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Characteristics of phosphorus adsorption for a titanium mesostructure synthesized with various surfactants

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Eutrophication due to excessive phosphorus in water has been considered one of the most important environmental problems. In this study, a titanium mesostructure, prepared with different surfactant templates, was tested to confirm its applicability as an adsorbent for the removal of phosphorus and to evaluate the phosphorus removal efficiency. An X-ray diffraction analysis, the phosphorus adsorption isotherm and a kinetic test were performed on the titanium mesostructure synthesized with various molar ratios of base material to surfactant and different surfactant templates. It was revealed that the mesostructure synthesized with the molar ratio of 1.00/0.25 was the most uniformly and clearly formed and had the maximum adsorption capacity.

Keywords: phosphorus; mesostructure; titanium; adsorption; surfactant

Introduction

Phosphorus is a very important element that is widely used in agriculture and industry. However, urban development and agricultural intensification have caused widespread phosphorus enrichment of surface water [1]. The negative effects of eutrophication due to the presence of anthropogenic phosphorus in surface water are well known. An optimal process for the removal of phosphorus from water needs to be developed to alleviate the eutrophication of lakes, rivers and oceans. General technologies for the removal of phosphorus from water include physical processes (settling, filtration), chemical precipitation (using aluminium, calcium, iron) [2] and biological processes (bacteria, algae) [3–5]. However, the chemical methods are expensive and produce large quantities of sludge, whereas biological processes need complex and strict control of the operating conditions [6]. Conversely, adsorption processes appear to be attractive tools for the removal of phosphorus because of the simplicity of their operation, the production of only small quantities of sludge, their potential for phosphorus recovery and their cost-effectiveness [6,7]. A variety of adsorbents have been developed for the removal of phosphorus, including aluminium oxide [6,8], zirconium oxide [9], hydrotalcite [10,11], ion exchange resins [12], clay minerals [13,14] and activated alumina [15]. In recent research, a mesostructure made of zirconium sulphate, using the surfactant hexadecyltrimethylammonium bromide (C_{16}TMA-Br) as a template, was found to be highly effective for the sorption of phosphate [16]. The zirconium mesostructure has a high specific surface area (>1000 m² g⁻¹) and exhibits a phosphorus sorption capacity higher than other adsorbents [16]. However, because the raw material required for the zirconium mesostructure is very expensive, its commercial use has been limited. For this reason, a more efficient and cost-effective material for the synthesis of inorganic mesostructures was investigated using titanium as a substitute material as it is stronger, denser and has a more stable mesostructure network than zirconium and has similar chemical affinities to those of zirconium [17]. The titanium mesostructure was found to be a potential adsorbent for phosphorus, but little is known about the sorption characteristics of the material, such as the maximum adsorption capacity and adsorption kinetics, or the conditions that are most favourable for the synthesis of the mesostructure. In this study, a titanium mesostructure was synthesized using different surfactant species and various molar ratios of inorganic to surfactant. In addition, their maximum adsorption capacity, adsorption kinetics and structural properties were also investigated.

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Materials and methods

Synthesis of titanium mesostructure

To investigate the effects of different surfactant species, which serve as the template of the mesostructure, on the adsorption characteristics of materials, titanium mesostructures were synthesized using different surfactant templates. Surfactant solutions were prepared by dissolving 2.50 g of do-decyltrimethylammonium bromide, hexa-decyltrimethylammonium bromide or octa-decyltrimethylammonium bromide (Sigma-Aldrich Chemical Co., Yongin, Korea) in 85 g of distilled water and then adding the solution to titanium oxysulphate–sulphuric acid complex hydrate dissolved in distilled water. All molar ratios of inorganic to surfactant were maintained at 1.0/0.5. The mixture was then vigorously mixed with a magnetic stirrer for two hours. During mixing, the formation of a white precipitate was observed. The solution containing the precipitate was placed in an oven at 100 °C for 48 hours and filtered through a 0.45 µm membrane filter. The precipitate was washed 5 times with 50 mL of distilled water and then dried at 80 °C for four hours. After drying, the material was ground into a fine powder using a pestle and mortar, and then used in the main experiments. The structural properties of each mesostructure were estimated using X-ray diffraction analysis (DMAX-2500, Rigaku, Tokyo, Japan).

To investigate the effect of the molar ratio on the sorption characteristics of the material, titanium mesostructures were synthesized at molar ratios of 1.00/0.25, 1.00/0.50 and 1.00/1.00. The inorganic solution containing the titanium was prepared by dissolving 4.55 g of titanium oxysulphuric acid hydrate complex (TiOSO$_4·$H$_2$SO$_4·$H$_2$O, Sigma-Aldrich Chemical Co., Yongin, Korea) in 15 g of distilled water. The surfactant solutions were prepared by dissolving 1.25, 2.50 and 5.00 g of do-decyltrimethylammonium bromide or hexa-decyltrimethylammonium bromide (Sigma-Aldrich Chemical Co., Yongin, Korea) in 85 g of distilled water. All other synthesizing sequences followed the procedures described above.

Phosphorus adsorption isotherm and kinetic tests

The maximum phosphorus adsorption capacities of the titanium mesostructures synthesized under various conditions were estimated using adsorption isotherm tests. Fifty millilitres of phosphorus solutions with initial concentration of 50, 100, 150 and 200 mg L$^{-1}$ were placed into 50 mL conical tubes containing 0.4 g of the adsorbent. The phosphorus solution was prepared by dissolving anhydrous potassium phosphate (K$_3$HPO$_4$, Sigma-Aldrich Chemical Co., Yongin, Korea) in distilled water. The tubes were shaken on a rotary air-shaker for 24 hours. After shaking, the liquid and solid phases were separated using a 0.45 µm membrane filter. The concentrations of phosphorus and sulphate in the aqueous phase were analysed via UV spectrophotometry. (Optizen, Mecasys Co., Daejeon, Korea).

To estimate the adsorption kinetics of the titanium mesostructure, 200 mL of phosphorus solution with an initial concentration n of 1000 mg L$^{-1}$ were placed into 50 mL conical tubes containing 0.4 g of the adsorbent. The tubes were shaken on a rotary air shaker and samples were taken from the liquid phase at predetermined time intervals (20, 40, 80, 160, 240 and 480 min). The filtered solutions were analysed for their residual phosphorus concentrations using UV spectrophotometry.

Modelling of equilibrium and kinetic adsorption

To quantify the adsorption capacity of the titanium mesostructure, the Langmuir adsorption isotherm (Equation (1)) and pseudo-second-order kinetic models (Equation (2)) [18] were used as both equilibrium and kinetic adsorption models as follows:

$$S = \frac{\alpha \beta C}{1 + \alpha C},$$

(Equation (1))

where $S$ and $C$ are the adsorbed and residual aqueous concentrations, and $\alpha$ and $\beta$ are the constants related to the binding energy (mg g$^{-1}$) and the maximum adsorption capacity (mg kg$^{-1}$), respectively. The kinetic rate equation can be written as:

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

(Equation (2))

where $k_1$ is the second-order reaction constant, $q_e$ is the amount of phosphorus sorbed at equilibrium (mg g$^{-1}$) and $q_t$ is the amount of phosphorus sorbed at time $t$ (mg g$^{-1}$).

Results and discussion

Structural properties of titanium mesostructures

Figure 1 show the X-ray diffraction patterns for the titanium mesostructures synthesized with the do-, hexa- and octa-decyltrimethylammonium bromide (C$_x$TMA-Br) surfactants as the templates. Depending on the length of the carbon chain, the appearance of the peak patterns was approximately similar. However, there were slight differences in the peak intensity and sharpness. In particular, the titanium mesostructure synthesized using hexa-decyltrimethylammonium bromide showed a relatively high intensity compared with the other structures, indicating that the hexagonally shaped pores in the material
were most clearly formed and were most orderly with hexa-decyltrimethylammonium bromide.

The X-ray diffraction patterns for the titanium mesostructures synthesized using do- and hexa-decyltrimethylammonium bromides, with molar ratios of 1.00/0.25, 1.00/0.50 and 1.00/1.00, are shown in Figures 2 and 3, respectively. In both cases, the peak patterns were relatively higher for the 1.00/0.25 molar ratio, which confirmed that the titanium mesostructures synthesized using do- and hexa-decyltrimethylammonium bromides had more uniform pore sizes than other molar ratios. The results of the equilibrium adsorption tests for the titanium mesostructure using the three kinds of surfactants are shown in Figure 4. Use of do- and hexa-decyltrimethylammonium bromides showed similar phosphorus adsorption capacities, but the use of octa-decyltrimethylammonium bromide gave a lower adsorption capacity.

**Phosphorus adsorption capacity of titanium mesostructure**

Figure 4 shows the phosphorus adsorption isotherms of the titanium mesostructures synthesized with different surfactant (C₇T-MA) templates.
showed a sharp increase in the adsorbed concentration for the lower range of equilibrium concentrations, but it reached its maximum capacity at around 400 mg L$^{-1}$, whereas that of the do-structure had an extended maximum capacity to a much higher value. This indicates that the binding energy ($\alpha$) of the octa-structure for phosphorus appeared to be very high compared with the other surfactants, as the steepness of the curve is representative of the extent of the binding energy (Table 1). In general, the highest adsorption capacity of the titanium mesostructure synthesized using do-decyltrimethylammonium bromide was due to its structure having the smallest pore size and shortest carbon chain length. The pores in the material are formed by the surfactant micelles, which serve as a template for the mesostructure, and the length of the carbon chain in the surfactant tail corresponds to the radius of the pores. The smallest pore size in the mesostructure would give the largest specific surface area of a material, which would increase the adsorption capacity for the target compound.

Tests for the adsorption of phosphorus by the titanium mesostructures were performed to investigate the effects of different molar ratios of inorganic to do- and hexa-decyltrimethylammonium bromide surfactant, and the phosphorus adsorption isotherms are shown in Figures 5 and 6. The Langmuir parameters for these isotherms are summarized in Tables 2 and 3. The maximum phosphorus adsorption capacities ($\beta$) were found for the titanium mesostructures synthesized with the molar ratio of 1.00/0.25: the adsorption capacity was more than twice that obtained at the other molar ratios. The shape of the pores in the materials might explain the different phosphorus adsorption capacities of the surfactants. As discussed above, the formation of the mesopores was most clear and ordered with the molar ratio of 1.00/0.25, which resulted in the highest phosphorus adsorption capacity. The maximum adsorption capacities of do- and hexa-decyltriethylammonium bromides were 404.78 and 392.06 mg g$^{-1}$, respectively. These values were much higher than the 47.83 mg g$^{-1}$ for layered double hydroxides amended with magnetic particles [19], 196 mg g$^{-1}$ for hydrotalcite [18], 79.4 mg g$^{-1}$ for synthetic HUD zeolite [20] and 51.74 mg g$^{-1}$ for zirconium mesostructure [16] reported in the literature.

\begin{table}[h]
\centering
\caption{Langmuir parameters for the titanium mesostructures synthesized using different surfactant species.}
\begin{tabular}{lcc}
\hline
Surfactant & $\alpha$ (kg L$^{-1}$) & $\beta$ (mg g$^{-1}$) & $R^2$
\hline
Do- (C$_{12}$TMA-Br) & 0.0124 & 77.89 & 0.953
Hexa- (C$_{16}$TMA-Br) & 0.0334 & 69.20 & 0.955
Octa- (C$_{18}$TMA-Br) & 0.0330 & 61.64 & 0.793
\hline
\end{tabular}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.pdf}
\caption{Phosphorus sorption isotherms of the titanium mesostructures synthesized using different molar ratios of titanium oxysulphate–sulphuric acid hydrate complex to do-decyltrimethylammonium bromide.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6.pdf}
\caption{Phosphorus sorption isotherms of the titanium mesostructures synthesized using different molar ratios of titanium oxysulphate–sulphuric acid hydrate complex to hexa-decyltrimethylammonium bromide.}
\end{figure}

\begin{table}[h]
\centering
\caption{Langmuir parameters for the titanium mesostructures synthesized using different molar ratios of titanium oxysulphate–sulphuric acid hydrate complex to do-decyltrimethylammonium bromide.}
\begin{tabular}{lccc}
\hline
Inorganic/surfactant & $\alpha$ (l kg$^{-1}$) & $\beta$ (mg g$^{-1}$) & $R^2$
\hline
1.00/0.25 & 0.0144 & 404.78 & 0.802
1.00/0.50 & 0.0114 & 162.07 & 0.857
1.00/1.00 & 0.0410 & 283.91 & 0.853
\hline
\end{tabular}
\end{table}

\textbf{Adsorption kinetics of titanium mesostructure}

Figure 7 shows the phosphorus adsorption kinetics of the titanium mesostructures synthesized with different
surfactant species. The kinetic parameters for the pseudo-second-order model are summarized in Table 4. The second-order reaction constant indicated that the titanium mesostructure synthesized with octa-decyltrimethylammonium bromide exhibited the fastest reaction rate except for the case of layered double hydroxides. This means that the reaction would proceed in a relatively short time. For octa-decyltrimethylammonium bromide, the equilibrium state was reached after around 40 min. However, the rates of the reactions for the do- and hexa- structures were found to proceed to 240 min. In other words, the reactions were rapidly completed during the early stage for the octa- structure with a large pore size, whereas the do- and hexa- structures, with relatively small pore sizes and uniformly formed pores allowed the diffusion of phosphorus into the interior adsorption sites [21].

The phosphorus adsorption kinetics of the titanium mesostructures synthesized with different molar ratios of do- and hexa-decyltrimethylammonium bromide is shown in Figures 8 and 9. The kinetic parameters for the pseudo-second-order model are summarized in Tables 5 and 6, respectively. The differences in the parameters due to changes in the inorganic to surfactant ratio were
not significant, as is shown in the tables. However, contrary to the result obtained from the equilibrium adsorption test, the phosphorus adsorption rate was found to be highest with for the 1.00/0.25 molar ratio. This conflicts with the results of a previous study [22] where an excessive amount of inorganics, in relation to the surfactant, caused clogging of pores and the formation of irregularly sized pores, which might block the diffusion of phosphate because of a bottle-neck effect.

**Conclusions**

In this study, we investigated the potential adsorption capacity of a titanium mesostructure using three kinds of surfactants species to remove phosphorus from aqueous solutions. It was found that the titanium mesostructure synthesized with the do-decyltrimethylammonium bromide (C_{12}TMA-Br) surfactant, with an inorganic to surfactant molar ratio of 1.00/0.25, was most uniformly and clearly formed and thus had the maximum sorption capacity and reaction rate. The pore size within the mesostructure decreased with increasing carbon chain length of the surfactant template used, thus yielding the maximum amount of phosphorus sorption and the greatest reaction.

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