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Chromate ion adsorption by agricultural by-products modified with dimethyloldihydroxyethylene urea and choline chloride

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Abstract

The use of cellulose-containing agricultural by-products modified with the cross-linking reagent dimethyloldihydroxyethylene urea (DMDHEU) and the quaternary amine, choline chloride, as anion exchange resins, has not been reported. The objective of the present study was to convert the readily available by-products, soybean hulls, sugarcane bagasse and corn stover to functional anion exchange resins using DMDHEU and choline chloride. Optimization of the modification method was achieved using soybean hulls as a substrate. The optimized method was additionally used to modify sugarcane bagasse and corn stover. Adsorption efficiency results with chromate ion showed that modification with both DMDHEU and choline chloride was required for the highest efficiencies. Adsorption capacities of the modified by-products were determined using chromate ion and found to be 1.97, 1.61 and 1.12 mmol/g for sugarcane bagasse, corn stover and soybean hulls, respectively. Competitive adsorption studies were conducted at 10 and 50 times US Environmental Protection Agency (US EPA) limits for arsenic, chromium and selenium in a simulated wastewater at pH 7. The results showed preferential adsorption of chromate ion over arsenate or selenate ion. Estimated product costs for the three resins ranged from \$0.88/kg to \$0.99/kg, which was considerably lower than the market costs for the two commercial anion exchange resins QA-52 and IRA-400 also used in this study. DMDHEU/choline chloride modification of the three by-products produced an anion exchange resin with a high capacity to adsorb chromate ion singly or competitively in the presence of other anions from aqueous solutions.
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Keywords: Soybean hulls; Sugarcane bagasse; Corn stover; Anion exchange resins; DMDHEU; Choline chloride; Chromium; Arsenic; Selenium

1. Introduction

Agricultural by-products are high volume, low-value, underutilized lignocellulosic materials that are generally poor anion exchange resins. However, through the introduction of quaternary ammonium groups, anion exchange properties can be enhanced (Marshall and Wartelle, 2004). Agricultural by-products contain high levels of cellulose, hemicellulose and lignin. Quaternization of these polymers, especially cellulose, involves the reaction of various quaternary amine-containing reagents with a primary alcoholic –OH group on glucose units within the polymer. Marshall and Wartelle (2004) quaternized soybean hulls with *N*-(3-chloro-2-hydroxypropyl trimethylammonium chloride) and produced an anion exchange with good removal efficiency toward arsenate, chromate, dichromate or selenate anions. Low and Lee (1997) quaternized rice husks to adsorb reactive dyes. Rice hulls quaternized in the same manner were

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used to remove Cr(VI) in the form of chromate ion from synthetic solutions, electroplating waste and wood preservative waste (Low et al., 1999).

Dimethyloldihydroxyethylene urea (DMDHEU) and choline chloride have been used to crosslink and add cationic character to cotton fabric. DMDHEU acts as a crosslinking agent that imparts wrinkle resistance to cellulose-containing fabrics (Harper and Stone, 1986). Choline chloride has been used to impart cationic character cotton and improve dyeability (Harper and Stone, 1986; Cardamone et al., 1996; Cardamone and Turner, 2000; Brodmann and Thackrah, 1999). There have been no previous reports in the literature that describe the application of DMDHEU and choline chloride for the modification of agricultural by-products to create centers of positive charge.

There are several anions of environmental concern to the US Environmental Protection Agency (US EPA) and three important anions contain chromium, arsenic or selenium (US EPA, 2002). Chromium is the most ubiquitous of these three elements and is widely used in electroplating, leather tanning, metal finishing, chromate preparation, textile dyeing, the canning industry, steel fabrication, wood preservatives, and paint and pigments (Ajmal et al., 1996; Garg et al., 2004). Chromium is primarily found in its hexavalent [Cr(VI)] or trivalent forms [Cr(III)]. The hexavalent form is 100 to 1000 times more toxic than the trivalent form and its accumulation in the environment is a great cause for concern (Low et al., 1999).

Several treatment methods have been used for chromium remediation, including adsorption, ion-exchange, and precipitation after reduction (Lee et al., 1995). Adsorbents from agricultural by-products are particularly advantageous due to their low cost and high availability as starting materials. Garg et al. (2004) used formaldehyde and sulfuric acid-treated sawdust to remove up to 88% of chromium as dichromate from a 200 mg/l solution. Lee et al. (1995) used copper coated moss to remove up to 66% of Cr(VI) from 20 mg/l solution. Yu et al. (2003) used maple sawdust as an adsorbent for low levels of chromium. Raji and Anirudhan, (1998) used polyacrylamide-grafted sawdust to remove Cr(VI) and As(III) from batch solutions. Selveraj et al. (2003) found that distillery sludge had a chromium adsorption capacity of 5.7 mg/g in batch studies.

The objective of this study was to investigate the use of the DMDHEU/choline chloride reaction using lignocellulosic-based agricultural by-products to enhance their ability to bind anions such as hexavalent chromium. Improved anion binding of agricultural by-products from the DMDHEU/choline chloride modification would extend this method beyond its current use in cellulose-based fabrics.

2. Materials and methods

2.1. Materials

Soybean hulls were obtained from Owensboro Grain Co., Owensboro, KY. Sugarcane bagasse was obtained from Nicholls State University, Thibodaux, LA. Corn stover was obtained from Iowa State University, Ames, IA. All by-products were milled in a Retsch SK cross beater mill (Glen Mills Inc., Clifton, NJ) and sieved to retain particles of 0.85–2.00 mm diameter. A quaternary ammonium, cellulose anion exchange resin (QA-52) was obtained from Whatman International Ltd. (Maidstone, England) and polystyrene-divinylbenzene-based, quaternary ammonium, strong anion exchange resin (Amberlite IRA-400) was purchased from Supelco (Bellefonte, PA).

2.2. Optimization of reaction conditions for DMDHEU/choline chloride quaternization

In order to optimize the modification of soybean hulls with DMDHEU and choline chloride with respect to chromate ion adsorption, 3 g samples of soybean hulls were mixed with varying concentrations of DMDHEU (2 to 12%) and choline chloride (2 to 12%) at 10 ml solution/g of soybean hulls. The pH was adjusted to between 4 and 4.5 and the samples were dried at 60 °C. The dried samples were heated between 120 and 200 °C for time periods between 0.5 and 6 h. They were then washed three times at a sample:water ratio of 1:40 and dried at 60 °C.

Product yields were determined on the final products in accord with the following equation:

$$\text{Product yield } (\%) = [(\text{Wt}_p/\text{Wt}_{sm})] \times 100,$$

where Wt_p = dry weight in g of the final product and Wt_{sm} = dry weight in g of the source or starting material.

2.3. Chromate ion adsorption

The adsorption of chromate ion was determined by batch analyses using 0.25 g samples of un modified or modified by-products in 25 ml of 20 mM Na_2CrO_4 (sodium chromate) solution adjusted to pH 3.

All suspensions were stirred at 300 rpm for 24 h at 25 °C. The solutions were filtered through 0.45 μm filters and diluted in 4% Ultrex HNO_3. No significant leaching of pigmented organic material from the by-products was visually observed after the batch assays were concluded. Chromium concentrations were determined on the filtrates after suitable dilutions using a Leeman Labs Profile ICP-AES spectrometer at 268 nm with an axial torch and dual view capabilities (Leeman Labs, Hudson,