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Thiol-incorporated activated carbon derived from fir wood sawdust as an efficient adsorbent for the removal of mercury ion: Batch and fixed-bed column studies

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ABSTRACT

The thiol-incorporated activated carbon (AC) was produced from fir wood sawdust by treating it chemically with phosphoric acid at five different impregnation ratios and used as adsorbent for Hg^{2+} ion in batch and fixed bed systems. The raw material and ACs samples were characterized by means of proximate and ultimate, FTIR, SEM, and BET analyses. The BET surface area of the prepared AC enhanced from 1273 m^2/g to 1789 m^2/g along with an increase in the impregnation ratio of H_3PO_4 from 1 to 1.5 g/g and then decreased to1593 m^2/g. AC-$H_{1.5}$ and the AC-S (modified AC) samples had the highest (1789 m^2/g) and lowest surface area (1162 m^2/g). The effects of various parameters such as contact time, adsorbent dose, pH and initial Hg^{2+} concentration for the removal of Hg^{2+} were studied in a batch process. The Hg^{2+} ion removal efficiency increased by increasing the adsorbent dosage from 0.25 to 2 g/L and the pH from 2 to 8. The equilibrium data fitted to the Freundlich, Langmuir and Redlich–Peterson isotherms, but gave a better fit to the Redlich–Peterson model. The maximum monolayer adsorption capacity of the mercury ion onto the AC-S sample (129 mg/g) was more than that onto the AC-$H_{1.5}$ (107 mg/g). The results showed that the adsorption process fitted the pseudo-second-order kinetic models. In a fixed-bed column adsorption, the effects of bed height, flow rate and Hg^{2+} concentration on the breakthrough curve were investigated, on which the adsorption capacity predicted both by the Yan and Thomas models was found to be satisfactory with that determined by integrating the total area above breakthrough curves. The desorption of AC adsorbent was investigated with several acids (HCl, HNO_3, H_2SO_4 and H_3PO_4) and bases (KOH, NaOH and $NaCO_3$).

1. Introduction

Water pollution caused by disposal of effluents containing heavy metal ions has become one of the most vexing environmental problems (Rao et al., 2009). Mercury is a heavy metal with the toxic effects for human and environment that has been identified as carcinogenic and mutagenic. The toxicity of mercury is dependent on the concentration and its chemical form (Tuzen et al., 2009a). Exposure to high concentrations of mercury leads to kidney and pulmonary disease,

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neurosis and chest pain (Zhang et al., 2005). The allowable amount of mercury in drinking water is 1 ng ml^{-1} that was recommended by the world health organization (WHO) (Tuzen et al., 2009c). Even a low level of mercury because of its capacity to accumulate in the food chain is harmful. The major sources of mercury pollution are the waste of the chlorine-alkali, pulp and paper, oil refinery, tire processing and fertilizer industries (Rao et al., 2009). Therefore, mercury must be removed from industrial wastewater before it is discharged into the environment. The conventional methods of removing any heavy metal are chemical precipitation, ion exchange, coagulation and flocculation, membrane filtration, electrochemical treatment and adsorption (O'Connell et al., 2008). Among these techniques, adsorption is considered as one of the important ones. Several adsorbents have been used for mercury removal from wastewater such as fly ash (Rio and Delebarre, 2003), lichen biomass (Tuzen et al., 2009b), moss biomass (Sari and Tuzen, 2009), sulfur-impregnated coal (Wajima and Sugawara, 2011), streptococcus pyogenes loaded Dowex optipore SD-2 (Tuzen et al., 2009c), glutaraldehyde cross-linked chitosan, barbital-glutaraldehyde cross-linked chitosan, (Kushwaha and Sudhakar, 2011), chitosan-coated diatomite (Caner et al., 2015), palm shell activated carbon (Ismaiel et al., 2013), waste antibiotic arterial activated carbon (Budinova et al., 2008), furfural activated carbon (Yardim et al., 2003), walnut shell activated carbon (Zabihi et al., 2009), and etc. Among these adsorbents, AC, due to its excellent properties, has become the most popular and widely used adsorbents for wastewater treatment (Ho and McKay, 2003). AC is a form of porous carbon with a high surface area, used extensively as adsorbent in removal of organic and inorganic pollutants from gas and liquid phases (Hayashi et al., 2005). For the elimination of contaminants, the efficiency of AC is subject to the criteria of surface area, pore volume, pore size distribution and surface chemistry (i.e., functional groups and polarity) (Nieto-Delgado et al., 2011), which are determined as a consequence of the phys1ical and the chemical properties of the precursor and the preparation method (Nahil and Williams, 2012). AC can be produced from a wide range of carbonaceous raw materials such as date stone (Bouhamed et al., 2012), alga (Padmesh et al., 2005), eucalyptus wood (Heidari et al., 2014a; Heidari et al., 2014b) and so forth. Out of these feedstocks, woody materials are significant sources for AC preparation, because they contain appropriate carbon fractions and low ash content (Wu and Tseng, 2006). The wood of fir is a good candidate for the production of activated carbon, because it is often used as pulp or in manufacturing plywood and rough timber, as a consequence has many residues. Some research has been carried out in this regard; for example, Lin et al. (2013) investigated the influence of heat pretreatment during impregnation on the production of AC from Chinese fir wood by H_3PO_4. Also, Wu and Tsengb (Wu and Tseng, 2006) prepared activated carbon from fir wood by KOH, using it as adsorbent, so as to remove dyes and phenols from water.

The purpose of this study was to investigate the mercury adsorption behavior of the AC-based fir wood sawdust in the batch and column modes. To achieve this objective, the AC was prepared with different impregnation ratios of the activating agent (H_3PO_4) to fir wood sawdust of 0.75, 1.0, 1.5, 2.0 and 2.5 g/g. Thus, the thiol-incorporated AC process was carried out with sulfur at a mass ratio of sulfur to H_3PO_4-impregnated AC of 1:3 g/g. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetry analysis (TGA), and BET surface area and proximate and ultimate analyses were used to characterize the adsorbent thus obtained. The effects of the various operational parameters of mercury removal in terms of adsorption capacity were evaluated.

Table 1 – Characteristics of fir wood sawdust.

Elemental analysis	%	Proximate analysis	%
Carbon	45.51	Moisture	12.18
Hydrogen	5.83	Volatile matter	74.69
Nitrogen	0.001	Ash	0.42
Oxygen	48.66	Fixed carbon	12.71
Thermal value (MJ/kg)	17.70	Compounds analysis. %	
		Cellulose	55.07
Density, g/cm^3	0.42	Hemicellulose	14.05
		Lignin	27.57
		Extractive material	3.30

2. Materials and methods

2.1. Feedstock and reagents

Fir wood sawdust, used as raw material for the production of AC, was acquired from the woodcraft factory in the north of Iran. The proximate and the ultimate analyses for the fir wood sawdust and its component percentage are summarized in Table 1. The chemical substances such as zinc chloride ($ZnCl_2$), 1,5-diphenylthiocarbazone(dithizone), hydrochloric acid (HCl), mercury chloride ($HgCl_2$), sulfuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium carbonate ($NaCO_3$) and cetyltrimethylammonium bromide (CTAB) were purchased from the Merck Company (Germany). Also, methanol and sodium acetate ($C_2H_3NaO_2$) were acquired from Scharlo (Spain) and New Chem Company (India), respectively.

2.2. Preparation of activated carbon

Prior to carrying out the experiments, the fir sawdust was sieved through a 60 mesh (<0.25 mm), then dried in oven at 110 °C for 24 h. In order to prepare the AC, the dried precursor of sawdust was impregnated with H_3PO_4 at five different mass ratios of H_3PO_4 to fir sawdust of 0.75, 1.0, 1.5, 2.0 and 2.5 g/g, used as an activating agent. The prepared sample was denoted as AC-$H_{0.75}$, AC-$H_{1.0}$, AC-$H_{1.5}$, AC-$H_{2.0}$, AC-$H_{2.5}$, respectively. The mixture was kept at room temperature for 1 h for completing the reaction between H_3PO_4 and sawdust, then, after drying at 110 °C for 24 h, it was carbonized under N_2 flow (100 ml/min) in a horizontal CVD furnace at 500 °C for 2 h. After this carbonization time and cooling the quartz reactor down to room temperature, the material, thus obtained, was washed with 100 ml of 0.1 M NaOH and distilled water (several times until it reached a neutral pH) in order to remove any residual H_3PO_4 and other formed inorganic matter. Then, it was dried again at 110 °C for 24 h and kept in a bottle for characterization and adsorption tests.

2.3. Synthesis of thiol-incorporated activated carbon

Among different prepared activated carbons, AC-H1.5 was chosen for a surface modification with thiol group to get