

Reduction of acidity and removal of metal ions from coal mining effluents using chitosan microspheres

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Abstract

Effluents from coal mining operations are not only highly acid but also depict elevated concentrations of metals which may contaminate the environment. Due to the polybasic characteristic of chitosan, this biopolymer is capable of both neutralizing and removing iron, aluminum and copper ions from such effluents. The present study aimed at evaluating the use of chitosan microspheres for their importance in continuous systems. The microspheres were prepared by the phase inversion method. Their average diameter and morphology were determined. Water samples from decantation pool (DP) and acidic mine drainage (AMD) effluents were treated using different amounts of microspheres. The pH and concentration of Fe, Al and Cu ions were evaluated both before and after treatment of effluent samples. The results revealed that the microspheres were capable of increasing the pH of DP and AMD samples from 2.34 and 2.58, respectively, to 6.20, i.e., close to neutrality. The treatment also resulted in full removal of the metals investigated.

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1. Introduction

The extraction, beneficiation and use of mineral coal produce effluents of elevated acidity (pH \sim 3.0) and significant concentration of metals, such as Fe, Al, Mn, Cu, Zn and Pb. These effluents are hazardous to the environment and may contaminate hydro resources, thus threatening the integrity of living organisms [1–3].

The recovery of aquatic environments contaminated by metals and/or chemical compounds is rather complex. It often requires a thorough evaluation of contaminant sources and toxic agents so the most appropriate remediation strategy can be selected. Among other options, chemical remediation methods can be employed to that end. These processes commonly consist of an initial step to correct the pH of the water followed by treatment measurements involving ionic resins and filtration columns in addition to adsorption and flocculation methods [4].

Chitosan is a natural copolymer consisting of 2-amino- β (1-4)-2-desoxy-D-glycopyranose and 2-acetamide- β (1-4)-2-desoxy-D-glycopyranose. It is prepared by the deacetylation of chitin, commonly found in shellfish exoskeletons and fungi [5]. The presence of a significant number of amine groups distributed along its polymeric chain grants chitosan characteristics of a polybase capable of neutralizing and removing various metallic ions from acid effluents [6,7]. As a result, no previous neutralization treatment is necessary to adjust the pH of effluents, thus reducing costs and shortening the remediation time.

Chitosan has also drawn special attention as it can be produced in a variety of morphologies including fibers, films, gels, membranes, nanoparticles and microspheres. Moreover, this biopolymer is also an efficient adsorbent to pollutants such as metallic ions [8–10], dyes [11–14] and phenols [15]. The adsorption capacity of chitosan is mainly controlled by its degree of deacetylation, which determines the fraction of free amine groups available to interact with the metallic ions in solution. In this scenario, the aim of the present study was to test chitosan microspheres as adsorbent to both neutralize the acidity and remove metallic ions from coal mining effluents.

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2. Materials and methods

2.1. Reagents and solutions

Chitosan with deacetylation degree of 90% was purchased from Purifarma Company (São Paulo, Brazil). Standard solutions 1000 mg L^{-1} for each metallic ion were prepared from Titrisol[®] ampoules (Merck). All glassware used in the preparation of solutions were washed with neutral detergent, rinsed with nitric acid 10% (v/v) for 24 h and re washed with distilled water. All solutions were prepared using distilled water and analytical grade reagents.

2.2. Preparation of chitosan microspheres

For the preparation of the microspheres, 25 g of chitosan were dissolved in 1000 mL of acetic acid 5% (v/v). A viscous solution was obtained and poured drop by drop using a peristaltic pump coupled to a NaOH 2.0 mol L^{-1} bath. The resulting gel microspheres were washed with distilled water to neutralize their pH and oven dried at 60°C [16].

The average diameter and morphology of the microspheres were analyzed by scanning electron microscopy (SEM) using a Philips-XL 30 system. The samples were placed onto stubs and coated with Au films using a P-S2 Diode Sputtering System to prevent charging. The average diameter of the microspheres was determined by measuring both vertical and horizontal axes of each sphere from a micrograph depicting 20 microspheres.

2.3. Effluent sampling and treatment

Both decantation pool (DP) and acidic mine drainage (AMD) effluent samples were collected from the intense coal mining operations held in Siderópolis, Southern Brazil. The samples were placed in polyethylene flasks with total volume of 5 L and stored in a cooler at 5°C . They were then filtered using an Advantec MFS vacuum filter system coupled to a $0.45 \mu\text{m}$ Schleicher and Schuell membrane to remove particulate material. Next, the pH of the samples was measured using a Corning-pH/ion analyzer 350 pH-meter. The initial concentration of Fe,

Al and Cu ions was determined by flame atomic absorption spectroscopy (FAAS) using a Varian-SpectrAA 50 system and hollow cathode lamps specific for each metallic ion.

Different amounts of chitosan microspheres, varying from 0.2 to 3.0 g, were poured in sealed Erlenmeyer flasks containing 100 mL of effluent samples. The flasks were constantly stirred at 25°C in a mini-shaker Marconi-MA 832 thermostatic bath for 24 h. After that, the pH and remaining concentration of Fe, Al and Cu ions were measured.

3. Results and discussion

3.1. Characterization of chitosan microspheres

The average diameter of the microspheres was $1.00 \pm 0.05 \text{ mm}$, as determined by SEM. Their morphology was nearly spherical with few pores (Fig. 1).

3.2. Characterization of effluent samples

The values of the pH and concentration of metal ions in untreated samples are summarized in Table 1. As it can be seen, both samples were highly acid and contained significant levels of metal ions, especially Fe (III). These results are similar data reported in Ref. [17].

The characteristic acidity of effluents is typically a result of the percolation of aquifers in sulfide minerals, especially pyrite (FeS_2). When in contact with air and water, pyrite oxidizes and dissociates. Consequently, Fe^{2+} is released and rapidly oxidizes to Fe^{3+} , which precipitates as hydroxides. After the onset of the reaction, a cyclic series of events takes place starting with the oxidation of Fe^{2+} to Fe^{3+} which is subsequently reduced by pyrite, releasing Fe^{2+} which increases the acidity of the solution [18].

In addition to iron, other metals, such as aluminum, manganese and copper, present in minerals associated to coal, can be solubilized and lixiviated as a consequence of the typically low values of the pH of effluents. Hence, the concentration of these elements is often high [19]. Therefore, the results obtained during sample characterization suggested that the effluents were

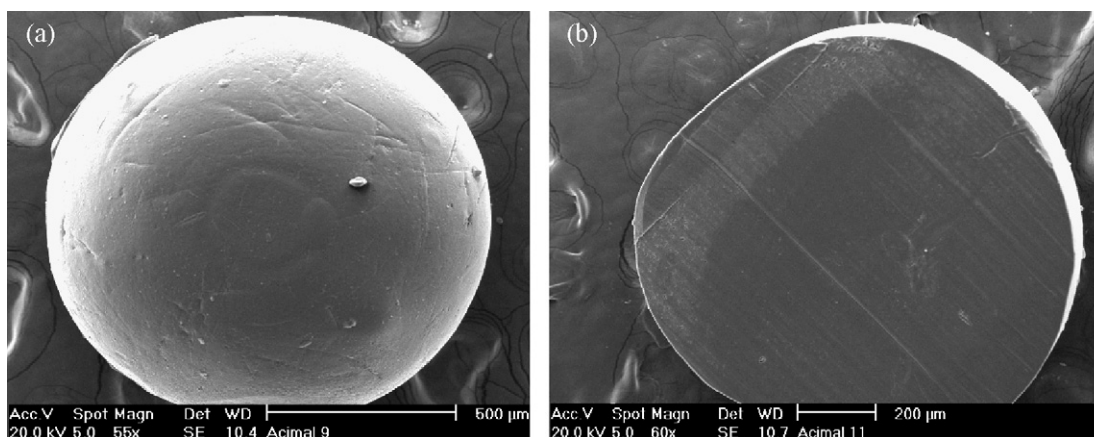


Fig. 1. SEM images of (a) outer and (b) inner region of microspheres.

Table 1
pH and metal concentration in untreated coal mining effluents

Parameter	DP	AMD
pH	2.34	2.58
Fe (III) (mg L ⁻¹)	446	112
Al (III) (mg L ⁻¹)	136	66
Cu (II) (mg L ⁻¹)	0.6	0.2

Evaluation of decantation pool (DP) and acidic mine drainage (AMD) samples.

potentially toxic and could endanger the ecosystem where they are disposed with no previous treatment.

3.3. Effluent treatment using microspheres

The variation of the pH as a function of the amount of chitosan microspheres used to neutralize the acidity of effluent samples is shown in Fig. 2. As it can be seen, the pH increased as the amount of microspheres increased. To raise the pH to 6.20, 0.5 and 2.0 g of microspheres were used for the AMD and DP samples, respectively. This difference can be attributed to the higher concentration of both iron and aluminum ions in DP effluents.

The isotherm of hydronium ions adsorbed by chitosan microspheres is shown in Fig. 3. The adsorption process is ruled by Eq. (1), where q_e is the amount adsorbed (mol g⁻¹), C_0 the initial concentration of solute, C_e its equilibrium concentration (mol L⁻¹), V the volume of the solution (L) and m is the mass of adsorbent (g) [20]:

$$q_e = \frac{C_0 - C_e}{m} V. \quad (1)$$

Experimental adsorption results suggested a typical Langmuir isotherm, with NH₂ groups as the main adsorption sites of the polymer. The protonation of such groups was responsible for reducing the acidity of the solution.

An analysis of the linear Langmuir isotherm yields the adsorption parameters characteristic of the system, i.e., the max-

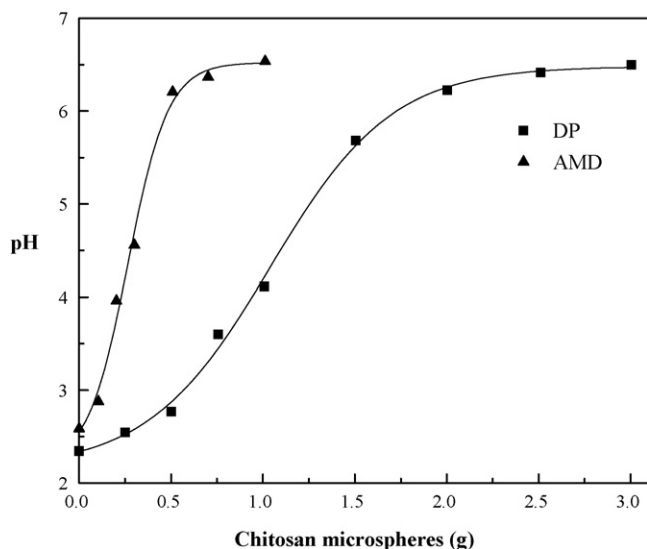


Fig. 2. Reduction of acidity of AMD and DP samples treated with different amounts of microspheres.

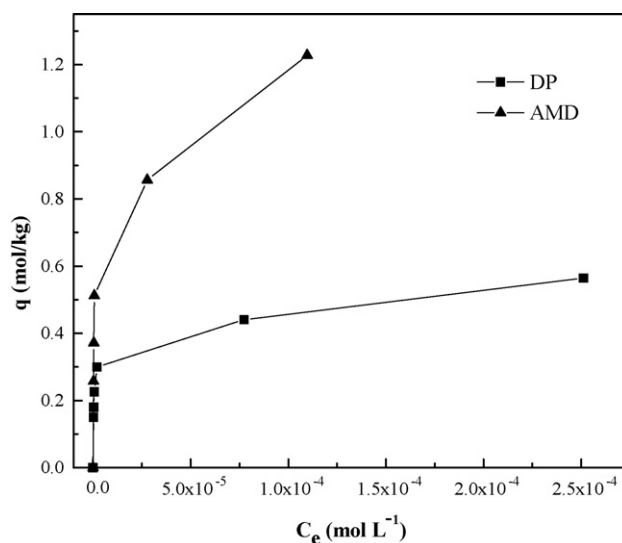


Fig. 3. Adsorption isotherm of H₃O⁺ ions by microspheres.

imum adsorption capacity is determined from the slope of the isotherm (q_m) whereas the Langmuir constant (K_L) is calculated from its intercept [21,22]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}. \quad (2)$$

A linearization of the isotherm resulted in Eq. (3) for DP and Eq. (4) for AMD effluents, respectively:

$$Y = 7.22 \times 10^{-6} + 1.78X \quad (R = 0.997) \quad (3)$$

$$Y = 2.65 \times 10^{-6} + 0.807X \quad (R = 0.994). \quad (4)$$

The slopes of these equations correspond to $1/q_m$ and their intercept to $1/K_L q_m$. The maximum surface saturation capacity of the adsorbent revealed that 1 kg of microspheres adsorbed 562 and 1239 mmol of H₃O⁺ for DP and AMD effluents, respectively. From the environmental standpoint, these results indicate significant neutralization of effluent acidity. The value of the Langmuir constant was 2.46×10^5 L kg⁻¹ for DP and 3.04×10^5 L kg⁻¹ for AMD, suggesting high affinity of the adsorbent for H₃O⁺ ions. These results are quite relevant since, contrary to conventional effluent treatments, no pre-neutralization of the pH was carried out. Therefore the use of chitosan microspheres lowers the costs associated to coal mining effluent treatment by reducing the number of steps of the process.

The removal of metals from DP samples treated with different amounts of chitosan microspheres is illustrated in Fig. 4. As it can be seen, 1.5 g of microspheres were necessary to fully remove Fe, Al and Cu ions from those samples. On the other hand, the total removal of these ions from AMD samples required 0.2, 0.5 and 0.7 g of microspheres, respectively. Higher amounts of chitosan microspheres were necessary to fully remove these metallic ions from DP samples, due to their elevated acidity compared to AMD samples.

The removal of metals from effluents can be associated to the formation of insoluble hydroxides and/or oxides as a result

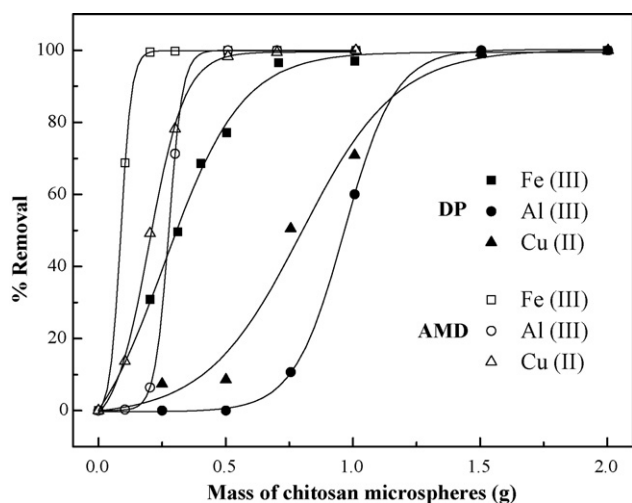


Fig. 4. %Removal of metal ions from DP and AMD effluents.

of the increase in pH. It can also be explained by the formation of a polymer–metal complex once the amine groups act as chelation sites for metallic ions [23,24]. Finally, it should be pointed out that the method presented herein is a relevant step towards reducing the effects of an important source of environmental contamination, since few other alternatives are currently available to treat coal mining effluents.

4. Conclusions

The results obtained in this study revealed that the chitosan microspheres is an alternative for the removal of acidity, Fe(III), Al(III) and Cu(II) from coal mining wastewater. The adsorbent can be regenerated by using sulfuric acid followed by sodium hydroxide, and therefore can be reused. Besides, recycled chitosan microspheres can be disposed in soil, since this biopolymer is rich in nitrogen and carbon with no damage to environment.

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