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Pre-concentration and separation of heavy metal ions by chemically modified waste paper gel

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Abstract

Iminodiacetic acid was immobilized on waste paper by chemical modification in order to develop a new type of adsorption gel for heavy metal ions. Adsorption behavior of the gel was investigated for a number of metal ions, specifically Cu(II), Pb(II), Fe(III), Ni(II), Cd(II), and Co(II) at acidic pH. From batch adsorption tests, the order of selectivity was found to be as follows: Cu(II) ≫ Fe(III) > Pb(II) > Ni(II) ≫ Co(II) > Cd(II). Column tests were carried out for pairs of metal ions to understand the separation and pre-concentration behavior of the gel. It was found that mutual separation of Ni(II) from Co(II) and that of Pb(II) from Cd(II) can be achieved at pH 3. Similarly, selective separation of Cu(II) from Cu(II)–Fe(III) and Cu(II)–Pb(II) mixtures at pH 1.5 and 2, respectively, was observed by using this new adsorption gel. In all cases, almost complete recovery of the adsorbed metal was confirmed by elution tests with HCl.

Keywords: Waste paper; Iminodiacetic acid; Chelating gel; Mutual separation; Pre-concentration

1. Introduction

In the field of separation and recovery of metal resources, biomass wastes, i.e., agricultural and forestry products (Malik et al., 2002; Babel and Kurniawan, 2003; Leyva-Ramos et al., 2005; Wartelle and Marshall, 2006) like rice husks, soybean hulls, sugarcane bagasse, corn stover, peanut hulls, coconut fibers, wood powder as well as marine products (Inoue et al., 1999; Ruiz et al., 2000; Guibal, 2004) such as crustacean shells (particularly chitosan) and algal biomass have been investigated for their capacity and efficiency to extract metal ions. In a number of cases, chitosan and its derivatives have proved to be excellent materials for separation of metal ions. However, the production of chitosan generates an offensive smell and a large amount of waste effluent containing protein materials. This consequently raises the production cost of chitosan and also affects the environment. Thus, from the viewpoint of low cost and green technology, exploring and developing a competent biomass material that can replace the use of a variety of petroleum-based ion exchange resins, chelating resins and extraction solvents is still a big challenge. For this purpose, we have selected and evaluated waste paper as an alternative biomass material, after simple chemical modification. Since waste paper originally possesses an amorphous structure and the breakdown of hydrogen bonds during recycling also increases the amorphous region, it is suitable for easy chemical modification.

To date, there has been very little work on waste paper for the purpose of separation and recovery of metal ions though a wide variety of sorbents based on chemically modified cellulose have been investigated (Navarro et al., 1996; Zih-Perenyi et al., 1998; Ighodalo and Solomon, 2000). The presence of larger amorphous regions and a

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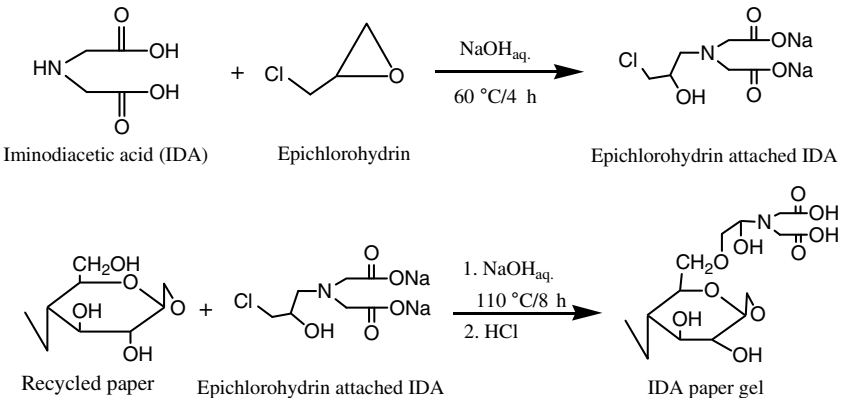

Scheme 1. Preparation of the waste paper gel.

significant proportion of lignin may provide some interesting features in adsorbents based on waste paper. Taking this into consideration, we have immobilized iminodiacetic acid (IDA), a well known chelating agent, onto waste paper cellulose to develop an adsorption gel and tested it for the separation and concentration of various metal ions. In the past, some studies have been made by immobilizing iminodiacetic acid on various forms of cellulose as feed material. Chan et al. (1992a,b) prepared iminodiacetic acid cellulose sorbents using cotton fabric and sawdust to investigate the mutual separation of Ni(II) and Co(II) though the selectivity for Ni(II) over Co(II) was not marked. Similarly, Gennaro et al. (1983) prepared iminodiacetic acid cellulose filters from ordinary filter paper disks and Gupta et al. (2002) utilized pure cellulose as the starting material for an iminodiacetic acid type of chelating cation exchanger. However, these adsorbents were found to be suitable for the simultaneous adsorption of various metal ions only and no scope for mutual separation of coexisting metal ions was found. In this context, we have prepared an iminodiacetic acid modified waste paper gel which is expected to exhibit a distinct ability for selective pre-concentration and mutual separation between coexisting metal ions.

2. Experimental

2.1. Chemicals

Waste newspaper was crushed by a Dalton model P-3S power mill to obtain a fiber-like material which was used as the feed material. Iminodiacetic acid was purchased from Dojindo Laboratories Co. Ltd., Japan and epichlorohydrin, from Kishida Chemical Co. Ltd., Japan. All other chemicals and reagents were of analytical grade and used without any purification.

2.2. Preparation of the adsorption gel

Pretreatment was necessary to remove greasy materials and ink from the paper and also to activate it for subsequent modification. For this purpose, the fiber-like material was washed many times with bio-cleans soap and water and treated with 20% NaOH solution for 5 h. It was washed again with water till neutral pH and dried in a convection oven at 60 °C for 24 h.

The pre-treated paper was chemically modified with iminodiacetic acid (IDA) according to a process developed by Sano and Murase (1980). At first, 2 g NaOH was dissolved in about 15 ml water in a 200 ml flask to which 2 g IDA and 2 ml epichlorohydrin were added with stirring. Reaction between these chemicals was carried out at 60 °C for 4 h in an oil bath. Then, 4 g NaOH was further added to the mixture and dissolved by stirring. The pretreated waste newsprint paper (2 g) was added subsequently and the reaction mixture was heated in the oil bath at 110 °C for 8 h. The product (about 1.84 g in fiber-like form) was filtered, washed with 0.5 M HCl followed by distilled water, and dried to obtain the chelating waste paper gel, abbreviated hereafter as waste paper gel. It was characterized by taking its IR spectrum and elemental analysis (Scheme 1).

2.3. Adsorption tests

A test solution containing 0.2 mM Cu(II) in 0.1 M HCl and 0.1 M HEPES (*N*-[2-hydroxyethyl]piperazine-*N*′-[2-ethanesulfonic acid]), a buffering agent, was prepared and the pH was adjusted to 3 by adding dilute NaOH solution. Ten samples were prepared by weighing 20 mg of the waste paper gel and adding 15 ml of the test solutions into each 50 ml sampling bottle. The mixtures were shaken for different time periods (from 5 min to 25 h) in a thermostated shaker maintained at 30 °C after which they were filtered and the filtrate was taken for analysis. The concentrations of the metal ions before and after the adsorption were measured by using a Shimadzu model AA-6650 atomic absorption spectrophotometer (AAS).

To observe the pH dependency of the adsorption of metal ions on the waste paper gel, batch-wise adsorption tests were carried out. Test solutions containing 0.2 mM