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Two fold modified chitosan for enhanced adsorption of hexavalent chromium from simulated wastewater and industrial effluents

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ABSTRACT

Ionic solid (Ethylhexadecyldimethylammoniumbromide) impregnated phosphated chitosan (ISPC) was synthesized and applied for enhanced adsorption of hexavalent chromium from industrial effluent. The compound obtained was extensively characterized using instrumental techniques like FT-IR, TGA-DTA, XRD, SEM, BET and EDX. ISPC showed high adsorption capacity of 266.67 mg/g in accordance with Langmuir isotherm model at pH 3.0 due to the presence of multiple sites which contribute for ion pair and electrostatic interactions with Cr(VI) species. The sorption kinetics and thermodynamic studies revealed that adsorption of Cr(VI) followed pseudo-second-order kinetics with exothermic and spontaneous behaviour. Applicability of ISPC for higher sample volumes was discerned through column studies. The real chrome plating industry effluent was effectively treated with total chromium recovery of 94%. The used ISPC was regenerated simply by dilute ammonium hydroxide treatment and tested for ten adsorption-desorption cycles with marginal decrease in adsorption efficiency.

1. Introduction

At present, heavy metal pollution in environment is of great concern towards the health of human beings (Flora, Gupta, & Tiwari, 2012). Chromium is not an omission. Chromium exists in trivalent and hexavalent states. Cr(III) is an essential nutrient for glucose, lipid and protein metabolism in mammals (Mertz, 1976) whereas Cr(VI) is highly toxic. Cr(VI) can easily diffuse in cell membranes and has tendency to cause adverse effect on human health (Katz & Salem, 2006). Exposure to Cr(VI) may lead to skin irritation, kidney, liver and gastric damage. It may cause lung cancer and is known as potential carcinogen. Effluents from various industries such as electroplating, tannery, petroleum, paints and dyeing industries contain Cr(VI) (Ma et al., 2012). Permissible limit of Cr(VI) in drinking water according to WHO guidelines is 0.05 mg/L (WHO, 1996). Therefore, for detoxification of Cr(VI), there is a need for an affirmative remediation. Conventional methods for the removal of Cr(VI) include chemical precipitation (Mirbagheri & Hosseini, 2005), redox reaction (Ölmez, 2009), mechanical filtration (Muthukrishnan & Guha, 2008), membrane separation (Korus & Loska, 2009), ion exchange (Zhang, Xia, Liu, & Zhang, 2015), and adsorption (Mohan, Singh, & Singh, 2006). Chemical methods require large amounts of chemicals and generate toxic sludge that needs further treatment. The adsorption method is preferred for the removal of heavy metals as it is economically most favourable. Use of biopolymers including cellulose and chitosan is a common practice for chromium detoxification. Properties like biocompatibility, biodegradability and good adsorption tendency enhance the utility of chitosan in pharmaceuticals, waste water treatment, flocculation etc (Alves & Mano, 2008; Dabrowski, 2001; Muzzarelli, 1973; Rinaudo, 2006).

Chitosan has also gained pronounced attention as biosorbents due to its physicochemical properties like chemical stability, high reactivity, excellent chelation behaviour and high selectivity towards pollutants (Elwakeel, 2010a, 2010b; Owlad et al., 2009). A modification of chitosan mainly involves the free amine group on deacetylated units and hydroxyl groups on C_3 and C_6 carbons of monomers units. These groups of chitosan can be grafted or crosslinked with organic and inorganic moieties to enhance the adsorption efficiency. Porous chitosan beads (Wan Ngah, Kamari, Fatinathan, & Ng, 2006), crosslinked chitosan beads (Zimmermann, Mecab̃o, Fagundes, Rodrigues, 2010), grafted chitosan (Sharma & Mishra, 2010), chitosan resin (Tan, He, & Du, 2001), magnetic chitosan resin (Elwakeel, 2010a, 2010b) and chitosan coated onto ceramic alumina (Boddu, Abburi, Talbott, & Smith, 2003) have

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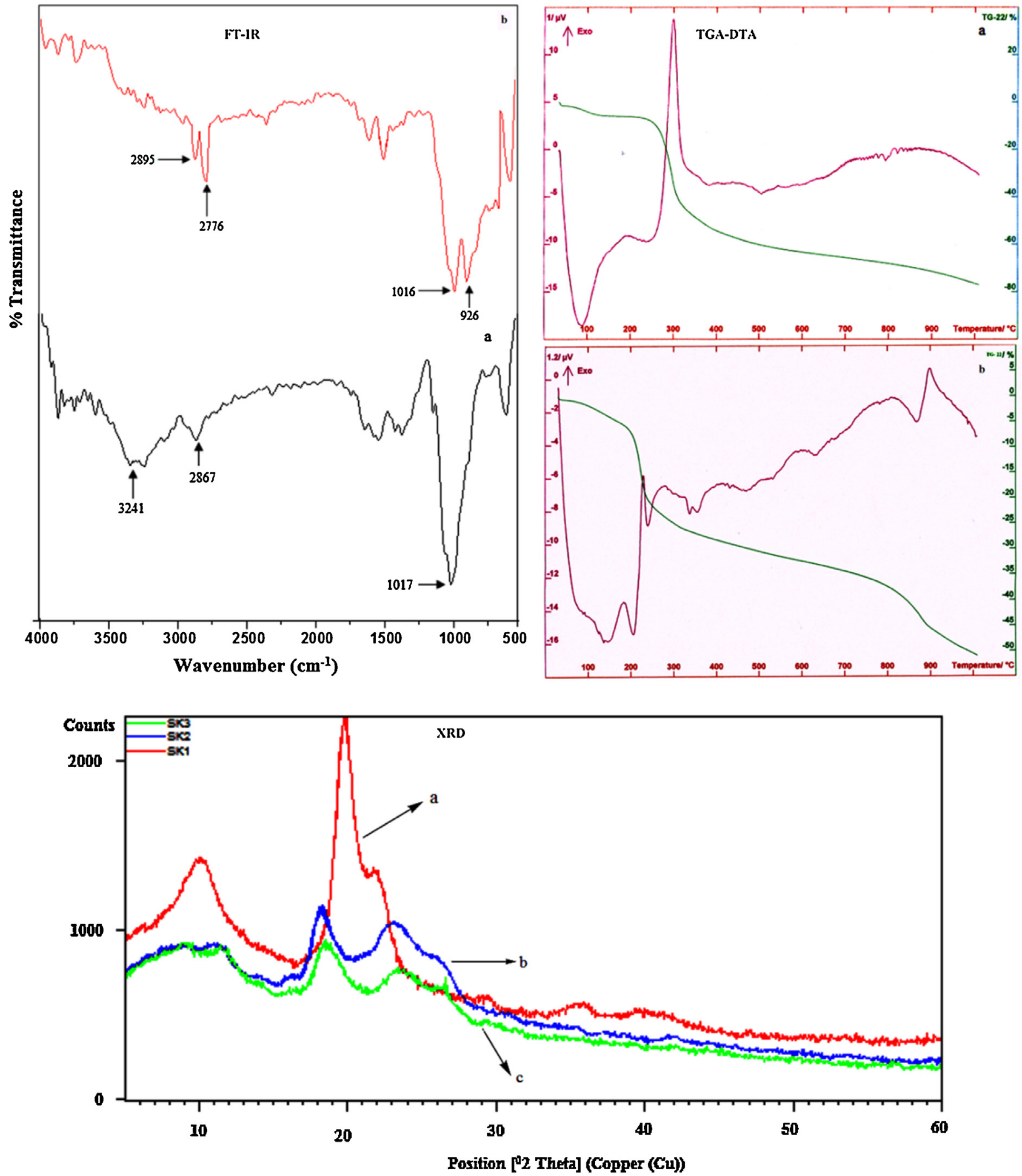

Fig. 1. FT-IR and TGA-DTA curves of (a) chitosan (b) ISPC and X-ray diffraction pattern of (a) chitosan (b) ISPC (c) ISPC with adsorbed Cr(VI).

been reported to show higher adsorption efficiency compared to untreated chitosan. Kahu et al. prepared a sulphate cross-linked chitosan for detoxification of chromium (Kahu, Saravanan, & Jugade, 2014). Anchoring of trialkyl amines on adsorbent has been reported in literature for the solid phase extraction of Cr(VI) (Kalidhasan, Kumar, Rajesh, & Rajesh, 2012; Kumar & Rajesh, 2013; Pinkert, Marsh, Pang, & Staiger, 2009; Shekhawat, Kahu, Saravanan, & Jugade, 2015).

Modification of adsorbent materials is based on two aspects-structural and functional. Both of these have been proved to enhance the adsorption capacity of the materials. In present study, we report two-fold modification on chitosan for admirable adsorption of Cr(VI). It involves crosslinking the polymeric chains with phosphate and functional modification with ionic solid ethylhexadecyldimethylammonium bromide. Crosslinking gives enhanced structural stability and porosity to the material while modification with ammonium salt leads to enhanced ionic interaction with the hydrogen-chromate species.

2. Experimental

2.1. Materials

Diphenylcarbazide, sodium hydroxide, dipotassium hydrogen phosphate, ethylhexadecyldimethylammonium bromide, and potassium dichromate were procured from Merck, India. Chitosan