Removal of copper, nickel and chromium mixtures from metal plating wastewater by adsorption with modified carbon foam

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HIGHLIGHTS

- Impregnation of Fe_2O_3 in carbon foam (CF) enhanced the adsorption of Cr.
- Fe_2O_3-CF adsorbed both cationic and anionic heavy metals simultaneously.
- There is no interference between adsorptions of Cr and Cu using Fe_2O_3-CF.
- The adsorption of Cu on Fe_2O_3-CF interfered the adsorption on Ni.
- Fe_2O_3-CF showed excellent removal of Cr and Cu in fixed-bed column test.

GRAPHICAL ABSTRACT
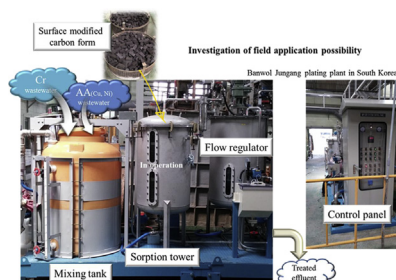
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ABSTRACT

In this study, the characterizations and adsorption efficiencies for chromium, copper and nickel were evaluated using manufacture-grade Fe_2O_3-carbon foam. SEM, XRD, XRF and BET analyses were performed to determine the characteristics of the material. Various pore sizes (12—420 μm) and iron contents (3.62%) were found on the surface of the Fe_2O_3-carbon foam. Fe_2O_3-carbon foam was found to have excellent adsorption efficiency compared to carbon foam for mixed solutions of cationic and anionic heavy metals. The adsorption capacities for chromium, copper and nickel were 6.7, 3.8 and 6.4 mg/g, respectively, which were obtained using a dual exponential adsorption model. In experiments with varying dosages of the Fe_2O_3 powder, no notable differences were observed in the removal efficiency. In a fixed-bed column test, Fe_2O_3-carbon foam achieved adsorption capacities for chromium, copper and

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nickel of 33.0, 12.0 and 9.5 mg/g, respectively, after 104 h. Based on these results, Fe₂O₃-carbon foam was observed to be a promising material for treatment of plating wastewater.

1. Introduction

Various industries use processes that include a finishing treatment consisting of metal compounds. These heavy metals can cause contamination in the discharged water. For example, the effluents from electroplating industries contain various types of toxic substances, such as cleaning agents, heavy metals and solvents. Among them, metals such as copper, nickel and chromium are harmful if they are discharged without treatment (Akbal and Camcı, 2011). Anthropogenic stresses, such as the above-mentioned heavy metals, cause adverse effects to several species of aquatic biota. Thus, National Primary Drinking Water Regulations (NPDWRs) are legally enforceable standards that apply to public water systems (USEPA, 2009).

Various physical, chemical and biological processes have been used for the treatment of heavy metals, including precipitation, adsorption, ion-exchange, biosorption, reverse osmosis and filtration (Ding et al., 2014; Ahmadi et al., 2015; Cho et al., 2015; Luo et al., 2015). Chemical coagulation, which is most commonly used and has been demonstrated to be effective in the treatment of industrial effluents, can induce secondary pollution from additional chemical substances and result in higher costs. Certain adsorption methods, such as ion exchange, can easily remove heavy metal ions (Katsumata et al., 2003). Recently, carbonaceous materials such as carbon nanotube and graphene oxide are frequently used as adsorbents for heavy metal removal from aqueous solutions (Chen and Wang, 2006; Chen et al., 2009a,b; Yang et al., 2011; Liu et al., 2011; Li et al., 2012, 2014a, 2014b). Chen et al. (2009a,b) showed that the adsorption capacity of MWCNT/iron oxide composites for Sr(II) is higher than that of iron oxides due to the high specific surface area. Li et al. (2012) reported that Cu(II) sorption capacity of GO/Fe₃O₄ is higher than that of MWCNTs, bentonite-polyacrylamide, spent activated clay, etc. These nano-sized carbon materials show great potential for the removal of heavy metal ions, but have a drawback due to the economic feasibility of the adsorbent. However, a disadvantage of this method is the cost of the adsorbent. Therefore, the development of economical adsorbents is valuable for field applications.

Among the carbonaceous materials, carbon foam has the properties of low coefficient of thermal expansion, tailorable electrical conductivity and chemical inertness (Spradling and Guth, 2003). Additionally, it is made from inexpensive precursor materials, such as coal and is manufactured on a large scale and competitively priced as various categories for such applications. Heavy metal removal using carbon foam has been reported in previous studies (Tondi et al., 2010; Burke et al., 2013). However, limited research has been performed on wastewater treatment using carbon foam. Hence, our previous study conducted an investigation for applications potentially related to the removal of cationic heavy metals using carbon foam and also showed regeneration methods of carbon foam using chemical and electrical methods (Lee et al., 2015). Further studies related to the treatment of heavy metals and metalloids, such as chromium and arsenic, which demonstrated anion characteristics in the aqueous phase, were conducted using various iron oxide materials (Jeong et al., 2007; Sheha and El-Shazly, 2010).

In this study, the efficiency of adsorption in removing the heavy metals copper and nickel as a cation and chromium as an anion from metal plating plant wastewater was investigated using two types of carbon foam.

2. Materials and methods

2.1. Preparation of the carbon foam and Fe₂O₃-carbon foam

Phenolic resin-based carbon foam and Fe₂O₃-carbon foam were co-developed with the Smithers-Oasis Korea Co. Ltd and the final products were supplied by the company. The syntheses procedure was a multistep process: First, 1.0 kg of phenol was added to a four-necked reactor, then, 1.5 kg of formaldehyde was poured into the reactor and stirred slowly, followed by 40 g of a base catalyst, and the contents were stirred for a further 2 h at 75 °C. The mixture was cooled to 35 °C and neutralized to pH 6-7 with dilute sulfuric acid. The moisture content was then adjusted to 9% through dehydration under a vacuum with reduced pressure. Second, 2 g of an alkyl ether type surfactant was mixed with the prepared phenolic resin, and the mixture was stirred slowly and thoroughly in a cylindrical mold. Third, 80 g of an organic acid curing agent and 20 g of a hydrocarbon foaming agent were added to the mixture, and the stirring rate was increased to 1000 rpm. The synthesized foam was aged in a convection oven at 60 °C. Finally, the dried foam was placed in an electric furnace and the air was removed with a vacuum pump. The sample was carbonized at a heating rate of 5 °C/min up to 900 °C under a nitrogen stream of 100 mL/min, held at the final temperature for 2 h, and slowly cooled in the nitrogen atmosphere. To prepare the Fe₂O₃-carbon foam, 100–300 g of iron (III) oxide powder (Fe₂O₃, Reagent grade, Daejung Chemicals, Korea) was added into the third step of the synthesis process and the other process was the same as described above.

2.2. Characterization of the carbon foam

The surface area, mesopore volume, and micropore volume were calculated from the N₂ isotherm based on the methods of Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), and Horvath-Kawazoe (HK). The surface morphology of the sample was investigated using a scanning electron microscope (SEM, Inspect F50, FEI, USA) at 10.00 kV. Nitrogen gas (N₂) adsorption-desorption experiments were performed using a surface area analyzer (nano-POROSITY-XQ, Mirae Scientific Instruments, Korea) after the sample was pretreated at 200 °C. The chemical composition of the carbon foam was determined using an X-ray fluorescence spectrometer (XRF, ZSX Primus II, Rigaku, Japan). Additionally, the crystalline structure of the sample was measured using an X-ray diffractometer (XRD, D-max 2500/PC, Rigaku, Japan) with a Cu Kα radiation and a fixed power source (40 kV and 200 mA). The diffraction data were collected over a 2θ range between 20° and 80° at a scanning rate of 0.5°/min.

2.3. Characterization of the wastewater

The wastewater used in this study was collected from the Banwol Jungang plating plant, Ansan, Korea. The typical wastewater characteristics of the raw feeding water are presented in Table 1.