Phosphate Removal from Swine Waste Water with Unburned Red Mud Ceramsite

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Abstract. Red mud, a waste tailing from the alumina industry, was calcined at different temperatures. The calcined red mud was used to prepare the unburned ceramsite as adsorbent to remove phosphate from the effluent of swine waste water treated with a sequencing batch reactor (SBR). Adsorption of phosphate to the unburned ceramsite made of raw red mud and activated red mud was studied as a function of dosage, pH and reaction time. The adsorption of phosphate to the red mud unburned ceramsite both in-roasting and roasting fit the Langmuir isotherm. Calcination of red mud enhanced the adsorption capacity of unburned ceramsite greatly. The pH has an obvious effect on the removal and high pH favors the removal of phosphate. The adsorption mechanism is suggested to include surface complexation reactions, and the mechanism of phosphate removal may include co-precipitation. Due to their low cost and high capability, it is concluded that the red mud unburned ceramsite may be an efficient adsorbent to remove phosphate from swine waste water.

1. Introduction
In recent years, with the rapid development of the livestock and poultry breeding, environmental pollution problems caused by livestock and poultry breeding waste water becomes more and more serious in China. Chemical oxygen demand (COD) in livestock and poultry breeding waste water is between 2500 and 46800mg/L, and total phosphorus content is between 32 and 293mg/L [1, 2]. Phosphorus (P) is usually considered to be the limiting nutrient in relation to the eutrophication of water bodies. For this reason, waste-water treatment plants have to meet maximum P discharge limits [3]. In order to meet the effluent quality standards, further treatment of the secondary effluent is required. Removal of phosphate from waste-water has been conducted by the chemical precipitation [4] or by the biological treatment [5]. More effective methods for phosphate removal are chemical treatments including phosphate precipitation with calcium, aluminum and iron salts [6, 7]. However they are still subjected to high costs of maintenance and problems of sludge handling, disposal, and neutralization of the effluent [8]. Various physical methods have been suggested including reverse osmosis, electrolyte-dialysis, contact filtration and adsorption [9]. Adsorption is comparatively handy and economical for this purpose. The application of low cost and available materials like fly ash...
[10,11], blast furnace slag [12], dolomite [13], dewatered alum sludge [14] and mesoporous structural material [15] have been widely investigated recently in waste-water treatment. The major advantage of using these materials or by-products for waste-water treatment is cost effectiveness.

The red mud is an industrial waste derived from an alumina factory in Sanmenxia city, Henan Province, China. The discarded red mud not only occupies a huge cultivated land but also leads to the environment destruction. It is noticed that, however, the red mud has large specific surface area, still contains certain amounts of calcium, iron oxides and alumina oxide [16, 17]. Then, it could possibly be used for removing phosphorus effectively in livestock and poultry breeding waste-water.

The objective of this work is to use the red mud ceramsite as an adsorbent for phosphorus removal from swine waste-water. The effects of adsorption isotherms, adsorbent dosage, solution pH, contact time and temperature on removal of phosphate were evaluated in batch experiments. The livestock and poultry breeding waste water treated with the conventional biological treatment of sequencing batch reactor (SBR) process, which was used in above experiments. The column flow-through adsorption tests were conducted with secondary effluents from a waste-water treatment plant. Such work will contribute to optimize the phosphate removal process using the red mud ceramsite.

2. Materials and methods

2.1. Materials

2.1.1. Red mud. The red mud in Bayer process was supplied by a company of Sanmenxia City, Henan Province, PRC. The chemical compositions of the raw mud are given in Tab.1.

| Chemical composition | CaO | SiO₂ | Fe₂O₃ | Al₂O₃ | TiO₂ | Na₂O | K₂O | MgO |
|----------------------|-----|------|-------|-------|------|------|-----|-----|
| Mass percent/%       | 36.82| 19.1 | 14.93 | 6.93  | 1.08 | 2.37 | 1.20 | 1.15 |

2.1.2. Waste water. The sampling waste waters were collected from a pig-breeding company in Bobai County of Guangxi Province, China. The characteristics of the treated water in Sequencing Batch Reactor (SBR) process are given in Tab.2.

| Water quality objective | COD | TP | TN | NH₄⁺-N | pH |
|-------------------------|-----|----|----|--------|----|
| Results/mg/L            | 150-230 | 4.3-13 | 12-14 | 0-1.6 | 8.0-8.7 |

Ammonia nitrogen is measured by means of Nessler's reagent spectrophotometry method, the total nitrogen is measured by means of ultraviolet spectrophotometry (Seal Analytical Ltd., UK) method with potassium persulfate oxidation, total phosphorus is measured by means of the analysis method with ascorbic acid using spectrophotometer(Seal Analytical Ltd., UK), chemical oxygen demand (COD) measured by means of potassium dichromate method using fast COD meter(Lovibond ET1255C), The solution pH is measured using a pH meter (Model 250, ThermoOrin, USA) [18].

2.2. Test method

2.2.1. Preparation method of unburned red mud ceramsite. 500g red mud is roasted at different temperature in a muffle furnace for 1.5h respectively, then cool to room temperature after roasting, and pass through 200 mesh sieve. The non-activated red clay and activated red clay are mixed with other auxiliary materials respectively, and pelleted into a sphere with a diameter of 5mm, and cured for 28d.
2.2.2. Adsorption test method. (1) Static adsorption test Take 500ml treated water sample into a 500ml conical taper bottle, add suitable amount of unburned red mud ceramsite, oscillate for 24h at 180r/min in air bath oscillator at room temperature. The precipitate is removed by centrifugation. The supernatant extract is used to determine the residual phosphorus concentration. The adsorption of phosphorus is calculated according to Formula 1.

\[ Q = (C_i - C_e) \frac{V}{m} \]  

In the Formula (1), Q is the amount of adsorption (mg/g); Ci is the initial pollutant concentration (mg/L). Ce is the concentration of pollutants in equilibrium (mg/L). V is the volume of waste water (L); m is the quantity of adsorbent (g).

(2) Dynamic adsorption test. Dynamic adsorption experiment device is shown in figure 1. In Fig 1, the adsorption column is an organic glass column which is 67 mm internal diameter and 100 cm high. The adsorption column has an outlet at the bottom and an inlet at the top. The phosphorous waste water is controlled by the creep pump.

The waste water flows constantly into the absorption column by the creep pump. Being the waste water against the flow, it can have full adsorption by red mud ceramsite. Then, the water flows to the cup for chemical analyses.

2.2.3. PH effect. Phosphate adsorption isotherm studies are carried out with 15g/100mL unburned red mud ceramsite at 25℃, at 200rpm for 24h. The effect of pH (ranging from 3.5 to 11.5) on phosphate adsorption was examined in a series of experiments using the same initial phosphate concentration.

2.2.4. Ceramsite dose effect. The effect of adsorbent dose on adsorption of phosphate was investigated with 100mL phosphate solution containing 11.45mg P/L at 25℃, and with the initial pH of 5.0 at 200rpm for 24h. Nine initial adsorbent dose (1, 2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20g/L) were tested for phosphate removal.

2.2.5. Adsorption time effects. The ceramsite dosage was maintained at a defined value of 15.0g/L, and the pH was maintained at a defined value of 5.0. The influence test of adsorption time (4, 8, 12, 16, 20, 24, 28, 32, 36, 40 and 48h) was investigated at 25℃ and 200rpm on the phosphorus removal.
3. Results and discussions

3.1. The adsorption isotherm
Using unburned red mud ceramsite as adsorption, the phosphorus removal efficiency in aqueous solution are investigated before investigating the phosphorus removal efficiency in waste water of livestock and poultry breeding. The adsorption isotherms are determined. The phosphorus saturated adsorption amount of the unburned red mud ceramsite in different initial concentration of solution are investigated respectively. Phosphorus adsorption capacity of the red mud ceramsite increased after roasting activation. The adsorption quantity rises with the increase of the activation treatment temperature.

The experimental results matched the Langmuir adsorption isotherm model. The Langmuir isothermal equation is shown in Formula 2:

\[ Q = \frac{Q_0 b C}{1 + b C} \]  

In the formula, \( Q \) is the amount of adsorption (mg/g). \( Q_0 \) is the saturation adsorption (mg/g); \( C \) is the equilibrium concentration (mg/L); \( b \) is the adsorption coefficient.

The Langmuir linear regression results are shown in Tab.3. From Tab.3, the adsorption isotherms are in line with the Langmuir adsorption isotherm. After being calcined and activated at 300℃, 500℃, 700℃ and 900℃ respectively, the phosphorus saturated adsorption amount of the modified unburned red mud ceramsite increased significantly compared with non calcined red mud.

| Tab. 3 Langmuir isotherm parameters for phosphate adsorption |
|-------------------------------------------------------------|
| \( Q_0 \)/mg/g | b  | \( R^2 \) |
| red mud in-calcined | 46.26 | 0.039 | 0.993 |
| red mud calcined at 300℃ | 60.70 | 0.033 | 0.981 |
| red mud calcined at 500℃ | 100.12 | 0.024 | 0.999 |
| red mud calcined at 700℃ | 130.59 | 0.019 | 0.960 |
| red mud calcined at 900℃ | 149.29 | 0.013 | 0.999 |

3.2. Effect of pH value
To study the influence of pH on the phosphate adsorption capacity of ceramsite, experiments were performed at various initial solution pH values, from 3.5 to 11.5. The obtained results were shown in Fig.2. It was found that the amount of phosphate adsorbed at pH 5.0 was the greatest. The phosphate adsorption by the red mud unburned ceramsite had a direct-relation with solution pH, i.e. the amount of phosphate adsorbed onto red mud unburned ceramsite decreased with decreasing or increasing pH.

The surfaces of Fe and Al metal oxides of red mud unburned ceramsite consist mainly of oxygen atoms and hydroxyl groups. It is primarily the hydroxyl group that determines the chemical properties (acid–base character) and the reactivity of these surfaces [20]. Phosphate cannot be ion exchanged onto red mud unburned ceramsite under alkaline or acidic conditions. This is likely attributed to the fact that a higher pH causes the unburned red mud ceramsite surface to develop more negative charges and thus would more significantly repulse the negatively charged species in solution. Under acidic conditions, the adsorptive capacity decreases due to a higher solubility of Al and Fe oxides. Therefore, the lower adsorption of phosphate at higher pH values resulted from an increased repulsion between the more negatively charged PO\(_4^{3-}\)species and negatively charged surface sites. That is why the maximum phosphate adsorption occurred at pH 5.0.

Within the pH scope from 3.5 to 5.0, the phosphorus removal rate increase gradually with the increase of pH value. The main reason is that the acidic conditions has the power to release Ca\(^{2+}\) of the red mud, and to remove phosphate by the precipitation of phosphate and Ca\(^{2+}\). The increase of pH value can reduce the Ca\(^{2+}\) release of the red mud, which led to the decrease of the removal of
Within the pH scope from 5.0 to 11.5, the phosphorus removal rate decrease gradually with the increase of pH value. The main reason could be that the condition of high pH value were more conducive to remove phosphorus by the insoluble precipitation of phosphate and calcium ions [19, 20].

**Fig. 2** Effect of pH value on phosphorus removal from effluent with different red mud ceramsite

In summary, In the case of acidic conditions, the equilibrium is carried out in the analytic direction, and the removal rate of phosphorus decreases with increase of H+ concentration. On the other hand, in alkaline conditions, as the OH- concentration increasing, the reaction is favorable to the adsorption direction, thus the removal rate increase.

3.3. Effect of ceramsite dosage

The relation between the amounts of phosphate adsorbed and unburned red mud ceramsite dose is shown in Fig.3. It is apparent that the phosphate removal rate in solution increased with increasing unburned red mud ceramsite dose for a given initial phosphate concentration. This result was anticipated because increasing adsorbent doses provide greater surface area. However, it is evident that the phosphate removal rate began to fall since unburned red mud ceramsite dose of 15g/L. That is to say, the optimal dosage of unburned red mud ceramsite is 15g/L.
3.4. Effect of adsorption time

Experiments were conducted to study the effect of varying phosphate time on phosphate removal by red mud unburned ceramsite. The result are shown in Fig. 4. It indicates that all curves have the similar shape. The removal rates of phosphorus are rapidly increased in the ceramsite made of red mud in-calcined or calcined within 24h of the adsorption reaction time. The removal rate of phosphorus with unburned ceramsite made of red mud calcined at different temperature were 76.2%, 82.3%, 86.1%, 91.3% and 96.2% respectively at 24h, thereafter the removal rate increased slowly. It can be seen from Fig. 4 that the removal rate of phosphorus in calcined red mud ceramsite is much larger than that of in-calcined red mud ceramsite at the same dosage and the same reaction time. Moreover, the higher the activation temperature is, the higher the ability of removal phosphorus in red mud ceramsite have. It indicates that high temperature roasting is conducive to improve the adsorption of phosphorus on red mud ceramsite.
3.5. Discussion on phosphorus removal mechanism

The results of the above tests show that the ability of removal phosphorus of the activated red mud increased and its adsorption dosage increased with the increasing calcination temperature. Experimental research shows the effect of the heat treatment on the red mud by X-ray diffraction (XRD) analysis. The results of XRD analysis are shown in Fig.5. It can be seen that the specific surface area of the red mud gradually increased when calcined from 300°C to 500°C. The increase of its specific surface area was favorable for the adsorption of phosphorus. Hence the effect of phosphorus removal of the red mud was significantly increased with the calcination treatment at 300°C and 500°C. However, when the temperature reaches 700°C and 900°C, the specific surface area of calcined red mud decreases gradually. But its removal ability still improved. The differential thermal analysis of red mud are carried out and the results are shown in Fig.5. It can be seen that the differential thermal analysis curve of the red mud has a strong peak from 690°C, which is mainly due to the decomposition of the carbonate in the red mud into the metal oxide [18]. Therefore, when the red mud calcined at 700°C and 900°C, the increase in the ability of removal phosphorus is mainly due to that transformation from the carbonate to oxides, which increases the content of the effective adsorption component in the red mud.
4. Conclusions

Present study indicates that red mud ceramsite may be an effective adsorbent for phosphate removal from livestock and poultry breeding waste water. The red mud ceramsite showed good performance for phosphorus removal. Due to its low cost and high adsorptive capacity, the red mud ceramsite possess the potential to be utilized for cost-effective removal of phosphorus from livestock and poultry breeding waste water. It was also found that the phosphate removal efficiency by red mud ceramsite depended on pH, adsorbent doses and adsorbent temperature.

1) The adsorption phosphorus on red mud calcined at different temperature or in-calcined are in accordance with Langmuir adsorption isotherm model.

2) The calcination activation increases the ability of the red mud ceramsite to remove the phosphorus in the livestock and poultry breeding waste water. The saturated adsorption capacity increases with the increase of the calcination temperature.

3) The removal ability of phosphorus is affected by pH value, and the high pH condition is favorable for the removal of phosphorus.

4) The mechanism of removal of phosphorus from red mud and activated red mud is the mechanism of surface complexation of metal oxides, and the removal mechanism of phosphorus also includes coprecipitation. The phosphorus removal mechanisms on the red mud ceramsite are surface complexation action and coprecipitation.

Acknowledgments

Authors would like to acknowledge key Project (No. 201705) from Wuhan Urban and Rural Construction Commission of Hubei Province, China.

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