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Pretreatment of landfill leachate by using the composite of poly ferric sulfate and bioflocculant MBFR10543

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ABSTRACT

In this study, considering humic acids (HA) removal as well as some traditional indexes such as COD, color, and turbidity removals from landfill leachate, potential of the composite of alkaline-thermal-treated sludge (as a bioflocculant) and poly ferric sulfate (PFS) was studied in leachate pretreatment. Results showed that this composite could remove COD, HAs, color, and turbidity from the leachate by 72.6, 79.3, 64.9, and 85.1%, respectively, under the condition of bioflocculant of 19.3 mg L^{-1}, PFS of 12.7 g L^{-1}, pH 6.9, and agitation speed of 202 rpm, which was optimized by response surface methodology. The appreciable removal of COD and HA indicated that the coagulation–flocculation process as a pretreatment could effectively remove recalcitrant compounds from landfill leachate.

Keywords: Bioflocculant; Poly ferric sulfate (PFS); Landfill leachate; Alkaline-thermal (ALT)-treated sludge; Response surface methodology (RSM)

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1. Introduction

As is well known, sanitary landfill still remained the commonest way for municipal solid waste disposal, which generated a high-strength liquid with complex and variable constituents referred to as landfill leachate [1–3]. Due to the dark color, high levels of organics (such as humic acids (HA)), and the presence of inorganic macro-constituents, the leachate cannot be effectively treated by conventional methods [4]. From this standpoint, the leachate treatment has been one of the most bothersome environmental issues to be solved [5]. At present, the chief methods for leachate treatment were biological and physical–chemical processes. Biological processes were regarded as the most efficient options to deal with leachate, such as membrane bioreactor (MBR) [6–8]. Nevertheless, the biological processes were only efficient in the treatment of young leachate, which was rich in volatile fatty acids, but they were hardly able to achieve a high efficiency in older leachate treatment, due to the major presence of non-biodegradable organics [9]. In addition, it cannot be denied that when ammonium nitrogen was considered a major pollutant in leachates, nitrification–denitrification was widely used for both young and old leachates (although an external biodegradable carbon source may be needed in the latter case) [10]. As an advanced beneficial physical–chemical process in leachate treatment projects, Fenton process can be used as an effective pretreatment method to remove large molecule organics, for example, Zhang et al. have dealt leachate by means of Fenton oxidation–MBR, in this case, integration of MBR to the effluent of Fenton reactor increased the average COD removal efficiency (RE) from 62.2 to 93.1% [11]. Fenton process presented some disadvantages in practical application such as complicated control process, toxic intermediates generated from the oxidation process, and high running cost. Coagulation–flocculation process has been regarded as a more effective alternative technology for the pre- or post-treatment of stabilized leachate to reduce pollutants load for the subsequent biological process [12].

Chemical flocculants were efficient in wastewater treatment by using coagulation–flocculation process, compared with aluminum salts, iron-based coagulants were found to be effective with a lower dose, coagulate in a wider pH range, and pose less health risks than aluminum counterparts in the event of an overdose [13]. Poly ferric sulfate (PFS), as a polymerized iron-based coagulant, was investigated for the stabilized leachate pretreatment in this study. Despite the effective flocculating performance, the widely used inorganic and organic flocculants in wastewater treatment have been reported to be toxic and non-readily degradable [14]. On the contrary, bioflocculant, secreted by micro-organisms during their active secretion and cell lysis, was a kind of environment-friendly material with the character of harmless and biodegradable, which has been considered as a potential solution to the toxicity to aquatic life and environment pollution in recent years [15–17].

It is reported that the composite of bioflocculant and chemical flocculant in a coagulation–flocculation process can reduce the risk brought by chemical flocculants, since their dose was decreased to the least [18], thus, in this study, the bioflocculant from alkaline-thermal (ALT)-treated sludge was selected to be composited with the PFS for the stabilized leachate pretreatment. The response surface methodology (RSM), a statistical technique for building multivariable equation and evaluating their optimal values [19,20], was employed to search the optimum conditions of the coagulation–flocculation process and to investigate the interactions of possible individual parameters including doses of the PFS and bioflocculant, solution pH, and agitation intensity. Landfill leachate was chosen as a representative sample, and the removal of four dependent parameters was settled as the response variables: HA removal combined with COD removal, which might reflect the decrease in recalcitrant organics more accurately, the removal of color and turbidity, as two conventional parameters in leachate pretreatment. The optimal conditions were their compromised result.

2. Materials and methods

2.1. Coagulant, bioflocculant, and leachate

Coagulant, PFS (19.5% $Fe_2(SO_4)_3$), supplied by Henan Jieyuan Water Treatment Material Co. Ltd., was a commercial product.

Bioflocculant-producing strain, *Rhodococcus erythropolis*, was deposited in China Center for Type Culture Collection. Bioflocculant MBFR10543, a kind of microbial flocculant, was harvested from ALT-pretreated sludge with suspended sludge solids concentration of $25\ \mathrm{g\ L^{-1}}$ by *Rhodococcus erythropolis*; this sludge was collected from the biofiltration unit at a swine wastewater treatment plant located in Fuhua pig farm, Hunan Province, China [21].

Landfill leachate samples used in this study were obtained from an old landfill site located in Luodai, Sichuan, China, and were stored at 4℃ to prevent the natural degradation of organics. The main physical–chemical characteristics of raw leachate are summarized in Table 1. It illustrated that the leachate was a highly turbid liquid with a high concentration of COD and HA, and the pH was higher than 7.0.

2.2. Experimental procedures

A standard jar test apparatus (ET-720, Lovibond, Germany) comprising six paddle rotors in 400-mL beakers was used for the coagulation–flocculation experiments. Leachate samples were taken and placed for about 1.5 h to return to room temperature before any test. Prior to adding PFS and bioflocculant, leachate samples were added into the beakers and the pH values were adjusted to the desired levels using $1.0\ \mathrm{mol\ L^{-1}}$ NaOH or HCl. PFS and bioflocculant were then added into the samples in turn, and the mixtures were immediately stirred at 200 rpm for 30 min. After agitation, all the samples were allowed to stand for 60 min. Thereafter, a 50-mL supernatant was withdrawn and filtered by 0.45-μm filter membrane for the measurement and analysis. The RE of parameters can be calculated according to the following equations:

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

where C_0 and C_e are initial and final parameters (COD, HA, color, and turbidity) concentrations of the leachate, respectively.

Table 1
Landfill leachate characterization before/after pretreatment

Parameters	Raw leachate	After treated by the composite	Model predictions	Standard deviation (%)	Discharge limited value[a]
COD (mg L^{-1})	9,853.6	2,825.8	2,699.9	4.5	100
HA (mg L^{-1})	554.3	118.5	114.7	3.2	–
Color	264.5	96.4	92.8	3.7	40
Turbidity (mg L^{-1})	923.6	134.2	137.6	2.5	–
SS (mg L^{-1})	4,475.2	1,357.8	1,381.5	1.7	30
Ammonium (mg L^{-1})	2,478.1	1,576.9	1,543.4	2.1	25
pH	7.6	7.2	6.9	4.2	–

[a] China national standard for pollution control on the landfill site of municipal solid waste wastewater discharge (GB 16,889-2008).

2.3. Analytical procedures

Conventional parameters, COD, color, and turbidity were determined according to APHA Standard Methods [22]. The measurement of HA was conducted by a UV–vis spectrophotometer (UV2800, Sunny Hengping Scientific Instrument Co. Ltd., Shanghai, China) at wavelength 630 nm. pH values of all samples were determined by a pH Meter (Hach-HQ11d, USA).

2.4. RSM experimental design, analysis, and optimization

Central composite design (CCD), the standard approach of RSM, was selected to investigate the interactions of factors including the bioflocculant dose (x_1), PFS dose (x_2), pH (x_3), and agitation speed (x_4). In order to obtain an effective range of the studied factors, some preliminary studies with wide bioflocculant dose, PFS dose, and initial pH ranges of 10–60 mg L^{-1}, 5–30 g L^{-1}, and 3–12 were carried out prior to the experimental design. The response variable (y) that represented removal efficiencies of the four dependent parameters (COD, HA, color, and turbidity) were fitted by a second-order model in the form of quadratic polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{m} \beta_i x_i + \sum_{i<j}^{m} \beta_{ij} x_i x_j + \sum_{i=1}^{m} \beta_{ii} x_i^2 \qquad (2)$$

where y is the response variable to be modeled, x_i and x_j are independent variables which determine y, β_0, β_i, and β_{ii} are the offset term, the i linear coefficient, and the quadratic coefficient, respectively. β_{ij} is the term that reflects the interaction between x_i and x_j. The actual design ran by the statistic software, Design-expert 7.1.3 (Stat-Ease Inc., USA), is presented in Table 2.

3. Results and discussion

3.1. Production and characteristics of the bioflocculant MBFR10543

It is clear that sludge treatments disintegrated the organic fractions and released soluble carbon into the sludge medium. Carbon sources and nitrogenous organic materials available in sludge medium changed with different treatment methods and therefore could change bioflocculants secretion pattern and yields [23,24]. Thus, before bioflocculant production, the sludge suspensions were treated by sterilization (ST), ALT, and acid-thermal (ACT) treatments, respectively. Sterilization was carried out by autoclaving (steam sterilization) at 121℃ for 30 min. In ALT treatment, first, pH value of the sludge solution was increased to 10 by using 1.0 mol L^{-1} NaOH at room temperature (25℃) and then autoclaved in the same procedure. In the ACT treatment, first, pH value was reduced to 2.0 using 1.0 mol L^{-1} HCl at room temperature (25℃) and then autoclaved in the same procedure. After autoclaving, pH value of all the sludge samples was adjusted to 7.0 using 1.0 mol L^{-1} HCl or NaOH. In our previous study, the specific carbon and nutrient contents released in the ALT sludge medium were more favorable to bioflocculants secretion as compared to that of ST and ACT sludge [21].

Table 2
Coded levels for four variables framed by the CCD

Factors	Codes	Code levels		
		−1	0	1
Bioflocculant (mg L^{-1})	x_1	10	20	30
PFS (g L^{-1})	x_2	5	10	15
pH	x_3	5	7	9
Agitation speed (rpm)	x_4	100	200	300

The bacterial strain was first inoculated in the sterilized sludge in a 250-mL Erlenmeyer flask, and was incubated on a reciprocal shaker at 150 rpm and 35℃ for 24 h. Subsequently, 2.0% V/V of the inoculum was used to inoculate the different pretreated sludge samples (ST, ALT, ACT treatments). These inoculated sludge and the control sample (without inoculating) were incubated in the same procedure to produce bioflocculant. After 60 h of cultivation, maximum bioflocculant of 2.9, 4.1, and 1.8 g L^{-1} were harvested from fermented broths of ST-, ALT-, and ACT-pretreated sludge, while a very low concentration of less than 0.15 g L^{-1} was obtained from the control sample. Studies conducted by Verma et al. have confirmed the fact that the soluble carbon and nitrogen concentrations increased after sludge treatments, and this increase was more obvious in the case of ALT-pretreated sludge as compared to ST- and ACT-pretreated sludge [25]. Thus, the bioflocculant significantly varied with different sludge pretreatments, and the bioflocculant from ALT-pretreated sludge was utilized directly in the pretreatment of landfill leachate.

Thermal stability of the bioflocculant depends on its active ingredients, as known to all, bioflocculants with sugars were thermostable, while those made of protein were generally sensitive to heat. In our previous study, the flocculating activity of the bioflocculant from ALT-pretreated sludge was decreased by about 60% after being heated at 80℃ for 30 min and by about 85% after being heated at 120℃ for 30 min. Poor heat stability indicated a protein backbone of the bioflocculant. Chemical analysis of the bioflocculant revealed that the total protein of the purified bioflocculant was 98.8% (W/W), including glutamic acid, alanine acid, and aspartic acid with a mass proportion series of 14.8, 17.3, and 12.6% (W/W), respectively, and there was almost no polysaccharide contained in the bioflocculant. Furthermore, it is found that the presence of hydroxyl, carbonyl, and carboxyl groups in the bioflocculant produced by using ALT-pretreated sludge was all preferable functional groups for the flocculation process in polyelectrolyte. The bioflocculant participated in the flocculation mainly through available hydroxyl, carbonyl, and carboxyl groups which induced very high binding capacity. The negative charge groups could react with the positively charged site of suspended particles in the wastewater, in this case, the particles can approach sufficiently close to each other so that attractive forces become effective [21].

3.2. Performance of the bioflocculant and coagulant

The removal efficiencies of COD, HA, color, and turbidity at the different doses of the bioflocculant and PFS varying from 10 to 60 mg L^{-1} and 5 to 30 g L^{-1}, respectively, are shown in Fig. 1. The behavior of leachate pretreatment as a function of solution's pH at the optimal dose of the bioflocculant and PFS from Fig. 1 is presented in Fig. 2.

In the bioflocculant flocculation process, it was observed that the removal efficiencies increased rapidly with the bioflocculant dose increasing from 10 to 30 mg L^{-1} when the solution pH was adjusted in the range of 6–8, and went to the values as high as 56.5, 62.7, 48.4, and 71.6% for COD, HA, color, and turbidity, respectively. The increasing bioflocculant dose above 30 mg L^{-1} had negligible effects on the increase in removal efficiencies (Fig. 1(a)), which may be attributed to the formation of aggregates at higher solid/liquid ratios or to the precipitation of particles [26]. In the same way, PFS got the best at 15 g L^{-1} (Fig. 1(b)), and the decline in removal efficiencies was observed when moving away from this point. As seen

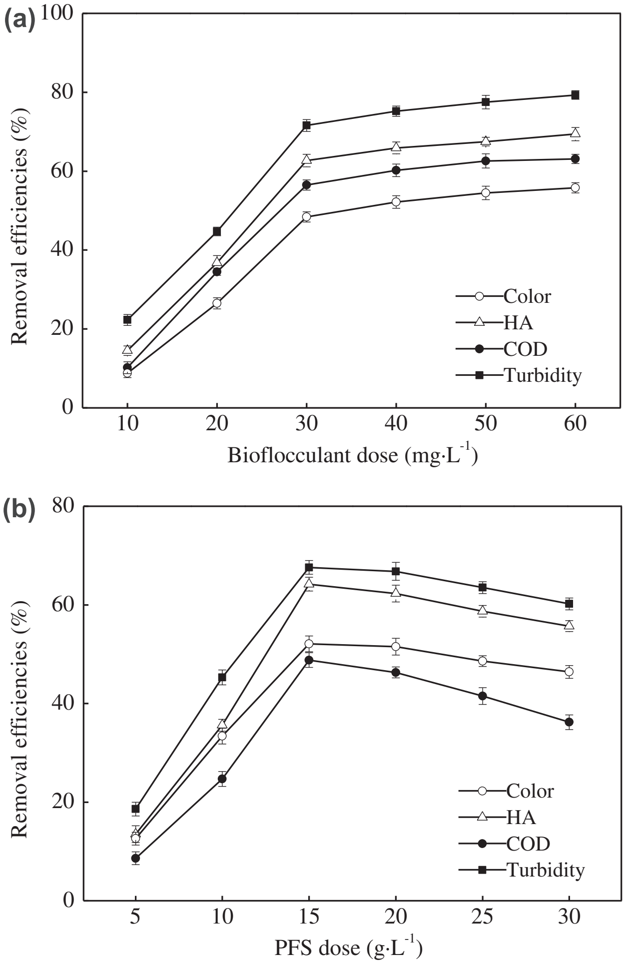

Fig. 1. Removal efficiencies at different doses of (a) bioflocculant and (b) PFS.

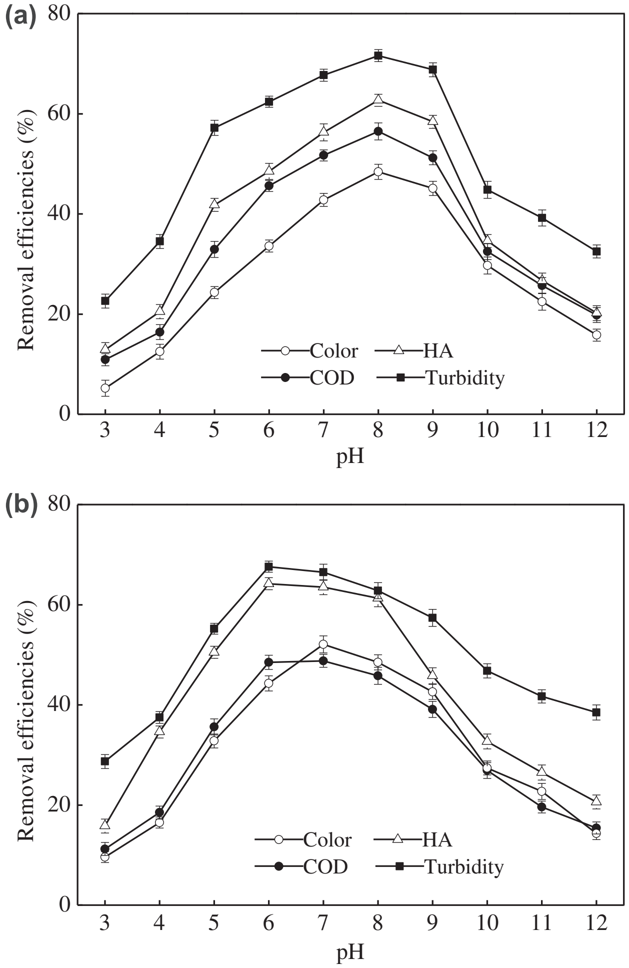

Fig. 2. Removal efficiencies changed with solution pH at the optimal dose of (a) bioflocculant and (b) PFS.

from Fig. 2(a), the decline in removal efficiencies was observed when moving away from the pH range of 6–8; as the pH values are above 8, negative charge density increased with the increase in pH, and hence increased electrostatic repulsion of the negatively charged particles and bioflocculant chains. In acidic environment, the hydrogen ions (H^+) concentration increased with the decrease in pH, which shares the functional groups of the bioflocculant, and thereby results in a depression of removal efficiencies. Meanwhile, it is well known that iron-based coagulants were effective in a wider pH range for coagulation, and in this study, PFS worked well in the pH range of 5–9 (Fig. 2(b)).

As it is mentioned above, the maximum doses of the bioflocculant and PFS in the RSM experiment were selected as 30 mg L^{-1} and 15 g L^{-1}, respectively, and the solution pH was adjusted in the range of 5–9.

3.3. Statistical analysis

To understand the influence of the bioflocculant dose, PFS dose, solution pH, and agitation speed on the corresponding responses (COD, HA, color, and turbidity removal efficiencies), the experiments were designed using RSM based on the performance of the bioflocculant and PFS in the leachate pretreatment. Following equations represent empirical relationship in the form of quadratic polynomial between the removal efficiencies and the four factors (x_1–x_4):

$$\begin{aligned} y_1 = {} & 69.60 + 2.25\,x_1 + 6.92\,x_2 - 1.08\,x_3 - 2.42\,x_4 \\ & - 4.75\,x_1x_2 - 4.25\,x_1x_3 - 1.75\,x_1x_4 - 4.00\,x_2x_3 \\ & + 4.50\,x_2x_4 - 2.00\,x_3x_4 - 6.47\,x_1^2 - 2.72\,x_2^2 \\ & - 16.22\,x_3^2 - 2.72\,x_4^2 \end{aligned} \tag{3}$$

$$\begin{aligned} y_2 = {} & 78.80 - 0.58\,x_1 + 4.25\,x_2 + 0.50\,x_3 - 0.50\,x_4 \\ & - 3.50\,x_1x_2 + 3.75\,x_1x_3 + 0.50\,x_1x_4 - 3.50\,x_2x_3 \\ & + 0.75\,x_2x_4 - 0.25\,x_3x_4 - 12.90\,x_1^2 - 6.65\,x_2^2 \\ & - 16.27\,x_3^2 - 5.03\,x_4^2 \end{aligned} \tag{4}$$

$$\begin{aligned} y_3 = {} & 63.80 + 2.00\,x_1 + 6.00\,x_2 - 2.17\,x_3 - 1.67\,x_4 \\ & - 5.00\,x_1x_2 - 3.50\,x_1x_3 + 2.00\,x_1x_4 + 5.50\,x_2x_3 \\ & + 3.00\,x_2x_4 + 0.50\,x_3x_4 - 8.07\,x_1^2 - 7.32\,x_2^2 \\ & - 16.57\,x_3^2 - 2.32\,x_4^2 \end{aligned} \tag{5}$$

$$\begin{aligned} y_4 = {} & 84.00 + 0.25\,x_1 + 5.08\,x_2 + 1.58\,x_3 + 0.083\,x_4 \\ & - 3.50\,x_1x_2 + 6.50\,x_1x_3 + 5.25\,x_1x_4 - 4.50\,x_2x_3 \\ & + 2.25\,x_2x_4 + 2.25\,x_3x_4 - 12.50\,x_1^2 - 6.25\,x_2^2 \\ & - 14.50\,x_3^2 - 3.50\,x_4^2 \end{aligned} \tag{6}$$

Statistical testing of these models was performed with Fisher's statistical method for analysis of variance (ANOVA) [27]. The results of ANOVA analysis in terms of coded variables for removal efficiencies of COD, HA, color, and turbidity indicated that all the final models were significant at 95% confidence level with values of Prob. $> F$ (<0.0001) less than 0.05 and values of $F_{\text{statistic}}$ of 19.11, 19.97, 26.67, and 20.58 (the ratio of mean square due to regression to mean square to real error) greater than $F_{0.01}(20, 29)$ of 2.57. There were only 0.01% chances that a "Model F-value" this large could occur due to noise. The lack of fit (LOF) test showed variation of the data around the adapted model, and the LOF will be significant ($p < 0.05$) if the model fits the data well. As presented in Table 3, all

Table 3
ANOVA results for the four responses

Responses (removal efficiency (%))	Item	Sum of squares	Degrees of freedom	Mean square	F-value	Prob. > F	p-value	R^2	Adjusted R^2	AP
COD	Model	2,847.93	14	203.42	19.11	<0.0001[a]				
	Lack of fit	147.83	10	14.78	49.28		0.0010[a]	0.9503	0.9005	13.80
HA	Model	2,779.47	14	198.53	19.97	<0.0001[a]				
	Lack of fit	136.42	10	13.64	19.49		0.0057[a]	0.9523	0.9046	15.00
Color	Model	2,946.36	14	210.45	26.67	<0.0001[a]				
	Lack of fit	103.67	10	10.37	6.10		0.0481[a]	0.9639	0.9277	18.59
Turbidity	Model	2,829.26	14	202.09	20.58	<0.0001[a]				
	Lack of fit	133.50	10	13.35	13.35		0.0117[a]	0.9537	0.9073	15.46

Notes: AP: adequate precision; R^2: determination coefficient; adjusted R^2: adjusted determination coefficient.

[a]Significance.

Table 4
Significance of quadratic model coefficient for the four responses

Responses (removal efficiency (%))	Independent variables	Coefficient estimate	Degrees of freedom	Standard error	Prob. > F
COD	x_2	6.92	1	0.94	<0.0001[a]
	x_1x_2	−4.75	1	1.63	0.0114[a]
	x_1x_3	−4.25	1	1.63	0.0208[a]
	x_1^2	−6.47	1	1.28	0.0002[a]
	x_3^2	−16.22	1	1.28	<0.0001[a]
HA	x_2	4.25	1	0.91	0.0004[a]
	x_1x_2	−3.50	1	1.58	0.0435[a]
	x_1x_3	3.75	1	1.58	0.0322[a]
	x_2x_3	−3.50	1	1.58	0.0435[a]
	x_1^2	−12.90	1	1.24	<0.0001[a]
	x_3^2	−16.27	1	1.24	<0.0001[a]
Color	x_2	6.00	1	0.81	<0.0001[a]
	x_1x_3	−5.00	1	1.40	0.0031[a]
	x_2x_3	−3.50	1	1.40	0.0259[a]
	x_1^2	−8.07	1	1.10	<0.0001[a]
	x_3^2	−16.57	1	1.10	<0.0001[a]
Turbidity	x_2	5.08	1	0.90	<0.0001[a]
	x_1x_2	−3.50	1	1.57	0.0423[a]
	x_1x_3	6.50	1	1.57	0.0010[a]
	x_1x_4	5.25	1	1.57	0.0048[a]
	x_2x_3	−4.50	1	1.57	0.0123[a]
	x_1^2	−12.50	1	1.23	<0.0001[a]
	x_3^2	−14.50	1	1.23	<0.0001[a]

[a]Significance.

the p-values (0.0010, 0.0057, 0.0481, and 0.0117 for the four empirical models) for LOF were less than 0.05, which suggested that there were almost no systematic variation unaccounted in the models, and there were 0.10, 0.57, 4.81, and 1.17% chances that a "LOF F-value" this large could occur due to noise. Moreover,

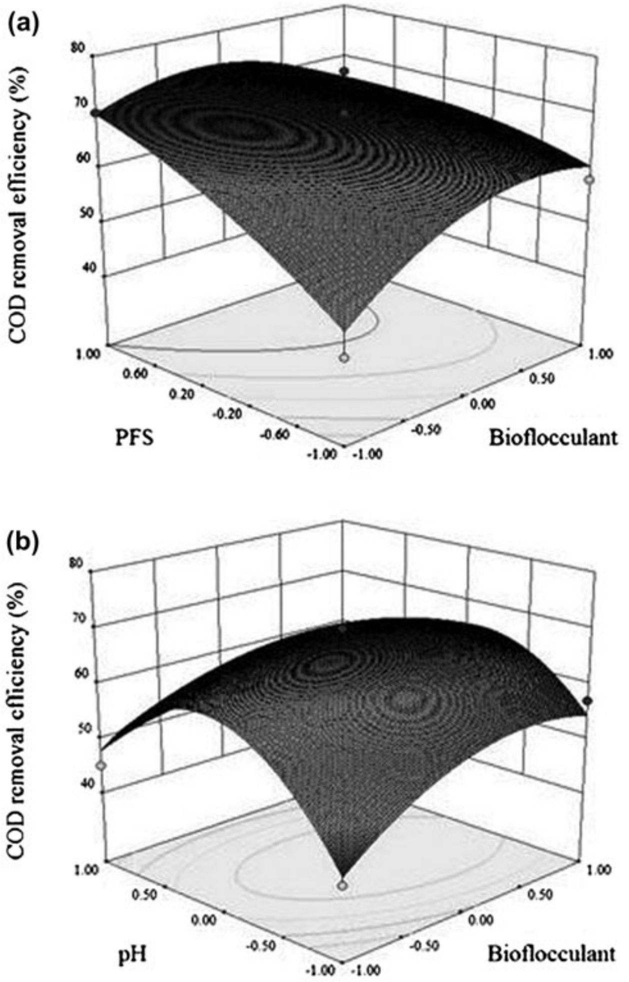

Fig. 3. Surface graphs of COD RE showing the effect of variables (a) bioflocculant–PFS and (b) bioflocculant–pH.

the “LOF *F*-value” of 49.28, 19.49, 6.10, and 13.35 implied the LOF was significant. Besides, as an evaluation of the model’s overall performance, all the determination coefficient R^2 values in this study were relatively high (0.9503, 0.9523, 0.9639, and 0.9537 for the four models), which indicated a good agreement between the model predicted and the experimental values (Table 3). Meanwhile, adjusted R^2, permitting for the degrees of freedom associated with the sums of the squares, should be an approximate value of R^2. The adjusted R^2 values were 0.9005, 0.9046, 0.9277, and 0.9073 for the four models, which were not significantly different with the determination coefficient R^2 values, showed that there were almost no chances that insignificant terms have been included in the model [28]. The values of 13.80, 15.50, 18.59, and 15.46 of adequate precision (AP) were found to be desirable for all models (AP greater than 4 is desirable), and this demonstrated that all predicted models could be used to navigate the design space defined by the CCD.

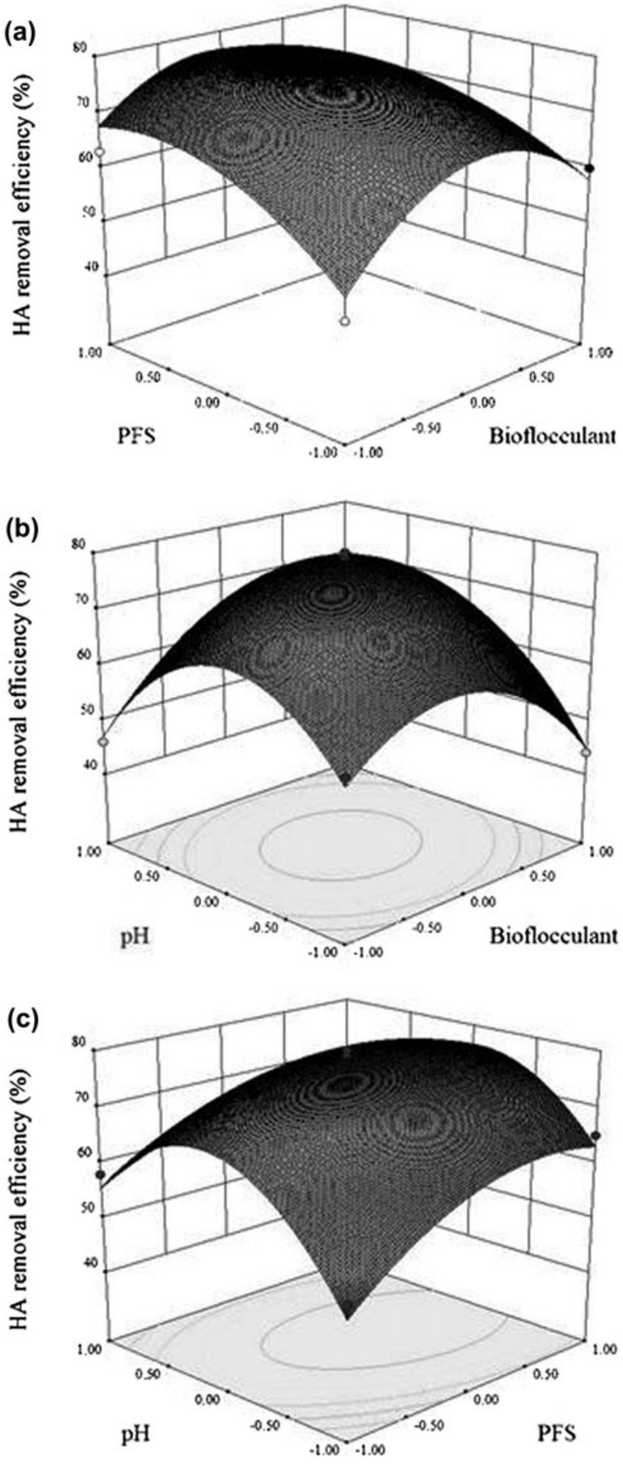

Fig. 4. Surface graphs of HA RE showing the effect of variables (a) bioflocculant–PFS, (b) bioflocculant–pH, and (c) PFS–pH.

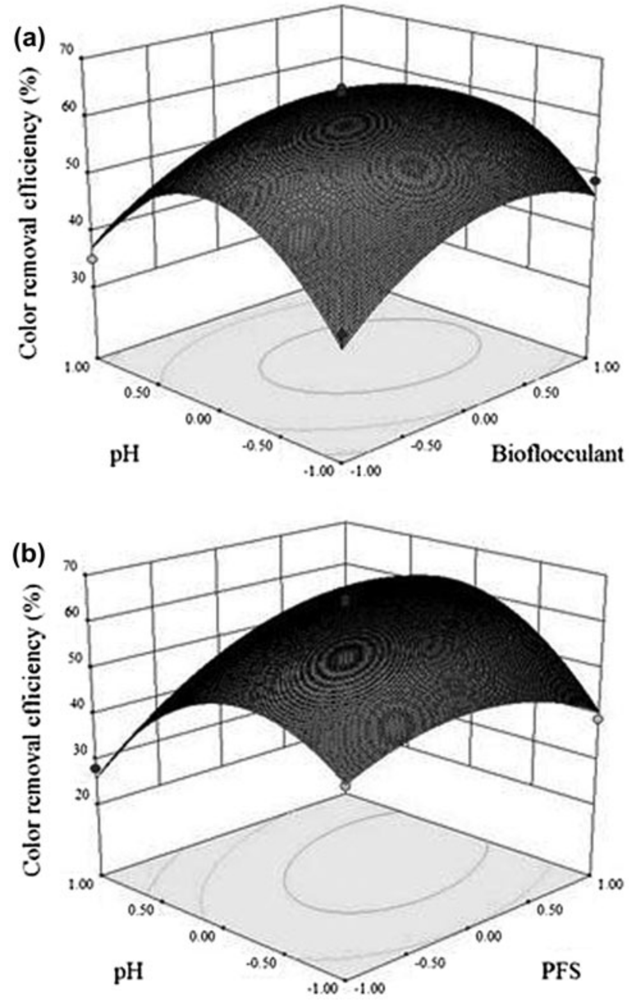

Fig. 5. Surface graphs of color RE showing the effect of variables (a) bioflocculant–pH and (b) PFS–pH.

The significance testing for the coefficient of the equations whose variables were in terms of coded factors is listed in Table 4. For all the four parameters, in the linear terms, PFS dose was significant, because the excessive PFS leads to the stabilization of the colloidal system again. Among the higher order effects, the quadratic terms of solution pH and bioflocculant dose were significant. Solution pH played a decisive role in the flocculating process has been proved in our previous study [26]; in acidic environment, the hydrogen ions concentration increased with the decrease in pH, which shares negative functional groups of the bioflocculant, and hence, the removal efficiencies declined. While in the strong alkaline environment ($pH > 10$), negative charge density increased with the increasing pH, and hence increased electrostatic repulsion of the negatively charged particles. As repulsion prevented particles from approaching the activity chain of the bioflocculant with the increased pH, there eventually results a depression of removal efficiencies. For the bioflocculant attributing to the absorption bridging action, particles adsorbed to a bioflocculant molecular chain, and they could be adsorbed simultaneously to other chains, leading to the formation of three-dimensional flocs, which were capable of rapid settling. Besides this, the flocculation might be attributed to a decrease in the electrostatic repulsion force between bioflocculant chains and particles by decreasing the negative charge on both the bioflocculant and particles surface by neutralizing in the presence of Fe^{3+}; eventually, the negative charge on suspended particles might be reversed from negative to positive. Thus, the negative charge groups could react with the positively charged site of suspended particles, in this case, the particles can approach sufficiently close to each other so that attractive forces become effective.

Figs. 3–6 depicted the interaction terms with a significant effect. The COD removal response on the bioflocculant–PFS doses surface in Fig. 3(a) showed that bioflocculant has an obvious effect on COD removal in composite process, and this agrees with the previous study using bioflocculant only. And it is predicted that at a low level of bioflocculant, COD removal was enhanced after the addition of PFS, and it can get to the peak ultimately. However, this target obviously becomes more difficult when the concentration of bioflocculant was kept at a high level [28]. This phenomenon suggested that the bioflocculant was a proper flocculant which could produce a positive effect on COD removal at low level of PFS for compounding. Fig. 3(b) showed that when the PFS dose and the top speed of agitation were kept at the central level, COD RE can get to the anticipant value at a small quantity of bioflocculant when pH value was in the range of 6.8–7.3 approximately. The HA removal response surfaces in Fig. 4(a) and (b) reflected almost identical points, the HA removal was enhanced by varying the doses of bioflocculant and PFS, and depended upon a neutral pH environment when the other two factors were kept at the central level. From Fig. 4(c), HA RE decreased when solution pH moved away from the optimal values. At low pH, PFS is more positively charged, and HA is more electroneutral because the proton is not likely to dissociate. Hence, the charge reversion (from negative to positive charge) of a fraction of the complexes restrained their removal. Fig. 5(a) showed the change of color removal with the bioflocculant dose and pH varying within the experimental ranges, while the PFS dose and the top speed of agitation were kept at central level. The curve and the curvature of the contour on the bottom also provided more evidence that the bioflocculant was relatively effective in natural pH environment. Fig. 5(b) showed that when the bioflocculant dose and agitation speed were kept at the central level, color RE can get to the anticipant value at a small quantity of PFS when solution pH value was in its optimal range, and also showed the decline of color RE when solution pH was moving away from the optimal values. The response surfaces in Fig. 6 illustrated that bioflocculant–PFS doses, bioflocculant–pH, bioflocculant–agitation speed, and PFS–pH were the interaction terms with a significant effect for turbidity removal. Fig. 6(a) provided more evidence that bioflocculant can improve the removal efficiencies when there was plenty of PFS for coagulation–flocculation process. However, PFS was not always a positive effect on turbidity removal. Excessive Fe^{3+} debased the size at a certain extent because they might occupy the absorption sites with negative charge on the bioflocculant molecules, then it could hinder the absorption bridging action which could increase the floc size. Fig. 6(b) showed the change in turbidity removal with the bioflocculant dose and pH when the PFS dose and the top speed of agitation were kept at central level. The curvature of the contour on the bottom also provided more evidence that the bioflocculant was relatively effective in natural pH environment. Fig. 6(c) showed that the turbidity removal was enhanced with the advance of bioflocculant and agitation speed, while the PFS dose and solution pH were kept at central level, agitation speed was significant based on the reasoning that a higher speed creates greater turbulence, and greater turbulence leads to better mixing [18]. Fig. 6(d) showed that the

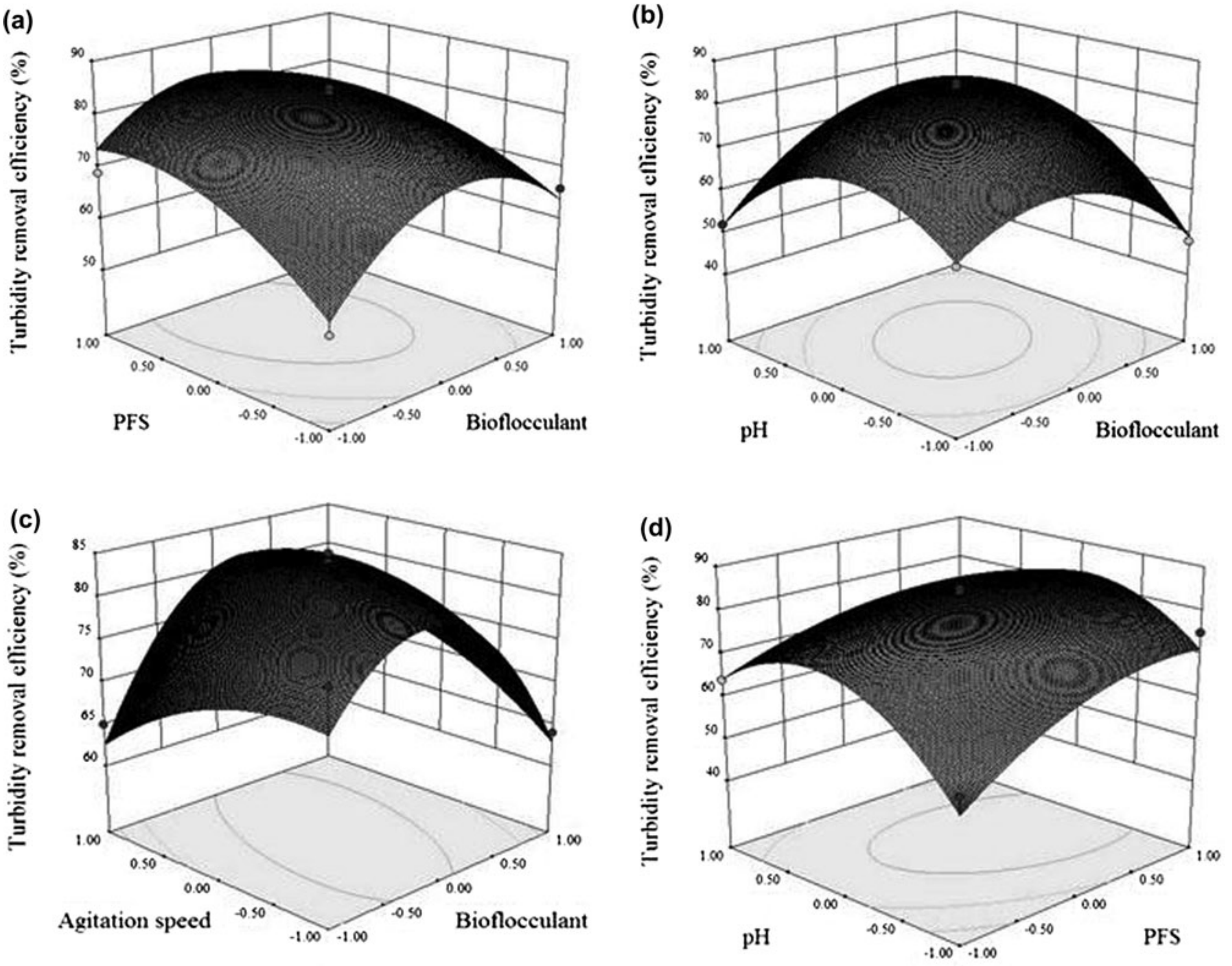

Fig. 6. Surface graphs of turbidity removal efficiency showing the effect of variables (a) bioflocculant–PFS, (b) bioflocculant–pH, (c) bioflocculant–agitation speed, and (d) PFS–pH.

Table 5
Elementary analysis of precipitates by EDS

Elementary	Wt.%	Elementary	Wt.%
C	31.2	Na	17.6
O	32.8	K	0.4
N	3.7	Mg	0.2
S	9.5	Ca	0.1
Cl	0.8	Si	0.3
P	0.3	Fe	2.7

turbidity removal varies with pH and PFS when the agitation speed and bioflocculant dose were at central level. At low level of pH, the influence of PFS on turbidity removal was inconspicuous. However, with the advance of pH, PFS showed a negative effect on turbidity removal gradually, and this might rise from the comprehensive effect between PFS and the bioflocculant.

3.4. Optimal coagulation–flocculation conditions

According to the target values of the four responses, COD, HA, color, and turbidity removal efficiencies of 100%, the optimal condition calculated from the regression equations was bioflocculant of 19.3 mg L^{-1}, PFS of 12.7 g L^{-1}, pH 6.9, and agitation speed of 202 rpm. Under this optimal condition, the composite flocculant could remove COD, HA, color, and turbidity from the leachate by 72.6, 79.3, 64.9, and 85.1%, respectively. The corresponding results (presented in Table 1) under the optimum process conditions showed that the composite flocculant has a great potential in landfill leachate pretreatment. Although the concentration of pollutants in the pretreated leachate by the composite declined obviously in comparison with raw leachate, the obtained results were still far from discharge limited according to Table 1. Therefore, to meet the national discharge standard, further treatment was required.

Additional experiments were carried out at the optimal conditions to check the agreement of the results acquired from models and experiments for the composite. As shown in Table 1, the residual COD, HA, color, and turbidity (measured by the removal efficiencies) achieved from the experiments were in close agreement with the model predictions (standard deviation < 5%). Thus, the use of the composite by RSM provides a feasible way to receive high removal efficiencies of pollutants from leachate.

3.5. Characterization of the precipitates

Elementary analysis of precipitates by EDS is listed in Table 5, it demonstrated that the pretreatment process by the composite of PFS and bioflocculant can not only remove organic substance, but also remove other pollutants in raw landfill leachate, such as metal ions, due to the adsorption or sweep flocculation of precipitates. Thus, the composite can be recommended for landfill leachate treatment in a large scale, providing a simpler, more controllable, and less reagent-consuming technique to the coagulation–flocculation process.

4. Conclusions

Potential of a composite flocculant was studied in landfill leachate pretreatment, the ALT-treated sludge as a bioflocculant was selected to be composited with PFS, and the RSM was applied to optimize the pretreatment conditions. Under the optimal condition of bioflocculant of 19.3 mg L^{-1}, PFS of 12.7 g L^{-1}, pH 6.9, and agitation speed of 202 rpm, the composite flocculant could remove COD, HA, color, and turbidity from the leachate by 72.6, 79.3, 64.9, and 85.1%, respectively. This study suggested that the composite of bioflocculant and PFS has a great potential to conventional flocculants in landfill leachate pretreatment.

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