

Application of Pisolite as inorganic Sorbent for Heavy Metals and Arsenic Removal from river waters

José Alves Pires ^{a)}, Achilles Junqueira Bourdot Dutra ^{b)}, Antonio Eduardo Clark Peres ^{a)},
Afonso Henriques Martins ^{a)}

^{a)} *Universidade Federal de Minas Gerais/Departamento de Engenharia Metalúrgica e de Materiais-UFMG.
Rua Espírito Santo 35 sala 206-AG, Centro, Belo Horizonte (MG), Brazil, CEP 30160-030.*

E-mail: aecperes@demet.ufmg.br, Phone: (5531)34091053, Telefax: (5531)34091815

^{b)} *Universidade Federal do Rio de Janeiro/Departamento de Engenharia Metalúrgica e de Materiais(PEMM).
Cidade Universitária-Centro de Tecnologia, sala F210, Ilha do Fundão, Rio de Janeiro (RJ), Brazil,
CEP 21941-972.*

Abstract

This paper presents experimental results concerning the removal of arsenic (29.6%), manganese (3.8%), iron (5.1%), and copper (2.2%) from aqueous solutions, using 1.0 g of pisolite as natural inorganic sorbent. Pisolite is a sedimentary rock composed of iron and manganese hydrated oxides occurring as waste material from manganese ore mining. Aqueous solutions containing copper, manganese, iron, and arsenic ions were used in the experiments, simulating the Velhas River waters (Minas Gerais State-Brazil). The results obtained were satisfactory, for the total mass of the extracted species was higher than the species concentrations found in the Velhas River waters.

Introduction

Pisolite is a mining waste containing aggregates of iron and manganese hydrated oxides which impart to the rock sorption characteristics for removal of cationic metal species present in aqueous solutions such as river waters (Pereira et al. 2005). Pisolite is a sedimentary rock formed from ooids (spherical grains composed of concentric layers) of diameter larger than 2 mm, but typically 5-8 mm. The name derives from the Hellenic word for pea. Being a natural material, pisolite is much cheaper than other inorganic sorbents regularly used in water treatment plants in Brazil.

This work reports the experimental results for arsenic, copper, iron, and manganese removal from aqueous solutions using pisolite as natural inorganic sorbent in a vertical sorption column system. The selection of species for the aqueous solution used in the experiments was based on the chemical composition of the Velhas River waters, used in water treatment plants in Minas Gerais State (Brazil). Treated water from Velhas River is supplied to a population of approximately 4,000,000 people.

Methods and Materials

The pisolite sample was supplied by the Brazilian mining company VALE and it was originally collected in a disposal area for manganese oxide mining wastes. The sample was submitted to physical and chemical characterization. Particle size analysis by screening, surface area determination by BET method, X-ray diffractometry (Philips equipment-USA, model PW1710), X-ray fluorescence spectrometry (Philips equipment-USA model PW2400) and zeta potential determination (Matec - Brazil, microelectrophoretic apparatus model 8050) were some of the analytical procedures used.

Sorption experiments were performed in glass columns 480 mm high, 9.0 mm of internal diameter and 25 mL of nominal 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 due to solution percolation requirements of the column.

Two litres of aqueous solution percolated the column bed of pisolite at the rate of 12.5 mL/min aided by a peristaltic pump Milan (Brazil), model 204, with an automatic flow rate control. Samples of aqueous solutions of the column outlet were collected each 40 minutes and sent for chemical analyses. The percentage of As, Cu, Fe, and Mn removal from the aqueous solution was determined by the difference of mass in solution before and after contact with the pisolite bed in the column.

The chemical composition of the pisolite sample used in the experiments was 12.60% Mn, 10.08% Fe, 20.07% SiO₂, 27.42% Al₂O₃, 0.12% K₂O, 0.11% CaO, and 0.02% MgO. The chemical composition was determined by atomic absorption spectrometry (AA) using a Perkin-Elmer equipment (USA), model Analyst 300.

Arsenic and heavy metals concentrations in the aqueous solutions used in the experiments were based on the chemical composition of the Velhas River water, disclosed by IGAM (2001). The concentration used in the aqueous solutions of the experiments was 450 mg/L Cu, 435 mg/L Mn, 168 mg/L Fe, and 50 mg/L As. These species were selected because they exhibited higher concentration than the limit of tolerance established by the Minas Gerais State legislation (COPAM, 1986). Besides, it was important to evaluate the saturation capacity of the pisolite when submitted to very high species concentration in solution. Saturation capacity is a very important parameter for natural sorbents used in water treatment plants because it reduces the time of sorbent replacement in the plant without processing interruption. The initial pH of the aqueous solutions was kept at 6.5 ± 0.2 , the same average initial pH of the Velhas River waters.

Results

The experimental results showed that the pisolite sample exhibited 71.78% retention in 2.36 mm, thus requiring a comminution operation to fit its particle size to the percolation requirements of the solution through the pisolite bed in the column.

The BET method was used for superficial area determination of the pisolite sample. The sample analyzed was finer than $38\mu\text{m}$ (<400 mesh) and the superficial area determined was $61.4\text{ m}^2/\text{g}$. This result can be considered satisfactory for an inorganic sorbent material when compared with results for other inorganic sorbents used for metal ions removal from aqueous solutions (Carneiro, 2003).

X-ray diffraction analysis of the pisolite sample used in the experiments showed that hydrated silicates, quartz and iron, manganese, magnesium and aluminum hydrated oxides were present ($\text{NaMn}_6\text{O}_{12}\cdot 3\text{H}_2\text{O}$ - todorokite, $\text{MnAl}_2(\text{SO}_4)_4\cdot 22\text{H}_2\text{O}$ - apjonite, $\text{Mn}(\text{Mg}_5\text{Al})(\text{Si},\text{Al})_4\text{O}_{10}$ - clinochlore, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ - nacrite). The sorption characteristics of pisolite for ions removal from aqueous solutions is given by the presence of iron and manganese hydroxides in its mineral structure (Helfferrich, 1995).

Results from the X-ray fluorescence analysis showed that Fe, Mn, Si, and Al were the major elements in the pisolite sample. Nickel and titanium were present in low concentrations, and Ca, K, Mg, Rh and Cd were detected just as traces. It was also showed that there were no species which could affect the sorption potential of the pisolite. Besides, no poisoning species were detected which could be released to the solution during the arsenic and heavy metals removal procedure.

Zeta potential measurements of the pisolite sample as a function of the initial pH of the aqueous solution exhibited a cationic sorbent behavior for aqueous solutions at pH 6.5, the average pH of the Velhas River waters. Regarding its cationic sorption characteristics, pisolite can be considered as capable of removing arsenic and heavy metals from aqueous solutions.

Figure 1 shows the experimental results for the individual removal of Cu, Mn, Fe, and As as a function of the time of contact between the aqueous solution containing just one of those species under study and the pisolite sample in the column bed.

The experimental results for the individual species removal showed that 2.0% of copper was extracted in the first 40 minutes of contact between aqueous solution and pisolite. For manganese, iron and, arsenic, the percentage of extraction was 3.2%, 3.6% and 40.0%, respectively, also for 40 minutes contact time. These results showed that pisolite exhibited stronger chemical affinity towards Mn, Fe, and As than for Cu. On the other hand, the saturation of pisolite with those elements should occur for times of contact larger than 160 minutes.

The simultaneous extraction of Cu, Mn, Fe, and As, present in the aqueous solution containing all four species together, by the contact with 1.0 g of pisolite in the column, was also investigated (Figure 2). The species concentrations used in the experiments were 228 mg/L Cu, 237 mg/L Mn, 875 mg/L Fe, and 27 mg/L As. The concentration of these species was lower than the concentration of solutions used in the experiments for individual species removal. The reason is the fact that the presence of all four species together in the same aqueous solution reduces the solubility of each element in the solution. Nevertheless, the concentration of the elements used in these experiments was higher than their concentration in the Velhas River waters. The arsenic removal from the solution containing all species in the feed solution, in the first 40 minutes of contact with pisolite, was much lower than the extraction percentage obtained in the experiment using the feed solution containing just arsenic. The same comment is valid for copper and manganese extraction.

Figure 1 Copper, manganese, iron and arsenic removal percentage by contacting aqueous solution with just one species and 1.0 g of pisolite in a column system. Aqueous solution concentration: (A) 450 mg/L Cu; (B) 435 mg/L Mn; (C) 1680 mg/L Fe, and (D) 50 mg/L As.

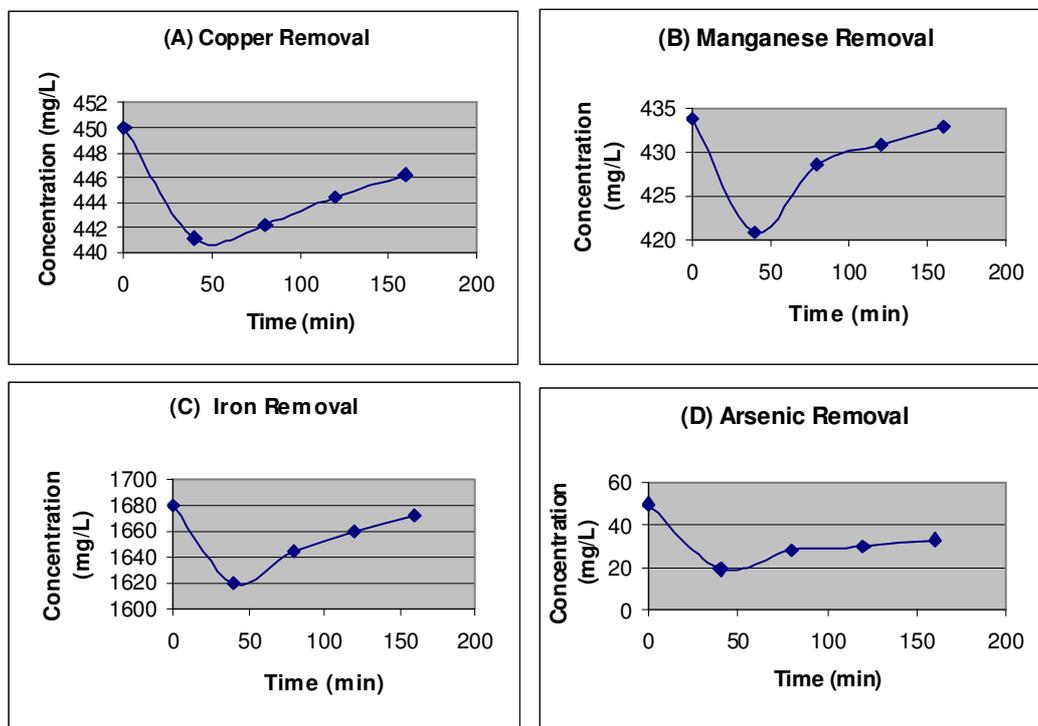
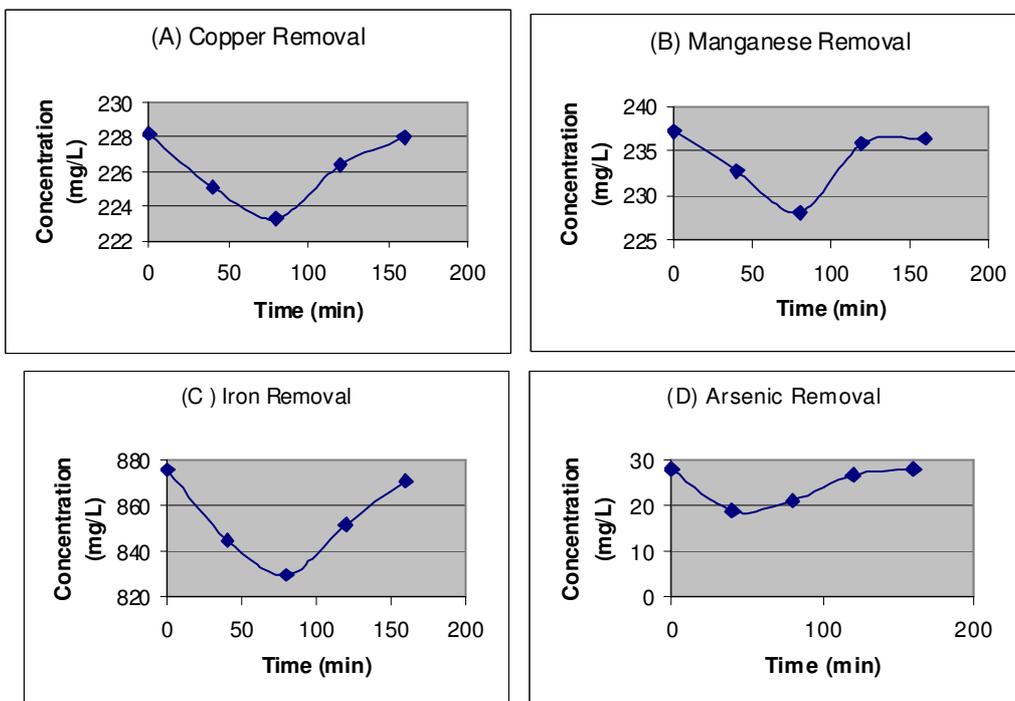


Figure 2 Copper, manganese, iron and arsenic removal percentage by contacting aqueous solution with all species and 1.0 g of pisolite in a column system. Species concentration in the feed solution: (A) 228 mg/L Cu; (B) 237 mg/L Mn; (C) 875 mg/L Fe and (D) 27 mg/L As.



The presence of all four species in the feed solution caused a higher saturation of pisolite for the experiments lasting 160 minutes. The final results showed that 2.2% Cu, 3.8% Mn, 5.1% Fe, and 29.6% As were extracted. Comparing these results with the values obtained for the feed solution containing just one species, copper reached percentages of extraction in the same order of magnitude. Manganese presented a slightly higher extraction in the system with all species in the feed solution. Iron had an increase in the percentage of extraction for the system with all species together in the feed solution, while arsenic had a lower extraction. However, pisolite still presented a strong chemical affinity for arsenic in both systems. All results can be considered as promising because the concentrations of As, Cu, Fe, and Mn used in all experiments were much higher than the concentration of these elements in the Velhas River waters. It is suggested the possibility of further research work to evaluate more deeply the feasibility of pisolite to be used as natural inorganic sorbent for arsenic and heavy metals removal at larger scale systems.

Conclusions

Arsenic removal from aqueous solutions containing Cu, Fe, Mn, and As was lower than the extraction from solutions containing just arsenic.

Pisolite showed potential to be used as natural inorganic sorbent to remove all the species in solution studied in this experimental work. In the feed system containing just one species in solution, pisolite removed 2.0% of copper in the first 40 minutes of contact between aqueous solution and pisolite. For manganese, iron and arsenic, percentages of extraction were 3.2%, 3.6% and 40.0%, respectively, for the same contact period.

In the feed solution containing simultaneously Cu, Mn, Fe, and As, the percentage of extraction results for contacting 1.0 g of pisolite in the column were 2.2% Cu, 3.8% Mn, 5.1% Fe, and 29.6% As.

Acknowledgments

Authors are grateful to VALE for supplying a pisolite sample used in the experiments and Millennium Institute Initiative Program – Water Project: A Mineral Approach (Brazilian Science Foundation-CNPq-Brazil) for the financial support.

References

- Carneiro, M.E.D.P. (2003) Evaluation of human and environmental contamination by arsenic and its immobilization onto iron and manganese oxides, PhD. Thesis, Federal University of Minas Gerais (UFMG), Belo Horizonte, Brazil, February, 139 pp (in Portuguese)
- COPAM (1986) Standard n^o. 10 Minas Gerais State Council for Environmental Policy (COPAM), Minas Gerais, Brazil, September 16, 16 pp (in Portuguese)
- Helfferich, F. (1995) Ion Exchange. Dover Publications, Inc., New York (USA), 624 pp.
- IGAM (2001) Report on water quality in Minas Gerais. Minas Gerais Institute for Water Management (IGAM), Minas Gerais, Brazil, <http://www.igam.mg.gov.br/aguas> (in Portuguese)
- Pereira, P.A.L., Dutra, A.J.B., Martins, A.H. (2005) Adsorptive Removal of Arsenic from River Waters Using Pisolite. CDROM 2nd International Symposium on Processing & Disposal of Mineral Industry Wastes (PDMIW'05), 13-15 June, Falmouth, UK, vol. I, 18 pp