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Ecological Engineering

Biosorption of heavy metal from aqueous solution using cellulosic waste orange peel

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A R T I C L E   I N F O

A B S T R A C T

This paper discusses the adsorption of copper ions Cu^{2+} from aqueous solutions onto cellulosic waste orange peel (CWOP).The adsorption process depends on solution pH, adsorbent dose, contact time, initial metal ions concentration and agitation speed. The adsorption kinetics were relatively fast and equilibrium was reached in 60 min. The adsorption equilibrium follows Freundlich adsorption isotherm model. The maximum adsorption capacity value of the (CWOP) for copper ions was 63 mg/g. The thermodynamic study showed that the adsorption of copper ions onto (CWOP) is spontaneous and exothermic. The external mass transfer kinetic model was applied to the experimental results and provided reasonable overall volumetric mass transfer coefficients.

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1. Introduction

The removal of heavy metal ions such as Cu^{2+} ions from waste water is essential because of their bioaccumulation tendency, toxicity, persistency and non–biodegradability in nature (Zhong et al., 2014; Caroll et al., 2013; Wang et al., 2009). The accumulation of Cu^{2+} in the human body also causes skin, brain, pancreas and heart diseases (Cai et al., 2014). Consequently, a great attention has been paid to the studies of effective Cu^{2+} removal from industrial effluents. Cu^{2+} in waste streams come mainly from electrical and semi-conductor industries, the manufacture of fungicides, mining, ore refining, antifouling paints, etc. Many Cu^{2+} waste water treatment methods have been reported in literature (Demirbas, 2008; Weng et al., 2016). These methods include chemical precipitation, ion exchangers (Yogeshwar et al., 2016), chemical oxidation/reduction, reverse osmosis, electro dialysis, ultra filtration, adsorption, etc. Adsorption, for instance, was considered as the best method to deal with low copper waste water concentrations. Many adsorbents such as zeolite, clay diatomite, wheat straw, activated carbon, montmorrillonite, waste biomass, etc. (Azzam et al., 2016; Bhatti et al., 2009; Hanif et al., 2009) were used. The aim of the present work is to evaluate the potential of cellulosic waste orange peel as an effective adsorbent for the removal of metal ions from aqueous solutions. The effect of operating variables such as

solution pH, adsorbent dose, contact time, initial metal ion concentration, and temperature on the percentage removal of metal ions by (CWOP) were investigated. Equilibrium isotherm, kinetic and thermodynamic parameters were evaluated and discussed in detail to understand the adsorption nature.

2. Experimental

2.1. Orange peel

Orange peel used in this study was collected from orange farms in Tunisia. It was sliced and crushed then sieved to a geometric mean size of 500 μm. Orange peel was not subjected to any form of pretreatment before use. Fourier Transformed InfraRed spectroscopy (FTIR) is a useful tool to study the interaction between an adsorbate and the active functional groups on the surface of the adsorbent. Chemical functional groups such as carbonyl, hydroxyle, amine, amide, etc. were identified as potential adsorption sites responsible for binding the metal ions to the adsorbent. FTIR spectra for (CWOP) is shown in Fig1. The surface morphology of the (CWOP), shown in Fig. 2, was zoomed 200 times using a Leo Gemini 1530 scanning electron microscopy.

2.2. Preparation of metal ion solutions

All the chemicals used were of Analytical Reagent (AR) grade and were procured from Merck. Stock solution of Cu (II) ions were prepared by dissolving the required quantity of salts such as

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Nomenclature

Ap	Surface area for mass transfer (m^{-1})
C_0	Initial concentration in aqueous solution (mg/L)
C_t	Concentration of metal ion solution at any time t (mg/L)
Cs	Concentration at the external surface (mg/L)
C_{eq}	Concentration of Cu^{2+} ions at equilibrium (mg/L)
d_p	Mean particle diameter (m)
K_L	Parameter of langmuir isotherm (L/mg)
k_f	External mass transfer coefficient (m/s)
K_f	Freundlich constant (L/mg)
m_s	Mass of adsorbent in solution (g/L)
m	Mass of dry adsorbent(g)
N	Stirring speed (rev/min)
1/n	Freundlich parameter
q_{eq}	Equilibrium concentration in solid phase (mg/g)
q_m	Maximum adsorbed per unit mass of adsorbent (mg/g)
R_L	Langmuir adsorption constant
T	Témpérature (°C)
t	Time (min)
V	Volume particle free liquid (L)
ΔG	Free energy of adsorption (J/mol)
ΔH	Change in entalpy (J/mol)
ΔS	Change in entropy (J/mol K)
ρ_p	Particle density (kg/m^3)
ε_p	Particle void age (%)

Fig. 2. IR spectrum of (CWOP).

pH-meter using a combined glass electrode. Fourier transform IR spectrometry (FTIR) analysis was used to identify the different chemical functional groups present in the (CWOP) and to determine which groups are responsible for the metal binding to (CWOP).

2.4. Batch adsorption experiments

Experiments of batch absorption were conducted in 250 mL conical flasks, at constant agitation speed. 100 mL of the solution was used in the concentration range of 50–500 mg/L (Guiza et al., 2014). The effect of pH was obtained by stirring 1 g/L of (CWOP) in a series of conical flasks containing 100 mL of metal ions solution with an initial concentration of 100 mg/L at different solution pH ranging from 2.0 to 7.0. The concentration of metal ions in the solution before and after adsorption was determined using an atomic absorption spectrometer (nov AA300).

2.5. Adsorption equilibrium experiments

Adsorption equilibrium experiments were carried out by stirring 50 mL to 500 mL with 1 g/L of (CWOP) at temperatures of 20 °C, 30 °C, 40 °C and 50 °C, a pH value of 5 at constant agitation speed (600 rev/min). The amount of metal ions adsorbed onto the (CWOP) at equilibrium, q_{eq} (mg/g) was calculated by the following relationship:

$$q_{eq} = \frac{(C_o - C_{eq})V}{m} \tag{1}$$

Where C_o and C_{eq} (mg/L) are the initial metal ions concentration and equilibrium metal ions concentration, respectively. V is the volume of metal ions solution (L) and m is the mass of (CWOP) used (g) (Guiza et al., 2004).

2.6. Adsorption kinetics experiments

Regarding the study of the kinetics of adsorption, we proceeded as follows. One liter of metal ions solution, studied at concentrations ranging from 10 to 40 mg/L, for different (CWOP) ranging from 0.4 to 1.2 g masses and for various speeds ranging from 200 to 600 rev/min at 20 °C at a pH of 5, was introduced in a jacketed reactor of 2 L volume maintained at constant temperature with a paddle stirrer Fig. 3.

Withdrawals over time were made to track the evolution of the concentration of Cu^{2+} remaining in solution. 5 mL was rapidly
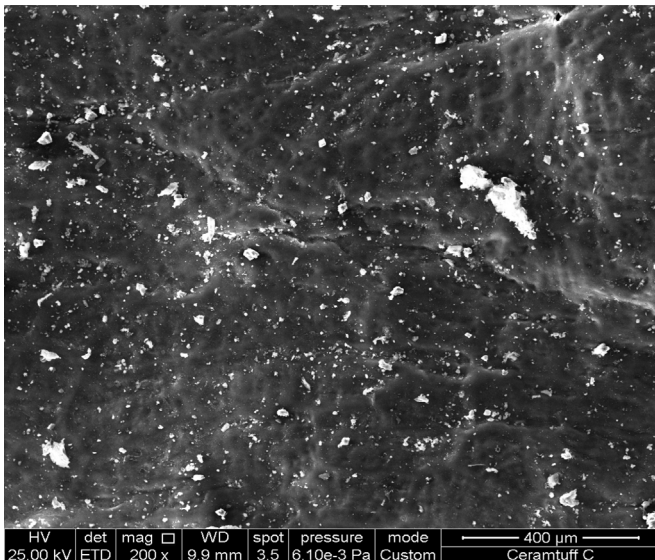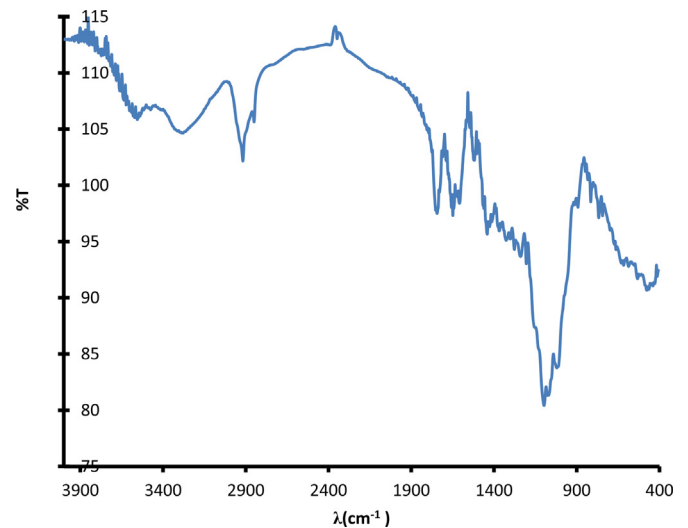

Fig. 1. SEM Image of (CWOP), (magnification of 200×).

$CuSO_4 \cdot 5H_2O$, in double distilled water. The prepared solution was diluted with double distilled water to obtain working solution

of different desired concentrations. The pH of each working solution was adjusted to the required value by using 0.1 M NaOH or 0.1 M HCl.

2.3. Apparatus

The concentrations of metal ions in the solutions before and after equilibrium were determined by an atomic absorption spectrometer (nov AA 300 Shimadzu. Japan). The details of this instrument are given in Table 1. The pH of solution was measured with Hana