

# Use of Red Mud to Removal Phosphorus from Biogas Slurry Implication for Practical Application

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**Abstract.** This study investigated a novel approach by using red mud (RM), an industrial waste of alumina production, to remove phosphate from biogas slurry. First, the important parameters, which affect the removal efficiency of phosphate and final pH of solution (pH<sub>f</sub>), such as initial pH (pH<sub>i</sub>), RM dosage, reaction time and phosphate concentration of biogas slurry were explored. The results indicated that the phosphate removal efficiency decreased first, and then increased with the increase of pH. And the highest and the lowest phosphate removal efficiency were 89.6% and 47.2%, respectively, at pH 2.1 and pH 6.9 under given conditions. RM dosage and contact time had a positive effect, whereas initial phosphate concentration had a negative effect on phosphate removal and pH<sub>f</sub>. Overall, the results of this work demonstrated that RM can be proposed as a cost-effective absorbent for the effective removal of phosphate from biogas slurry.

## 1. Introduction

Excess phosphorus, mainly from untreated wastewater, has been identified as one of the major factors that causing the deterioration of water quality and subsequent eutrophication in water bodies [1, 2]. Biogas slurry is a kind of wastes generated from household scale biogas installations. High concentration of phosphate nutrition is one of its most important characteristics and the total phosphate of anaerobic biogas slurry could reach 6.6~7.6 g L<sup>-1</sup> which far exceed the Class A of Sewage Synthesis Discharges Standard 0.5 g L<sup>-1</sup> (GB8978-1996). On the one hand, phosphorus is an essential nutrient for the growth of plants and animals; therefore biogas slurry is widely used in agriculture as fertilizers in China [3]. On the other hand, a large amount of phosphate from untreated biogas slurry is a particularly important cause of water eutrophication [4]. Owing to the more stringent regulation of phosphate discharge, it is essential to develop cost-effective treatment methods for phosphate removal from biogas prior to its discharge into water bodies to avoid any kind of problems [5].

Phosphorus removal technologies mainly include chemical precipitation [6], biological processes [7], and adsorption processes [8]. Among these methods, adsorption has been demonstrated to be an effective method for phosphate removal due to production of less sludge, high efficiency and simple and easy operation [9]. Furthermore, considerable attention has been paid based on economic and environmental concerns to the study of using different types of low-cost and easily available, such as superabsorbent resins [10], ferric sludge [11], fly ash [12], red mud [13,14], as alternative adsorbents for sorption of phosphate from wastewater in recent years.



Among these sorbents, RM (RM) with a relatively larger surface area ( $162.5 \text{ m}^2 \text{ g}^{-1}$ ), composed of aluminum oxide, iron oxide, calcium oxide and silica, is a highly alkaline waste generated in the production of alumina [13, 15]. With the rapid development of the alumina industry, more and more RM is being produced. Roughly 1-2 tons RM were produced for each ton of alumina [15, 16]. Large amounts of RM were discharged into environment arbitrarily. Since there is large number of industrial alkali, fluoride and heavy metals and other potential pollutants in RM, long-term stockpiling of RM would not only occupy scarce land resources, but also easily lead to serious pollution of the surrounding soil and groundwater due to the leakage of alkaline (pH 10-12.5) leachate [16]. Therefore, final disposal of RM is facing a huge challenge due to its negative environmental effects. In the past decades, RM, as an economically and environmentally viable alternative, was widely utilized for various applications such as land composting, cement, building material additive and metal recovery and many comprehensive investigations [18].

In addition, RM is also a good adsorbent for pollutants removal, such as phosphate [14], arsenate [17], dyes [19], from aqueous solution. One of the main advantages of phosphate removal by using RM over the other chemical treatment is the abundance of RM and its easy availability [14]. In contrast to the abundant research conducted to the phosphate removal efficiency of RM from water, there are few studies having been reported on the use of RM to adsorb phosphate from biogas slurry. The application of RM for phosphate removal in biogas slurry may be a good way to achieve goals both of disposing and reusing of RM.

## 2. Materials and methods

### 2.1. Materials

The 100 mesh particle sized, washed, and air-dried RM used in this study was obtained from Shandong Aluminium Corporation in Zibo, Shandong Province, China. The average chemical composition of RM was listed in Table 1 [14]. This table showed that RM is primarily composed of Ca, Si, Fe and Al oxides. Other minor elements such as Mg, K, Ti and Na are also precipitated as solid phases. And the biogas slurry in this study was taken directly from anaerobic fermentation residues.

Table 1. Average composition of RM used from calcination method (% by wt.)

Constituent	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>
Red mud	18.08	15.30	8.26	38.02	1.63	3.55	0.36	4.51

### 2.2. Methods

In order to determine phosphate removal capacity and effect on  $\text{pH}_f$  of the RM, batch experiments were conducted. And the experimental procedure was as follows: adding biogas slurry 150mL with a certain concentration to a series of 200mL glass beakers, and then adding fine powdered RM into the beakers. The flocculation experiment was conducted with an initial 2-min rotation at 200 rpm, immediately followed by 15-min rotation at 60 rpm. Then, samples were left for 30 min to allow complete precipitation in the jars, and its super-stratum clear fluid was filtered with  $0.45 \mu$  micro-pore filter membrane for measurement of phosphate concentration.

Sorption of phosphate was measured using the ascorbic acid method with a HACH DR/4000U spectrophotometer, according to APHA standard methods [20]. A pH meter (Orion) was used to measure the pH of the solutions. All chemicals and reagents used were of analytical reagent grade. And all experiments were conducted in triplicate and the average values were used for data analysis.

### 3. Results and Analysis

#### 3.1. Effect of pH

For the removal of phosphate from aqueous by adsorption, pH is considered to be an important parameter which affects surface charge of the adsorbent and the degree of ionization and specification of adsorbate [21]. The impact of different pH values, through adjusting the pH value of the biogas slurry by using 0.01 mol l<sup>-1</sup> NaOH solution or HCl, on the phosphate removal and pH<sub>f</sub> was shown in Fig.1(a). It was obviously observed that there was a sharp decrease of phosphate removal efficiency with increase of pH up to around pH 6.87, and thereafter an increase was observed from pH 6.87 to 11.04. The highest and the lowest phosphate removal efficiency were 89.58% and 47.23%, respectively, at pH 2.08 and pH 6.87. And that is, compared with acid and alkaline condition, the phosphate removal efficiency was the lowest under neutral condition.

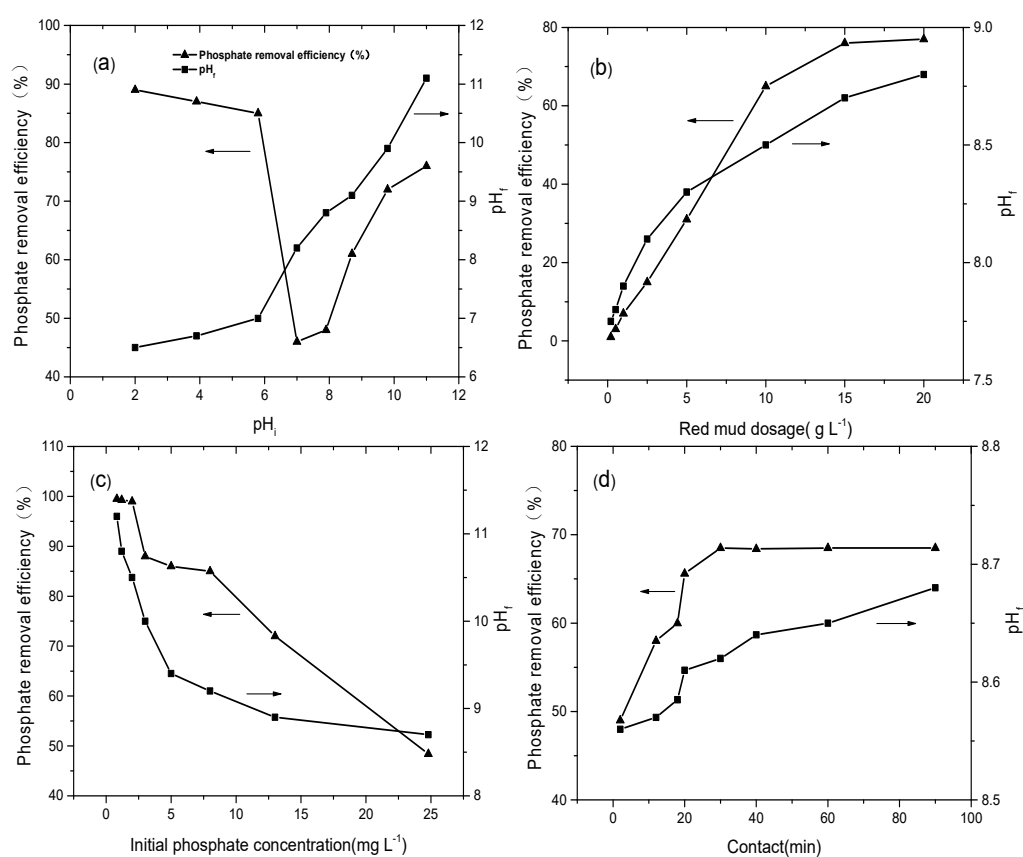


Fig.1 (a) Effect of initial pH (RM dosage: 10.0 g L<sup>-1</sup>, initial phosphate concentration: 10mg L<sup>-1</sup>, contact time 30 min, agitation speed: 200 rpm, temperature 25°C). (b) RM dosage (pH<sub>i</sub> 3.0, initial phosphate concentration: 10mg L<sup>-1</sup>, contact time 30 min, agitation speed: 200 rpm, temperature 25°C). (c) initial phosphate concentration (pH<sub>i</sub> 3.0, RM dosage: 10 g L<sup>-1</sup>, contact time 30 min, agitation speed: 200 rpm, temperature 25°C) and (d) contact time on phosphate removal efficiency and pH<sub>f</sub> (pH<sub>i</sub> 3.0, RM dosage: 10.0 g L<sup>-1</sup>, initial phosphate concentration: 10mg L<sup>-1</sup>, agitation speed: 200 rpm, temperature 25°C)

#### 3.2. Effect of Dosage

The effect of RM dosage on the removal of phosphate from biogas slurry was shown in Fig. 1(b). As seen from Fig.1(b), it can be clearly seen that increasing RM dosage resulted in higher phosphate

removal efficiency. When the quantity of RM was less than  $10 \text{ g L}^{-1}$ , the phosphate removal efficiency rapidly increased with increase of RM dosage (from 0.27% to 66.28%), and thereafter it increased slowly. And the phosphate removal efficiency reached to 76.37% when the RM dosage increased to  $20 \text{ g L}^{-1}$ .

The increase in the adsorption capacity of RM treated phosphate in the biogas slurry was attributed to the pH values and active components of RM. On the one hand, more surface area and adsorption functional sites are available under higher RM dosage conditions and so higher phosphate removal efficiency could be achieved [14]. On the other hand, the alkaline property ( $\text{OH}^-$ ) of RM is the other active component in phosphate adsorption. And it was used for the conversion of acidic phosphate compounds and so the pH of the solution did not raise a lot. Therefore, in order to increase pH to an adequate value for satisfactory phosphate removal, more RM should be added into the biogas slurry [22].

### 3.3. Effect of Initial Phosphate Concentration

Phosphate removal efficiency for different phosphate concentrations was presented in Fig. 1(c). As shown in Fig.1(c), the phosphate removal efficiency decreased with increasing initial phosphate concentration for a given RM dosage. The phosphate removal efficiency reached to 99.54% when the initial phosphate concentration was  $0.82 \text{ mg L}^{-1}$ , while it was only 48.44% when the initial phosphate concentration was  $24.68 \text{ mg L}^{-1}$ . These results may be anticipated due to buffering properties of phosphate compound and insufficient calcium ions in the solution.

As can be seen from Fig.1(c),  $\text{pH}_f$  value decreased with increase of phosphate concentration. This can be explained by the change of orthophosphate compounds with pH (i.e. conversion of  $\text{H}_3\text{PO}_4 \Rightarrow \text{H}_2\text{PO}_4^- \Rightarrow \text{HPO}_4^{2-} \Rightarrow \text{PO}_4^{3-}$  with increasing pH).  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  are the predominant aqueous species at pH 3.0.  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  may also be present at the same pH but typically at concentrations less than  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  [14]. Lots of research has shown that more RM were needed to add water in order to increase the  $\text{pH}_f$  that was suitable for the formation of the insoluble phosphate compounds when the initial phosphate concentration increased [22].

### 3.4. Effect of Contact Time

Contact time affected the effective elements dissolution efficiency of RM and the reaction extent between RM and biogas slurry. The influence of contact time on phosphate removal was shown in Fig.1(d). Obviously, the phosphate removal process could be divided into two steps at the time of 30 min. 68.60% of removal efficiency was achieved at the first step (during the beginning 30 min). In this step, phosphate seemed to be removed through surface adsorption [23], and the more available vacant adsorption sites added advantageous effects on this removal process [24]. The second step started from 30 min to the equilibrium, about 90 min. With the increase of contact time, the increase in phosphate removal tended slowly gradually and maintained at a steady level, implying that phosphate was possible monolayer-adsorbed on the surface of RM. The longer reaction time, the higher utilization efficiency of RM and the higher reaction extent between RM and biogas slurry would be attained. But if the reaction time was too long, a little increase in the effective compositions of the RM would be observed and more energy would be needed mainly due to the decrease in vacant adsorption sites on the surface of RM, and this would be not economic [13]. Therefore, the optimum reaction time of RM and biogas slurry in phosphate removal was determined 30 min. As it was observed,  $\text{pH}_f$  increased with increase of contact time and this may be due to the fact that phosphate adsorption on RM released hydroxyl ( $-\text{OH}$ ) into solution [25].

## 4. Conclusions

RM, a solid waste material from the aluminum industry, was used as an adsorbent to remove phosphate from biogas slurry. Based on the experimental results, the conclusions can be drawn as follows: the phosphate removal efficiency decreased with increasing pH up to around pH 6.87, and then increased with the increase pH from 6.87 to 11.04 under given conditions; RM dosage was found to have the most positive influence on the removal efficiency of phosphate and  $\text{pH}_f$ , and the maximal phosphate removal

efficiency could reach to 76.37% at RM dosage of 20 g L<sup>-1</sup>; The phosphate concentration of biogas slurry had a negative influence for the removal efficiency of phosphate and pH<sub>f</sub>. The maximum and minimum phosphate removal efficiency was 99.54% and 47.98% when the initial phosphate concentration was 0.82 mg L<sup>-1</sup> and 24.68 mg L<sup>-1</sup>, respectively; the removal efficiency of phosphate increased with the increase of contact time, and attained a steady level when the contact time was 30 min.

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