Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Acid activation pine cone waste at differences temperature and selective removal of Pb^{2+} ions in water

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ARTICLE INFO

Article history:
Received 23 September 2015
Received in revised form 26 November 2015
Accepted 4 December 2015
Available online 15 December 2015

Keywords:
Regeneration
Acid-treatment
Ion exchange
Adsorption cost
Lead
Pine cone

ABSTRACT

This study reports potential application of pine cones (PC) and acids treated pine cone at as adsorbents for removal of Pb^{2+} ions in water. Two different types of acids were used for the treatment of PC at different activation temperature, with the following combination of hydrochloric -acid treated PC at 25 °C (PC-H25) and 50 °C (PC-H50); phosphoric-acid treatmented PC at 25 °C (PC-P25) and 50 °C (PC-P50). The basic physicochemical properties of PC, both before and after acid treatment, were characterized using scanning electron microscopy (SEM), Fourier-transformed infrared spectroscopy (FTIR) and elemental analysis (EA). Bath adsorption experiments on Pb^{2+} ions were optimized in term of pH, adsorbent dose, reaction time and initial concentration of Pb^{2+} ions. It was estimated through adsorption isotherm analysis that adsorption capacities of PC-H25, PC-P25, PC-H50 and PC-P50 on Pb^{2+} ions were 132.6, 108.2, 148.3 and 119.8 mg/g, respectively. Desorption studies revealed the promising regeneration potential of PC, PC-H25, PC-H50, PC-P25 and PC-P50. It was found that the percentage removal of Pb^{2+} was maintained at more than 60% as compared to the initial value, even after 5 adsorption–desorption cycles. Furthermore, the adsorption costs required for removal of Pb^{2+} ions using PC, PC-P25, PC-P50, PC-H25, PC-H50 were estimated to be 1.6, 11.5, 17.5, 6.7 and 8 US$/kg, respectively. Based on these findings, PC and acid-treated PC could be used as low-cost, eco-friendly and effective adsorbents for the Pb^{2+} removal from water.

1. Introduction

The primary threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, and arsenic (Namasivayam and Senthilkumar, 1995; Manahan, 1994; Volesky, 1990; Bailey et al., 2008; Gloaguen and Morvan, 1997; Necip et al., 2012). The presence of these heavy metals in the environment is of significant concern due to their toxicity and adverse health effects on humans and other living creatures. Lead is a particularly dangerous chemical as it can accumulate in individual organisms as well as entire food chains. Children are particularly susceptible to lead exposure due to its high gastrointestinal uptake and ability to permeate the blood–brain barrier (Bailey et al., 2008; Aklil et al., 2004; Sánchez et al., 1999; Gaballah and Kilbertus, 1998; Low et al., 2000; Gloaguen and Morvan, 1997). The major source of

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http://dx.doi.org/10.1016/j.psep.2015.12.002

lead pollution in wastewater is from the discharge of waste from acid battery manufacturing, metal plating, printing, metallurgical alloying, and lead mining. Additional important source include cable coverings, plumbing, ammunition, fuel additives, paint pigments, PVC plastics, X-ray shielding, crystal glass production, and pesticides. Some technologies and methods for heavy metal ion removal from wastewater have been developed, including ion exchange, evaporation and concentration, chemical precipitation, reverse osmosis, adsorption, and electrodialysis (Pagnanelli et al., 2001; Kapoor et al., 1999). From an economy and efficiency perspective, adsorption methods are regarded as the most promising methods given their low operating costs, minimized chemical volumes, and high efficiencies.

Activated carbon was first used to treat water over 2000 years ago, and is one of the most widely used adsorbents for removing heavy metals. However, its high cost poses an economical problem, which has in recent years resulted in research concerning the production of alternative adsorbents to replace activated carbon. Many studies have focused on the various natural materials that are able to remove heavy metals from water (Kumar and Dara, 1981; Orhan and Büyükgüngör, 1993; Wang et al., 2009; Sen Gupta et al., 2009; Mata et al., 2009; Salim et al., 2008; Aydin et al., 2008; Prasad and Freitas, 2000; Ajmal et al., 1998, 2003; Khalid et al., 1999; Hasar, 2003; Gloaguen and Morvan, 1997; Gaballah and Kilbertus, 1998; Low et al., 2000; Bailey et al., 2008). Adsorbents from agricultural waste, forestry waste, and industrial waste have all been shown to work for water treatment and are being considered as potential alternatives to existing technologies for the removal and/or recovery of toxic metals. The major advantages of this adsorption method includes its effectiveness for reducing the concentration of heavy metal ions to very low levels and the use of cheap adsorbent materials (Katsumata et al., 2003; Bailey et al., 2008; Orhan and Büyükgüngör, 1993; Ho et al., 1996; Necip et al., 2011; Kaya et al., 2016).

Coniferous forests account for 42% of the total forested land in Korea. Within coniferous forests in Korea, red pine and pitch pine comprise the majority of tree species. While the large amounts of pine cones in Korea have been regarded as forestry waste, they have the potential to serve as adsorbent material for heavy metal removal. In general, chemically modified or treated pine cones exhibited better adsorption capacities for heavy metal ions than unmodified pine cones (Ofomaja and Naidoo, 2011a,b; Ofomaja et al., 2009, 2010a, 2010b; Vasconcelos and Beca, 1994). Chemicals used for modification of pine cones include NaOH (Ofomaja et al., 2010c, 2010b), KOH (Ofomaja et al., 2010b), $Ca(OH)_2$ (Ofomaja and Naidoo, 2011b), and organic compounds (Argun et al., 2008), most of which were able to successfully treat pine cones to achieve a high adsorption capacity for heavy metals removal. This study investigated the feasibility of using pine cones, considered a forestry waste in Korea, as an adsorbent for Pb^{2+} ions from aqueous solution using pine cones treated with HCl and H_3PO_4 at activation temperatures of 25 °C and 50 °C.

2. Materials and methods

2.1. *Adsorbent preparation*

Pine cone samples were collected from a mountainous area located 500 m from the University of Ulsan in Ulsan, South Korea. Collected pine cones were washed with deionized water to remove impurities such as dirt, sand, and leaves. Pine cones were then dried at 90 °C for 12 h. The dried pine cone samples were sieved using mesh (DA-354) to obtain a uniform particle size range between 150 and 200 μm. The sieved pine cones were then stored in an airtight plastic container until they were used for acid treatment.

Size segregated pine cones of 10 g were mixed with 100 mL of 0.5 M HCl or H_3PO_4 at room temperature. The reaction mixture was stirred with a magnetic stirrer for 12 h at 25 °C or 5 h at 50 °C. The acid treated pine cones were then filtered and repeatedly washed with distilled water. The resulting washed cones were dried overnight in an oven at 50 °C and used for physical and chemical property characterization.

2.2. *Chemical, reagents, and analytical methods*

All of the chemicals used in this study were of analytical reagent grade (obtained from Daejung Chemical and Metals Co. LTD., South Korea) and used as received without further purification. Aqueous solutions of $Pb(NO_3)_2$, HCl and H_3PO_4 were prepared by dissolving lead nitrate, $Pb(NO_3)_2$ (Merck), and respective acids in deionized distilled water. The pH measurements were performed with a Digital pH meter (Orion 5Star). The concentration of Pb^{2+} ions were measured using an atomic absorption spectrophotometer (VARIAN AA240) at $\alpha = 217$ nm and slit width 1 nm under an air–acetylene flame. Scanning electron micrographs (SEM Hitachi 4700 microscope) were taken for the surface morphology analysis of pine cones and acid-treated pine cones. Infrared spectra (Perkin-Elmer infrared spectrophotometer) were obtained using a Nicolet Nexus 470 FTIR spectrometer in the 4000–500 cm^{-1} region in transmission mode and IR samples were prepared in the form of pellets with KBr at ambient conditions. Final analysis was performed using an elementary analyzer (Elementar Analysensysteme GmbH, Germany), and provided composition information of the pine cone samples studied in terms of the weight fraction (wt%) of contained elements including carbon (C), hydrogen (H), oxygen (O), and sulfur (S).

2.3. *Adsorption experiments*

Batch experiments for adsorption studies to remove lead ions (Pb^{2+}) from aqueous solutions were performed in 250 mL Erlenmeyer flasks, which were agitated in a Shaking water bath (HST-205SW at 120 rpm) at room temperature for 20 ± 1 °C.

2.3.1. *Optimization of pH*

In order to evaluate the effect of pH on metal uptake by acid-treated pine cones, we adjusted the pH of the experimental solutions from 2 to 6.5. The solution pH values adjusted to the required values with 0.1 M HNO_3 and 0.1 M NaOH. Solutions containing initial concentrations of 200 mg/L of lead ions and 0.5 g of adsorbent were used to determine the optimal pH.

2.3.2. *Optimization of reaction time*

Adsorption experiments were performed in 100 mL of a solution of 200 mg/L Pb^{2+}, and the contact time was varied from 10 to 150 min. After adsorption for a given reaction time, the concentration of Pb^{2+} that remained was analyzed.

2.3.3. *Optimization of Pb^{2+} initial concentration*

Batch tests were conducted at different initial concentrations of Pb^{2+} ions ranging from 100 to 1000 mg/L with an adsorbent dose of 0.5 g and a reaction time of 60 min. The equilibrium