Removal of phosphate from wastewater using alkaline residue

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A B S T R A C T

Alkaline residue (AR) was found to be an efficient adsorbent for phosphate removal from wastewater. The kinetic and equilibrium of phosphate removal were investigated to evaluate the performance of modified alkaline residue. After treatment by NaOH (AR-NaOH), removal performance was significantly improved, while removal performance was almost completely lost after treatment by HCl (AR-HCl). The kinetics of the removal process by all adsorbents was well characterized by the pseudo second-order model. The Langmuir model exhibited the best correlation for AR-HCl, while AR was effectively described by Freundlich model. Both models were well fitted to AR-NaOH. The maximum adsorption capacities calculated from Langmuir equation were in following manner: AR-NaOH > AR > AR-HCl. Phosphate removal by alkaline residue was pH dependent process. Mechanisms for phosphate removal mainly involved adsorption and precipitation, varied with equilibrium pH of solution. For AR-HCl, the acid equilibrium pH (< 6.0) was unfavorable for the formation of Ca-P precipitate, with adsorption as the key mechanism for phosphate removal. In contrast, for AR and AR-NaOH, precipitation was the dominant mechanism for phosphate removal, due to the incrase on pH (> 8.0) after phosphate removal. The results of both XRD and SEM analysis confirmed $CaHPO_4 \cdot 2H_2O$ formation after phosphate removal by AR and AR-NaOH.

Introduction

Phosphorus is considered as one of the key nutrient elements that cause eutrophication in aquatic environments. Superfluous phosphate discharge from domestic, industrial and agricultural wastewater into natural water bodies often leads to the overgrowth of phytoplankton and depletion of dissolved oxygen, which not only destroys the aquatic life but also disrupts the balance of the aquatic ecosystem (Mustafa et al., 2008). Therefore, it is of value to remove the phosphate before discharging wastewater into natural water environment. During the past decades, various techniques, including biological treatment and chemical precipitation have been reported for phosphorus removal. Comparing with these traditional methods, adsorption is considered as a more effective way to such removal due to its high removal efficiency, economical operation and less residue production (Morse et al., 1998; Ding et al., 2012).

In recent years, increasing attention has been paid to several low-cost and easily available adsorbents derived from natural materials and industrial by-products for removal of phosphate, such as apatite (Bellier et al., 2006; Molle et al., 2005), dolomite (Karaca et al., 2006), limestone (Johansson, 1999), zeolite (Sakadevan and Bavor, 1998), fly ash (Lu et al., 2009; Pengthamkeerati et al., 2008; Xu et al., 2010), red mud (Huang et al., 2008), Aleppo pine (Benyoucef and Amrani, 2011), sugarcane bagasse (Carvalho et al., 2011), paper residue (Wajima and Rakovan, 2013), phosphate mine (Jellali et al., 2011), eggshell (Köse and Kvanç, 2011), blast furnace slag (Kostura et al.,

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2005). Alkaline residue, a by-product of the Solvay method for the production of soda ash, is one of the well-known waste materials. Despite a large portion of alkaline residue is used in relevant industry, such as road construction, soil nutrient amendment or preparation of precipitated calcium carbonate, there is still a considerable portion is disposed of in open dumps or landfills directly (Gao et al., 2007). Every year, relatively massive area of lands in China is being covered up by alkaline residue, and a series of environmental problems have been caused, such as groundwater pollution or dust pollution. Therefore, finding an interesting potential market to reuse alkaline residue may be an economically valuable solution to this problem. Many previous studies have been focused on using alkaline residue to treat wastewater, and the results of laboratory investigations showed that alkaline residue is an effective adsorbent for removal of anionic dye, ammonia-nitrogen and heavy metals from wastewater (Zhu et al., 2007; Şener, 2008; Cao et al., 2006, 2009). However, little research has been conducted to focus on the removal of phosphate. Alkaline residue mainly comprises of calcium carbonate, calcium sulfate, calcium hydroxide, magnesium hydroxide and other substances, which enables alkaline residue to strongly adsorb or precipitate phosphate. Hence, alkaline residue could be considered as a candidate material for phosphorus removal from wastewater.

The objective of this study was to investigate the feasibility of using alkaline residue and chemically modified alkaline residue as adsorbents for phosphate removal from wastewater. The effects of operating parameters, such as contact time and initial phosphate concentration, on the removal were investigated. Moreover, the adsorption kinetic and equilibrium isotherms models were used to fit experimental data. In addition, the mechanisms involved in the phosphate removal process were explored based on X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis.

1 Materials and methods

1.1 Materials

Alkaline residue (AR) used for the experiments was obtained from distiller wastewater provided by Lianyungang Soda Ash Plant, China. Prior to use, the sample was oven-dried at 80°C for 48 hr. The dried sample was treated in a 1 mol/L solution of NaOH or 1 mol/L solution of HCl at a solution to alkaline residue ratio of 10:1 by weight. The mixed samples were then cured at 100°C for 2 hr. After treatment, the mixtures were filtered, washed several times with deionized water, oven-dried at 105°C for 24 hr and sieved for particle size less than 0.15 mm. The final solid products were stored in a desiccator and designated as AR-NaOH (treated by NaOH) and AR-HCl (treated by HCl).

The stock phosphate solution (1000 mg P/L) was prepared by dissolving potassium dihydrogen phosphate (KH_2PO_4) in deionized water. All experimental phosphate solutions were prepared by proper dilution of this stock solution. All the reagents and chemicals used in this study were of analytical grade.

1.2 Analytical methods

The concentration of phosphate was analyzed by molybdenum blue method (Lenore et al., 1999) by using UV-Vis spectrophotometer (LAMBDA 25, PerkinElmer, USA) at a wave length of 880 nm. The concentration of calcium was analyzed by inductively coupled plasma mass spectrometry (ICP-AES) (Optima 7000DV, PerkinElmer, USA) with argon as carrier gas. The pH value of solution was measured using pH meter (FE20, Mettler Toledo, USA).

X-ray fluorescence spectrometer (XRF) (LAB CENTER XRF-1800, Shimadzu, Japan) was used to determine the chemical composition of materials. The surface area of materials was measured by BET apparatus (ASAP 2020, Micromeritics Instrument, USA), using nitrogen gas as the adsorbate at 77 K. The morphological structure of materials was examined by X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany) and scanning electron microscope (SEM) (S-4800, Hitachi, Japan). The particle size distribution of alkaline residue was carried out using a Particle Size Analyzer (ZetaPALS, Brookhaven Instruments, USA).

1.3 Phosphate removal experiments

1.3.1 Phosphate removal calculation

At a giving time, t (min), the phosphate adsorption capacity, q_t (mg/g), was calculated as follows:

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

where, C_0 (mg P/L) and C_t (mg P/L) are the concentration of phosphate in the initial solution and at time t, respectively, V (L) is the volume of solution, and m (g) is the weight of the sample added to the solution.

1.3.2 Batch kinetic and equilibrium studies

To investigate the kinetics and equilibrium of the phosphate removal by alkaline residue, 0.1 g of AR-HCl, AR and AR-NaOH were respectively placed into 250 mL capped conical flasks containing 100 mL phosphate solution with initial concentration of 50 mg P/L and original pH 5.2, and then vibrated at a constant speed of 200 r/min using an air bath thermostatic oscillator. The shaking was interrupted momentarily at predetermined time intervals of 10, 30, 60, 120, 180, 360, 540, 900 and 1440 min. For the equilibrium study, 0.1 g of sample was added into conical flask containing 100 mL phosphate solution with various concentrations (50, 100, 200, 300, 400, 600 and