Adsorption of arsenate, phosphate and humic acids onto acicular goethite nanoparticles recovered from acid mine drainage

Regina F.P.M. Moreira[a,*], Solange Vandresen[a], Danielle B. Luiz[a], Humberto J. José[a], Gianluca Li Puma[b]

[a] Department of Chemical Engineering and Food Engineering (EQA), Laboratory of Energy and the Environment (LEMA), Federal University of Santa Catarina (UFSC), Campus Universitário, Trindade, CP 476, Florianópolis, Santa Catarina, 88040-900, Brazil
[b] Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom

ABSTRACT

Acicular goethite nanoparticles (AGNs), obtained from the active treatment of acid mine drainage (AMD) on an industrial scale, were evaluated with respect to their capacity to adsorb the contaminants arsenate, phosphate and humic acids (HAs) in aqueous solution. Kinetics and equilibrium constants that describe the adsorption process were investigated. The adsorption capacity decreased in the order: HAs $(37 \, mgC \, g^{-1}) > As(V) \, (20 \, mg \, As(V) \, g^{-1}) >$ phosphate ions $(13 \, mgPO_4^{3-} \, g^{-1})$. The adsorption capacity of the AGNs produced from acid mine drainage to remove arsenate, phosphate or humic acids are similar to those found for other synthetic iron oxides produced under controlled conditions at the laboratory scale. This study demonstrates the valorization of the AGNs product derived from acid mine drainage slurry waste arising from the mining of coal as an effective adsorbent materials for water treatment.

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1. Introduction

Acid mine drainage (AMD) arising from the mining of metals or coal, represents a serious environmental problem when left uncollected and untreated. Typically, in Brazil, each ton of coal produces 2.5 m^3 of AMD, which contains 2 to 15 g L^{-1} of iron [1]. AMD causes the degradation of surface and ground waters, soils and sediments, and poses a serious hazard to aquatic biota and to humans. AMD is formed when sulfide minerals, predominantly pyrite (FeS_2) but also arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S), among others, are exposed to oxygen and water, causing an oxidation reaction that produces sulfuric acid (H_2SO_4). The waters are characterized by a low pH and high concentrations of iron, and often, other metals and toxic chemicals such as SO_4^{2-}, CO_3^{2-}, Al^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Cr^{3+}, As^{3+}, As^{5+}, Pb^{2+}, Cd^{+2} and Hg^{2+}. Futhermore, naturally occurring bacteria such as *Acidithiobacillus ferrooxidans* can accelerate AMD production considerably [2,3].

As a result of the gravity of the environmental damage that AMD poses, new emerging methods for the treatment of AMD have been investigated, including the use of fly-ash zeolite, fuel cell technologies, peat-humic agent, microfiltration and electrodialysis [2,4–6], besides the traditional method of remediation involving alkaline neutralizing agents such as anhydrous ammonia, hydrated lime, sodium hydroxide, sodium carbonate and limestone, which cause the precipitation of the heavy metals in the AMD in the form of hydroxides and/or oxides sludge [7]. In parallel, potential applications for the recovered AMD sludge are currently being sought, such as its use as pigments [8] and as adsorbent materials [9–11].

The application of iron oxides or hydroxides as adsorbents for the removal of water contaminants is well documented, however, it is desirable to develop greener and low cost sources of iron, reusing industrial waste rich in iron, thus avoiding the synthesis of iron adsorbents from analytical-grade chemicals [12]. Iron compounds such as hematite, goethite, iron oxide-coated materials [13] and iron oxide pillared clays [14] are the preferred group substances for anion adsorption, such as arsenate or phosphate,

* Corresponding author at: Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Campus Universitário, Trindade, PO box 476, Florianópolis, SC, 88040-900, Brazil.
E-mail address: regina.moreira@ufsc.br (R.F.P.M. Moreira).

Nomenclature

AGN	Acicular goethite nano-particles
AMD	Acid mine drainage
k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1})	Adsorption rate constants of pseudo-first and pseudo-second order
K_F,n (dimensionless)	Freundlich parameters
q_t	Amount adsorbed at time t (mg g^{-1})
q_e	Amount adsorbed at equilibrium (mg g^{-1})
q_m	Monolayer adsorption capacity (mg g^{-1})
b	Langmuir constant (L mg^{-1})
BET	Brunauer-Emmett-Teller method
BJH	Barret-Joyner-Hallenda method
ST	Saito-Foley method
C	Concentration of adsorbate at equilibrium (mg L^{-1})
Co	Initial concentrations of adsorbate (mg L^{-1})
EDS	Energy dispersive X-ray spectrometer
HAs	Humic acids
pH_{pzc}	Point of zero charge
SEM	Scanning electron microscopy
V	Initial volume of adsorbate solution (L)
w	Mass of adsorbent (g)
C_o and C_e	Concentrations of adsorbate–initial and at equilibrium, respectively (mg L^{-1})

because they lead to low leaching of adsorbed anions from exhausted adsorbent.

In this study, we evaluate a new application of acicular goethite nanoparticles (AGNs), which is produced from the treatment of 60 m^3 per day AMD and at high purity (>80%), as adsorbent for environmental remediation of water contaminated with arsenate, phosphate and humic acids. This is in response to strict limits of 10 μg L^{-1} on arsenic in drinking water dictated by the US Environmental Protection Agency, the World Health Organization (WHO) and the European Commission [15]. Arsenic is an environmental contaminant associated with the highest risks of morbidity and mortality worldwide, both because of its toxicity and the number of people exposed [16] and dangerously high levels of arsenic have been identified in many water supplies around the world [17]. Excess phosphorous is associated with algal blooms events, which can cause high economic damage in coastal oceans and lakes [18] in addition to the formation of extremely toxic species in drinking water [19]. Sewage and urban waste-waters commonly contain 10–30 mg L^{-1} of phosphate ions and

biological and physico-chemical treatments are the most commonly used methods for their removal. Although widely applied, these methods have disadvantages including excessive sludge production, high chemical demand and difficulty in achieving regulatory guideline levels, since only 75%–85% of the phosphate is typically removed. These problems are not encountered when adsorption methods are used [20]. Finally, color-causing humic substances have long been a problem for the water supply industry, since trihalomethanes (THMs), haloacetic acids (HAAs) and other halogenated organic compounds can be formed during the chlorination of water supplies [21]. These problems highlight the need to remove these compounds from water and wastewaters.

2. Materials and methods

2.1. AGN recovery from AMD

The chemical sludge was obtained from the treatment of AMD at a coal mine located in the state of Santa Catarina in southern Brazil. The adsorbent was prepared from the AMD following the protocol described in Madeira [1]. In this process, 60 m^3 h^{-1} of AMD collected from a coal mine in the southern state of Santa Catarina (Brazil) was treated, generating a chemical sludge at a flow rate of 4–35 tonn day^{-1} with the percentage of iron oxides being greater than 80%. Briefly, the active treatment consists of an AMD (pH 2.5; [Fe^{2+}] = 2.5 g L^{-1}; [SO$_4^{2-}$] = 9.0 g L^{-1}; [Al^{3+}] = 33.5 mg L^{-1}; [Mn^{2+}] = 72.4 mg L^{-1}) pre-neutralization step with lime (Ca(OH)$_2$) at pH 2.7, to yield the selective precipitation of aluminum hydroxides and CaSO$_4$, followed by the addition of NaOH to reach pH 3.2. The result is a precipitate rich in iron, referred to herein as acicular goethite nanoparticles (AGNs). The AGN was washed multiple times with distilled water until the pH of the washing water became constant (pH = 4.0), it was filtered through a cellulose membrane in a press filter, dried at 90 °C for 5 h and stored for further use.

2.2. AGN characterization

The point of zero charge (pH_{pzc}) of the AGNs was measured used two methods. In the first method, 50 mL of NaCl 0.01 mol L^{-1} were placed in Erlenmeyer bottles and appropriate amounts of HCl or NaOH were added to obtain pH values between 2 and 12. AGNs (0.15 ± 0.01 g) were added to each bottle, subjected to agitation for 48 h and then filtered through a Buchner funnel with qualitative filter paper. The final pH of the filtrate was plotted against the initial pH and the pH at which the curve intercepted the line $pH_{initial} = pH_{final}$ was taken as the pH_{pzc}. The same procedure was repeated using a 0.1 mol L^{-1} NaCl solution. In the second method, 1.00 ± 0.01 g of AGNs were placed in 50 mL Erlenmeyer flasks and 20 mL of distilled water (free of CO$_2$) were then added. The bottles were placed under constant stirring for 24 h (Dist, DI 951, Brazil) and filtered through a Buchner funnel with qualitative filter paper. The final pH was measured with a pH meter (Micronal, model B474) and this was regarded as the pH_{pzc}.

The porosity and specific surface area of the AGNs were measured in a Quantachrome Autosorb-1C nitrogen adsorptometer, via nitrogen adsorption and desorption at 77 K. The total surface area was calculated from the adsorption isotherm using the BET equation [22]. The pore size distribution was obtained from the desorption isotherm following the BJH method [23]. Micropore analysis was carried out by the SF method [24].

Microscopic images and the elemental composition of the AGNs were obtained using a scanning electron microscope (JEOL JSM-6390LV) equipped with an energy dispersive X-ray spectrometer (EDS). For the preparation of the AGNs, a small amount of powder was added to acetone and the mixture was sonicated to disperse