Adsorption removal of zinc (II) from aqueous phase by raw and base modified Eucalyptus sheathiana bark: Kinetics, mechanism and equilibrium study

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Abstract

In this study, potential application of abundantly available agricultural by-product Eucalyptus sheathiana bark in its raw and sodium hydroxide (NaOH) modified form to remove Zn²⁺ from its aqueous solutions was investigated by considering parameter identification and optimization, reusability, equilibrium, kinetic and thermodynamic studies. The adsorbent was characterized by SEM-EDX, FTIR, XRD, BET surface area and bulk density and point of zero charge were also determined. The process was strongly pH dependent and the adsorption percentage of Zn²⁺ was increased with an increase in solution pH from 2.5 to 5.1. Conversely, the adsorption percentage of Zn²⁺ decreased with the increase in adsorbent dosage, initial metal concentration, temperature and ionic strength. Kinetic measurements showed that the process was multistep, rapid and diffusion controlled. It was found to follow the pseudo-second-order rate equation. Equilibrium adsorption studies showed that both Freundlich and Langmuir models are applicable for both raw and base modified eucalyptus bark. MPSD error function was used to treat the equilibrium data using non-linear optimization technique for evaluating the fit of the isotherm equations. The maximum sorption capacity of modified eucalyptus bark was 250.00 mg/g at 30°C which was comparative to other adsorbents. Various thermodynamic parameters indicate that the process was spontaneous and physical in nature. Desorption studies were also performed to determine possible recovery potential of Zn²⁺ and the re-usability of the biomass and to identify the mechanism of adsorption.

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1. Introduction

The main sources of zinc entering the environment are from the wastewater discharging through many industrial sectors such as the manufacturing of brass and bronze alloys, purifying zinc, lead and cadmium ores, steel production, coal burning and burning of wastes (Bhattacharya et al., 2006). Zinc is also present in high concentration in wastewater of pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, etc. that causes serious problem to the environment (Bhattacharya et al., 2006). Zinc is an essential element for life and acts as a micronutrient when present in trace amounts (Sen and Gomez, 2011). The maximum contamination levels (MCLs) of heavy metals for surface or groundwater to be used in the drinking supply set up by The United States Environmental Protection Agency (USEPA) was a maximum acceptable concentration of zinc is 0.8 mg/L (Nguyen et al., 2013). Beyond the permissible limits, Zn²⁺ is toxic and the symptoms of zinc toxicity include irritability, muscular stiffness, loss of appetite and nausea (Safe Drinking Water Committee and National Research Council, 1977). Various advanced chemical or physical treatment processes such as electrocoagulation, ion exchange, irradiation, ozonation, membrane separation, advanced oxidation, adsorption on activated carbon are applied for the removal of heavy metal ions including Zn²⁺ ions from aqueous solutions. Most of the treatment processes have their own advantages and disadvantages. Among all these
hydroxide solution has been the most popular method of improving surface properties and removing soluble organic components of plant wastes applied for adsorption (Ofomaja et al., 2009). Dilute sodium hydroxide solution treatment onto lingo cellulosic agricultural waste adsorbents is known to solubilize a small fraction of the lignin and soluble organics in the plant waste (Wartelle and Marshall, 2000); improving the penetration of modifying agents into the biosorbent matrix and thereby increasing porosity and changing surface properties and hence metal sorption capacity (Ofomaja et al., 2009). Several investigators reported the effectiveness of chemically modified agricultural biomass in the removal of metals and dyes and authors are encouraged to go through a few recently published review articles such as Afroze et al. (2015a), Gautam et al. (2014), and Hubbe et al. (2011).

Eucalyptus trees are evergreen, fast growing and abundantly available worldwide. Due to the high number of eucalyptus trees, massive amounts of barks are disposed each year in Australia as waste material. Cost consideration of an adsorbent is an important parameter for selection and design of an adsorption process. In general, a sorbent can be assumed to be “low cost” if it requires little processing and is abundant in nature, or waste material either from industry or agricultural by-product with almost no economic value. Eucalyptus bark is freely available, non-hazardous in nature and with throughput price which fulfills the precursor to become a low cost adsorbent alternative to costly commercial adsorbents. Hence the utilization of this agricultural solid waste as adsorbent is of great significance in liquid-phase contaminant separation and also in efficient solid waste management. Previously eucalyptus barks were used in the adsorptive removal of Cu(II), Cr(III), Cd(II), Ni(II) (Saliba et al., 2002), and Hg(II) (Ghodbande and Hamdouli, 2008) from aqueous phase. It was observed that eucalyptus bark is an efficient sorbent for the removal of these metal ions. Therefore the aim of this present research work were to (a) evaluate the effectiveness of raw and chemically NaOH treated eucalyptus bark biomass in the removal of Zn(II) metal ions from its aqueous solution; (b) to study the equilibrium, kinetics, mechanism and thermodynamics of Zn(II) adsorbate onto raw and chemically treated adsorbent under various physico-chemical process conditions; (c) identify the main surface and morphological and functional groups characteristics of treated adsorbents and their mechanistic contribution towards capacity of adsorbents; (d) assess the reusability and applicability of treated eucalyptus bark in the Zn(II) adsorption; and (e) comparison of treated eucalyptus bark adsorbents capacity with other published adsorbents including commercial activated carbon.

2. Materials and methods

2.1. Materials

2.1.1. Raw adsorbent

Eucalyptus barks were collected from Eucalyptus sheathiana trees at the campus of Curtin University, Perth, Western Australia between February and March 2013. The barks were washed repeatedly with distilled water to remove impurities such as sand and leaves, and then dried at 105 °C for 24 h in an oven. The dried biomass was ground using a mechanical grinder and the resultant powder was sieved and the particles below 106 μm were collected, stored in an airtight plastic container and used for conducting adsorption experiments.

2.1.2. Chemical modification of eucalyptus bark adsorbent and characterization

A weighed amount (50 g) of raw eucalyptus bark powder was contacted with 500 mL of 0.1 M sodium hydroxide (NaOH) solution to prepare base modified eucalyptus bark powder. The whole slurry was stirred overnight with a magnetic stirrer and then the powder was filtered and rinsed with distilled water. This procedure was repeated twice to ensure removal of conventional technologies, adsorption has been recognized as one of the versatile effective technique practiced widely for heavy metal infested wastewater treatment because of its operational simplicity, sludge free operation and reuse potential of adsorbents during long-term applications (Acharaya et al., 2009; Bharathi and Ramesh, 2013). In recent years, a number of non-conventional cost effective biomass based adsorbents alternative to costly activated carbon such as pine chips (McLaughlin et al., 2015), watermelon rind (Liu et al., 2012), Cedrus deodara sawdust (Mishra et al., 2012), cashew nut shell (Senthil Kumar et al., 2012), potato peels (Taha et al., 2011), orange waste (Pérez Marín et al., 2010), eucalyptus leaf biomass (Mishra et al., 2010), Citrus reticulata (Kinnow waste (Boota et al., 2009), carrot residue (Nasernejad et al., 2005), almond shell, olive and peach stones (Ferro-Garcia et al., 1988) have been used for Zn2+ adsorption from its aqueous solution. Readers are encouraged to go through review article by Yagub et al. (2014) and Nguyen et al. (2013) in this research area. The application of agricultural solid wastes as effective adsorbents offer several advantages; their easy availability in large quantities, requirement of less processing time, renewable in nature, low cost, eco-friendly and good adsorption potential due to their unique chemical composition makes the adsorption process more attractive for heavy metal and dye remediation (Choi et al., 2012; B. Singha and Das, 2013; Sud et al., 2008). In most of the situations direct use of these raw biomass adsorbents is restricted due to their low adsorption capacity. Therefore pre-treatment of adsorbent is also commonly used to increase the adsorption capacity of these materials (Bhattacharya et al., 2006). Pretreatment with dilute sodium