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Combined chemical coagulation–flocculation/ultraviolet photolysis treatment for anionic surfactants in laundry wastewater

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ABSTRACT

In this work, a combined chemical coagulation–flocculation/ultraviolet photolysis process was used to separate and oxidative degrade the linar alkylbenzene sulfonate (LAS), an anionic surfactant in laundry wastewater, aiming at making the effluent dischargeable with suitable characteristics. Mineral ash, $ZnCl_2$, and Praestol-650 (P-650) were chosen as the coagulant-sorbent, the complex former and the cationic high-molecular flocculants, respectively. The dosages of three components were optimized through the response surface methodology (RSM). The optimum parameters values obtained from RSM were further proved by a successful parallel trial with the actual laundry wastewater. Results showed that the maximum LAS removal efficiency of 71.26% and 74.58% were achieved for the self-made LAS wastewater and the actual laundry wastewater when the dosages of $ZnCl_2$, ash and P-650 was 29.54, 1936.35 and 196.38 mg/L, respectively. The effect of solution pH in LAS ultraviolet photolysis process was also investigated. Results indicated that the alkaline medium is beneficial to LAS photolysis removal. These results support the applicability of the combined chemical coagulation–flocculation/ultraviolet photolysis process for LAS removal due to its efficient and rapids treatment rate, high adsorption and extraction capacity, and acceptable catalytic oxidation ability using Zn^{2+} salts and mineral ash as specific coagulant and Praestol-650 as cationic high-molecular flocculant.

Introduction

Surfactants used as surface-active matters can effectively decrease the surface tension of liquids. Those surface activities of surfactants derive from the amphiphilic structures that posses both hydrophilic and hydrophobic parts in one molecule [1]. Synthetic surfactants are widely used in many industrial applications such as metal processing, textile, food, pharmaceuticals and paper industries [2]. Surfactants are can be classified into four groups depending on the charge of the hydrophilic part: nonionic (0), anionic (−), cationic (+) and zwitterionic (±) [3].

Linar alkylbenzene sulfonate (LAS) is a typical anionic surfactant, which are extensively used in household products, detergents, personal care products, industrial processes and pesticide formulations [4,5]. It can also be found in the sewages of many enterprises including laundries, car washing facilities and railway transport facilities [6]. LAS were referred as water pollutants of the third group of dispersibility of Kylsky's classification of water impurities (diameter of particles from 1 to 10 nm) [6]. It is reported that in domestic sewage, the LAS concentration may vary from 1 to 18 mg/L [7], and the concentration in laundry wastewater may vary from 17 to 1024 mg/L [8]. Under low concentration they exist in water in the form of molecules and ions, forming the homogeneous systems. Under high concentration and in the presence of particulate, fine-dispersed pollutants and oil products, however, they form colloid structures and act simultaneously as the stabilizers of emulsions and suspensions.

Due to the biotoxicity and non-biodegradability, wastewaters containing surfactants need to be treated before discharging into the aquatic environment, in terms of public and environmental health [2]. Generally, LAS are also considered as the dangerous and undesirable substances in water body. Even accumulated in small amounts (0.8–2.0 mg/L), LAS would produce a strong toxic effect on flora and fauna, destroy the organoleptic property and prevent the self-purification process of water body [9]. On the other hand, a

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Table 1
Chemical components of the mineral ash.

Component	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SO_3	TiO_2	MnO	K_2O	Na_2O
Content (wt%)	50.64	37.57	5.15	0.80	1.72	0.30	1.15	0.068	0.67	0.44

study of the possibility for wastewater reuse is essential because of its large quantities in the laundering process of industrial laundries. Laundry wastewater possesses the potential for reclamation and reuse. Such reclamation and reuse of laundry discharge is important to save water supply and significantly improve urban environments [10]. In this context, many technologies such as adsorption, ion exchange, membrane filtration, precipitation, coagulation, flocculation, and oxidation treatments have been proposed to treat LAS in laundry wastewater [9–21]. Among the currently used techniques, precipitation/coagulation had received considerable attention due to its high removal efficiency and low-cost. A great number of liquid and solid organic/inorganic coagulants and flocculants are available [11,16–18]. In addition, the advanced oxidation processes (AOPs) such as ozonation, photocatalysis, Fenton and ultraviolet irradiation [11,15,19–21] had been widely utilized to improve the removal efficiency of LAS. However, it is difficult to meet with the national environmental quality standard of China (GB 3838-88) after treated by the conventional methods. Also, it is difficult to develop a single and an effective treatment method due to the diversity and the unique physicochemical properties of the laundry wastewater.

In present work, a combined chemical coagulation–flocculation/photolysis process was proposed. Mineral ash, $ZnCl_2$ and Praestol-650 (P-650) were chosen as coagulant-sorbent, complex precursor and cationic high molecular flocculants, respectively. The dosages of the three components were optimized through the response surface methodology (RSM). The novel mechanism of coagulation–flocculation process was also proposed. In the photolytic process, the influence of the solution pH was investigated and the products after photolysis were also analyzed by gas chromatography. Results indicated that the combined chemical coagulation–flocculation/ultraviolet photolysis process is an environmentally friendly strategy for laundry wastewater treatment.

Material and methods

Chemicals and wastewater samples

In RSM experiments, the simulated anionic surfacant wastewater was self-made using LAS (alkyl benzene sulfonates, R-$C_6H_4SO_3H$ (322 g/mol), where R refers to the alkyl chain (hydrophobic region) ranging from 4 to 10 carbon atoms and another part (hydrophilic region) corresponding to a sulfonated aromatic ring). Owing to the high concentration of LAS, the laundry wastewater was generally diluted to obtain an influent LAS concentration of approximately 12.0–14.0 mg/L, below the inhibitory value of 50 mg/L in biochemical treatment processes [22]. So, the initial concentration of LAS in this work was selected as 13.8 mg/L, which is at concentration below its critical micelle concentration (CMC) of 2.0 mM [23]. Mineral ash obtained from Beihai thermal power plant, Dalian, was used as the coagulant-sorbent and its composition was listed in Table 1. $ZnCl_2$ and Praestol-650 were chosen as complex precursor and cationic high molecular flocculants, respectively. Solution pH was adjusted by using sulfuric acid and sodium hydroxide.

Experimental procedures

Coagulation–flocculation experiments

Coagulation–flocculation experiments were carried out in a classical jar test apparatus. $ZnCl_2$, mineral ash and P-650 were added successively into 400 mL wastewater. Then, the wastewater was vigorously mixed for 5 min at 200 rpm, followed by slow mixing for 30 min at 30 rpm, and allowed to settle for 30 min. Finally, the supernatant was taken out for measurement and subsequent ultraviolet photolysis. After the optimization of three components dosages through RSM, three parallel coagulation–flocculation/ultraviolet photolysis experiments were carried out with the actual laundry wastewater obtained from the launderette in Dalian University of Technology, China. The initial composition of the laundry wastewater is shown in Table 2.

Response surface methodology

The dosages of $ZnCl_2$, ash and Praestol-650 were optimized by the RSM in order to obtain the maximal removal efficiency of AS. A Box–Behnken design [21] was chosen to evaluate the combined effect of three independent variables. The contents of $ZnCl_2$, ash and Praestol-650 were termed as X_1,X_2 and X_3, respectively. The minimum and maximum ranges of variables were investigated and the full experimental plan with respect to their values is listed in Table 2. The coded values of the three independent variables together with the responses are shown in Table 3. An empirical second-order polynomial model for three factors was in the following form:

$$Y_i = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i<1}^{n} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is residual contents of LAS (mg/L); X_i the variable parameters in codes, β_o, β_i, β_{ii} and β_{ij} the parameters of the regression model; ε the random error associated with this measure [24]. Design-Expert software was used to attain the coefficient parameters estimated by the multiple linear regression analysis, generating response surface contour plots and analyzing the data collected by the performing analysis of variance (ANOVA).

Photolysis experiments

Ultraviolet photolysis experiments were carried out using a high pressure mercury lamp (quartz tube, power supply 220 V/36 W, frequency = 50 Hz, λ = 253.7 nm) as the light source at room temperature. The distance between the lamp and wastewater was 5 cm. The volume of wastewater was 200 mL, the width of the wastewater layer was 3 cm and the irradiation time was 30 min.

Table 2
The initial composition of the laundry wastewater.

Laundry wastewater ingredients	Concentration (mg/L)
LAS	19.68
Suspension substances/optical density	126.6/0.76
Oil products (oil P)	3.70
Chemical oxygen demand (COD)	280
pH	9.0–9.5