

Adsorptive removal of arsenic from river waters using pisolite [☆]

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Abstract

This work presents the experimental results for arsenic removal from aqueous solutions using pisolite as a natural inorganic sorbent, a waste mineral product from Brazilian manganese ore mines. A pisolite sample was submitted to physical and chemical characterization; particle size analysis by screening, X-ray diffractometry, X-ray fluorescence, surface area determination by the Brunauer–Emmett–Teller (BET) method and atomic absorption spectrophotometry (AA) for the determination of the species concentration in the pisolite and in the aqueous solution samples from the experiments.

Column and batch tests to contact pisolite and aqueous feed solutions were carried out for evaluation of the pisolite's performance as a natural sorbent for arsenic removal. Experiments using activated pisolite and aqueous feed solutions prepared with Velhas River water were also performed. In the column system, 1.0 g of pisolite removed 1.41 mg of As (4.05% As extraction) from 630 ml of the aqueous feed solution and 1.0 g of activated pisolite extracted 3.51 mg of As (11.6% As extraction). Results for the batch tests with 100 ml of aqueous feed solution and 1.0 g of pisolite removed 1.29 mg of As (24.7% As extraction) and 1.0 g of activated pisolite extracted 3.17 mg (58.2% As extraction).

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1. Introduction

Environmental poisoning due to the emission of waste metals from the mineral processing industry in the last few decades has been and continues to be of growing concern. With stricter environmental standards and policies for solid, liquid, and gas emissions the demand for more effective low cost removal methods has arisen.

Arsenic is a very dangerous specie which has a great capacity for contaminating the environment; contaminat-

ing soils, waterways the ecosystem and causing disease in man kind, for example several types of cancer. In the last decade, discussions in Brazil about the presence of trace concentrations of arsenic and heavy metals in drinking water have been brought to light. In the State of Minas Gerais, Brazil, an institutional project called “Waters from Minas Gerais”, has been set up in the last 3 years and has been instrumental in highlighting the source of contamination in our waterways. This project has enabled scientists to identify the quality of the water used in Minas Gerais. In the case of arsenic and some heavy metals, an increase in their concentration has been detected in river water, which is used in the water treatment plants which supply several cities and counties. For instance, Velhas River (Minas Gerais, Brazil) is regularly used in water treatment plants which supply The City of Belo Horizonte (Capital of Minas Gerais). Arsenic concentrations in The Velhas River water

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Table 1
Chemical composition of Velhas River water sample

Specie	Concentration (mg/l)
Cu	0.04
Mn	0.91
Fe	0.66
As	0.05
Pb	0.015
Ni	0.013
Hg	0.02

is around 0.05 mg/l but in some areas, the arsenic concentration can even be much higher which from a pollution point of view can be critical (www.igam.mg.gov.br/aguas) (Norma no. 10, 1986; Relatório da Qualidade das Águas de Minas Gerais nos anos de 1997, 1998 e 1999; Relatório da Qualidade das Águas em Minas Gerais no ano de 2001). Table 1 shows the chemical composition of a Velhas River water sample.

The search for new decontamination procedures and sorbent materials which will reduce levels of heavy metal concentrations has been established in the legislation bill and has assumed a high level of relevance in Brazil. With the above in mind the search for low cost natural sorbents which are capable of diminishing arsenic and heavy metal concentrations in waterways to tolerable levels is the main goal of research efforts.

Pisolite is a mining waste product, which is basically an iron and manganese oxide mineral aggregate. Due to the presence of iron and manganese oxides, pisolite has sorption characteristics for the removal of cationic metal species present in aqueous solutions (Pires et al., 2004). For example this characteristic assumes an important role in the extraction of some heavy metals and arsenic from river water. It is important to emphasize that pisolite is much cheaper than most inorganic sorbents regularly used in water treatment plants in Brazil.

This work presents the experimental results at bench laboratory scale for pentavalent arsenic species (As^{+5}) removal from aqueous solutions using pisolite as a natural inorganic sorbent in vertical sorption column and batch tests. Some experiments were also carried out using activated pisolite, i.e. pisolite having a higher superficial area caused by the heating of natural pisolite to extract the crystallized water from the sorbent structure. Arsenic concentration used in the aqueous solution of the experiments was 50 mg/l, i.e., 1000 times higher than the concentration found in Velhas River water. This high concentration was used in the tests to evaluate the performance of pisolite for arsenic removal when submitted to severe conditions of poisoning. Some tests were also carried out using aqueous solutions prepared with samples of Velhas River water and the addition of arsenic (50 mg/l) to evaluate the influence of organic compounds, biological organisms and other inorganic species normally found in Velhas River water.

2. Methods and materials

The pisolite sample used in the aforementioned experiments was supplied by Vale do Rio Doce Mining Co. (CVRD-Brazil) and was originally collected from a manganese oxide mining waste disposal area.

The pisolite sample was submitted to the following analytical procedures. Physical and chemical characterization; particle size analysis by screening, surface area determination by Brunauer–Emmett–Teller (BET) method, X-ray diffractometry (Philips equipment-USA, model PW1710), X-ray fluorescence spectrometry (Philips equipment-USA model PW2400) and zeta potential (Matec-Brazil, model 8050).

Table 2 showed the results for the chemical composition of a pisolite sample used in the experiments by atomic absorption spectrometry (AA) using a Perkin–Elmer equipment (USA), model Analyst300.

Column tests were performed in a glass burette 480 mm high, 9.0 mm of internal diameter and 25 ml of nominal volume capacity. The column bed had 1.0 g of pisolite in the particle size ranging from 0.425 mm to 0.600 mm. This particle size was selected in accordance with the solution percolation requirements of the column.

Two liters of aqueous solution (50 mg/l As^{+5}) was percolated through the column bed of pisolite (or activated pisolite) at 3.5 ml/min rate by means of a peristaltic pump (Milan-Brazil, model 204) with an automatic control rate. Samples of aqueous solutions from the outlet column were collected every 40 min and sent for chemical analysis for the determination of species concentration. The percentage of arsenic removal from the aqueous solution was determined by the difference between the mass of arsenic present in the aqueous feed solution before contacting with the pisolite in the column bed and the mass of arsenic present in the aqueous solution in the exit stream of the column divided by the initial mass of arsenic present in the aqueous feed solution. This percentage is also the percentage of arsenic adsorbed onto the pisolite.

Batch tests were carried out in 250 ml glass Erlenmeyers flasks with 1.0 g of pisolite (or activated pisolite) in a particle size range from 0.50 mm to 0.59 mm (28–32 mesh) and 100 ml of aqueous solution 50 mg/l As^{+5} . Pisolite and aqueous solution were stirred at about 250 rpm at room temperature in a controlled environment incubator shaker (New Brunswick Scientific. Inc.-USA, model G-25KC). Samples

Table 2
Chemical composition of a pisolite sample used in the experiments

Specie	Mass (%)
Mn	12.60
Fe	10.08
SiO ₂	20.07
Al ₂ O ₃	27.42
K ₂ O	0.12
CaO	0.11
MgO	0.02

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