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Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles

Jing Hu, Guohua Chen, Irene M.C. Lo*

Environmental Engineering Program, School of Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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Abstract

Hexavalent chromium existing in the effluent is a major concern for the metal-processing plant. In this study, a new method combining nanoparticle adsorption and magnetic separation was developed for the removal and recovery of Cr(VI) from wastewater. The nanoscale maghemite was synthesized, characterized, and evaluated as adsorbents of Cr(VI). Various factors influencing the adsorption of Cr(VI), e.g., pH, temperature, initial concentration, and coexisting common ions were studied. Adsorption reached equilibrium within 15 min and was independent of initial Cr concentration. The maximum adsorption occurred at pH 2.5. The adsorption data were analyzed and fitted well by Freundlich isotherm. Cr(VI) adsorption capacity of maghemite nanoparticles was compared favorably with other adsorbents like activated carbon and clay. Competition from common coexisting ions such as Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, NO_3^-, and Cl^- was ignorable, which illustrated the selective adsorption of Cr(VI) from wastewater. Regeneration studies verified that the maghemite nanoparticles, which underwent six successive adsorption–desorption processes, still retained the original metal removal capacity. In addition, the adsorption mechanisms were investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopic techniques.

Keywords: Adsorption; Chromium; Common ion effect; Desorption; Freundlich isotherm

1. Introduction

Hexavalent chromium species, Cr(VI), are highly toxic agents that act as carcinogens, mutagens, and teratogens in biological systems (Dupont and Guillon, 2003). Metal-processing wastewater often contains a considerable amount of hexavalent chromium mainly from rinsing of plated articles, dragout from the chromium bath, and spent chromate passivation solutions, which can pose a severe threat to public health and the environment if discharged without adequate treatment (Ouki and Neufeld, 1997). USEPA recommends that the levels of chromium in water should be reduced to 0.1 mg/L (Ayuso et al., 2003). For compliance with this limit, it is imperative for industries to reduce the chromium in their effluents to an acceptable level before discharging into municipal sewers. A variety of methods have been developed for removal of chromium compounds from industrial wastewater. Hexavalent chromium usually exists in wastewater as oxyanions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) and does not precipitate easily using conventional precipitation methods. Currently, chemical redox followed by precipitation is the most widely used

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*Corresponding author. Tel.: 852 23587147; fax: 852 23581534.
E-mail address: cemclo@ust.hk (I.M.C. Lo).

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technique for Cr(VI) removal (Aravindhan et al., 2004). This is achieved by reduction of hexavalent chromium to the less toxic trivalent state by applying a reducing agent such as ferrous sulfate, and subsequent precipitation of the trivalent chromium. This approach has three direct disadvantages: higher waste treatment equipment costs, significantly higher consumption of reagents, and significantly higher volume of sludge generated. This method also has two indirect disadvantages: a potential hazard to the environment due to landfill leachate and the difficult recovery of metals for re-use. Especially, many small/medium-scale plants do not segregate chromium waste streams from the rest of the wastewater and consequently, they must handle all waste streams through the chemical reduction system. The mixing of wastewater streams raises the practical difficulties of compliance, and ultimately will increase the scale and cost of wastewater treatment. Furthermore, the effectiveness of precipitation methods depends strongly on the composition of the wastewater. The presence of organic and inorganic compounds can decrease the heavy metal removal efficiency. Besides the chemical precipitation method, ion exchange, reverse osmosis, and electrodialysis are efficient for Cr(VI) ion removal although the cost is relatively high (George, 1985).

As one of the most promising techniques for removal of chromium from industrial wastewaters, adsorption technology has been employed for many years and the effectiveness of various adsorbents has been demonstrated (Periasam et al., 1991; Chand et al., 1994; Lazaridis and Asouhidou, 2003). In principle, adsorption cannot only remove heavy metals but also recover and recycle them back into the industrial process (Singh and Tiwari, 1997). The adsorbed material, toxic or valuable, is recovered in a concentrated form for disposal or reuse. The solid adsorbent can often be regenerated for reuse (Wang et al., 2003). Activated carbon as the most common adsorbent used in the adsorption process shows higher efficiency for the adsorption of organic than inorganic matters. The spent activated carbon is either landfilled or regenerated at rather high temperatures commonly used by commercial regenerators (Long and Yang, 2001). However, the regeneration loss may be as much as 10%, even with well-operated systems. Also, regeneration usually affects the properties of the carbon. Generally, the capacity of carbons is expected to be near 90% of the original value after regeneration (Cooney, 1999). As a result, the regeneration of this kind of adsorbent is limited because of its high cost, loss of capacity, and operating difficulties. Thus, there is a need to explore more suitable adsorbents for regeneration and recovery purpose.

In this study, a new method combining nanoparticle adsorption with magnetic separation has been developed for the removal and recovery of Cr(VI). Maghemite nanoparticles were chosen for new adsorbents by considering the main advantages: (1) maghemite nanoparticles can be produced in large quantity using the sol–gel method; (2) it can be expected that the adsorption capacity of magnetic nanoparticles is higher by considering the larger surface area and highly active surface sites; (3) it is possible that the uptake process occurs via external adsorption, resulting in a very short adsorption time; and (4) the easy separation of metal-loaded magnetic adsorbent from treated water can be achieved via an external magnetic field. Our previous work on the use of magnetite (Fe_3O_4) nanoparticles for the removal of Cr(VI) had partially verified these advantages. Nanoscale Fe_3O_4 was effective for the removal of Cr(VI) from wastewater, but chemical adsorption occurred in the process (Hu et al., 2004). Thus, the regeneration of this kind of adsorbent and recovery of adsorbate became difficult and inefficient. In the present study, another kind of magnetic nanoparticles, maghemite (γ-Fe_2O_3) nanoparticles, were synthesized and employed. Therefore, the objectives of this study were to (1) investigate the removal and recovery of Cr(VI) by synthesized maghemite nanoparticles and (2) understand the mechanism of Cr(VI) adsorption onto nanoscale maghemite.

2. Materials and methods

2.1. Synthesis and characterizations of adsorbent

In the laboratory, maghemite nanoparticles were prepared by developing the existing sol–gel method from Kang et al. (1996). First, 200 mL of purified, deoxygenated water (resistivity of 17.8 MΩ-cm) was bubbled by nitrogen gas for 30 min. Then 5.2 g $FeCl_3$ and 2.0 g $FeCl_2$ were dissolved in the above mixture with mechanical stirring. Under the protection of nitrogen gas, 1.5 M NH_4OH solution was added dropwise into the above mixture under vigorous stirring. After an initial brown precipitate, a black precipitate was formed. When pH reached 8.0, the stirrer was turned off and magnetite settled gradually. The black precipitate was isolated by an external magnetic field of 3000 G with the supernatant decanted. To obtain the pure and neutral products, synthesized materials were rinsed with ultrapure water three times. Finally, magnetite nanogel was obtained by adding 1 mL of 25% tetramethylammonium hydroxide into the precipitate. To get the maghemite nanogel, freeze-dried magnetite particles were dispersed in 99% octyl ether and the mixture was then heated to 250 °C under an air atmosphere and maintained at this temperature for 2 h. Red–brown γ-Fe_2O_3 nanogel was collected via external magnetic field after adding ethanol. The synthesized nanoparticles were then characterized before their applications.