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A novel approach for methylene blue removal by calcium dodecyl sulfate enhanced precipitation and microbial flocculant GA1 flocculation

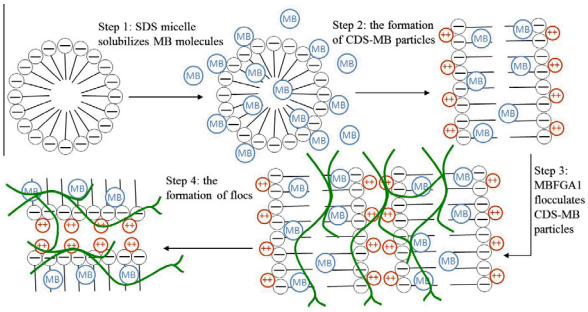
Zhaohui Yang *, Min Li, Mingda Yu, Jing Huang, Haiyin Xu, Yan Zhou, Peipei Song, Rui Xu

College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

HIGHLIGHTS

- A novel approach for the efficient removal of MB was proposed.
- SDS solubilization and Ca^{2+} effect were combined to reduce the solubility of MB.
- MB precipitated from aqueous solution by adsorbing onto the Ca $(DS)_2$ particles.
- The $Ca(DS)_2$ particles adsorbed MB were flocculated by MBFGA1.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach was proposed for the removal of methylene blue (MB), a soluble cationic dye, from aqueous solution by calcium dodecyl sulfate ($Ca(DS)_2$) enhanced precipitation which was based on the solubilization of sodium dodecyl sulfate (SDS) on MB and Ca^{2+} effect on SDS micelles, and microbial flocculant GA1 (MBFGA1) flocculation. The independent and interactive effects of factors, such as SDS, Ca^{2+} and MBFGA1 dosages, on the MB removal and interaction between SDS and Ca^{2+} were investigated. The response surface methodology (RSM), environmental scanning electron microscope (ESEM) and energy dispersive spectrometer (EDS) analysis were employed to discuss the interaction mechanism between SDS and Ca^{2+}, and MB removal mechanism. The results showed that MB and SDS removal efficiency could reach 98.63% and 88.97%, respectively, with pH (10), MB (50 mg/L), SDS (8 mM), Ca^{2+} (5 mM) and MBFGA1 (4 mL/L). Under the optimal conditions, residual SDS and Ca^{2+} concentrations in the upper phase were 0.88 mM and 1.27 mM, respectively, which reached the *K*sp of $Ca(DS)_2$. The concentration consumption ratio between SDS and Ca^{2+} was 2.0. The interaction between SDS and Ca^{2+} was depended on the SDS-Ca^{2+} concentration ratio in aqueous solution rather than the CMC of SDS. When Ca^{2+} concentration was relatively sufficient, SDS micelles containing the solubilized MB (SDS-MB micelles) would disassemble to generate MB loaded $Ca(DS)_2$ particles (CDS-MB particles) which would be flocculated by MBFGA1. Whereas, when SDS concentration was superfluous relatively, SDS micelles formed in the upper phase would redissolve the CDS-MB particles in flocs.

1. Introduction

Dyes and pigments are widely used in the textile and leather dyeing, printing, pharmaceutical, and cosmetic industries [1,2]. Discharge of the dyes to the environment have aroused serious

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
E-mail address: yzh@hnu.edu.cn (Z. Yang).

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concerns all over the world due to the toxicity of dyeing effluents, such as carcinogenic and mutagenic action to aquatic biota and humans [1]. Furthermore, the dyes in surface water are aesthetically displeasing, imped sunlight penetration and reduce the dissolved oxygen, which cause annoyance to the aquatic biosphere [3]. Therefore, it is important to remove the dyes from wastewater to an acceptable level before discharging into the natural environment.

In recent years, several physical, chemical and biological methods, including adsorption [2,4,5], photo-catalytic degradation [6], biodegradation [7], micellar-enhanced ultrafiltration (MEUF) [1,8–10] and flocculation [11,12] have been developed to reduce the pollution and hazards of dyes. Among these methods, flocculation is considered as an attractive and favorable technique because its low capital cost, short detention time and good removal efficiency [3,13]. However, the main limitation of the conventional flocculation technique is that it cannot remove soluble dyes like methylene blue (MB) effectively as a main treatment [3]. Thus, it is crucial to reduce the solubility of MB, a soluble cationic dye, before employing flocculation technology.

Recently, sodium dodecyl sulfate (SDS), a widely used anionic surfactant, has been employed to improve the MB removal efficiency in the micellar enhanced ultrafiltration technique [1,9,10] and the surfactant enhanced adsorption technique [14,15], which owing to the micellar solubilization of SDS on MB molecules. That is when SDS concentration is equal to or higher than its critical micellar concentration (CMC), SDS monomers will assemble to form micelles which are capable of solubilizing MB molecules [1]. Furthermore, the interaction between SDS and calcium ion has been studied in many literatures [16–18]. These researches show that the interaction was depended on the CMC of SDS. Below its CMC of 8 mM, SDS monomers will react with calcium ions to generate precipitation, which is governed by the solubility product of calcium dodecyl sulfate (CDS), whereas, above the CMC, the precipitated CDS will be redissolved gradually by SDS micelles [16,18]. Though the solubilization of SDS and the interaction of SDS with calcium ion have both been researched widely, to our best knowledge, there is no research to combine those two chemical properties of SDS to reduce the solubility of MB.

In this study, the solubilization effect of SDS on MB and the calcium ion effect on SDS micelles containing the solubilized MB (SDS-MB micelles) were combined, for the first time, to make MB precipitate from aqueous solution in a form of suspended particles, which then were flocculated by microbial flocculant GA1 (MBFGA1). MBFGA1, a kind of microbial flocculant, is produced from *Paenibacillus polymyxa* GA1 with being eco-friendly, high security and high efficiency for removing Kaolin suspension which has been studied in our previous work [19–21]. The main objective of this research had two aspects: the one was to investigate the independent and interactive effects of factors, including SDS, calcium ions and MBFGA1 dosages, on the MB removal efficiency and the interaction between SDS and calcium ions, the other was to explore the interaction mechanism between SDS and Ca^{2+}, MB removal mechanism and flocculation mechanism based on the experimental results.

2. Materials and methods

2.1. Materials

The cationic dye, MB (DaMao Chemicals, China) was prepared by dilution of 1 g/L stock solution. Fresh diluents were used in each experiment. The anionic surfactant, SDS (Sinopharm Chemicals, China) was prepared at the concentration of 100 g/L. The critical micelle concentration (CMC) is 8 mM in distilled water [22]. $CaCl_2$ (Sanpu Chemicals, China) was prepared at the concentration of 10 g/L to provide Ca^{2+} which was crucial during the MB removal process. Microbial flocculant GA1 was harvested from the fermentation liquid of *Paenibacillus polymyxa* GA1 with high flocculation activity [19–21] and the fermentation liquid contained 15.56 g/L effective components. Unless otherwise stated, all reagents used were of analytically pure grade. The distilled water was used in all experiments.

2.2. MB removal experiment

1000 mL of MB solution was prepared at the concentration of 50 mg/L (Fig. S1). Then the pH of the MB solution was adjusted to 10 (Fig. S2) by NaOH and HCl, which was discussed specifically in the Supplementary Material. Subsequently, pre-determined amounts of SDS, $CaCl_2$ and MBFGA1 were added into the 1000 mL MB solution in 1000 mL beaker in turn. Then the beaker containing the mixture was fixed on the floc-tester (ET-720. Lovibond. Germany). After that, the mixture was stirred with 5 min rapid mixing at 200 rpm, followed by 30 min slow mixing at 40 rpm and 1 h settlement period. Water samples were collected at a depth of 2 cm in the upper phase for the zeta potential measurement and the concentration determination of MB, SDS and Ca^{2+}.

2.3. Analysis and calculations

The zeta potential and MB concentration were directly measured by Zetasizer (Nano-ZS90, Malvern, England) and UV spectrophotometer (UV-2550, SHIMADZU, Japan) at 665 nm, respectively. However, the water samples should be filtered through 0.45 μm filter membrane before the concentration measurements of SDS and Ca^{2+} were taken. The SDS concentration was analyzed by a double phase titration following ISO-2271-1989 using benzethonium chloride (J&K Chemicals, China) as standard and an indicator consisting in a mixture of ethidium bromide and acid blue 1 (Aladdin Industrial Corporation, China). The ethidium bromide was HPLC pure. Chloroform (Sinopharm Chemicals, China) was used to provide the double phase. The Ca^{2+} concentration was analyzed by EDTA (Sinopharm Chemicals, China) titrimetric method following ISO-6058-1984. All experiments were performed in triplicates for the mean calculation and the results were reproducible within 5%.

The removal efficiency (RE) of MB, SDS and Ca^{2+} all followed the equation:

$$\mathrm{RE}\,(\%) = (C_0 - C_e)/C_0 \times 100 \tag{1}$$

where C_0 denotes the initial concentration (dosage) of MB, SDS and Ca^{2+}; C_e denotes the final concentration in the upper phase of MB, SDS and Ca^{2+}.

We defined the concentration consumption of SDS or Ca^{2+} as:

$$\mathrm{Q} = C_1 - C_2 \tag{2}$$

where C_1 is the initial dosage of SDS or Ca^{2+} (mM); C_2 is the final concentration in the upper phase of SDS or Ca^{2+} (mM).

The concentration consumption ratio (CT) between SDS and Ca^{2+} was defined as:

$$\mathrm{CT} = Q_s/Q_c \tag{3}$$

where Q_S and Q_C are the concentration consumptions of SDS and Ca^{2+} (mM), respectively, which follows the Eq. (2).

Generally, at low SDS concentration, Ca^{2+} could react with SDS monomers as follows:

$$Ca^{2+} + DS^{-} \leftrightarrow Ca(DS)_2 \tag{4}$$