



## Adsorptive Removal of Phosphate by Calcined Kanuma Clay from Aqueous Solution

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### ABSTRACT

The phosphate removal capacity of Kanuma clay, an inexpensive and abundantly available in Japan, has been investigated. Kanuma clay was calcined at temperature of 600°C, and laboratory-scale batch experiments were conducted to evaluate the efficiency for phosphate removal from aqueous solution. The major factors of the removal process, such as adsorption isotherms, adsorption kinetics, temperature, pH and desorption were investigated. The results showed that calcined Kanuma clay was of capable in phosphate removal. The phosphate adsorption matched the Freundlich isotherms model well, and the process can be well described by pseudo-second-order kinetic model. The adsorption process was exothermic process which removal capacity decreased with the increase of temperature. The adsorption capacity was the best at pH value of 6, and the adsorbed phosphate on the calcined Kanuma clay could be hardly desorbed in normal pH condition. These results showed that calcined Kanuma clay processed great potential for phosphate removal from aqueous solution.

*Keywords:* Low cost; easy operation; eutrophication treatment; hydroxides; soils fertilization

### 1. INTRODUCTION

As well known, the majority of phosphorus used in living and production activities of human beings is finally discharged into natural water body through phosphorus cycle. The content of phosphorus was an important factor in water environment because of its importance as nutrient element in water environments. A large amount of phosphorus in water body is always responsible for eutrophication which caused by algal bloom (Gao et al., 2009; Jin et al., 2005; Xiong et al., 2011), that always happened in lakes, reservoirs and coastal areas. Eutrophication could easily cause several environmental damages which was hardly in controlling, such as esthetic problem (Peleka

and Deliyanni, 2009), dissolved oxygen decreasing and destroyed aquatic ecosystems led to death of aquatic animals (Biswas et al., 2007). The regulations limits of phosphors discharging were performed in many nations to prevent those problems.

In past decades, phosphorus removal from wastewater was widely developed: including chemical precipitation through  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  (Katz and Dosoretz, 2008), activated sludge through microorganism (Vaiopoulou et al., 2007), ion exchange (Liu et al., 2002) and crystallization as hydroxyapatite (HAP), magnesium ammonium phosphate (MAP) or brushite (DCPD) (Moreno and Varughese, 1981). Those methods achieved high efficiency of phosphorus removal, but still defects

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such as, high cost, low efficiency and complicated operation. On the contrary, adsorption method was increasingly utilized in many research of phosphorus removal because of its low cost and convenient operation. Diverse absorbents were used for phosphorus removal, such as, peat (Xiong and Mahmood, 2010), alunite (Özacar, 2003a), palygorskite (Ye et al., 2006), red mud (Liu et al., 2007), hydroxides (Das et al., 2006), smectites (Karageorgiou et al., 2007), dolomite (Karaca et al., 2006), ferric sludge (Song et al., 2011), etc.

Kanuma clay, a kind of inorganic soil (geomineral), was very abundant in Japan, which was widely used in agriculture and horticulture. Kanuma clay had functional physical and chemical abilities with high permeability, water retention ability and porous. It was rarely used for pollutant removal, especially for phosphorus controlling. Therefore, an attempt was performed to investigate the efficiency of phosphorus removal through Kanuma clay from polluted aqueous solutions. The adsorption isotherms, adsorption kinetics, effect of temperature on adsorption, effect of pH on adsorption, and desorption capacity were discussed in this study.

## 2. MATERIALS AND METHODS

### 2.1 Preparing of the phosphate absorbent

The absorbents used in present study were obtained from Kanuma city, Tochigi prefecture, Japan. It was manually smashed and sieved, the particles less than 300  $\mu\text{m}$  were selected. The samples were washed by distilled water for five times and calcined at temperature of 60°C. The obtained samples were modified through a calcination treatment at temperature of 600°C for 2 hours to form more metal oxide and porous (the flammable organics and cellulosic in Kanuma clay could be burned out and left more porous). The calcination could also remove most of organism and formed

more porous which could be functioned in adsorption process. The morphological structure of the dewatered Kanuma clay was examined by X-ray diffractometer (XRD, RINT2200, Rigaku, Japan) and scanning electron microscope (SEM, JSM-5600, JEOL, Japan); also, BET (Brunauer-Emmett-Teller) was analyzed by specific surface area analysis device (Coulter SA3100, US) using  $\text{N}_2$  method.

### 2.2 Adsorption isotherm experiments

Phosphate adsorption isotherms study was carried out. An amount of 1g prepared samples were put in a centrifuge tube (50mL) with series initial concentrations of phosphate (anhydrous  $\text{KH}_2\text{PO}_4$ , analytical grade). The concentrations were 0, 0.5, 1, 2, 5, 10, 15, 20, 30, 40 and 50 mg P/L, respectively. The centrifuge tubes were set in a thermostat at a temperature of  $25 \pm 1^\circ\text{C}$ . Centrifugations were performed after equilibrium at 5000 rpm for 5 min. Supernatant liquid was obtained for phosphate concentration analyzing. The adsorption isotherms could be calculated.

### 2.3 Kinetic experiments

Phosphate adsorption kinetics was measured in a thermostat at a temperature of  $25 \pm 1^\circ\text{C}$ . An amount of 1g samples were put into a series of centrifuge tubes with the concentration of 10 mg P/L phosphate solution (anhydrous  $\text{KH}_2\text{PO}_4$ , analytical grade) for 50 mL. The time intervals were 5, 10, 20, 30, 90, 120, 180, 300, 420, 600, 840, 1020, 1320 and 1440 min, respectively. Centrifugations were performed immediately each time, and supernatant liquids was obtained for phosphate concentration analyzing after centrifugation.

### 2.4 Effect of pH on phosphate adsorption

Twenty mL phosphate solutions (10 mg P/L anhydrous  $\text{KH}_2\text{PO}_4$ , analytical grade) were added in 12 centrifuge tubes in a thermostat at

a temperature of  $25 \pm 1^\circ\text{C}$ , and 1 g of calcined Kanuma clay was added respectively. Different amount of 0.1 M HCl and NaOH were used to adjust pH value range from 2 to 12, all the centrifuge tubes were capped to avoid evaporation, the pH value were determined after 24 h.

### 2.5 Effect of temperature on phosphate adsorption

The effect of temperature on phosphate adsorption was investigated at fixed amount of adsorbent and initial concentration of 10 mg P/L. An amount of 1g samples were added in centrifuge tubes with 50 mL phosphate solution. The pH of the suspension was adjusted to 6. The centrifuge tubes with the content were capped and set in a temperature thermostat at different temperature (5, 25 and  $35^\circ\text{C}$ ). At the end of 24 h treatment time, centrifugations were performed after equilibrium at 5000 rpm for 5 minutes. Supernatant liquids were obtained and filtered through a  $0.45\mu\text{m}$  membrane filter for phosphate concentration analyzing.

### 2.6 Desorption studies

The desorption studies of Kanuma clay on phosphate adsorption were also investigated. An amount of 1g prepared samples were put in a centrifuge tube (50mL) with series initial concentrations of phosphate (anhydrous  $\text{KH}_2\text{PO}_4$ , analytical grade). The concentrations were 1, 2, 5, 10 and 15 mg P/L, respectively. The centrifuge tubes were set in a thermostat at a temperature of  $25 \pm 1^\circ\text{C}$ . The equilibrium concentration of phosphate adsorption were determined after 24 h, the adsorbent used was filtered and dried for 2 hours at  $60^\circ\text{C}$ , and added into 5 centrifuge tubes with 50mL distilled water/0.1 M NaOH solution, respectively. All the centrifuge tubes were shaken at 200 rpm in a temperature controlled orbital shaker to enhance reaction equilibrium at room tempera-

ture of  $25 \pm 1^\circ\text{C}$ . The equilibrium concentration of phosphate desorption were determined after 24 h, centrifugation also executed before concentration analyzing.

## 3. RESULTS AND DISCUSSION

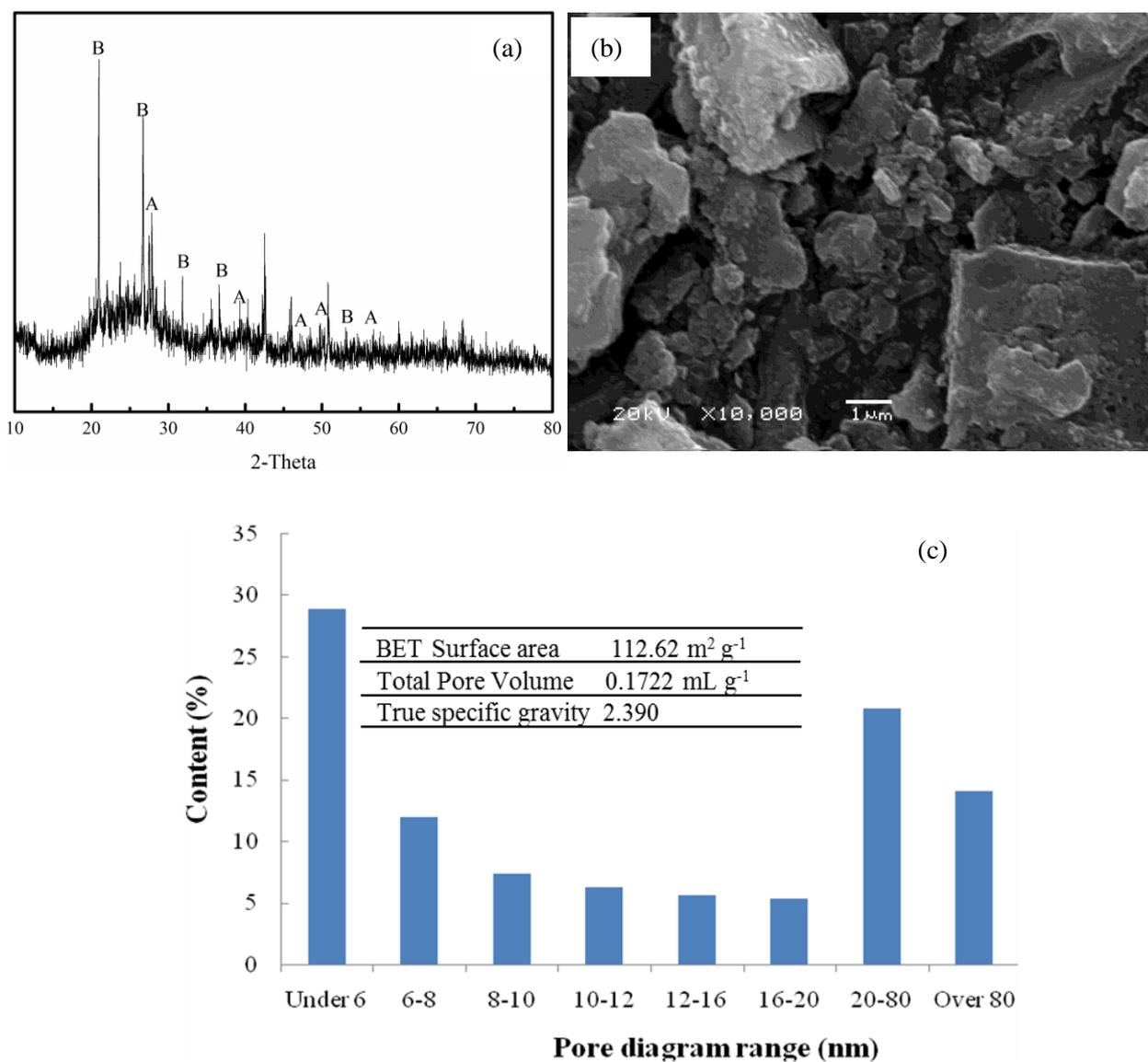
### 3.1 XRD and SEM analysis of Kanuma clay adsorbent

The reflections of XRD spectrums (Fig.1a) were complex and overlapped for some of them because of the complex component in calcined Kanuma clay. The XRD patterns were strong with distinct reflections, implying a higher crystallinity degree of majority content. According to the XRD data analyzing, the curve described above might be defined as boehmite (JCPDS74-1895) and goethite (JCPDS 81-0463). The majority products would be metal oxide (divalent and trivalent).

The scanning electron microscope (SEM) observation of calcined Kanuma clay adsorbents (Fig.1b) clearly revealed a fragmented and porous surface texture, which indicated the adsorbent was highly porous with larger specific surface area which would play a positive effect on adsorption sites by phosphate adsorption process on calcined Kanuma clay; The pore-size distribution and specific surface area (Fig.1c) of calcined Kanuma clay further confirmed its porous nature. The specific surface area of calcined Kanuma clay was largely higher than similar materials, such as fly ash, slag, red mud with the value of 0.66, 1.11,  $14.09\text{ m}^2/\text{g}$  (Agyei et al., 2000; Liu et al., 2007), respectively; and also a little higher than that of raw Kanuma mud with the value of  $107.04\text{ m}^2/\text{g}$ . This might be caused by the high temperature calcination that flammable substance, such as organisms/cellulosic was burned and left a large amount of pore which enhanced the specific surface area, but still a great gap exists when it was compared with activated carbon with a huge specific surface area of  $880.65$

m<sup>2</sup>/g (Wang et al., 2014), although a lower specific surface area showed in Kanuma clay, but the functional groups (hydroxyl) were richer in Kanuma clay than that of activated carbon. Thus, Kanuma clay could also be used for phosphate removal even it kept a low spe-

cific surface area. Fig. 1c exhibited that the majority pore diameter in Kanuma clay was ranged from 2 to 50nm, thus according to IUPAC classification, calcined Kanuma clay is a typical mesoporous material (Rouqu  rol et al., 1994).



**Figure 1** (a) Scanning electron microscope micrographs of calcined Kanuma clay adsorbents: 20kV, x1000; (b) XRD spectrums patterns of Kanuma Clay: A: goethite; B: boehmite; (c) Pore size distribution (nm)

### 3.2 Adsorption isotherm

The equilibrium uptake capacity of phosphate  $q_e$  (mg/g) was calculated by following equation (1):

$$q_e = \frac{(C_i - C_e) \times V}{1000w} \quad (1)$$

Where  $C_i$  and  $C_e$  are the initial and equilibrium phosphate concentrations (mg/L),  $V$  is the volume of phosphate solution (mL),  $w$  is the mass of adsorbent (g), respectively.

The following two models (Langmuir (2) and Freundlich (3) isotherms) were used to describe the adsorption isotherm of phosphate on the sediments, the linear forms of the Langmuir isotherm and the Freundlich isotherm can be presented by:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \frac{1}{C_e} \quad (2)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

Where  $q_e$  is equilibrium phosphate concentration on adsorbent (mg/g),  $C_e$  is equilibrium phosphate concentration in solution (mg/L),  $Q$  is monolayer capacity of the adsorbent (mg/g),  $b$  is adsorption constant,  $K_f$  (mg/g) is the Freundlich constant, and  $n$  (dimensionless) is the Freundlich exponent. While Langmuir isotherm parameters  $Q$  and  $b$  could be obtained by plotting  $(1/q_e)/(1/C_e)$ , Freundlich isotherm parameters could be obtained by plotting  $\log q_e/\log C_e$ .

The Langmuir and the Freundlich isotherm equation were often used to demonstrate the monolayer and complicated adsorbents process. From a comparison of isotherm constant and  $R^2$  value, the Freundlich isotherm model matching plots with determination coefficient  $R^2$  0.961 was better than the Langmuir isotherms model. This result suggests that the phosphate adsorption through calcined Kanuma clay was a complicated adsorption process with a diverse energetic distribution of

adsorption sites and with interaction between adsorbed mass, or alternatively a heterogeneous mixture of several minerals in calcined-Kanuma clay had different affinities for Phosphate. The comparison of  $Q$  values between Kanuma clay and other materials were summarized (Table 1). The phosphate adsorption capacity of Kanuma clay was comparatively higher than most of other adsorbents, Therefore, calcined Kanuma clay exhibited the potential capability for phosphate adsorption from aqueous solution.

### 3.3 Adsorption kinetics

In order to determine the rate constant for adsorption, the pseudo-first-order (4) and pseudo-second-order kinetic model (5) had been used, which can be described by following equations:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (4)$$

Where  $q_e$  and  $q_t$  are the adsorption capacities at equilibrium, and time  $t$  (mg/g), respectively.  $k_1/\text{min}$  is the rate constant for the pseudo-first-order adsorption.  $k_1$  and  $q_e$  are determined from the slope and intercept of the straight line of  $\log(q_e - q_t)/t$ , respectively.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (5)$$

Where  $q_e$  is the equilibrium loading capacity (mg/g) for the pseudo-second-order adsorption,  $k_2$  is the equilibrium rate constant of pseudo-second-order adsorption (g/mg/min). The values of  $k_2$  and  $q_e$  are calculated from a plot of  $(t/q_t)/t$ .

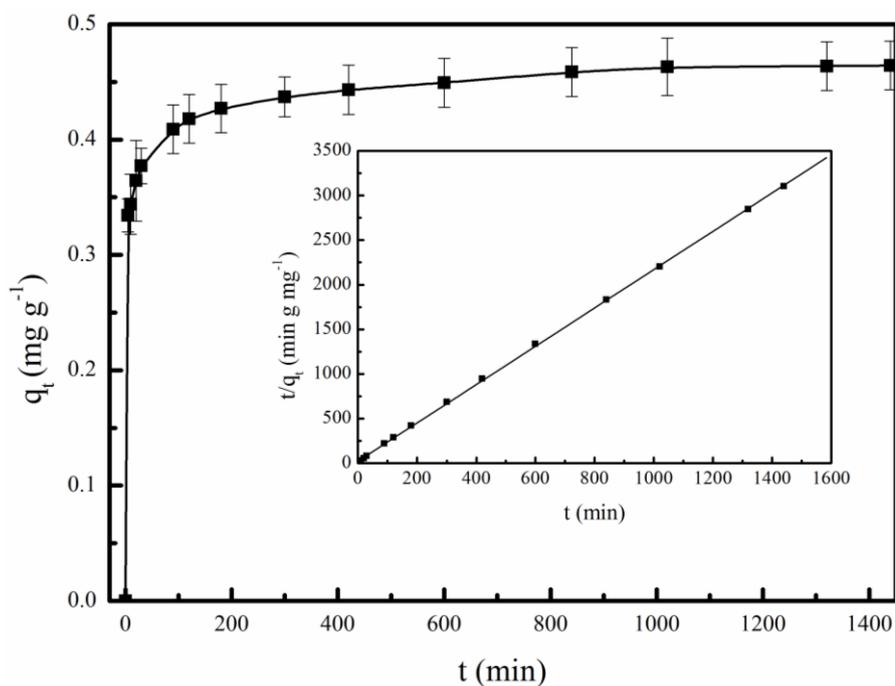
According to the kinetic experiment, the phosphate adsorption on calcined Kanuma clay consisted of two phases of which named as phase I and phase II (Fig.2). The phase I was finished in preliminary 180 min and about 92.02% of adsorption equilibrium was completed in this phase. The phosphate was rapidly

adsorbed until 180 min maybe fitted with the large concentration phosphate gradient and vacant adsorption function sites. On the other hand, the phase II could be extended over 17 hours until the phosphate adsorption to equilibrium, the phase II might be driven by the inner diffusion adsorption of the calcined Kanuma clay and to the possibility of chemical precipitation reaction with metal component in Kanuma clay, such as Fe, Al, Ca, etc.(Huang,

2004; Özacar, 2003b; Xiong and Mahmood, 2010; Zhao et al., 2011).The process kinetic was fitted to the pseudo-first-order and pseudo-second-order model, the results showed that the adsorption process could be more described by the pseudo-second-order model with the correlated coefficient of 0.9992. The maximum adsorption capacity in this condition was 0.4642 mg/g.

**Table 1** Comparison of adsorption capacity with other adsorbents.

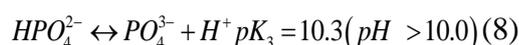
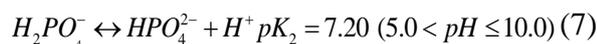
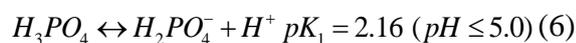
Adsorbent	Q(mg/g)	Source
Na-natural zeolite	2.19	Wu et al., (2006)
Steel furnace slag	1.43	Xiong et al., (2008)
Goethite	6.42	Borggaard et al., (2004)
Red mud	0.58	Huang et al., (2008)
Kanuma clay	2.24	This study



**Figure 2** Effect of contact time and pseudo-second-order kinetic model

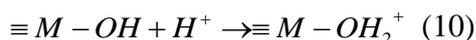
### 3.4 Effect of pH on phosphate adsorption

Phosphate dissociation equilibrium in aqueous solution is pH-dependent, which can be presented as (Haghsresht et al., 2009):

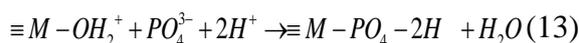
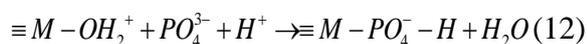
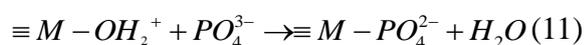


The phosphate adsorption by calcined Kanuma clay could be profoundly affected by the change of pH value. The best removal efficiency of phosphate was found at pH value of 6 (Fig. 3) when calcined Kanuma clay was used as adsorbent. The phosphate uptake decreased sharply with the increasing of pH value, especially at pH of 12. On the other hand, the phosphate uptake also decreased slowly with the decreasing of pH value. Fe and Al presented as oxides and hydroxides that fixed to the silicate were significantly contained in calcined Kanuma clay. Phosphate is usually considered to be removed through an inner-sphere ligand exchange mechanism (Collins et al., 1999). Considering that different phosphate species dominated in different pH solutions, the following reactions may be included in phosphate removal through calcined Kanuma mud adsorption:

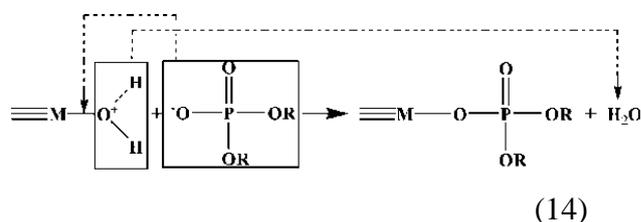
Surface hydroxyl deprotonation and protonation (Zhang et al., 2007):



Phosphate-hydroxyl monodentate and protonation of adsorbed phosphate:



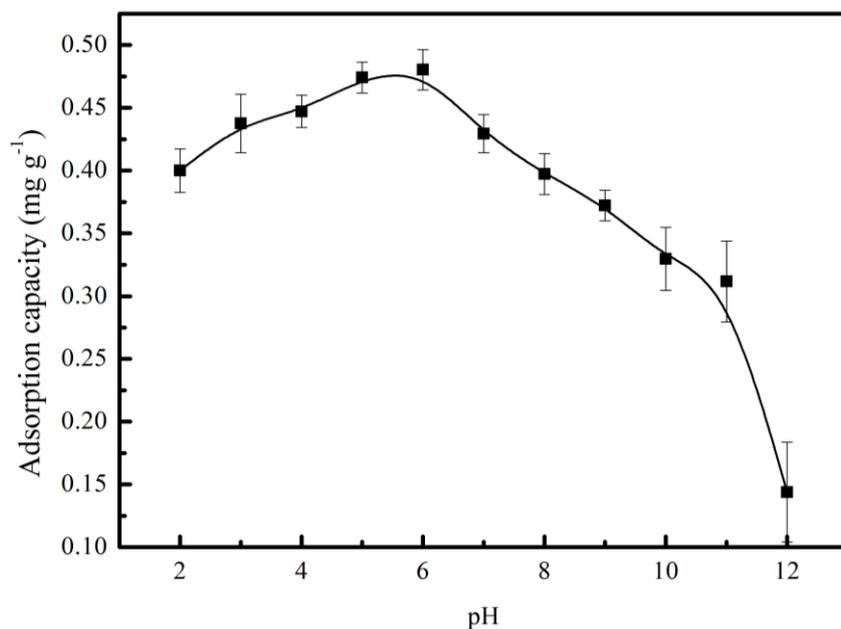
The overall reaction could be expressed as:



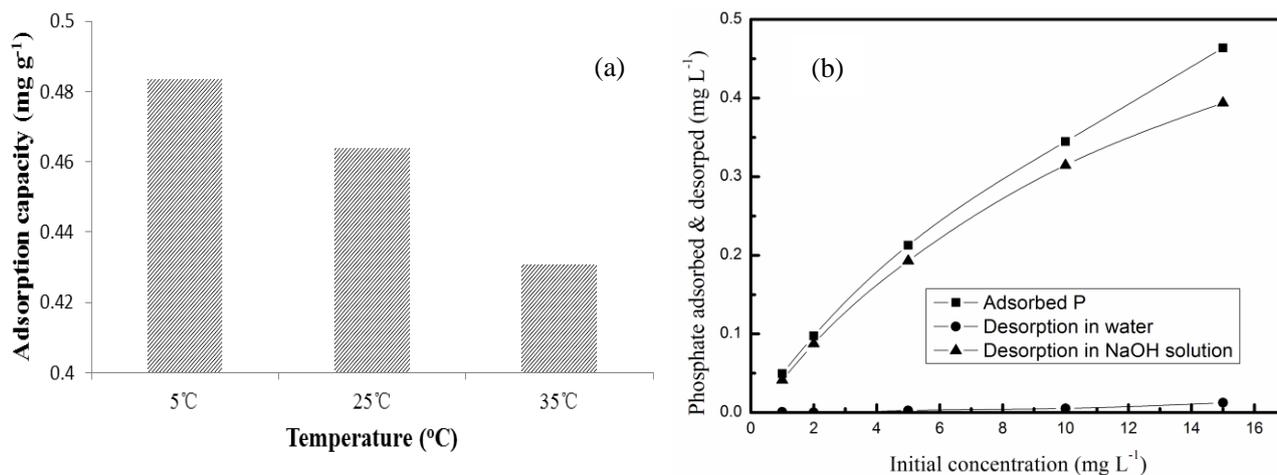
Where M is metal component, such as Al, Fe, Ca, etc.

In suitable pH, protonation executed on the metal oxide and supplied sufficient adsorption sites (Eq. 10). While pH value decreased, phosphate distribution was  $H_2PO_4^-$  and  $HPO_4^{2-}$  (Eq. 6 and 7), the phosphate could be removed through Eq. 12 and Eq. 13, and with the pH continuously decrease, the metal oxides/hydroxides became unstable and started to dissolve which led to the number decreasing of adsorption sites for phosphate adsorption. While pH value increased, the phosphate distribution was  $HPO_4^{2-}$  and  $PO_4^{3-}$  (Eq. 8), the phosphate would be absorbed through reaction which described by Eq. 11 and Eq. 12. With the increase of pH, the huge amount of  $OH^-$  caused deprotonation of oxide/hydroxides, that may destroy the hydroxyl groups (Eq. 9), and the materials would carry more negative electric charge, it caused phosphate releasing and decreasing of phosphate adsorption due to the electrostatic repulsion; moreover, high pH decreased the adsorption capacity of phosphate on the adsorbent surface because of their competition adsorption with  $OH^-$  ions was likely to play an important role.

The results were similar to the result by Özacar (2003b) that maximum phosphate adsorption occurred at pH 5 using alunite, and also similar to results of Xiong and Mahmood (2010) that maximum phosphate adsorption occurred at pH 6.5 and the adsorption amount decreased with either decreasing or increasing pH using peat as a phosphate adsorbent.



**Figure 3** Effect of pH on phosphate adsorption



**Figure 4(a)** The effect of temperature on phosphate adsorption; (b) The results of desorption

### 3.5 Effect of temperature on phosphate adsorption

The effect of temperature on phosphate adsorption was investigated (Fig.4). The phosphate adsorption in aqueous solution increased with the decreasing of temperature by Kanuma clay, especially in higher temperature.

The adsorption capacity was 0.4308 mg/g at

35°C and increased to 0.4638 mg/g at 25°C, 0.4836 mg/g at 5°C, respectively. These results agreed with the reports on phosphate adsorption by peat (Xiong and Mahmood, 2010) and fly ash (Ugurlu and Salman, 1998); but opposite with the results of Zamparaset al. (2012) by bentonites, the adsorption capacity of bentonites decreased with the decreasing of temperature, indicated that the adsorption reaction

was of endothermic nature and the ion-exchange mechanism was favored at higher temperatures. Likewise, the process of phosphate adsorption by Kanuma clay was an exothermic process of which decreasing of temperature enhance the phosphate uptake.

### 3.6 Desorption study

The phosphate desorption experiments were performed with 5 initial phosphate concentrations (1, 2, 5, 10 and 15 mg/L) at pH value of 6 and room temperature. The used Kanuma clay was soaked in water to investigate the desorption capacity in neutral pH condition. The results showed that adsorbed phosphate by calcined Kanuma clay could be hardly desorbed in neutral pH condition (Fig.4b). However, the desorption of adsorbed phosphate was necessary in some cases for phosphorus resources reclamation. Thus, 0.5 mol/L NaOH solutions was utilized as eluent to figure out that whether adsorbed phosphate could be desorbed; the results were also shown in Fig. 4b. It showed that adsorbed phosphate could be well desorbed by NaOH solution. Over 89.02% of adsorbed phosphate was desorbed. The NaOH solution was rich in phosphate which could reclaim phosphorus by other method, such as distillation and crystallization (Song et al., 2006).

Therefore, calcined Kanuma clay was a suitable adsorbent for phosphate removal. The phosphorus could also be reclaimed by using NaOH as eluent. In addition, no further treatment was required for the phosphate adsorbed Kanuma clay, considering the widely using in agriculture and horticulture; it could be reused as a fertilizer (Karageorgiou et al., 2007).

## CONCLUSIONS

According to this study, the calcined Kanuma clay exhibited great phosphate adsorption ability. The adsorption process consisted of a fast and a slow process, the former finished in 180 min and the latter extended to 24 h even more. The Freundlich isotherm model and pseudo-second-order model can well describe the adsorption process. The phosphate adsorption efficiency mainly depended on pH and temperature, which adsorption amount was the best at pH of 6 and comparatively low temperature can enhance the adsorption efficiency; adsorbed phosphate could be hardly desorbed when solution pH was in neutral condition, and more than 89.02% of phosphate could be reclaimed when 0.1 M NaOH solution was used as eluent. The phosphate was removed through anion-exchange ion exchange mechanism. Besides, the calcined Kanuma clay which adsorbed phosphate is friendly to the environment, there is no need further treatment for phosphate adsorbed Kanuma clay, and the adsorbed adsorbent can be reused as soils fertilization.

## ACKNOWLEDGEMENTS

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