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Application of response surface method as an experimental design to optimize coagulation–flocculation process for pre-treating paper wastewater

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ABSTRACT

The response surface methodology (RSM) was employed to study the pre-treatment of paper wastewater with polyaluminum chloride (PAC) as the coagulant and cationic polyacrylamide (c-PAM), as the flocculant in the coagulation–flocculation (CF) process. In addition, the three quadratic models of the three factors of PAC dosage, PAM dosage, and pH were established with the chemical oxygen demand (COD), total suspended solids (TSS), and sludge volume index (SVI) as three responses. The optimal conditions obtained from the compromise of the three desirable responses are PAC 3689 mg/L, PAM 39.9 mg/L, and pH 5.4, respectively. From zeta potential measurement, it was concluded that charge neutralization is the main mechanism of coagulation at slightly acid pH, and c-PAM is very effective in the bridge effect. Additionally, the results offered a certain reference value for the practical application of the CF process using hybrid PAC and c-PAM in stabilized paper pretreatment for COD and TSS removal.

Introduction

The pulp and paper industry is a major water-intensive chemical process industry. It is a significant contributor of pollutants to the environment. Some of the raw materials (e.g. fibers, water, fillers, retention aids, dyes, fluorescent whitening agents (FWA), sizing agent, starch, wet strength agent) that are used for production of the paper (printing and information paper, wrapping paper, sanitary tissue) may enhance the organic load of the wastewater [1,2]. Coagulation–flocculation is widely used for wastewater treatment, as it is efficient and involves a simple operation. Chemical coagulation followed by sedimentation is a proven technique for the treatment of high suspended solids wastewater especially those formed by colloidal matters [3]. The coagulation/flocculation process can be used as a pretreatment prior to biological treatment in order to enhance the biodegradability of the wastewater during the biological treatment [4].

Coagulation/flocculation is a commonly used process in wastewater treatment in which compounds such as Alum, polyaluminum chloride (PAC) and/or polymer are added to wastewater in order to destabilize the colloidal materials and cause small particles to agglomerate into larger settleable flocs [5]. Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids removal in wastewater treatment has rapidly grown [5,6]. Flocculations of suspended particles occur via charged amide or carboxylic groups. Polyacrylamide (PAM) is a commonly used polymeric flocculant because it is possible to synthesize polyacrylamides (PAMs) with various functionalities (positive, neutral, or negative charge) that can be used to produce good settling performance at relatively low cost [7]. Research and practical applications have shown that optimal coagulation will lower the pollution load [8,9]. As a result of the smaller load, the wastewater treatment plant could be designed to be more energy efficient at with smaller footprint and with lower investment costs [10]. Accordingly, several studies have reported the coagulation–flocculation process for the treatment of industrial wastewater (paper-recycling [11], pulp mill [12], pulp and paper mill [13], landfill leachate [14], textiles [15], etc.) especially with respect to the performance optimization of coagulant (Alum, PAC, PACl, $FeSO_4$, $FeCl_3$)/flocculant (Chitosan-g-PDMC, g-PAM-gPDMC, PVP-g-PAM) and the determination of economical and optimal conditions using the response surface method (RSM).

In the coagulation/flocculation process, many factors can influence the efficiency of the process, such as the type and

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dosage of coagulant/flocculant, pH, mixing speed and time, temperature, and retention time, etc. [16–18]. The optimization of these factors can significantly increase the process efficiency. In conventional multifactor experiments, optimization is usually carried out by varying a single factor while keeping all other factors fixed at a specific set of conditions [19]. While it is time-consuming, the true optimum cannot be reached since the interactions among variables is ignored. On the other hand, the response surface methodology (RSM) method has been proposed to determine the influences of individual factors as well as their interactive influences. The RSM is a statistical technique for designing experiments, building models, evaluating the effects of several factors, and searching optimum conditions for desirable responses. With RSM, the interactions of possible influencing parameters on treatment efficiency can be evaluated with a limited number of planned experiments [20,21].

The main objective of this work was to optimize the coagulation–flocculation process and investigate the interactive effects of experimental factors, including coagulant dosage, flocculant dosage, and pH. For this purpose, paper wastewater was selected as the target to be treated by the coagulation–flocculation process which was optimized by RSM. The COD and TSS of treated wastewater and the sludge volume index (SVI) were chosen as the dependent output variables. The compromise optimal conditions for the three responses were also obtained using the desirability function approach.

Materials and methods

Wastewater measurements and analyses

The experiments were carried out at a laboratory bench scale using a jar test apparatus. Statistically designed experiments were used to optimize of the two most effective operating variables in the coagulation–flocculation process, namely the coagulant dosage and pH. The wastewater was collected from the wastewater treatment plant equalization tank of a paper mill in Deajon, Korea. Wastewater samples were characterized and the results of the analyses are given in Table 1. The collected samples were stored at 4 °C. Characterization was carried out immediately after the samples arrived in the laboratory. Table 1 shows the characteristics of the samples determined according to the Standard Methods [22]. The variation of Zeta potential during the process of coagulation–flocculation using PAC and c-PAM was measured by Zetasizer 2000 (Malvern Instruments Ltd., Company, England).

Coagulation–flocculation process

Polyaluminum chloride (PAC) was used as a coagulant in this work. The PAC was in the powder form, with the formula $Al_2(SO_4)_3 \cdot 16H_2O$, and was supplied by Sigma. PAM was used as the flocculant, while cationic polyacrylamide (c-PAM) with a very high linear molecular weight (7×10^5 to 9×10^5) and low charge density (2–2.5) was used as the flocculant.

PAM was supplied by Yixing Cleanwater Chemicals Co., Ltd. in China. Distilled water was used to prepare all the PAM feedstock solutions of 0.1%. The pH was adjusted using 0.1 M HCl or 0.1 M NaOH immediately before dosing of the coagulant. To investigate the removal efficiencies of COD and TSS, sludge volume index (SVIs) by jar tests were used to perform the coagulation–flocculation process. The experiments were carried out using 2 L square jars, with six paddle stirrers (Ewha Tech., Korea). The time and speed for rapid and slow mixing were set with an automatic controller as follows: rapid mixing at 250 rpm ($G = 550\ s^{-1}$) for 1 min after coagulant addition, followed by slow mixing at 30 rpm ($G = 22\ s^{-1}$) for 30 min, and then settling for 30 min. After settling, the supernatant was analyzed for the COD and TSS was determined following the Standard Methods and manufacturer's instructions for the instrument. The remaining portion of the treated wastewater samples was used to determine the SVI.

Experimental design

A response surface methodology was used to determine the relationship between the coagulation–flocculation process responses (COD and TSS removals, and SVI) with the most important variables (PAC dosage, PAM dosage, and wastewater pH). As shown in Fig. 1, this rotatable experimental plan was carried out as a central composite design (CCD) consisting of 20 experiments. For three variables ($n = 3$) and three levels (low (−), medium (0), and high (+)), the total number of experiments was 20 determined by the expression: $2n$ ($2^3 = 8$: factor points) + $2n$ ($2 \times 3 = 6$: axial points) + 6 (center points: six replications), as shown in Fig. 2.

The ranges and the levels of the variables investigated in this study are given in Table 2.

A complete set of the experimental design is shown in Table 3. As shown in Table 3, the three-factor CCD was implemented to investigate the effects of the three independent operating variable conditions [X_1 (PAC dosage: 1000–5000 mg/L), X_2 (PAM dosage: 10–50 mg/L), and X_3 (pH: 2–10)] on the responses Y [% of COD removal (Y_1), % of TSS removal (Y_2), and % of SVI (Y_3)].

A full second-order polynomial model obtained by multiple regression technique for three factors by using the SAS package (SAS Institute, Cary, NC, USA) and the MINITAB package (Minitab Institute, USA) was adopted to describe the response surface. The real values of the independent variables (X_i) were coded to z_i

Table 1
Chemical characteristics of the paper[a] wastewater used.

Parameter	Unit	Range	Mean[b]
Temperature	°C	30–45	42
pH	–	7.2–8.3	7.8
TCOD[c]	mg/L	2940–3521	3257
SCOD[d]	mg/L	298–382	345
TSS	mg/L	745–1050	825
Turbidity	NTU	520–825	752

[a] Paper (tissue, printing, newsprint, etc.).
[b] Values show the average values of 10 samples.
[c] Total chemical oxygen demand.
[d] Soluble chemical oxygen demand.

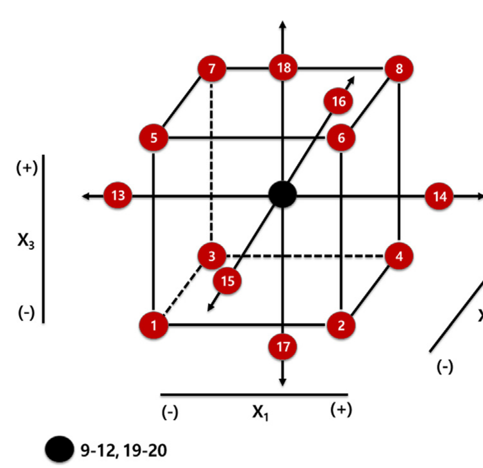

Fig. 1. Schematic diagram of central composite design (CCD) as a function of X_1 (PAC dosage), X_2 (PAM dosage), and X_3 (initial pH) according to the 2^3 factorial design with six axial points and six central points (replication) as shown in Table 3.