

Improvement of the process of removing phosphorus from high-phosphorus distillery effluent by ferric chloride using response surface methodology and three-step method

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ABSTRACT

The purpose of this study was to optimize the coagulation–flocculation effect of a wastewater treatment system using the response surface methodology (RSM) and three-step method to minimize phosphorus concentration in the distillate wastewater. In order to minimize the concentration of total phosphorus (TP), experiments were carried out using 3³-factorial designs with three levels and three factors. A Box–Behnken design, which is the standard design of RSM, was used to evaluate the effects and interactions of three major factors (Fe:P (w/w) ratio, coagulation pH and fast mixing speed (FMS)) on the treatment efficiency. A multivariable quadratic model developed for studying the response indicated that the values for optimum conditions for Fe:P (w/w) ratio, coagulation pH and FMS were 2.40, 6.48 and 100 rev min⁻¹, respectively. Under optimal process conditions, the TP concentration in the distillery effluent was reduced from 10 mg L⁻¹ to 0.215 mg L⁻¹, representing a removal efficiency of 97.85%. Based upon the statistical evaluation of results, it is inferred that RSM can be used as an appropriate approach to optimize the coag-flocculation process. Meanwhile, the study has shown that, for the equivalent dose of ferric chloride, the average three-step effect is better than that of the one-time addition.

Key words | distillery effluent, ferric chloride, RSM, three-step method

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INTRODUCTION

Chinese liquor is one of the most important parts of traditional Chinese wine culture. With rapid social development and improved living standards, the demand for liquor has increased. Therefore, a lot of distillery effluent is being generated by distilleries. Distillery effluent is characterized by high concentration of suspended solids, chemical oxygen demand and phosphorus (Billore *et al.* 2001; Moletta 2005; Nataraj *et al.* 2006). Most of the distillery effluents are usually discharged directly without treatment, and lead to environmental pollution, which includes contamination of land and water resources. The high-phosphorus distillery effluent entering into the natural water body is significantly involved in eutrophication, which allows the algae to multiply, and results in microbial overgrowth and dissolved oxygen consumption (Correll 1998; Smith *et al.* 1999). In addition, the proliferation of large numbers of cyanobacteria may pose a potential hazard to humans and animals, as

some of the cyanobacteria produce and release toxins, which are called cyanobacterial toxins (Codd *et al.* 1999; Dao *et al.* 2016). Therefore, it is necessary to remove phosphorus from distillery effluent before discharge. At present, in high-phosphorus wastewaters, phosphorus is removed mainly by a combination of chemical and biological methods. However, with this simple treatment it is difficult to meet the most stringent water discharge requirements. Therefore, it is urgent to optimize the chemical process in high-phosphorus wastewater treatment to remove phosphorus.

The coag-flocculation method has been widely used for removing phosphorus from wastewaters due to its advantages of simple operation, high efficiency and low cost. Iron and aluminum salts are the phosphorus removing agents, which are commonly used in coag-flocculation processes (Ebeling *et al.* 2003; Verma *et al.* 2012; Irfan *et al.*

2013; Kim *et al.* 2015). Compared with alum, iron salts are more promising for practical application to remove phosphorus because of their relatively low cost and high phosphorus removal efficiency (Huang *et al.* 2016). The process of treating industrial or agricultural high-phosphorus wastewater is accomplished by using the coag-flocculation method as shown in Figure 1.

Previous studies have demonstrated that ferrous or ferric salts are commonly used as flocculants for phosphorus removal in wastewater treatment (Priyantha & Perera 2000; Zhang *et al.* 2015; Wang *et al.* 2016). Seida *et al.* (2002) successfully synthesized iron-based layered double hydroxides which removed more than 80% of the phosphate from wastewater. Ivanov *et al.* (2009) studied the reduction of iron ore using iron-reducing bacteria to remove phosphate from sewage water and obtained a phosphorus removal efficiency of about 90%.

The optimization of the coagulant dosage is of great significance to improve the efficiency of phosphorus removal and reduce the operational cost. Considering both the influences of individual factors and their interactions, response surface methodology (RSM) has been proposed as a potential solution. RSM is an empirical statistical modeling technique used to design experiments, build models, and find the optimum conditions for an ideal response, while involving a limited number of planned experiments (Gulati *et al.* 2010). Recently, RSM has also been used to study the optimization of coagulant dosage and flocculant in the coag-flocculation process (Khayet *et al.* 2011; Trinh & Kang 2011; Agbovi & Wilson 2017; Momeni *et al.* 2018).

In order to reduce the cost of phosphorus removal, this study uses RSM or the three-step method to optimize the coag-flocculation process for phosphorus removal in treating high-phosphorus wastewater. The study was conducted with the following objectives: (1) to evaluate the feasibility

of ferric chloride coagulant for removing phosphorus from distillery effluent; (2) to design the coag-flocculation experiments using Box–Behnken design and optimize the coagulant dosage using RSM; (3) to design the three-step experiments to reduce the cost of phosphorus removal.

MATERIALS AND METHODS

Materials and water samples

All reagents used in the experiments were of analytical reagent grade and used without further purification. Ferric chloride hexahedron ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0%) and HCl (35–37%) were purchased from Tianjin Sailboat Chemical Reagent Technology Co. Ltd (China), while sodium hydroxide (NaOH, 97%) was obtained from Tianjin Chemical Reagent Factory (China). Furthermore, sodium bicarbonate (NaHCO_3 , 99.9%) was purchased from Tianjin Yongda Chemical Reagent Co. Ltd (China). The concentration of phosphorus in the distillery effluent was 10 mg P L^{-1} .

Phosphorus removal experiments

Various factors affecting the removal of phosphorus using ferric chloride include Fe:P (w/w) ratio, fast mixing time (FMT), fast mixing speed (FMS) and pH. These parameters were investigated using batch experiments. All experiments were performed in triplicate. The phosphorus removal rate was calculated using Equation (1):

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

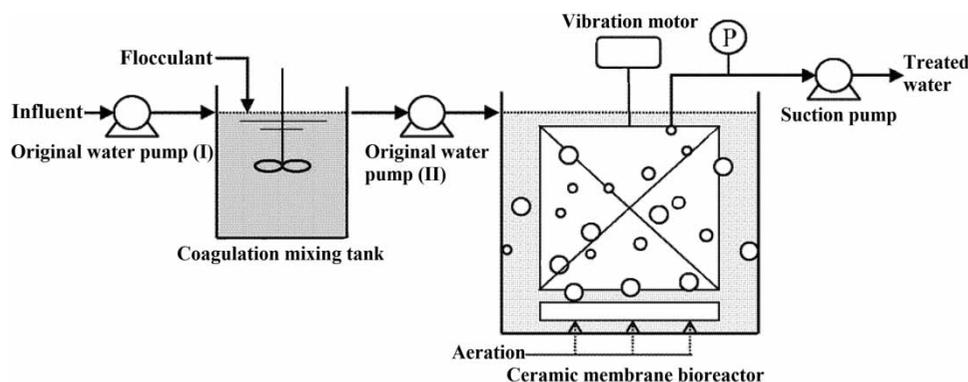


Figure 1 | Phosphorus-containing wastewater treatment process.

where C_0 and C_e are the initial and equilibrium phosphorus concentrations in mg L^{-1} , respectively.

Effect of Fe:P (w/w) ratio

Batch experiments were conducted using different volumes of 10 g L^{-1} FeCl_3 . These values were 1, 2, 3, 4, 5 and 6 mL. Each FeCl_3 solution was added into a 500 mL beaker containing 400 mL of distillery effluent (10 mg P L^{-1}), and was then mixed using a magnetic stirrer (IKA, RO5, Germany) at 200 rev min^{-1} and 25°C for 5 min. After the mixture was permitted to stand for 40 min, 25 mL of the supernatant was withdrawn and then subjected to total phosphorus concentration measurement using ammonium molybdate spectrophotometry (absorbed light at 700 nm) method using a UV-Vis spectrophotometer (UV-2550, Hach Co., USA). The performance of ferric chloride for phosphorus removal was then evaluated.

Effect of fast mixing time

In order to investigate the effect of FMT on the removal of phosphorus using ferric chloride, batch experiments were carried out at six different FMTs (2, 3, 4, 5, 6 and 7 min), and using 400 mL of distillery effluent (10 mg P L^{-1}).

Effect of fast mixing speed

In order to investigate the effect of FMS on the removal of phosphorus, batch phosphorus removal experiments were carried out at five different FMSs ($150, 200, 250, 300$ and 350 rev min^{-1}), using 400 mL of distillery effluent (10 mg P L^{-1}) for each FMS.

Effect of pH

The experiment was designed to investigate the effects of different pH values (with the range of 5–10) on the removal of phosphorus using ferric chloride. Four hundred millilitres of distillery effluent (10 mg P L^{-1}) with different initial pH values was used in the batch experiments.

Optimization using Box–Behnken design

Box–Behnken experimental design with three levels and three factors combined with RSM (Beker et al. 2013), is a collection of mathematical and statistical techniques for designing experiments. The design is a useful approach

that can be utilized to study the effect of various factors influencing the responses, in which the factors can be simultaneously varied during a small number of experiments (Adinarayana & Ellaiah 2002). Since FMT has negligible effect on the phosphorus removal using ferric chloride, this factor was not considered in RSM. Other factors included Fe:P (w/w) ratio, pH and FMS, and were assigned as independent factors. The efficiency of ferric chloride for phosphorus removal at equilibrium was assigned as the response to the modified process (dependent variable). The values of these factors were for three levels of $-1, 0$ and $+1$, which represented low (Zhang et al. 2011), central and high values, respectively (Table 1). The values of Fe:P (w/w) ratio (X_1), pH (X_2) and FMS (X_3) were set as the input factors. Table 2 shows the coded levels of factors that were employed in these experiments.

Design-Expert 10 (Stat-Ease Inc., USA) was used to design the experiments. The sequential model-fitting test was carried out to find a suitable model. The Box–Behnken model, which is composed of a second-order polynomial model, was identified, and all possible interactions between the selected factors were expressed using Equation (2).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i^2 + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + \epsilon \quad (2)$$

Simulating the three-step method to remove phosphorus from distillery effluent

First, 400 mL of distillery effluent was taken in a beaker. Then 0.8 mL of 10 g L^{-1} ferric chloride solution was added into the beaker, and mixed using a magnetic stirrer (IKA, RO5, Germany) at 200 rev min^{-1} and 25°C for 30 min. After the mixture was allowed to stand overnight, 25 mL of the supernatant was withdrawn and subjected to total phosphorus concentration measurement using ammonium molybdate spectrophotometry (absorbed light at 700 nm) method using a UV-Vis spectrophotometer

Table 1 | Response surface factor levels

No.	Independent factors	Code	Levels		
			-1	0	1
1	Fe:P(w/w)	A	2.0	2.2	2.4
2	Fast mixing speed	B	100	150	200
3	pH	C	6	7	8

Table 2 | Experimental design and results of response surface

Run	Factor 1 A: Fe:P (w/w/)	Factor 2 B: FMS (rev min ⁻¹)	Factor 3 C: pH	% Removal
1	2.0	100	7	87.75
2	2.4	100	7	94.50
3	2.0	200	7	80.25
4	2.4	200	7	86.00
5	2.0	150	6	56.25
6	2.4	150	6	73.00
7	2.0	150	8	78.75
8	2.4	150	8	73.00
9	2.2	100	6	85.00
10	2.2	200	6	47.75
11	2.2	100	8	61.00
12	2.2	200	8	89.50
13	2.2	150	7	86.25
14	2.2	150	7	85.50
15	2.2	150	7	86.57
16	2.2	150	7	89.50
17	2.2	150	7	86.25

(UV-2550, Hach Co., USA). The experiments were performed three times to ensure the repeatability of results.

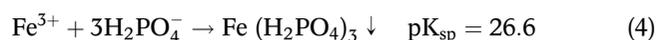
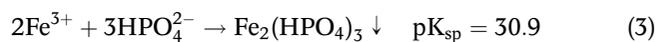
RESULTS AND DISCUSSION

Phosphorus removal experiments

Effect of Fe:P (w/w)

Batch experiments were performed to determine the optimal of Fe:P (w/w) ratio for phosphorus removal. According to Figure 2(a), the phosphorus removal rates rapidly increased with the increase in Fe:P (w/w) ratio from 0.4 to 2.15. In contrast, when the Fe:P (w/w) ratios were greater than 2.15, the phosphorus removal rate remained nearly unchanged, indicating that the optimal Fe:P (w/w) ratio is at 2.15. For Fe:P (w/w) ratio of less than 2.15, with the increase in the amount of ferric chloride, the volumes of flocs increased due to the increasing content of absorbed phosphorus, which then induced further complexation on the surface of flocs. As a result, the phosphorus anions in water were further reduced. The process can be explained using the reactions expressed in Equations (3)–(6) (Lijklema 1980; Smith *et al.* 2008; Szabó

et al. 2008). On the other hand, when Fe:P (w/w) ratio was greater than 2.15, the hydrolysis of ferric chloride may be inhibited due to high acidity in water, which was caused by ferric chloride. As a result, flocs no longer formed, and thus the rate of phosphorus removal did not show significant differences.



Effect of fast mixing time

An appropriate FMT allows better dissolution and spread of ferric chloride in water, and also increases the possibility of contact between the phosphorus and flocs, thus enhancing the removal of phosphorus. In order to examine the effect of FMT on the efficiency of ferric chloride in phosphorus removal, the phosphorus removal experiment was conducted by changing the FMT within the range of 2–7 min. The corresponding results are shown in Figure 2(b), which shows that with the increase of FMT, the phosphorus removal slightly fluctuated between the values of 76% and 85%, and reached a small peak at 6 min. It appears that the effect of FMT on the phosphorus removal is insignificant and can be ignored. Therefore, it was not considered in the optimization of RSM using the Box–Behnken experimental design.

Effect of fast mixing speed

At a certain appropriate FMS, the rate of phosphorus removal using ferric chloride can be increased because the solution is more homogeneous, which enhances the probability of contact between the hydrated iron complex ions and the phosphate anion. In order to determine the optimum value for FMS, the phosphorus removal was performed at various FMS values, within the range of 150–350 rev min⁻¹. The results shown in Figure 2(c) demonstrate that the removal of phosphorus increased from 77.00% to 84.50% with the increase in FMS from 150 to 200 rev min⁻¹. The phosphorus removal is optimum at the FMS of 200 rev min⁻¹, after which the effect of FMS on phosphorus removal becomes insignificant. Therefore, the results indicate that the optimum FMS is 200 rev min⁻¹ for achieving the highest efficiency of phosphorus removal.

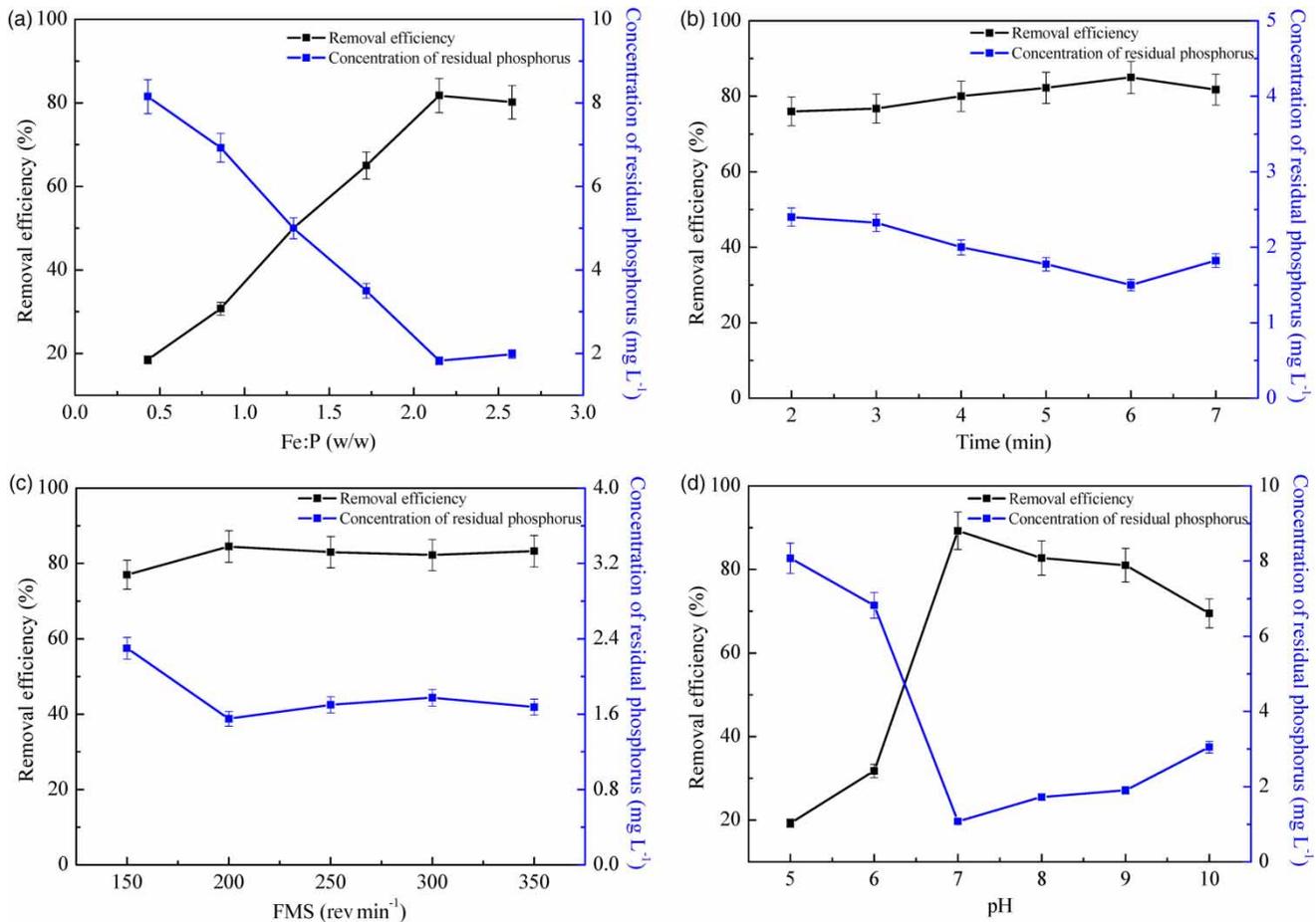


Figure 2 | Effect of individual factors on phosphorus removal. (a) Effect of dosage of ferric chloride; (b) effect of fast mixing time; (c) effect of fast mixing speed; (d) effect of pH.

Effect of pH

The quantity of flocs formed during phosphorus removal varies with pH (Lijklema 1980; Zinatizadeh *et al.* 2006; Nie *et al.* 2015). Therefore, phosphorus removal at different pH, ranging from 5.0 to 10.0, was examined to study the effect of pH. Figure 2(d) illustrates the effect of solution pH on phosphate removal by ferric chloride. It is generally known that the negatively charged phosphate (usually H_2PO_4^- or HPO_4^{2-}) is selectively trapped by flocs through formation of the inner-sphere complexes, and HPO_4^{2-} tends to form stronger bidentate complexes than H_2PO_4^- (Zeng *et al.* 2008). As shown in Figure 2(d), as the pH is from 5 to 7, the H_2PO_4^- in the water is converted to HPO_4^{2-} , so the efficiency of phosphorus removal is increased. However, in alkaline conditions, the negatively charged sites on the surface of flocs became dominant and the negatively charged phosphate species increased (Cumbal & Sengupta 2005), which resulted in the repulsion between the phosphate ions and the flocs. As a result, phosphate adsorption dropped remarkably.

When the pH increased from 5.0 to 7.0, the phosphorus removal increased from 19.25% to 89.25%. However, the phosphorus removal quickly declined from 89.25% to 69.50% when the pH was increased from 7.0 to 10.0. Therefore, the optimal pH for the removal of phosphorus using ferric chloride was found to be 7.0.

Analysis of variance

Table 3 presents the results of the analysis of variance (ANOVA) of the second-order polynomial equations and the corresponding regression coefficients. The analysis showed that the model had an F value of 114.19 with Prob far greater than F of 0.0001, which indicates that the model is significant and partly practical. Adequate precision compares a range of the predicted values of design space, and in turn, is desirable (Mohajeri 2010). In the present work, adequate precision of 37.983 indicates that the model is acceptable. Additionally, the experimental R^2 value of 0.9932 is comparable to the model's R^2 value of

Table 3 | ANOVA for phosphorus removal

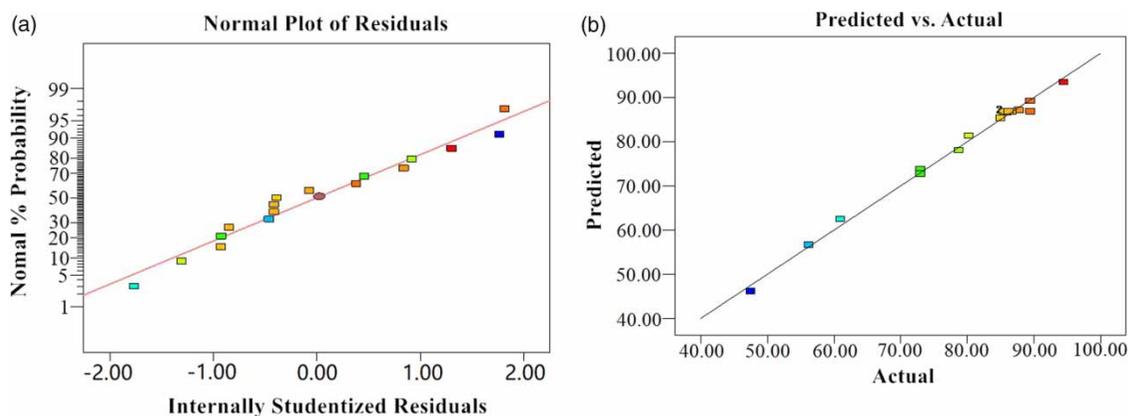
Source	Sum of squares	df	Mean square	F Value	Prob > F	Comment
Model	2,717.85	9	301.98	114.19	<0.0001	SD = 1.63
A: Fe:P	69.03	1	69.03	26.10	0.0014	Mean = 79.22
B: speed	78.13	1	78.13	29.54	0.0010	CV = 2.05
C: pH	205.03	1	205.03	77.53	<0.0001	Press = 157.96
AB	0.25	1	0.25	0.095	0.7674	R ² = 0.9932
AC	126.56	1	126.56	47.86	0.0002	R ² _(adj) = 0.9845
BC	1,089.00	1	1,089.00	411.78	<0.0001	AP = 37.983
A ²	0.053	1	0.053	0.020	0.8911	
B ²	0.63	1	0.63	0.24	0.6398	
C ²	1,144.58	1	1,144.58	432.79	<0.0001	
Residual	18.51	7	2.64			
Lack of fit	8.94	3	2.98	1.24	0.4043	
Pure error	9.57	4	2.39			
Cor total	2,736.36	16				

df, degrees of freedom; SD, standard deviation; CV, coefficient of variation; Press, predicted residual error sum of squares; AP, adequate precision; Cor total, totals of all information corrected for the mean.

0.9845, which indicates that the model is in good agreement with the experimental data (Adinarayana & Ellaiah 2002). Moreover such an R² value indicates that the model can explain about 99% of the experimental data. The significant lack of fit observed in this study is suitable for the model. Depending on the results, the response surface model constructed for predicting the efficiency of ferric chloride in phosphorus removal can be considered accurate. The final regression model is based on the defined factors, A, B and C, which can be expressed using Equation (7).

$$R = 86.85 + 2.94A - 3.12B + 5.06C - 0.25AB - 5.63AC + 16.50BC - 0.11A^2 + 0.39B^2 - 16.49C^2 \quad (7)$$

Suitability of the model, which provides adequate approximation of the real system, is confirmed based upon the diagnostic plots. Such plots, which include normal probability plots of studentized residuals and the plot of predicted value versus actual value, are used to judge the adequacy of a model. Figure 3(a) shows the normal probability plot of the studentized residuals in phosphorus removal. Studentized residuals represent a normal probability plot, in which the residuals follow a normal distribution, while the points follow a straight line, and some scattered data points can generally be expected. The data are evenly distributed (Figure 3(a)), and the predicted values are in good agreement with the experimental values (Figure 3(b)).

**Figure 3** | (a) Normal plot of residuals; (b) plot of predicted v/s actual.

Three-dimensional response surface plot

Wu *et al.* (2009) have reported that the three-dimensional (3D) response surface is a function of two factors, while all other factors remain unchanged. This helps in understanding the main effects as well as interaction effects of the two factors. In addition to the 3D response surface, the corresponding contour map can help visually verify the influence of experimental variables on the response (Szabó *et al.* 2008). In order to better understand the interaction effects between the flotation variables, a 3D response surface map of the measured response was

generated based on Equation (2) (Figure 4(a)–4(f)). Moreover, contour plots can further clarify the relationship between the dependent and independent variables, while one variable in each graph remained unchanged at the center level. Therefore, three response 3D maps and three corresponding contour maps were generated.

Figure 4(a) and 4(b) show the two-dimensional contour map and the 3D response surface relationship between Fe:P (w/w) ratio (A) and FMS (B) at the center level of pH (C). The phosphorus removal increased with the increase in Fe:P (w/w) ratio (A). Similar trends were observed in the two-dimensional contour map and 3D response surface

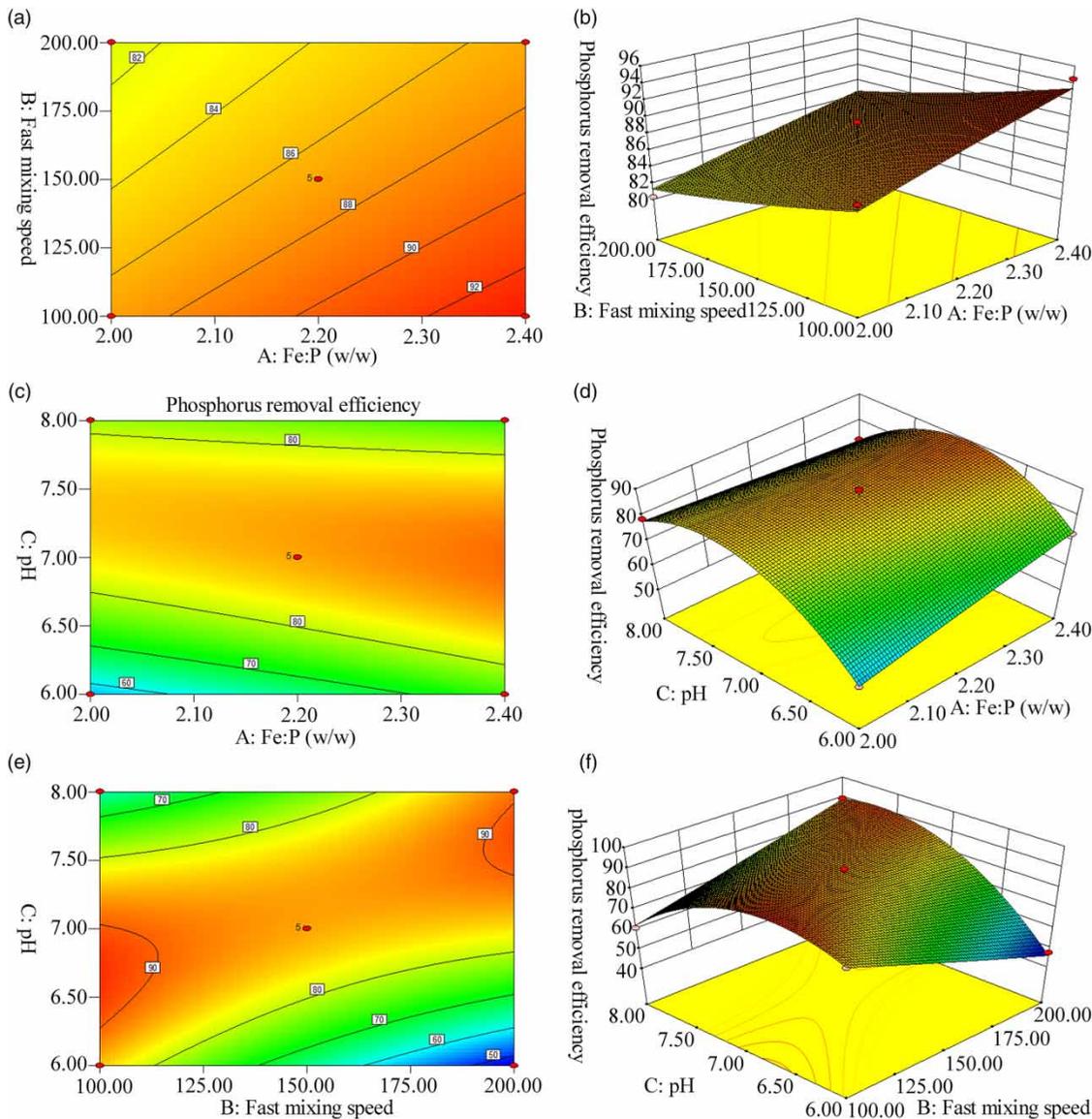


Figure 4 | Three-dimensional surface and two-dimensional contour plots of phosphorus removal. (a) and (b) Effect of Fe:P (w/w) and fast mixing speed; (c) and (d) effect of Fe:P (w/w) and pH; (e) and (f) effect of pH and fast mixing speed.

relationship between Fe:P (w/w) ratio (A) and pH (C) at the center level of FMS (B), which are shown in Figure 4(c) and 4(d). The efficiency for phosphorus removal initially increased and then decreased with the increase in pH value. Figure 4(e)–4(f) display the two-dimensional contour map and 3D response surface relationship between FMS (B) and pH (C) at the center level of Fe:P (w/w) ratio (A). Similarly, efficiency in phosphorus removal increases and then decreases with increasing pH.

Optimization of phosphorus removal conditions

The optimization of numerical conditions for phosphorus removal was performed using Design-Expert software. Each operational condition (Fe:P (w/w), pH and FMS) was chosen within the range at which the response (phosphorus removal) was maximized (indicating the highest performance). The software combines the desired unique value into a single number, and then maximizes its function. The model prediction shows that, for 97.85% removal of phosphorus, the Fe:P (w/w), pH and FMS values were 2.40, 6.48 and 100 rev min⁻¹, respectively.

Simulation of the three-step method to remove phosphorus from distillery effluent

As can be seen from Figure 5, after every addition of 8 mg ferric chloride to 400 mL distillery effluent, the total phosphorus concentration was reduced, and the efficiency of phosphorus removal reached 99.0% after three repetitions. If ferric chloride is added only once to distillery effluent, and the efficiency of phosphorus removal of more than

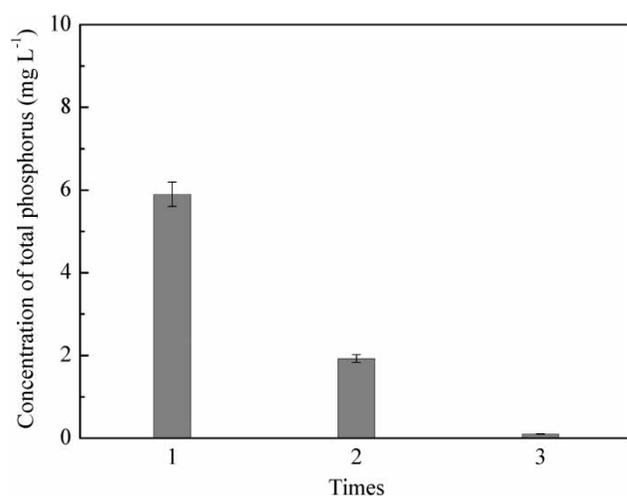


Figure 5 | Using three-step method to remove phosphorus in distillery effluent.

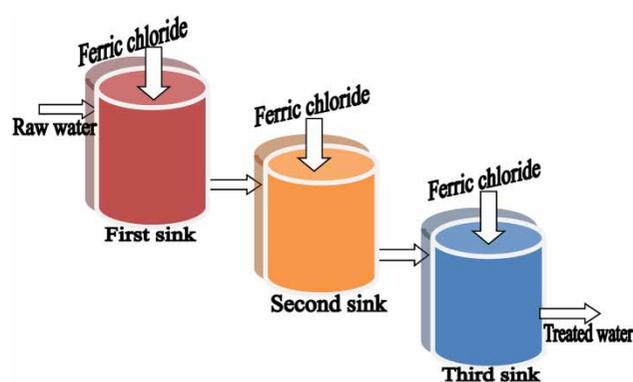


Figure 6 | Simulating the industrial treatment of distillery wastewater using three-stage treatment.

90% is desired, the dosage of ferric chloride should be increased to 125 mg L⁻¹. Compared with one-time dosage of ferric chloride, the use of the three-step method to treat distillery effluent can reduce its operational cost. Figure 6 shows the industrial process of phosphorus removal.

CONCLUSION

The presence of phosphorus in distillery effluent is one of the reasons for hindering its reuse for farming and drinking. The Coag-flocculation employed in this study is able to reduce phosphorus concentration below the World Health Organization permissible level of 0.5 mg L⁻¹. The RSM was successfully applied to optimize the phosphorus removal from aqueous solution. At optimal operating conditions of Fe:P (w/w) ratio = 2.40, pH = 6.48 and FMS = 100 rev min⁻¹, 97.85% removal of phosphorus was achieved. Moreover, compared with the one-off dosage, the three-step process treatment can save 50% of the cost in terms of ferric chloride when treating the same amount of distillery effluent.

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