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Chemical modification of rice husk by quaternized hexadecylpyridinium for removal of chromate oxyanions from aqueous solution

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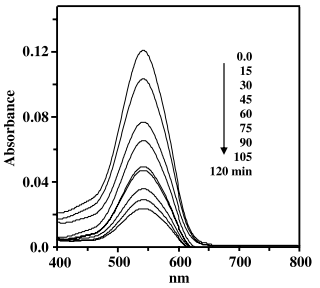
HIGHLIGHTS

- Removal of Cr(VI) ions using HDPBr modified rice husk is proposed.
- The adsorption of Cr(VI) onto HDP^+/RH involved intraparticle diffusion.
- The adsorption was described by the pseudo-second order kinetic model.
- Langmuir model was employed to fit the adsorption isotherm.
- A strong IR peak at 3429 cm^{-1} due to Cr(III)-OH is developed for HDP^+Cr(VI)/RH.

GRAPHICAL ABSTRACT



UV–Vis spectra of the effect of contact time on the adsorption of Cr(VI) from aqueous solution by HDP^+/RH.

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ABSTRACT

Rice husk was chemically modified with synthesized hexadecylpyridinium bromide (HDPBr) to enhance Cr(VI) adsorption capacity of the obtained surfactant modified rice husk (HDP^+/RH). The structure of as-synthesized HDPBr surfactant was confirmed with ^1H NMR spectroscopy. The interaction between the HDPBr molecules and the RH surface was investigated by X-ray diffraction (XRD), FTIR spectroscopy, scanning electron microscopy (SEM) and nitrogen adsorption at −196 °C. HDP^+/RH brought about decrease in the values of specific surface area, pore radius, pore size and pore volume compared with those of pure RH, indicating pore narrowing through grafting of HDPBr on the RH surface. The IR spectrum of HDP^+/RH exhibited new frequency peaks at 1614, 1490, 1115 and 1043 cm^{-1} due to vibration of pyridinium ion, fact that is indicative of the successfully anchoring of the surfactant molecules through hydrophobic bonding to the cellulose chains in RH. The adsorption of Cr(VI)-oxyanions onto RH and HDP^+/RH was investigated by batch studies at

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20 and 50 mg L^{-1} initial concentration. HDP^+/RH was evaluated as an efficient adsorbent for the Cr(IV)-oxyanions than RH, which rapidly attained equilibrium after 45 min compared with the latter at 110 min. This allows evidence for the electrostatic interaction between the Cr(VI)-oxyanions and HDP^+-promoted RH. The adsorption data fitted reasonably with the Langmuir and Freundlich models for HDP^+/RH, similarly the pseudo-second-order model shows a better fitting. The intraparticle diffusion analysis suggests that adsorption of Cr(VI) ions by HDP^+/RH involved intraparticle diffusion which contributed to the rate of the process.

1. Introduction

In recent years, the levels of toxic heavy metals in surface and ground waters have been steadily increasing due to the pollution of industrial wastewater discharges which represent a significant environmental hazard. These toxic metals include cadmium, chromium, lead, and mercury. Among all these metals, chromium species as Cr(VI) is a common contaminant in waste waters arising from industrial processes such as electroplating, production of steel, leather tanning or paint-making; due to its carcinogenic properties, it has been regulated in many countries (Malkoc et al., 2006). It is much more toxic than trivalent chromium because of its solubility in almost the whole pH range and greater mobility than Cr(III) (Vieira et al., 2008). Cr(VI) forms several species, the relative proportions of which depend on both pH and total Cr(VI) concentration. Within the normal pH range in natural waters, Cr(VI) exists mainly as CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$. Its concentrations in industrial wastewater vary from 0.5 to 270.0 mg L^{-1} (Patterson, 1985). As a guideline, World Health Organization (WHO) recommended a maximum level of 0.050 mg L^{-1} for Cr(VI) in drinking water and the National Institute for Occupational Safety and Health (NIOSH) proposed that the levels of chromium should be reduced to 10^{-3} mg L^{-1} (Afkhami and Conway, 2002; EU and WHO, 2008).

The methods employed for the removal of Cr(VI) from wastewater include reduction, precipitation, reverse osmosis, ion exchange and electrodialysis (Kobya, 2004; Ranganathan, 2000). However, these treatment methods are not widely practiced due to their high operation costs and problems in the disposal of the residual metal sludge (Bishnoi et al., 2004). Adsorption is an economically feasible alternative approach, which is effective and versatile in removing chromium, particularly when combined with appropriate regeneration steps (Dakiky et al., 2002). The use of activated carbon as an adsorbent is still very popular and different grades are available, but are quite expensive (Gupta et al., 2001).

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view (Babel and Kurniawan, 2003; Bailey et al., 1999). Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, when these materials the end of their lifetime, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for natural sorbents. One of the new developments in recent years for the removal of harmful toxic heavy metals from water and wastewater is to use rice straw which is an effective adsorbent and, besides, to reduce or eliminate rice straw burning as the means for disposal.

To enhance the capacity of substrates to adsorb cations, many functional/surface modification methods have been introduced which include chemical or physical treatment (Krishna et al., 2000; Li and Bowman, 2001; Bingol et al., 2004). Among these methods, the surface modification method using surfactants can significantly enhance the capacities of substrates to absorb heavy metals (Torres et al., 2012; Namasivayam and Sureshkumar, 2008; Deng et al., 2013; Zhao et al., in press; Miranda et al., 2014). These studies were based on their properties as surfactants and catalysts. There is no data in the literature about the synthesis of adsorbent materials containing quaternary ammonium groups synthesized through the quaternization of amino-functionalized rice straw applied to chromium oxyanions removal. In this study, adsorption of Cr(VI) ion onto HDP^+/RH was tested as a function of contact time, initial Cr(VI) concentration and solution pH in batch mode. The sorption kinetics and isotherms of these materials were described. Characterization at elucidating the HDPBr dopant and the HDP^+/RH interaction with Cr(VI) oxanion species was done using XRD, FT-IR, N_2 adsorption and SEM studies.

2. Experimental

2.1. Materials

The materials used were potassium chromate [Merck], 1,5-diphenylcarbazide [Merck], 1-bromohexadecane [Fluka], pyridine [Fluka] and ethanol (Adwic).

2.2. Cleaning rice husk

Dry raw rice husk (RH), as obtained from rice field, was firstly cleaned by sieving to eliminate residual rice and clay particles, washed thoroughly with distilled water, filtered and air-dried in room temperature. Chemical composition of the