Treatment of eutrophication-inducing substance by modified inorganic based mesostructure

Seung-Yeon Lee, Jae-Woo Choi, Sang-Hyup Lee, Ki-Bong Lee, Dong-Ju Kim, Seok-Won Hong

1 Water Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea. *(Corresponding author)
2 Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea.
3 Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, Republic of Korea.

Abstract— In this study, mesoporous silica was synthesized and attached with several functional groups, such as amine, aluminum and titanium. Whole samples were tested to investigate the adsorption capacity for phosphate. The structure of synthesized materials was analyzed by X-ray diffractions (XRD), Fourier transform-infrared (FT-IR) and surface area analysis, Brunauer-Emmett-Teller (BET). To determine the maximum adsorption capacities and sorption rates for phosphate, the equilibrium and kinetic tests were conducted in batch condition. Among functionalized SBA-15, pure SBA-15 hardly adsorb phosphate but NH2-SBA-15, Al-SBA-15 and Ti-SBA-15 showed good performances for the removal of phosphate. The maximum adsorption capacity of NH2-SBA-15 for phosphate was most efficient compared to the other adsorbents. This study could provide information on the most ideal modification of SBA-15 for the practical removal of phosphate.

Keywords:-Functionalization, mesoporous silica, phosphate, removal

I. INTRODUCTION

Phosphorous (P) poses threats to human life as well as being a valuable resource for humans. Phosphorous is an important element in the composition of human bodies and a material widely used to improve human life, such as fertilizers, detergents and pesticides. However, the excess residues from their uses flow into natural waters, such as rivers, lakes and streams, where they enrich the water ecosystem with mineral nutrients. This abundant nutrition results in streams, where they enrich the water ecosystem with mineral nutrients.

In water, phosphorous exists in the form of phosphate, which is an anion molecule bonded to oxygen and hydrogen. Using the chemical characteristics of phosphorous, phosphate in water can be removed using various methods, such as chemical precipitation [3,4], biological processes [5], adsorption [6-10] and ion exchange [11,12]. Of these methods for phosphate removal, chemical precipitation, with Ca, Al, and Fe, is currently the most widely used. Biological processes are also applied for the removal of phosphate. However, both these methods are inappropriate for the removal of low phosphate concentration, and due to the high costs and generation of large amounts of sludge, their applications are limited as practical phosphate removal method. For the elimination of low phosphate concentrations in water bodies, adsorption methods are used as alternatives for the control of phosphate. Various adsorbents have been studied and used for the adsorption of phosphate for many decades, such as red mud [8], fly ash [10], hydrotalcite [7], activated alumina [6], zeolites [9] and ion exchange resin [11,12].

Currently, mesoporous materials are used as adsorbent for the removal of phosphate. Due to their characteristics, such as large surface areas and abundant reactive ionized surfaces, synthesized mesoporous materials could replace zeolites, which have an exhaustibility as a mineral. Moreover, mesoporous materials have characteristics, such as the simplicity of controlling their pore size, highly uniformed pore and various functional groups improved the adsorption capacity of these materials. Based on their several advantages, mesoporous materials are applied for the removals of heavy metal, ionized materials, organic/inorganic compounds and CO2 [13-17]. Meanwhile, mesoporous silica is widely used as a base material for the grafting of functional groups, because it can be easily synthesized, has good reactivity to organic/inorganic groups and is low cost. Therefore, mesoporous silica has been used as a practical adsorbent material in terms of its economics and efficiency [18].

In this study, the modification of mesoporous SBA-15 and its application to phosphate removal were investigated. Pure SBA-15 was synthesized, with various functional groups attached under identical conditions to modify and improve the affinity for phosphate. In addition, from the equilibrium and kinetic adsorption tests, the potential of the modified SBA-15 for commercialization as phosphate adsorbents was established. Based on the results, the characteristics and mechanisms of phosphate removal by the modified SBA-15 were investigated and compared.
II. MATERIALS AND METHODS

Synthesis of pure SBA-15

Pure SBA-15 was synthesized according to the procedure reported by Anunziata et al. [18]. Triblock copolymer, P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)), was used as the SBA-15 template material. Four grams of P123 was dissolved in 30 g of distilled water, with 120 g of 2 M HCl slowly added. This solution was stirred for 24 h at room temperature, then heated to 315 K and 8.5 g of TEOS (Tetraethyl orthosilicate) slowly added under vigorous stirring for a further 20 h. The resulting mixture was reacted in hydrothermal condition, which was an autoclave at 373 K for 24 h. The solid product was filtered, washed with distilled water and ethanol, and then dried overnight at 353 K. After drying process, the final product was calcined at 823 K for 5 h.

Synthesis of functionalized SBA-15

Functionalized mesoporous SBA-15 was obtained using the post-synthesis method employing precursors for each functional group, with the amount of each functional group fixed at 1:0.05 = SBA-15:functional precursor molar ratio to compare their capacities for the removal of phosphate.

Amine-SBA-15. 1.1 g of pure SBA-15 was dispersed in toluene, with 0.22 mL of N-[3-(Trimethoxysilyl)propyl]ethylenediamine added. The mixture was refluxed for 24 h. The final product was filtered, washed by Soxhlet extraction in toluene and dried for 6 h at 353 K.

Aluminum-SBA-15. 5 g of pure SBA-15 was dispersed in 125 mL of distilled water containing 1.684 g of aluminum nitrate nonahydrate (Al(NO₃)₃·9(H₂O)). The mixture was stirred for 24 h at room temperature and filtered. The product was then calcined at 813 K for 2 h.

Titanium-SBA-15. 0.566 g of TBOT (Tetrabutyl orthotitanate) was added to a mixture of 40 mL of glycerol (99 wt%) and 7.5 mL of 20 % TPAOH (Tetrapropylammonium hydroxide). To this solution, 2 g of pure SBA-15 was added, with the resultant mixture stirred at 373 K for 72 h. The product was then filtered, washed with deionized water and calcined at 773 K for 4 h.

Equilibrium adsorption test

To investigate the maximum adsorption capacities of functionalized SBA-15 for phosphate, equilibrium adsorption tests were conducted. 0.1 g of each functionalized SBA-15 was reacted with 50 mL of solutions containing various phosphate concentrations (10, 25, 50, 75 and 100 mg L⁻¹). The reactions were conducted in 50 mL conical tubes on the rotary shaker for 1 h, after which, 5 mL of each sample was taken and analyzed. To confirm the reproducibility of results, the tests were repeated in triplicate, with the results based on the averages of experimental data.

Kinetic adsorption test

Kinetic adsorption tests were conducted to determine the phosphate adsorption rates. 0.1 g of functionalized SBA-15 was reacted in a conical tube with 50 mL of 50 mg L⁻¹ phosphate solution on a rotary shaker at 50 rpm for 24 h. Samples were collected at specific time intervals and analyzed until the concentration reached at equilibrium stage. To confirm the reproducibility of results, the tests were repeated as for the equilibrium test.

Adsorption isotherm model

To calculate the adsorption capacity of the functionalized SBA-15, the Langmuir isotherm model (Eq. 1) was used:

\[ q_e = \frac{Q_{\text{max}} \cdot b \cdot C_e}{(1 + b \cdot C_e)} \]  

where, \( q_e \) and \( C_e \) are the amount and concentration adsorbed at equilibrium, \( b \) the Langmuir constant related to the binding energy (L mg⁻¹) and \( Q_{\text{max}} \), the maximum adsorption capacity (mg g⁻¹) [24].

Assuming that one adsorbate was sorbed onto three surface sites of the material under examination condition, the sorption rate equation would be as shown below:

\[ q_t = q_0 - \left(\frac{q_0 - q_i}{1 + 2kt}\right)^2 \]

where, \( q_i \) is the amount adsorbed at equilibrium (mg g⁻¹), \( q_0 \) the initial amount (mg g⁻¹) and \( q_i \) the amount adsorbed at time \( t \) (mg g⁻¹) and \( k \) the pseudo-third order constant (min⁻¹).

Analytical methods

The low angle 2θ XRD peaks of the synthesized SBA-15 were analyzed within the range 0.5-10° (GADDS, German). The BET surface analyses were conducted using a TriStar3000 (Micromeritics, USA) at 77 K. Before the BET analysis, a degassing procedure was conducted for 24 h at 423 K. The structures of samples were analyzed using High-resolution transmission electron microscopy (FEI Tecnai F20). Samples were dissolved in ethanol and evenly dispersed prior to the analyses. FT-IR spectroscopy (Mattson Infinity Gold FT-IR spectrometer) was used to obtain spectra at a 4.00 cm⁻¹ frequency resolution. To observe the changes in the phosphate concentration, an ion chromatography system (ICS-1100, Dionex, USA) was used, with 0.45 μm membrane filters employed to remove the solids from the samples prior to analyse.

III. RESULTS AND DISCUSSION

Characterization of inorganic mesostructures

Fig. 1 shows the low-angle XRD patterns of the synthesized SBA-15. Pure SBA-15 exhibited three peaks, which
represented Bragg diffraction peaks (100), (110) and (220), to prove the SBA-15 characteristics. Functionalized SBA-15 samples also exhibited strong peaks (100), indicating the pore characteristics [15,18]. However, due to their functional groups, the intensities of the secondary and tertiary peaks of the functionalized SBA-15 were lower or even non-existent. This indicated that the well arranged mesoscopic orders greatly reduced by the functional groups due to thicken of the pore walls of SBA-15, with the pore sizes becoming naturally disordered and decreased.

Fig. 1.Powder X-ray diffraction of the functionalized SBA-15.

Table 1 described the overall BET results of the functionalized SBA-15 samples. The BET results confirmed that all the synthesized SBA-15 samples were within the mesoscopic range. Especially, the pure SBA-15 had the largest surface area and pore size. As the functional groups were grafted onto the pure SBA-15, the surface areas and pore sizes decreased. This fact indicated that the functional groups were attached to the surfaces of the pores and naturally concealed the pores. These results supported that of XRD mentioned above.

Table 1. The BET Results of the SBA-15.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$(m$^2$/g)</th>
<th>$V$(cm$^3$/g)</th>
<th>$D_A$(nm)</th>
<th>$D_{BET}$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure-SBA-15</td>
<td>1076.78</td>
<td>1.718</td>
<td>6.723</td>
<td>6.048</td>
</tr>
<tr>
<td>NH$_2$-SBA-15</td>
<td>361.64</td>
<td>0.296</td>
<td>3.934</td>
<td>3.837</td>
</tr>
<tr>
<td>Ti-SBA-15</td>
<td>638.66</td>
<td>0.691</td>
<td>4.774</td>
<td>4.297</td>
</tr>
<tr>
<td>Al-SBA-15</td>
<td>842.46</td>
<td>0.642</td>
<td>3.052</td>
<td>2.966</td>
</tr>
</tbody>
</table>

To confirm the ordered structure of SBA-15, the results of TEM are shown in Fig. 2. According to TEM images, the mesoscopic hexagonal arrays were well ordered and arranged. As the functional groups were attached to pure SBA-15, the images became darker than that for the pure SBA-15. Because the functional groups caused thickening of the pores, the pores of the functionalized SBA-15 became smaller and darker than those of pure SBA-15. The TEM images confirmed the functionalization of SBA-15.

Fig. 2.TEM images of the functionalized SBA-15 (a) Pure-SBA-15; (b) NH$_2$-SBA-15; (c) Al-SBA-15; (d) Ti-SBA-15.
The FT-IR spectra provided information on the functional groups grafted onto the SBA-15. Fig. 3 shows the FT-IR spectra of the synthesized SBA-15. All samples exhibited Si-O, Si-OH peaks (960 cm\(^{-1}\) and 1100-1000 cm\(^{-1}\), respectively) representative of the silica bonds in pure SBA-15. Each of the functional groups exhibited adsorption peaks at different wavelength ranges in the FT-IR spectra according to their characteristics. The peaks at 850-750 cm\(^{-1}\) corresponded to NH\(_2\) groups, proving the successful grafting of amine groups onto SBA-15 [19,20]. Compared with pure SBA-15, Si-O peaks (960 cm\(^{-1}\)) of Ti-SBA-15 became stronger which was attributed to Ti-O-Si bonding and indicated that Ti condensation had occurred. In the case of Al-SBA-15, as the pure SBA-15 became impregnated with Al, the Al component weakened the silanol peaks (960 cm\(^{-1}\) and 1100-1000 cm\(^{-1}\)) [6]. These peak changes indicated that each function group had become suitably chemically attached to the pure SBA-15.

![FT-IR spectra of the functionalized SBA-15.](image)

### Isotherm study

The phosphate adsorption isotherms are shown in Fig. 4 and the equilibrium parameters for Langmuir isotherm model are shown in Table 2. The amount of adsorbed phosphate, \(Q\) (mg per g of adsorbent), was plotted against the phosphate equilibrium concentration (mg per liter). For the various phosphate concentrations, the pure SBA-15 displayed a very little amount of phosphate adsorbed concentration. These slight changes were a small amount, they could be regarded as a possible error of the analysis. This implies that pure SBA-15 had no phosphate adsorption capacity or affinity for phosphate. Meanwhile, as shown in Fig. 4, NH\(_2\)-SBA-15, Al-SBA-15 and Ti-SBA-15 were appropriately fitted to the Langmuir isotherm model. Al-SBA-15 had a high phosphate adsorption capacity, with a maximum \(Q_{\text{max}}\) of 39.49 mg g\(^{-1}\) within the measured range. Ti-SBA-15 and NH\(_2\)-SBA-15 also showed good performances for the adsorption of phosphate, with maximum \(Q_{\text{max}}\) of 13.34 and 16.22 mg g\(^{-1}\), respectively. Compared with other phosphate adsorbents, such as activated alumina, iron oxide and ion resin, which exhibited adsorption capacities of 17.50 [21], 2.00 [22] and 8.21 [23] mg g\(^{-1}\), respectively. The Ti and NH\(_2\) modified mesoporous materials could be good adsorbents for the removal of phosphate [21]. According to Table 2 and Fig. 4, as the binding energy \(b\) increased, the maximum adsorption capacity also increased. Al-SBA-15 had a high binding energy and maximum adsorption capacity, and was also shown to be an efficient adsorbent within each equilibrium concentration range. In addition, the high binding energy of NH\(_2\)-SBA-15 resulted in the effective adsorption phosphate at low concentrations.

![Equilibrium adsorption isotherms of the SBA-15.](image)

### Table 2. Constants of the Langmuir isotherms for the adsorption of phosphate.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(Q_{\text{max}}) (mg/g)</th>
<th>(b) (L/mg)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure-SBA-15</td>
<td>0.4567</td>
<td>0.7661</td>
<td>0.0923</td>
</tr>
<tr>
<td>NH(_2)-SBA-15</td>
<td>65.789</td>
<td>0.0798</td>
<td>0.9959</td>
</tr>
<tr>
<td>Ti-SBA-15</td>
<td>16.216</td>
<td>0.0111</td>
<td>0.9653</td>
</tr>
<tr>
<td>Al-SBA-15</td>
<td>39.601</td>
<td>0.0666</td>
<td>0.9729</td>
</tr>
</tbody>
</table>

### Adsorption kinetics

The results of kinetic adsorption tests are shown in Fig. 5 and the kinetic parameters from the modeling in Table 3. From the equilibrium adsorption tests, pure SBA-15 absorbed no phosphate as a function of time. However, marked differences were observed in the phosphate adsorptions between NH\(_2\)-SBA-15, Ti-SBA-15 and Al-SBA-15. In the case of NH\(_2\)-SBA-15, phosphate adsorption occurred and reached at equilibrium state within 60 min. This was because the phosphate adsorption
originated from fast reactions, such as hydrogen bonding and electrostatic interactions. The hydrogen on the amine group reacted with the oxygen on the phosphate via hydrogen bonding. Simultaneously, the cationic (\(-NH_3^+\)) form on the surface preferentially reacted with the anionic form of phosphate. For this reason, the phosphate adsorption by NH\(_2\)-SBA-15 reached its equilibrium state in a short time [20]. Similar to NH\(_2\)-SBA-15, Ti-SBA-15 adsorbed phosphate via hydrogen bonding. The adsorption reaction occurred rapidly, but the lower distribution of hydrogen in Ti-SBA-15 decreased the amount of phosphate bonding to the oxygen on the phosphate.

Because of the delay stage, the phosphate was adsorbed slowly onto Al-SBA-15. Although each different functionalized SBA-15 sample had different mechanisms for phosphate removal, the pseudo-third-order model suitably fitted all the kinetic results. According to Table 3, the experimental and model parameters had similar values. This indicated that a pseudo-third-order reaction was ideal for both adsorbents and their adsorption rates could be predicted and calculated from this model.

IV. CONCLUSION

Mesoporous SBA-15 functionalized via various modifications were synthesized and tested to assess their adsorption capacities for phosphate. Pure SBA-15 exhibited no phosphate adsorption ability. With the same amount of each functional group attached to SBA-15, Al-SBA-15 was shown to be an efficient adsorbent for the removal of phosphate. The NH\(_2\)-SBA-15 and Ti-SBA-15 also exhibited good adsorption capacities for phosphate. SBA-15 functionalized with aluminum, titanium and amine were all suitably fitted to the Langmuir model, with maximum adsorption capacities of 39.49, 16.22 and 13.34 mg g\(^{-1}\), respectively. From the analysis of the kinetic data, the SBA-15 samples were well fitted to the pseudo-third-order model and were proven as effective adsorbents for the removal of phosphate. Especially, NH\(_2\)-SBA-15 and Ti-SBA-15 were able to quickly adsorb phosphate, and Al-SBA-15 efficiently removed phosphate in water. Due to their characteristics of phosphate removal, functionalized SBA-15 could be used as selective adsorbents for the removal of phosphate in water.

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REFERENCES


