Extended abstract No. 107

CAPACITY ADSORPTION OF ARSENIC(V) ON PEAT: A POSSIBLE REMEDIATION

Lílian Karla de Oliveira[1,2], Camila Almeida Melo[1,2], Leonardo Fernandes Fraceto[2], María Aurora Armienta Hernández[3], André Henrique Rosa[2]

[1]Departamento de Química Analítica, Instituto de Química, UNESP, Rua Prof. Francisco Degni, 55, Araraquara, São Paulo, Brazil, CEP 18087-180. [2]Departamento de Engenharia Ambiental, Unesp, Av. Três de Março, 511, Sorocaba, São Paulo, Brazil, CEP 18087-180. [3]Investigador Titular "C" del Instituto de Geofísica, Universidad National Autonoma del Mexico, Cidade do México

SUMMARY

The purpose of this work was to evaluate the adsorption of arsenic ions by peat collected in the state of Sergipe, Brazil. The peat samples were characterized by ^{13}C NMR and elemental analysis. The adsorption experiments were performed in batches at three different pH levels in the peat samples and arsenic concentration of 2 mg l^{-1} of. The equilibrium time of adsorption of arsenic in peat samples was reached in 24 hours. The peat samples showed good adsorption capacity with the highest adsorption capacity observed at pH 5.5. Adsorption kinetics followed the model of pseudo-second order and slow kinetics.

INTRODUCTION

Arsenic is a naturally occurring element that presents high toxicity. Its mobility in the environment is due to natural processes and anthropogenic activities. By presenting great health benefits, several studies have developed techniques for arsenic removal from the environment. Currently the main approaches are ion exchange, adsorption, organic methods and photo-catalytic oxidation (Li et al., 2010; Pakzadeh & Batista, 2011; Mirza et al., 2010; Nguyen et al., 2008)

Recently, natural attenuation, a process that involves applying natural products, little or no toxicity, that degrade and/or retain contaminating compounds without human intervention, has been widely used to minimize the damage caused by several of these contaminants (Wang & Mulligan, 2006). The main advantage of natural attenuation is the use of natural processes that occur in the environment without the need for large investment to remedy or detoxify a particular environment. Natural peats, continuously formed by complex humification processes from vegetable residues are important sources of refractory organic carbon in environments. These have a high content of humic substances, natural complexing with large amounts of oxygen clusters that are responsible for reactions with inorganic compounds.

In this sense, the objective of this work was to evaluate the adsorption of arsenic ions and peat collected in the State of Sergipe, Brazil for possible remediation of areas contaminated with this metal.

MATERIAL AND METHODS

Samples were collected in a peatland in Serra de Itabaiana, Sergipe State, Brazil, at a depth of 0 to 20 cm from the surface by composite sampling (n=5). The samples were stored in polythene bags, dried, crushed, homogenized and passed through a 2 mm sieve. The samples were characterized by ^{13}C NMR with cross-polarization (CP) and magic angle spinning (MAS), using a Bruker Avance III 400 MHz spectrometer, with 5 kHz rotation, a contact time of 2 ms, a relaxation time of 5 s, and a scan number of 11000. For elementary analysis a Thermo Finnigan Flash EA 1112 elemental analyzer was used and the oxygen contents were determined by difference.

In the adsorption batch the peat was added to a beaker together with arsenate ion at a concentration of 2 mg l^{-1}. The pH was adjusted to different values with dilute HCl and/or NaOH solution. Aliquots were removed at predetermined time intervals and stored for later analysis by atomic absorption with graphite furnace atomization using a Varian AA240Z. After batching, the equilibrium pH was measured.

RESULTS

Table 1 shows the results of the elemental analysis and atomic ratios. The results obtained are consistent with those reported in the literature. In general, the lower ratio H/C indicates increased aromaticity. On the other hand, the ratio O/C presents sugar content, so the lower the ratio the less the amount of carbohydrates. The sample of peat in the study presented 0.95 H/C ratio and 0.63 O/C, that are similar to those found in the literature for peat with a small degree of aromaticity (Fernandes et al., 2010). The C/N ratio indicates the origin of organic matter in natural environments, considering that lower than 20 ratios indicate that plants promote the decomposition process, while ratios higher that 20 indicate microbial activity. The ratio for the peat under study was 14.4 suggesting that microbial activity is responsible for the decomposition process (Giovanela et al., 2010). The results of the ^{13}C NMR analysis can be observed in Table 1.

Table 1. Elemental analysis and ^{13}C NMR

Elemental analysis	
C	24.3
H	1.9
N	2.0
O	20.2
H/C	0.95
O/C	0.63
C/N	14.4
^{13}C NMR - Chemical shift δ assignments (%)	
C aliphatic (0-65)	54.1
Ethers, -OH, sugars (65-110)	14.3
C aromatic (110-140)	19.4
Phenols (140-160)	4.7
-COOH (160-190)	2.7
-CO (190-220)	4.8

The spectrum ^{13}C NMR was divided into 6 regions, 0-65 ppm were attributed to aliphatic carbons, 65-110 ppm to alkyl carbon and regions of 110-140 ppm and 140-160 ppm to the aromatic carbon and phenolic carbon as well as in the regions of 160-190 and 190-220 to carboxylic carbon and carbonyl carbon, respectively. From table 1 note that the sample presents highest percentages of saturated carbons (54%) compared to the aromatic (19%), carbon and low values of carboxylic and phenolic groups, groups responsible for links with arsenic ions (Fernandes et al., 2010).

It is known that pH is a determining factor in the ability of peat to absorb ions due to the presence of phenolic (-OH) and carboxylic groups (-COOH); these sites are responsible for ion links on peat. The anion adsorption is favoured at low pH and cations. In this sense, the study of hydrous ions on peat was conducted at three different pH levels. Figure 1 demonstrates the effect of pH on arsenic adsorption by peat.
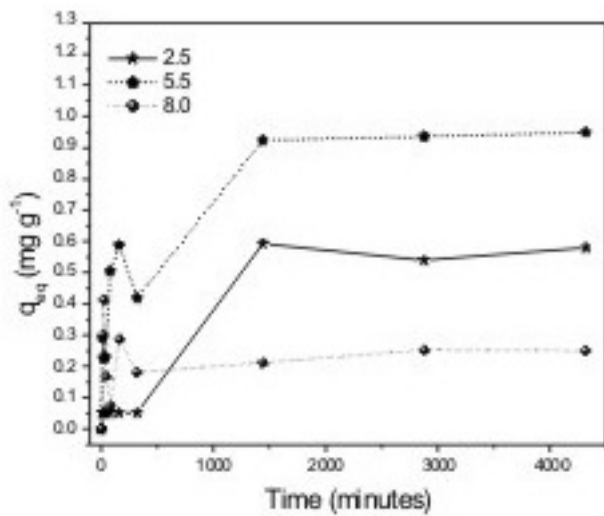

Figure 1. Effect of pH on arsenic adsorption of arsenate in peat

Arsenic adsorption equilibrium time in peat samples (time after which further changes in concentration was not observed) in pH 2.5 and 5.5 was reached in 24 hours. For pH 8.0 the equilibrium time was 320 minutes. The adsorption process was dependent on the pH with the higher adsorption in the range of pH: 8.0< 2.5< 5.5. The greatest values found in pH 5.5 compared to 2.5 can be explained by increased ionization of active sites on the organic matter. Already the lowest values at pH 8.0 can be explained by the fact that $HAsO_4^{2-}$ is found in solution at this pH value. At high pH active sites with negative charge will be dominant, increasing the repulsion effects on the adsorption process.

In order to examine the rate of the adsorption process the data from batch studies were applied to pseudo-first order and pseudo-second order kinetic models. Equations 1 and 2 express the model first and second order, respectively (Ho & McKay, 2000; Ho, 2006).

$$\frac{1}{q_t} = \frac{k_1}{q_{eq}}\frac{1}{t} + \frac{1}{q_{eq}} \qquad \text{(Equation 1)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \qquad \text{(Equation 2)}$$

The values of rate constants and coefficients to pseudo first-order models and pseudo second order can be viewed in Table 2. The correlation coefficients (R^2) show that the best fit model was the pseudo second order, an indication that the adsorption process follows the chemisorptions and/ or ion exchange mechanism (Ho, 2006). The values of the rate constant followed the order of increasing pH: 5.5< 8.0< 2.5; this can also be observed in Figure 2 where equilibrium time is reached at 320 minutes at pH 8.0. Initial adsorption rates also obeyed the order pH 2.5< 5.5< 8.0.

Table 2. Values for the pseudo-first and -second order reaction kinetics of adsorption of arsenate in peat

	Pseudo-first order			Pseudo-second order			
	k_1 (min^{-1})	q_{eq} (mg g^{-1})	R^2	k_2 (min^{-1} g mg^{-1})	q_{eq} (mg g^{-1})	R^2	h^1 (mg g^{-1}min^{-1})
2.5	16.29	0.055	0.520	0.003	0.360	0.770	3.9×10^{-4}
5.5	18.55	0.310	0.662	0.021	0.428	0.972	3.8×10^{-3}
8.0	2.000	0.110	0.080	0.133	0.126	0.997	2.11×10^{-3}

The pH 5.5 showed better retention of arsenate in peat (about 22%), and the adsorption capacity values found for pH 2.5, 5.5 and 8.0 were 0.36, 0.43 and 0,13 mg g^{-1} respectively.

Figure 2 compares the initial and equilibrium pH during the adsorption process. It appears that when the adsorption is made at pH 2.5 a small increase is observed in the final pH, which can be explained by the fact that peat removes H^+ ions along with the arsenate. Already in adsorptions that occur at pH 5.5 and 8.0 it was noted a decrease in pH at equilibrium. This decrease indicates that the predominant mechanism in adsorption of arsenate in peat is ion exchange that occurs by reaction between the metal and the H^+ ions of peat that is transferred into the solution, causing a decrease in pH.
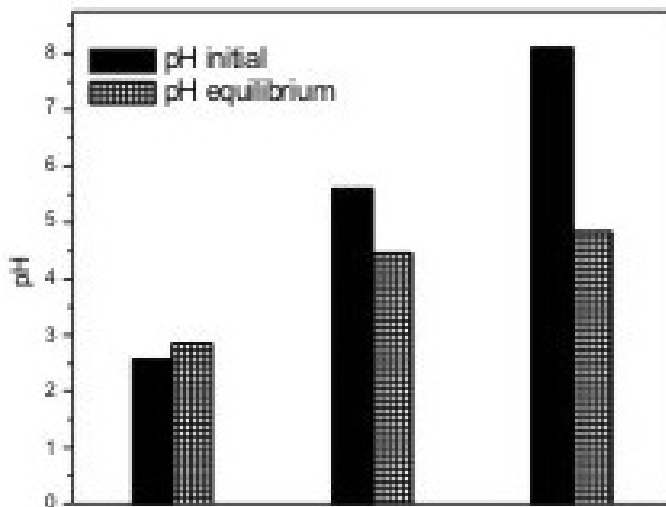

Figure 2. Comparing the initial and equilibrium pH in adsorption process of arsenate in peat

4

CONCLUSION

The peat samples showed good adsorption capacity with highest adsorption capacity observed at pH 5.5. The adsorption kinetics followed the model of pseudo-second order with slow kinetics. The results show that the use of peat as an adsorbent for arsenic might be a viable alternative in the decontamination of this metal.

ACKNOWLEDGEMENTS

REFERENCES

Fernandes, A. N, Giovanela, M., Esteves, V. I. and Sierra, M. M. S. (2010) Elemental and spectral properties of peat and soil samples and their respective humic substances. Journal of Molecular Structure, **971**, 33–38.

Giovanela, M., Crespo, J.S., Antunes, M., Adamatti, D.S., Fernandes, A.N., Barison, A., Silva, C.W.P., Guegan, R., Motelica-Heino, M. and Sierra, M.M.D. (2010) Chemical and spectroscopic characterization of humic acids extracted from the bottom sediments of a Brazilian subtropical microbasin.. Journal of Molecular Structure **981**, 111–119.

Ho, Y. S. (2006) Review of second-order models for adsorption systems. Journal of Hazardous Materials, **136**, 681-689.

Ho, Y. S. and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Research, **34**, 735-742.

Li, Y., Wang, J., Luan, Z. and Lian, Z. (2010). Arsenic removal from aqueous solution using ferrous based red mud sludge. Journal of Hazardous Materials,**177**, 131–137.

Mirza, N., Mahmood, Q., Pervez, A., Ahmad, R., Farooq, R., Shah, M. M. and Azim, M. R. (2010) Phytoremediation potential of *Arundo donax* in arsenic containing synthetic water. Bioresource Technology, **101**, 5815–5819.

Nguyen, T.V., S. Vigneswaran, S., Ngo, H.H., Kandasamy, J. and Choi, H.C. (2008) Arsenic removal by photo-catalysis hybrid system. Separation and Purification Technology, **61**, 44-50.

Pakzadeh, B. and Batista, J.R. (2011) Surface complexation modeling of the removal of arsenic from ion-exchange waste brines with ferric chloride. Journal of Hazardous Materials, **188**, 399-407.

Wang, S.; Mulligan, C. N. (2006) Journal of Hazardous Materials, **138**, 459-470.