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NOTE

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Decontamination of synthetic solutions containing heavy metals using chemically modified sawdusts bearing polyacrylic acid chains

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Abstract New materials containing carboxylate groups have been synthesized by grafting polyacrylic acid onto sawdust. These new adsorbents were subjected to continuous extraction of different metal ions using packed columns to determine their maximum binding capacities. They exhibit binding capacities 15–40 times higher than unmodified sawdusts for removal of Cu^{2+}, Ni^{2+}, and Cd^{2+} chosen as representative heavy metal ions. Cation desorption and adsorbent regeneration could be effected by elution with a diluted HCl solution; water as an eluent has no effect on metal desorption.

Key words Acrylic acid · Chemical modification of wood · Ion-exchange resin · Heavy metal · Sawdust

Introduction

Increased industrial activity raises the question of waste water treatment, particularly concerning heavy metal ions. Several methods were developed to remove metal ions from aqueous solutions.[1] Among them, precipitation, ion exchange and adsorption, solvent extraction, and foam flotation are commonly used. Most do not lead to satisfactory decontamination with respect to their operational costs. It has been also reported that natural substances such as barks,[2–6] sawdusts,[7,8] and other agricultural by-products[9–11] can be used advantageously for scavenging heavy metal ions. All these natural substances, considered by-products, are inexpensive and easily available; but they have relatively low binding capacities. Therefore, chemical modifications of these materials have been proposed to improve their ability to adsorb heavy metals. Treatment of barks by nitric or sulfuric acid and formaldehyde prevents leaching of extractives into water and improves their ability to adsorb heavy metals.[12–16] Wood-polyethylenimine composite and its derivative containing dithiocarbamate group exhibited improved ability for the adsorption of mercury (Hg^{2+}) and copper (Cu^{2+}) from water.[17] Sawdusts treated with dyes such as procion red or procion yellow have been used to remove heavy metals from waste water.[18]

We recently described the use of esterified sawdust bearing a carboxyl group for the adsorption of Cu^{2+} from aqueous solution (Fig. 1).[19] The highly porous and hydrophilic structure of wood combined with the chelating properties of carboxyl groups allows us to obtain efficient adsorbents for removal of heavy metals. More recently we reported a new method to graft polyacrylic acid chains onto sawdust using $KMnO_4$ as initiator[20] to obtain inexpensive adsorbents (Fig. 2). The present study describes preliminary results concerning the use of such modified sawdusts to remove Cu^{2+}, Ni^{2+}, and Cd^{2+} from water.

Materials and methods

Materials

Wood meal (mixture of *Picea abies* and *Fagus sylvatica*, particles size <1 mm) was used without extraction.

Chemical modification

Dried sawdust (15 g) was mixed with 750 ml 0.016 M $KMnO_4$ solution at room temperature for 30 min. The sawdust was then filtered, washed with distilled water, and transferred into a 500-ml flask containing 5 or 20 ml of acrylic acid in 250 ml hexane.

Graft co-polymerization was carried out by mechanical stirring for 2 h at 69°C. The mixture was then filtered on a Büchner funnel and the wood washed with acetone

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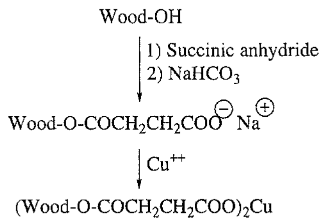

Fig. 1. Adsorption of Cu^{2+} from agueous solution using esterified sawdust bearing carboxyl group

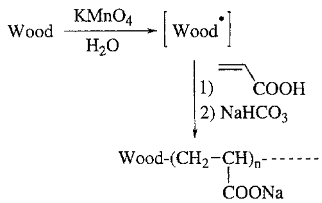

Fig. 2. Method to graft polyacrylic acid chains onto sawdust using $KMnO_4$ as initiator to obtain inexpensive adsorbents

(100 ml). To remove unreacted chemicals and homopolymer, the resulting sawdust was mixed with 500 ml hot distilled water, stirred for 2 h at room temperature, filtered on a Büchner funnel, and washed with acetone (200 ml) before drying to a constant weight at 70°C.

Ion-exchange capacities

Theoretical binding capacities were estimated by two methods based, respectively, on weight gain and titration. Weight percent gain (WPG) was calculated as follows:

$$\mathrm{WPG} = \frac{(m_1 - m_0)}{m_0} \times 100$$

where m_0 is the oven-dried mass (g) of sawdust used for the reaction, and m_1 is the oven-dried mass (g) of sawdust obtained after the reaction.

The acid value according to gain mass ($\boldsymbol{A}_{\mathrm{GM}}$) was calculated as follows:

$$A_{\mathrm{GM}}\left(\mathrm{mEqH}^+/\mathrm{g}\right) = \frac{(m_1 - m_0)}{72 \times m_0} \times 1000$$

The titration of carboxylic acids grafted on wood was determined according to a procedure described in the literature.[21] Sawdust (150 mg) was mixed with 5 ml 0.1 N H_2SO_4 in 50 ml distilled water and titrated using 0.1 N NaOH with phenolphthalein as indicator. The acid value according to titration (A_T) was obtained by the following equation:

$$A_{\mathrm{T}}\left(\mathrm{mEqH}^+/\mathrm{g}\right) = \frac{(v_1 - v_0) \times 0.1}{m_0}$$

where v_1 is the volume (ml) of the 0.1 N NaOH titration solution used, v_0 is the volume (ml) of the 0.1 N NaOH solution used for neutralizing 5 ml of 0.1 N H_2SO_4 solution, and m_0 is the sample weight (g).

Adsorption of heavy metals from water

Copper, nickel, and cadmium were selected as representative heavy metal ions based on their high toxicity and their use in electroplating factories and industry. Synthetic solutions containing Cu^{2+}, Ni^{2+}, and Cd^{2+} were prepared by dissolution of chloride salts in distilled water and used without pH adjustment, which were pH 4.9, 5.9, and 5.7, respectively. Modified sawdust was treated with saturated $NaHCO_3$ solution, for 1.5 h, filtered, washed with distilled water, and dried for 48 h at 70°C before use.

Saturation of the adsorbent was carried out as follows: Percolating columns (7.8 cm length, 1.2 cm internal diameter) were packed with 1 g of sawdust wetted with water and allowed to drain.

The solutions of metal salts (1 l at 1000 ppm of metal) were passed through the closed circuit columns with a flow rate of 1 ml min^{-1} for 24 h. Saturated sawdusts were then washed with 90 ml distilled water. A sample (0.2 g) was dried for 48 h at 70°C, mineralized using 30% H_2O_2 solution (10 ml, 20°C, 24 h) followed by $HClO_4$ 15N (10 ml, 200°C), and the amount of metal analyzed by emission spectrometry (ICP, inductively coupled plasma).

Results and discussions

The quantities of metal ions sorbed onto sawdusts are given in Table 1. The removal capacity of the adsorbents for divalent heavy metals (C_{GM} or C_{T}) can be estimated from the acid value on the basis of the formation of a divalent ionic complex according to the formula:

C_{GM} (mEq/g) = $A_{\mathrm{GM}}/2$ or C_{T} (mEq/g) = $A_{\mathrm{T}}/2$

Theoretical binding capacities are different depending on the method used for their determination. For weakly modified sawdust (WPG 2.8%), the capacity estimated from the weight gain is lower than that estimated from titration, which can be explained by the loss of low-molecular-weight compounds from wood. For strongly modified sawdust (WPG 31.2%), the estimated capacity according to weight gain is higher, indicating that the carboxyl groups are not all ionized in the same manner during titration. Quantities of heavy metal ions fixed on modified sawdust are important compared to those on unmodified sawdust and approximately the same for the three metals studied (~1.6 mEq/g). They are in good agreement with the theoretical values calculated according to $\boldsymbol{A}_{\mathrm{T}}$ for strongly modified sawdust and are higher in all cases for weakly modified sawdust, indicating the formation of monovalent ionic complexes probably due to the distance between the carboxyl functions, which makes difficult the formation of divalent complex. Saturated columns were subjected to continuous elution with distilled water (1 ml min^{-1} for 48 h) to determine the stability of the fixation between metal and modified wood. For the three metals, less than 1% of metal was desorbed after 48 h. Regeneration of the columns can be realized using diluted HCl solution (pH 3, 1 ml min^{-1} for

Table 1. Quantities of heavy metal ions sorbed on sawdust

Adsorbent	Acid value (mEq H^+/g)		Removal capacity (mEq/g)		Metal sorbed on sawdust					
					Cu^{2+}		Cd^{2+}		Ni^{2+}	
	A_{GM}	A_T	C_{GM}	C_T	mg/g	mEq/g	mg/g	mEq/g	mg/g	mEq/g
Unmodified sawdust	–	–	–	–	2.0	0.03	4.9	0.04	2.7	0.05
Modified sawdust (WPG = 2.8%)	0.39	0.89	0.195	0.445	46.9	0.74	76.1	0.68	39.8	0.68
Modified sawdust (WPG = 31.2%)	4.33	3.63	2.165	1.815	104	1.63	168.0	1.49	97.3	1.66

WPG, weight percent gained; A_{GM} and A_T, acid value according to gain mass and titration, respectively; C_{GM} and C_T, removal capacity based on A_{GM} and A_T, respectively

Table 2. Quantities of heavy metals desorbed using HCl solution after 48h

Adsorbent	percent of metal desorbed		
	Cu^{2+}	Ni^{2+}	Cd^{2+}
Unmodified sawdust	98	100	98
Modified sawdust (WPG 2.8%)	98	98	99
Modified sawdust (WPG 31.2%)	95	95	87

48h), which causes desorption of heavy metals initially bonded to wood, allowing us to envisage further utilization. The quantities of metal desorbed after 48h are given in Table 2. The behavior of modified sawdust is similar in all points to that of commercially available weakly acidic cation exchangers. The total exchange capacity can be modulated by the quantity of acrylic acid used and can reach values of about 4mEq/g, which is of the same order as that of commercial ion-exchange resins.

Conclusions

Graft co-polymerization of acrylic acid onto sawdust allows us to obtain efficient adsorbents for the removal of heavy metals from water. The low cost of these adsorbents prepared from agricultural or industrial by-products and their adsorptive ability make their use promising for depollution of industrial waste waters. Moreover, for nonvolatile metals, saturated sawdusts could be incinerated, which constitues a satisfactory depollution solution with respect to waste storage.

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