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Adsorption kinetics and isotherms of phosphate and its removal from wastewater using mesoporous titanium oxide

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Abstract. The adsorption of phosphate onto mesoporous TiO_2 was investigated in order to reduce phosphorus concentrations in wastewater and provide a potential mode of phosphorus recovery. Three equilibrium isotherms were used to optimize and properly describe phosphate adsorption (R^2>0.95). The maximum capacity of phosphate on the adsorbent was found to be 50.4 mg/g, which indicated that mesoporous TiO_2 could be an alternative to mesoporous ZrO_2 as an adsorbent. A pseudo-second order model was appropriately fitted with experimental data (R^2>0.93). Furthermore, the suitable pH for phosphate removal by TiO_2 was observed to be in the range of pH 3-7 in accordance with ion dissociation. In contrast, increasing the pH to produce more basic conditions noticeably disturbed the adsorption process. Moreover, the kinetics of the conducted temperature study revealed that phosphate adsorption onto the TiO_2 adsorbent is an exothermic process that could have spontaneously occurred and resulted in a higher randomness of the system. In this study, the maximum adsorption using real wastewater was observed at 30℃.

Keywords: equilibrium isotherm; kinetics; mesoporous TiO_2 adsorbent; phosphate adsorption; wastewater

1. Introduction

Phosphates are crucial for all living creatures and are extensively used in industry and agriculture (Ozacar 2006). However, phosphorus is a resource that is nonrenewable and irreplaceable. Therefore, the recover and reuse of this limited resource is a priority for sustainable development (Cheng *et al.* 2009). Phosphorus is found in natural waters and wastewaters owing to human activities, such as industrial, domestic, and agricultural activities, that continuously increase the amount of phosphorus in these bodies of water (Henry and Heinke 1989). A phosphorus concentration increase to more than 0.1 mg/L may cause eutrophication (Henry and Heinke 1989), in which excessive growth of organisms, such as algae, reduces the soluble oxygen concentration in waters and has a detrimental effect on aquatic life (Genz *et al.* 2004). Therefore, it

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is important not only to address the recovery of phosphorus, but also its removal from wastewater (Ebie *et al*. 2008).

Phosphorus removal by chemical means has been a considerable concern since the late 1960s (Onar *et al.* 1996). However, it is difficult to recover phosphate, as opposed to removal, using these processes as some of them also produce excess amounts of sludge, which require subsequent disposal (Urano and Tachikawa 1991, Ratanatamskul *et al.* 2012). Adsorption is an alternative technology that appears to be more technically and economically feasible for such recovery operations as well as for ultra-high removal. Metals, such as iron, aluminum, calcium, manganese, lanthanum, and zirconium, have been used to study the adsorption of phosphate onto their oxides and/or hydroxides (Chitrakar *et al*. 2006, Cheng *et al.* 2009).

For adsorption, the use of highly porous material is more effective because of ion exchange that occurs on the surface of the materials. A mesoporous material containing pores with diameters between 2 and 50 nm have shown their utility as high capacity adsorbent materials (Choi *et al.* 2012). Mesoporous structures have been synthesized using surfactant micelles as a template, thereby resulting in these structures having high surface areas and definite pore size distribution (Davis 2002, Stein 2003, Jutidamrongphan *et al.* 2012). The advantages of adsorption using mesoporous materials over those of other technologies, i.e., coagulation or chemical precipitation, are that additional sludge is not produced, additional reagents to overcome high alkalinity are not required, and the pH of the discharged wastewater is unaffected (Urano and Tachikawa 1991, Choi *et al.* 2012). As phosphate adsorbents, zirconium-based mesostructured materials have been broadly studied (Iwamoto *et al.* 2002, Lee *et al.* 2007). However, the selection of an appropriate adsorbent should be carefully considered; the economic feasibility of these absorbents has not been fully verified because of the high cost of zirconium. Therefore, various low-cost materials have also been investigated in several studies to reduce the production costs of zirconium-based mesostructured materials (Falcaro *et al*. 2004, Naidich 2000, Choi *et al.* 2012). Titanium-based mesostructures have received attention in terms of their heterogeneous reactions, which are facilitated by the support of reagents on various solid inorganic surfaces (Esumi *et al.* 1998). Mesoporous TiO_2 has been found to be effective in arsenic removal (Haron *et al.* 2006) but has hardly been used for the removal of phosphate.

Hence, in the present study, mesoporous TiO_2 was reviewed and selected as an interesting alternative adsorbent for phosphate. This work focused on the equilibrium isotherm and adsorption kinetics of phosphate onto TiO_2 adsorbent. The influences of pH and temperature on phosphate removal from wastewater were evaluated with the aim of utilizing this technology in practical applications.

2. Materials and methods

The mesoporous TiO_2 adsorbent is a new material and was synthesized by the following procedure. Titanium (IV) isopropoxide (11.76 g) and 2,4-pentanedione (4.14) were used as the titanium precursor. Four grams of the triblock copolymer (as a surfactant) was dissolved in 100 mL of distilled water at 40℃. After the surfactant had been dissolved sufficiently, 1.5 g of sulfuric acid was added. The dissolved surfactant was mixed dropwise with the prepared titanium precursor. For hydrothermal treatment, the reaction was carried out at 100℃ for 24 h without stirring. After the reaction was finished, the precipitate mixtures were washed three times with ethanol and distilled water remove excess surfactant. Calcination of mesoporous TiO_2 was carried out to remove the surfactant at 550℃ for 6 h.

All reagents used in this study were of analytical grade. KH_2PO_4 was used to prepare a standard phosphate stock solution. All of the adsorption studies were carried out using a batch method at an initial pH of 6.5-7.5. An adsorption experiment was conducted in a shaking incubator (JSSI-100C, JS Research Inc., South Korea) under specific conditions. For the equilibrium test, a mass of 0.02 g of the adsorbent was used with 50 mL of KH_2PO_4 solution. For the kinetic study, a mass of 0.1 g of the adsorbent was added to 250 mL of KH_2PO_4 solution in 300-mL flasks. The flasks were shaken for 24 h with the amount of phosphate adsorbed at equilibrium, q_e (mg/g), calculated as follows

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q_e (mg/g) is the amount of phosphate adsorbed onto the adsorbent at equilibrium, C_o (mg/L) is the initial phosphate concentration, C_e (mg/L) is the phosphate concentration at equilibrium, V is the volume of the solution (L), and W is the weight of adsorbent (g).

The phosphate adsorption characteristics were evaluated with the use of equilibrium isotherms and kinetics, including the influence of pH and temperature, which were investigated in batch experiments. Equilibrium isotherms are able to reveal adsorption capacities via several models. In this study, two- and three-parameter models were applied to predict adsorption characteristics.

Secondary wastewater used in this experiment was collected from the aeration tank of an animal wastewater treatment plant in Hongseong, South Korea. The initial phosphate concentration of the raw wastewater was in the range of 17-25 mg/L. For use in this experiment, wastewater was diluted 2.5 times to maintain a phosphate concentration $\leq$10 mg/L. The concentration of phosphate was determined using the ascorbic method (APHA, 2005) via UV/VIS spectrophotometry (Smart Plus SP 1900, Young Woo Inst., South Korea) at a wavelength, λ, of 880 nm.

3. Results and discussion

3.1 Adsorption isotherms

The adsorption isotherms of phosphate ions onto the new mesoporous TiO_2 adsorbent were analyzed by two two-parameter equilibrium adsorption models (Freundlich and Langmuir models) and a three-parameter model (Langmuir-Freundlich combination model). The determined model parameters are summarized in Table 1. Phosphate adsorption onto the adsorbent was relatively well explained by all models tested, though the three-parameter model could best describe the

Table 1 Equilibrium isotherm parameters

Freundlich model ($q_e=KC_e^{1/n}$)	K 3.018	$1/n$ 0.482		R^2 0.989
Langmuir model ($q_e=q_m bC_e/(1+bC_e)$)	q_m (mg/g) 50.434	b (g/mg) 0.0136		R^2 0.959
Langmuir-Freundlich model ($q_e=q_m bC_e^{1/n}/(1+bC_e^{1/n})$)	q_m (mg/g) 322.58	b (g/mg)$^{1/n}$ 0.0102	$1/n$ 0.483	R^2 0.995

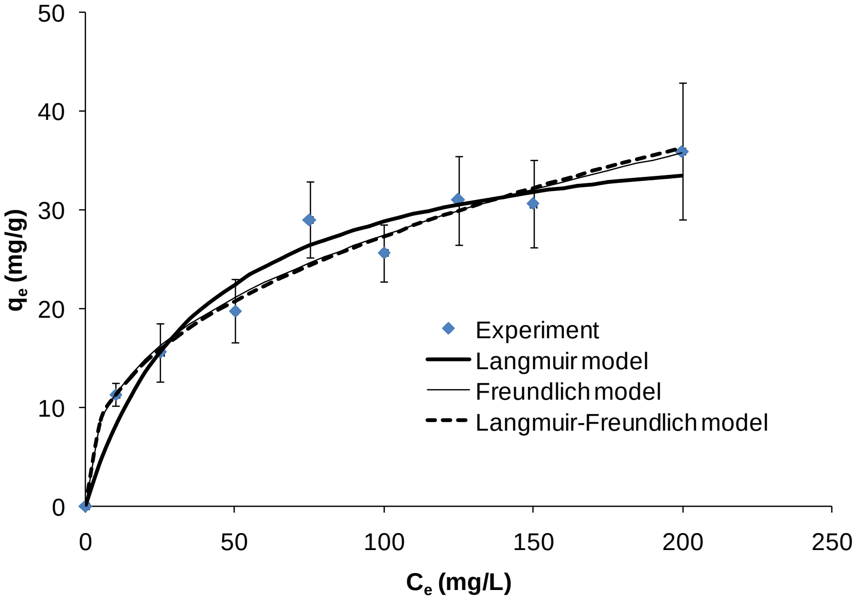

Fig. 1 Phosphate adsorption onto mesoporous TiO_2

Table 2 Comparison of the phosphate adsorption capacity

Adsorbent	Optimum pH	Removal capacity (q_m, mg/g)	Reference
Activated alumina	5.5	13.80	Genz *et al.* (2004)
Hydrotalcite	6.9	47.30	Kuzawa *et al.* (2006)
Iron oxide tailings	6.6	8.00	Zeng *et al.* (2004)
Amorphous ZrOH	6.0	17.00	Chitrakar *et al.* (2006)
Mesoporous ZrO_2	10.0	29.7	Liu *et al.* (2008)
Mesoporous TiO_2	3.0-7.0	50.4	This study

experimental data (R^2=0.995; Fig. 1). The two-parameter model equations (Freundlich and Langmuir models) have been more practically used compared to the three-parameter equations of the Langmuir-Freundlich combination model owing to the complexities inherent in models involving more parameters (Peleka and Deliyanni 2009).

The maximum capacity of the Langmuir model was 50.4 mg/g; this value was significantly higher than those found by Zeng *et al.* (2004) who observed an iron oxide tailing when natural adsorbents were used. It should also be noted that mesoporous TiO_2 had a higher phosphate adsorption capacity than mesoporous ZrO_2. Table 2 summarizes the adsorption characteristics of the adsorbents compared to several other natural oxides and developed adsorbents.

3.2 Adsorption kinetics

To investigate the adsorption mechanism and the rate-controlling steps, the adsorption kinetics were also evaluated. In the kinetics experiment, concentration changes of the phosphate ions were

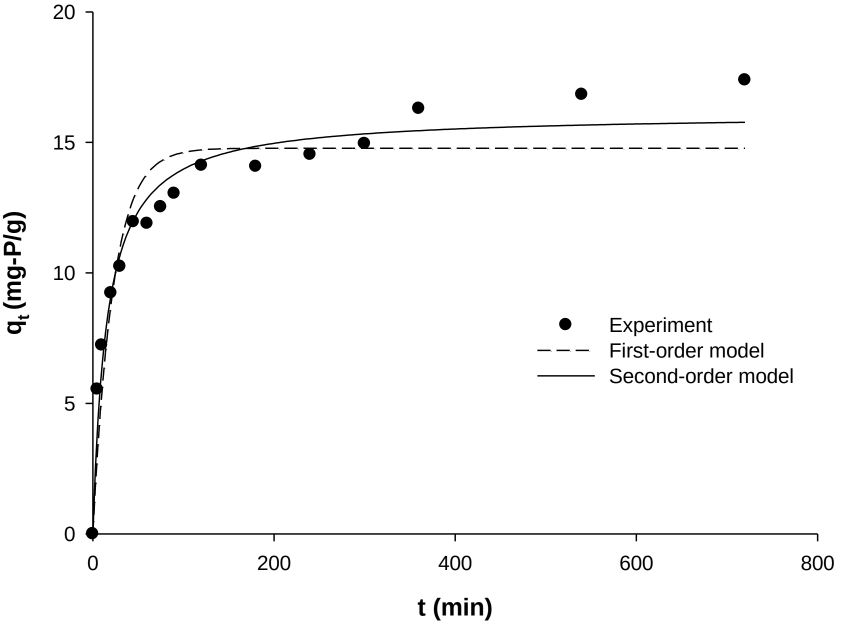

Fig. 2 Plot of kinetic adsorption of phosphate onto TiO_2 adsorbent

Table 3 The kinetic parameters of phosphate adsorption on mesoporous TiO_2 adsorbent

$q_{e, exp}$ (mg/g)	First-order equation			Second-order equation		
	$q_{e, 1st}$ (mg/g)	k_1 (1/min)	R^2	$q_{e, 2nd}$ (mg/g)	k_2 (g/mg·min)	R^2
20.44	15.53	0.086	0.840	16.96	0.0031	0.927

measured during the adsorption period. The adsorption reactions were completed within 100 minutes under the stated experimental conditions. To determine the kinetic parameters, two common models were used to fit the experimental results, which were formulated as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where q_e (mg/g) is the amount of phosphate adsorbed at equilibrium, q_t (mg/g) is the amount of phosphate absorbed at time t, k_1 is the rate of absorption, and k_2 is the rate constant of the second-order adsorption kinetics.

The kinetic parameters were calculated by non-linear regression, using SigmaPlot software, as shown in Fig. 2 and Table 3. Kinetic data showed that the adsorption process could reach equilibrium in a short time span, and the first- and second-order equations applied had better agreement with the experimental data for adsorption. The maximum adsorption of approximately 17 mg/g could be attained at a rate of 0.0031 g/mg·min. The pseudo second-order model was favored as it had a high correlation coefficient ($R^2 \cong 0.93$) and has been recommended by several previous works.

3.3 Effect of pH on adsorption

The effect of pH on phosphate adsorption from secondary wastewater of an animal wastewater treatment plant was investigated to use this technology in practical applications. Normally, the pH of a solution plays an important role in the physicochemical reaction at the water-solid surface (Cheng *et al.* 2009). Theoretically, phosphate dissociation equilibria in liquid are pH-related and could be represented as (Perrin and Dempsey 1974)

$$H_3PO_4 \overset{K_1}{\leftrightarrow} H_2PO_4{}^- + H^+ \overset{K_2}{\leftrightarrow} HPO_4{}^{2-} + 2H^+ \overset{K_3}{\leftrightarrow} PO_4{}^{3-} + 3H^+ \tag{4}$$

where pK_1=2.15, pK_2=7.20, and pK_3=12.33. Likewise, the surface charge state of TiO_2 also depends on pH conditions. The isoelectric point of TiO_2 has been defined as a pH of approximately 6.5 (Haron *et al.* 2006). Therefore, the surface hydroxyl groups of TiO_2 exists in the forms of $TiOH^+$ and TiO^- in acidic and basic conditions, respectively (Lee *et al.* 2003). From the Freundlich equation, the value of n was calculated and found to be 2.1. The n value is associated with the surface heterogeneity and sorption capacity of the adsorbent (Mustafa *et al.* 2006). As the n value was in the range of 1-10, it implies that the adsorbent performed well. Moreover, n refers to the stoichiometry of the sorption reaction. The reaction might possibly take place as the following (Mustafa *et al.* 2006)

$$TiOH^+ + H^+ \Leftrightarrow TiOH_2{}^+ \tag{5}$$

$$TiOH_2{}^+ + \frac{1}{n}P^{-n} \Leftrightarrow TiOH_2{}^+ + \ldots\frac{1}{n}P^{-n} \tag{6}$$

In acidic conditions, both $H_2PO_4^-$ and HPO_4^{2-} were competently adsorbed onto the solid. Furthermore, it was believed that $TiOH_2^+$ preferred to react with the doubly charged HPO_4^{2-} rather than the singly charged $H_2PO_4^-$. In contrast, even $TiOH^+$ reacted with the triply charged PO_4^{3-}

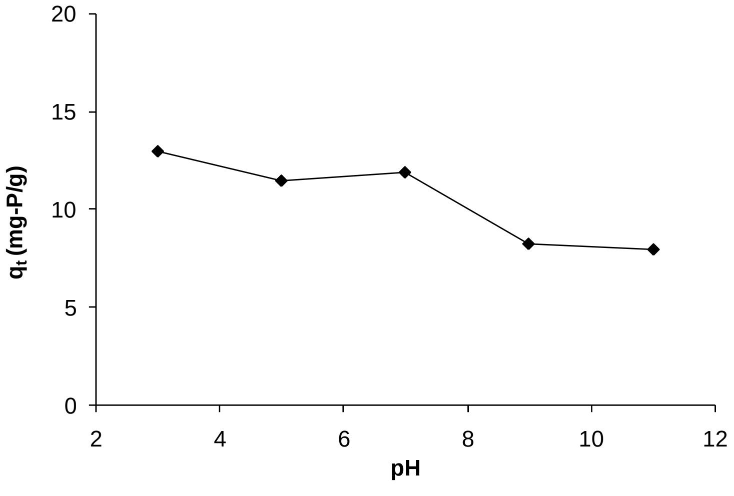

Fig. 3 The effect of pH on adsorption

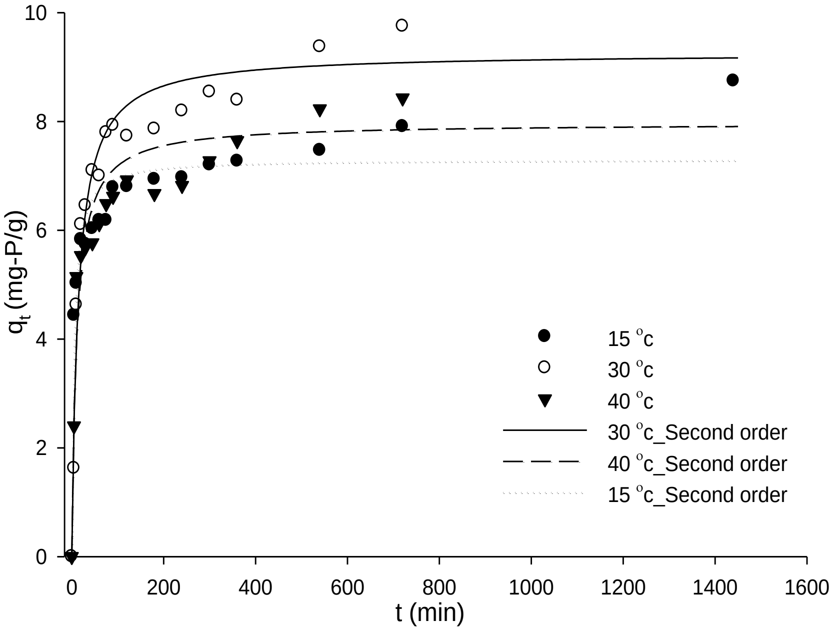

Fig. 4 The influence of temperature on phosphate adsorption onto TiO_2 adsorbent

properly; however, in basic conditions, some dissociated TiO^- disturbed the ion exchange reaction and resulted in lower sorption as shown in Fig. 3. The primary explanation for sorption reduction under strong basic conditions has focused on hydroxyl formation and not electrostatic repulsion (Lee *et al.* 2003). Additionally, in fact, salts of $H_2PO_4^-$ and HPO_4^{2-} may be crystallized from solution by adjusting the pH to approximately 5.5 and 10, respectively. This supposition elucidated that the concentrations of the two ions reached a maximum at pH 5.5 and 10, thereby impacting the decreased adsorption (Fig. 3). Although the phosphate adsorption showed a pH dependency, the mesoporous TiO_2 adsorbent was obviously effective for the removal of phosphate ions in the pH range of 3.0-7.0. The maximum phosphate adsorption was at pH 3.0.

3.4 Effect of temperature

Generally temperature is counted by an important factor of adsorption because it affects mass transport process at liquid-solid interfaces. Different temperatures (15, 30, and 40 °C) were tested to investigate effect of temperature on adsorption of phosphate from secondary wastewater from an animal wastewater treatment plant onto TiO_2 adsorbent (Figure 4). Estimated kinetic parameters were compared at each temperature. The adsorption kinetics implied that phosphate removal by TiO_2 adsorbent was an exothermic process that could spontaneously occur and result in higher randomness of the system.

Phosphate adsorption by TiO_2 adsorbent may be a result of both physical and chemical sorption. High temperature was favorable for phosphate adsorption owing to endothermic process (Liu *et al.* 2011). Adsorption curves fitted with the pseudo-second order model (R^2>0.92) revealed that the ambient temperature was appropriate for kinetic adsorption. Notably in this study, ambient temperature (30°C) showed the best kinetic adsorption and reached 10.6 mg/g. Additionally, it was

Table 4 Effect of temperature on the kinetic parameters

Temperature (℃)	$q_{e,\,exp}$ (mg/g)	$q_{e,\,2\mathrm{nd}}$ (mg/g)	$k_{2\mathrm{nd}}$ g/mg·min)	R^2
15	8.74	8.62	0.0039	0.994
30	10.57	10.53	0.0026	0.994
40	10.46	10.10	0.0018	0.980

observed that $k_{2\mathrm{nd}}$ values (Table 4) decreased with increasing temperature. It is feasible that microorganisms existed in the real wastewater and actively utilized a portion of the phosphate at moderate temperature (Cheng *et al.* 2009), which would have induced a corresponding phosphate reduction from wastewater.

4. Conclusions

The development of phosphate adsorption technology using mesoporous TiO_2 adsorbent was established. The equilibrium isotherm and adsorption kinetics of phosphate onto TiO_2 adsorbent were investigated. The maximum adsorption capacity was found to be 50.4 mg/g for phosphate, which was high when compared to existent adsorbents. The pseudo-second order model was favored as it had a high correlation coefficient ($R^2 \cong 0.93$). The effects of pH and temperature on phosphate adsorption were evaluated. It was discovered that, in acidic conditions (pH 3-7), the adsorption capacity elevated with decreasing pH, which was affected by ion dissociation in terms of charge of phosphate and $TiOH^+$ reaction. In contrast, increasing pH under basic conditions noticeably disturbed the sorption process. Furthermore, the results of the temperature study demonstrated that the phosphate adsorption onto TiO_2 adsorbent is an exothermic process that could occur spontaneously and result in higher randomness of the system. Moderate temperature (30°C) suitably supports the adsorption kinetics in real wastewater; both chemical processes and typical microorganism function aids in adsorption.

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