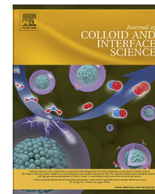




Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Assessment of microbial products in the biosorption process of Cu(II) onto aerobic granular sludge: Extracellular polymeric substances contribution and soluble microbial products release



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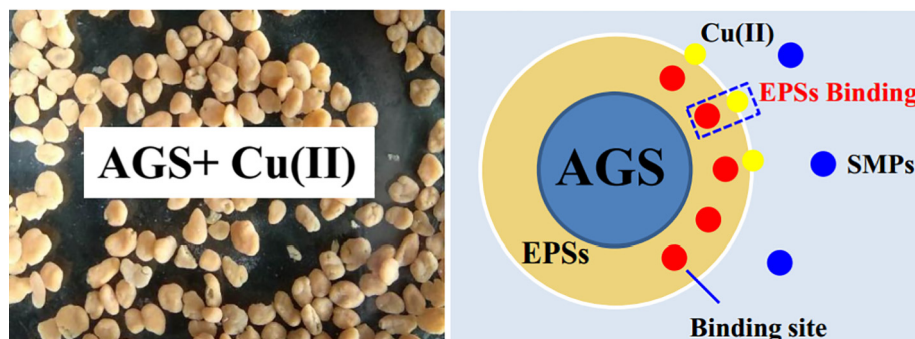
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GRAPHICAL ABSTRACT

Responses of microbial products from AGS during biosorption process



ARTICLE INFO

Article history:

Received 7 February 2018

Revised 11 May 2018

Accepted 14 May 2018

Keywords:

Aerobic granular sludge

Extracellular polymeric substances (EPSs)

Soluble microbial products (SMPs)

Heavy metal

Biosorption

ABSTRACT

In the present study, the responses of microbial products in the biosorption process of Cu(II) onto aerobic granular sludge were evaluated by using batch and spectroscopic approaches. Batch experimental data showed that extracellular polymeric substances (EPSs) contributed to Cu(II) removal from an aqueous solution, especially when treating low metal concentrations, whereas soluble microbial products (SMPs) were released under the metal stress during biosorption process. A three-dimensional excitation-emission matrix (3D-EEM) identified four main fluorescence peaks in the EPS, i.e., tryptophan protein-like, aromatic protein-like, humic-like and fulvic acid-like substances, and their fluorescence intensities decreased gradually in the presence of Cu(II) during the sorption process. Particularly, tryptophan protein-like substances quenched the Cu(II) binding to a much higher extent through a static quenching process with less than one class of binding sites. According to the synchronous fluorescence spectra, the whole fluorescence intensity of released SMP samples expressed an increased trend with different degrees along with contact time. Two-dimensional correlation spectroscopy (2D-COS) suggested that the fulvic-like fluorescence fraction might be more susceptible to metal exposure than other fractions. The result of molecular weight distribution demonstrated that the SMPs released from the

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biosorption process differed significantly according to contact time. The result obtained could provide new insights into the responses of microbial products from aerobic granular sludge with heavy metal treatment.

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1. Introduction

With the rapid development of population growth and industrialization worldwide, heavy metal pollution is of specific concern due to its toxicity, bioaccumulation tendency and persistence in nature [1]. In recent years, a great number of heavy metals are generated from many industries such as tanning, battery preparation, mining, surface finishing, energy and fuel production, electric appliance manufacturing, etc., and these industries create serious environmental pollution, threatening human health [2,3]. Due to the non-biodegradability of heavy metals, wastewater containing heavy metals is often pre-treated by various physicochemical processes, including chemical precipitation, ion exchange, membrane separation, reverse osmosis and sorption [4].

Among these pretreatments, sorption is regarded as one of most cost-effective and environment-friendly technologies for removal or recovery of heavy metal ions from aqueous solutions [5,6]. Until the present, various low-cost biosorbents have been developed by utilization of bacteria, waste sludge, bioflocs, biomass, fungi, etc. [7,8]. Compared to activated sludge, aerobic granular sludge has the advantages of a denser microbial structure and better settling capacity, meaning that aerobic granular sludge could easily be separated from the aqueous environment after metal pollutant treatment [9,10]. Therefore, aerobic granular sludge as a promising biosorbent has been applied successfully for treating various toxic chemicals in wastewater [11,12].

Specifically, microbial products, including extracellular polymeric substances (EPSs) and soluble microbial products (SMPs, or soluble EPSs), are excreted by sludge microorganisms due to the metabolic activity of bacterial cultures during their growth, decay or in a response to environmental conditions in wastewater treatment systems [13]. EPSs are located at or outside the cell surface, while SMPs are the soluble cellular polymeric components dissolved in aqueous solution, irrespective of their origins [14]. EPSs are well-known to play a significant role in affecting the physicochemical properties of aerobic granular sludge, including structure, stability, deposition, retention, flocculation, settling, dewatering, and biofouling [15,16]. Specifically, EPSs have been extensively applied as an effective adsorbent for treating heavy metal from wastewater because of their abundant functional groups and binding sites [17]. Therefore, the presence of EPSs in aerobic granular sludge is considered beneficial for migration and removal of heavy metals through a complexation process [18].

Although EPSs contribute to remove heavy metal from aqueous solution, SMPs may be released from microorganisms as by-products under the stress of toxic compounds during the sorption process. SMPs are generally accepted to be composed of hydrolysis products of EPSs and decay products of active cells, which are the major components of soluble organic matter in the effluents from wastewater treatment plants [19]. Hence, the release of SMPs from aerobic granular sludge under conditions of heavy metal exposure may negatively affect the quality of the biosorption-treated effluent [14]. However, to the best of our knowledge, limited information is available about the production of SMPs in the biosorption process of heavy metal onto aerobic granular sludge. Therefore, it is essential to study SMP release in-depth, not only in terms of improving the comprehension of the sludge-based biosorption process but also providing possible information for reducing sec-

ondary pollution through the optimization of operational parameters.

Based on the above discussion, the objective of this study was to evaluate the role and characterization of microbial products in the biosorption process of heavy metal onto aerobic granular sludge by using batch and spectroscopic approaches. To achieve this purpose, a combined use of excitation-emission matrix (EEM), synchronous fluorescence spectra, two-dimensional correlation spectroscopy (2D-COS), and molecular weight (MW) distribution was employed to characterize the properties of EPSs and SMPs in the biosorption process. The result obtained could provide better understanding of the responses of microbial products of sludge-based biosorbents during the heavy metal treatment process.

2. Materials and methods

2.1. Aerobic granular sludge

Aerobic granular sludge was obtained from our laboratory-scale sequencing batch reactor (SBR), which was operated for more than one year for treating high ammonia-nitrogen wastewater. The detailed composition of influent wastewaters could be found in the literature reported by Wei et al. [20]. The average size of the aerobic granular sludge used for sorption experiments was approximately 1.5 mm. Before the sorption experiment, the aerobic granular sludge was collected at the end of the aeration process and washed three times using deionized water to remove the surface-soluble ions.

2.2. Batch sorption experiments

In the present study, all chemicals were of analytical-reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. Cu(II) was selected as a target for biosorption onto aerobic granular sludge from the view point of sorption kinetics and sorption isotherms. Detailed biosorption kinetics experiments were carried out in a 250-mL Erlenmeyer bottle containing approximately 0.25 g (dry weight) of aerobic granular sludge and 100 mL of Cu(II) solution (100 mg/L) at 25 °C. The initial pH of the mixed solution was adjusted to 5.0 by using 0.1 mol/L HCl and NaOH to avoid precipitation. The samples were taken at different time intervals in the range of 0–360 min. The adsorption isotherm experiment was carried out with different initial concentrations of Cu(II) from 25 to 1200 mg/L for 5 h to ensure equilibrium at 25 °C.

After the batch sorption experiments, the mixed solution was first centrifuged at 5000 rpm for 10 min, and the Cu(II) concentration in the supernatant was measured to obtain the amount of Cu(II) sorbed onto the aerobic granular sludge. Then, the remaining aerobic granular sludge was used to extract EPSs, and the Cu(II) analyzed in the extracted EPS solution was recognized as Cu(II) adsorbed by EPSs. The Cu(II) adsorbed by sludge could be obtained by subtracting the amount absorbed by EPS from the total adsorption of aerobic granular sludge, as similarly reported by Xu et al. [21].

2.3. Fluorescence spectra

EPS and SMP samples were extracted at various reaction times during biosorption kinetics experiments. More detailed EPS

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