



Research article

Novel biosorbent with high adsorption capacity prepared by chemical modification of white pine (*Pinus durangensis*) sawdust. Adsorption of Pb(II) from aqueous solutions



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ABSTRACT

The natural sawdust (NS) from white pine (*Pinus durangensis*) was chemically modified by a hydrothermal procedure using citric, malonic and tartaric acids. The adsorption capacity of modified sawdust (MS) towards Pb(II) was considerably enhanced due to the introduction of carboxylic groups on the surface of MS during the modification, and the adsorption capacity was almost linearly dependent on the concentration of carboxylic sites. The NS surface was acidic, and the MS surface became more acidic after the modification. At $T = 25\text{ }^{\circ}\text{C}$ and $\text{pH} = 5$, the maximum adsorption capacity of the optimal MS towards Pb(II) was 304 mg/g, which is exceptionally high compared to NS and other MS reported previously. The adsorption capacity of MS was considerably reduced from 304 to 154 mg/g by decreasing the solution pH from 5 to 3 due to electrostatic interactions. The adsorption of Pb(II) on MS was reversible at $\text{pH} = 2$, but not at $\text{pH} = 5$. The contribution percentage of ion exchange to the overall adsorption capacity ranged from 70 to 99% and 10–66% at the initial pH of 3 and 5, respectively. Hence, the adsorption of Pb(II) on MS was mainly due to ion exchange at $\text{pH} = 3$ and to both ion exchange and electrostatic attraction at $\text{pH} = 5$.

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1. Introduction

Lead is one of the four heavy metals that can cause serious harmful effects on the human health resulting in damages to the kidneys, nervous system, reproductive system, liver and brain. Lead is used extensively in the production of car batteries, pigments, paintings, welding, ammunition and ceramics. Due to these applications, high lead concentrations are frequently found in surface, underground and residual waters (Emsley, 2003; Wang et al., 2009).

The removal of Pb(II) from aqueous solutions is usually achieved using technologies such as adsorption, ion exchange, chemical precipitation, ultrafiltration and electrochemical deposition (Lin and Juang, 2002; Li and Bowman, 2001; Valcárcel-Cases and Gómez-Hens, 1988; Volesky, 2003). These separation processes are not entirely economically feasible due to their relatively high costs. Therefore, it is important to study new processes, which are

more efficient and economical.

In recent years, biosorption has been successfully employed to eliminate heavy metals polluting water solutions. Several low-cost biosorbents have been tested for the removal of heavy metals from water solutions. Among these biosorbents are sugarcane bagasse (Demirbas, 2008), coconut husk (Hasan and Ahmad, 2006), peanut husk (Chamarthy et al., 2001), banana stem (Annadurai et al., 2002), spent grain (Low et al., 2000), bagasse fly ash (Srivastava et al., 2006) and coir pith (Namasivayam and Kadirvelu, 1998).

The sawdust is a biomaterial mainly composed of cellulose (40–50%), hemicellulose (20–40%) and lignin (20–40%) (Lee, 1992; López-Miranda et al., 2009). The sawdust is a biowaste of the wood industry, and its accumulation constitutes a serious pollution and health problem (Akunwa et al., 2014; Malström et al., 1999).

Recently, the use of sawdust from different species of wood for removing heavy metals from aqueous solutions has attracted much attention (Adouby et al., 2007; Akunwa et al., 2014; Bulut and Tez, 2007; Li et al., 2007; Prado et al., 2010; Taty-Costodes et al., 2005; Šćiban et al., 2006). Li et al. (2007) studied the adsorption of Pb(II), Cr(III) and Cu(II) on poplar sawdust at $\text{pH} = 4$ and $T = 25\text{ }^{\circ}\text{C}$. The adsorption capacities of the poplar sawdust were 21.05, 5.25 and

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6.58 mg/g for Pb(II), Cr(III) and Cu(II), respectively. The effect of the temperature on the adsorption of Pb(II), Cd(II) and Ni(II) from water solution on walnut sawdust at constant pH = 4, was investigated by Bulut and Tez (2007) and found that the adsorption capacity of the sawdust was slightly affected by the temperature in the range of 25–60 °C.

The adsorption capacity of sawdust towards heavy metals can be enhanced by modifying the physicochemical properties of its surface. The modification has been carried out using various reagents such as formaldehyde (Baral et al., 2006); hydrochloric, sulfuric and phosphoric acids (Argun et al., 2007; Jeon and Kim, 2009; Meena et al., 2008); sodium hydroxide (Ściban et al., 2006); and citric and tartaric acids (Gode et al., 2008; Yang et al., 2010). Jeon and Kim (2009) modified oak sawdust with phosphoric acid to adsorb Pb(II) from a water solution and reported a maximum adsorption capacity of 192 mg/g at pH = 4. Recently, Yang et al. (2010) investigated the adsorption of various metallic cations (Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)) from aqueous solutions on pine (*Pinus desiniflora*) sawdust modified with 6 M solutions of citric and tartaric acid. At pH = 4.5 and T = 24 °C, the capacities of the sawdust modified with citric acid for adsorbing Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) were 12.8, 15.1, 9.80, 48.5 and 9.16 mg/g, respectively, while those of the sawdust modified with tartaric acid were 11.8, 11.2, 7.63, 38.3 and 9.22 mg/g. Besides, it was observed that the adsorption capacity augmented by increasing the solution pH (Yang et al., 2010). In all the cases, the chemically modified sawdust presented a higher adsorption capacity than that of the natural sawdust.

This work was aimed at enhancing the adsorption capacity of sawdust towards Pb(II) from aqueous solution by modifying the sawdust surface. The modification was carried out by a hydrothermal method and using solutions of citric, malonic and tartaric acids. The carboxylic groups were bound to the sawdust surface during the modification. Moreover, the effect of the degree of modification, solution pH and temperature on the capacity of sawdust for adsorbing Pb(II) was also analyzed in detail and the adsorption mechanism of Pb(II) on modified sawdust was as well elucidated.

2. Materials and methods

2.1. Sawdust and stock solution of Pb(II)

The natural sawdust (NS) used throughout this work was from white pine (*Pinus durangensis*). The NS was washed several times with deionized water to remove dust, and it was dried in an electric oven at 80 °C for 24 h. Subsequently, the NS was milled with an analytic mill, sieved to an average particle diameter of 0.16 mm, and stored in a plastic container.

A Pb(II) stock solution of 1000 mg/L was prepared in a 1000 mL volumetric flask by dissolving a particular mass of reagent grade Pb(NO₃)₂ (JT Baker) in deionized water.

2.2. Modification of sawdust

The sawdust (NS) was modified by a hydrothermal method using aqueous solutions of citric (C), malonic (M) and tartaric (T) acids, and the method was as follows. A portion of 20 g of NS and 200 mL of an organic acid solution were added to an Erlenmeyer flask. The concentrations of the C, M and T acids were 0.5, 1 and 2 M. In a magnetic heating plate, the solution and NS were heated at T = 60 °C and continuously stirred for 2 h. Afterwards, the solution and modified sawdust (MS) were allowed to cool down to room temperature, and then the MS was separated by decanting the acid solution. Immediately, the MS was heated in an oven at 80 °C for 12 h. The MS was allowed to cool down and was washed repeated

times with deionized water until the pH of the washing solution remained constant. A similar hydrothermal method was applied to the modification of corncob (Leyva-Ramos et al., 2012).

Depending on the organic acid and its concentration used in the modification, the MS were designated as MSC2, MSC1, MSC0.5, MSM2, MSM1, MSM0.5, MST2, MST1 and MST0.5. The third letter of the denomination represents Citric (C), Malonic (M) and Tartaric (T) acids, and the last numbers correspond to the molarity of the acid solution.

2.3. Chemical composition of natural and modified sawdust

The moisture and ash contents were determined by standard gravimetric methods (AOAC, 1990). The ether extract of wood was quantified by successive extractions with cyclohexane, acetone, methanol and water, and the lignin was quantitatively assessed by the method proposed by Runkel and Wilke (1951). The total content of cellulose and hemicellulose was quantified as holocellulose by the method proposed by Wise (Bernabé-Santiago et al., 2013).

2.4. Characterization of natural and modified sawdust

The morphologies of the particles and surface of NS and MS were examined by a Scanning Electron Microscope (SEM), Philips, XL-30-SFEG. The textural properties (surface area, pore volume and mean pore diameter) were determined using a surface area and porosimeter analyzer, Micromeritics, ASAP 2010; and the surface area was calculated by the N₂-BET method.

The surface functional groups of the NS and M were identified by Infrared Spectroscopy. The IR spectra were obtained with a Fourier Transform Infrared (FTIR) spectrophotometer, Thermo-Scientific, Nicolet iS10, and using the technique of Attenuated Total Reflectance (ATR).

2.5. Determination of active sites

The concentration of the active sites of the NS and MS were determined by the acid-base titration method proposed by Boehm (1994). The total acidic and basic sites were neutralized with 0.01 N NaOH and HCl solutions, respectively. The total acidic sites comprised the carboxylic, phenolic and lactonic sites. Additionally, the carboxylic and lactonic sites were titrated with a 0.01 N Na₂CO₃ solutions, and the carboxylic sites with a 0.01 N NaHCO₃ solutions. The phenolic sites were evaluated by subtracting the carboxylic and lactonic sites from the total acidic sites.

The procedure for determining the active sites can be described as follows. A portion of 0.1 g of the adsorbent and 45 mL of a neutralizing solution were added to a plastic bottle. After five days, a 40 mL sample of the neutralizing solution was taken out and was titrated with a 0.1 N NaOH or HCl solution, as required. The titration was performed by triplicate using an automatic titrator, Mettler-Toledo, model DL50, and the experimental error for the titration was calculated to be less than 1%.

2.6. Determination of surface charge distribution and point of zero charge

The surface charge of the NS and MS was determined by the procedure described below. Twenty three neutralizing solutions with pH ranging between 2 and 12 were prepared by adding between 0 and 7.2 mL of 0.1 N NaOH and HCl solutions to 100 mL volumetric flasks and filling up to the mark with a 0.1 N NaCl solution. In a 50 mL polypropylene bottle, 0.1 g of the biosorbent and 45 mL of the various neutralizing solutions were added, and then nitrogen was bubbled for 2 min to prevent the formation of

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