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Biosorption of copper ions from aqueous solution using rape straw powders: Optimization, equilibrium and kinetic studies

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ABSTRACT

In this paper, the adsorption behaviors of Cu(II) from the aqueous solution using rape straw powders were studied. The effects of initial Cu(II) concentration, pH range and absorbent dosage on the adsorption efficiency of Cu(II) by rape straw powder were investigated by Box-Behnken Design based on response surface methodology. The values of coefficient constant of the nonlinear models were 0.9997, 0.9984 and 0.9944 for removal Cu(II) from aqueous solution using rape straw shell, seed pods and straw pith core, respectively, which could navigate the design space for various factors on effects of biosorption Cu(II) from aqueous solution. The various factors of pH and biosorbents dosage were the key factors that affecting the removal efficiency of Cu(II) from aqueous solution. The biosorption equilibrium data presented its favorable monolayer adsorption Cu(II) onto shell, seed pods and straw pith core, respectively. The pseudo-second order kinetic model was the proper approach to determine the adsorption kinetics. The biosorption of Cu(II) onto surfaces of rape straw powders were confirmed and ion-exchanged in the adsorption process by energy dispersive spectrometer. The critical groups, —OH, —CH, $—NH_3^+$, $—CH_3$, —NH and —C—O, exhibited by the infrared spectra results, changed to suggest that these groups played critical roles, especially $—CH_3$ in the adsorption of copper ions onto rape straw powders. The study provided evidences that rape straw powders can be used for removing Cu(II) from aqueous water.

1. Introduction

The problem of environment heavy pollution has become one of the severe environment problems, particularly in the heavy pollution aquatic system to be a matter of seriously focused on. Under certain conditions, lower concentration of metals may accumulate to toxic levels through the routes of the human food chain and the biosphere from the environment, which lead to disturb the biochemical processes and health hazards to human being, plants and animals (Anastopoulos et al., 2015; Vijayaraghavan et al., 2008; Peng et al., 2010; Ofomaja et al., 2010; Ekmekyapar et al., 2006). Heavy metals, such as mercury, copper, lead, cadmium, chromium, zinc, nickel, are widely used in the field of industries like as electroplating, electrolysis, mining, smelting metalliferous, fertilizer, pesticide industry, leather working, energy and fuel production (Vijayaraghavan et al., 2008; Peng et al., 2010; Ekere et al., 2016). Among the heavy metals, copper is an essential micronutrients and beneficial to organisms at the lower concentration. But, excessive intake of copper can cause lasting damage to kidneys, reproductive system, nervous system, encephalopathy and blood system for effects of cytotoxicity and neurotoxic to human beings (Ofomaja et al., 2010; Ekere et al., 2016). Therefore, it's reveal important practical significance to remove copper from effluents, before discharging it into water bodies.

An array of suitable treatment technologies including oxidation-reduction, iron co-precipitation, ion exchange, and adsorption have been applied to remove copper ions from aqueous solution (Yahaya et al., 2009; Tsekova et al., 2010). Among the above methods, biosorption has been regarded as a cost-effective technology to remove heavy metals at low metal concentrations because of its advantages such as low-cost of sources, good adsorption effect, easily desorption, good recycling, and environmental-friendly operation (Anastopoulos et al., 2015; Vijayaraghavan et al., 2008; Ekmekyapar et al., 2006; Ekere et al., 2016). In recent years, various waste materials from plant derivatives, fungus, bacteria, yeast and fruit-based by-products were used to remove copper ions from aqueous water such as chaff (Anastopoulos and Kyzas 2015; Han et al., 2006), wheat straw (Dang et al., 2009), pine cone powder (Ofomaja et al., 2010), mushroom (Kan et al., 2015), *Aspergillus niger* (Tsekova et al., 2010), *Pycnoporus sanguineus* (Yahaya et al., 2009), *Sargassum wightii* (Vijayaraghavan et al., 2008), *Bacillus sphaericus* (Tuzen et al., 2007), *Spirogyra species* (Gupta et al., 2006), *Saccharomyces cerevisiae* (Peng et al., 2010), Cellulose xanthogenate (Zhou et al., 2011), anaerobic granular (Hawari and

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Mulligan, 2006). However, it's few of the reports about the efficiency of adsorption of copper ions from the aqueous solution using rape straw powders, unless justly one short communication (Zhou et al., 2011) and a research (Wang et al., 2012). To the best of our knowledge, no previous works has found to investigate the combined effects of various factors, namely initial metal ion concentration, adsorbent particle size, adsorbent dosage and contact time, on the removal of copper ion from aqueous solution using the three parts of rape straw powders with response surface methodology (RSM).

China is a major producer of *Brassica campestris L* all over the world. In 2014, the rape planting area was about 7.1 million hectares, rapeseed output and rape straw yield were about 1300 million tons and 3900 million tons, respectively (Liu et al., 2015). The rape straw is residue as a byproduct, after oil extraction from *Brassica campestris L*. Otherwise, rape straw is commonly used as organic manure for returning to the field, decorative material for manufacturing sheet and providing fuel for heat energy that generation greenhouse gases and fogs. In addition, the researchers reported that rape straw containing hydroxyls, carboxylic, amino, carbonyl, methylene, amide and thiol functional groups, which have strong interaction of the metal ions with functional groups (Zhou et al., 2011; Liu et al., 2015). Thus, the powders of *Brassica campestris* L. could be effective potential adsorption material for removing heavy metal ions from industrial sewage.

In this paper, the Box-Behnken Design used to investigate effects of initial concentration, pH range and absorbent dosage on the removal rates of copper ions using rape straw powders by response surface methodology (RSM). The models of equilibrium models and kinetic models were applied to assess the behaviors of biosorption on removal copper ions from the aqueous solution by rape straw powders.

2. Materials and methods

2.1. Biosorbent preparation

Harvested rape straw was obtained from *Brassica campestris L* growing areas in Xindu district (30°45′8″N, 104°6′36″E), Chegndu city, Sichuan province (China) in June 2015. Rape straw was cleaned in deionized water several times to removing sand, stones and soil. Then, rape straw was separated to three different parts (shell, seed pods and straw pith core) after dried in an oven at 40 °C for 72 h, and afterward were all crushed mechanically in a grinder. The rape straw powders were passed through sieves of sizes of 0.355 mm and 0.180 mm, and then stored respectively in polyethylene boxes at 40 °C for further use.

2.2. Reagents

Reference material of copper (1000 μg mL^{-1}) was purchased from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials, China. Other analytic grade of reagents such as sodium hydroxide, hydrochloric acid and cupric nitrate, which all were purchased from ChengDu Kelong Chemical Co., Ltd., China.

The stock solution of copper (1000 mg L^{-1}) was prepared with dissolving constant weight weighed 3.802 g cupric nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) in 1000 mL deionized water. The test solution concentrations were obtained by diluting the stock solution with distilled water (≥18.2 MΩ cm), and the range of test solutions for pH from 2 to 6 were adjusted to desired values by adding 1 M HCl and NaOH solutions with a pH meter (Fangzhou pH-320 m).

2.3. Biosorption experiments

2.3.1. Box–Behnken Experiment design

Response surface methodology (RSM) is a collection of statistical and mathematical techniques based on fitting a polynomial equation to the experimental data. It can be well applied when a response or a set of responses of interest are affected by several factors (Bezerra et al., 2008; Cobas et al., 2014). In this work, Box–Behnken design were carried out to evaluate efficacy of rape straw powders as biosorbent for removal Cu (II) at various factors of initial Cu(II) concentration (30.0–90.0 mg L^{-1}), pH (2.0–6.0) and biosorbents dosage (1.0–5.0 g L^{-1}) with a stirring speed of 350 rpm during contact time of 120 min and holding at temperature of 20 °C. Each influenced factor was adjusted only at three levels (coded −1, 0, +1) and to evaluate effects of each influenced factors and interactions between influenced factors for removal rates of Cu(II) from aqueous solution by rape straw powders with RSM.

Box–Behnken design is a three-level full factorial designs, which grants the efficient estimation of the first-order and second-order coefficients of the mathematical model, to simultaneously optimize the levels of independent variables for reaching the best system performance (Bezerra et al., 2008; Cobas et al., 2014). The number of experiments required for Box–Behnken design according to following expression to be calculated, Eq. (1); the commonly form of the second-order polynomial equation is presented in Eq. (2):

$$N = 2k(k-1) + c_p \tag{1}$$

Where k is the number of influenced factors, and c_p is the central points, respectively.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta x_i + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_{ij} + \varepsilon \tag{2}$$

Where Y is the research of predicted response value, β_0 is the intercept, β_j is the linear coefficient, β_{jj} is the quadratic coefficient, β_{ij} is the interaction coefficient, X_i and Y_j are independent factors and ε is the random error.

2.3.2. Equilibrium isotherm and kinetics studies

The various factors of removal Cu(II) from the aqueous solution were investigated using absorbents by the batch study. During equilibrium isotherms experiments, 3 g L^{-1} of biosorbent were added into 50 mL of copper solution with pH of 5.0, initial concentration ranged from 25 to 500 mg L^{-1} in polyethylene plastic pipe, and then were shaken at 350 rpm lasting for 120 min under the conditions of various temperatures 20 °C, 30°Cand 40 °C, respectively. During the kinetic study, 3 g L^{-1} of biosorbent were added into 50 mL of Cu(II) solution with initial concentration of 300 mg L^{-1}, pH of 5.0, and temperature of 20 °C in a polyethylene plastic pipe sealed were shaken at 350 rpm for different predetermined time (5, 10, 20, 30, 60, 90 and 120 min).

Ended the adsorption experiment, the absorbents were separated from the solutions with cellulose nitrate membrane filters (0.45 μm pore). The metal concentrations of filtrate (before and after biosorption Cu(II)) were determined by flame atomic absorbent spectrometer (analytikjena Zeenit 700p). The Cu(II) uptake capacities (mg of metal per g of dried biosorbent) were calculated according to mass balance as following expression, Eq. (3); the removal rates of Cu(II) from the aqueous solution using dried biosorbent determined as follows, Eq. (4).

$$q_t = \frac{(C_o - C_t)}{m} V \tag{3}$$

$$p = \frac{C_o - C_t}{C_o} \times 100\% \tag{4}$$

Where C_o and C_t are the concentrations of the Cu(II) in the initial solution (mg L^{-1}) before and after biosorption after predetermined equilibrium period, respectively; m is the dry weight of the biosorbent (g) and V is the volume of Cu(II) aqueous solution (L).

2.4. Methods of characterization

2.4.1. Determination of pH_{PZC}

The pH_{PZC} of rape straw powders (0.180 mm) were determined by the previous method described (Nayak et al., 2017). 0.1 g of rape straw