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Biosorption of copper, zinc, cadmium and chromium ions from aqueous solution by natural foxtail millet shell

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ABSTRACT

The industrial effluents discharge including heavy metals drain into the river, which has given rise to many problems of hazarding aquatic ecosystems and human health. Biosorption serves as the adsorption of heavy metals onto a natural adsorbent, it is becoming a potential alternative for toxic metals removal from industrial effluents in the last decades. The objectives of present research were to investigate the biosorption behaviors and the mechanisms of copper (Cu), zinc (Zn), cadmium (Cd) and chromium (Cr) ions, respectively onto foxtail millet shell as a new natural biosorbent in aqueous solution. The effects of pH (2.0–6.0), contact time (5.0–240.0 min), initial metal ions concentration (25.0–300.0 mg/L), particle size (0.25–2.0 mm) and biosorbent dosage (1.0–6.0 g/L) on the adsorption efficiency of the target metals using foxtail millet shell were evaluated in batch experiments. The models of isotherms and kinetics were used to assess the removal behaviors of Cu, Zn, Cd and Cr ions from aqueous solution by foxtail millet shell. The results showed that the best fitting equilibrium isotherm models for Cu, Zn, Cd and Cr ions were Freundlich (Cu and Zn) and Langmuir (Cd and Cr), respectively under the proper adsorption conditions. The maximum biosorption capacities were 11.89, 10.59, 12.48 and 11.70 mg g^{-1} of Cu, Zn, Cd and Cr, respectively by terms of Langmuir model. The kinetics of biosoption the target metal ions processes were best explained by pseudo-second-order kinetic model. Furthermore, pseudo-second-order and intraparticle diffusion models were cooperative mechanism during the whole biosorption. In addition, the pores on the surface of the shell were covered and then became smooth after biosorption through Scanning electron microscope (SEM) revealed, which demonstrated that the target metal ions were adsorbed by foxtail millet shell. The results of Energy dispersive spectrometer (EDS) further gave evidences that Cu, Zn, Cd and Cr ions were adsorbed onto surface of the adsorbent, respectively. Analysis of Fourier transform infrared spectroscopy (FTIR) demonstrated that various functional groups, such as C—H, C=O, C=C, C—O, O—S—O and Si—O groups were engaged in the interaction between foxtail millet shell and Cu, Zn, Cd and Cr ions. This paper provided evidences that foxtail millet shell was a potential and efficient biosorbent on removal of Cu, Zn, Cd and Cr ions from aqueous solutions, due to its high biosorption availability, capacity and low cost.

1. Introduction

Widespread industrialization and the production of various chemicals have led to a global declination in environmental quality. Heavy metals are used generally in the many industrial activities, such as pesticide, sludge, fertilizers and smelting industries. It's their subsequent release, via aqueous effluents, into the environment that has given rise to many problems of hazarding aquatic ecosystems and human health (Ofomaja et al., 2010; Anastopoulos, Kyzas, 2015; liu et al., 2018). Heavy metals are non-biodegradable in nature and then constantly accumulated in living organisms, which can easily enter into the human body through the channel of food chain, leading to cardiovascular, nerve, kidney and other systemic diseases (Pillai et al., 2013; Anastopoulos, Kyzas, 2015; liu et al., 2018). Though some metals are essential for plants and animals, they can also be very harmful to living organisms when they exceed the standard or exceed a certain limited value (Ofomaja et al., 2010; Ekere et al., 2016). Thus, an array of suitable treatment technologies have been applied to alleviate heavy metal pollution in water environment, which were coagulation and precipitation (Jamaleddin et al., 2010), reduction, flotation (Zouboulis et al., 1997), activated carbon (Toles et al., 2000), reverse osmosis, ion exchange and electron dialysis (Canet et al., 2002). However, these technologies above on are either expensive or inefficient at lower concentration's level of heavy metals. As a result, many researchers are

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studying alternative new technologies for removing trace metals from industrial effluents, including photocatalyst degradation (Rajabi et al., 2016) and Biosorption (Yahaya et al., 2009). Biosorption, as an alternate method, is becoming one of the potential methods to remove heavy metals from aqueous solutions in the last decades (Yahaya et al., 2009). The technology might overcome the disadvantages of conventional physicochemical technologies with advantages of the reusability, low operating cost, short operation time and without secondary pollution (Anastopoulos, Kyzas, 2015; Ekere et al., 2016). During the last decade, a lot of researches have been reported using economical and efficient biosorbents such as bacteria, fungi, algae and nanoparticles on application of metal ions absorption (Shamsipur et al., 2013; Rajabi et al., 2015). To greatly improve the application of biosorption in the removal for heavy metals and solve the problem of the difficult recovery of biosorbent from aqueous solutions, many scholars have adopted the method of preparing the adsorbent into magnetic nanoparticles (Rajabi et al., 2015). In addition, the study can be clearly demonstrated on the mechanism and behaviors of biosorption heavy metals onto the adsorbents by the method of new quantum dot fluorescein which can be used to effectively mark the target heavy metal ions in recent years (Shamsipur and Rajabi, 2013; Rajabi et al., 2018).

Foxtail millet (*Setaria italica*, synonym *Panicum italicum L*), is an annual grass grown for human food which is the second largely crop of millet, as the main grain in northern China, and mainly planted in the middle and upper reaches of the Yellow River. In 2015, planting area of foxtail millet was about 0.839 million hectares, of which yield were nearly 2.0 million tons in China. The shell of foxtail millet is mainly used for raising livestock, discarded or returning to the field because of its limited nutritional value. Our preliminary experimental results showed that foxtail millet shell taken a high bonding affinity with target heavy metals, because there were various functional groups on their cell walls (like as hydroxyls, methylene, carbonyl, carboxylic, amino and thiol functional groups) which could strongly bond with metal ions. Thus, foxtail millet shell was chosen as a biosorbent which could provide another economical source of biosorbent on removal of the metals from aqueous solutions because it can be put in use directly without the need for careful preparation.

In previous study, the only one report has been published about that foxtail millet shell has a good adsorption capacity of lead ions (Zehua et al., 2017). To our best know, complex aquatic environment not only have lead ions, but other diverse ions such as copper (Cu), zinc (Zn), cadmium (Cd) and chromium (Cr) ions and so on. The adsorption capacities of more heavy metal ions onto foxtail millet shell would be needed to further research in aqueous solutions. Therefore, the aims of this work were to study the potential efficiency of foxtail millet shell as a biosorbent to remove Cu, Zn, Cd and Cr ions in aqueous solutions. The adsorption efficiency of the target metals using foxtail millet shell were investigated in batch experiment because the various factors of important parameters would have significant effects on biosorption efficiency, namely pH, contact time, particle size, initial concentration and biosorbent dosage. To understand the biosorption behaviors of Cu, Zn, Cd and Cr ions in aqueous solutions onto foxtail millet shell, the kinetics and equilibrium isotherms of biosorption were also determined. Moreover, to study the mechanism of biosorption before and after biosorption process, the morphology and surface structure of the cells were observed by Scanning electron microscope (SEM) and Energy spectrometer (EDS). Fourier transform infrared sectroscopy (FTIR) analyses were preformed to study possible functional groups and potential binding sites on the cell walls of foxtail millet shell.

2. Material and methods

2.1. Biosorbent

Foxtail millet shell was collected from a local farm in Jinxiang county, Shandong province, China in October 2016. Raw foxtail millet shell as biosorbent was washed several times by distilled water to clean dust away, and then put it into oven dried at 40.0℃for 24 h. The dried shell was milled mechanically and was measured by passing through different sizes of sieves (0.18–0.25 mm, 0.25–0.35 mm, 0.35–0.85 mm and 0.85–2.00 mm). Finally, the sieved shell powders were stored in polythene contains, respectively at 40.0 °C for future using.

2.2. Reagents

All reagents were at least analytical grade and were purchased from Chengdu Kelon chemical reagent factory, China. The stock solutions (1000 mg/L) of Cu, Zn, Cd and Cr ions were prepared by dissolving amounts of $Cu(NO_3)_2{\cdot}3H_2O$ (1.900 g), $Zn(NO_3)_2{\cdot}6H_2O$ (2.293 g), $Cd(NO_3)_2{\cdot}4H_2O$ (2.566 g) and $CrCl_3{\cdot}6H_2O$ (1.399 g), respectively in 500 mL distilled water. The solutions of different concentrations were obtained by diluting the stock solutions with deionized water in various batch experiments.

2.3. Experiments

Batch operations were employed to investigate the effects of pH, contact time, initial metal ion concentration, particle size and biosorbent dosage on the efficiency of the biosorption of the target heavy metal ions. The pH of solutions were adjusted to 2.0–6.0 using a small amount of 10% HCL and 1 M NaOH as required during the biosorption process with a pH meter (Fangzhou pH-320 m, China). Biosorption studies were performed by various factors of contact time (5.0–240.0 min), initial metal ion concentrations (25.0–300.0 mg/L), particle sizes (0.18–0.25 mm, 0.25–0.35 mm, 0.35–0.85 mm and 0.85–2.00 mm) and biosorbent dosages (1.0–6.0 g/L) with holding at the pH of 5.0 set.

During the kinetic study, 4.0 g/L dried biomass (particle size 0.25–0.35 mm) were added to 30.0 mL of each metal ion solution with initial concentration of 100 $mg{\cdot}L^{-1}$, pH of 5.0 and temperature of 25.0℃ in a polyethylene plastic pipe sealed, and then were shaken at 350 rpm for different predetermined time (5, 10, 20, 30, 60, 90, 120 and 240 min). In the equilibrium isotherms research, 4.0 g/L dry foxtail millet shell (particle size 0.25–0.35 mm) were added to 30.0 mL of each metal ion solution with pH of 5.0, predetermined time of 120.0 min and temperature of 25.0℃in a polyethylene plastic pipe sealed, and then were shaken at 350 rpm for different initial concentrations (25, 50, 100, 150, 200 and 300 mg/L).

Afterwards, the each metal ion solution was filtered through a cellulose nitrate membrane filters (0.45 μm filter) and every metal ion concentration was determined by atomic absorption spectrometer with flame atomization (analytikjena Zeenit 700p, Germany). The final metals concentrations in the remaining solution were analyzed and metal uptake (q_t) were calculated using the following mass balance Eq. (1) and the percentage biosorption (p) of metal ions were calculated as follows Eq. (2) (Tsekova et al., 2010).

$$q_t = \frac{(C_0 - C_t)}{m}V \tag{1}$$

$$p = \frac{C_o - C_t}{C_o} \times 100\% \tag{2}$$

Where C_O is the initial metal concentration (mg/L), C_t is the equilibrium concentration of metal solution (mg/L), V is the volume of solution (L), and m is the mass of biosorbent (g).

2.4. Biosorbent characterizations

2.4.1. Measuring of surface area

The surface areas of foxtail millet shell were investigated by test of nitrogen physisorption isotherms using a QuadraSorb Station 2 device (USA) when experiment was measured at 77 K. Before the