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Research Paper

Preparation and characterization of magnetic biosorbent based on oil palm empty fruit bunch fibers, cellulose and *Ceiba pentandra* for heavy metal ions removal

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ABSTRACT

This study prepared, characterized and developed agro-based magnetic biosorbents (AMBs) from *Ceiba pentandra* (RKF), oil palm empty fruit bunches (EFB) and celluloses (CEL) extracted from EFB, using a novel, simple and cost-effective preparation technique for the removal of Pb(II), Cu(II), Zn(II), Mn(II) and Ni(II) ions from aqueous solutions. There has been no report on the methods to prepare and the use of magnetic biosorbent based on these biomaterials. The morphological, chemical and magnetic characterization suggested successful preparation of AMBs with good dispersion of magnetic nanoparticles on the surface of the base materials with clear magnetic properties. Optimum sorption was achieved between pH 5–7, and increase in initial ion concentration and solution temperature resulted in increased ion uptake. AMBs regeneration was successfully performed for 5 adsorption/desorption cycles. The magnetic biosorbent based on kapok showed the best Pb(II) removal efficiency of 99.4% and 49 mg/g adsorption capacity compared to 98.2% for cellulose and 97.7% for EFB. The magnetic biosorbents exhibited 10.3% higher removal efficiency than the raw sorbents.

1. Introduction

Heavy metal ions are considered as environmental health hazards, as they are placed in the top 10 in the directory of "Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances", based on the poisonousness of the material and its potential exposure from contaminated air, water and soil. A number of international agencies that include Centre for Disease Control (CDC) (Yantasee et al., 2007), World Health Organization (WHO) (Chen et al., 2013; Sharma et al., 2012), Food and Agricultural Organization (FAO) and International Agency for Research on Cancer (IARC) are dealing with the hazardous impacts of heavy metal exposure. This has made detection and bio-monitoring crucial components of environmental pollution, control and remediation strategies (Aragay et al., 2011).

Some heavy metals are essential for many biological activities at the micronutrient level, but higher concentrations have the ability to produce a range of toxic effects. In actual fact, lead, cadmium, chromium, arsenic, and mercury are even considered as toxic compounds at low concentrations (Bagal-Kestwal et al., 2008). Although harmful effects of these substances have been known for a long time, indiscriminate disposal of heavy metals are still continuing and even increasing, especially in developing countries. Among various contaminants present in the ground and surface water, inorganic heavy metals are the most difficult to remove due to their small ionic size, complicated state of presence, low concentration in high volume and competition with other non-poisonous inorganic kinds (Bailey et al., 1999).

Adsorption is among the most common methods for heavy metal ions removal due to its simplicity, feasibility and effectiveness. It is also widely utilized for both inorganic and organic material removal (Ali, 2012; Ali et al., 2012; Faust and Aly, 2013). In most cases, highly porous materials such as adsorbents can provide sufficient sorption surface area. The major bottleneck, however, is the intraparticle diffusion which causes reduced available space, leading to a decreased adsorption capacity. As the adsorption property of an adsorbent is highly affected by its intrinsic properties, modification or functionalization will significantly change the sorbent surface area, pore size distribution and surface functional groups. It is therefore necessary to develop biocompatible materials with large surface area, active surface sites and low intraparticle diffusion rate (Mahdavian and Mirrahimi, 2010). Adsorption via magnetic biosorbents (MBSs) has attracted much attention and reported as effective and applicable for field application

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due to its simple operation (Nalbandian et al., 2016). MBSs can be applied to adsorb pollutants from aqueous or effluents, which can later be separated from the medium by using a magnetic field for possible reuse for several cycles. MBSs can be designed as nano-sorbent materials for water pollution removal such as heavy metals and dyes. The advantages include a high number of active surface sites, large surface area, low intraparticle diffusion rate, high adsorption capacities and most importantly reusability, which make their utilization for water treatment more economical (Nassar, 2010; Tan et al., 2012).

In practical engineering applications, having consistent supply of raw materials at large industrial scale is of paramount importance. As environmental protection is of increasing global concern, effort to develop greener remediation technique based on biosorption has gained traction. Biosorption involves the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solutions (Volesky, 2007). Agricultural-based biosorbents are therefore attractive for economics reason and ease of applications, as these are mainly made up of cellulose, hemicellulose and lignin with high contents of hydroxyl groups and admixture of other functional groups like carboxyl, sulfhydryl carboxyl, acetamido, phenolic, structural polysaccharides, amino groups, ester and alcohols that could all enhance heavy metals ion adsorption (Okoro and Okoro, 2011). These functional groups substitute hydrogen ions for metal ions or contribute an electron pair to form complexes with the metal ions in the solutions. These binding groups make agricultural lignocellulosic wastes a promising source of adsorbent materials to remove heavy metal ions from water and wastewater (Jiménez-Cedillo et al., 2013). Natural materials such as water bamboo husk (Asberry et al., 2014), *Eucalyptus* pulp (Squissato et al., 2017), phthalate-functionalized sugarcane bagasse (do Carmo Ramos et al., 2016), oil palm empty fruit bunches (Daneshfozoun et al., 2014a, 2016), cellulose (Daneshfozoun et al., 2014b), *Ceiba pentandra* (Afzaal et al., 2014; Abdullah et al., 2015), chitosan (Tran et al., 2010), hydroxyapatite (Feng et al., 2010) and moss peat (Bulgariu et al., 2008), are among biosorbents developed for heavy metal ion sorption.

Conversion of agro-wastes into valuable products such as composite materials (Abdullah et al., 2016) or as adsorbent to remove inorganic pollutant can resolve both environmental problems: 1) reducing or recycling the wastes and 2) remediating the environment. Oil palm (Elaeis guineensis Jacq), a kind of monoecious plant, has been a cash crop in Malaysia since 1917. Palm oil has become a major contributor to the total oil and fat production in the world − increasing from 13% in 1990 to 28% in 2011 (MPOC, Malaysian Palm Oil Council 2012). Each plant can produce approximately 150 kg of fresh fruit bunches (FFB) per year and the weight of the FFB may vary from 10 to 40 kg, depending on the number of compactly bound fruitlets in the bunch (Yusoff, 2006). After the fruit has been detached from the FFB for oil extraction, the rest is called an oil palm empty fruit bunch (OPEFB). A total of 77.2 million tonnes of biomass are generated from oil palm processes, out of which, the 19.8 million tonnes on wet basis or 6.93 million tonnes on a dry basis, are OPEFB (Foo et al., 2011), making them the most abundant wastes from palm oil industries.

Ceiba pentandra (L.) Gaertn. or Kapok, from the Bombaceae family, is another agro-fibers with a high potential to be developed as sorbent materials (Abdullah et al., 2010). A mature Kapok tree bears hundreds of pods that are up to 15 cm long and filled with fibrous seeds. In contrary to cotton, which is lignified and not attached to the seed grains, kapok fiber is made up of single-celled plant hairs (Zheng et al., 2015). Kapok fibers are light brown/yellowish silky fibers which are moisture resistant, quick-drying, and buoyant, and have found applications for oil sorption (Abdullah et al., 2010) and palm oil mill effluent (POME) treatment (Afzaal et al., 2014; Abdullah et al., 2015). Natural biopolymers such as oil palm fibers, kapok and cellulose provide high capacity and selectivity for environmental remediation applications due to their different functional groups representation in the structure (Gómez-Pastora et al., 2014). The magnetic lignocellulose-based materials can resolve the continued-use issues, create high surface area-to-volume ratio and increase adsorption capacity and efficiency (Feng et al., 2010). Surface functionalized magnetic nanoparticles (MNPs) and the composite materials can further improve the costly synthesis of MNPs for wider application. The composite with core–shell nanostructures are more effective since the shell prevents the core from particle–particle combination and increases the dispersion stability of nanostructures in the suspension medium (Gómez-Pastora et al., 2014).

The objectives of this study were to develop, prepare and characterize the magnetic biosorbent based on OPEFB fibers, celluloses extracted from OPEFB and kapok fibers. To the best of our knowledge, there has yet to be any report on heavy metal ion removal using magnetic biosorbents based on these agro-materials. The OPEFB magnetic biosorbent was studied for Pb(II), Cu(II), Zn(II), Ni(II) and Mn(II) ions removal from aqueous solution. The Pb(II) ion removal efficiency was compared with Cellulose and kapok. The parameters optimized included the contact time, pH, effects of initial ion concentration and temperature and the sorbent reusability.

2. Materials and methods

2.1. Raw materials and chemicals

The raw OPEFB fibers used in this study were obtained from the FELCRA Nasaruddin Palm Oil Mill, Bota, Perak, Malaysia. The purely extracted cellulose was obtained from OPEFB fibers as reported earlier (Abdullah et al., 2016; Nazir et al., 2013). Raw kapok fiber was collected from Telok Belanja Village in Dungun, Terengganu, Malaysia. Fe_2O_3 nano-particles (5–50 nm sizes) were purchased from Merck (USA). Stock solutions of Pb(II), Cu(II), Zn(II), Ni(II) and Mn(II) were prepared from the required amount of $Pb(NO_3)_2$, $CuCl_2$, $ZnSO_4$, $NiCl_2$ and $MnCl_2$ (Merck) and dissolved in distilled water at room temperature. Other chemical reagents such as NaOH and HCl were all of analytical grade.

2.2. Preparation of magnetic biosorbent

The raw OPEFB and cellulose fibers were homogenized to the size of 0.2 mm by bench top ring mill (Rocklabs LTD, New Zealand). The fine-sized OPEFB samples were obtained by two cycle grinding of the shredded OPEFB using a grinder and a hammer mill (Janke & Kunkel). Subsequently, the ground fibers were subjected to a Planetary Mono Mill (FRITSCH GmbH) to finally achieve the size ranging from 0.005–0.02 mm.

In the case of a fine-sized raw kapok fiber (RKF) preparation, the fibers were separated out from the seeds, and the visible dust particles were removed manually. The fibers were dried in an oven at 70 °C until the moisture content was reduced to less than 1%. The dried fibers were then cut into small part, and every 3 g of the fibers were milled for 30 min at the speed of 450 rpm, in order to obtain an average size of 0.1–0.002 mm using the Planetary Mono Mill (FRITSCH GmbH).

A mixture of 50 mg of Fe_2O_3 nanoparticles and 100 mL of fine-sized base-materials (5 mg/ml) in deionized water was sonicated using an Ultrasonic Homogenizer machine (150VT, biologist, USA) for 5 min and then shaken on an orbital shaker for another 10 min before it was sonicated again. The mixture was subjected to this cycle for 3 times and placed on a permanent magnet (4000 G) to recover the magnetic sorbents. The recovered MBSs were washed with deionized water and stored at room temperature.

2.3. Characterization

2.3.1. Morphology

Morphology, shape and size of the biosorbent were analyzed using FESEM (VP- FESEM, Carl Zeiss, Supra 55VP). An Energy-dispersive X-ray (EDX) joined to the FESEM was used for elemental analysis. As the