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Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies

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ABSTRACT

The efficacy of coconut dregs residue, a by-product from coconut milk production factory, to adsorb Cu(II), Ni(II) and Pb(II) ions from aqueous solutions was investigated. The effects of experimental parameters such as solution pH, contact time and initial metal concentration on adsorption process were examined in batch experiments. The equilibrium data were best described by the Langmuir isotherm model, while the dynamical data followed the pseudo-second order kinetic model. The Freundlich constant (n) and separation factor (R_L) values suggest that the metal ions were favourably adsorbed onto biosorbent. The affinity of the biosorbent for metal ion was in the order of Pb(II) > Cu(II) > Ni(II), both in single- and multi-metal systems. The characterisation studies were carried out using scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDX) and Fourier transform infrared spectrometer (FTIR). Complexation between metal ions and binding sites of the biosorbents was the main adsorption mechanism. Coconut dregs residue removed Cu(II) better than bamboo derived activated carbon, a commercial activated carbon, from electroplating effluent.

Introduction

The release of industrial effluents containing excessive amount of toxic metals to the environment have caused serious problems with regards to water quality. Heavy metals such as Cr, Cu, Ni, Pb and Zn can be found in the effluents of metal plating, battery manufacturing, and leather finishing, mining and smelting industries [1]. Heavy metals are non-biodegradable and carcinogenic contaminants. Therefore, their presence in the environment can be harmful or nuisance to living organisms [2]. For example, high intake of Cu can cause severe mucosal and central nervous system irritation, kidney and liver dysfunction, anaemia and gastrointestinal diseases [3]. According to Bahadori et al. [4], there were 10 countries had serious water contamination issues in 2010. The top 5 countries were Brazil, USA, China, Indonesia and Japan. Due to rapid industrialisation, water pollution is becoming a serious environmental issue in Malaysia. Mohamed and Jahi [5] studied the implication of manufacturing industries within Langat Drainage Basin, Selangor. They reported that there were about 330 factories located in Langat Drainage Basin, ranging from the manufacture of agricultural end products to high-tech products such as consumer electronics. The electrical and electronic industries were reported to predominate with 53 industries, followed by factories manufacturing industrial and engineering products, building materials, chemicals, textile and fabrics, and furniture. They highlighted the rapid decline of the river's water quality, particularly metal concentration, beginning of 1991.

In order to maintain the quality of the water, several techniques have been developed to purify industrial effluents before being discharge to the main streams [6]. These techniques include membrane filtration, solvent extraction, ion-exchange, chemical precipitation, oxidation and electrodeposition [7,8]. However, many of these techniques are not practical to implement due to several drawbacks such as high operating cost, high energy consumption, low selectivity and generate toxic slurries [9]. Therefore, physicochemical approach by using adsorption method has been proposed to solve this problem.

Adsorption has been regarded as a promising and cost-effective method for heavy metals removal. This technique does not

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generate solid residues and suitable for a wide range of metal ion concentrations [2,10]. Activated carbon has been widely used as an adsorbent because it has large surface area and high adsorption capacity [11]. In spite of its excellent ability to treat industrial effluents, activated carbon is costly [12]. Therefore, alternative adsorbents derived from natural materials, agricultural and industrial wastes that are available in large quantities and cheap need to be utilised [13,14].

Coconut dregs residue is the waste obtained from coconut milk production and easily available at low-cost [15]. After extracting most of the milk from the coconut, the remaining product is called coconut dregs residue. This waste can be used to feed animal or just let to decompose on the field [15]. It was estimated that about 555,120 t of coconut have been produced in 2008 in Malaysia. From this value, approximately 510,000 t of coconut has been used [16]. So, the application of coconut dregs residue for water clean-up can offer a good solution for its disposal.

In this study, the potential of coconut dregs residue as a biosorbent to sequester Cu(II), Ni(II) and Pb(II) ions from aqueous solutions was evaluated. The effects of experimental parameters such as solution pH, contact time and initial metal concentration on metal ion adsorption were investigated. The equilibrium adsorption data were fitted with the Freundlich and Langmuir isotherm models. The adsorption rates were determined using the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models. The characteristics of the biosorbents and possible binding mechanism(s) involved were studied using SEM, EDX and FTIR.

Materials and methods

Preparation of biosorbent

The coconut dregs residue was obtained from a coconut milk production factory in Banting, Selangor. The residue was washed thoroughly with deionised water and dried in an oven at 70 °C for 7 days. The dried material was then ground and sieved through 150–250 μm size fractions using an American Society for Testing and Materials (ASTM) standard sieve. The ground material was kept in self-sealing plastic bags to avoid moisture effects.

Preparation of stock solutions

The stock solutions of 1000 mg/L were prepared by dissolving appropriate amount of $Cu(NO_3)_2{\cdot}2.5H_2O$ (HmbG Reagent Chemicals), $Ni(NO_3)_2{\cdot}6H_2O$ (Bendosen Laboratory Chemicals) and $Pb(NO_3)_2$ (Bendosen Laboratory Chemicals) salts in 0.1 mol/L KNO_3. In this study, 0.1 mol/L KNO_3 was used as an electrolyte to control the ionic strength. The stock solutions were then diluted to the required concentrations. Cu, Ni and Pb atomic absorption spectrometer (AAS) standard calibration solutions were obtained from Fisher Scientific. All reagents used were analytical reagent grade, and deionised water was used throughout this study.

Characterisation studies

The surface area and pore diameter of coconut dregs residue were determined using a Quantachrome Autosorb 1 Surface Analyser. The surface area was determined according to the Brunauer–Emmett–Teller (BET) multipoint technique [17], meanwhile the Barrett, Joyner and Halenda (BJH) technique was applied for pore diameter analysis [18]. The surface area and pore diameter of coconut dregs residue were measured as 0.38 m^2/g and 1.83 nm, respectively. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the pore of the biosorbent corresponds to micropores ($d < 2$ nm).

The presence of functional groups in the coconut dregs residue was confirmed using a Thermo Nicolet 6700 FTIR Spectrometer. A Hitachi SU 8020 UHR field emission scanning electron microscope (FESEM) was used to observe the surface morphology of coconut dregs residue before and after interaction with metal ions. The coconut dregs residue was first coated with platinum to avoid electron charging during analysis. The elemental composition in the coconut dregs residue was examined using a Horiba energy dispersive X-ray (EDX) spectrometer. The CHN analyses of the biosorbent were determined using a Thermo Electron Flash EA 1112 Series CHNS/O Analyzer. The biosorbent contains 42.73% of C, 13.08% of H and 5.74% of N.

The pH of the zero point charge (pH_{zpc}) of soya dregs was determined by the acid–base titration approach outlined by Huang and Ostovic [19] and Jha et al. [20]. The experiment was conducted in the presence of 1.0, 0.1 and 0.01 mol/L NaCl electrolytes, and 0.1 mol/L HCl and 0.1 mol/L NaOH solutions were used as the titrants.

Adsorption studies

Batch adsorption experiments were carried out in 250 mL conical flasks by adding approximately 0.5 g of biosorbent in 50 mL of metal ion solution of the required concentration. The samples were equilibrated by shaking at 120 rpm using a Protech orbital shaker (model 720). The samples were then separated through filter paper (Filtre Fioroni 601, 125 mm). The concentration of metal ion in the supernatant was measured by using a PerkinElmer AAnalyst 400 atomic absorption spectrometer.

The effect of solution pH was studied in the pH range of 3.0–7.0. Appropriate amount of 0.1 mol/L of HCL or NaOH solution was used to adjust the pH of 100 mg/L metal ion solutions. The pH readings were measured using a Thermo Scientific, Orion 2-Star pH meter. To study the effect of contact time, 10 sets of 100 mg/L of metal ion solutions were equilibrated with biosorbents for a period of time (between 15 and 240 min). The effect of initial metal concentration was conducted by adding biosorbents in 50 mL of metal ion solution ranging from 5 to 100 mg/L. The mixture was then equilibrated for 60 min.

The competitive adsorption study was accomplished in multi-metal system. The coconut dregs residue was added to 50 mL solution containing 25 mg/L of Cu(II), Ni(II) and Pb(II). The suspension was equilibrated for 4 h at a constant agitation speed. The concentration of each metal ion in the supernatant was measured using AAS, and the dried filtrate was characterised, as discussed in Section Characterisation studies.

All experiments were run in triplicates and metal free blanks were used as controls. The adsorption capacity at equilibrium was calculated using Eq. (1):

$$q_e = \left(\frac{C_0 - C_e}{W}\right)V \quad (1)$$

where q_e is the amount of metal ion adsorbed by the biosorbent (mg/g), C_0 is the initial concentration of metal ion (mg/L), C_e is the equilibrium concentration of metal ion (mg/L), W is the weight of the biosorbent (g), and V is the volume of metal ion solution (L).

The percentage ion removal for the adsorption process was estimated using Eq. (2):

$$\text{Removal}(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (2)$$

Industrial effluent treatment

The effectiveness of coconut dregs residue to remediate metal contaminated water was examined using an industrial effluent. The industrial effluent sample was collected from an electroplating