A Simple Method for Synthesis of Triamine-SiO$_2$ Material toward Aqueous Nitrate Adsorption

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This study describes a facile route for preparation of mesoporous silica at ambient condition using cheap and available commercial SiO$_2$ precursor. The mesoporous material was then loaded with amine (Amine-P-SiO$_2$) and applied for nitrate removal in aqueous solution. The materials were characterized by XRD, TGA, FTIR, and SEM to explore the properties. Effects of pH, nitrate concentration, adsorbent dosage, and temperature on the nitrate adsorption capacity were investigated. Amine-P-SiO$_2$ material was superior to commercial adsorbent (Akualite A420) for nitrate adsorption with capacity reaching 32.5 mg/g and relatively stable after 10 cycles of adsorption-desorption. Moreover, the adsorption follows Langmuir model, proving that this chemical adsorption could effectively remove nitrate from aqueous solution for water and advanced wastewater treatment applications.

Keywords:
Triamine/ Mesoporous silica/ Amine-P-SiO$_2$/ Aqueous nitrate adsorption

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1. INTRODUCTION

The increase of domestic water use causes a pressure on water treatment and the shortage of clean water due to climate change and water pollution from anthropogenic sources. Nitrate ion exists naturally in the nitrogen biogeochemical cycle and serves as an essential nutrient for plants on Earth. However, the increase of nitrate pollution causes many issues for both environment and human health. Nitrate concentration in drinking water is limited by WHO guideline at 45 ppm and by every country. Therefore, the removal of nitrate contaminant from water has attracted many attentions and proposed with various methods. Conventional approaches such as biological treatment, ion exchange, adsorption, reverse osmosis, electrochemical, and chemical methods show several limitations (Tyagi et al., 2018) while advanced methods using nanotechnology such as reduction by zero valent iron (Araújo et al., 2016), catalytic and electrocatalytic reduction (Martinez et al., 2017; Garcia-Segura et al., 2018), photocatalytic reduction (Tugaeon et al., 2017; Bahadori et al., 2018), adsorption (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013; Singh et al., 2018) emerge as potential technologies. Among these methods, adsorption using new and effective nanomaterials could be a very promising technology, which can remove nitrate from water and wastewater. The development of ion exchange has recently attracted many attentions (Banu and Meenakshi, 2017; Kalaruban et al., 2016; Nujić et al., 2017). Moreover, mesoporous silica (e.g., SBA-15 and MCM-48) modified by amine has been proven as effective materials for nitrate removal from water (Hamoudi et al., 2007; Safia et al., 2012; Saad et al., 2007). However, the application of these materials is limited due to the complicated procedure for synthesis and high production cost. Therefore, the development of simple and cheap adsorbents is necessary for effective and efficient nitrate removal and recovery in water environment.

In the present work, a simple process for synthesis of new and cheap mesoporous silica was proposed from available commercial SiO$_2$. The materials were then grafted with amine and applied for removal of nitrate in water. The effect of
environmental conditions on the nitrate removal efficiency and adsorption capacity was investigated, including solution pH, initial nitrate concentration, adsorbent dosage, and adsorption temperature. The adsorption capacity of the synthesized materials was compared with commercial ion exchange resin (Akualite A420) and the durability test was also conducted.

2. METHODOLOGY

2.1 Material synthesis and characterization

Analytical-grade chemicals and in-lab deionized (DI) water were used in this study. HF, SiO₂, NaOH, and HCl were from Xilong (China). Triaminesilane (N1-(3-trimethoxysilylpropyl) dimethylenetriamine), pentane and toluene solvents, KBr powder, and nitrate (stock solution of 1,000 mg/L) were from Merck (Germany). Commercial Akualite A420 resin bought from China was used as a reference material.

Commercial silica (industrial grade) was purchased from Ho Chi Minh City, Vietnam. This silica was pretreated by washing with DI water, drying at 100 °C, and sieving with mesh size from 20 to 50 μm (named as SiO₂ in this study). The mesoporous structure of silica was created by using chemical reaction of HF and SiO₂. In a typical procedure, 20 g of SiO₂ powder was added into 1 L of 5% (vol/vol) HF solution under continuous stirring at ambient condition. After 30 min of reaction, the remaining solid SiO₂ powder was filtered and washed with DI water. The mesoporous silica (named as P-SiO₂) was finally obtained by drying at 100 °C for 4 h.

The amine-loaded materials (i.e., Amine-P-SiO₂ and Amine-SiO₂) were synthesized by grafting of triaminesilane onto P-SiO₂ and SiO₂ materials, respectively, following a synthesis procedure described in the literature (Thanh, 2016). In a typical experiment, a mixture of 150 mL toluene and DI water (continuous stirring at 85 °C) was added with P-SiO₂ (or SiO₂) at ratio of 0.3 mL DI water per 1 g of P-SiO₂ (or SiO₂). The mixture was then added with triaminesilane with ratio of 3 mL/g silica and stirred continuously for 16 h. After that, the mixture was filtered and the obtained solid material was washed by toluene and subsequently pentane. The material was finally dried at 100 °C for 1 h and named as Amine-P-SiO₂ (or Amine-SiO₂).

The materials were then characterized by Fourier transform infrared spectroscopy (FTIR, Bruker), thermogravimetric (TGA, Q500), X-ray diffracttrolley (XRD, D2 Phaser), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Brunauer-Emmett-Teller (BET, BET-202A Porous Materials). Detailed condition of these analyses and material sample pretreatment can be found in our previous studies (Phan et al., 2018; Thanh, 2016).

2.2 Nitrate adsorption experiment

The nitrate removal ability of amine-grafted materials was evaluated using batch nitrate adsorption test. Adsorbent was added into 50 mL of nitrate solution and shaken at 120 rpm and 25±0.5 °C. After reaching the equilibrium, the solid material was collected by centrifuging at 10,000 rpm. The effects of adsorbent amount (0.005-0.10 g), pH (2-10), and nitrate concentration (5-100 mg/L) on the adsorption capacity were investigated. All experiments were replicated three times and the average results were reported. Nitrate concentration was analyzed using a SPECORD 210 Plus UV-Vis spectrophotometer (Analytik Jena) via brucine-sulfanil colorimetric method.

The regeneration of adsorbents was carried out by brine desorption technique. Typically, 1000 mL of HCl solution (0.1 M) was used to regenerate the adsorbent (1 g) for 3 h at ambient condition. The material was then washed with distilled water.

2.3 Adsorption isotherms, thermodynamics, and kinetics

In order to study the nitrate adsorption on the surface of Amine-P-SiO₂ material, both the Langmuir and Freundlich isotherm models were applied. The Langmuir isotherm is based on the monolayer adsorption of nitrate ions on adsorbent surface. The Freundlich isotherm describes both multilayer adsorption and adsorption on heterogeneous surfaces. The Langmuir model (1) and Freundlich model (2) are presented as the following equations:

\[ q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (1)

\[ q_e = K_f C_e^{1/n} \]  \hspace{1cm} (2)
Where $C_e$ (mg/L) and $q_e$ (mg/g) are equilibrium concentration and amount of nitrate adsorbed, respectively. $Q_{\text{max}}$ (mg/g) and $K_L$ (L/mg) are the maximum capacity and equilibrium constant. $K_f$ ((mg/g)(L/mg)$^n$) and $n$ are Freundlich constants.

In this study, chi-square analysis was also applied for the calculated results from model ($Q_{\text{max,cal}}$) and experimental data ($Q_{\text{max,exp}}$) as in Equation (3).

$$\chi^2 = \sum \frac{(Q_{\text{max,exp}} - Q_{\text{max,cal}})^2}{Q_{\text{max,cal}}}$$

Thermodynamic parameters were calculated from equilibrium condition at different adsorption temperatures (293-318 K), as following equations (Duranoğlu et al., 2012):

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$K = \frac{C_{Ae}}{C_e}$$

$$\ln K = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Where $C_{Ae}$ and $C_e$ (mg/g) are the nitrate amount on adsorbent and solution phases, respectively. $\Delta G^o$ (kJ/mol), $\Delta H^o$ (kJ/mol), and $\Delta S^o$ (kJ/mol.K) are Gibbs free energy, enthalpy, and entropy changes, respectively, calculated from Equation (6) using the plot of $\ln K$ vs. $1/T$.

3. RESULTS AND DISCUSSION

3.1 Material characterizations

FTIR was used for identification of surface functional groups of Amine-P-SiO$_2$ and Akualite A420 materials, as shown in Figure 1. The FTIR peak at around 3,442 cm$^{-1}$ was observed for both Akualite A420 and Amine-P-SiO$_2$ for -OH stretching vibration. In Akualite A420, other peaks was found at 3,018 and 2,922 cm$^{-1}$ of C-H bonds and -CH$_2$ groups (Sowmya and Meenakshi, 2013), 1,601 cm$^{-1}$ of styrene ring C-C bonds (Lazar et al., 2014), 1,481 cm$^{-1}$ of methyl group of quaternary nitrogen (Wołowicz and Hubicki, 2009; Gandhi et al., 2011), and 1,039 and 1,128 cm$^{-1}$ of benzene ring (Lee et al., 2003). For Amine-P-SiO$_2$, FTIR peaks were found at 1,480 cm$^{-1}$ of amine group, which is similar to Akualite A420. The other characteristic peaks of organic and silica were observed at wavenumbers of 3,420 (-OH), 2,930 (C-H), 1,650 (C=C), 1,030-1,130 (Si-O-Si), and 650-840 cm$^{-1}$ (Si-H) (Ibrahim et al., 1980), which indicates the successful grafting of amine groups onto the surface of porous P-SiO$_2$ material.

![Figure 1. FTIR spectra of Amine-P-SiO$_2$ and ion exchange resin (Akualite A420)](image-url)

The BET adsorption - desorption isotherms of nitrogen at 77 K for P-SiO$_2$ support and Amine-P-SiO$_2$ material are plotted in Figure 2, which follow type IV IUPAC isotherm for mesoporous materials. The BET surface area of supports amine-loaded materials is summarized in Table 1. There was a remarkable increase of 20 times in surface area of silica material after treated with HF (i.e., from 32.5
(SiO$_2$) to 675.8 m$^2$/g (P-SiO$_2$)). This proves that HF treatment is a very effective method for generation of mesoporous silica from commercial silica. After loading with amine, the surface area of Amine-P-SiO$_2$ slightly decreased to 625.7 m$^2$/g; however, it was still 18 times higher than that of Amine-SiO$_2$.

Figure 2. Nitrogen adsorption - desorption isotherm of P-SiO$_2$ and Amine-P-SiO$_2$

Table 1. Surface area and amine loading of silica materials

| Sample            | Surface area (m$^2$/g) | Amine loading (%) |
|-------------------|------------------------|-------------------|
| SiO$_2$           | 32.5                   | -                 |
| P-SiO$_2$         | 675.8                  | -                 |
| Amine-SiO$_2$     | 34.6                   | ~ 1.6             |
| Amine-P-SiO$_2$   | 625.7                  | ~ 6.4             |

Figure 3 presents the thermogravimetric curves of Amine-P-SiO$_2$ in temperature range of 30-1,000 °C. The mass loss can be divided into three stages. The first mass loss of ~16% in range of 30-200 °C with peak at 50-100 °C was the loss of water and highly volatile compounds. The second mass loss of ~34.6% in range of 200-430 °C was attributed to the hydroxyl group dehydration and other volatile compounds loss. The major loss of amine group (6.4%) was observed in the third stage with temperature range of 450-620 °C. The amine contents of P-SiO$_2$ and SiO$_2$ were then calculated to be 6.4% and 1.6%, respectively (Table 1). This was due to the higher surface area of P-SiO$_2$ support or silicon density on silica support surface as compared to SiO$_2$ material.

Figure 3. Thermogravimetric curves of Amine-P-SiO$_2$

3.2 Adsorption tests of nitrate removal

The nitrate removal test using amine-loaded silica materials was evaluated using batch adsorption experiment. The effect of environmental conditions such as initial solution pH, concentration, dosage, and temperature on the adsorption capacity was investigated. When pH increased from 2 to 8 (Figure 6), nitrate removal capacity was higher than 18 mg/g and reached maximum capacity of 19 mg/g at pH 5. However, the capacity of nitrate removal decreased significantly to 15 mg/g at pH 10. This could be explained by the effect of solution pH value on the surface charge of adsorbent and nitrate species. Under acidic condition, NO$_3^-$ ions tend to combine with H$^+$ ions in solution to form HNO$_3$, which
reduces the electrostatic attraction between nitrate and positively charged functional groups on the surface of Amine-P-SiO$_2$ adsorbent (Song et al., 2016). Meanwhile, the poor adsorption capacity of Amine-P-SiO$_2$ under basic condition could be due to the competition of OH$^-$ and nitrate ions for the same adsorption sites (Battas et al., 2019). When the pH of the solution increases, many OH$^-$ ions exist, which can make the adsorbent surface more negatively charged, thereby hindering the ion exchange of NO$_3^-$ on the adsorption sites of material by electrostatic repulsion.

**Figure 4.** SEM images of (a) P-SiO$_2$ and (b) Amine-P-SiO$_2$, (c) EDS spectrum, and (d, e, f, and g) SEM mapping images of Amine-P-SiO$_2$ for Si, O, C, and N elements

**Figure 5.** XRD pattern of P-SiO$_2$ and Amine-P-SiO$_2$ materials

The effect of Amine-P-SiO$_2$ dosage on nitrate adsorption is shown in Figure 7. It is obvious that adsorption efficiency continuously increased with the increase of the adsorbent dosage. However, the rapid increase was only observed for low dosage range of 0.1-0.2 g/L and the efficiency then increased slowly in dosage range of 0.2-2.0 g/L. On the other hand, the adsorbent capacity of Amine-P-SiO$_2$ reached the highest value of 66.0 mg/g at the lowest dosage of 0.1 g/L, but decreased to 10 mg/g...
at the highest dosage of 2.0 g/L. Since there was limited nitrate ion in the solution, adding more amount of adsorbent would result in a decrease of adsorption capacity and an adsorbent dosage of 0.6 g/L with high adsorption capacity and efficiency was chosen for further experiments.

**Figure 7.** Effect of Amine-P-SiO$_2$ dosage on nitrate removal (Condition: temperature: 25±0.5 °C, pH 5, nitrate concentration: 15 mg/L)

The comparison on nitrate removal of Amine-P-SiO$_2$, Amine-SiO$_2$, and anion exchange resin (Akualite A420) is presented in Figure 8(a). Amine-P-SiO$_2$ showed a superior adsorption capacity of 32.5 mg/g, which was 1.71 and 1.31 times higher than that of Akualite A420 and Amine-SiO$_2$, respectively. The higher nitrate adsorption capacity of Amine-P-SiO$_2$ confirmed the successful and effective modification of SiO$_2$ surface by HF solution. However, the loading and utilization of amine was not effective and needed to be optimized in the future since the surface area and amine loading of Amine-P-SiO$_2$ was around 20 and 4 times, respectively, higher than those of Amine-SiO$_2$. Moreover, both amine-loaded silica materials had higher adsorption capacity than Akualite A420, proving the strong affinity of nitrate (from the solution) and amine group (on the surface of silica materials). The used Amine-P-SiO$_2$ and Akualite A420 were then regenerated using 0.1 M HCl solution and applied for durability test. As demonstrated in Figure 8(b), Amine-P-SiO$_2$ was more stable than Akualite A420 and the decline in adsorption of these materials was 20% and 50%, respectively, after 10 cycles of adsorption-desorption. This is a notorious advantage of Amine-P-SiO$_2$ as compared to Akualite A420 ion exchange resin for commercialization of the product in the future

**3.3 Adsorption isotherms, thermodynamics, and kinetics**

Figure 9 illustrates the adsorption isotherms using Amine-P-SiO$_2$. Langmuir and Freundlich models were applied to understand the adsorption of nitrate. The calculated parameters for these two models are summarized in Table 2. As seen in Table 2, the Langmuir model fit better with the experimental data due to its higher correlation coefficients of 0.9849-0.9992 and smaller $\chi^2$ values of 10.215-23.280. The maximum capacities ($Q_{\text{max}}$) for nitrate ion were then calculated to be 45.2-99.0 mg/g in temperature range of 288-318 K, respectively. These results indicated that nitrate removal mainly follows monolayer adsorption on Amine-P-SiO$_2$ adsorbent surface (Yousef et al., 2011). The adsorption process would be the chemical interaction of amine functional groups on the surface of the material and the nitrate ion. This also suggests that the improvement of the adsorption capacity in the future should be focused on the increase of surface amine groups on the material.
Figure 8. (a) Nitrate sorption capacities of different materials and (b) Cyclic tests for Amine-P-SiO$_2$, and Akualite-A420 (Condition: temperature: 25±0.5 °C, pH 5, dosage: 0.6 g/L, nitrate concentration: 50 mg/L)

Figure 9. Adsorption isotherms at different temperatures (Condition: pH 5, Amine-P-SiO$_2$ dosage: 0.6 g/L)

Table 2. Parameters of Langmuir and Freundlich adsorption isotherms

| Isotherm model | Model parameters | Adsorption temperature (K) |
|---------------|------------------|---------------------------|
|               |                  | 288 | 293 | 298 | 303 | 308 | 313 | 318 |
| Langmuir      | $Q_{max}$ (mg/g) | 45.249 | 53.476 | 57.471 | 70.922 | 74.627 | 86.957 | 99.010 |
|               | $K_L$ (L/mg)    | 0.034 | 0.029 | 0.036 | 0.028 | 0.033 | 0.030 | 0.029 |
|               | $R^2$           | 0.9911 | 0.9849 | 0.9979 | 0.9905 | 0.998 | 0.999 | 0.9992 |
|               | $\chi^2$       | 10.215 | 15.918 | 11.289 | 12.206 | 16.067 | 20.244 | 23.280 |
| Freundlich    | $K_f$ ((mg/g)(L/mg)$^n$) | 3.215 | 3.181 | 4.146 | 3.806 | 4.876 | 4.999 | 5.442 |
|               | $n$             | 1.853 | 1.759 | 1.837 | 1.693 | 1.786 | 1.716 | 1.685 |
|               | $R^2$           | 0.980 | 0.980 | 0.968 | 0.989 | 0.979 | 0.981 | 0.979 |
|               | $\chi^2$       | 5.149 | 4.851 | 15.499 | 38.635 | 40.808 | 75.475 | 212.39 |
As observed in Figure 9 and Table 2, nitrate removal increased with the increase of temperature. Thermodynamic parameters of nitrate adsorption on Amine-P-SiO₂ at different temperatures are showed in Table 3. The values of ΔG° < 0, ΔH° < 0, and ΔS° < 0 indicated that nitrate adsorption is an spontaneous but endothermic process (Milmile et al., 2011) and the adsorption increases the disorder and randomness of the system. Moreover, the adsorption of nitrate using Amine-P-SiO₂ was more favorable at higher temperatures where ΔG° value decreased and became more negative (Katal et al., 2012).

Table 3. Thermodynamic parameters of nitrate adsorption on Amine-P-SiO₂ at different temperatures (nitrate concentration: 15 mg/L)

| ΔH° (kJ/mol) | ΔS° (kJ/mol) | ΔG° (kJ/mol) | R² |
|--------------|--------------|--------------|----|
| 18.852       | 124.5188     | -17.632      | 293 |
| 18.694       | 124.5188     | -17.632      | 303 |
| 19.500       | 124.5188     | -18.877      | 308 |
| 20.745       | 124.5188     | -19.500      | 318 |

4. CONCLUSIONS

A new Amine-P-SiO₂ material was successfully synthesized using a simple and low-cost route. The surface modification of silica precursor by HF reaction and amine loading was demonstrated by material characterization using TGA, XRD, FT-IR, BET, SEM and EDS-mapping. Results showed that Amine-P-SiO₂ had high nitrate adsorption of 32.5 mg/g (1.71 times higher than Akualite A420) and followed Langmuir isotherm as chemical adsorption. Amine-P-SiO₂ could be a new and very potential material for water and advanced wastewater treatment applications.

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REFERENCES

Araújo R, Castro ACM, Santos Baptista J, Fiuza A. Nanosized iron based permeable reactive barriers for nitrate removal - Systematic review. Physics and Chemistry of the Earth. Parts A/B/C 2016;94:29-34.

Bahadori E, Compagnoni M, Tripodi A, Freyria F, Armandi M, Bonelli B, Ramis G, Rossetti I. Photoreduction of nitrate from waste and drinking water. Materials Today: Proceedings 2018;5(9, Part 2):17404-13.

Banu HT, Meenakshi S. Synthesis of a novel quaternized form of melamine - formaldehyde resin for the removal of nitrate from water. Journal of Water Process Engineering 2017;16:81-9.

Battas A, Gaidouni AE, Ksakas A, Kherbeche A. Adsorption study for the removal of nitrate from water using local clay. The Scientific World Journal 2019;2019:1-10.

Bhatnagar A, Sillanpää M. A review of emerging adsorbents for nitrate removal from water. Chemical Engineering Journal 2011;168(2):493-504.

Duranoglu D, Trochimczuk AW, Beker U. Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer. Chemical Engineering Journal 2012;187:193-202.

Gandhi MR, Kalaivani G, Meenakshia S. Sorption of chromate and fluoride onto duolite a 171 anion exchange resin - a comparative study. Elixir Pollution 2011;32:2034-40.

Garcia-Segura S, Lanzarini-Lopes M, Hristovski K, Westerhoff P. Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications. Applied Catalysis B: Environmental 2018;236:546-68.

Hamoudi S, Saad R, Belkacemi K. Adsorptive removal of phosphate and nitrate anions from aqueous solutions using ammonium-functionalized mesopo-rous silica. Industrial and Engineering Chemistry Research 2007;46(25):8806-12.

Ibrahim DM, El-Hemaly SA, Abdel-Kerim FM. Study of rice-husk ash silica by infrared spectroscopy. Thermochimica Acta 1980;37(3):307-14.

Kalaruban M, Logathanathan P, Shim WG, Kandasamy J, Naidu G, Nguyen TV, Vigneswaran S. Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies. Separation and Purification Technology 2016;158:62-70.

Katal R, Baei MS, Rahmati HT, Esfandian H. Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk. Journal of Industrial and Engineering Chemistry 2012;18(1):295-302.

Lazar L, Bandrabur B, Tataru Fărmuş R-E, Drobotă M, Bulgariu L, Gutt G. FTIR analysis of ion exchange...
resins with application in permanent hard water softening. Environmental Engineering and Management Journal 2014;13(9):2145-52
Lee B, Bao L-L, Im H-J, Dai S, Hagaman EW, Lin JS. Synthesis and characterization of organic-inorganic hybrid mesoporous anion-exchange resins for perrenate (ReO₄⁻) anion adsorption. Langmuir 2003;19(10):4246-52.

Loganathan P, Vigneswaran S, Kandasamy J. Enhanced removal of nitrate from water using surface modification of adsorbents: A review. Journal of Environmental Management 2013;131:363-74.

Martinez J, Ortiz A, Ortiz I. State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates. Applied Catalysis B: Environmental 2017;207:42-59.

Milmile SN, Pande JV, Karmakar S, Bansiwal A, Chakrabarti T, Biniwale RB. Equilibrium isotherm and kinetic modeling of the adsorption of nitrates by anion exchange Indion NSSR resin. Desalination 2011;276(1):38-44.

Nujić M, Milinković D, Habuda-Stanić M. Nitrate removal from water by ion exchange. Croatian Journal of Food Science and Technology 2017;9(2):182-6.

Phan PT, Nguyen TT, Nguyen NH, Padungthon S. Triamine-bearing activated rice husk ash as an advanced functional material for nitrate removal from aqueous solution. Water Science and Technology 2018;79(5):850-6.

Saad R, Belkacemi K, Hamoudi S. Adsorption of phosphate and nitrate anions on ammonium-functionalized MCM-48: Effects of experimental conditions. Journal of Colloid and Interface Science 2007;311(2):375-81.

Safia H, Abir EN, Maissa B, Khaled B. Adsorptive removal of nitrate and phosphate anions from aqueous solutions using functionalised SBA- 15: Effects of the organic functional group. The Canadian Journal of Chemical Engineering 2012;90(1):34-40.

Singh NB, Nagpal G, Agrawal S, Rachna. Water purification by using Adsorbents: A Review. Environmental Technology and Innovation 2018;11:187-240.

Song W, Gao B, Xu X, Wang F, Xue N, Sun S, Song W, Jia R. Adsorption of nitrate from aqueous solution by magnetic amine-crosslinked biopolymer based corn stalk and its chemical regeneration property. Journal of Hazardous Materials 2016;304:280-90.

Sowmya A, Meenakshi S. Removal of nitrate and phosphate anions from aqueous solutions using strong base anion exchange resin. Desalination and Water Treatment 2013;51(37-39):7145-56.

Thanh NT. Amine-bearing activated rice husk ash for CO₂ and H₂S gas removals from biogas. KKU Engineering Journal 2016;43(S3):396-8.

Tugaoen HON, Garcia-Segura S, Hristovski K, Westerhoff P. Challenges in photocatalytic reduction of nitrate as a water treatment technology. Science of the Total Environment 2017;599:1524-51.

Tyagi S, Rawtani D, Khatri N, Tharmavaram M. Strategies for nitrate removal from aqueous environment using nanotechnology: A Review. Journal of Water Process Engineering 2018;21:84-95.

Wołowicz A, Hubicki Z. Sorption of palladium(II) complexes onto the styrene-divinylbenzene anion exchange resins. Chemical Engineering Journal 2009;152(1):72-9.

Yousef RI, El-Eswed B, Ala’a H. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies. Chemical Engineering Journal 2011;171(3):1143-9.