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Role of extracellular polymeric substances in biosorption of dye wastewater using aerobic granular sludge

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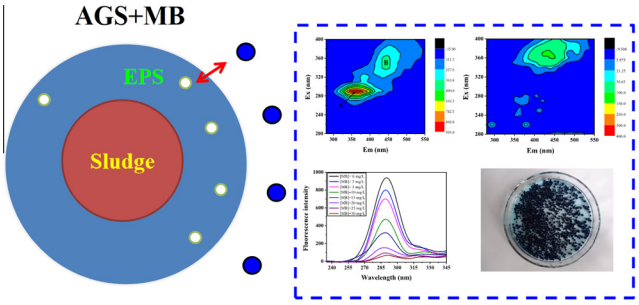
HIGHLIGHTS

- Biosorption of methylene blue onto aerobic granular sludge was studied.
- Extracellular polymeric substances gradually quenched during sorption process.
- The main fluorescence quenching was caused by tryptophan residues.
- Quenching type belonged to a combined dynamic and static quenching.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the role of extracellular polymeric substances (EPS) in biosorption of dye wastewater was evaluated using aerobic granular sludge as biosorbent. Based on the experimental data, the removal efficiencies of methylene blue (MB) by EPS and Sludge were 9.38 and 80.72%, respectively, implying that EPS made a certain contribution for MB removal. The adsorption rates of EPS, Sludge, and total Sludge + EPS for MB were better fitted with pseudo-second order kinetic model, and the equilibrium adsorption isotherm data agreed well with Langmuir model. The interaction between EPS and MB was explored by a combined three-dimensional excitation–emission matrix (3D-EEM) and synchronous fluorescence spectra. 3D-EEM indicated that protein- and humic acid-like substances were the main peaks of EPS, and gradually quenched with increased MB concentrations. According to synchronous fluorescence spectra, the main fluorescence quenching was caused by tryptophan residues, and the type belonged to a combined dynamic and static quenching.

1. Introduction

Textile dye wastewater is well known to contain strong color, high pH, temperature and chemical oxygen demand (COD), which is regarded as a main source of environmental pollution (Daneshvar et al., 2006). Moreover, dye is one of the most obvious indicators of wastewater pollution during biological treatment because of its low biodegradability (Gupta, 2009). Thus, dye-containing wastewater is usually pretreated by physical or chemical methods such as oxidation, precipitation, catalysis, coagulation, and sorption etc. (Papić et al., 2004).

Recently, biosorption has attracted researchers' attention as an environment-friendly and cost-effective technology to remove dye pollutant from wastewater (Liu et al., 2012). Activated sludge,

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being a typical low-cost biosorbent, has been successfully applied for purifying industrial wastewater due to its free availability and high biosorption capacity (Göbel et al., 2005). However, activated sludge is of small particle size, low density, poor mechanical strength and little rigidity, which may be difficult to achieve solid–liquid separation in real application (Gao et al., 2010). Compared with conventional activated sludge, aerobic granular sludge has the advantages of high surface area, excellent settle ability, dense and porous microbial structure, and thus can be easily separated from aqueous environment after removing dyestuffs (Wei et al., 2013). Therefore, aerobic granular sludge plays a promising role in adsorption of toxic chemicals (Adav et al., 2008).

Additionally, extracellular polymeric substances (EPS) are essential for keeping microbial aggregates together in aerobic granular sludge, which are composed of complex high-molecular-weight mixture of polymers in a three-dimensional matrix (Sheng et al., 2010). Polysaccharides (PS) and proteins (PN) are the major components of EPS influencing the physicochemical properties of sludge in biological wastewater treatment systems (Guo et al., 2012). EPS are regarded as an effective adsorbent and extensively used for treating various wastewaters because of their abundant functional groups and binding sites (Liu et al., 2001). Thus, it is postulated that EPS can make a certain contribution for dye removal from aqueous environment in sludge biosorption process. However, till now, little information has been available for this point.

Therefore, the objective of this study was to explore the role of EPS in the biosorption of dye from wastewater using aerobic granular sludge as biosorbent. Methylene blue (MB) was selected as the target pollutant to evaluate the function and effect of EPS in dye removal process. The combined use of three-dimensional excitation–emission matrix (3D-EEM) fluorescence spectroscopy and synchronous fluorescence spectra was employed to elucidate the interaction between EPS and MB. The obtained results could also provide more information for understanding the key component of EPS for contribution the dye removal in biological treatment system.

2. Methods

2.1. Parent SBR operation

Aerobic granular sludge was cultured in a lab-scale sequencing batch reactor (SBR) with a working volume of 17 L. A synthetic high-strength nitrogen wastewater was used in this study (Wei et al., 2014b). The volumetric exchange ratio and hydraulic retention time (HRT) of the granular reactor were 50% and 12 h, respectively. Before biosorption tests, aerobic granular sludge was collected at the end of aeration process, and washed three times with deionized water to remove the surface soluble ions.

2.2. Experimental design

In this study, the total adsorption of MB onto aerobic granular sludge could be attributed to EPS sorption and sludge sorption (the residual aerobic granular sludge after EPS extraction). For biosorption kinetic experiment, around 0.25 g (dry weight) of aerobic granular sludge was added into each 100 mL mixed solution containing 100 mg/L of MB. The initial pH of the mixed solution was adjusted to 6.0 using 0.1 mol/L HCl or NaOH and then stirred for 5–300 min. The isotherm experiment was carried out with different initial concentrations of MB from 25 to 1500 mg/L for adsorption equilibrium. Blank samples (containing only deionized water and corresponding aerobic granular sludge) were prepared and monitored as a control.

After the adsorption procedure, the supernatant MB was measured first to obtain the total adsorption of aerobic granular sludge (Sludge + EPS). The remained sludge was then used to extract EPS. MB concentration in the extracted EPS solution was measured and recognized as MB adsorbed by EPS. The MB adsorbed by sludge was determined by subtracting the amount adsorbed by EPS from the total adsorption amount of aerobic granular sludge.

The removal efficiency and the amount of MB adsorbed q_t (mg/g) were given according to the following Eqs. (1) and (2):

$$\text{Removal efficiency } (\%) = \frac{(c_0 - c_t)}{c_0} \times 100\% \quad (1)$$

$$q_t = \frac{(c_0 - c_t) \times V}{m} \quad (2)$$

where c_t (mg/L) is the concentration of adsorbate at time t (min), V (L) is the volume of adsorbate solution, m (g) is the mass of adsorbents, q_t (mg/g) is the adsorbed amount at time t (min).

2.3. EPS extraction and 3D-EEM

A heat method was used to extract the sludge EPS and the detailed procedure could be found in the previous literature (Li and Yang, 2007). All 3D-EEM spectra of EPS samples were measured using a luminescence spectrometer (LS-55, Perkin-Elmer Co., USA). EEM of excitation spectra were subsequently scanned from 200 to 400 with 10 nm increment by varying the excitation wavelength from 280 to 550 nm.

2.4. EPS and MB blinding test

In order to understand the mechanism of fluorescence quenching between EPS and MB, blinding tests of synchronous fluorescence spectra of EPS before and after binding with a series of concentrations of MB were conducted. Firstly, aerobic granular sludge samples (approximate 0.25 g dry weight for each sample) were resuspended into 30 mL deionized water to extract EPS. After that, 2 mL EPS solution was added into a 10 ml centrifugal tube, and 2 mL different concentrations of pre-determined MB solution and 6 mL deionized water were successively added to ensure the final MB concentrations varying from 3 to 30 mg/L. The pH value was adjusted to 6.0 and the temperature was set at 25 °C. Finally, the solutions were mixed for 4 h using an oscillator to before spectral analysis. Synchronous fluorescence spectra of all samples were analyzed by simultaneous scanning the excitation and emission wavelength from 250 to 350 nm with a constant offset ($\Delta\lambda$) at 60 nm. The scanning speed was set at 1200 nm/min for all the fluorescence measurements.

2.5. Analytical methods

The analytical methods of suspended solids (SS) and volatile suspended solids (VSS) were by using the standard methods (APHA, 1998). The analysis of MB in the filtered solutions was performed using a UV/vis spectroscopy (TU-1901, Purkinje General Instrument Co., Ltd. China) at 664 nm. All the samples were monitored immediately in this study. The adsorption experimental results were carried out in duplicate ($n = 2$) and the mean values were presented here. The experimental error of results was within ±5%.