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Removal of arsenic from gold cyanidation process waters by use of cerium-based magnetic adsorbents

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ABSTRACT

Cerium-based magnetic adsorbents (referred to as $Fe_3O_4@CeO_2/(OH)_x$) were synthesised via a simple chemical precipitation method. Scanning electron microscopy – energy dispersive spectrometry (SEM-EDS) showed that the synthesised particles had an average size of approximately 300 nm. The particles consisted of crystalline magnetite cores coated with poorly ordered cerium oxide as identified by their X-ray diffraction (XRD) patterns. A saturation magnetization of approximately 40 emu/g was determined by a superconducting quantum interference device (SQUID), making $Fe_3O_4@CeO_2/(OH)_x$ easy to separate magnetically. The Brunauer-Emmett-Teller (BET) specific surface area of the final product was approximately 91.38 ± 1.47 m^2/g. Systematic adsorption tests showed that both As(III) and As(V) could be rapidly removed by $Fe_3O_4@CeO_2/(OH)_x$ with the Langmuir maximum adsorption capacities of 79.1 mg/g for As(III) and 25.5 mg/g for As(V) at a pH value of 9, in arsenic-only solutions. A simultaneous adsorption of 51.2 mg/g for As(III) and As(V) was obtained in simulated process waters from gold cyanidation. 1.0 mol/L NaOH solution was used as a regenerant to investigate the regeneration and reuse of $Fe_3O_4@CeO_2/(OH)_x$, and over 60% of its initial adsorption capacity was retained after five consecutive adsorption–desorption cycles. Therefore, the readily synthesised $Fe_3O_4@CeO_2/(OH)_x$ microparticles, with their high degree of magnetic separability and exceptional arsenic adsorption capacity, can be considered a promising arsenic scavenger in certain industrial applications.

1. Introduction

It is common knowledge that arsenic is toxic and carcinogenic, posing a severe threat to both human health and the environment. As a result, the world total demand for arsenic and its products continuous to decline. For example, the practice of wood or timber preservation with copper chrome arsenate has ceased in North America. Likewise, arsenic has been abandoned by most large glass manufacturers for fining and the use of arsenic in semiconductors remains limited (Edelstein, 2015).

Therefore, at present, arsenic enters the environment principally through natural pathways, such as chemical and physical weathering, volcanic emissions, etc., as well as anthropogenic pathways, such as mining, metallurgy, coal combustion, pesticides, etc. (Martin et al., 2014).

The gold industry is strongly associated with the release of arsenic, since arsenic is frequently a significant component in gold deposits (Asselin and Shaw, 2016). Arsenic exists primarily in nature as sulphides, such as arsenopyrite (FeAsS), and copper sulfosalts, specially enargite (Cu3AsS4) and tennantite ((Cu,Fe)12As4S13), which are all main sources of arsenic in most gold ores.

Gold cyanidation, as the most commonly used process for gold extraction, can be adversely affected by arsenic (Kyle et al., 2011; Kyle et al., 2012). Although arsenic cannot form any stable complex with cyanide, arsenic-bearing sulfide minerals can be completely oxidised to arsenites ($AsO_3{}^{3-}$) and arsenates ($AsO4^{3-}$) or partially oxidised to thioarsenites ($AsS_3{}^{3-}$) and thioarsenates ($AsS_4{}^{3-}$) by oxygen in leaching solutions, under the alkaline conditions typically present in gold cyanidation. This additional oxygen consumption by arsenic species has a significant impact on cyanidation, leading to retardation or prevention of gold dissolution (Marsden and House, 2006). At the same time, free cyanide is likely to be involved in further oxidation of thioarsenites and thioarsenates to form thiocyanates (SCN^-), causing a loss of lixiviant (Hedley and Tabachnick, 1950).

In addition, all these oxidation products can be attached to the gold surface so as to hinder the interaction of gold with cyanide and oxygen in the leaching solutions. After leaching, gold recovery can also be influenced by arsenic species via competitive adsorption onto activated

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carbon (Lorenzen et al., 1995). In tailing dams, both As(III) and As(V) can be present at high concentrations in alkaline solutions. According to the literature (Haffert and Craw, 2008), the more toxic As(III) species is significantly more soluble than the As(V) species in tailings waters. Despite the limited information of the deportment of arsenic in tailing dams, one may predict that arsenic species can be very troublesome for subsequent treatment, particularly As(III).

In order to address the problems caused by arsenic in aqueous solutions, a number of processes has been proposed and tested. The most common of these is precipitation, for instance, by use of schwertmannite (Paikaray and Peiffer, 2012; Raghav et al., 2013), basic ferric arsenate sulfate (Gomez et al., 2013), ferrous arsenate (Raghav et al., 2013; Sadiq et al., 2002), ferrihydrite (Raghav et al., 2013), solidification and stabilization in cements (Burton et al., 2010; Yoon et al., 2010), and aluminium phosphate-encapsulation of scorodite (Lagno et al., 2010). Other techniques, including adsorption, ion exchange, reverse osmosis, as well as coagulation with microfiltration, were also investigated (Kartinen and Martin, 1995; Lin et al., 2006; Mohan and Pittman (2007); Pereira et al., 2007). Recently, some interesting research findings on arsenic immobilization were reported, such as As(III)/As(V) removal by calix[4]pyrrole (de Namor et al., 2017), Fe-Mn wastes produced by a water treatment plant for arsenic immobilization (Lewińska et al., 2018), arsenic removal by perilla leaf biochar (Niazi et al., 2018), Friedel's salt used for arsenic removal (Li et al., 2017) and arsenite and arsenate immobilization by preformed and concurrently formed disordered mackinawite (Vega et al., 2017). However, most of these methods are not suitable for treatment of gold cyanidation waters, owing to the high alkalinity, the low arsenic concentration and the complex chemical composition of the water (Nishimura and Robins, 2000; Tahija and Huang, 2000).

Adsorption is one of the most commonly used methods for removing arsenic species from aqueous solutions, but the vast majority of related studies are aimed at drinking water under near neutral pH that is markedly different from the alkaline conditions prevalent in gold cyanidation.

Previous studies have shown that titanium oxide and zirconium oxide can be used as effective arsenic scavengers in alkaline process waters during gold processing (Feng et al., 2017a; Feng et al., 2017b). It was also reported that cerium oxide is an efficient arsenic adsorbent over a pH range from 3 to 11 (Li et al., 2012; Basu and Ghosh (2013); Basu et al. (2013)), showing outstanding adsorption performance, particularly towards As(III) under alkaline conditions. Cerium oxide in combination with other materials, such as activated carbon (Yu et al., 2017) and manganese oxide (Gupta et al., 2011; Gupta et al. (2012)) and other nanobiocomposites (Nath et al., 2016; Zhang et al., 2016) have likewise shown good performance. Moreover, despite the rare earth terminology, cerium dioxide and other cerium salts are cheap and abundant, and could potentially be cost competitive adsorbents.

As to the adsorption mechanism, both As(III) and As(V) can be adsorbed onto the surface of cerium oxide by the formation of negatively charged inner sphere complexes with the surface hydroxyl groups (Li et al., 2012). To facilitate the separability, the cerium oxide particles were coated onto the surfaces of magnetite microparticles via a simple chemical precipitation method. The resultant cerium-based magnetic microparticles were used for studying on removing arsenic species from both arsenic-only solutions and simulated process waters of gold cyanidation. The targeted arseniferous solutions in this study were gold cyanidation process waters after destruction of cyanide. Based on a survey of several gold processing plants in Western Australia, the pH values of the process waters in this stage range from 7 to 9. Accordingly, adsorption tests on the effect of pH were conducted within a pH range of 7–11, while adsorption kinetics and isotherms were determined at a pH of 9, which was typical of the water samples from local gold mines. These composite particles are referred as Fe3O4@CeO_2/$(OH)_x$ in this study, owing to the uncertainty with regard to the exact structure of the cerium species, as discussed in Section 3.1.2 in this paper. Finally, desorption tests were conducted to evaluate the reusability of Fe3O4@CeO_2/$(OH)_x$.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich (Australia) and used without further treatment, unless otherwise stated. Stock solutions of As(III) and As(V) were prepared from sodium (meta)arsenite ($NaAsO_2$) and sodium arsenate dibasic heptahydrate ($Na_2HAsO_4·7H_2O$), respectively, at a concentration of 1 g/L. HCl and NaOH solutions (both 0.1 mol/L) were used for pH adjustment. Deionised water (resistivity > 18 MΩ·cm at 25 °C) was used to prepare all solutions.

2.2. Preparation of Fe_3O_4@CeO_2/$(OH)_x$ adsorbents

Fe_3O_4@CeO_2/$(OH)_x$ was synthesised via a simple chemical precipitation method at room temperature, as outlined below. First of all, 1 g of Fe_3O_4 microparticles (100–200 nm) was ultrasonically dispersed in a 200 mL aqueous solution of 0.025 mol/L $Ce(NO_3)_3·6H_2O$, followed by adding a 100 mL aqueous solution of 0.25 mol/L NaOH dropwise under mechanical stirring (800 rpm) for 2 h. After that, the resultant particles were separated magnetically and rinsed repeatedly with deionised water. Finally, the final product of approximately 2g of Fe_3O_4@CeO_2/$(OH)_x$ microparticles, was dried in an oven at 60 °C overnight.

2.3. Analytical techniques

A scanning electron microscope – energy dispersive spectrometer (SEM-EDS, Zeiss Neon 40ESB) was used to analyse the surface structure and morphology of Fe_3O_4@CeO_2/$(OH)_x$. A small amount of the synthesised particles was dispersed in deionised water by ultrasonication. One drop of this suspension was subsequently transferred onto an aluminium stub and air dried, prior to sputter coating with 3 nm of platinum. Finally, the prepared sample was analysed by SEM and EDS at acceleration voltages of 15 kV and 30 kV, respectively.

Phase identification was carried out on an X-ray diffractometer (XRD, Panalytical Empyrean) using Co Kα radiation. The powder sample was scanned by an applied current of 40 mA and a voltage of 45 kV with scattering angles of 5–90 °2θ.

Magnetic properties were determined on a superconducting quantum interference device (SQUID, Quantum Design MPMS 3) without any sample pretreatment at room temperature. The Brunauer-Emmett-Teller technique (BET, Micromeritics TriStar 3000) was used to study the specific surface area of Fe_3O_4@CeO_2/$(OH)_x$ with N_2 as the adsorbate, at −195.85 °C, while a Zetasizer Nano ZS (Malvern Instruments) was used to measure the surface zeta potentials of particles for estimating their approximate points of zero charge. Arsenic concentrations in solution was determined by using an inductively coupled plasma – optical emission spectrometer (ICP-OES, Agilent 735-ES).

2.4. Adsorption tests

Batch adsorption tests were carried out at 25 °C by agitating 0.05 g of Fe3O4@CeO_2/$(OH)_x$ with 50 mL of an arsenic-containing solution in a sealed flask held in a shaking bath. As(III)-only (100 mg/L) and As(V)-only (100 mg/L) solutions with pH values ranging from 7 to 11 were used to investigate the effect of pH on the adsorption performance of Fe3O4@CeO_2/$(OH)_x$. The contact time was set as 24 h. In the study of adsorption kinetics, the solutions containing 100 mg/L either As(III) or As(V) were treated with Fe3O4@CeO_2/$(OH)_x$ for 0.5 h, 1 h, 2 h, 4 h, 6 h, 12 h and 24 h, respectively, at pH 9. For the equilibrium isotherms, the adsorption tests were conducted for 24 h in the As(III)-only and As(V)-