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Magnetite modified with amine polymer to adsorb indium ions

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ABSTRACT

Indium is one of the contaminants of the optoelectronics industry, and adsorption is a potential treatment method for this pollutant. A magnetic adsorbent manufactured from magnetite (Fe_3O_4) can be easily recovered from treated water by magnetic force without requiring further downstream treatment. In this research, the surface of magnetite is modified with oleic acid, methyl methacrylate and ethylenediamine (EDA/MMA/OA/Fe_3O_4). A magnetic adsorbent (EDA/MMA/OA/Fe_3O_4) made by magnetite modified with oleic acid, methyl methacrylate and ethylenediamine was used to adsorb indium ions solution in a batch system. The indium ions adsorption behavior by EDA/MMA/OA/Fe_3O_4 was in good agreement with both the Langmuir and Freundlich adsorption isotherm. The maximum adsorption capacity (q_m) and Gibbs free energy of indium ions at 298 K was 54.18 mg g^{-1} and −17.94 kJ mol^{-1}, respectively. A pseudo-second-order model could best describe the adsorption kinetics, and the derived activation energy was 5.96 kJ mol^{-1}. The optimal condition of indium ions desorption from EDA/MMA/OA/Fe_3O_4 was provided by 0.01 M HNO_3 in aqueous solution.

1. Introduction

More than one-half of indium consumption in the world is for indium-tin oxide (ITO) coatings [1]. Indium has numerous industrial applications, such as the manufacture of liquid crystal displays, solar cell, semiconductor devices, a low-temperature solder and an infrared photodetector [2,3]. TFT-LCD manufacturing is one of the major industries in Taiwan; the wastewater from the etching process typically contains a concentration of indium metal [1]. Indium and its compound are suspected to be carcinogenic to human beings, damaging the heart, kidney and liver [4]. Therefore, removing indium ions is very necessary before discharging wastewater into water bodies.

Various techniques such as chemical precipitation [5], solvent extraction techniques [6,7], electrochemical analysis techniques [1,8], ion exchange [9] and adsorption [10,11] have been employed for the removal of indium ions from wastewater. Among these available approaches, adsorption methods have proven to be more promising since indium ions are recovered in the form of highly pure indium ions during the regeneration of the adsorbent. In addition, after desorption of indium ions, the adsorbent can be reused for the removal and recovery of indium ions.

An innovative technology that has gained increasing attention involves solid-liquid phase separation and employs adsorbents with magnetic properties. Magnetic separation is now widely used in the fields of medicine, diagnostics, molecular biology, bioinorganic chemistry and catalysis [12]. Furthermore, the method of magnetic separation is beneficial to the environment because it does not produce contaminants such as flocculants [13]. Conventional magnetic adsorbents are generally commercial carriers made of magnetite particles modified with polymer [14] or organosilane [15], in which suitable functional groups are present on the adsorbent surface. Most polymers with surface functional groups have been reported in the past few years, including chitosan, methacrylic acid, acrylamide and 1-hydroxy-4-(prop-2-enyloxy)-9,10-anthraquinone [16,17]. However, there are few papers studying the preparation of ethylenediamine-modified magnetic particles to remove indium ions from waste water. In this study, magnetic adsorbents (EDA/MMA/OA/Fe_3O_4) made by magnetite modified with oleic acid, methyl methacrylate and ethylenediamine were used to adsorb indium ions solution in a batch system. Several techniques, such as Fourier transform infrared spectroscopy (FTIR), vibrating sample magnetometer (VSM) X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were used in the characterization of the materials. In addition, the pH effect, adsorption isotherm and adsorption kinetic of this magnetic adsorbent were examined using indium ions as the model contaminant. This will open up a potential broad application in wastewater treatment.

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2. Materials and methods

2.1. Materials

Ferric chloride ($FeCl_3$) and ferrous sulfate7-hydrous ($FeSO_4.7H_2O$) were purchased from Ferak (Berlin, Germany). Ammonium hydroxide (NH_4OH), Alcohol (C_2H_5OH) and oleic acid (OA, $CH_3(CH_2)_7CH.CH(CH_2)_7COOH$) were purchased from a Pharmaceutical Company in Japan. Acetonitrile (CH_3CN) was purchased from J.T. Backer (USA). Methyl methacrylate (MMA, $C_5H_8O_2$), 2,2-azodiisobutyronitrile (AIBN, $C_8H_{12}N_4$), ethylene dimethacrylate (EDMA, $C_{10}H_{14}O_4$), polyvinyl pyrrolidone (PVP, $(C_6H_9NO)_n$) and ethylenediamine (EDA, $C_2H_8N_2$) were obtained from Acros Organics (Belgium, USA). Indium (III) nitrate hydrate ($In(NO_3)_3.XH_2O$) was purchased from Sigma-Aldrich (USA). All the other chemicals were of a reagent grade and were purchased from several suppliers.

2.2. Instruments

Amine groups anchored on the support surface could be determined by a UV-VIS colorimetric method (UV-1800, Shimadzu, Japan). The specific surface area and pore diameter of the adsorbents were measured by the BET method using a particle size analyzer (ASAP 2000C, Micromeritics, USA). The functional groups of the synthesized adsorbents were confirmed using an FTIR spectrometer (Spectrum 100, Perkin Elmer, USA). The magnetic behavior was analyzed using a vibrating sample magnetometer (VSM, Lake Shore 7407, Lake Shore, USA). The crystal lattice structure of the material was determined by XRD (Theta Probe, Thermo Scientific, UK). The polymer coverage of the magnetic polymer particles was measured using a Thermogravimetric Analyzer (TGA, TA Instruments Q-500, Thermo, England). The concentrations of indium ions were determined by standard spectrophotometric methods using a polarized zeeman atomic absorption spectrophotometer (Z-2000, Hitachi, Japan).

2.3. Synthesis of adsorbents

In this study, magnetic polymer particles (MMA/OA/Fe_3O_4) were synthesized by using methyl methacrylate (MMA, molecule structure is shown in Fig. 1) as the functional monomer, ethylene glycol dimethacrylate (EDGMA) as the cross-linking agent, polyvinyl pyrrolidone (PVP) as the stabilizer, 2,2-azodiisobutyronitrile (AIBN) as the radical initiator and ethanol as the solvent. A mixture of $FeSO_4.7H_2O$ and $FeCl_3$ was dissolved in distilled water in a 1 L beaker with stirring under nitrogen atmosphere. An appropriate amount of ammonia water was added to the aqueous solution to control the pH at 8.8 under mechanical stirring. An appropriate amount of H_2SO_4 was added in the aqueous solution at 85 °C to adjust the pH to 6.3. Oleic acid (OA) was then added slowly via a burette to the magnetite suspension solution due to avoid the oxidation of magnetite, and the magnetite covered with oleic acid (Fe_3O_4/OA) was maintained at 85 °C for 30 min under mechanical stirring [18]. The prepared OA/Fe_3O_4 was then dried at 105 °C for 2 days and stored in desiccators until further use in the following experiments. The previously synthesized OA/Fe_3O_4 (25.0 g) was suspended in 500 mL of ethanol with a 60.0 mmol solution of ethylene glycol dimethacrylate, and then, 1.2 g of polyvinyl pyrrolidone was added to prepare the prepolymerization solution. 2,2-azodiisobutyronitrile was added to the prepolymerization solution with a nitrogen purge gas at 70 °C for 30 min. After polymerization, the MMA/OA/Fe_3O_4 was separated by applying an external magnetic field and then vacuum dried for 2–3 days. However, MMA/OA/Fe_3O_4 modified with amine functional groups (EDA/MMA/OA/Fe_3O_4) was synthesized by using ethylenediamine (EDA) and acetonitrile as a solvent (as shown in Fig. 2). 40 g of MMA/OA/Fe_3O_4 particles was placed in 500 mL of acetonitrile in a four-necked round-bottomed flask, and then, 150 mL of ethylenediamine (EDA) was added with a nitrogen purge gas at 80 °C for 12 h. EDA/MMA/OA/Fe_3O_4 was separated by applying an external magnetic field and vacuum dried for 2–3 days after washing with distilled water.

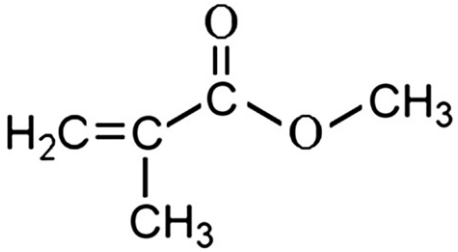

Fig. 1. Molecule structure of oleic acid (OA).

2.4. Adsorption experiments

Adsorptions of indium ions from aqueous solutions were investigated in batch experiments. Effects of the pH (1.0–6.0), kinetic experiments (0–90 min), adsorption isotherm (initial concentration 400–800 mg L^{-1}) and thermodynamic studies (283–313 K) on adsorption were studied. All the adsorption isotherm experiments were carried out at 298 K, in which the pH was maintained at a constant value during the whole reaction time. The adsorbent concentration was kept constant at 0.5 g in a 50 mL solution, and the equilibrium time was considered as 24 h [19]. After adsorption reached the equilibrium, the adsorbent was separated via an external magnetic field. The concentrations of indium ions in the aqueous solution were analyzed using an atomic absorption spectrophotometer.

2.5. Desorption experiments

The experiments for desorption efficiency were carried out with HNO_3 solutions in the concentration range of 0.005–2 M. A 1.0 g amount of the EDA/MMA/OA/Fe_3O_4 adsorbent adsorbed with indium ions was placed into 100 mL of a HNO_3 solution with thermostatic shaking, and desorption was allowed for a time period up to 24 h. The desorption efficiency (DE) was determined from the following equation: $DE = \frac{C \times V}{q \times m} \times 100\%$, where C(mg L^{-1}) is the concentration of indium ions in the desorption solution, V is the volume of the desorption solution, q (mg g^{-1}) is the amount of indium ions adsorbed on the adsorbents before desorption experiment and m (g) is the amount of the adsorbent used in the desorption experiments.

3. Results and discussion

3.1. Characterization of magnetic adsorbent

3.1.1. FT-IR analysis and UV absorbance

The FTIR spectra of Fe_3O_4, OA/Fe_3O_4, the prepared polymer-magnetic adsorbent (MMA/OA/Fe_3O_4) and the prepared polymer-magnetic modified with amine groups (EDA/MMA/OA/Fe_3O_4) are shown in Fig. 3. The results exhibited basic characteristic peaks of these three adsorbents at about 576 cm^{-1} (Fe-O vibration), which were attributed to the presence of Fe-OH in Fe_3O_4 [15]. In the spectrum of OA/Fe_3O_4, the peak at 3300 cm^{-1} was attributed to the O-H stretching of the carboxylic acid group of oleic acid. The peaks at 1728 and 1259 cm^{-1} were attributed to carboxyl groups (C = O and C-O) of MMA/OA/Fe_3O_4 and EDA/MMA/OA/Fe_3O_4. The results confirmed that methyl methacrylate was successfully coated on the surface of OA/Fe_3O_4. On the other hand, OA/Fe_3O_4, MMA/OA/Fe_3O_4 and EDA/MMA/OA/Fe_3O_4 showed C-H bands at 2986, 1523 and 1425 cm^{-1}. These bands are known to be the characteristic bands of CH_2 groups