A novel tablet porous material developed as adsorbent for phosphate removal and recycling

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ABSTRACT

In the present study, a novel tablet porous material (TPM) was developed from Kanuma clay (K-clay), corn starch, and calcium oxide. Laboratory-scale batch experiments were conducted to evaluate the phosphate adsorption capacity of TPM from aqueous solution. The adsorption isotherms, adsorption kinetics, phosphate recycling, and major factors such as temperature, pH, and dosage were investigated. The phosphate adsorption results fitted the Freundlich isotherm model very well, and the adsorption process was an endothermic and spontaneous reaction which could be described by a pseudo second-order kinetic model. The maximum phosphate adsorption capacity was 4.39 mg g^{-1}, and its equilibrium could be attained in 2 h. The solution pH had little effect on TPM phosphate removal when pH varied from 5.0 to 9.0. 70.29% of adsorbed phosphate could be recycled when 0.2 N HCl was used as eluant, and the present developed TPM could be recovered and reused for 5 times. This novel developed TPM is a promising adsorbent than other clay mineral materials for phosphate removal from wastewater.

1. Introduction

A large amount of phosphate discharged from untreated wastewaters, fertilizer industries, etc. into water body is often responsible for algal bloom and eutrophication [1–3], especially in lakes, reservoirs, and coastal areas. These excessive phosphate discharges may bring about environmental issues such as esthetic problems, excessive dissolved oxygen consumption, and deteriorated aquatic ecosystems [4]. In addition, environmental toxin such as microcystin would be produced in eutrophication process. The microcystin accumulated in the body of aquatic animals and transferred into human body led to hepatocellular carcinoma [5]. On the other hand, P element is necessary for human beings, and the lack of P will limit food production for our growing world population [6]. Besides, phosphate can also be used in other areas, such as photocatalysis [7], electrochemistry [8], and bioceramics [9]. Phosphorus as an un-renewable resource is estimated to be depleted in 50–100 years based on current global reserves [10]. So, P recycling from wastewater and reusing is important and urgent.

Various technologies have been developed for phosphate removal in wastewater treatment, mainly including enhanced biological phosphorous removal process (through the biomass growth of phosphate accumulating organisms), chemical precipitation, ion exchange, phosphate crystallization, and adsorption [11–15]. Among these technologies, adsorption may be the most promising process when taking P removal efficiency, operation convenience, P recycling, and reusing into consideration. Diverse adsorbents were tested for phosphate removal, such as peat [16], palygorskite [17], alunite [18], mussel shells [19], active red mud [20], ferric sludge [21], dolomite [22], and resin [23]. Although effective phosphate removals have been achieved, these adsorbents cannot be widely applied in practice due to their difficulties in separation from aqueous phase (powder materials, such as bentonite and red mud) or high cost (resin). Thus, some new, effective, and low-cost adsorbents are still necessary to be developed to solve the above mentioned problems.

Kanuma clay (K-clay), a kind of geomaterial abundant in Japan, is widely used in agriculture and horticulture. K-clay possesses some functional physical–chemical properties such as high permeability, water retention, and porous structure. The composition of K-clay mainly consists of metal oxides, such as SiO_2, Al_2O_3, Fe_2O_3, MgO, and CaO [24]. The metal oxides can be hydrolyzed into metal ions and hydroxyl in aqueous solution, which would enhance the inner-sphere ligand ion exchange for phosphate adsorption. Thus, K-clay seems to be an effective adsorbent for phosphate adsorption. However, little information could be found about its adsorption potential for phosphate removal and the regeneration after adsorption.

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In this study, a tablet porous material (TPM) was developed from K-clay, corn starch, and calcium oxide to remove phosphate. Its physical, chemical, and surface characteristics, isotherms model, and kinetic model were investigated. In addition, some influencing factors (such as dosage, pH, and temperature) and TPM regeneration were also discussed.

2. Materials and methods

2.1. Synthesis of tablet porous material

K-clay (bought from the Makino Store, Kiyosu, Japan) was manually smashed and sieved, and the particles less than 300 μm were selected and used in this study. Corn starch and CaO (analytical reagent) were supplied by Wako Pure Chemical industries Ltd., Japan.

The TPM was synthesized as the following chart (Fig. 1), and the developed TPM was cooled to room temperature and used in the following experiments.

2.2. Phosphate adsorption experiments

A stock solution of 50 mg L^{-1} phosphate was prepared by dissolving KH_2PO_4 (anhydrous, analytical grade) in deionized water. All the adsorption experiments were conducted more than triplicate in 50 mL test tubes in a thermostat (except the thermodynamics experiments); considering practical condition, all experiments were performed without shaking.

2.2.1. Isotherms experiment
A number of 0.2 g TPMs were added into test tubes, respectively, under initial phosphate concentrations range from 5 to 50 mg P L^{-1} and initial pH 7.0. Then, the test tubes were set in the thermostat (25 ± 1 °C).

2.2.2. Kinetic experiment
One gram TPM was individually dosed into test tubes containing 50 mL of 10 mg P L^{-1} phosphate solution. The sampling time intervals were 5, 10, 20, 30, 90, 120, and 180 min, respectively (initial pH 7.0, 25 ± 1 °C).

2.2.3. Effect of pH
Fifty milliliters of phosphate solutions (10 mg P L^{-1}) were added, respectively, in 11 test tubes with 1 g TPM dosed. 0.1 M HCl or NaOH was used to adjust the initial solution pH ranged from 2.0 to 12.0. All the test tubes were capped to avoid evaporation, and the pH values were determined after 2 h (25 ± 1 °C).
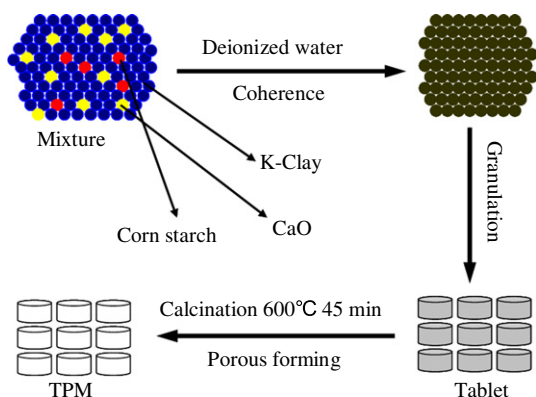
2.2.4. Thermodynamics and effect of temperature
The thermodynamics and influence of temperature on phosphate adsorption onto TPM were carried out at temperatures ranging from 288.15 to 308.15 K with an initial phosphate concentration between 5 and 20 mg L^{-1}. (initial pH 7.0, a fixed TPM dose of 4 g L^{-1}.)

2.2.5. Effect of dosage
Phosphate solution (20 mg P L^{-1}) was used for adsorption under different TPM dosage (initial pH 7.0, 25 ± 1 °C). The TPM dosage varied from 5 to 50 g L^{-1}.

2.3. TPM regeneration and phosphate recycling test

In this trial, 50 mg P L^{-1} of phosphate solution was used for TPM adsorption. After adsorption, the TPMs were collected and used for phosphate desorption. HCl (0.2 N and 0.5 N) and NaOH (0.1 N) were utilized to test the possibility of phosphate recycling and TPM regeneration.

2.4. Analytical methods

TPM was characterized by Energy Dispersive X-ray Spectroscopy and scanning electron microscope (SEM XL40 series philips, Holland) to obtain its physical, chemical, and surface characteristics; Brunauer–Emmett–Teller (BET) specific surface area was obtained by a analysis device (Coulter SA3100, US) using the He–N_2 method. All the equilibrium phosphate concentration was analyzed with the ascorbic acid method (4500-P E) [25].

3. Results and discussion

3.1. Characterization of TPM

Fig. 2a is the photo of pristine TPM (Φ7 mm, H2 mm); the SEM images of TPM adsorbents (before and after phosphate adsorption) are illustrated in Fig. 2b and c. The images obviously showed that porous texture and structure were widely developed at the surface of TPM; it might be molded during the incineration process in which corn starch would be burned off leaving porous structure in TPM. The result indicated TPM would naturally develop a comparatively larger specific surface area that plays a positive effect on adsorption sites in phosphate adsorption onto TPM. Furthermore, the surface feature of TPM after phosphate adsorption was different with raw TPM to a certain degree, assuming that metal-hydroxyl-phosphate ligand component [26] and phosphate-metal chemical precipitation [27] might bring about these morphological changes of TPM surface during phosphate adsorption.

The EDX result was shown in Fig. 2d, and the detailed composition of TPM was summarized in Table 1.

Clearly, TPM was mainly composed of metal oxides such as Al_2O_3, SiO_2, and CaO. Al_2O_3 was reported as a good adsorbent for phosphate by surface precipitation [28], and the added CaO in TPM could be transformed into calcium hydroxides in aqueous solution and supplied large amount of functional groups (Ca^{2+}, OH$^-$) to enhance the chemical precipitation and inner-sphere ligand exchange process.

The result of specific surface area of TPM and K-clay (Table 1) showed that BET surface area was 107.04 m^2 g^{-1} for raw K-clay and decreased to 15.401 m^2 g^{-1} for TPM, due to the fact that the particle size of raw K-clay lower than 300 μm while the diameter of TPM was about 7 mm. The specific surface area of TPM was similar with red mud, 14.09 m^2 g^{-1} [20] but lower than hydrotalcite, 44 m^2 g^{-1} [29]. In addition, the pore size distribution (Fig. 2e) indicated that TPM was a typical mesoporous material according to IUPAC classification [30]. The proportion of pore diameter in

Fig. 1. The procedure of TPM synthesis. Mass ratio of K-clay:corn starch:CaO was 4:0.5:1.