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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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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:

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

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, NH). All ion exchange material was dried to a moisture content of approximately 10% or less before adsorption analyses were conducted. Untreated, DMDHEU modified, choline chloride modified and DMDHEU/choline chloride modified by-products were compared to the two commercially available anion exchange resins, QA-52 and IRA-400 for their ability to adsorb chromium.

2.4. Adsorption isotherms

Adsorption capacity measurements were determined on modified soybean hulls, corn stover and sugarcane bagasse for their ability to adsorb chromate ion over the concentration range of 0.5 to 35 mM. Concentrations of chromium were determined by ICP-AES as described above. The isotherms were evaluated using the non-linear Langmuir model as given by the following equation (Kinniburgh, 1986):

$$q_e = KC_eQ_o/(1 + KC_e),$$

where C_e is the equilibrium chromate ion concentration in solution, q_e is the amount of chromate ion adsorbed per g of resin, Q_o is the adsorption capacity of the resin for chromate ion and K is the affinity or association constant of chromate ion for the resin. Langmuir parameters Q_o and K were determined by non-linear regression analysis of the adsorption isotherms using Sigma Plot v. 8.0 (SPSS, Chicago, IL). The regression analysis also determined the correlation coefficient (r^2) and the "goodness of fit" parameter (p) for each adsorption isotherm.

2.5. Determination of competitive anion adsorption

Competitive adsorption studies were carried out at pH 7 and 25 °C for 24 h with stirring at 300 rpm using 0.25 g of DMDHEU/choline chloride-treated by-product. Solution concentrations were prepared to be 10 or 50 times the US EPA drinking water limits for total chromium (0.100 mg/l), arsenic (0.050 mg/l) and selenium (0.050 mg/l) (US EPA, 2002). After incubation, the solutions were filtered, diluted with acid and analyzed at ICP-AES wavelengths of 268, 194 and 196 nm for Cr, As and Se, respectively.

2.6. Nitrogen analyses

Nitrogen analyses were conducted on a Leco Model FP-428 Nitrogen Analyzer (St. Joseph, MI). Values are expressed as percent dry weight.

3. Results and discussion

3.1. Optimized resin properties

In order to optimize reaction conditions of reactant concentrations and reaction time and temperature, the concentrations of DMDHEU and choline chloride employed by Cardamone et al. (1996) were used as a starting point. Fig. 1 shows maximum adsorption of chromate ion occurring at a reaction temperature of 180 °C using 4% DMDHEU and 6% choline chloride. Fig. 2 demonstrates chromate ion adsorption as a function of reaction time for the 0.5 to 6 h time interval. Chromate ion adsorption varied little over this time interval and 2 h was chosen as a convenient value. Time and temperature conditions of 2 h and 180 °C were then used to optimize concentrations of DMDHEU and choline chloride. Mixtures of varying DMDHEU and choline chloride concentrations from 2 to 12% were used to modify soybean hulls. Fig. 3 shows maximum adsorption of chromate ion occurs at 10% DMDHEU when the choline chloride concentration is fixed at 6%. When the choline chloride concentration was varied and the DMDHEU concentration was fixed at 4%, a maximum concentration was observed at 8%. Therefore, process conditions were developed whereby these two reagent concentrations were used, namely, 10% DMDHEU and/or 8% choline chloride. Therefore, soybean hulls were treated with 10% DMDHEU and/or 8% choline chloride at 180 °C for 2 h. These process conditions were also applied to two additional agricultural by-products, namely, sugarcane bagasse and corn stover, and the resulting resins were evaluated for adsorption of chromate ion. We recognize that our process conditions developed for soybean hulls may not be optimal for either sugarcane bagasse or corn stover. However, when one set of modification conditions are

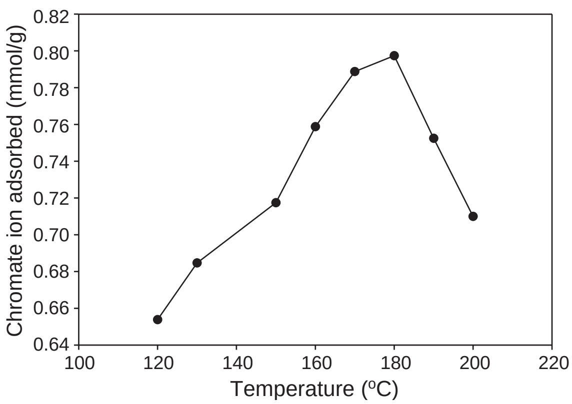

Fig. 1. Chromate ion adsorption for modified soybean hulls at reaction temperatures from 100–200 °C. Reaction conditions: 4% DMDHEU and 6% choline chloride for 2 h.

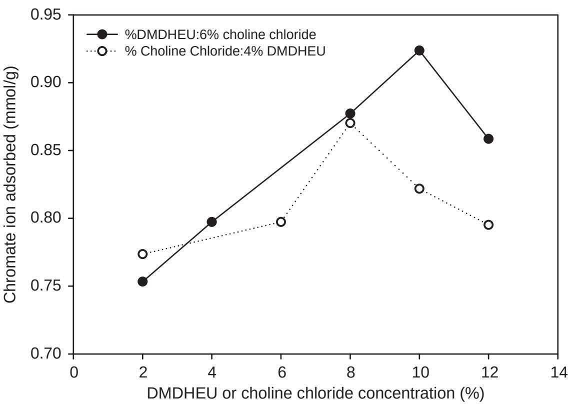

Fig. 2. Chromate ion adsorption for modified soybean hulls at reaction times from 0.25–6 h. Reaction conditions: 4% DMDHEU and 6% choline chloride at 180 °C.

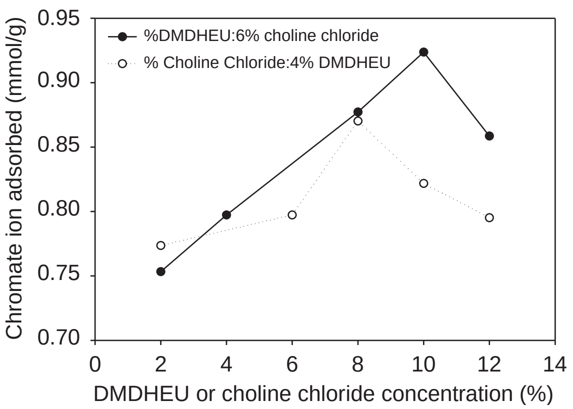

Fig. 3. Chromate ion adsorption for modified soybean hulls at different DMDHEU or choline chloride concentrations. Reaction conditions: 180 °C for 2 h.

used, all three by-products were treated identically and can be compared directly.

Structures for the reagents employed in this study and a reaction scheme are shown in Fig. 4. This reaction scheme represents the most likely scenario as explained below. As depicted in Fig. 4, DMDHEU acts as a crosslinking reagent between cellulose and choline chloride. Reaction between cellulose and DMDHEU and between DMDHEU and choline chloride is thought to occur through the removal of water (dehydration) and formation of ether linkages among the primary alcoholic –OH groups on cellulose, DMDHEU and choline chloride.

Table 1 shows high product yields for by-product treatment with DMDHEU only, and a combined treatment with both DMDHEU and choline chloride. Apparently DMDHEU binds readily to the by-products by crosslinking cellulose and perhaps little mass is lost

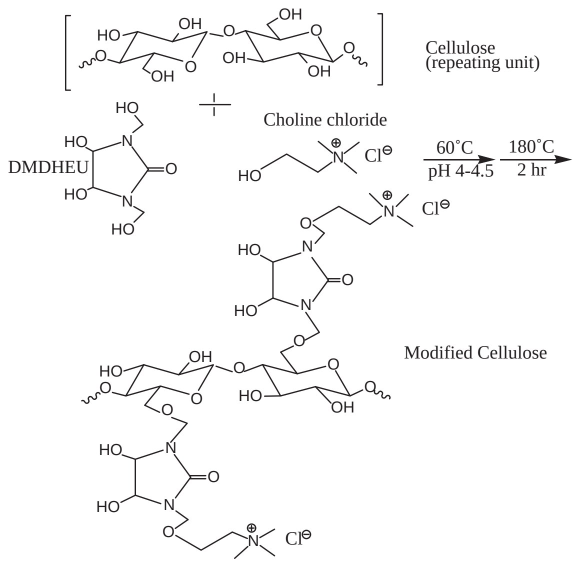

Fig. 4. Reaction scheme for the reaction among by-product cellulose and the reagents DMDHEU and choline chloride.

Table 1
Product yield, chromate ion adsorption and %N added to by-products treated with DMDHEU or choline chloride (CC) or DMDHEU and choline chloride compared to two commercial anion exchange resins

Chemical modification and adsorbent material	Product yield (%)	Chromate ion adsorption (mmol/g)	Nitrogen content (%)
Untreated			
Soybean hulls	N/A	0.26	1.83
Sugarcane bagasse	N/A	0.35	0.45
Corn stover	N/A	0.35	0.88
DMDHEU only			
Soybean hulls	103	0.51	9.17
Sugarcane bagasse	164	0.44	8.92
Corn stover	170	0.49	9.21
Choline chloride only			
Soybean hulls	66	0.51	2.17
Sugarcane bagasse	88	0.60	0.88
Corn stover	85	0.70	1.52
DMDHEU-CC			
Soybean hulls	107	0.81	6.86
Sugarcane bagasse	129	1.04	5.64
Corn stover	98	1.05	7.00
Commercial resins (Synthetic)			
Amberlite IRA-400	N/A	2.14	4.67
(Cellulose-based)			
Whatman QA-52	N/A	0.72	1.50

through subsequent washing of the modified product. The addition of choline chloride only generated lower yields as there may be less binding of choline chloride to cellulose than with DMDHEU alone. The mixture of DMDHEU and choline chloride as reactants produces products with yields that are near or above 100%. It is possible that since DMDHEU reacts with choline chloride, cellulose crosslinking with DMDHEU is decreased, therefore product yields are lower than with the reaction of DMDHEU alone.

Table 1 also shows chromate ion adsorption for the three unmodified and modified by-products at an anion concentration of 20 mM at pH 3. Selveraj et al. (2003) reported that the maximum adsorption of chromate ion occurs at pH 3. A high concentration of chromate ion (20 mM) was used to determine the effect of high anion loading on adsorption. Untreated by-products exhibit low levels of chromate ion adsorption, which is increased by treatment with DMDHEU only. A large increase in nitrogen content was observed upon the addition of the cross-linking agent. Each DMDHEU provides two nitrogen atoms per molecule, but there was still a considerable increase in %N. There appeared to be no relationship between chromate ion adsorption and the amount of DMDHEU added to the by-products. Since DMDHEU does not provide cationic sites, the mechanism of chromate adsorption upon addition of this reagent is not known.

The addition of choline chloride by itself to the by-products also improved chromate ion adsorption compared to the untreated samples, but the nitrogen content after reaction were considerably less than with DMDHEU (Table 1). However, unlike the case with DMDHEU, there appeared to be an increase in chromate ion binding as the nitrogen content increased. Moreover, much smaller amounts of N added in the case of choline chloride compared to DMDHEU resulted in generally more chromate ion bound to the resins compared to DMDHEU. The choline chloride addition may have been small but it was more effective than the addition of DMDHEU for chromate ion adsorption. Choline chloride carries a center of positive charge, whereas DMDHEU does not (Fig. 4). This could explain the difference in effectiveness.

The addition of DMDHEU and choline chloride to the reaction mixture produced a product with the greatest chromate ion adsorption compared to other untreated and treated samples (Table 1). The amount of N incorporated into these samples was high, whereby an increase in nitrogen also showed an increase in chromate ion adsorption. Under these reaction conditions, choline chloride and DMDHEU may be competing for binding sites on the cellulose in the by-products. Considering the relative ease with which DMDHEU reacts with by-product cellulose, DMDHEU may be the major reactant with the polymeric glucose in cellulose. Choline chloride may then react with DMDHEU to a greater extent than it reacts with polymeric glucose, thereby increasing the degree of choline chloride addition and, hence, generating increased chromate ion binding.

The chromate ion adsorption values from products exposed to DMDHEU and choline chloride were compared with two commercially available anion exchange resins (Table 1). The best experimental resin in terms of chromate ion adsorption, namely, corn stover, adsorbed 46% more chromate ion than the cellulose-based resin Whatman QA-52. However, the corn stover-based resin adsorbed 51% less chromate ion than the synthetic resin IRA-400.

3.2. Adsorption isotherms

Adsorption isotherms for chromate ion adsorption by the three modified by-products are given in Fig. 5. Adsorption capacities and association constants were obtained from the isotherms using the non-linear Langmuir model (Table 2). Both correlation coefficients (r^2) and the "goodness of fit" parameter (p) indicated the Langmuir model adequately represented the data (Table 2). Chromate ion adsorption was highest for sugarcane bagasse and lowest for soybean hulls, although all modified by-products had adsorption capacities that exceeded 1.00 mmol/g.

3.3. Competitive ion adsorption studies

Competitive ion adsorption studies were conducted on the DMDHEU and choline chloride modified by-products in order to determine their effectiveness in adsorbing several anions from solution. In addition to

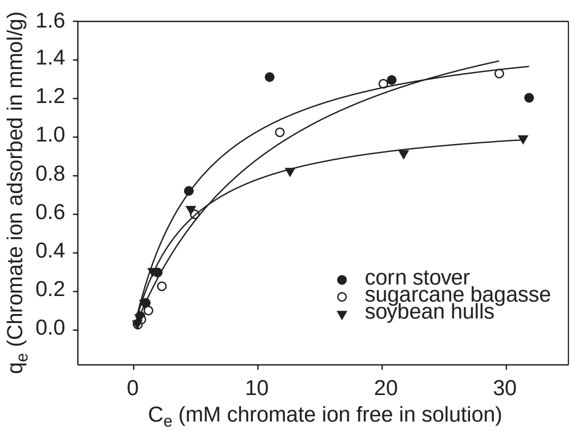

Fig. 5. Adsorption isotherms for chromate ion using DMDHEU and choline chloride modified corn stover, soybean hulls and sugarcane bagasse. The adsorption isotherms were generated at pH 3 with concentrations ranging from 0.5 to 35 mM.

Table 2
Adsorption capacities and association constants[a] for chromate ion adsorption on quaternized agricultural by-products

Adsorbent material	Adsorption capacity (mmol/g resin)	Association constant (L/mmol)	r^2	p
Soybean hulls	1.12 ± 0.04	4.39 ± 0.59	0.99	0.0001
Sugarcane bagasse	1.98 ± 0.18	12.2 ± 2.6	0.99	0.0001
Corn stover	1.61 ± 0.19	5.57 ± 2.10	0.95	0.0002

[a]Adsorption capacities and association constants were obtained from adsorption isotherms using the Langmuir model in the non-linear form. The adsorption isotherms were generated at pH 3.

Table 3
Competitive anion adsorption at 10X and 50X US EPA limits for chromium, arsenic and selenium in a simulated wastewater at pH 7

	Cr (%)	As (%)	Se (%)
10X US EPA limits			
Untreated by-products			
Soybean hulls	13[a]	0.0	0.4
Sugarcane bagasse	0.0	5.3	0.0
Corn stover	16	0.0	0.0
50X US EPA limits			
Untreated by-products			
Soybean hulls	15	0.0	3.7
Sugarcane bagasse	6.5	0.0	0.0
Corn stover	13	0.0	0.0
10X US EPA limits			
DMDHEU-CC			
Soybean hulls	76	0.7	3.4
Sugarcane bagasse	97	13	35
Corn stover	98	23	27
50X US EPA limits			
DMDHEU-CC			
Soybean hulls	42	0.0	3.3
Sugarcane bagasse	96	0.0	12
Corn stover	97	6.7	33

[a]Values given as percent of initial ion concentration removed.

chromium, arsenic and selenium were chosen due to their status as priority pollutants. Table 3 shows that very little of the three anions were adsorbed at pH 7 by the untreated by-products. Adsorption values at pH 7 are important because it is in the required pH range of 6 to 9 for wastewater that is being prepared for discharge in Louisiana (Louisiana Department of Environmental Quality, 2003). Modified sugarcane bagasse and corn stover adsorbed over 95% chromate ion in a competitive environment at both 10X and 50X anion levels. Modified soybean hulls removed considerably less chromate ion from solution than either corn stover or sugarcane bagasse. Both arsenic (as arsenate) and selenium (as selenate) were removed to a much less degree than chromate ion by all modified by-products.

This competition study concentrated on the fate of three environmentally important anions in a laboratory prepared solution in the presence of by-product-based and commercial anion exchange resins. Ultimately, if these by-product-based resins are to be considered for commercialization, extensive evaluations need to be carried out with different wastewater streams. In this case, the effectiveness of the resins for chromate ion may change, since wastewater normally carries chloride, sulfate and nitrate anions, which may affect resin performance.

3.4. Estimated product cost

Estimated product cost is based on a reaction between by-product and a mixture of 10% DMDHEU and 8% choline chloride. Recycling of the reactants was not included in the cost. Cost estimates are given for all three modified by-products because they differed in yield (Table 1) and are listed in Table 4. Manufacturing costs for the by-product-based resins are compared to bulk costs for QA-52 and IRA-400 (Table 4). Estimated manufacturing costs were calculated on a by-product feed rate of 10,000 kg/day, which yielded 10,700 kg/ day, 12,900 kg/day or 9,800 kg/day of quaternized soybean hulls, sugarcane bagasse or corn stover, respectively. Given a 320 day/yr production schedule, the yearly output would be 3,424,000, 4,128,000 or 3,136,000 kg for modified hulls, bagasse or stover, respectively.

Manufacturing costs for all the quaternized by-products were considerably lower than the market costs for the two commercial anion exchange resins. Also, the cost to remove one mmol of chromate ion from solution was about 3 to 4 times lower compared to the synthetic resin IRA-400 and about 500 to 600 times lower than the cellulose-based resin QA-52.

4. Conclusions

Three agricultural by-products, soybean hulls, sugarcane bagasse, corn stover, were quaternized by the

Table 4
Estimated product or manufacturing cost[a] for quaternized agricultural by-products compared to market prices for two commercial resins

Product	Product cost ($/kg)	Cost/mmol chromate ion adsorbed ($/mmol)[c]
Soybean hulls	0.99	1.22
Sugarcane bagasse	0.88	0.85
Corn stover	0.97	0.92
QA-52	436[b]	606
IRA-400	7.50	3.50

[a]Estimated costs were comprised of raw material costs and other costs. Raw material costs were: soybean hulls = \$0.06/kg; sugarcane bagasse = \$0.01/kg; corn stover = \$0.01/kg. Annual costs were \$192,000, \$32,000 or \$32,000 for hulls, bagasse or stover, respectively. DMDHEU was valued at \$1.41/kg for a 28% solution and choline chloride was priced at \$0.73/kg for a 70% solution, resulting in annual costs of \$754,000 and \$311,000 for DMDHEU and choline chloride, respectively. Other costs were based on utilities, labor, supplies, general works and depreciation of capital costs of a citric acid modification process that utilizes a similar process scheme (Marshall et al., 2001). The other costs are estimated at \$0.62/kg.

[b]Market or bulk prices for QA-52 and IRA-400.

[c]Based on the adsorption values given in Table 1.

addition of DMDHEU and choline chloride. The combination of reagents was found to be necessary for modification in order to ensure the greatest level of chromate ion binding. These modified by-products demonstrated chromate ion adsorption that surpassed a cellulose-based anion exchange resin but was less than a synthetic, commercially available anion exchange resin. The quaternized hulls, bagasse and stover preferred chromate ion to arsenate or selenate ion when all three ions were present in a simulated wastewater. Product or manufacturing cost for the by-product-based resins was relatively low compared to the market costs for the commercial products, based on the low cost of the starting materials and the reagents used for quaternization. In applications requiring removal of hexavalent chromium, by-product-based resins should be considered compared to commercial resins on the basis of high efficacy and low cost.

The results presented in this study can form the basis for further studies involving ion exchange columns or contactors with actual wastewater containing the chromate ion. Questions to be answered include appropriate contact times, sorbent regeneration and the ultimate fate of the chromate anion once removed from the sorbent. Studies are underway in our laboratory to answer these questions.

Disclaimer:

Mention of names of companies or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture over others not mentioned.

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