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Research article

Production of bioflocculants prepared from formaldehyde wastewater for the potential removal of arsenic

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ABSTRACT

A novel bioflocculant (MBF-79) prepared using formaldehyde wastewater as carbon resource was investigated in the study. The optimal conditions for bioflocculant production were determined to be an inoculum size of 7.0%, initial pH of 6.0, and formaldehyde concentration of 350 mg/L. An MBF-79 of 8.97 g/L was achieved as the maximum yield. Three main elements, namely C, H, and O, were present in MBF-79 with relative weigh percentages of 39.17%, 6.74%, and 34.55%, respectively. The Gel permeation chromatography analysis indicated that the approximate molecular weight (MW) of MBF-79 was 230 kDa. MBF-79 primarily comprised polysaccharide (71.2%) and protein (27.9%). Additionally, conditions for the removal of arsenic by MBF-79 were found to be MBF-79 at 120 mg/L, an initial pH 7.0, and a contact time 60 min. Under the optimal conditions, the removal efficiencies of arsenate (0.5 mg/L) and arsenite (0.5 mg/L) were 98.9% and 84.6%, respectively. Overall, these findings indicate bioflocculation offers an effective alternative method of decreasing arsenic during water treatment.

1. Introduction

Bioflocculants are extracellular polymeric substances (EPS), which comprise glycoproteins, polysaccharides, and proteins produced by microorganisms during their growth (Aljuboori et al., 2013). Bioflocculants are advantageous over inorganic flocculants and chemically synthetic high polymer flocculants in numerous applications including wastewater clarification, purification of carbohydrates from plant biomass, paper production, chemical operations, dewatering and thickening in mineral operations, due to their nontoxic, harmless, and biodegradable properties (Aljuboori et al., 2015; Bala Subramanian et al., 2010; Zhao et al., 2013). However, a major bottleneck for its commercial application is the high production cost compared with inorganic flocculants and synthetic high polymer flocculants (Zaki et al., 2013; Tang et al., 2014). Hence, industrial-scale production and application of bioflocculants as potential alternatives to the synthetic ones have yet to be achieved. Although several investigations using inexpensive substrates for bioflocculant production have been conducted (Zhang et al., 2013, 2007; Zhong et al., 2014), there have been no studies of the production of bioflocculants from formaldehyde wastewater.

Formaldehyde, which is colorless and has a characteristic pungent irritating odor, is an important precursor to many other materials and chemical compounds. Commercial solutions of formaldehyde in water, commonly known as formol or formalin, have been used as disinfectants, for the preservation of biological specimens and for the embalming of human remains. Formaldehyde is also commonly used in nail hardeners and/or nail varnish. Although formaldehyde wastewater is very harmful to ecological systems and human health, it is a potentially inexpensive medium and a rich source of carbon and other nutrients that have the potential for use as bioflocculants. Hence, the microorganisms that use wastes as substrates for the production of interesting materials not only contribute to the production of these value added compounds, but also focus on the minimization of waste disposal.

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Although most bioflocculants can be used to flocculate Kaolin suspension, they show different flocculating ability for other particles, metals or colloids in aqueous solution (Nie et al., 2011; Patil et al., 2011; Peng et al., 2014). It is noteworthy that the use of bioflocculants for the flocculation of arsenic has seldom been reported in the literature.

Arsenic-contaminated wastewater represents a great threat to the environment and human health. In aquatic systems, the predominant forms of As are the inorganic species arsenate and arsenite, with the latter being more labile and 25–60 times more noxious than the former (Al Rmalli et al., 2005). Owing to the high virulence of arsenic, the World Health Organization (WHO) has lowered the permissible limit of arsenic in drinking water from 50 to 10 μg/L (Altun et al., 2014). Some inorganic flocculants or coagulants, such as the $Fe_2(SO_4)_3$, have been found to be effective in arsenic removal, and charge neutralization has been demonstrated to play a key role in the flocculation process (Wang et al., 2007).

Therefore, the present study was conducted to: (1) isolate and identify bioflocculant-producing strains from formaldehyde wastewater sludge; (2) produce bioflocculant using strains isolated from formaldehyde wastewater; (3) evaluate the performance of this bioflocculant and its application to arsenic removal.

2. Materials and methods

2.1. Isolation and identification of bioflocculant-producing microorganisms

Bioflocculant-producing strains were isolated from recycled activated sludge samples (pH 5.2–5.7) taken from a formaldehyde wastewater treatment plant located in Jiangsu, China. Each isolated strain was cultivated in screening medium (50 mL) containing 2% w/w formaldehyde, 0.5% $(NH_4)_2SO_4$, 0.5% K_2HPO_4, 0.2% KH_2PO_4, 0.05% $MgSO_4$ and 0.01% NaCl with oscillation (200 rpm) at 30 °C for 3 d. Next, 1 mL of fermentation broth was added into 100 mL kaolin suspension (4 g/L) in a 250-mL beaker and the flocculating activities of the suspensions were measured. Culture broths propitious to flocculating rate were further explored. Seven strains were found to produce flocculants, among which ZCY-79 exhibited the excellent flocculating activity in kaolin suspension. Therefore, ZCY-79 was inoculated onto an isolation slant culture-medium and cultivated at 30 °C for 4 d, after which it was preserved at 4 °C for further study. PCR amplification of the 16S rDNA was conducted by Takara Biotechnology Co., Ltd (Gong et al., 2008).

2.2. Bioflocculant production and flocculating activity tests

Formaldehyde wastewater (COD_{Cr} = 8100 mg/L, pH 5.5, formaldehyde 1000 mg/L) was collected from the primary sedimentation tank of the JiHua Chemical Plant in Jiangsu, China. The culture medium consisted of 1 L diluted formaldehyde wastewater (formaldehyde = 400 mg/L) containing 0.5% $(NH_4)_2SO_4$, and 5 g yeast extract. Prior to cultivation, the formaldehyde wastewater was diluted to the desired formaldehyde concentration, after which the initial pH of formaldehyde wastewater medium was adjusted to the determined value. Batch anaerobic fermentations were conducted in a 5-L stirred tank reactor (14 cm ID × 45 cm height) at 30 °C for 10 d with agitation at 120 rpm.

2.3. Optimization of culture conditions for bioflocculant production

To further optimize the production of MBF-79, central composite experimental design (CCD) was used to optimize conditions of fermentation of bioflocculant using formaldehyde as the substrate (Ugbenyen et al., 2014). In the design, three independent variables were the formaldehyde concentration, inoculum size, and initial pH, respectively. Twenty experiments were conducted using a face central composite design to investigate the optimum factors which contributed to the bioflocculant production (Table 1). Each of these three significant variables was assessed at five different levels (−1.682, -1, 0, +1, +1.682). The average yield which obtained in these experiments was used as the response variable (Y) and all the experiments were conducted in triplicate.

The second-order model for the three quantitative factors can be described as follows:

$$Y = \beta_0 + \sum \beta iX_i + \sum \beta iiXi^2 + \sum \beta ijXiXj, ...i, j = 1, 2, 3, ..., k \quad (1)$$

where Y is the predicted response, β_0 is the offset term, βi is the linear effect, β_{ii} is the quadratic effect and β_{ij} is the interaction effect, Xi and Xj are input variables which influence the response variable Y.

2.4. Characteristics of the bioflocculant

The polysaccharide concentration of the purified biopolymer was determined by the phenol–sulfuric method (Kurane and Matsuyama, 1994; Ghosh et al., 2009). The total protein content of the purified bioflocculant was measured by the Bradford method using bovine serum albumin as a standard (Li et al., 2009). Neutral sugar, amino sugar and uronic acid content were determined using the standard methods (de Alexandre Sebastiao et al., 2013; Fujita et al., 2000). The monosaccharide composition of the purified biopolymer was analyzed after hydrolysis with 3 M Trifluoroacetic Acid at 100 °C for 4 h using Thin Layer Chromatography with ethyl acetate, pyridine, acetic acid and water (5:5:1:3, v/v) as a solvent. Monosaccharide was detected by spraying with aniline phthalic acid reagent and heating at 110 °C for 5 min (Cosa et al., 2012). Gel filtration chromatography, equipped with a Waters 2410 Reactive Index Detector, was conducted in a glass column to determine the molecular weight of the bioflocculant.

2.5. Jar testing for arsenic removal

All chemicals used in this work were analytical grade and were dissolved in deionized water (18.4 MO). A standard Jar Tester was used for the flocculation tests in arsenic solution dosed with MBF-79/$FeCl_3$. Flocculants were added into 1.0 L of arsenic solution (0.5 mg/L arsenate + 0.5 mg/L arsenite) and then fixed on a jar testing device (TA2-2, Wuhan Hengling Co. Ltd.) at room temperature 20 °C. The jar testing procedure involved a 2-min rapid mixing stage at 200 rpm followed by a slow stir phase at 40 rpm for 30 min to promote the collision of particles and hence floc growth, which resulted in a 60-min settlement period. Sodium hydroxide and sulfuric acid were employed to adjust the pH of the solutions to the predetermined level before the jar test. These experiments were performed in triplicate. After each test, the supernatant was separated by filtration with a 0.22-μm pore size membrane filter, and arsenic in the solution was analyzed by inductively coupled

Table 1
Independent variables for the MBF-79 production.

Factors	Coded levels				
	−1.682	−1.000	0	1.000	1.682
Formaldehyde concentration (mg/L)	63	200	400	600	736
Initial pH	4.3	5.0	6.0	7.0	7.7
Inoculum size (%)	3.3	5.0	7.5	10	11.7