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Characterization of red mud granular adsorbent (RMGA) and its performance on phosphate removal from aqueous solution

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A B S T R A C T

Red mud granular adsorbent (RMGA), which was applied to remove phosphate from aqueous solution in this research, was manufactured with red mud (a solid waste from alumina industry) as the main raw material. Based on the combined adsorption–regeneration experiment, RMGA sintered at 1000 °C was selected for further characterization. Through the process of sintering, both the alkalinity and the surface of RMGA were ameliorated. X-ray diffraction analysis showed that the components with —OH and $—SO_4$ were the functional groups for phosphate adsorption. The removal of phosphate by RMGA was weakly affected by the common coexisting ions in solution (such as Cl^-, NO_3^- and SO_4^{2-}), but strongly depended on pH and contact time. RMGA performed relatively better at pH_i (the initial pH in solution) of 3.0–6.0, and equilibrium could be reached after 7 h. The kinetics studies presented that phosphate removal by RMGA mainly followed the pseudo second-order model. The initial phosphate removal rate was faster at lower pH_i, since the electrostatic repulsion between RMGA and phosphate was enhanced as pH increased. The pH in solution rose during phosphate removal process, and the mechanism for phosphate removal was divided into two stages: the removal of phosphate within 1 h was mainly attributed to phosphate adsorption on RMGA; while that after 1 h was the combined effect of adsorption and precipitation, which resulted in the appearance of the maximum phosphate removal capacity (6.64 mg g^{-1}) at pH_i 5.00.

1. Introduction

Phosphate is a limiting nutritional factor for plant growth, but it will induce eutrophication to rivers and lakes if it is excessively supplied. According to a report in 2004, more than 40% of the receiving surface waters around the world are facing eutrophication problems [1]. Moreover, as P is considered as a nonrenewable and irreplaceable resource that will be scarce in the future [2], it is of great importance to remove and collect phosphates from the drainage basin before being dispersed into environment. An efficient method of reducing phosphates during wastewater treatment is the fundamental factor to prevent eutrophication in surface water. Various physical, chemical and biological techniques have been applied to remove dissolved phosphate from wastewater, such as adsorption or ion exchange [3], coagulation [4], precipitation–microfiltration [5] and aerobic–anaerobic–anoxic systems [6]. Among them, thanks to the comparatively simple and economical process as well as the less sludge producing and easy disposing operation, adsorption methods are considered promising [7].

In recent decades, various adsorbents have been studied for their application in phosphate removal, which include modified natural minerals like bentonite [8] and montmorillonite [9], agricultural residues like shells [10] and wheat-straw [11], industrial wastes like fly ash [12] and red mud [13], etc. Among these materials, red mud is a highly alkaline waste residue of bauxite via the alumina producing process, and one to two tons of red mud is generated for per ton alumina production [14]. Only in China, approximately 28.9 million tons of alumina was created during 2010 [15], and red mud is produced even more. Because of the alkaline in it as well as the lack of proper disposal methods, large amount of red mud is cumulated continuously, and this results in serious environmental problems. Since red mud is a potential adsorbent, the application of it in water treatment for phosphate removal is a good way, by which both the objects of disposing and reusing red mud can be obtained.

Recently, powdered red mud has been studied by many researchers, which performed well for phosphate removal due to its relatively larger surface area and higher calcium, aluminum, and iron content [16]. However, the characteristics such as easy-blocking and hard-recovering prevent the application of powdered red mud in practical column techniques [17], so the project of making red mud into a granular adsorbent has been put forward.

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Because the cohesiveness of red mud is not strong enough for granulation, some researchers have created granular red mud employing additives (such as Na_2SiO_3 [18]), which plays the role of adhesive, but this method is not very satisfactory in economic concern. Based on these attempts, we intend using clay, which is a natural cementing agent [19], instead of those expensive chemical adhesives to reduce the high cost in granular red mud producing.

In this research, red mud granular adsorbent (RMGA) was developed from red mud as the main raw material. Bentonite (a kind of clay) and starch were employed as natural additives instead of expensive chemical agent. For the purpose of accumulating basic operating data, the removal of phosphate from aqueous solution using RMGA was investigated according to adsorption experiments conducted in capped conical flasks. Through the regeneration experiment, RMGA sintered at 1000 °C (RMGA-1000 °C) was selected for further study. RMGA was characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) microanalysis. The influences of some operation parameters on phosphate removal were investigated, including initial pH, coexisting ion and contact time as well as the kinetics studies.

2. Material and methods

2.1. Materials

In this research, raw materials for RMGA producing included dewatered red mud, bentonite and starch, all of which were under 100 mesh particle sized (less than 0.149 mm). Red mud, the main raw materials, was obtained from Shandong Aluminium Industry Corporation in Zibo, Shandong Province of China. Bentonite and starch played the role of cementing agent and aperture producer, respectively, taking the place of expensive chemical additives. The powdered materials were evenly blended at a mass ratio of 90:5:5, and mixed with pure water to a paste. The raw granules were manufactured to small cylinder particles of 1.5-mm-long and 1.5-mm-wide, according to the preparation procedures in our previous research [20]. Then, they were preheated at 400 °C for 20 min in a muffle furnace and subsequently sintered at the relevant temperature (950 °C, 1000 °C, 1050 °C, etc.) for 10 min in a tubular furnace. After being naturally cooled down to room temperature, various RMGA were obtained as desired.

2.2. Sample description

The phosphates concentration in solution was determined via the ascorbic acid method with a 722E visible range spectrophotometer, according to the method published in *Monitoring and Analysis Methods of Water and Wastewater* [21].

The chemical composition of two raw materials – dewatered red mud and bentonite, was determined by the energy dispersive X-ray analysis (EDAX), using a PV9100 X-ray energy spectrometer which connected with an S-520 scanning electron microscope. XRD patterns of powdered red mud and selected RMGA samples were obtained with a D/max-ra X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA over the 2θ range of 10–70°. The zeta potential was measured in pH controlled deionized water at pH of 3.0 and 10.0 with a JS94H electrophoresis meter. The specific surface area of RMGA was measured with a QUADRASORB SI automated surface area analyzer, and the pore size distribution of RMGA was determined with a JW-BK122 W static nitrogen aperture meter, both according to the BET nitrogen gas sorption method. The micrograph of selected samples were observed using a 26 kV X650 SEM at a magnification of 1 × 2000.

2.3. Phosphate removal studies

Phosphate solutions were prepared by potassium dihydrogen phosphate (KH_2PO_4) of guaranteed grade, and the concentration of element P was 50 mg L^{-1}. The other reagents used in this research were of analytical grade, and deionized water was applied for the preparation of all solutions. The initial pH (pH_i) in phosphate solution was adjusted to the relevant value of 1.0–13.0 with 1.0 mol L^{-1} HCl or NaOH solutions as required in different tests. The batch adsorption experiments were conducted by shaking 25 mL of the selected phosphate solution with 0.1 g RMGA (the designed adsorbent dosage was 4 g L^{-1}) in the covered Erlenmeyer flasks for a definite time (5–480 min), using a stable temperature horizontal shaking bath that was regulated at temperature of 27 ± 1 °C (300 K) and stirring speed of 100 rpm. After operation, the final pH (pH_f) in solution was measured with a PHS-25C acidometer, and the concentration of P was analyzed by the ascorbic acid method [21]. At the same time, considering that phosphate may be adsorbed slightly by the glass container, blank tests were carried out under the same conditions without using RMGA, and P in these solutions was measured to represent the initial phosphate concentration.

The phosphate removal capacity (q) of RMGA was evaluated by

$$q = (C_i - C_f)V/m \tag{1}$$

where q signifies the amount of P removed by per unit mass of RMGA (mg g^{-1}); C_i and C_f are the initial and final concentrations of elemental P in solution (mg L^{-1}), respectively; V is the volume of phosphate solution (L); and m indicates the weight of dry RMGA (g).

3. Results and discussion

3.1. Components analysis of raw materials

The chemical composition of two raw materials determined by EDAX is shown in Table 1: calcium oxide was the dominant component in red mud with 31.12% in mass, and the other principal components were the oxides of Si, Fe, Al and Na; while for bentonite, SiO_2 was dominant with mass percentage of 66.18%, and the results were similar with our previous research [20]. The mass ratio of chemical compositions in mixed raw materials was calculated according to their corresponding proportion in red mud (90%), bentonite (5%) and starch (5%).

In order to investigate the component variation in granules during sintering process, the chemical composition of RMGA-1000 °C was determined by EDAX. The result is shown in Table 1, and it was found that the percentage of the compositions in RMGA did not agree well with those in mixed raw material. After being sintered, about 30% of mass in raw granules was reduced due to the evaporation of crystal water, the carbonization of starch as well as the decomposition of calcite or some other components [22,23]. In addition, according to the range of Riley's foaming composition in ceramics production [6], the total ratio of CaO and Na_2O (both are flux component) in raw granule was much higher than demand, so they were comparatively easy to be melted and released during sintering. As a result, the percentage of CaO and Na_2O in RMGA decreased obviously while that of the other composition increased. Therefore, the alkalinity of RMGA was also reduced to some extent at the same time.

To identify the mineralogical structure of selected samples, XRD was used hereon. Fig. 1a shows the XRD pattern of red mud. It can be seen that the main crystalline phases of red mud included calcium oxide, iron oxide, alumina, bayerite ($Al(OH)_3$) and nepheline ($(Na,K)AlSiO_4$) [23,24]. When raw granules were sintered at