for removing As(V) by varying the pH, shaking time and arsenate/sorbent ratio.

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Materials and methods

Materials

The pozzolane (POZ) used in this study was obtained from Los Romanes, Aguascalientes, México, which is located on 102°04′ West longitude and 22°15′ North latitude.

Obtaining solid fractions from natural pozzolane

Ten grams of natural pozzolane was vigorously shaken with 250 mL of distilled water for 10 min in a beaker. The suspension was then left to settle for 20 min. It was then poured into centrifuge tubes and the phases were allowed to separate. Sediment was observed at the bottom of the beaker after the pouring step was complete. After centrifuging, the liquid was discarded and the tubes were placed into a boiling water bath to dry the solid. This dried solid was referred to as POZ1. The sediment left in the beaker was also dried in a boiling water bath; this solid is referred to as POZ2.

Preparation of Fe-modified pozzolane

A 10 g sample of POZ was put in contact with 250 mL of 0.1 N $FeCl_3$ aqueous solution in a 500 mL rounded flask. The suspension was refluxed for 8 h, then cooled to room temperature. The brown–red suspension was poured into a beaker while the non-suspended dark-red residue was left in the rounded flask. The brown–red suspension was centrifuged and the residual solid was separated. To eliminate chloride ions, this solid was suspended in distilled water within the same centrifuge tube and centrifuged for two more hours. The supernatant was discarded. This operation was repeated six or seven times until chloride ions were not detected by a $AgNO_3$ test. The centrifuge tubes containing the brown–red solid were dried in a boiling water bath. Once recovered in a ceramic dish, the brown–red solid, referred to as Fe-POZ1, was dried again at 80 °C for 24 h and then heated at 150 °C for 5 h.

The dark-red residue observed at the bottom of the rounded flask was also poured into a beaker. It was then washed with distilled water five or six times until chloride ions were no longer detected with the $AgNO_3$ test. After washing, the solid was dried at room temperature for 24 h. This dark-red solid, referred to as Fe-POZ2, was also thermally treated according to the procedure for Fe-POZ1.

Isolation of Fe-POZ

Ten grams of POZ with 250 mL of 0.1 N $FeCl_3$ aqueous solutions was refluxed for 8 h. The brown–red suspension and the dark-red residue were poured together into a beaker. Vigorous stirring prevented the separation of the solid fraction. The suspension was then poured into centrifuge tubes and centrifuged for 2 h. After centrifugation, the supernatant was discarded and then the iron modified pozzolane was washed to remove chloride ions. The obtained material was referred to as Fe-POZ. The pozzolanic materials POZ, Fe-POZ, Fe-POZ1 and Fe-POZ2 were all used for adsorbing As (V).

As(V) solution

As(V) adsorption experiments were performed with a concentration that simulates real contaminated ground water: 0.1 ppm of $Na_2HAsO_4{\cdot}7H_2O$ aqueous solution (pH values of 2.5, 5.5 and 7.5).

Characterization

Scanning electron microscopy

The samples were mounted directly onto sample holders for scanning electron microspcopy. The images were observed at 20 KeV with a Phillips XL30 electron microscope.

X-ray diffraction

Powder diffractograms for non-modified pozzolane (POZ) and iron modified pozzolane materials were obtained with a Siemens D500 diffractometer coupled to a copper-anode X-ray tube. JCPD files were used to identify the compounds.

Specific area and total pore volume

The specific areas and total pore volume of solid samples were determined by the N_2 Brunauer-Emmett-Teller (BET) method, using a specific area analyzer Micromeritics Gemini 2375.

Elemental composition of the pozzolane and iron modified pozzolane

The chemical composition of the pozzolane materials was determined with an EDS system that was coupled to the electron microscope. The Fe content in the natural and modified pozzolane was determined with instrumental neutron activation analysis (INAA). In this analysis, the photopeak of 1099 keV from ^{59}Fe, produced by the nuclear reaction $^{58}Fe(n, \gamma)^{59}Fe$, was utilized to determine the ^{59}Fe radioactivity with a gamma spectrometer.

As (V) uptake

Kinetic

Two hundred milligram samples of each pozzolane material were shaken in separate glass vials, with 20 mL of 0.1 ppm $Na_2HAsO_4{\cdot}7H_2O$ aqueous solution (pH values of 2.5, 5.5 and 7.5), at 20 °C, and for time periods ranging from 5 min to 24 h. After shaking, the suspension was centrifuged for phase separation. The liquid was recovered with a pipette and the solid was discarded. The arsenic content in the liquid was determined as described below.

Isotherm

For the isotherms, samples from 5 to 200 mg of Fe-POZ1 were contacted with 20 mL of 1 mg/L $Na_2HAsO_4{\cdot}7H_2O$ solution, for 3 h at 20 °C, and pH of 5.5. The measurements of As in each solution were performed as described in the next paragraph. The experimental data were examined using Langmuir and Freundlich adsorption models.

Arsenic quantitative analysis

The arsenic was quantified in the remaining solutions using an atomic absorption spectrometer, model GBC 932 plus, with a hydride system. The wavelength used to measure arsenic was 193.7 nm. For each experiment, and before determining the residual arsenic in the liquid samples, an arsenic calibration curve was obtained using arsenic standard aqueous solutions.

Results and discussion

Characterization

Scanning electron microscopy

No morphological changes were observed in the Fe-modified pozzolanic material after the original pozzolane was treated with the $FeCl_3$ solution.

X-ray diffraction

The XRD analysis showed that natural pozzolane predominantly contains quartz (JCPDS file 33-1161), sanidine (JCPDS file 10-0357), anorthite (JCPDS file 10-1202) and albite (JCPDS file 20-0572). After the Fe-modification process was applied, the composition of the Fe-POZ changed slightly: silicon oxide hydrate (JCPDS file 20-1049) and iron oxide (JCPDS file 40-1139) were detected by XRD, in addition to the compounds found in the natural tuff. XRD patterns of Fe-POZ1 and Fe-POZ2 showed the same composition than Fe-POZ.

Specific area and total pore volume

The specific area and pore total volume of the studied fractions are smaller in the original pozzolanic materials than in their Fe modified analog. On the other hand, Fe-POZ1 and Fe-POZ2 have higher specific areas than their corresponding POZ1 and POZ2 fractions, Table 1.

Elemental composition of the pozzolane and iron modified pozzolane

The elemental composition (EDS semiquantitative analyses) of POZ1 and POZ2 are similar. The main components of these materials are O, Si, Al, Na, K, Ca (Table 2) and Fe (Table 3). The iron content in both pozzolane fractions varies from 0.8 to 2.6% wt. When the POZ1 and POZ2 were treated with $FeCl_3$ solution, the iron content increased in the corresponding obtained fractions Fe-POZ1 and Fe-POZ2; however the Fe-POZ1 sample contained more iron than the Fe-POZ2 sample. The Fe content in POZ1, POZ2, Fe-POZ1 and Fe-POZ2 samples determined by INAA is similar to that measured with EDS (Table 3).

Table 1 Specific area and total pore volume for POZ and Fe-POZ samples

Sample	Specific area (m^2/g)	Total pore volume (cm^3/g)
POZ	0.5564	0.0016
POZ1	1.9471	0.0048
POZ2	0.0819	0.0004
Fe-POZ	2.3262	0.0049
Fe-POZ1	16.9321	0.0458
Fe-POZ2	0.3486	0.0006

Table 2 Elemental composition of pozzolane materials obtained by EDS analyses

Element	wt. %			
	POZ1	Fe-POZ1	POZ2	Fe-POZ2
O	45.44 ± 0.71	38.68 ± 2.53	49.13 ± 4.80	47.84 ± 0.50
Na	1.51 ± 0.15	0.97 ± 0.15	1.23 ± 0.15	1.22 ± 0.29
Al	6.70 ± 0.23	5.76 ± 0.39	6.68 ± 0.15	6.29 ± 0.38
Si	37.18 ± 0.64	29.52 ± 1.41	35.84 ± 3.05	36.75 ± 1.35
Cl	ND	0.96 ± 0.04	ND	0.14 ± 0.10
K	5.99 ± 0.21	4.29 ± 0.36	5.69 ± 1.32	5.19 ± 0.15
Ca	0.57 ± 0.02	0.39 ± 0.11	0.50 ± 0.21	0.45 ± 0.06

Table 3 Amount of iron in each pozzolane materials obtained by EDS and INAA

Sample	Fe content (%)	
	EDS	INAA
POZ	–	1.11
POZ1	2.58 ± 1.05	1.39
POZ2	0.89 ± 0.16	0.90
Fe-POZ	–	7.23
Fe-POZ1	19.39 ± 4.69	11.63
Fe-POZ2	2.07 ± 0.44	0.98

As(V) uptake

Kinetic

Figure 1 shows that As(V) is adsorbed efficiently (80%) in the original POZ sample, particularly at pH 5.5, which could be found in groundwater. At pH 2.5, the adsorption value decrease to 50%. At a higher pH value (7.0), the As(V) adsorption is very slow. It requires about 18 h to reach equilibrium. On the other hand, it was expected that the Fe treatment improves the pozzolanic adsorption behavior. Therefore, the two fractions Fe-POZ1 and Fe-POZ2 that were obtained with the $FeCl_3$ treatment were studied in more detail. The results obtained with Fe-POZ1 are shown in Fig. 2. With the Fe-POZ1 sample, it is possible to rapidly retain 100% of the As(V) present in solution at a pH value of 5.5; a complete equilibrium distribution was attained in less than an hour. For comparison, retention of 83% was observed for Fe-POZ at the same initial pH (5.5) of the arsenic solution, and about 10 h are required to reach the equilibrium distribution. On the other hand, with the Fe-POZ2 sample, up to 87.5% of the

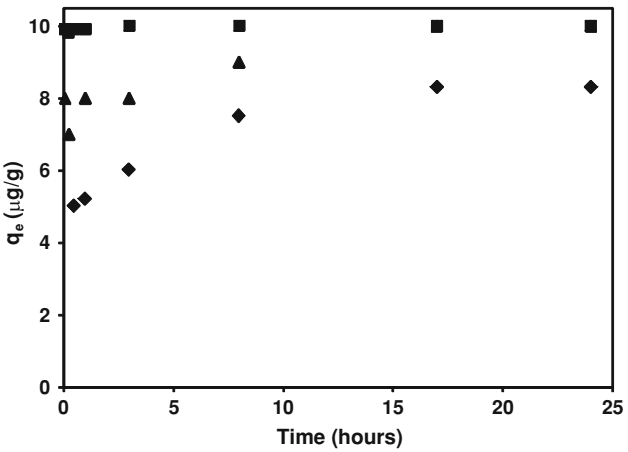

Fig. 2 Kinetics of As(V) uptake on Fe-POZ1 at different pH values as a function of time. (*filled diamond*) pH 2.5, (*filled square*) pH 5.5, (*filled triangle*) pH 7.0

As(V) was retained at equilibrium under the same experimental conditions. The adsorption process is very slow and at least 17 h are required to reach the equilibrium distribution of As(V) (this result is not shown in Figs. 1 and 2). Considering that this system presents similar characteristics to those found in the literature [13], the experimental data were fit to pseudo-second order kinetic model [14]. In this work, the obtained correlation coefficient is 0.98. The maximum adsorbed quantity of arsenic adsorbed at equilibrium by the pozzolane (q_e) varies with the pH value; however, the composition of the pozzolane material also plays a role in this process. As the pH increased, the q_e value also increased. This value is higher in the Fe-POZ1 than in the POZ material (Fig. 3). This is likely because the iron content in each sample enhances the arsenic adsorption behavior. The pseudo second order rate constant depends on the pH value of the arsenic solution in contact

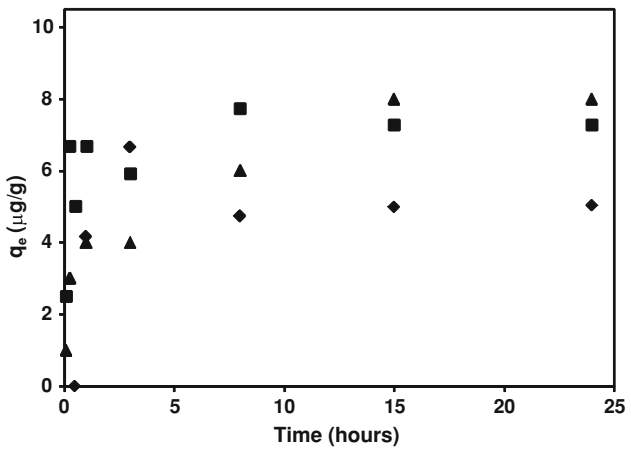

Fig. 1 Kinetics of As(V) uptake on POZ at different pH values as a function of time. (*filled diamond*) pH 2.5, (*filled square*) pH 5.5, (*filled triangle*) pH 7.0

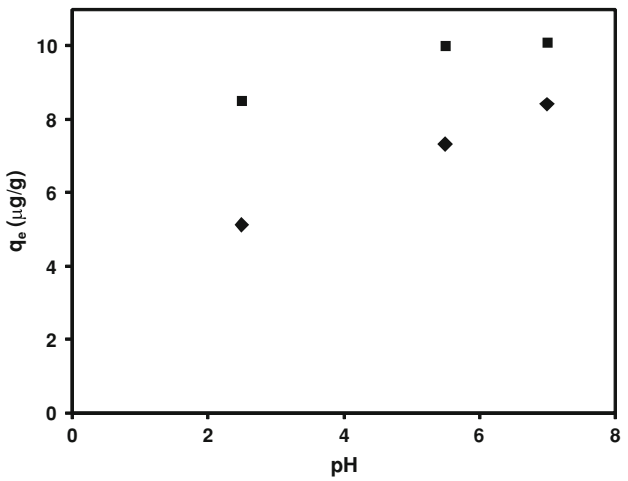

Fig. 3 Maximum amounts (q_e) of As adsorbed by (*filled diamond*) POZ and (*filled square*) Fe-POZ1 as a function of the pH

Table 4 Kinetic constant of pseudo-second order for different pozzolanic materials at several pH values

pH	Pseudo-second order kinetic constant k (g/μgh)	
	POZ	Fe-POZ1
2.5	359	783
5.5	2460	250000
7.0	390	2760

with the pozzolane material. This constant is higher at pH 5 for both Fe-POZ1 and POZ (Table 4). This result can be related to the arsenic chemical species in solution at different pH values. The chemical characteristics of each pozzolane material affect the arsenic adsorption kinetics.

Table 5 shows the As(V) equilibrium adsorption in the different samples studied at different initial pH values of the Na_2HAsO_4 aqueous solution (0.1 ppm). At pH 5.5, As(V) sorption on the original POZ was 7.42 μg/g, while on the Fe-POZ the As (V) adsorption rose to 8.1 μg/g. In the separated fractions, As(V) adsorption improved considerably for the Fe modified samples, from 4.92 μg/g for POZ1 to 10.0 μg/g for Fe-POZ1 and from 0.24 μg/g for POZ2 to 8.7 μg/g for Fe-POZ2. Experiments performed at pH 2.5 and 7.5 show the same trend.

The arsenic chemical species present in the very dilute aqueous solutions at pH values of 2.5, 5.5 and 7.5, were simulated with MEDUSA [15]. At pH values of 2.5 and 5.5, the $H_2AsO_4^-$ ion is the main arsenic chemical species adsorbed onto the Fe-modified pozzolane. At pH 7.5, the main arsenic chemical species adsorbed is the $HAsO_4^{2-}$ ion. The Fe-POZ1 sample, which contains the highest amount of Fe (11.63%) and has the highest specific area (16.9321 m^2/g) of the solids surveyed in this work, adsorbs the most arsenic. The high specific surface area is related to a number of surface –Fe−OH groups available as active sites for the arsenic anionic species. In contrast, Fe-POZ2 shows a lower arsenic adsorption because its Fe-content (0.98 wt. %) and specific surface area (0.3486 m^2/g) are lower. Natural pozzolane (POZ) shows good arsenic retention. This is probably because its surface components, among them iron (Table 3), become hydroxylated when the natural tuff is contacted with the arsenic aqueous solution. It is clear from Table 5 that the arsenic removal from aqueous solution is enhanced by the use of Fe-modified pozzolane; specifically, Fe-POZ1 has the best performance in removing As (V).

Table 5 As(V) equilibrium sorption on pozzolanic materials

Sample	As(V) equilibrium sorption (μg/g)		
	pH 2.5	pH 5.5	pH 7.5
POZ	5.01	7.42	8.0
POZ 1	8.0	4.92	3.82
POZ2	3.58	0.24	0.71
Fe-POZ	7.60	8.1	5.80
Fe-POZ1	8.3	10	10
Fe-POZ2	6.5	8.7	4.9

Adsorption isotherms

The effect of the initial mass of Fe-POZ1 on the adsorption of As(V) at pH 5.5 was investigated by determining the amount of As(V) adsorbed per unit weight of the Fe-POZ1. The results are shown in Fig. 4, where Ce is the As(V) equilibrium concentration and q_e is the equilibrium adsorption of As(V) on the Fe-POZ1 sample.

As(V) adsorption data were examined with the Freundlich and Langmuir adsorption isotherms [16]. The arsenate adsorption data on Fe-POZ1 did not fit the Langmuir isotherm but fit the Freundlich isotherm. The logarithm of the amount adsorbed at equilibrium (log q_e) has been plotted versus the logarithm of As(V) concentration (log C_e) in solution at equilibrium with pH 5.5. The regressed line is described by the Freundlich equation

$$\text{Log } q_e = 1/n \text{ log } C_e + \text{Log } K$$

where K and 1/n ($0 < 1/n < 1$) are the Freundlich constants corresponding to the adsorption capacity and intensity of adsorption, respectively. These constants can be estimated by the intercept and the slope (<1) of the straight line, respectively. The correlation coefficient was 0.9410 and the values of K and 1/n, computed by using the least square technique, were 42.46 μg g^{-1} and 0.6331, respectively. The value of 1/n (<1) found in this work confirms that the Freundlich isotherm is valid for the As(V) adsorption data. Furthermore, this suggests than the adsorbent surface is heterogeneous with an exponential distribution of the active centers. These results are similar to those obtained by

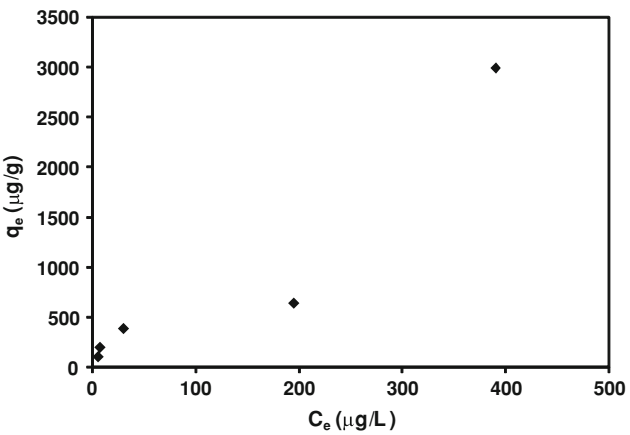

Fig. 4 Adsorption isotherm of arsenate on Fe-POZ1

Macedo-Miranda and Olguín [17] for As(V) adsorption on zeolite materials.

The iron (III) oxide surface has a high affinity for As(V) and is capable of forming inner-sphere bidentate, binuclear As(V)–Fe(III) complexes, as suggested by Su and Puls [18]. The pH dependence of As adsorption is usually explained in terms of the ionization of both adsorbates and adsorbents. In the pH range of 3–6, $H_2AsO_4^-$ is the predominant species (as was mentioned above) and, presumably, the major species being adsorbed. The iron oxide surfaces exhibit a net positive charge in this pH range and anionic adsorption of As(V) is enhanced by coulombic attractions.

The reaction mechanisms just mentioned may also explain As(V) adsorption on Fe-modified pozzolane. The coulombic attraction could specifically explain the high As(V) retention on the fraction Fe-POZ1 that is observed when the initial pH of the arsenic solution was 5.5.

Conclusions

The main conclusion from this study is that pozzolane has the capacity to adsorb As(V) when contacted with arsenate aqueous solutions. Arsenate adsorption was improved in the iron modified pozzolane. This shows that arsenate adsorption both depends on the iron content of the adsorbent as well as the pH value of the arsenate solution. The best As (V) adsorption results were obtained with Fe-POZ1 and an As(V) aqueous solution at an initial pH of 5.5.

The benefits and novelty of using Fe-Modified pozzolane include its low cost, chemical resistance and low solubility in a pH wide interval.

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