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Competitive adsorption of metals on cabbage waste from multi-metal solutions

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HIGHLIGHTS

- Modified Langmuir model described well the multi-metal adsorption system.
- Adsorbent from cabbage waste is effective for Pb(II) and Cd(II) adsorption.
- High interference among the metals was observed in a multi-metal system.
- Adsorption capacity was suppressed by the presence of other metal ions.
- The highest reduced in adsorption capacities were found for Pb(II), Zn(II) and Cd(II).

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ABSTRACT

This study assessed the adsorption capacity of the agro-waste ‘cabbage’ as a biosorbent in single, binary, ternary and quaternary sorption systems with Cu(II), Pb(II), Zn(II) and Cd(II) ions. Dried and ground powder of cabbage waste (CW) was used for the sorption of metals ions. Carboxylic, hydroxyl, and amine groups in cabbage waste were found to be the key functional groups for metal sorption. The adsorption isotherms obtained could be well fitted to both the mono- and multi-metal models. In the competitive adsorption systems, cabbage waste adsorbed larger amount of Pb(II) than the other three metals. However, the presence of the competing ions suppressed the sorption of the target metal ions. Except the case of binary system of Cd(II)–Zn(II) and Cd(II)–Cu(II), there was a linear inverse dependency between the sorption capacities and number of different types of competitive metal ions.

1. Introduction

Untreated and uncontrolled discharge of heavy metal containing wastewaters into the natural environment could be toxic to humans, animals, plants, and to urban ecosystems (Ahmad et al., 2010; Pamukoglu and Kargi, 2006). Cu(II), Pb(II), Cd(II) and Zn(II) are used in various industries and some are micronutrients necessary for living organisms at trace level. However, an increase in the intake of these metals can cause health problems such as gastrointestinal disturbance, liver and kidney failure, Wilson’s disease and insomnia, birth defects, kidney and liver damage, Itai-Itai disease, cancer, hypertension, encephalopathy, seizures and mental retardation, kidney damage, disruption of the nervous system, reduces haemoglobin production, depression, lethargy, neurologic signs such as seizures and ataxia (Han et al., 2009; Kurniawan et al., 2006; Laus and de Fávere, 2011). In addition, the presence of heavy metals in surface and groundwater ecosystem can inhibit the growth of aqueous organism and stop any beneficial use of the water bodies. These metal ions, and their supplementary complexes, could accumulate in the body of fishes and other aquatic organisms, and finally could reach to the human body by bio-accumulation, bio-concentration and bio-magnification through the drink and food chains (Hu et al., 2007). Removal of heavy metal ions from wastewater is now a major global concern for both industry and environmental protection agencies. Hence, it is crucial to control the level of heavy metals in wastewaters before its disposal into the nature.

A wide range of techniques such as membrane separation, chemical coagulation, extraction, ion-exchange, electro deposition, and chemical precipitation and electrochemical techniques have been employed to remove heavy metals from water and wastewater. Each process has its own pros and cons; however, in general the physico-chemical processes require costly reagents. Because these techniques require the use of expensive chemicals, they

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can be significantly expensive especially for removing heavy metals present in low concentrations (Popuri et al., 2009; Nghiem et al., 2006). Adsorption process is widely used to efficiently remove heavy metals from wastewater with high solute loadings and even at dilute concentrations (<100 mg/L) (Popuri et al., 2009). Among the adsorbents, activated carbon is commonly used as a commercial adsorbent for removing heavy metals from wastewater. However, this is still an expensive material, requiring costly regeneration. This has prompted the search for an inexpensive yet effective alternative adsorbent.

Removal of heavy metals by biosorption is a relatively new and an emerging technology in the field of water treatment by sorbent materials (biosorbents) (Vieira and Volesky, 2010), derived from a suitable agro-biomass can be used for the effective removal and recovery of heavy metals from wastewater streams (Raize et al., 2004). Extensive studies have been commenced in recent years with the aims of finding alternative and economically feasible biosorbents for wastewater and water treatment. At a large scale, economic sorbents can be defined as materials which are abundant in nature or can be found as a by-product or waste from agro-industry, are cheap and effective and normally do not require significant pre-processing. Recent studies on the removal of heavy metals have reported the use of numerous types of biomass/biomaterials. Several mechanisms may govern biosorption of metals that differ qualitatively and quantitatively from species to species, origin, and processing procedure of biomass/biomaterials (Karthikeyan et al., 2007). Biomass/biomaterials comprise several chemical or functional groups such as acetamido, amino, amido, sulfhydryl, sulfate, and carboxyl etc. which could attract and sequester the metals from solution (Karthikeyan et al., 2007; Vieira and Volesky, 2010). Major biosorption mechanisms include ionic interactions and exchanges and formation of complexes between metal cations and ligands contained in the structure of the cell wall biopolymers, as well as precipitation on the cell wall matrix of the biosorbents, surface adsorption, dissolution, and subsequent precipitation (complexation); ion exchange; and biosorption (Vieira and Volesky, 2010; Prasad et al., 2008). Pearson's concept of hard and soft acid and base theory (HSAB) and by Irving-William's series could be used to explain the binding characteristics of metallic cations during biosorption (Karthikeyan et al., 2007).

First time by this investigation, cabbage-biosorbent is used to determine the biosorption capacities of most commonly available heavy metals in wastewater such as Pb(II), Cd(II), Cu(II) and Zn(II) ions in single, binary, ternary and quaternary solutions while establishing the applicable isotherm model and antagonism mechanism.

2. Methods

2.1. Materials

Cabbage wastes were collected from Campsie Fruits World (Campsie, NSW, Australia). Copper (II) nitrate [$Cu(NO_3)_2$, 99.0%], cadmium(II) nitrate [$Cd(NO_3)_2$, 98.0%], lead(II) nitrate [$Pb(NO_3)_2$, 99.0%], and zinc(II) nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] were purchased from Sigma–Aldrich (St. Louis, MO, USA). Analytical grade chemicals were used as received.

2.2. Methods

2.2.1. Preparation of biosorbent and characterisation

The cabbage waste was cut into small pieces and washed twice with tap and then distilled water. After air drying, cabbage was dried further at 105 °C for 24 h. Subsequently, the dried cabbage was ground into powder (75–300 μm) and kept in air-tight containers for experiments. A BET surface area of cabbage waste was measured by Micrometric Gemini 2360, UK. The functional groups on thus prepared biosorbent were determined by an FTIR instrument (SHIMADZU FTIR 8400S, Kyoto, Japan). For the FTIR analysis, the testing pellet comprised 1% (w/w) of the biosorbent in KBr. The surface morphology of cabbage was scanned with a scanning electron microscope (SEM) instrument (JEOL, JSM-35CF, UK).

2.2.2. Metals solutions and measurement

A stock solution of Pb(II), Cd(II), Cu(II) and Zn(II) were obtained by dissolving the exact quantity of $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ in Milli-Q water. The test solutions containing single ions were prepared by diluting 1000 mg/L of stock solutions of metal ions to the desired concentrations. The ranges of concentrations of both metal ions prepared from stock solutions varied between 1 mg/L and 500 mg/L.

For the investigation with binary metal solutions, the desired combinations of Cu(II)–Pb(II), Pb(II)–Cd(II), Cd(II)–Zn(II), Cd(II)–Cu(II), Cu(II)–Zn(II) and Pb(II)–Zn(II) ions were obtained by diluting 1000 mg/L of stock solutions of metal ions and mixed them in the test medium. Before mixing the biosorbent, the pH of each test solution was adjusted to the required value with 0.1 N H_2SO_4/NaOH. Similarly, the ternary solutions of Pb(II)–Cd(II)–Zn(II), Cu(II)–Pb(II)–Cd(II), Cu(II)–Pb(II)–Zn(II) and Cu(II)–Cd(II)–Zn(II) were quaternary solution of Cu(II)–Pb(II)–Cd(II)–Zn(II) was prepared with required dilutions from the stock solutions.

The concentrations of heavy metal ions in solution were determined by Atomic Adsorption Spectroscopy (AAS) (Contra®AA 300, Analytikjena, Germany) after samples were filtered with Whatman™ GF/C-47 mm ϕ circle filters (GE Healthcare, Buckinghamshire, UK).

2.3. Adsorption experiments

2.3.1. Effect of pH

The metal adsorption was carried out with 10 mg/L metal concentrations at pH values of 2–9.5 for each metal (Pb(II), Cd(II) Cu(II), and Zn(II)). The solutions were adjusted to the desired pH values using 0.1 N HNO_3 and 0.1 N NaOH. A 0.5 g of dried cabbage powder was combined with 100 mL of metal solutions in 250 mL flasks (with paraffin cover) and these flasks were shaken at 120 rpm for 120 min at room temperature (20 °C). These experiments were conducted in three replicates.

2.3.2. Adsorption isotherm

Adsorption isotherm experiments were studied at eight concentrations ranging from 1 to 500 mg/L at initial pH 6.0, at room temperature for a contact time of 120 min. A 50 mg of dried cabbage powder was weighed into the flasks and 100 mL of metal solutions was poured to these flasks. Then the flasks were shaken at 120 rpm. After 120 min, 30 mL of water samples were withdrawn after filtering with Whatman™ filters for AAS analysis.

2.3.3. Single, binary, ternary and quaternary adsorption equilibrium isotherms

The most popular biosorption model is Langmuir model. It is not only use for prediction of single metal adsorption but also for multimetals adsorption. It is the best model for adsorption on the monolayer adsorption onto biosorption. This model is used for metals adsorption onto cabbage waste. The theoretical formulations are given below. The equilibrium data for a single metal adsorption can be normally interpreted by the Langmuir isotherms (Langmuir, 1918), which is represented mathematically as follows: