Calcined Scallop Shells for Phosphate Adsorption in Aqueous Solution

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Summary

Adsorption of phosphate from aqueous solution has been conducted using calcined scallop shells (CSS), and XRD spectra, TG/DTA signals and pore properties (BET) of CSS were characterized. The influences of calcination temperature of scallop shells, pH, adsorption time and concentration on the phosphate adsorption using CSS were studied in batch adsorption experiment. The XRD spectra showed that CaO appeared after calcination at 800°C, the TG/DTA result exhibited decreasing weight around 38% from 600 to 800°C and BET surface area portrayed increasing value after calcination process at 800°C. The solution pH on the phosphate adsorption had no significant effect by calcination at 800°C (CSS-800). A comparison of kinetic models applied to the adsorption data by CSS-800 was evaluated with pseudo-first order and pseudo-second order model, and the experimental data were fitted well to pseudo-second order kinetic model, while the result of isotherm studies had an approach to Langmuir method with linear regression of 0.998. The adsorption amount of CSS-800 was 30 times higher than scallop shell without calcination.

Key words: Adsorption, calcination, calcium, phosphate, scallop shells

INTRODUCTION

Excessive discharge of nitrate and phosphate into water body results in excess algal growth, which in turn causes eutrophication¹⁾. Eutrophication occurs when phosphate concentration reaches 0.02 mg/L²⁾. In wastewater treatment process, various physical and biological treatments have been conducted^{3,4)}. Other phosphorus removal techniques are chemical treatments like adsorption, chemical precipitation, ion exchange and electrodialysis. Among these techniques, adsorption method has supreme advantage to others from the viewpoint of high efficiency, low cost, high availability of different adsorbents and ease of operation and maintenance⁴⁻⁶⁾. Over the past few years, several studies have been widely conducted for the application of the low cost and abundant available material in wastewater treatment such as alunite⁴⁾, wood charcoal⁷⁾, shell⁸⁾ and others^{2,9)} for adsorbent material. Scallop shell has high potential for being adsorbent material and has been proven to be phosphate adsorbent³⁾. The primary component of scallop shell contains calcium carbonate (CaCO₃), which will be converted to CaO via thermal decomposition (calcination). CaO is used in industries and daily practice such as wastewater

treatment, construction material and so on¹⁰⁾. Therefore, calcination process is expected to enhance amount of phosphate adsorption. The calcination of limestone will decompose carbonate to produce lime and CO₂ according to the following reaction¹¹⁾.

Phosphate adsorption using scallop shells without calcination as adsorbent achieved 23 mg/g (0.242 mmol/g)³⁾. In this study, we attempted to increase the phosphate adsorption capacity of scallop shell through calcination method. The objective of this research was to perform the removal of phosphate in aqueous solution by calcined scallop shells (CSS) and to examine its optimum condition in batch adsorption system mode. The scope included calcination temperature and time of scallop shell, solution pH, kinetic and isotherm studies, together with characterization of modified scallop by XRF, XRD, TG/DTA and nitrogen adsorption-desorption isotherm method (BET) analysis. Moreover, the reuse of scallop shells was attempted from the viewpoint of recycle waste, furthermore it is a very abundant and inexpensive material. This removal system is expected to be an effective phosphate removal method with low cost material.

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MATERIALS AND METHODS

Adsorbents preparation

Scallop shells were collected from Aomori Prefecture, close to the south of Hokkaido. The samples were ground and rinsed with deionized water for several times. The samples were dried at 110°C for 24 h in an oven. The dried scallop shells were calcined in a furnace at 600, 800 and 1,000°C for 5 h. After that, the calcined scallop shells (CSS) were ground and screened through a set of sieves to 150 μm . Stock solutions were prepared by dissolving anhydrous dipotassium hydrogen phosphate (K_2HPO_4) in distilled water to get 1,000 $\text{mg-PO}_4^{3-}/\text{L}$. This stock solution would be diluted if necessary.

The chemical characteristics of calcined scallop shells were investigated by X-ray fluorescence, XRF (ZSX Primus IV, Rigaku, Japan). Calcination of scallop shells was analyzed with a Thermal Gravimetric Analysis, TG/DTA (Seiko EXSTAR 6000, Hitachi, Japan). Exact 78.094 mg powdered scallop shells (without calcination) were taken for TG/DTA Thermal Gravimetric Analysis. The temperature range began from 30°C until 1,100°C with heating rate of 10°C/min. Mineralogical composition of the scallop shells was determined by X-ray diffraction/XRD (M18X-HF-SRA, Mac Science, Japan) instrument. The specific surface area of the scallop shells powder was measured by using nitrogen adsorption-desorption isotherm method (BELSORP-mini II, MicrotracBEL, Japan). The BET equation was used to estimate the specific surface area (S_{BET}). The micropore volume (V_{micro}) result was obtained by applying the subtracting pore effect method with α_s -plot. The mesopore volume (V_{meso}) was calculated by the difference between total pore volume (V_{total}) and V_{micro} . The pore size distribution (D_{avg}) was determined by Dollimore and Heal method. The prepared samples were labelled as CSS-T, where T is calcination temperature (°C).

Batch adsorption

The influence of calcination temperature on the phosphate removal using scallop shells was examined for various temperatures at 600, 800 and 1,000°C. Adsorption experiments were implemented with 0.03 g from different calcined shell samples and 50 mL phosphate solution (350 $\text{mg-PO}_4^{3-}/\text{L}$, original pH 8.5) at 25°C for 24 h in water bath shaker with 100 rpm. As comparison, pure CaCO_3 was prepared with calcination temperature at 600°C, 800°C and 1,000°C, then the sample was used for phosphate adsorption with the same condition as CSS.

Since the best result for calcination temperature of scallop shell was obtained at 800°C, this temperature was applied through all adsorption experiments. In the study examining the influence of solution pH, 0.3 g adsorbent and 15 mL of 300 $\text{mg-PO}_4^{3-}/\text{L}$ were mixed and shaken at 25°C for 24 h using thermostatic water bath shaker with 100 rpm. Initial pH was adjusted by adding 0.1 M NaOH or 0.1 M HCl and measured with pH meter (D-51, Horiba, Japan). The isotherm tests were performed with 0.3 g of adsorbent and 50 mL phosphate solution at 50–1,000 $\text{mg-PO}_4^{3-}/\text{L}$ at 25°C and at pH 8.5 of the solution for 24 h. Kinetics experiments were carried out to reveal the effect of time on the adsorption process and to identify the adsorption rate. Kinetics experiments were conducted at 25°C for 1 h and shaken at 100 rpm. The samples (0.3 g adsorbent, 50 mL of 350 mg/L phosphate solution, and original pH 8.5) were taken at predetermined time

intervals.

All of the adsorption procedures were performed in Erlenmeyer flask and shaken at 100 rpm using thermostatic water bath shaker (NCS-3000 Eyela, Rikakikai, Japan). After adsorption process, the loaded adsorbent samples were refined and the phosphate concentration in supernatant was determined spectrophotometrically (UV-2550, Shimadzu, Japan) using molybdovanadate method. The amount of adsorbed phosphate was calculated by

$$q = (C_0 - C_e) \frac{V}{m} \quad (2)$$

where q is the amount of phosphate ions adsorbed (mg/g), C_0 and C_e (mg/L) are the concentration of phosphate at the initial and equilibrium, respectively, V is the volume of solution (L) and m is the mass of the adsorbent (g).

RESULTS AND DISCUSSION

Characterization of calcined scallop shells

XRF analysis

Elemental compositions of scallop shell were analyzed by XRF. The results were depicted in Table 1. It showed that CaCO_3 was main compound of scallop shells. The results presented no major differences of CaCO_3 between scallop shells and CSS-600, indicating that calcination process had not occurred on this temperature. On the other hand, CaO amount on CSS-800 was more than 98%. CSS-800 and CSS-1000 exhibited increasing value of CaO in small amount. Elemental composition of original shells had a concordance with the previous study which treated scallop shells contained 98 wt.%^[12].

XRD analysis

Upon calcination, the scallop shells turned completely in white (CSS-800), which implied the decomposition and release of some impurities such as proteins. XRD results of scallop shells are depicted in Fig. 1. The peaks were compared to the Joint Committee on Powder Diffraction Standards (JCPDS). It represented the main peak of calcium carbonate at $2\theta=24^\circ, 29^\circ, 32^\circ, 39^\circ, 43^\circ, 47^\circ$ and 48° (JCPDS 85-1108) for scallop shell. CSS-600 demonstrated that all diffraction peaks were attributable to CaCO_3 . After heating the scallop shells at 800°C, the new peaks obtained at $2\theta=34^\circ, 51^\circ, 54^\circ, 63^\circ$ and 64° (JCPDS 48-1467) were of calcium oxide. Calcium hydroxide was observed at $2\theta=17^\circ$ and this peak would be due to the existence of Ca(OH)_2 from interaction between CaO and water vapor in the air after sample decomposition. Sharma et al.^[13] reported that the XRD spectra of

Table 1 Chemical composition of scallop shells and CSS (wt%) by XRF

Sample	CaCO_3 or CaO	Na_2O	SO_3	SrO	MgO	P_2O_5	SiO_2	Al_2O_3	K_2O
Scallop Shell	98.2 (CaCO_3)	0.66	0.41	0.35	0.16	0.11	0.06	0.05	ND
CSS-600	98.1 (CaCO_3)	0.99	0.29	0.31	0.14	0.15	ND	ND	ND
CSS-800	98.4 (CaO)	0.66	0.29	0.26	0.21	0.14	ND	ND	ND
CSS-1000	98.9 (CaO)	ND	0.44	0.25	0.18	0.15	ND	ND	0.05

Fig. 1 XRD spectra of scallop shell and calcined scallop shell after calcination, a) scallop shells, b) CSS-600 c) CSS-800 (before adsorption) d) CSS-800 (after adsorption). CaCO_3 (▲); CaO (■); Ca(OH)_2 (●); $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (◆)

Ca(OH)_2 appeared at $2\theta=14.772^\circ$ and 17.869° for a calcined eggshell catalyst. These results were in accordance with previous result that CaO was formed during calcination.

Peak of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ was detected from CSS-800 (after adsorption) and it revealed that there was chemical interaction between CaO in scallop shells and phosphate solution. $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ peak was expressed at $2\theta=25.7^\circ$, which was relevant with previous study⁹. Calcium can react with PO_4^{3-} and form Ca-P bonding such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) or brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$)¹⁴.

TG/DTA analysis

Figure 2 depicts the decomposition temperature of the uncalcined scallop shells. As the temperature increased, the weight of scallop shells decreased. The maximum weight loss occurred from 600°C to 850°C (around 38%). A significant weight loss was observed at the temperature of 865°C . It would be related with decomposition of calcium carbonate by emitting carbon dioxide. DTA curve showed that the decomposition process will begin at 636°C and decompose completely at 822°C . These results led to considering calcination tempera-

Fig. 2 TG/DTA curves of scallop shell (uncalcined)

Table 2 Surface structure properties of scallop shell and phosphate removal of CSS

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)	D_{avg} (nm)	Phosphate removal (%)
Scallop shell	3.76	3×10^{-3}	6×10^{-3}	9×10^{-3}	9.62	2.9
CSS-600	2.36	1×10^{-3}	5×10^{-3}	6×10^{-3}	9.97	3.0
CSS-800	10.70	14×10^{-3}	10×10^{-3}	24×10^{-3}	9.18	86.5
CSS-1000	5.35	5×10^{-3}	4×10^{-3}	9×10^{-3}	7.30	90.3

ture as critical point for decomposition process. Sawai et al.¹⁵⁾ evaluated thermal gravimetry of the scallop shell powder heated from ambient temperature to 1,000°C and our TG/DTA results were similar to the previous data.

Surface area and pore volume analysis

Table 2 was observed that the increase of BET surface area correlated with weight loss steps in the TG/DTA results and calcination process could expand the surface area on scallop shells. CSS-600 exhibited a slight reduction of BET surface area and total pore volume compared with scallop shell. This result conveyed that calcination method at 600°C did not give significant impact on scallop shell. The remarkable increase of CSS-800 compared to the scallop shell was probably caused by crystal growth of CaO. This implied the decomposition of CaCO_3 as expressed in Eq. (1). The development of the pore volume was induced by calcination of shells at high temperature. It was indicated by the rise of total pore volume of CSS-800 compared with scallop shell. In our study, calcination process at heating temperature of 800°C enhanced 2.85 times higher surface area than without calcination.

CSS-1000 portrayed deflation of surface area significantly compared with scallop shell. The higher calcination temperature tended to agglomerate CaO particles. If agglomeration occurred, the volume of the product will be shrunk and surface area will be declined. It was supported by reduction of total pore volume of CSS-1000 after increasing total pore volume of CSS-800. Temperature had a strong effect on shrinkage tendency during calcination process¹⁶⁾. Köse and Kivanç¹⁷⁾ conducted calcination process on waste eggshells, and indicated that calcination process increased 3.7 times surface area. In our study, calcination process at heating temperature of 800°C enhanced 2.85 times higher surface area than without calcination. From this study together with the result of previous study, it deduces that calcination process can enhance the surface area.

Calcination temperature of scallop shells and phosphate adsorption ability of CSS

The phosphate removal ability of CSS-600, CSS-800 and CSS-1000 was also exhibited in Table 2. It represented that phosphate removal would be increased with the rise of calcination temperature. There was a significant difference in phosphate removal of CSS-600 and CSS-800. It coincided with the result of TG/DTA, in which the decomposition process would begin at 600°C. Phosphate removal increased on CSS-800 because decomposition occurred significantly at 800°C. After 800°C, calcium carbonate had changed into CaO. These phosphate removals (Table 2) support the TG/DTA result.

Agglomeration might occur on CSS-1000 so that the pore volume will be shrunk and the surface area will be declined. However, the

agglomeration of CSS did not affect adsorption amount significantly because phosphate removal of CSS-1000 increased slightly compared to CSS-800. CSS-600 and CSS-800 had different phosphate removal of around 83.5%. Meanwhile, by the same temperature raise, CSS-1000 had merely 3.8% of difference with CSS-800. Due to the viewpoint of energy efficiency, CSS-800 became the most excellent adsorbent among the other materials.

We also conducted phosphate adsorption with pure CaCO_3 through calcination process. The results showed that trend of phosphate removal with CSS had concordance to pure CaCO_3 treated by calcination process. It depicted that adsorption amount of phosphate was almost similar between CSS and pure CaCO_3 (treated by calcination process). Utilization of pure CaO as references showed that CaCO_3 had the main role of phosphate adsorption with calcined scallop shells as adsorbent.

Influence of solution pH

The influence of solution pH on the removal of phosphate has been conducted. pH value acted as a decisive aspect in the determination of phosphate species in the aqueous solution system. The relationship between pH value and phosphate species can be shown in the following equations¹⁸⁾:

The results implied that phosphate removal of CSS-800 was almost constant at pH 3–11. It showed that after equilibrium condition, the pH tended to reach base condition ($\text{pH}_e > 11$). When phosphate solution at $\text{pH} > 11$, PO_4^{3-} was being the main species at aqueous solution. It is known that calcium phosphate precipitation dominantly happened at higher pH¹⁹⁾. Phosphate precipitation typically occurs in alkaline conditions. Thus, the increase in pH and the presence of Ca in the scallop shell would result in PO_4^{3-} precipitation, as $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, hydroxyapatite.

Adsorption kinetics

In order to investigate the adsorption mechanism, pseudo-first order and pseudo-second order models were applied to fit the experimental data. The pseudo-first order equation can be written as²⁰⁾:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

where q_e and q_t are the amount of phosphate adsorbed (mmol/g) at equilibrium and time t , respectively, and k_1 is the rate constant of first order adsorption (h^{-1}). Straight lines were obtained by plotting $\log(q_e - q_t)$ against t . Slopes and intercepts of the plots were reflected as the values of the rate constant k_1 and q_e , respectively.

The pseudo-second order equation is conveyed by the form²¹⁾:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 is the pseudo-second order rate constant ($\text{g}/\text{mmol} \cdot \text{h}$). The values of equilibrium adsorption capacity (q_e) and the second order

Fig. 3 Effect of contact time on scallop shell (■), CSS-600 (●) and CSS-800 (▲)

constant (k_2) can be decided by the slope and intercept of plot t/q_t versus t , respectively.

The results demonstrated that among these two models, pseudo-second order kinetic model had the highest R^2 value. This kinetic model was used as the best fit equation for the description of the mechanism of phosphate adsorption (Fig. 3). The coefficient of determination for the pseudo-second order kinetic model was 0.999 with q_e 4.96 mmol/g and k_2 21.4 g/mmol h, meanwhile coefficient of determination for pseudo-first order kinetic model was 0.588 with q_e 0.247 mmol/g and k_1 1.25 1/h. The result showed that pseudo-second order model is better to describe the rate of adsorption of the prepared sample than the pseudo-first order model. Amount of phosphate adsorption (q_e) required 1 h to achieve the equilibrium point. Moreover, the pseudo-second order kinetic model can justify the adsorption mechanism due to the calculated q_e values which agreed very well with the experimental value. Similar results were also reported by other workers^{5,14}. Through the kinetic models, adsorption mechanism and the rate controlling steps can be determined. Results obtained from pseudo-second order model showed that diffusion process within the particles of scallop is being the predominant process in the controlling step. Other than that, electrostatic attraction and ion exchange may take a partial role of phosphorus removal⁹.

Adsorption isotherms

Langmuir and Freundlich isotherm equations were used to obtain b (Langmuir constant) and K (capacity constant by Freundlich), respectively. The Langmuir equation²² was applied for the adsorption data of the CSS:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (8)$$

where q_e is the amount of phosphate adsorbed at equilibrium (mmol/g), C_e is concentration at the equilibrium (mmol/L), Q_0 and b are

Fig. 4 Langmuir isotherm plot for phosphate adsorption with CSS and scallop shells, q_e : amount of phosphate adsorbed at equilibrium and C_e : concentration at equilibrium

Langmuir constants related to monolayer adsorption capacity and energy of sorption, respectively. The Langmuir model considers that the adsorption occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules.

The Freundlich equation is represented by the following equation²³:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (9)$$

where K ((mmol/g)(L/mmol)^{1/n}) is the Freundlich capacity constant and n is the Freundlich intensity constant. This model is applicable for non-ideal adsorption on heterogeneous surfaces. Freundlich adsorption describes multilayer adsorption which has heterogeneous surface with interaction between the adsorbed molecules. The experimental data were fitted very well to Langmuir isotherms with linear regression of 0.998 rather than Freundlich isotherm with linear regression of 0.362. It represented homogenous surface by monolayer adsorption. Previous studies^{4,20} have shown that adsorption follows Langmuir isotherm.

The phosphate adsorption amount was declined with increasing phosphate concentration. The adsorption amounts of phosphate on CSS-800 were presented in Fig. 4. The optimum adsorption amount was established to be 5.08 mmol/g through Langmuir isotherm. Moreover, adsorption amount of phosphate using scallop shell was 0.170 mmol/g (without calcination) which was close to the magnitude in previous study³. It portrayed that the adsorption amount of CSS-800 is 29.8 times higher than scallop shell without calcination.

CONCLUSION

Calcination process would release carbon dioxide and change CaCO_3 to CaO . This calcium can react with PO_4^{3-} and it could

decrease phosphate concentration in aqueous solution. XRF results showed CaCO_3 as the main chemical component of the scallop shell and CSS-600. The TG/DTA and investigation of calcination temperature showed that calcination or decomposition process occurred at 800°C and XRD spectra showed the existence of CaO after calcination at 800°C . The phosphate removal of CSS-800 was almost constant at $\text{pH } 3 - 11$. The equilibrium pH tended to reach base condition ($\text{pH}_e > 11$). The pseudo-second order kinetic was well described by experimental data of phosphate adsorption by CSS-800. The Langmuir equation was concordant with the adsorption data. Phosphate adsorption capacity with scallop shells was enhanced from 0.170 mmol/g to 5.08 mmol/g due to calcination. It can be concluded that calcination method on scallop shell can increase phosphate removal. It is revealed that CSS-800 is a low-cost and abundant adsorbent with high adsorption amount ability for phosphate adsorption in aqueous solution.

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