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ScienceDirect
Bioresource Technology 99 (2008) 6464–6470
BIORESOURCE TECHNOLOGY

A study in the adsorption of Fe^{2+} and NO_3^- on pine needles based hydrogels

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Received 4 May 2007; received in revised form 15 November 2007; accepted 16 November 2007
Available online 31 December 2007

Abstract

Novel supports for use as cation and anion adsorbents were prepared from lignocellulosics using pine needles and their carboxymethylated forms by network/hydrogel formation with acrylamide and *N*,*N*-methylene bisacrylamide. The hydrogels thus prepared were further functionalized by partial alkaline hydrolysis with 0.5 N NaOH and were characterized by FTIR, SEM and nitrogen analysis. Adsorption of Fe^{2+} on these hydrogels was carried as a function of time, temperature, pH and ionic strength. The hydrogel having the maximum adsorption capacity was loaded with Fe^{2+} at the conditions those afforded maximum uptake and was used as novel anionic adsorbent for NO_3^-. The water uptake capacities and biodegradability of the hydrogels before and after the ion loading was studied to evaluate the possible end-uses of these hydrogels as alternate materials in the removal of ionic species from water.

Keywords: Adsorbents; Hydrogels; Ion uptake; Pine needles; Water uptake

1. Introduction

Recently bio-wastes have been reported as efficient biosorbents of heavy metal ions. The leaves, bark, fibres or saw dust are used as such or are subjected to suitable pre-treatment or are chemically modified to meet performance requirements of their end-use. Recent reports include use of spent grain (Low et al., 2000), cork and yohimbe bark wastes (Villaescusa et al., 2000), palm sheath (Iqbal et al., 2002), crude coniferous barks (Vázquez et al., 2002; Martin-Dupont et al., 2002, 2006), rice husk (Kumar and Bandyopadhyay, 2006) and coir fibres (Conrada and Hansenb, 2007). Juniper wood and bark have been recently reported for the removal of Cd^{2+} from aqueous solutions at different pH (Shin et al., 2007). The latter was observed to show 3–4 times higher adsorption capacity.

The underlying mechanism of the metal ions uptake by lignocellulosics is generally adsorption, as cations are attracted to the negatively charged active sites spread throughout a lignocellulosic. Though the hydroxyl and carbonyl groups are present in abundance on the lignocellulosics, yet these are not effective sites for binding of the metal ions since most of these are unavailable due to the operation of intermolecular forces. Tiemann et al. (1999) reported use of X-ray absorption spectroscopy to investigate Cr^{3+} and Ni^{2+} ligands in alfalfa biomass. They established that the carboxyl groups plays important role in the binding of heavy metals. From the FTIR spectroscopy analysis it was deducted that that the carboxylate ion is the major functional group in the juniper fibre responsible for the Cd^{2+} adsorption (Min et al., 2004). The mechanism of the metal ion uptake on the bio-waste based supports has also been studied by using DRIFT spectroscopy. It was concluded there from that that the higher Cd^{2+} uptake

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doi:10.1016/j.biortech.2007.11.044

on the juniper bark as compared on the juniper wood was due to the surface concentration of the carboxyl groups on the former. The ion exchange with Ca^{2+} ions was also reported to contribute to the overall adsorption mechanism (Shin et al., 2007).

However, in the native form, the efficacy of the lignocellulosis is not high due to the lack of accessibility of ionic species in the bulk, especially in the lignified regions. The hydroxyl groups of cellulose are also not available for co-ordination by the ions due to the high crystallinity of the cellulose. Hence, adsorption of ions remains more or less a surface phenomenon. Hence, pre-treatment or derivatization of the cellulose backbone is often attempted to improve the sorption processes in the bulk of the sorbents. The surface modification by chemical treatment usually increases the adsorption capacity of lignocellulosics (Simkovc et al., 1996). The ground corncobs modified with citric acid or phosphoric acid before were used for the selected removal of metal ions from the aqueous solutions (Vaughan et al., 2001). Reddad et al. (2002) compared binding properties the Ni^{2+} and Cu^{2+} of the native and modified sugar beet pulp. The effective removal of Cu^{2+} and Pb^{2+} by tartaric acid modified rice husk from aqueous solutions was reported by Wong et al. (2003). Min et al. (2004) reported that for effective Cd^{2+} sorption, the ideal concentration for the pre-treatment juniper was about 0.5 M of sodium hydroxide. Martin-Dupont et al. (2004) reported enhancement of Pb^{2+} binding capacities of Douglas fir bark after chemical modification. The high adsorption capacity for Cu^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} were reported for bark flour from *Pinus ponderosa* crosslinked with citric acid and consolidated into pellets (Oh and Tshabalala, 2007). Flax shive a lignocellulosic by-product was chemically activated to carbon and subsequently exposed to phosphoric acid in order to improve binding of Cd^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+} and Zn^{2+} ions. The performance of the activated carbon in the removal of Mg^{2+} was greater than a commercial drinking water filtration carbon, but lesser than that of the filters containing cation exchange resins (Marshall et al., 2007).

Grafting and network formation with monomers having active groups like $–CO_2NH_2$, $–CO_2H$ or $–SO_3H$ is often carried to improve the performance of lignocellulosics or cellulosics for use in metal ion uptake studies (Chauhan and Mahajan, 2002; Chauhan and Lal, 2003; Chauhan et al., 2005; Chauhan et al., 2006; Chauhan et al., 2007). The functional groups anchored on the backbone polysaccharide by grafting and network formation can operate via adsorption, ion exchange and the presence of these groups increases water absorption capacities of the backbone biopolymer and that also enhances metal ions partitioning between the functionalized biopolymer and the solution phase. In a novel attempt Chauhan and Mahajan (2002) reported that the metal ion uptake capacities of cellulosics based hydrogels got enhanced many times by functionalization of the anchored $–CONH_2$ by partial saponification. However, despite many such breakthroughs in the use of lignocellulosics or cellulosics as supports for the removal of cations from the aqueous solutions, there is scant information on the use of these materials as anion exchangers or anion adsorbents. For use as anion exchanger, a material should possess cationic moieties, generation of which requires derivatization reactions and use of many auxiliary chemicals. However, there are reports where a novel approach using the principle of geochemistry of existence of the some anions and Fe^{2+} ions has been reported for removal of anions from aqueous solutions. The modified starch based hydrogels loaded with Fe^{2+} have been reported as novel anion adsorbents (Chauhan et al., 2007). On the same analogy, in the present article we report use of novel hydrogels based on the total pine needles. Pine needles constitute a huge perennial renewable bioresource of the Western and Central Himalayas. At present this vast forest waste is not put to any use. In our earlier studies we used pine needles as a feedstock of cellulose to prepare hydrogels for the sorption of Fe^{2+}, Cu^{2+} and Cr^{6+} from aqueous solutions (Chauhan and Mahajan, 2002; Chauhan et al., 2005; Chauhan et al., 2006). However, in the present communication, the whole needles have been used to prepare an active, cost-effective and green hydrogels supports by functionalization with carboxymethylation and network formation. These supports were used both as cation (Fe^{2+}) and anion (NO_3^-) adsorbents. The hydrogels characterized by nitrogen analysis, FTIR, water uptake and by biodegradation studies. The biodegradability studies shows that the hydrogels were biodegradable as functionalization of the pine needles by carboxymethylation and network formation, and even after loading of the ionic species.

2. Experimental

2.1. Materials

Acrylamide and *N*,*N*-methylenebisacrylamide (Merck, Mumbai, India), Ammonium persulphate (analytical grade, Glaxo, Mumbai, India), tetramethylethylene diamine (S.D. Fine Mumbai, India), and monochloroacetic acid, ferrous sulphate, potassium nitrate (analytical grade, BDH, India) were used as received.

2.2. Carboxymethylation of pine needles

Pine needles were dried and crushed to fine powder. Carboxymethylation of total pine needles (T_{pn}) was carried out as follows. 10 g of pine needles were stirred with 18% NaOH for 1 h and 2-propanol was added to it. The contents were transferred to a bi-necked flask fitted with a separating funnel and it was heated for 45 min at 70 °C. Chloroacetic acid 14 g was dissolved in 2-propanol and added in the flask dropwise for a period of 20–30 min. It was kept undisturbed at 70 °C for 2.5 h and then cooled and neutralized with acetic acid followed by extraction with methanol. The carboxymethylated fraction was labeled T_{CMC}. The solubility of T_{cmc} was found to 67% that checked by dissolving 1 g of it in 100 mL of water. The