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Removal of arsenic from alkaline process waters of gold cyanidation by use of γ-Fe_2O_3@ZrO_2 nanosorbents

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ABSTRACT

Arsenic is a problem in gold mining, as it can adversely affect operations and poses a health hazard. Although a number of technologies has been developed for its removal, none of them is effective under all conditions. Adsorption in particular, is a promising approach, but most methods have concentrated on the purification of water under neutral or acidic conditions. In gold mining and metallurgical processing waters, these adsorbents tend to be less effective. In this study, the removal of As(III) and As(V) from simulated mining process waters by use of composite nanoparticles is considered. The particles consisted of γ-Fe_2O_3 cores coated with ZrO_2. The maximum Langmuir adsorption capacities of As(III) and As(V) were 62.2 mg/g and 18.3 mg/g, respectively, at a pH of 9. In the alkaline process waters from a gold cyanide leaching plant, adsorption of 42.3 mg/g for As(III) and As(V) collectively, remained satisfactory, despite the presence of multiple competitive ions. Moreover, the particles retained their capacities well after multiple cycles of regeneration.

1. Introduction

As is well-known, arsenic is a poison posing a severe threat to human health. Arsenic constitutes approximately 0.00015% of the Earth's crust in the form of > 300 minerals, making it the 53rd most abundant element (Emsley, 2001). In general, the most common arsenic minerals in association with gold are sulfides, such as realgar (As_4S_4), orpiment (As_2S_3) and arsenopyrite (FeAsS).

Large quantities of arsenic are mobilized by mining and metallurgical activities, such as mineral excavations, ore transportation, smelting, refining and waste and wastewater disposal around mines (Kwon et al., 2017; Langsch et al., 2012; Sun et al., 2015) Apart from the well-documented health hazards of arsenic associated with gold mining (Asselin and Shaw, 2016; Seitkan and Redfern, 2016), the presence of arsenic can also adversely affect the extraction of gold.

More specifically, the deportment of arsenic in gold leaching by cyanidation can lead to a number of undesirable outcomes (Kyle et al., 2012; Kyle et al., 2011). Arsenic does not form any stable complex with cyanide, but under alkaline conditions present in gold cyanidation, arsenic sulfides are oxidised to arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) and the partially oxidised thioarsenite (AsS_3^{3-}) and thioarsenate (AsS_4^{3-}) in the presence of oxygen.

This increased oxygen consumption could significantly influence cyanidation, leading to retardation or prevention of gold dissolution (Marsden and House, 2006). Moreover, free cyanide ions might participate in further oxidation of thioarsenites and thioarsenates to form thiocyanates (Hedley and Tabachnick, 1950). These oxidation products attached to the surface of metallic gold hinder the interaction of gold with cyanide ions and oxygen. Arsenic could also affect gold adsorption onto activated carbon through competitive adsorption (Lorenzen et al., 1995).

Removal of arsenic from mining process waters is therefore a prime concern and a number of technologies have been developed for this purpose. Precipitation with trivalent iron salts and lime is most commonly applied in mining effluents for arsenic removal (e.g. Hamberg et al., 2016). However, the immobilization of arsenic removed in this way may not be guaranteed (Pantuzzo and Ciminelli, 2010). Other methods, such as coagulation and coprecipitation, ion exchange and adsorption are also used, but none of these technologies is effective under all conditions.

Adsorption is a promising approach for removal of arsenic from water. Several adsorbents have been proposed for arsenical removal, including activated carbon from pyrolytic tyre char (Mouzourakis et al., 2017), mesoporous alumina (Han et al., 2013), biochar supported by zerovalent iron (Wang et al., 2017), Fe_2O_3 nanoparticles (Luther et al., 2012), as well as titania functionalised magnetic adsorbents (Feng et al., 2017a, 2017b).

Among various adsorbents, zirconia, an inexpensive, nontoxic,

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chemically unreactive and water-insoluble inorganic material, is widely recognized as a strong adsorbent for arsenic species (Xu et al., 2013; Zheng et al., 2012a; Zheng et al., 2012b), particularly As(III) species (Cui et al., 2012; Luo et al., 2013). The adsorption mechanism of arsenic species onto zirconium oxide has been investigated by several research groups. Cui et al. (2012), Ma et al. (2011) and Zheng et al. (2009) have studied zirconium-based arsenic adsorbents with Fourier-transform infrared (FTIR) spectroscopy before and after arsenic adsorption.

Despite different forms of the adsorbents, the FTIR spectra showed similar results, i.e. hydroxyl groups ($-$OH) were present on the surface of the adsorbents before arsenic species were loaded and the corresponding peak shifted after arsenic adsorption, indicating the involvement of the hydroxyl groups during arsenic adsorption. Moreover, an As—O bond associated peak appeared after arsenic uptake. In addition, X-ray photoelectron spectroscopy (XPS) analyses on their adsorbents before and after arsenic adsorption suggested that the adsorption of arsenic species onto zirconium-based adsorbents is derived from the formation of inner-sphere complexes.

Most of these studies on zirconium-based arsenic adsorbents have focused on drinking water at neutral or slightly acidic pH values. No reports have been found to deal with mining process waters, which tend to be strongly alkaline. In this work, a functionalised magnetic nanosorbent (γ-Fe_2O_3@ZrO_2) was synthesised and its use in the removal of arsenic from process waters of gold cyanidation was evaluated for gold mines in Western Australia.

Owing to the alkaline environment of process water from gold cyanide leaching, the adsorption tests on the effect of pH in this study were conducted within a pH range of 7 to 11, while adsorption kinetics and isotherms were carried out at pH 9, which is typical of process water samples from local mines.

Moreover, a simulated solution with high ionic strength and complex chemistry was used to validate the adsorption performance of γ-Fe_2O_3@ZrO_2. Finally, experimental results from adsorption and desorption tests indicate that γ-Fe_2O_3@ZrO_2 is a suitable adsorbent for arsenic species under alkaline conditions. As a consequence, it has potential application in the gold industry for the treatment of arsenic-bearing process waters.

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 ($Na_2HAsO_4{\cdot}7H_2O$), respectively, at a concentration of 1 g/L. HCl and NaOH solutions (both 0.1 mol/L) were used for pH adjustment. All solutions were prepared with deionised water (resistivity $>$ 18 MΩ·cm at 25 °C).

2.2. Preparation of γ-Fe_2O_3@ZrO_2 nanosorbent

Fig. 1 schematically illustrates the theoretical process of the ZrO_2 coating onto the γ-Fe_2O_3 nanoparticles based on a previous study with a few modifications (Peng et al., 2015). Specifically, 1 g of γ-Fe_2O_3 ($<$ 200 nm) nanoparticles were ultrasonically dispersed in a solution containing 400 mL deionised water, 300 mL ethanol and 10 mL ammonia water (28%) to form a homogenised suspension. Next, an aqueous solution of $ZrOCl_2{\cdot}8H_2O$ (1.5 g dissolved in 10 mL of deionised water) was added dropwise for 10 min and then the mixture was stirred mechanically at 800 rpm for 6 h. After that, the product was collected by a hand-held magnet and rinsed repeatedly with ethanol and deionised water. The resultant particles were dried in an oven at 60 °C overnight. The final weight of the nanosorbents was approximately 1.7 g, making the molar ratio of Fe to Zr around 2.2:1.

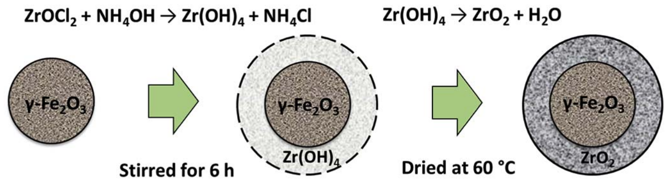

Fig. 1. Schematic illustration for the synthesis of γ-Fe_2O_3@ZrO_2.

2.3. Analytical techniques

A scanning electron microscope - energy dispersive spectrometer (SEM-EDS, Zeiss Neon 40ESB) was employed to visualise the morphology and surface structure of γ-Fe_2O_3@ZrO_2. One drop of the nanoparticles suspension was put on an aluminium stub and air dried, before the sputter coating with 3 nm of platinum. The prepared sample was then analysed by SEM and its attached EDS at acceleration voltages of 5 kV and 30 kV, respectively. X-ray diffraction (XRD, Panalytical Empyrean) was used to analyse its phase composition qualitatively. The powder sample was scanned by an applied current of 40 mA and a voltage of 45 kV with Co Kα radiation. Magnetic measurements were conducted on a superconducting quantum interference device (SQUID, Quantum Design MPMS 3) without any sample pretreatment at room temperature. The Brunauer-Emmett-Teller method (BET, Micromeritics TriStar 3000) was used for determining the specific surface area of γ-Fe_2O_3@ZrO_2 with N_2 as the adsorbate, at low operating temperature. Surface zeta potentials of the particles were measured via Zetasizer Nano ZS (Malvern Instruments) for approximate determination of the points of zero charge. The concentration of arsenic in solutions was analysed by use of 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 γ-Fe_2O_3@ZrO_2 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 γ-Fe_2O_3@ZrO_2. 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 γ-Fe_2O_3@ZrO_2 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)-only solutions at pH 9 with different initial arsenic concentrations.

In the competition adsorption tests, a simulated gold cyanidation process water spiked with arsenite and arsenate in a 1:1 molar ratio (As(III)/As(V)) was used. The total arsenic in this solution was 83.9 mg/L. The pH of the simulated solution was approximately 9 without any adjustment. The adsorption time was 24 h.

After adsorption, the adsorbents were separated magnetically and the remaining arsenic concentration was determined by ICP-OES.

2.5. Regeneration and reuse

Five consecutive adsorption-desorption cycles were conducted in duplicate to investigate the reusability of γ-Fe_2O_3@ZrO_2. The adsorption tests were carried out in the simulated process waters of gold cyanidation containing both As(III) and As(V) until equilibrium was attained. After adsorption, the magnetically separated nanosorbents were gently rinsed with deionised water for several times, then redispersed in 50 mL of regenerant, i.e. 1.0 mol/L NaOH solution, and shaken for 2 h. Prior to the next adsorption cycle, the treated particles were washed