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Removal of phosphate from etching wastewater by calcined alkaline residue: Batch and column studies

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ABSTRACT

The present study explored the effectiveness of calcined alkaline residue in removing phosphate from etching wastewater. Alkaline residue was calcined at various temperatures between 400 and 1000 °C with 100 °C interval for 2 h, and the highest phosphate sorption capacity was achieved at 800 °C. The pH impact, sorption kinetics, isotherms and thermodynamics of phosphate adsorption on AR800 (alkaline residue calcined at 800 °C) were investigated by batch tests. The kinetics was evaluated with the Lagergren pseudo-first-order and pseudo-second-order models, and the experimental data fitted well with the pseudo-second-order model, indicating chemisorption was the rate-limiting step of sorption process. The equilibrium data were further analyzed by the Langmuir, Freundlich and Dubinin–Radushkevich models. Equilibrium sorption of phosphate onto AR800 fitted best with the Langmuir model, and the maximum sorption capacity was 139 mg/g. The thermodynamic parameters, such as ΔG°, ΔH° and ΔS°, were also calculated, which confirmed that the removal of phosphate from etching wastewater by AR800 was a spontaneous and endothermic process. Moreover, fixed-bed column experiments were carried out to optimize flow rate, bed height and initial phosphate concentration. It was found that the breakthrough curves were well described by Thomas model. The results above show AR800 has high potentialities to be used as an adsorbent for phosphate removal from etching wastewater in large-scale.

1. Introduction

Thin-film transistor liquid crystal display (TFT-LCD) manufacturing industry is becoming more and more flourishing in China. The processes of TFT-LCD manufacturing, including deposition, photolithography and etching, often require large quantities of water and generate significant amount of wastewater. The wastewater from etching process typically contains high concentration of phosphate. Excessive phosphorus is often responsible for eutrophication, which leads to short- and long-term environmental and navigational problems in water bodies [1]. The concentration of phosphorus in effluents that discharge directly is regulated by national and international waster standard authorities with maximum limits ranging from 0.1 to 2.0 mg P/L, and many established at 1.0 mg P/L [2]. In response to these strict effluent quality standards, several physical, biological and chemical methods have been used for the phosphate removal from wastewater. However, physical methods for phosphate removal are generally either too expensive or inefficient [3]. Additionally, biological methods, although inexpensive, usually require more complex plant configurations and operating regimes [4]. Chemical removal techniques are widely accepted methods for phosphate removal, especially the adsorption process. Recently, the utilization of industrial by-products and other low cost materials as adsorbents for phosphate removal have been widely investigated, such as fly ash [5,6], calcite [7], steel slag [8], blast furnace slag [9], iron oxide tailings [10] and oyster shell [11].

Alkaline residue, the common by-product from soda ash production of the Solvay method for the production of soda ash, was usually deemed as waste. Lianyungang Soda Ash Plant, one of China's largest soda ash plants, provides about 350,000 tons alkaline residue every year. Although a large portion of alkaline residue is used in cement production and road construction, a considerable portion alkaline residue is disposed in open dumps or landfills directly [12]. However, with the available landfill space

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reduced, the cost of land disposal for waste is increased in industrial countries. Hence, finding an interesting potential market to reuse alkaline residue may be an economically valuable solution to this problem. In recent years, the application of alkaline residue as environmental adsorbents to remove anionic dyes [13,14], heavy metals [15] and ammonium [16] from wastewater has been paid more attentions. But little research was conducted to focus on removing phosphate from wastewater.

Many previous studies have demonstrated that sorption performance of calcium carbonate rich materials can be enhanced by modifying its texture by means of thermal treatments [17–19]. This work was to explore the feasibility of using calcined alkaline residue for removal of phosphate from etching wastewater. The phosphate adsorption properties (pH effect, sorption kinetics, sorption isotherms and sorption thermodynamics) were investigated utilizing batch experimental methods. Also, a laboratory scale fixed-bed column system has been carried out to predict the column breakthrough curves and obtain basic engineering data.

2. Materials and methods

2.1. Materials

Alkaline residue was collected from Lianyungang Soda Ash Plant, China. It was soaked and washed thoroughly in deionized water to remove soluble salts. The samples were dried at 105 °C for 24 h in an air dry oven, and then sieved for particle size less than 0.15 mm. The dried powder samples were prepared by thermal treatments for 2 h over a range of calcination temperatures (400–1000 °C) in an electric furnace under air atmosphere. Finally, the obtained cooled samples were stored in a desiccator and designated as AR (alkaline residue), AR400 (calcination temperature was 400 °C), AR500 (calcination temperature was 500 °C), etc.

The wastewater (pH 1.7), containing about 70, 000 mg/L phosphate, was provided by a TFT-LCD manufacturing company in Nanjing, China. The desired concentrations in experimental processes were obtained by dilution with deionized water.

2.2. Batch experiments

To select the optimum material, raw and calcined alkaline residue with different temperatures were used. The experiments were performed with 250 mL conical flasks containing 100 mL wastewater (50 mg P/L, pH 5.5) and 0.1 g various calcined alkaline residue in an air batch thermostatic rotary shaker for 2 h. The temperature and rotational speed of shaker were remained at 25 °C and 200 rpm, respectively. After phosphate adsorption, the suspensions were filtered through 0.45 μm membrane filter and the filtrates were analyzed for residual phosphate concentration via an UV–vis spectrophotometer (LAMBDA 25, Perkin Elmer, USA) at wavelength of 800 nm using molybdenum blue method [20]. The uptake of phosphate by alkaline residue at time t (min), q_t (mg/g), was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 and C_t are the concentration (mg P/L) of phosphate in the initial solution and at time t, respectively, V is the volume (L) of solution, and W is the weight (g) of the sample added to the solution. According to results, AR800 was found as the optimum sample and then applied throughout all removal experiments.

To determinate the pH impact on adsorption, 0.1 g AR800 was contacted with 100 mL wastewater (60 mg P/L) at 25 °C for 2 h with continuous shaking. 0.1 M HCl or NaOH was used to adjust the initial solution pH ranged from 2.5 to 11.5.

For kinetic studies, 0.1 g AR800 was loaded in 250 mL conical flasks containing 100 mL wastewater (50 mg P/L and pH 5.5). Then the flasks were capped and agitated on a thermostatic shaker at 200 rpm and 25 °C. Samples were withdrawn at predetermined time intervals for the analysis of residual phosphate concentration in solution.

For adsorption isotherm studies, 0.1 g AR800 was separately added to 100 mL wastewater with various concentrations of 50, 75, 100, 130, 160 and 200 mg P/L. The mixtures were shaken at 200 rpm for 2 h. During these experiments, the temperature and pH were fixed at 25 °C and 5.5, respectively.

For adsorption thermodynamics studies, 0.1 g of AR800 was equilibrated with 100 mL wastewater containing 60 mg P/L at 293, 313 and 333 K for 2 h. The rotate speed and pH were maintained at 200 rpm and 5.5, respectively.

2.3. Column experiments

Fixed-bed column experiments were performed in a laboratory scale glass column with an internal diameter of 1 cm and a length of 25 cm, where quartz sand and AR800 were mixed with a weight ratio of 20:1 in order to improve the penetrate performance. Quartz sand was thoroughly washed by deionized water and dried at 110 °C for 24 h. Glass wool was placed in the bottom and top of column to avoid any loss of AR800. The wastewater was fed in upwards through the column by peristaltic pump. The effluent solutions were collected from the top of the column at defined time intervals and analyzed for phosphate concentration. The three parameters were chosen for this study: flow rate, bed height and initial phosphate concentration. All the sorption column experiments were carried out at 25 ± 1 °C. Operation of the column was stopped when the effluent phosphate concentration equals approximately influent phosphate concentration. The value of the total mass of phosphate retained in the column, q_{total} (mg) can be calculated from the area under the breakthrough curve:

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \tag{2}$$

where C_{ad} is the concentration (mg P/L) of phosphate removal.

Equilibrium metal uptake or maximum capacity of the column, q_e (mg/g), is calculated as the following:

$$q_e = \frac{q_{total}}{m} \tag{3}$$

where m is the dry weight (g) of adsorbent in the column.

2.4. Analytical methods

The chemical compositions of alkaline residue and calcined alkaline residue were determined by X-ray fluorescence spectrometer (XRF) (LAB CENTER XRF-1800, Shimadzu, JPN). The BET surface area and pore volume were measured by BET apparatus (ASAP 2020, Micromeritics Instrument, USA), using nitrogen gas as the adsorbate at 77 K. The morphology was observed by a scanning electron microscope (SEM) (S-4800, Hitachi, JPN). Zeta potential measurement of calcined alkaline residue was carried out by using a Zeta meter (ZetaPALS, Brookhaven Instruments, USA).

3. Results and discussions

3.1. Characterization

The raw alkaline residue was white powder, while the alkaline residue became grayish after treatment at 800 °C. The results of the component variation between AR and AR800 were shown in Table 1. It could be found that calcium oxide was the dominant

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