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Adsorption characteristics of Copper (II), Zinc (II) and Mercury (II) by four kinds of immobilized fungi residues

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ABSTRACT

This study investigated the adsorption characteristics of Copper (II), Zinc (II) and Mercury (II) by immobilized *Flammulina velutipes*, *Auricularia polytricha*, *Pleurotus eryngii* and *Pleurotus ostreatus* residues. Lagergren model, elovich and intraparticle diffusion model were used to present the adsorption kinetics, and it was proved that Langmuir isotherm model and pseudo-second order kinetics are the best suitable model with high correlation coefficient to characterize the adsorption process of Copper (II), Zinc (II) and Mercury (II). The results showed that adsorption process finished in 120 min at pH 6.0. The adsorption rate of Cu^{2+}, Zn^{2+} and Hg^{2+} were reached to 53.8–84.1% of total in the initial 60 min, and finished in 120 min. Ion exchange and complexation of *F. velutipes* were the main mechanisms for adsorption of metal ions by characterizations of Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR). In addition the functional group of cell walls such as hydroxyl, amide, carbonyl, phosphoric played a critical role in ions adsorption of edible mushroom residues. Cu^{2+}, Zn^{2+} and Hg^{2+} in wastewater could be efficiently removed by *F. velutipes* residue with removal ratio of 73.11%, 66.67% and 69.35%, respectively.

1. Introduction

The production of Copper (Cu), Aluminum (Al), Lead (Pb), Zinc (Zn), Nickel (Ni), Magnesium (Mg), Titanium (Ti), Tin (Sn), Antimony (Sb) and Mercury (Hg) reached 19.17 million T in China during 2006, and ranked first worldwide for consecutive 5 years (AQSIQ, 2014). The large amount of industrial and municipal wastewater have consequently brought about serious pollution to soils and aquatic systems (Garg et al., 2007), it's influence tend to persist indefinitely and also will circulates and accumulates through the food chain. Copper, Zinc and Mercury are considered to be the main and priority hazardous substances. Excessive intake of Cu disrupt metabolic of human body, cause the damages to liver and gallbladder of the human body (Zang et al., 2014), whereas Zinc is high toxicity to aquatic organisms, it decline aquatic organisms memory, brings dysfunction to pancreas and kidney (Hein, 2003). In addition, Mercury is considered to be directive priority hazardous substance by the water framework that causes "hydrargyria" damaging the nervous system, brain, lungs and kidney of human body (Graeme and Pollack, 1998). The Minamata tragedy in Japan caused by mercury accumulation and transfer to human body, resulted intoxicating more than 20 thousand people (Meng and Hu, 2000).

It is challenging to solve the problem of heavy metal contamination in aquatic system, the microbial cell are attracted with considerable attention due to cheap and efficient adsorbent (Volesky, 2000; Yue and Charles, 2006; Umrania, 2006). However, microbial cell is hard to separation from dilute solutions which may cause second pollution. Appropriate chemical or physical means can be used to locate free microbial cells or enzymes in a limited area which maintains adsorbent activity and helps achieves microbial cell recycle (Luo et al., 2002). Many researches showed that immobilized microorganisms significantly increase the tolerance and degradation to toxic substances than suspension cells (Singh et al., 2012), Ma Pei found that immobilized *edodes Lentinus* gains a significantly higher adsorption amount than the pure one ($943\ mg\ g^{-1} > 14.9\ mg\ g^{-1}$) (Ma et al., 2013). Iqbal and Edyvan presented the removal rate of Zn^{2+} by immobilized *Phanerochaete Chrysosporium* is 16.1% higher than the pure one (Iqbal and Edyvan, 2004).

The global mushroom production as per FAO Statistics was estimated at about 2.18–3.41 million tons over period of last ten years (1997–2007). Since there was an increase of about 56% world mushroom production in last decades and guess time rates can be put on

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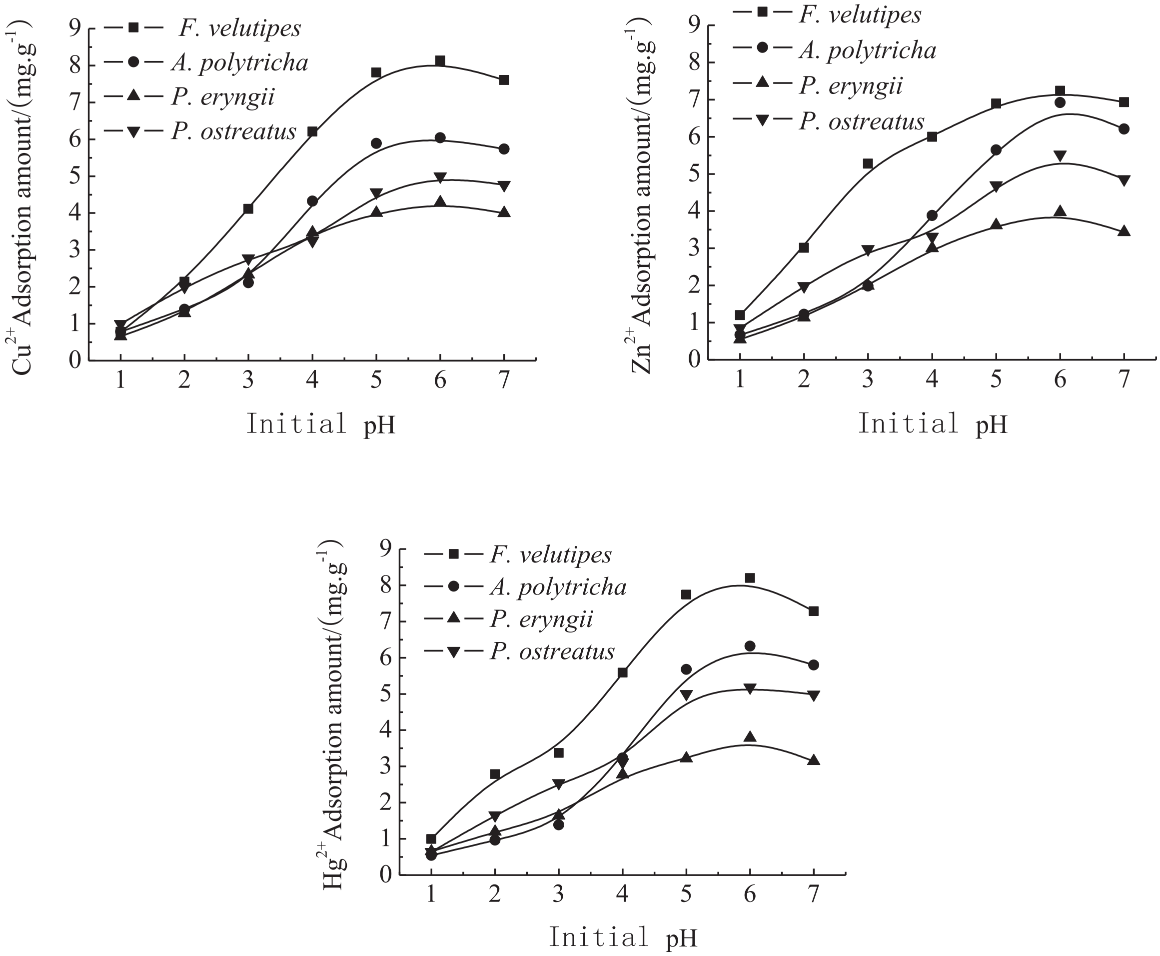

Fig. 1. Effect of solution pH on Cu^{2+}, Zn^{2+} and Hg^{2+} adsorption by immobilized edible mushroom residues.

current production to be around 3.5 million tons (Wakchaure, 2011). The study found that 5 kg fungus residues are produced per 1 kg of edible fungi production (Paredes et al., 2009), thus, global mushroom waste production is about 17.5 million tons. However, the inefficient recycling ratio of the edible mushroom residues resulted in serious environmental pollution as well as waste resources. The adsorbent of mushroom residues for heavy metal ions shows a promising prospects (Grag et al., 2007), and edible mushroom residue have been widely studied for metal ions adsorption (Ma et al., 2013; Iqbal and Edyvan, 2004; Bhatti et al., 2009). Regrettably, as the concentration of Copper (II) and zinc (II) is lower than 10 mg $L^{-1}$and 10 mg L^{-1} in wastewater respectively, the removal of metal ions become difficult, and lead to a unsatisfying discharging concentration of wastewater (Zhang et al., 2015; Xu et al., 2006).

In the present study, four kinds of immobilized plain edible mushroom have been used for the removal of copper, zinc and mercury from aqueous solution. The adsorption studies were performed for determining the impact of pH and sorption isotherms. In addition, the Lagergren, Elovich, Intraparticle diffusion kinetics model, Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) were used for the characterization of adsorbents and the sorption mechanisms. The results were also validated in water of Qingyi river Sichuan province, China.

2. Materials and methods

2.1. Biomass preparation and pretreatment

Adsorbent materials of *F. velutipes, A. polytricha*, *P. eryngii* and *P. ostreatus* residue were collected from mushroom production based in Jintang County, Professional planting cooperatives of *A.* polytricha in Qinglong Town; Food market in Chengdu, Sichuan province, China, respectively. We cut and washed the inedible stipe of mature sporophore and dried them at 60 ℃, then, the residues were triturated using a grinder (BJ-150, Baijie), sieved (< 0.15 mm) and stored at room temperature in desiccator. PVA-SA was used to immobilize biological material via the method described by Ma (Ma et al., 2013).

2.2. Metal ion solution and analysis

Stock cooper, zinc and mercury solution of 1000 mg L^{-1} were prepared by dissolving 0.1000 g, 0.1000 g and 0.1354 g of Cu, Zn and $HgCl_2$ in 2 mL of HNO_3 solution (V:V = 1:1) respectively, which were diluted with deionized water to 1 L. Working metal ion solution of 10 mg L^{-1} was prepared by diluting the stock metal ion solution. The total metal concentration in solution was determined by using an inductively coupled plasma optical emission spectrometry (ICP-OES, 8300, PerkinElmer Optima, USA).

2.3. Batch adsorption studies

All batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks with 25 mL metal ion solution. 1 mol L^{-1} NaOH, and 0.1 mol L^{-1} HCl solutions were used to adjust and maintain the pH of the metal ion solutions. Metal ion solutions were filtered through 40 µm qualitative filter paper after adsorption experiments. All experiments were conducted a control with no biomass.