Journal of Hazardous Materials 235–236 (2012) 116–122

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Kinetics and thermodynamics of adsorption for Cd on green manufactured nano-particles

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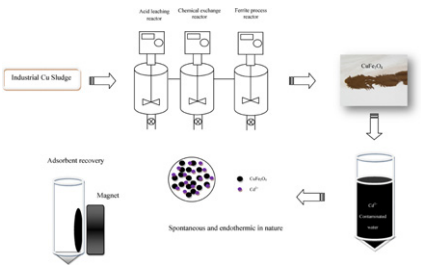
HIGHLIGHTS

- A novel technology for fabricating $CuFe_2O_4$ was developed from industrial Cu sludge.
- The manufactured $CuFe_2O_4$ was effective in removing Cd^{2+} from contaminated water.
- The adsorbent can be rapidly recovered by a magnet because of its soft magnetism.
- Increasing pH has positive effects on the Cd^{2+} removal in the pH ranges of 2–6.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 April 2012
Received in revised form 12 July 2012
Accepted 14 July 2012
Available online 20 July 2012

Keywords:
Magnetic nano-particles
$CuFe_2O_4$
Industrial sludge
Cd adsorption
Kinetics and thermodynamics

ABSTRACT

Magnetic nano-particles $CuFe_2O_4$ were successful manufactured from industrial sludge by combination of acid leaching, chemical exchange, and ferrite process. For the first time these recycled nano-particles were used as adsorbent to investigate the kinetics and thermodynamics for adsorption of Cd in aqueous solutions. These experimental results showed that Cd^{2+} adsorption efficiency increased from 0.85 to 99.9% when pH increased from 2 to 6. The maximum adsorption capacity of Cd^{2+} was found to be 17.54 mg g^{-1} under the conditions at pH 6.0, contact time 30 min, and temperature 318 K. The pseudo-second-order kinetic model provides the best correlation with the experimental data compared to the pseudo-first-order model. The Langmuir model yields a better fitting than the Freundlich model for Cd^{2+} adsorption on $CuFe_2O_4$ nano-particles under investigated temperatures. The thermodynamic constants of the adsorption process were evaluated, ΔG°, ΔH° and ΔS° is −6.05 kJ mol^{-1} (at 318 K), 0.71 kJ mol^{-1}, and 4.53 J mol^{-1} K^{-1}, respectively. These results imply that Cd^{2+} adsorption onto $CuFe_2O_4$ is feasible, spontaneous and endothermic in nature.

1. Introduction

Heavy metals have many industrial applications due to their technological importance [1]. However, they are often detected in industrial wastewaters owing to the improper treatment technologies. Presence of metal ions in natural waters is of special concern as they can accumulate in different components of environments, representing a serious threat to human health concerns [2]. The removal of heavy metals from wastewaters thus becomes an important issue in industrial plants all over the world.

Cadmium (Cd) is one of the most toxic pollutants in aquatic systems. Due to its non-degradable property, it cannot be removed easily from water systems by self-purification and could pose a serious threat to environment and human health [3]. The long period accumulation (30 years) of Cd through food chain relationships can lead to a serious osteoporosis-like bone disease known to the Japanese as “itai-itai byo” or “ouch-ouch disease” [4]. The Cd concentration in un-contaminated freshwater is ranged between

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0304-3894/$ – see front matter.
http://dx.doi.org/10.1016/j.jhazmat.2012.07.030

10 and 100 ng L^{-1} in natural waters [5]. However, much higher Cd (μg L^{-1}–mg L^{-1} level) may be found in other aquatic systems because of anthropogenic influences, such as metal surface treatment, electroplating, pigments, and mining activities. Thus, an effective and economic technology for Cd removal from water systems has become an important issue for both human health and aquatic ecosystems.

Conventional technologies of Cd removal from aqueous solutions usually involve physico-chemical treatments such as precipitation, adsorption, membrane filtration and ion exchange [6–9]. Some problems associated with these technologies have limited their industrial applications. For instance, the precipitation methods generate a large amount of sludge, causing an increase in treatment cost. The membrane system has high treatment cost owing to frequent change of membranes. Adsorption is the most popular method among the above-mentioned technologies [10–12]. It has been applied as an economic and effective technology for water purification in industrial plants. Suitable selection of adsorbent is one of the key points for developing a proper adsorption technology as specific type of adsorbent may play a dominant role in the adsorption process.

This study demonstrates the Cd removal efficiency using the magnetic nano-particles recycled from the sludge in printed circuit board (PCB) industry. The nano-particles, magnetic Cu–Fe oxide, contain Cu^{2+} and Fe^{3+} in the spinel structure. Our earlier investigation has recycled successfully of copper powder from PCB sludge by combination of acid leaching and chemical exchange [13]. After these combinations of technologies, ferrite process has been conducted not only to make sure the supernatant but also the sludge can meet the environmental regulations. The sludge generated from ferrite process hence is regarded as a general industrial waste due to its high stability in natural environments. If there is no other resourced use for the sludge, it could be disposed directly to the sanitary landfills.

A series of batch experiments were conducted to evaluate the capability of the manufactured nano-particles for Cd removal in aqueous solutions under various conditions. The adsorbent characterization including particle size, crystalline phases, surface area, and saturation magnetization were studied in detailed. Further kinetics and thermodynamics of adsorption of Cd on magnetic nano-particles were also investigated. The information obtained in this work shows great potential for developing a cost-effective adsorbent for immobilizing Cd using magnetic nano-particles.

2. Materials and methods

2.1. Manufacturing of magnetic nano-particles

A green low-cost adsorbent, $CuFe_2O_4$, was manufactured from PCB sludge by combination of acid leaching, chemical exchange, and ferrite process. Our previous work shows the detailed procedure for the preparation of $CuFe_2O_4$ [13]. Briefly, acid leaching was conducted using 500 g industrial sludge and 10 L diluted sulfuric acid was added for extracting copper from solids. Fe powder was used as sacrificed metal to substitute Cu^{2+} in the liquid during chemical exchange. To ensure the supernatant qualities fulfill the effluent standards, ferrite process was performed after chemical exchange. A green low-cost adsorbent, $CuFe_2O_4$, was thus manufactured after the ferrite process. The main corresponding reaction of acid leaching, chemical exchange, and ferrite process is described as Eqs. (1)–(3), respectively.

$$\text{Cu-sludge} + H_2SO_4 \rightarrow Cu^{2+} + \text{sludge} \quad (1)$$

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \quad (2)$$

$$Cu^{2+} + 2Fe^{2+} + 6OH^- + 1/2O_2 \rightarrow CuFe_2O_4 + 3H_2O \quad (3)$$

The manufactured green low-cost adsorbent was collected using a magnetic separation method by taking advantage of its magnetism. The $CuFe_2O_4$ was then washed with de-ionized water several times until the solution pH reached near 7. The solids were then dried at 323 K for 24 h in an oven and stored for further tests.

2.2. Characterization of the adsorbent

The physical/chemical characteristics of the adsorbent used in this study were elucidated using standard procedures. The crystal phases were determined by XRD (D8 Advance, Bruker, Germany) using graphite monochromatic copper radiation over the 2θ range 20–80°. The Brunauer–Emmett–Teller (BET) surface areas and the porosity of the adsorbents were obtained from nitrogen adsorption isotherms at 77 K using an ASAP 2010 analyzer (Micromeritics, USA). The surface morphology and particle size were examined by scanning electron microscopy (SEM, JSM-6330, Japan). The saturation magnetization of the nano-particles was measured using a Superconducting Quantum Interference Device (MPMS-XL7, Quantum Design, USA) at 298 ± 1 K.

2.3. Batch adsorption procedure

Batch adsorption was conducted in order to evaluate the process and the states of equilibrium of Cd mobilization. The Cd solution was prepared by dilution of the stock standard solution (Cd solution 1000 mg L^{-1}). All batch adsorption experiments were performed according to the following procedures: 10 mL Cd solution and fixed amount of nano-particles were poured into 15 mL centrifuge tubes. The centrifuge tubes were then put on the shaft of a rotary shaker after the caps were tightened. The rotating speed was set at 30 rpm and the temperature was controlled at 298 ± 1 K. The metal uptake q_t (mg g^{-1}) was determined by the following equation [14]:

$$q_t = \frac{C_o - C_t}{m_{ads}} \quad (4)$$

where C_o and C_t are the metal concentration in liquid phase at the initial and at time t (mg L^{-1}), respectively; m_{ads} is the adsorbent amount remaining in the solution (g L^{-1}).

The pH of solutions were controlled at 2.0 ± 0.1, 3.0 ± 0.1, 4.0 ± 0.1, 5.0 ± 0.1, and 6.0 ± 0.1 by adding dilute NaOH or HNO_3 solutions. The solid and liquid phases were magnetically separated using a magnet with 4000 Gauss. The Cd concentrations in the filtrate were determined by ICP-OES (iCAP 6500, Germany). The adsorbed amount of Cd on the nano-particles was determined using the differences between the initial and the equilibrium Cd concentrations in solutions.

2.4. Magnetic separation

Compared to the traditional solid–liquid separation method, such as centrifugal technique, magnetic separation enjoys advantages of effectiveness and rapidness. The magnetic behavior of our nano-particles was measured at 298 ± 1 K by a Superconducting Quantum Interference Device (SQUID, MPMS-XL7, Quantum Design, USA). The saturation magnetization was found to be of 62.52 emu g^{-1}. No remanence was detected in these samples, confirmed that the manufactured nano-particles are superparamagnetic. Fig. 1 shows that these magnetic nano-particles could be separated toward the magnet within 30 s. More than 98.7% nano-particles can be recovered from solution by a strong magnet (Table S1). When the external magnetic field was removed, the nano-particles could be well dispersed again by physical shaking.