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Removal of nickel ions from aqueous solutions by manganese dioxide derived from groundwater treatment sludge

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ABSTRACT

In this study, manganese dioxide (MnO_2) derived from groundwater treatment sludge was used in the adsorption of nickel (Ni(II)) ions from aqueous solutions. The synthetic MnO_2 was prepared via permanganate reduction using manganese extracted from the sludge by reductive acid leaching and hydroxide precipitation. Scanning electron microscopy images showed aggregated micron-sized MnO_2 particles. Fourier transform infrared analysis of MnO_2 revealed functional groups at 3,396 cm^{-1}, 1,630 cm^{-1}, 1,427 cm^{-1} and 468 cm^{-1} bands. Zeta potential measurements at the pH range of 2–8 confirmed the net negative surface charge of MnO_2 particles. Moreover, Ni(II) adsorption by MnO_2 was best described by the Langmuir isotherm model, as indicated by the high values for the coefficients of determination ($R^2 > 0.9703$). The separation factor (R_L) for the range of pH values and initial Ni(II) concentrations considered in this study indicated that Ni(II) adsorption by MnO_2 was favorable. The kinetic data of Ni(II) adsorption by MnO_2 at pH 6.5 and initial Ni(II) concentrations from 10 to 200 mg L^{-1} conformed to the pseudo-second order adsorption kinetic model, with $R^2 > 0.9997$. Chemisorption occurred through the complexation of Ni(II) ions with available MnO_2 functional groups. The thermodynamic study at temperatures of 298.15, 308.15 and 318.15 K revealed that Ni(II) adsorption by MnO_2 was spontaneous and thermodynamically favorable for initial Ni(II) concentrations ranging from 50 to 200 mg L^{-1}. Overall, Ni(II) adsorption by MnO_2 was endothermic, as indicated by the positive ΔH° values. In addition, MnO_2 had good affinity towards the Ni(II) ions, as shown by the positive ΔS° values at all Ni(II) concentrations. Simple cost analysis revealed that the MnO_2 production from groundwater sludge was economically viable and may be scaled up for commercial applications.

1. Introduction

The electroplating industry is one of the significant contributors of water pollution due to the heavy metal species in its high volume rinse water (Almazán-Ruiz et al., 2015). Nickel is one of the toxic and hazardous heavy metals found in rinse waters at concentrations ranging from 900 to 1,583 ppm (Sulaiman and Othman, 2017). Its removal from contaminated waters is of extreme importance in order to prevent nickel-induced diseases and abnormalities, such as birth defects, embolism, chronic bronchitis, anemia, diarrhea, encephalopathy, hepatitis, lung and kidney damage, gastrointestinal distress, pulmonary fibrosis, renal edema, skin dermatitis, and central nervous system dysfunction (Futalan et al., 2011; Zhang and Wang, 2015). Nickel and other heavy metals can be removed from contaminated waters by chemical separation, membrane processes, electro-chemical treatment, electro-deposition and adsorption (Ghaee et al., 2012). However, most of these metal separation strategies are expensive and ineffective in treating wastewaters with low concentrations of heavy metal pollutants (Mangaleshwaran et al., 2015). In such cases, adsorption has several advantages, including lower cost, easier operation, and higher

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efficiency compared to other technologies (Xu et al., 2016). Some of the adsorbents used in nickel removal from wastewaters include activated carbon and biochar (Higashikawa et al., 2016; Pap et al., 2017), non-conventional low-cost materials, nanomaterials, composites and nanocomposites (Raval et al., 2016).

Manganese dioxide has high potential for heavy metals removal from aqueous media via adsorption. The utilization of manganese dioxide, or compounds containing manganese dioxide, as heavy metal adsorbent has been explored in previous studies. For example, δ-MnO_2 with magnetic properties has been used for the removal of Cd(II), Ni(II) and Pb(II) ions from aqueous solution (Calderon Rosas et al., 2010); nanosized hydrous manganese dioxide (HMO) impregnated onto a porous polystyrene cation exchanger resin for enhanced lead removal (Su et al., 2009); manganese oxide-coated sand (MOCS) for removing Cu(II) and Pb(II) (Han et al., 2006); hydrous manganese dioxide-poly (N-hydroxymethyl acrylamide/2-hydroxyethyl acrylate) (HMO-P(HMAm/HEA)) hydrogel to effectively remove Pb(II), Cu(II), Cd(II) and Ni(II) from water (Zhu and Li, 2015); manganese dioxide for sorption of As(III) and As(V) (Ajith et al., 2013), and α- and δ-phase manganese dioxide nanoadsorbents for arsenate adsorption (Singh et al., 2010).

Manganese dioxide can be obtained from various sources. Some types are naturally-occurring and can be found in marine sediments (Schippers and Jorgensen, 2001), or extracted from mine ores (Devi et al., 2000). Other types are synthetic and can be prepared as colloidal particles (Altaf et al., 2009), or doped on other materials such as silica gel (Varma et al., 1997) or titanium dioxide (Villaseñor et al., 2002). In the studies conducted on the synthesis of manganese dioxide, the manganese was obtained from commercially-available reagents, such as potassium permanganate and manganese sulfate. Among these are water-soluble colloidal MnO_2 (Perez-Benito and Arias, 1992) and in-situ formed MnO_2 (Qin et al., 2011). There are, however, other sources of manganese that have not been explored. In particular, groundwater treatment sludge contains significant amount of manganese that may be recovered and used for other purposes such as pollution prevention.

Recovery of manganese from groundwater treatment sludge can add value to the solid waste material. This insoluble product of groundwater oxidation contains high concentrations of manganese and iron precipitates, and are formed by aeration or by application of chemical oxidants, such as chlorine, hypochlorite, chlorine dioxide, ozone or potassium permanganate (Kan et al., 2012). Current disposal options for this solid waste are not sustainable and do not consider extraction of these heavy metal components (Razali et al., 2007; Vaezi and Batebi, 2001).

Reductive leaching, which makes use of strong acid and reducing agent, is a potential process that can be applied to the groundwater treatment sludge to recover its manganese content. This process has already been explored in the extraction of manganese from mine ores (Nayl et al., 2011). Various acids and reductants have been considered in previous studies, such as sulfuric acid and sawdust (Hariprasad et al., 2007), nitric acid and molasses (Lasheen et al., 2009), sulfuric acid and methanol (Momade and Momade, 1999), sulfuric acid and cane molasses (Su et al., 2008), sulfuric acid and glucose (Trifoni et al., 2001), and sulfuric acid and hydrogen peroxide (Jiang et al., 2003).

In this study, manganese dioxide was synthesized using manganese derived from groundwater treatment sludge. This process involved reductive leaching of the manganese from the sludge using sulfuric acid and hydrogen peroxide, purification of the manganese sulfate by precipitation of the iron content, and synthesis of the manganese dioxide by permanganate reduction. To date, groundwater treatment sludge has not yet been considered as secondary source of manganese, and no study has reported on the application of reductive leaching and hydroxide precipitation processes for the recovery of the manganese from the sludge. The purpose of the present research is to investigate the potential of groundwater treatment sludge as source of manganese for the synthesis of manganese dioxide for the specific application of nickel removal from contaminated solutions.

2. Materials and methods

2.1. Chemicals

All solutions were prepared using analytical grade chemicals. Deionized water (18.2 MΩ-cm) for the preparation of solutions was obtained with Purelab Ultra by ELGA LabWater (UK). EMSURE® sulfuric acid from Merck (Germany), with a concentration of 95–97%, and hydrogen peroxide from Shimakyu's Pure Chemicals (Osaka, Japan), with a concentration of 35%, were used to prepare the solutions required in the reductive leaching. Riedel-de Haën potassium hydroxide pellets from Sigma-Aldrich (Czech Republic) with 85% purity was used to prepare the solutions required in the precipitation of metals for the recovery of manganese. Potassium permanganate from J.T. Baker (USA) with 99% purity was used in the synthesis of manganese dioxide. Merck Uvasol® Potassium Bromide for IR spectroscopy (Darmstadt, Germany) was used for the FTIR spectroscopy analysis of the solid products after manganese dioxide synthesis. EMSURE® fuming hydrochloric acid, from Merck (Germany), with a concentration of 37%, and Riedel-de Haën potassium hydroxide pellets from Sigma-Aldrich (Czech Republic), with 85% purity, were used to prepare the solutions required in the pH adjustment for the analysis of the zeta potential of the MnO_2 sample, as well as in the adsorption experiments. Nickel (II) nitrate from Ferak. Laborat GmbH (Germany), with 97% purity, was used to prepare the solutions for the adsorption experiments.

2.2. Manganese dioxide synthesis

The groundwater treatment sludge used in the manganese dioxide synthesis was obtained from Changhua Water Treatment Plant located in central Taiwan. The sludge was dried in a Memmert UFE 400 laboratory oven (Germany) for 24 h at 105 °C to remove the moisture. Reductive leaching experiments were carried out in a 125-mL glass stoppered Duran Erlenmeyer flask placed on a PC-420D stirring hot plate by Corning, Inc. (USA). Dried sludge (3 g) was leached using 50 mL of 0.3 mol L^{-1} sulfuric acid and 5 mL of 0.8 mol L^{-1} hydrogen peroxide. The leaching process was conducted at 5 min leaching time, 150 rpm agitation rate and 25 °C operating temperature. Temperature adjustment of the aqueous sulfuric acid solution was first carried out in the flask. The dried sludge sample was added to the agitated aqueous sulfuric acid solution at the required temperature. Leaching started after hydrogen peroxide was added to the solution. After the leaching process, the slurry was filtered using Whatman 40 ashless filter paper from GE Healthcare (UK) with nominal particle retention of 8 μm. Manganese recovery was carried out in a 50-mL Pyrex beaker by precipitating the iron in the leachate using 0.4 mol L^{-1} KOH. The KOH solution was added dropwise into the agitated leachate until the pH 4.0 was achieved. EZ-DO 6011 waterproof pH tester by G&B (Taiwan) was used to measure the pH of solutions. At the end of the precipitation process, the slurry was filtered using Whatman 40. The filtrate from the precipitation process was stirred continuously while adding stoichiometric amount of $KMnO_4$ solution drop-wise to produce manganese dioxide, according to Eq. (1) (Qin et al.,