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Metal adsorption by agricultural biosorbents: Adsorption isotherm, kinetic and biosorbents chemical structures

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ABSTRACT

Biosorption of Cu(II), Co(II) and Fe(III) ions from aqueous solutions by rice husk, palm leaf and water hyacinth was investigated as a function of initial pH, initial heavy metal ions concentration and treatment time. The adsorption process was examined by two adsorption isotherms: Langmuir and Freundlich isotherms. The experimental data of biosorption process were analyzed using pseudo-first order, pseudo-second order kinetic models. The equilibrium biosorption isotherms showed that the three studied biosorbents possess high affinity and sorption capacity for Cu(II), Co(II) and Fe(III) ions. Rice husk showed more efficiency than palm leaf and water hyacinth. Adsorption of Cu(II) and Co(II) was more efficient in alkaline medium (pH 9) than neutral medium due to the high solubility of metal ion complexes. The metal removal efficiency of each biosorbent was correlated to its chemical structure. DTA studies showed formation of metal complex between the biosorbents and the metal ions. The obtained results showed that the tested biosorbents are efficient and alternate low-cost biosorbent for removal of heavy metal ions from aqueous media.

1. Introduction

Industrial processes including: mining [1], electroplating [2], and battery manufacturing [3], release several heavy metals in the ecosystems. Heavy metals are considered as toxic pollutants, due to their accumulation in animals, fished and plants. This accumulation causes various diseases, biological and genetic disorders. Accumulated heavy metal ions are non-biodegradable, so that they must be removed from the environment to keep their abundance at the minimum standards for living organisms. Many physico-chemical methods have been developed for the removal of heavy metals from aqueous solutions including: metal extraction [4], ion exchange process [5], chemical precipitation of metals in form of insoluble salts [2] and membrane separation [6]. These methods have several difficulties included in their high operating costs, lack of selectivity, imperfect removing of metal ions, in addition to the production of wastes during their production. Original metal removal methods have limitation at low metal ions contamination lower than 50 ppm. Development of efficient and low-cost separation processes is therefore of most importance. Alternative relevant technique used in heavy metals removal from aqueous media is the adsorption process. The limitations which considered when choosing suitable adsorbents are: the adsorption and regeneration abilities, market availability, and kinetic parameters. Adsorption capacity parameter is very important for estimation of process costs. Regeneration of the sorbent is important in cyclic processes when the used sorbents are expensive. Kinetic parameters allow determining the rate of the sorption process. Recent studies showed that common agricultural waste products or natural polymers can be used as potential biosorbents for the removal of heavy metals. Several studies showed that various lignocellulose biomaterials, plant biomass [7], tobacco dust [8], coconut shells powder [9], short hemp fibers [10], rice [11], and nut shells [12] have been studied. Chitin rich wastes, such as crab carapaces [13] or shrimp shells [14] have also shown a potential for the removal of toxic metals. In recent years, some industrial and agricultural wastes, such as Neem oil cake [15], sugar-beet pectin [16], and waste activated sludge [17] have been examined in the removal of heavy metals from aqueous solutions. The adsorption process of metal ions from the environment comprised several physico-chemical processes including: electrostatic interactions, metal ion exchange, and ion complexation [18]. Description of the adsorption process makes use of numerous models to determine the sorbent volume. There are many models that allow describing both the equilibrium, and the kinetics of adsorption. Models most commonly

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described in the literature include the Langmuir and Freundlich models describing the process equilibrium, and the pseudo-second order model describing the process kinetics. In this study, the adsorption of Cu(II), Co(II), and Fe(III) metal ions on three biosorbents: rice husk, palm leaf, and water hyacinth was studied. The adsorption isotherms and kinetics of the adsorption process were studied. The influences of pH, initial metal ions concentration and immersion time were studied at 25 °C.

2. Materials and methods

2.1. Chemicals

The used chemicals were analytical grade. Stock solutions of Cu(II), Co(II), and Fe(III) were prepared in deionized water using copper nitrate ($Cu(NO_3)_2{\cdot}6H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), and ferric chloride ($FeCl_3{\cdot}6H_2O$). All the working solutions were prepared by diluting the stock solution in deionized water.

2.2. Biosorbents

Three biosorbents were used in this study: rice husk, palm leaf, and water hyacinth (Nile rose). The three biosorbents were collected from their natural places. The different biosorbents were washed with distilled water several times and dried to 50 °C for 3 days. After drying, the biosorbents were crushed and sieved to obtain particle size between 0.5 and 1 mm.

2.3. Adsorption studies

For each experiment, 1 g of biosorbent was added in 250 mL of metal solution (500 ppm) in 500 mL Erlenmeyer flask. The flasks were stirred (175 rpm) at 25 °C for different time intervals of: 30, 60, 120, 180 and 240 min. After the treatment, biosorbents were separated by vacuum filtration. Several experiments were conducted to evaluate the effect of pH on biosorption at neutral and alkaline medium (pH 7 and 9) at 500 ppm solution of the different metal ions. Values of pH were adjusted by NH_4OH and HCl solutions. The effect of initial metal ion concentration was determined by using different concentrations (100, 300, 500 ppm). The residual metal concentrations remained in solutions after the treatments were determined by atomic absorption spectroscopy (AAS).

2.4. Data processing

The amount of heavy metal ions adsorbed by the different biosorbents was calculated from the initial and final concentrations and the volume of solution according to the following equation, as in [19]:

$$Q_e = \frac{V(C_o - C_e)}{m}$$

where, V: volume of solution (L), C_o: initial metal ion concentration (mg/L), C_e: equilibrium concentration (mg/L), m: weight of the used adsorbent (g). Q_e: the quantity of metal ions in (mg) adsorbed by 1 g of biosorbent in (1 g).

Adsorption efficiencies of the different biosorbents determine the efficiency of each biosorbent in adsorbing the metal ions from the medium. Adsorption efficiency was expressed using the following equation [20]:

$$E\% = \frac{C_o - C_e}{C_o} \times 100$$

Table 1
Adsorption efficiency of Cu(II), Co(II), and Fe(III) metal ions at pH 7 and 9, using rice husk, palm leaf, and water hyacinth at 25 °C.

pH	Metal	Immersion time, h	Rice husk	Palm leaf	Water hyacinth
7	Cu(II)	0.5	96.8	94.7	90.7
		1	97.8	95.4	93.3
		2	98.1	95.8	93.9
		3	98.2	96.1	94.8
		4	98.4	96.2	95.1
	Co(II)	0.5	96.5	93.7	91.8
		1	97.1	95.6	92.4
		2	97.6	96.2	92.6
		3	97.8	96.4	93.4
		4	97.9	96.6	94.0
	Fe(III)	0.5	95.0	91.4	91.1
		1	96.7	94.1	93.0
		2	97.0	95.2	93.4
		3	97.3	96.0	93.3
		4	97.5	96.8	93.5
9	Cu(II)	0.5	98.0	98.1	97.8
		1	98.9	99.0	98.6
		2	99.1	99.4	98.7
		3	99.2	99.5	98.8
		4	99.2	99.6	98.8
	Co(II)	0.5	98.4	98.0	97.6
		1	99.2	98.9	98.2
		2	99.4	99.1	98.7
		3	99.4	99.1	98.8
		4	99.4	99.1	98.8
	Fe(III)	0.5	98.3	96.8	95.8
		1	98.6	97.5	96.9
		2	98.6	97.7	97.4
		3	98.6	97.7	97.5
		4	98.6	97.8	97.5

Error ratio = ±0.5%.

3. Results and discussion

The adsorption efficiencies of the different biosorbents were tested at different biosorbent amounts of 0.1, 0.3, 0.5, 0.7, and 1 g/L. The maximum adsorption efficiency of the different biosorbents was obtained at 1 g/L.

3.1. Factors affecting adsorption of heavy metals by adsorbents

3.1.1. Effect of immersion time

The ability of metal ions extraction from their solution phase depends on the immersion time of biosorbent in the medium. The influence of immersion time on the adsorption process can be represented by the relation between the adsorption efficiency (E%) and immersion time plot for the different metal ions. Fig. 1 represents the variation of the adsorption efficiency of Cu(II), Co(II), and Fe(III) metal ions using the three biosorbents (rice husk, palm leaf, and water hyacinth) at different immersion time of: 30, 60, 120, 180, and 240 min. It is clear that the adsorption efficiencies of Cu(II), Co(II), and Fe(III) metal ions are at the minimum values after 30 min of immersion. The adsorption efficiencies were gradually increased by increasing the immersion time to reach to the maximum values after 240 min of immersing the different biosorbents in the metal ions solutions. Table 1 lists the adsorption efficiencies of Cu(II), Co(II) and Fe(III) metal ions using rice husk, palm leaf, and water hyacinth. The maximum adsorption efficiencies were recorded for Cu(II) metal ions at 96.8%, 92.6% and 90.2% using the three biosorbents at pH 7. Similarly, increasing the immersion time for 4 h of immersion, the adsorption efficiencies of Co(II) and Fe(III) metal ions were increased. Increasing the immersion time has two functions which incorporated to increase the adsorption efficiency. First, increasing the immersion time increases the swelling of the biosorbent fibers which increases their contact area. Second,