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New insight into adsorption characteristics and mechanisms of the biosorbent from waste activated sludge for heavy metals

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ABSTRACT

The adsorption characteristics and mechanisms of the biosorbent from waste activated sludge were investigated by adsorbing Pb^{2+} and Zn^{2+} in aqueous single-metal solutions. A pH value of the metal solutions at 6.0 was beneficial to the high adsorption quantity of the biosorbent. The optimal mass ratio of the biosorbent to metal ions was found to be 2. A higher adsorption quantity of the biosorbent was achieved by keeping the reaction temperature below 55°C. Response surface methodology was applied to optimize the biosorption processes, and the developed mathematical equations showed high determination coefficients (above 0.99 for both metal ions) and insignificant lack of fit (p = 0.0838 and 0.0782 for Pb^{2+} and Zn^{2+}, respectively). Atomic force microscopy analyses suggested that the metal elements were adsorbed onto the biosorbent surface via electrostatic interaction. X-ray photoelectron spectroscopy analyses indicated the presence of complexation (between $-NH_2$, –CN and metal ions) and ion-exchange (between –COOH and metal ions). The adsorption mechanisms could be the combined action of electrostatic interaction, complexation and ion-exchange between functional groups and metal ions.

Introduction

Heavy metals are widely used in mining, industrial and agricultural activities. Wastewater from these activities contains metal ions, which can cause serious environmental and public problems (Majumdar et al., 2008; Sun et al., 2011). Zn^{2+} and Pb^{2+} are common heavy metal ions found in electroplate, smelt, and hardware industrial wastewater. Being reported to influence cell apoptosis (Chen et al., 2000), zinc is one of the 13 metals in the list of Priority Pollutants according to the United States Environmental Protection Agency (Ramos et al., 2002). Influencing the gastrointestinal tract and nervous system (Rozada et al., 2008), lead is one of the 11 hazardous priority substances in the list of pollutants among the Water Framework Directive (Kallis, 2001). Therefore, removal and reclamation of heavy metals from wastewater show a wider significance for both environment protection and resource reuse.

Various conventional technologies, *i.e.*, precipitation, oxidation, reduction, adsorption, filtration, flocculation, sedimentation, osmosis, ion-exchange and biosorption, have been used for treating the wastewater contaminated by heavy metals (Bhatnagar and Minocha, 2010; Chen et al., 2000). Among the

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available techniques, biosorption plays a significant role in the removal of heavy metals due to excellent adsorbability, eco-friendliness, cost-effectiveness, and easy availability of biosorbents (Vilar et al., 2008). In recent years, biosorbent extracted from the waste activated sludge (WAS) which contains a significant amount of natural organic macromolecule substances were successfully used to remove the metal ions from wastewater (Comte et al., 2008; Guibaud et al., 2006; Zhang et al., 2014). The removal of heavy metals by the biosorbent is attributed to a large number of negatively charged functional groups such as carboxyl, hydroxyl, amino, phosphate and sulfate (Liu and Fang, 2003). In our previous studies, the removal of Cu^{2+} and Cd^{2+} from aqueous single-metal solutions by the biosorbent from WAS after short-time aerobic digestion were investigated, and the results indicated that the biosorbent was an excellent adsorbent for heavy metals and short-time aerobic digestion could obviously improve the yield of biosorbent from WAS (Zhang et al., 2014; Zhou et al., 2016). However, the influencing mechanisms of key factors on the biosorption need to be further clarified, and the adsorption mechanisms of the biosorbent for heavy metals need more effective and comprehensive evidences.

Atomic force microscopy (AFM) is always used to investigate the materials at an atomic scale, which can measure the interatomic forces and electromagneic forces (Binnig et al., 1986). The AFM 3D (three-dimensional) view can be used to analyze the surface feature, which is more advantageous than scanning electron microscope (SEM) (Singh et al., 2013). Thus, AFM is believed to be an effective tool for determining the physical properties of adsorbent chain, such as shape, persistent length and end-to-end distances of the chain (Mandal et al., 2011). On the other hand, since X-ray photoelectron spectroscopy (XPS) can provide rich information about element composition via measuring photoelectron binding energy (Hollander and Jolly, 1970), it has been employed as a convenient and sensitive probing method for tracking the surface composition variations before and after chemical modification or adsorption (Yao et al., 2014). XPS is also a strong tool for analyzing the interaction between adsorbate and adsorbent, which can provide a direct chemical characterization of the surface layer (2–5 nm depth) (Ojeda et al., 2008; Zhu et al., 2012). Accordingly, the combined utilization of AFM and XPS would offer a new insight into the adsorption mechanisms of the biosorbent for heavy metals.

In this study, the biosorbent from WAS after short-time aerobic digestion was used as a novel biosorbent for the removal of Pb^{2+} and Zn^{2+} from aqueous single-metal solutions. The aims were to ascertain the influencing mechanisms of key factors on the biosorption characteristics, then to optimize the biosorption process by using response surface method (RSM), and further to explore the adsorption mechanisms of the biosorbent by combined utilization of AFM and XPS.

1. Materials and methods

1.1. Chemicals and biosorbent

All the used chemicals were of analytical grade. $Pb(NO_3)_2$ was obtained from Runjie Chemistry Reagents Co. Ltd. (Shanghai, China). $Zn(NO_3)_2{\cdot}6H_2O$ was obtained from Haituo experimental instrument Co. Ltd. (Changzhou, China). The stock solutions of Pb^{2+} and Zn^{2+} were prepared by dissolving $Pb(NO_3)_2$ and $Zn(NO_3)_2{\cdot}6H_2O$ in distilled water at an initial concentration of 1000 mg/L, respectively.

WAS samples were collected from the secondary settling tank back-flow sludge from a full-scale municipal WWTP in Shanghai, China. After gravity concentration of the sludge, its main parameters were as follows: pH 6.8–7.5, suspended solids (SS) 9.0 ± 1 g/L, and the ratio of volatile suspended solids to suspended solids (VSS/SS) 65% ± 8%. The detailed preparation process of the biosorbent from the sludge is as follows (Zhang et al., 2014; Zhou et al., 2016). Extraction of biosorbent was carried out with ultrasound followed by centrifugation. The ultrasound reactor was equipped with a transducer (20 kHz, diameter of 13 mm). During ultrasonic treatment (power density 2.7 kW/L, pulse 4 sec), the tip of the transducer was immersed at about 10 mm deep into the 100-mL sludge samples to be processed for 2 min, and the temperature was maintained at about 298.15 K. Then, the treated sludge samples were centrifuged twice at 10,800 ×*g* with a temperature of 277.15 K for 10 min every time. The supernatant was used as the biosorbent. The biosorbent with the yield of 342 mg from 1.0 L of the aerobic digested sludge (SS 8.04 g/L, VSS/SS 71.8%) consisted of protein (54.76%, W/W), polysaccharide (30.43%, W/W), and nucleic acid (14.81%, W/W). The ratio of protein content to polysaccharide content in biosorbent is 1.34.

1.2. Adsorption experiments of heavy metals onto the biosorbent

The adsorption experiments were carried out by adding the biosorbent into 200-mL Erlenmeyer flasks containing 50 mL of $Pb(NO_3)_2$ or $Zn(NO_3)_2{\cdot}6H_2O$ solutions with 20 mg/L of metal ions. Since this concentration was commonly reported in former studies (Chen et al., 2000; Comte et al., 2008; Zhu et al., 2012), it was chosen in this study for easy comparison between this biosorbent and other adsorbents. After adding the biosorbent, the flasks were sealed to prevent the change in volume of the solutions during the experiments. The flasks were agitated in an isothermal shaker. After shaking the flasks for 30 min, the samples were taken out with a syringe by suction. The obtained solutions with residual metal ions were separated from the precipitates prior to analysis by centrifugation at 5000 r/min for 10 min. The experiments were conducted in triplicate and the negative controls (without biosorbent) were simultaneously carried out to ensure that the adsorption was caused only by the biosorbent. The removal efficiency (R_e, %) and the adsorption quantity (q_e, mg/g) of metal ions by the biosorbent under equilibrium status were calculated using Eqs. (1) and (2), respectively.

$$R_e = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the liquid phase concentrations of the metal ions at time 0 and equilibrium status, respectively; V (mL) the volume of the solution, and W (g) the mass of the biosorbent.