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Research article

Treatment of chemical cleaning wastewater and cost optimization by response surface methodology coupled nonlinear programming

Yang Yang [a], Zhen Zhou [a, *], Chenjie Lu [a], Yunke Chen [a], Honghua Ge [a, **], Libing Wang [b], Cheng Cheng [a]

[a] College of Environmental and Chemical Engineering, Shanghai University of Electric Power, 2588 Changyang Road, Shanghai, 200090, China
[b] Shanghai Ahill Chemical Products Co., Ltd, 1038 Guoshun Road, Shanghai, 200090, China

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ABSTRACT

The real alkaline cleaning wastewater (ACW) was treated by a process consisting of neutralization, NaClO oxidation and aluminum sulfate (AS) coagulation, and a novel response surface methodology coupled nonlinear programming (RSM-NLP) approach was developed and used to optimize the oxidation-coagulation process under constraints of relevant discharge standards. Sulfuric acid neutralization effectively removed chemical oxygen demand (COD), surfactant alkylphenol ethoxylates (OP-10) and silicate at the optimum pH of 7.0, with efficiencies of 62.3%, >82.7% and 94.2%, respectively. Coagulation and adsorption by colloidal hydrated silica formed during neutralization were the major removal mechanisms. NaClO oxidation achieved almost complete removal of COD, but was ineffective for the removal of surfactant OP-10. AS coagulation followed by oxidation can efficiently remove OP-10 with the formation of Si-O-Al compounds. The optimum conditions for COD ≤100 mg/L were obtained at hypochlorite to COD molar ratio of 2.25, pH of 10.0 and AS dosage of 0.65 g Al/L, with minimum cost of 9.58 $\$/m^3$ ACW. This study shows that the integrative RSM-NLP approach could effectively optimize the oxidation-coagulation process, and is attractive for techno-economic optimization of systems with multiple factors and threshold requirements for response variables.

1. Introduction

Chemical cleaning is extensively used in a large variety of household and industrial applications, such as heat exchangers, oil and gas facilities, chemical equipments, multistage flash evaporators, etc (Motamedi et al., 2013; Senn et al., 2014). The chemical cleaning wastewater (CCW) is generated from cleaning and rinsing steps with residual cleaners and dirties removed (Senn et al., 2014), and must be properly treated. Alkaline cleaning wastewater (ACW) emerges as the most intractable CCW because of the complex ingredients of cleaners (Senn et al., 2014) and substantial dissolution of oil and grease under alkaline conditions. The high pH and high chemical oxygen demand (COD) of ACW certainly cause damages to the environment if untreated, and also prevent its combined treatment with other wastewaters considering its low biodegradability (Olmez-Hanci et al., 2011) and large flow rate in a short period. In addition, surfactants, in particular potential endocrine disrupting compounds alkylphenol ethoxylates (Chen et al., 2007; Reis et al., 2013), are widely used in alkaline cleaning solutions (Neamtu et al., 2009). The surfactants discharged with ACW tend to adsorb and hence accumulate onto soil sediments, imparting serious ectoxicological risks (La Guardia et al., 2001; Olmez-Hanci et al., 2011). Therefore, ACW should be properly treated before discharged into waters.

Various methods have been developed for the removal of surfactant, COD and heavy metals from CCW, including coagulation, adsorption, advanced oxidation process (AOP), electrocoagulation, etc (da Silva et al., 2015; Jangkorn et al., 2011; Kaleta and Elektorowicz, 2013; Karci et al., 2013; La Guardia et al., 2001; Mohan, 2014; Olmez-Hanci et al., 2011). Kaleta and Elektorowicz (2013) found that coagulation-adsorption (i.e. powdered activated carbon) process achieved efficient removal of anionic surfactant from water, and Jangkorn et al. (2011) confirmed the effectiveness of coagulation for surfactant and COD removal from consumer products wastewater. da Silva et al. (2015) compared effects of

* Corresponding author.
** Corresponding author.
E-mail addresses: zhouzhen@shiep.edu.cn (Z. Zhou), gehonghua@shiep.edu.cn (H. Ge).

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direct photolysis and three AOPs on nonylphenol ethoxylate, and found that photo-assisted electrochemical oxidation achieved highest degradation efficiency. Karci et al. (2013) observed that photo-Fenton process ensured complete removal of nonionic surfactant nonylphenol decaethoxylate and yielded toxicologically safer degradation products. Although those intensive efforts mentioned above are very helpful to understand removal mechanisms and to control contamination of surfactants, the accumulation of knowledge to develop a systematic treatment process for CCW is insufficient. Senn et al. (2014) reported a successful treatment of real ACW by a coagulation-photo-Fenton process, but the solid-liquid separation limited its practical applications and there is a lack of sufficient information on surfactant removal. Considering cleaning campaign usually conducted in 1–3 days, and organic matters in the real CCW are partially and slowly biodegradable (Olmez-Hanci et al., 2011), rapid and efficient physicochemical and chemical technologies are required to control its contamination timely. Detailed research on surfactant transfer and transformation in the treatment process is also needed to investigate its removal mechanisms from real CCW.

Treatment cost is another major obstacle for pollutants removal from real CCW. As a powerful mathematical and statistical tool for process optimization, response surface methodology (RSM) has been widely used in various wastewater treatment processes, such as AOPs (Körbahti and Rauf, 2009; Olmez-Hanci et al., 2011), coagulation-flocculation (Taheri et al., 2013; Wang et al., 2011), precipitation (Ren et al., 2015), etc. However, the economic costs of factors, which usually determine the feasibility of the optimized condition, are not incorporated in the RSM model. Furthermore, in many cases, the optimization target only requires the response variable above or below a threshold value rather than reaching the extreme value, and selecting the optimum condition from an infinite number of solutions has plagued the further application of RSM optimization. To overcome the shortcomings of RSM application, the nonlinear programming (NLP) (Birgin et al., 2016) can be employed by constructing an objective function, and combing NLP with RSM would be able to achieve the cost minimization in a certain constraint established by RSM model.

The main objective of this study was to treat the real ACW by using the neutralization-oxidation-coagulation process. The removal mechanisms of COD and surfactant in the process were also investigated by characterization of dissolved organic matters (DOM), and morphology and composition of precipitates. The integrative RSM-NLP approach was employed to minimize treatment cost of the oxidation-coagulation process. The results of this study are expected to provide an effective process for real ACW treatment, and a novel optimization strategy for other complex wastewater treatment processes.

2. Materials and methods

2.1. Materials

The ACW was obtained from a full-scale cleaning process to remove oil and grease from the surface of stainless steel parts, which generates wastewater of 50 m^3 in a cleaning period of two days. The original cleaning solution was prepared by Shanghai Ahill Chemical Products Co., Ltd, with the components declared by the provider consisting of sodium hydroxide, sodium carbonate, alkylphenol ethoxylates (OP-10), sodium metasilicate, and sodium tripolyphosphate. The characteristics of the ACW are as follow: pH of 12.5, COD of 2954.0 mg/L, conductivity of 71.5 mS/cm, surfactant of 46.5 mg/L and silicate of 1.21 g/L.

2.2. Batch experiments

The ACW was strong alkaline, contained high concentration of grease, COD and mineral impurities. Therefore, neutralization was utilized as a pre-treatment process to transform pollutants (e.g. oil and grease) dissolved under alkaline conditions to particulate form, which could be separated from ACW by settling. The supernatant of neutralized ACW was treated by an oxidation process to remove COD, and then coagulated for the further removal of residual pollutants. Batch experiments were implemented to investigate effects of each process on pollutants removal using a flocculator (ZR4-6, China) at 20 ± 0.5 °C.

2.2.1. Neutralization and settling process

Eight samples of well-mixed ACW were adjusted to the desired pH (4.0, 5.0, 6.0, 6.5, 7.0, 7.5, 8.0 and 8.5) with 98% sulfuric acid, and then stirred at 100 rpm for 30 min. Then the solution was settled down for 10 min, and COD concentrations of the supernatant were measured to determine the optimum pH with maximum COD removal. Then 10 L well-mixed ACW was neutralized to the optimum pH by sulfuric acid for further treatment.

2.2.2. Oxidation process

In the oxidation process, the neutralized ACW was treated by sodium hypochlorite (NaClO). Nine oxidation tests were conducted with different molar ratios of hypochlorite and COD (HCR) (0, 0.38, 0.75, 1.13, 1.69, 2.25, 2.81, 3.38 and 4.50) at stirred rate of 100 rpm for 60 min. Then the oxidized ACW was sampled for analysis before the following coagulation treatment.

2.2.3. Coagulation process

The nine oxidized ACW samples were further coagulated by aluminum sulfate (AS) at dosage of 0.6 g Al/L to confirm effects of coagulation afterwards on organic matters removal. Furthermore, the oxidized ACW at HCR of 1.28 was coagulated under dosages ranged from 0.2-1.2 g Al/L and different pH values of 9.0–11.5. After dosing AS, the wastewater was stirred at 100 rpm for 10 min, and then settled for 30 min. Settling volume for 30 min (SV_{30}) was measured to indicate the settleability of coagulated samples. The supernatant was taken for water quality analysis, and the settled precipitates were also treated for composition and morphological analysis.

2.3. Response surface optimization experiments

Based on results of the batch experiments of NaClO oxidation and coagulation, the three-factor three-level Box-Behnken experimental design was used to investigate effects of factors influencing pollutants removal from ACW. HCR (0.375–2.25), pH (9–11.5) and AS dosage (0.2–1.2 g Al/L) were chosen as the three factors of response surface experiment, and COD concentration in the coagulated ACW was selected as the response variable. In total, 17 runs were conducted for the experimental design and are shown in Table S1. Experimental design and analysis of variance (ANOVA) were performed using the Design Expert 8.0 software.

Based on the data obtained from the RSM experiments, the relationship between response variables and the set of factors is usually fitted by a second-order polynomial model given in Eq. (1).

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} X_i X_j \quad (1)$$

where, Y is the response variable; X_i and X_j represent the coded independent variables; k is the number of factors; b_0 is the constant