



# Thermodynamics of binding interactions between extracellular polymeric substances and heavy metals by isothermal titration microcalorimetry

Peng Yan<sup>a,b</sup>, Jia-Shuai Xia<sup>c</sup>, You-Peng Chen<sup>a,b,\*</sup>, Zhi-Ping Liu<sup>c</sup>, Jin-Song Guo<sup>a,b</sup>, Yu Shen<sup>a,b</sup>, Cheng-Cheng Zhang<sup>c</sup>, Jing Wang<sup>d</sup>

<sup>a</sup>Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China

<sup>b</sup>Key Laboratory of Reservoir Aquatic Environment, Chinese Academy of Science, Chongqing 400714, China

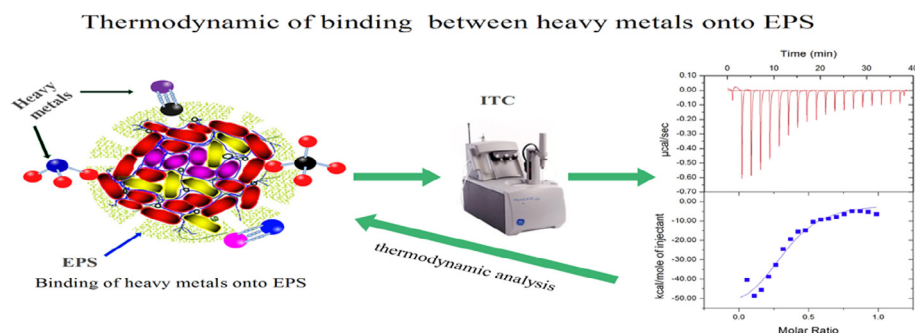
<sup>c</sup>Key Laboratory of the Three Gorges Reservoir Region's Eco-Environments of MOE, Chongqing University, Chongqing 400045, China

<sup>d</sup>Chongqing Jianzhu College, Chongqing 400072, China

## HIGHLIGHTS

- The thermodynamics of binding between EPS and heavy metals was investigated.
- Extracellular proteins were major participants in EPS/heavy metal binding.
- EPS/heavy metal binding was spontaneous and driven mainly by an enthalpy change.
- Divalent cations impeded EPS/heavy metal binding by electrostatic interaction.
- Trivalent cations competed with heavy metal ions for EPS binding sites.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 6 December 2016

Received in revised form 14 February 2017

Accepted 15 February 2017

Available online 20 February 2017

### Keywords:

Extracellular polymeric substances

Heavy metals

Isothermal titration calorimetry

Biosorption

## ABSTRACT

Extracellular polymeric substances (EPS) play a crucial role in heavy metal bio-adsorption using activated sludge, but the interaction mechanism between heavy metals and EPS remains unclear. Isothermal titration calorimetry was employed to illuminate the mechanism in this study. The results indicate that binding between heavy metals and EPS is spontaneous and driven mainly by enthalpy change. Extracellular proteins in EPS are major participants in the binding process. Environmental conditions have significant impact on the adsorption performance. Divalent and trivalent cations severely impeded the binding of heavy metal ions to EPS. Electrostatic interaction mainly attributed to competition between divalent cations and heavy metal ions; trivalent cations directly competed with heavy metal ions for EPS binding sites. Trivalent cations were more competitive than divalent cations for heavy metal ion binding because they formed complexing bonds. This study facilitates a better understanding about the interaction between heavy metals and EPS in wastewater treatment.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Rapid industrial development often results in the discharge of large quantities of heavy metals into aquatic environments

\* Corresponding author at: Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China.

E-mail address: [ypchen@cigit.ac.cn](mailto:ypchen@cigit.ac.cn) (Y.-P. Chen).

(Wang and Chen, 2009). Heavy metal pollution has aroused intense concern because of the significant hazard posed by such metals to human health and the environment (Li and Yu, 2014). Bio-adsorption is an efficient and cost-effective method of removing heavy metal ions during wastewater treatment; heavy metals are adsorbed by activated sludge and then removed from wastewater along with waste sludge (Vijayaraghavan and Yun, 2008). Unfortunately, heavy metals have been widely detected in effluents from wastewater treatment plants and represent a major source of aquatic ecosystem pollution because they cannot be efficiently removed by the conventional activated sludge process (Kamel et al., 2012). The process parameters of conventional activated sludge systems have not been optimized for efficient bio-adsorption of heavy metals because the interaction mechanism between heavy metals and activated sludge remains unclear (Laurent et al., 2009). Therefore, to better engineer such heavy metal biosorption processes, in-depth understanding of the behaviors and mechanisms of heavy metal adsorption by microbial extracellular polymeric substances (EPS) is essential (Li and Yu, 2014).

EPS, a complex high-molecular mixture of biopolymers secreted by microorganisms, mainly consists of extracellular proteins, polysaccharides, and humus acid substances, and which is the major component of activated sludge flocs (Sheng et al., 2010). EPS contains abundant negatively-charged functional groups and efficiently adsorbs heavy metal ions via electrostatic attraction, complexation, ion exchange, surface precipitation and other types of interaction (Gutnick and Bach, 2000; Guibaud et al., 2005; Pagnanelli et al., 2009; D'Abzac et al., 2010). Therefore, EPS play an important role in heavy metal bio-adsorption in the activated sludge process (Comte et al., 2008; Zhang et al., 2013; Wei et al., 2017). However, little is known about the mechanisms of metal adsorption by EPS because the process is markedly and easily affected by EPS properties, metal species, and environmental conditions; moreover, analytical tools suitable for identifying the complex interactions between EPS and heavy metals are unavailable (Li and Yu, 2014). In particular, the specific mechanisms through which EPS properties and solution chemistry affect metal adsorption remain unknown. In addition, significant controversy exists regarding the impacts of EPS on heavy metal sorption by activated sludge. These gaps in knowledge have severely restricted the application of bio-adsorption as a means of removing heavy metals in wastewater treatment plants (WWTPs). Considerable difficulties remain with regard to achieving efficient removal of heavy metals by activated sludge adsorption in the wastewater treatment process.

The adsorption behaviors of heavy metal ions on EPS are usually investigated using batch adsorption experiments with chemical analysis in previous studies (Wei et al., 2011; Zhang et al., 2013). However, this approach has the weaknesses of slow, lower accuracy and sensitivity. The recent development of sensitive analysis techniques has provided tools suitable for revealing the characteristics of binding between EPS and heavy metal ions. For example, surface plasmon resonance (SPR) has been employed to investigate the kinetics of bio-adsorption (Zhang et al., 2016), but, it is expensive (chip consumption) and cannot obtain thermodynamic parameters. Isothermal titration calorimetry (ITC), a microcalorimetric technique, is now widely used to obtain thermodynamic information about biochemical binding processes because it is sensitive, fast, accurate, label-free, lossless, and performed *in situ* (Perry IV et al., 2005; Sheng et al., 2013a). Because all physical, chemical, and biological processes are accompanied by heat exchange, thermodynamic characteristics can reveal the interactions underlying such processes. The thermodynamic characteristics of the binding between heavy metals and macromolecules can be directly obtained by microcalorimetry (Eichenbaum et al.,

2000). The energetic processes associated with the binding reaction can be characterized by thermodynamic analysis based on ITC (Spuches et al., 2005). Thus, thermodynamic parameters can be determined quantitatively by fitting experimental data with a binding model with equilibrium constants, the molar enthalpy of binding, and reactant concentrations (Sheng et al., 2013a).

In this study, ITC was used to systematically investigate the interaction between EPS and heavy metal ions with the goals of (1) evaluating the contribution of the main components of EPS to bio-adsorption of heavy metals; (2) assessing the effects of environmental conditions, including temperature (T), ionic strength (IS), concentration of heavy metal ions, and the presence of different valence cations, on adsorption performance; and (3) identifying competitive behavior between different valence cations and heavy metal ions during the bio-adsorption process. The results of this study provide detailed insight into the interaction mechanism between EPS and heavy metal, improving the bio-adsorption performance of activated sludge in wastewater treatment by optimizing process parameters.

## 2. Materials and methods

Bovine serum albumin (BSA), glucan, and humic acid sodium (HA-Na) were used as model EPS substances (proteins, polysaccharides, and humic acids) in the binding experiments (Ang and Elimelech, 2007; Xu et al., 2013). Cadmium (Cd) and zinc (Zn) were investigated in this study because they are the most commonly detected heavy metals in aqueous environments (Ha et al., 2010; Wei et al., 2016).

### 2.1. Chemicals

BSA, glucan, and HA-Na were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China).  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All chemical reagents were of analytical grade.

### 2.2. Binding experiments

Before the binding tests, all solutions were made with Tris-HCl buffer (1 M, pH 7.4). All standard solutions of model EPS substances (BSA, glucan, and HA-Na) were produced at a concentration of 1 g/L. Different concentrations of the heavy metal solutions were prepared (0.15–1.5 mM) to meet the requirements of each assay. Ionic strength (5 mM, 50 mM, or 500 mM) was adjusted with NaCl solution. The experimental temperature was maintained at a predetermined value (20, 25 or 37 °C).  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  (5 m Eq/L) solutions were prepared for the competitive binding experiments.

### 2.3. ITC analysis

The thermodynamic characteristics of the binding between heavy metals and model EPS substances were investigated using an ITC-200 calorimeter (MicroCal Co., USA). All solutions were degassed for 20 min under vacuum before titration to prevent bubbles in the solution, which can interfere with heat measurement. Binding experiments were carried out with a working volume of 200  $\mu\text{L}$  at a predetermined value with a stir rate of 1000 rpm. The syringe volume and power compensation were 40  $\mu\text{L}$  and 5  $\mu\text{cal/s}$ , respectively. For each experiment, there was an initial thermal equilibration time of 60 s, after which 19 injections were made. The first injection was 0.4  $\mu\text{L}$ , while the titration duration was 0.8 s. The remaining titrations were completed in 2-mL aliquots injected over 4 s with 240 s between injections. The heat released during dilution and binding, as well as the background

Download English Version:

<https://daneshyari.com/en/article/4997563>

Download Persian Version:

<https://daneshyari.com/article/4997563>

[Daneshyari.com](https://daneshyari.com)