Removal of phosphate from aqueous solution by red mud using a factorial design

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ABSTRACT

The purpose of the work is to study the adsorption of phosphate on red mud from aqueous solutions using 2^3 full factorial designs. The important parameters, which affect the removal efficiency of phosphate and final pH of solution (pH_f), such as phosphate concentration, initial pH of solution (pH_i) and the red mud dosage were investigated. The effects of individual variables and their interaction effects for dependent variables, namely, phosphate removal efficiency and pH_f were determined. The results of the study showed that phosphate removal efficiency and pH_f were found to be 97.6% and 10.9 with optimal reaction conditions initial phosphate concentration 25 mg l^{-1} , red mud dosage 1.5 g l^{-1} , pH_i 3.0, respectively. It was found that adequate amount of calcium ions and higher final pH than 9 are ideal conditions for maximum phosphate removal.

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1. Introduction

Phosphate in wastewaters is an essential nutrient for the growth of photosynthetic algae and other biological organisms in water bodies. But excess phosphate concentration in the effluent discharge can lead to eutrophication of the receiving confined water bodies [1]. Eutrophication can in turn disturb the balance of organisms present in the water and affect water quality, mainly through oxygen depletion as the algae decay. A reduced oxygen level harmful affects fish and other aquatic life, microorganism and insects' growth as well as it causes natural resorts degradation. Consequently, the amount of phosphate in domestic and industrial discharges must be controlled using wastewater treatment technology.

In wastewater treatment technology, many methods have been developed for phosphate removal [2], which include physical [3], chemical [4] and biological methods [5]. Physical methods have proved to be either too expensive, as in the case of electrodialysis and reverse osmosis [3], or inefficient, removing only 10% of the total phosphorus [4]. Enhanced biological treatment can remove up to 97% of the total phosphorus and it is low-cost. But the variability in chemical composition and temperature of wastewater would make the implementation of this process not

feasible for wastewater treatment [5]. Chemical removal techniques are the most effective and well-established methods up to date. Lime, aluminum sulfate, and ferric chloride are common precipitants used for phosphate removal [2]. However, the cost associated with the use of metal salts and sludge production may hinder the widespread application [6]. Therefore, alternative techniques for phosphate removal are being developed. Recently, attention has been focused on phosphate adsorbents because of the most economical and applicable of adsorption. Successful results have been obtained using fly ash [5,7,15], aluminum oxide [8–10], iron oxide [11–14], slag [16,17], red mud [18,19], silicates [20,21], activated carbon [22], and gas concrete [23].

Red mud emerges as a residue during alkaline-leaching of bauxite in Bayer process. Roughly 1–2 tons of red mud residue are produced for a ton of alumina [24]. About 10–20 million tons of caustic red mud must be disposed of annually in China during recent years [25]. Since the plant began to process, red mud has accumulated over years and causes a serious environmental problem due to its high alkalinity and large amount.

Many have studied the application of red mud in wastewater treatment and red mud has been found to remove fluoride [26], chromium [27], hexavalent [28], dyes [29], heavy metals [30], and phosphate [5,31] from aqueous solution. Due to the high percentages of calcium, aluminum and iron, red mud is a good candidate for use as an economic adsorbent for large-scale use. In this study, phosphate was removed using original red mud. One of the main advantages of phosphate removal by using red mud over the other

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chemical treatment is the abundance of red mud and its easy availability.

Many previous studies showed that phosphate precipitates with calcium as apatites and especially hydroxyapatites (HAP). Because the extent of HAP formation is critically dependent on factors such as degree of supersaturation, pH and initial phosphate concentration [32,33], it is necessary to study the effect of red mud dosage, initial pH of solution (pH_i) and phosphate concentration on the final pH (pH_f) which directly affects the formation of HAP.

This study examined the effect of original red mud on phosphate removal. The influence of phosphate concentration, pH_i and red mud dosage on the removal efficiency of phosphate using experimental design methodology was investigated. The main effects and their interactions of the parameters considered were studied by using a 2^3 factorial design.

2. Materials and methods

2.1. Materials

The red mud used in this study was obtained from Shandong Aluminium Corporation, Shandong, China. Before batch experiments were performed the red mud was first sieved and the particles smaller than 100 mesh were kept for further consideration in the trials without any further treatment. The average chemical composition of red mud was listed in Table 1. This table showed that red mud is primarily a mixture of Ca, Si, Fe and Al oxides and the CaO content is the highest. The single-point N_2 -BET method indicated that the specific surface area of a typical red mud sample was about $14.76 \text{ m}^2/\text{g}$.

The standard phosphate solutions used in the experiments were prepared from a stock solution of 1 g P l^{-1} anhydrous KH_2PO_4 . The determination of phosphate has been measured using the ascorbic acid method with a HACH DR/4000U spectrophotometer, according to APHA standard methods [34]. A pH meter (Orion) was used to measure the pH of solutions in experiments and pH adjustments of solutions have been done by diluted HCl and NaOH. The chemicals used for this study were analytical reagent-grade or better and all experiments were conducted in duplicate and the average values were used for analysis.

2.2. Experimental procedure

In order to determine phosphate removal capacity and effect on pH_f of the red mud, batch experiments were conducted. The experimental procedure was as follows: a defined volume of the phosphate stock solution with a concentration 1 g P l^{-1} in PO_4^{3-} was diluted to the experimental concentration by adding tap water of very low hardness. The pH of the solution was then adjusted to the desired value and a defined amount of adsorbent was added. The mixture was stirred at 200 rpm at room temperature ($20 \pm 1^\circ \text{C}$) for 4 h, which were performed under the same experimental con-

Table 1

Average composition of red mud used (wt.%).

Constituent	% (w/w)
SiO_2	18.08
Fe_2O_3	15.30
Al_2O_3	8.26
CaO	38.02
MgO	1.63
Na_2O	3.55
K_2O	0.36
TiO_2	4.51

Fig. 1. Effect of initial pH on phosphate removal (a) and pH_f (b) (red mud dosage: 1 g l^{-1}).

ditions for each factorial design experiment. The suspensions were agitated for 4 h, sufficient time to reach equilibrium, according to previous study [5]. After equilibrium, the samples were centrifuged and the supernatants were analyzed for phosphate. The pH_f of the solution was also measured.

The red mud before and after adsorption were identified by X-ray diffraction (XRD). The analysis was performed in a Rikaku TTR-III diffractometer at room temperature, with $\text{Cu K}\alpha$ radiation at a scan speed range of 0.2° s^{-1} . The XRD patterns were recorded in the 2θ range of 10 – 90° .

3. Results and discussion

3.1. The effect of initial pH on phosphate removal

For the removal of phosphates from aqueous solutions by adsorption, pH is considered to be an important parameter. Solutions containing 1.5 g l^{-1} red mud were adjusted to various pH values ranging from 1.0 to 11.0. Effect of pH_i on the phosphate removal percentage and pH_f is shown in Fig. 1(a) and (b). As seen from Fig. 1, the removal of phosphate strictly increases as the pH_i increases up to 3.0 and thereafter, a decrease is observed. Maximum phosphate removal occurs at pH_i of 3.0. It was observed that pH_f values of the solution at pH_i of 3.0 were measured as 11.3, 9.1, and 7.3, respectively with corresponding percentages of phos-

Table 2Remaining Ca^{2+} concentrations (mg l^{-1}) in solution and phosphate removal efficiency (%) after equilibrium for 50 mg l^{-1} phosphate concentration.

pH_i	Red mud dosage (g l^{-1})								
	0.25			0.5			1.0		
	Ca^{2+}	pH_f	Removal efficiency	Ca^{2+}	pH_f	Removal efficiency	Ca^{2+}	pH_f	Removal efficiency
1.0	57.9	1.2	5.2	131.3	1.3	10.4	227.1	1.3	22.5
3.0	45.9	7.0	12.8	43.5	7.8	30.5	31.8	9.1	71.8
5.0	21.2	8.5	6.5	18.9	9.9	17.5	13.8	10.2	53.5

phosphate removal of 87.1, 71.8, and 61.4% for 25, 50 and 100 mg l^{-1} of phosphate concentrations.

PH is an important factor regarding the amount of CaO in the red mud, especially in a strongly acid medium due to the high concentration of hydrogen ions [35]. The effect of pH_i on Ca^{2+} concentrations remaining in the solution and phosphate removal efficiency in the solution at different red mud dosages decrease with the pH_i increasing. High Ca^{2+} amount is released into the solution at pH_i 1.0, but the pH_f may be too low to form insoluble phosphate compounds because of low pH_i . The pH_f is high enough to form the insoluble phosphate compound at pH_i 5.0, but Ca^{2+} amount released into the solution is low and so phosphate removal efficiency is lower since Ca^{2+} in the solution is inadequate. Consequently, highest phosphate removal efficiency was achieved at pH_i 3.0.

As seen from Fig. 2, the red mud before and after reaction have been checked by XRD and the XRD results showed that phosphate precipitates with calcium as apatite. The Fe_2O_3 in red mud may be an important factor for phosphate removal (as iron phosphate). However, the red mud contained more CaO (38.02%) than Fe_2O_3 (15.30%) in this paper, CaO in the red mud play major role on phosphate removal. In addition, the paper mainly explains the mechanism of phosphate removal using red mud by phosphate precipitates with calcium as apatite. So the paper does not take a consideration of Fe_2O_3 in red mud for phosphate removal.

3.2. The effect of adsorbent dosage

The effect of red mud dosage on the removal of the phosphate from aqueous solution at pH_i 3.0 is shown in Fig. 3.

Fig. 2. X-ray diffraction patterns of the red mud (A) before adsorption and (B) after adsorption. Phosphate precipitates with calcium are marked by (P).

Fig. 3. Effect of red mud dosage on phosphate removal (pH_i 3.0).

Initial phosphate concentrations were varied from 10 to 100 mg l^{-1} . It is apparent that the phosphate removal efficiency increases with increasing the red mud dosage for a given initial phosphate concentration. As initial phosphate concentration increases, more red mud is needed to add water in order to increase the pH_f that is suitable for the formation of the insoluble phosphate compounds. The pH_f values decrease with increasing phosphate concentration for a given red mud dosage. The change of orthophosphate compounds with pH can explain this. H_3PO_4 and H_2PO_4^- are the predominant aqueous species at pH 3.0. HPO_4^{2-} and PO_4^{3-} may also be present at the same pH but

Fig. 4. Effect of initial phosphate concentration on phosphate removal (pH_i 3.0).

Fig. 5. Effect of phosphate/red mud ratios on phosphate removal (a) and pH_f (b) and the relationship between final pH and removal efficiency (c).

typically at concentrations less than H₃PO₄ and H₂PO₄⁻. The red mud does not make the pH of the solution increase too much for the conversion of acidic phosphate compounds use the alkaline property of red mud. Therefore, more red mud is needed to increase pH to an adequate value for satisfactory phosphate removal.

3.3. The effect of initial phosphate concentration

Fig. 4 gives phosphate removal efficiency of red mud as a function of phosphate concentration at pH_i 3.0. As shown in Fig. 4, the phosphate removal efficiency decreases with increasing initial phosphate concentration for a given red mud dosage. This result is anticipated due to buffering properties of phosphate compound and insufficient calcium ions in the solution as discussed in the previous section.

3.4. The effect of phosphate/red mud ratios

From the previous section, it was found that red mud dosage and initial phosphate concentration have a consideration effect on the phosphate removal. So, red mud dosage and initial phosphate concentration should be considered together to study the effect of them on the phosphate removal. The effect of phosphate/red mud ratios on phosphate removal and pH_f is shown in Fig. 5(a) and (b), respectively. The relationship between final pH and removal efficiency is shown in Fig. 5(c). As seen from Fig. 5(b), pH_f has strictly reduced with increasing phosphate/red mud ratios. As discussed previously, an adequate amount of calcium ions and pH higher than 9 are needed to supply for adequate phosphate removal. So phosphate removal efficiency is decreased due to low calcium ions and pH_f. It was found that pH 9 was a critical value to form hydroxyapatites [33]. As Ca²⁺ amount decreases at higher phosphate/red mud rates than 20, phosphate removal efficiency decreases. More red mud must be added to water for satisfactory phosphate removal under the condition of high phosphate and low pH_i.

3.5. Factorial design evaluation

A 2³ full factorial design (three factors each, at two levels) was employed to evaluate the importance and interactions of the pH_i, red mud dosage and initial phosphate concentration. The response variables in this study are the removal efficiency of phosphate and pH_f. Notation that the factors used in this work have never been investigated simultaneously using factorial designs, and they were chosen for their roles, as determined previously using one-variable-at-a-time experimental procedures. All factorial designs were executed in random order to correctly evaluate experimental errors. The matrix of three variables is varied at two levels (+1, -1). The higher level of variable was designed as '+' and the lower level was designed as '-'. For ease of notation, the effects were designed as in Table 3 which shows the values of the factors selected in this study. This factorial design results in eight tests with all possible combinations of A, B and C. Phosphate removal efficiency (Y₁) and pH_f (Y₂) were measured for each of these tests as shown in Table 4.

Table 3
Factors and levels used in the 2³ factorial design study.

Factor	Low level (-1)	High level (+1)
Phosphate concentration, A (mg l ⁻¹)	25	50
Red mud dosage, B (g l ⁻¹)	0.25	1.5
pH _i , C	3.0	7.0

Table 4

Experimental design matrix and results for the phosphate removal efficiency and pH_f .

Run number	Factor			Y_1	Y_2
	A	B	C		
1	−1	−1	−1	15.2	7.4
2	1	−1	−1	8.8	6.9
3	−1	1	−1	97.6	10.9
4	1	1	−1	65.0	8.9
5	−1	−1	1	6.0	9.5
6	1	−1	1	3.0	7.8
7	−1	1	1	90.1	12.0
8	1	1	1	55.0	10.6

A first-order model with interaction terms was chosen to fit the experimental data in Table 4:

$$Y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{123}ABC \quad (1)$$

where Y = predicted response, b_i = coefficients, A = phosphate concentration (mg l^{-1}), B = red mud dosage (g l^{-1}) and C = pH_f . The statistical calculations (t -test, F -test, analysis of variance (ANOVA) and multiple regressions) were performed using Microsoft Excel. Regression analysis was performed to fit the response function (phosphate removal efficiency and pH_f) with the experimental data (Table 5).

The mathematical models representing phosphate removal efficiency (Y_1) and pH_f (Y_2) in the experimental region studied can be expressed by Eqs. (2) and (3), respectively. Table 6 shows the analysis of variance for the models used to estimate phosphate removal efficiency and pH_f as a function of phosphate concentration, red mud dosage and pH_f . The regressions are all statistically significant at the 95% confidence level. The models representing phosphate removal efficiency (Y_1) and pH_f (Y_2) presented high determination coefficients ($R^2 = 0.999, 0.998$) explaining 99.9 and 99.8% of

the variability in the response, respectively. This is the proof that the models describe well, the region studied:

$$Y_1 = 42.595 - 9.645A + 34.335B - 4.065C - 7.285AB - 0.745ABC \quad (2)$$

$$Y_2 = 9.2575 - 0.7A + 1.3475B + 0.735C - 0.14AB + 0.2325ABC \quad (3)$$

The factorial design results show that red mud dosage had the strongest effect on phosphate removal efficiency and pH_f . Increasing red mud dosage increases phosphate removal efficiency and pH_f . The b_2 coefficient is the largest positive coefficient for all the model equations (see Eqs. (2) and (3)). It is known that the larger the coefficient, the larger is the effect of related parameter. The positive sign also shows that there is a direct relation between the

Table 5

Results of regression analysis for phosphate removal efficiency (Y_1) and pH_f (Y_2).

	Coefficient	Significance effect	t -value
Phosphate removal efficiency (Y_1)			
Intercept	42.595	0.230489	−
A	−9.645	0.230489	−41.8459
B	34.335	0.230489	148.9661
C	−4.065	0.230489	−17.6364
AB	−7.285	0.230489	−31.6068
ABC	−0.745	0.230489	−3.23226
pH_f (Y_2)			
Intercept	9.2575	0.057581	−
A	−0.7	0.057581	−12.1567
B	1.3475	0.057581	23.40163
C	0.735	0.057581	12.76452
AB	−0.14	0.057581	−2.43134
ABC	0.2325	0.057581	4.037758

Table 6

Regression analysis for phosphate removal efficiency and pH_f by first-order model fitting (ANOVA).

Source	d.f.	Sum of squares	Mean square	F -value
Phosphate removal efficiency (Y_1)				
Model	5	10736.55	2147.31	5052.494
Residual	2	0.85	0.425	
Core total	7	10737.4		
pH_f (Y_2)				
Model	5	23.3571	4.67142	176.1139
Residual	2	0.05305	0.026525	
Core total	7	23.41015

Fig. 6. Interaction effect of phosphate concentration and red mud dosage (a) and red mud dosage and pH_f (b) for phosphate removal efficiency. The balls represent a certain weight for the response variable and the values are the average of the response variables.

Fig. 7. Interaction effect of phosphate concentration and red mud dosage (a) and red mud dosage and pH_i (b) for pH_f. The balls represent a certain weight for the response variable and the values are the average of the response variables.

parameter and dependent variable. The b_1 coefficient is the largest negative coefficient for Y_1 and Y_2 . Increasing phosphate concentration decreases phosphate removal efficiency and pH_f and its increase decreases the removal rates due to low pH as shown in Fig. 3.

Eqs. (2) and (3) are also seen that two-variable or three-variable interactions are significant. Evidence of large negative (AB) and positive (ABC) interactions is very strong and therefore cannot be ignored from the model. Figs. 6 and 7 illustrate the possible positive and negative two-variable interactions among the variables A, B, C for Y_1 and Y_2 . These results support the findings related to the effect of phosphate/red mud dosage ratios in Section 3.4. Because it has been found that the lower phosphate/red mud ratios, the higher removal rates, i.e., low phosphate and high red mud dosage.

The maximum removal efficiency of phosphate and pH_f was found to be 97.6% and 10.89 with optimal reaction conditions initial phosphate concentration 25 mg l⁻¹, red mud dosage 1.5 g l⁻¹, and pH_i 3.0.

4. Conclusion

The results of this study indicate red mud is an effective adsorbent for the removal of phosphate in aqueous solutions. Phosphate removal efficiency of the red mud increases with increasing red mud dosage at initial pH 3.0. It was thought that adequate amount of calcium ions and higher final pH than 9 are ideal conditions for maximum phosphate removal. As the result of this study, red mud dosage was found to have the most positive influence on the removal efficiency of phosphate and pH_f. For phosphate concentration, this factor has a negative influence. The pH_i has a negative effect for the removal efficiency of phosphate and positive for pH_f. The interaction between phosphate concentration and red mud dosage was significant for the removal efficiency of phosphate and pH_f.

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