

# Removal of Nitrate Using Synthetic Nano Composite ZnO/Organoclay: Kinetic and Isotherm Studies

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**ABSTRACT:** This study was conducted to investigate organoclay prepared using montmorillonite clay with zinc oxide (ZnO) nanoparticles and a long-chain organic surfactant hexadecyltrimethyl ammonium bromide for the removal of nitrate ion from aqueous solutions. Adsorbents were evaluated by X-Ray Diffraction (XRD), Fourier Transform Infra Red (FT-IR), Transmission Electron Microscopy, Brunauer-Emmett-Teller, Emission Scanning Electron Microscopy, Energy Dispersive X-ray (EDX) spectroscopy devices and adsorption isotherms of nitrate ion on the best adsorbent were measured at the aqueous concentrations of 40 to 150 mg/25 mL. Activated montmorillonite-ZnO showed a much higher adsorption capacity than other materials. The laminated ZnO and modified surfactant enhanced nitrate ion, thus retaining silicates capacity, montmorillonite (17.24 mg/g) < montmorillonite by laminated ZnO (54.05 mg/g) < montmorillonite modified by surfactant (86.95 mg/g) < montmorillonite loaded by ZnO and surfactant (119.92 mg/g). The adsorbents for the removal of nitrate ion were studied and then regenerated with HCl solution (0.1 M) to be reused in adsorption. Adsorption data of nitrate ion could be interpreted using Langmuir isotherm and pseudo-second-order kinetic model. Therefore, activation of Montmorillonite/ZnO could be used as a suitable adsorbent to separate nitrate ion from wastewater and groundwater.

**KEYWORDS:** Removal; Nitrate; Nano composite; ZnO/montmorillonite; Kinetic; Isotherm.

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## INTRODUCTION

A primary environmental issue is the quality of surface water, sediments, and groundwater. Water quality covers the biological, physical, radiological, and chemical characteristics that are determined due to different human, industrial, and agricultural uses [1, 2]. These physical, chemical or biological components that affect water quality are known as water quality parameters (phosphate, arsenic, sediments, etc.) [3]. Majority of these parameters is calculated as concentration (in milligrams) of contaminants in 1 L of water (mg/L) or (ppm). Water is mostly contaminated by a range of tenacious organic chemicals from dependent and independent sources [4], such as pesticides, herbicides, and hormones [5]. In recent years, nitrate, which is a contaminate of drinking water produced using agricultural fertilizers, fossil fuel combustion, etc., has grown drastically. The recommended nitrates ion level in drinking water is below 50 ppm; especially for kids because of their immature digestive system [6]. The most commonly used treatment methods for the elimination of nitrate are chemical denitrification [7], ion exchange [8], reverse osmosis [9], and adsorption by some materials, e.g., activated carbon [10], chitosan derivations [11] nanoscale zero valent iron [12-16] and bimetallic nanoparticles [17, 18]. The technology that is related to adsorption with no chemical degradation is of high interest due to its efficiency and it can be successfully used to eliminate various types of inorganic anions such as fluoride [19, 20], bromide [21], and nitrate [22, 23] from waters. Today, clay minerals have an important role in modern industry; they are widely used in a range of applications such as polymer nano composites [24, 25], catalysts [26-28], electrochemical sensors [29], adsorbents, and ion exchangers [30, 31]. Clay minerals are a kind of sedimentary rocks [32] with a lot of variety like kaolinite, illite, montmorillonite, and other aluminum silicates [33, 34]. Montmorillonite is a complex hydrated silicate of Al, Mg, and Na [35, 36]. Clays are widely used because of their specific properties such as high degree of swelling, high cation exchange capacity, and strong adsorption capacity. Clays have some advantages in addition to their unique physical and chemical properties. They are locally available, recyclable, and environmentally friendly and they are also not harmful to human health. As an environmental use of clay minerals,

they are used to remove heavy metal ions, nitrate and perchlorate ions from wastewater [37]. Zinc oxide (ZnO) surface modification of clay minerals is demanded significantly [38]. Several methods can be used for the surface modification of clay minerals, such as cation exchange reaction, solid-state reaction, grafting of organic compounds, the intercalation of organic cations in the interlayer region of the clay, and sol-gel process [39-41]. The arrangements of organic cations within the montmorillonite interlayers are different depending on the length of organic ion alkyl chain. These arrangements may be in bilayer, monolayer, paraffin-type monolayer, and paraffin-type bilayer forms [42]. In the present study, the changes in the structure of montmorillonite clay with ZnO and a long-chain organic surfactant hexadecyltrimethylammonium bromide (HDTMAB) for the removal of nitrate ion from water were investigated. These changes on the clay surface were studied using X-ray diffraction, FE-SEM, TEM, and FT-IR spectroscopy. The objective of this research was to investigate montmorillonite clays capability to remove nitrate ion from aqueous solution under different experimental conditions including initial concentration of nitrate, contact time, solution pH, adsorbent weight, and surfactant content. Source water contaminated with nitrates is associated with spring water in the area of chemistry that its concentration is 120 mg/25mL.

## EXPERIMENTAL SECTION

### *Chemical material*

Calcium montmorillonite (94%) was collected from Saraian Bentonite Mine. Hexadecyltrimethylammonium bromide (HDTMAB),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{NH}_4\text{OH}$  were purchased from Merck Co. (Germany). All chemicals used were of analytical grade. Distilled water was also used for the experiments.

### *Preparation of Montmorillonite Clay (MC)*

MC was washed using distilled water and was separated from sand and  $\text{SiO}_2$  using sieves (mesh 800). MC was completely dispersed in concentrated sulfuric acid solution by stirring vigorously for 72 h. Then, it was rinsed with diluted ammonia and deionized water with the adjusted pH of 7. The suspension was centrifuged and the upper solution was decanted off, and the residue was calcined at  $900^\circ\text{C}$  for 2 h and at  $400^\circ\text{C}$  for 4 h.

The sample was then pulverized and sieved to a very uniform powder.

#### **Modification of MC by laminating ZnO nanoparticles (Montmorillonite/ZnO (MZ))**

MC (50 g) was added to 1000 ml of zinc nitrate solutions with different concentrations (4 to 16 g) and the resultant suspension was dissolved. Subsequently, 1 M sodium hydroxide solution was added drop wise into the solution in order to obtain an alkaline medium (pH ~ 12.50) [43]. Finally, the sample was rinsed off and centrifuged using distilled water to remove any non-adhesive impurities, and then it was calcinated in a furnace at 400°C for 4 h. The sample was removed from the furnace and sieved to 10 µm sieves.

#### **Activation of MZ and MC with HDTMB (AMZ and AMC)**

MC and MZ were added to a solution containing different HDTMB surfactants levels (4, 6, and 8% w/w) separately and were vigorously stirred at 70°C for 24 h. HDTMAB exchanged montmorillonite was prepared using a conventional ion exchange reaction of the montmorillonite and an aqueous solution of HDTMAB bromide. To remove bromide ion, the samples were washed with a solution of double distillation water and alcohol (ratio 1:1 v/v). The resulting solids were separated by centrifugation and were washed using deionized water for several times, and dried at 50°C for 3 days. To prepare a uniform adsorbent, the sample was then sieved to 10 µm sieves. In total, 11 adsorbents were prepared with the ratios as shown in Table 1.

#### **Characterization process and instrumentals**

Characterization processes were carried out on the samples. X-Ray diffraction (XRD) pattern was measured by a “Philips X’pert”, using Cu K $\alpha$  radiation at 40 kV and 30 mA. “Zeiss-Sigma VP-500 with Oxford Instrument” Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray spectroscopy (EDAX) for samples were studied. “Zeiss-EM10C-100 KV, Germany” Transmission Electron Microscopy (TEM) was used to characterize the microstructure and morphologies of the samples. Using Brunauer-Emmett-Teller (BET) porosity analyser JW-BK122W (Beijing JWGB Sci. & Tech. Co., Ltd.), the specific surface area

was calculated using the single-point method ( $p/p_0=0.2$ ). Fourier Transform Infra Red (FT-IR) spectroscopy was performed on a Thermo Nicolet FT-IR spectrometer (America) using KBr powder and UV-Vis Spectrophotometer (Cary-100-UV-Vis spectrophotometer, Varian) was used to study the adsorption of nitrate ion with modified montmorillonite.

#### **Adsorption of nitrate ion**

##### *Batch study of nitrate ion adsorption*

The ability of the synthesized montmorillonites (MC, MZ<sup>(2-8)</sup>, A<sup>(4-8)</sup> MC and A<sup>(4-8)</sup> MZ<sup>(2-8)</sup>) to be adsorbed was evaluated by measuring the adsorption of the nitrate solution. In a typical procedure, different amounts of montmorillonite samples (0.4, 0.6, 0.8, 1 and 1.2 g) were mixed with 25 mL of the solution of different nitrate ion concentrations (40, 60, 80, 100, 120, and 150 mg/25mL) with an initial pH value of about 7. The suspensions were prepared at room temperature with continuous stirring at 150 rpm and removal process was measured for 1 h with 10 min intervals. The nitrate ion concentration in the aqueous phase was prepared by dissolving 8145.16 mg from KNO<sub>3</sub> salt in 1000 mL double distillation water. All samples were washed three times using double distillation water. The removal of nitrate ion was estimated using a UV-Vis spectrophotometer at 220 nm after being centrifuged. The nitrate ion adsorption by montmorillonite was calculated using Eq. (1):

$$q_e = (C_i - C_e)V/m \quad (1)$$

Where  $q_e$  is the nitrate ion adsorption (mg/g),  $C_i$  is the initial concentration (mg/L),  $C_e$  is the equilibrium concentration (mg/L),  $V$  is the nitrate ion solution volume (L), and  $m$  is the quality of sorbents (g). The results were mean of three independent measurements.

##### *Recovery of adsorbents*

Montmorillonite samples saturated by nitrate, in three stages can be recycled. Montmorillonites were washed with acidic solutions and the pH was adjusted to 7 by leaching and the activated surfactant process was added to a solution containing HDTMB surfactant, then it was vigorously stirred at 70°C for 24 h and dried at 50°C for 3 days [44]. The concentrations of the nitrate ion solution were obtained by measuring absorbance at 220 nm using UV-Vis spectrophotometer. This method of nitrate ion

**Table 1: Specifications of absorbers at this work.**

Identification Code	Component Composition	Symbol
MC	Montmorillonite Clay	Base
MZ <sub>2</sub>	MC +ZnO 97.8%+2.2%	
MZ <sub>4</sub>	MC +ZnO 95.6%+4.4%	
MZ <sub>6</sub>	MC +ZnO 93.4%+6.6%	MZ-OPTIMUM
MZ <sub>8</sub>	MC +ZnO 91.2%+8.8%	
A <sub>4</sub> MZ <sub>6</sub>	HDTMAB 4%, (MC +ZnO) 92%	
A <sub>6</sub> MZ <sub>6</sub>	HDTMAB 6%, (MC +ZnO) 94%	AMZ-OPTIMUM
A <sub>8</sub> MZ <sub>6</sub>	HDTMAB 8%, (MC +ZnO) 92%	
A <sub>4</sub> MC	HDTMAB 4%,MC96%	
A <sub>6</sub> MC	HDTMAB 6%,MC94%	
A <sub>8</sub> MC	HDTMAB 8%,MC92%	AMC-OPTIMUM

adsorption determination was used to compare these sorbents and reuse condition in acidic to saturation investigation.

## RESULTS AND DISCUSSION

### ZnO lamination on MC

The results of ZnO loading on montmorillonite with different concentrations (2.2 to 8.8% w/w) for the removal of nitrate ion from aqueous water were investigated. ZnO loading amount increases with the increases of the primary ZnO percentages. The maximum loaded amount of ZnO on MC (~1.62 meq) for MZ<sub>6</sub> and (~2.17 meq) for MZ<sub>8</sub> was observed, thus showing bilayer formation surfactant on the external surface of montmorillonite. Simultaneously, adsorption studies and characterization have been performed on MZ<sub>(2-8)</sub> and A<sub>(4-8)</sub>MZ<sub>(2-8)</sub> adsorbents.

### Surfactant configuration on MC and MZ

The results of surfactant loading on montmorillonite are given as supplementary data MC and MZ, meaning that the surfactant loading amount increases as the initial surfactant percentages increase. The maximum sorption of 8% (w/w) was obtained for HDTMAB. The maximum loaded amount of HDTMAB on MC (~0.186 meq) and on MZ (~0.160 meq) was observed, thus showing bilayer formation of surfactant on the montmorillonite external surface. Thus, adsorption studies and characterization were performed on adsorbents with different percentages of surfactant A<sub>(4-8)</sub>-MC and A<sub>(4-8)</sub>MZ<sub>(2-8)</sub>.

### Material characterization

Identification of clays before and after treatment with ZnO nanoparticles and hexadecyltrimethyl ammonium bromide was documented. X-Ray Diffraction (XRD) data were obtained using Cu- $\alpha$  radiation source in the range of 2 $\theta$  Bragg angle: 20-70°. The X-ray patterns of sample powders MC, MZ<sub>6</sub>, A<sub>8</sub>MC and A<sub>6</sub>MZ<sub>6</sub> products are as shown in Fig. 1.

The diffraction data show that the highest peak intensity for montmorillonite (2 $\theta$ =19.7°) is in line with a spacing of 4.5 Å. The comparison of the diffraction patterns of ZnO and surfactant-modified from montmorillonite with their corresponding unmodified forms shows the integrity in the structure of the material before and after ZnO and surfactant treatment. Using Scherrer's formula (Equation 2), the powder size of the products was calculated by X-ray line broadening technique.

$$D = 0.9\lambda / \beta \cos \theta \quad (2)$$

Where D is the grain diameter,  $\beta$  is the half-intensity width of the relevant diffraction,  $\lambda$  is the X-ray wavelength, and  $\theta$  is the diffraction angle. The results showed that the number of phases and particle size of montmorillonite is modified by ZnO nanoparticles and HDTMAB surfactant. By comparing diffraction patterns of montmorillonite (MC) and modified montmorillonite with ZnO nanoparticles (MZ<sub>6</sub>), coating montmorillonite with ZnO nanoparticles has been observed to cause

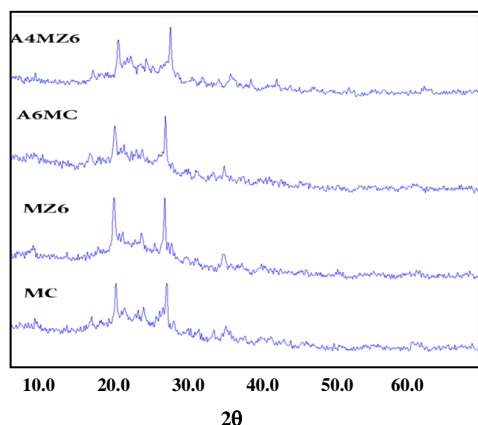


Fig. 1: XRD patterns of samples MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub>.

decrease in crystalline size from 55 to 47 nm. By comparing the diffraction patterns for surfactant modified forms of montmorillonite-ZnO nanoparticles (A<sub>6</sub>MZ<sub>6</sub>) and unmodified forms (MZ<sub>6</sub>) shows that the addition of HDTMAB to montmorillonite increased crystalline size from 47 to 49 nm and the addition of HDTMAB to montmorillonite (A<sub>8</sub>MC) decreased crystalline size from 55 to 52 nm. The chemical composition of the used materials has been investigated for metal ions Zn, Na, Al, K, Si, O, and C using EDS (as supplementary data A<sub>6</sub>MZ<sub>6</sub>). The results obtained by EDS analysis conform with the weight percentage of the initial rate and composition of these metals. FE-SEM micrograph of MC shows the spherical shape crystals together with aggregated particles and the SEM micrograph of montmorillonite shows the homogeneous flakes such as crystals micrograph MZ<sub>6</sub>. It also shows the crystal hexagonal wurtzite type [45] of the presence of ZnO on bar layers montmorillonite (Fig. 2). The addition of HDTMAB to montmorillonite and MZ<sub>6</sub> caused flat layers hexagonal to be aggregated. TEM observations as shown in Fig. 2 showed that the prepared products MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> have nano-size crystals. Fig. 3 shows the FT-IR spectra of four adsorbents. Silicates show a typical infrared spectroscopic pattern because of the internal vibrations of Si-O, Al-O tetrahedron which is not sensitive to other structural vibrations and is the primary unit of the structure. Robust vibration bands at 950 to 1250 and 420 to 500 cm<sup>-1</sup> are ascribed to (Si, Al)-O stretching and bending modes, respectively [42]. Structural stability of these samples is well presented

by the appearance of major peaks at almost the same position in all adsorbents. In fact, two intense bands around 2850 and 2920 cm<sup>-1</sup> [42] show the surfactant loading on A<sub>8</sub>MC and A<sub>6</sub>MZ<sub>6</sub>. The vibration bands are at 479 cm<sup>-1</sup> as regards to Zn-O in MZ<sub>6</sub> and A<sub>6</sub>MZ<sub>6</sub>. The results can be obtained by comparing the FT-IR spectrum between surfactant and composite produced by the interaction of montmorillonite and surfactant in A<sub>8</sub>MC, and the composite obtained from montmorillonite - surfactant and zinc oxide (A<sub>6</sub>MZ<sub>6</sub>). First, there was no proper interaction between surfactant and montmorillonite. The absence of indices in FT-IR spectrum is very poor in the stretching vibration area associated with the aliphatic surfactant chain in the 2850 and 2910 cm<sup>-1</sup> region. By adding zinc oxide to the composite, there is a great interaction between the surfactant and the montmorillonite, and this interaction can be seen by varying the stretching vibrational value of the methylene and methyl groups of surfactant from 2848 cm<sup>-1</sup> in the surfactant spectrum to 2850 cm<sup>-1</sup> in the composite A<sub>6</sub>MZ<sub>6</sub>. Secondly, the effect of interaction in A<sub>6</sub>MZ<sub>6</sub> by the increase in nitrate ion absorption from the proper performance of surfactants in the composite structure is indicated.

The specific surface areas for samples MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> were 151, 88, 45, and 168 m<sup>2</sup>/g, respectively when measured using BET. It is obvious that the surface area of modified montmorillonite with surfactant and ZnO A<sub>6</sub>MZ<sub>6</sub> increased when compared with unmodified clays.

### Nitrate ion adsorption optimization

#### Effect of nitrate ion solution pH

The effect of pH environment in the range of 2-10 in the absorbing nitrate solution with a concentration of 120 mg/25mL witnesses were examined. The appropriate nitrate ion solution pH was adjusted with NaOH 0.1 N and HCl 0.1 N. Montmorillonites adsorbent was combined with the solution at room temperature with continuous stirring for 30 min. Results in Fig. 4 show decrease in pH from 2 to 10 for all the samples. This can be due to the fact that decrease in pH (above 7) is equal to the hydroxide ions increase within the solution and the presence of hydroxide ion prevents the connection between nitrate ions on adsorption sites on montmorillonites [42]. On the other hand, alkaline pH

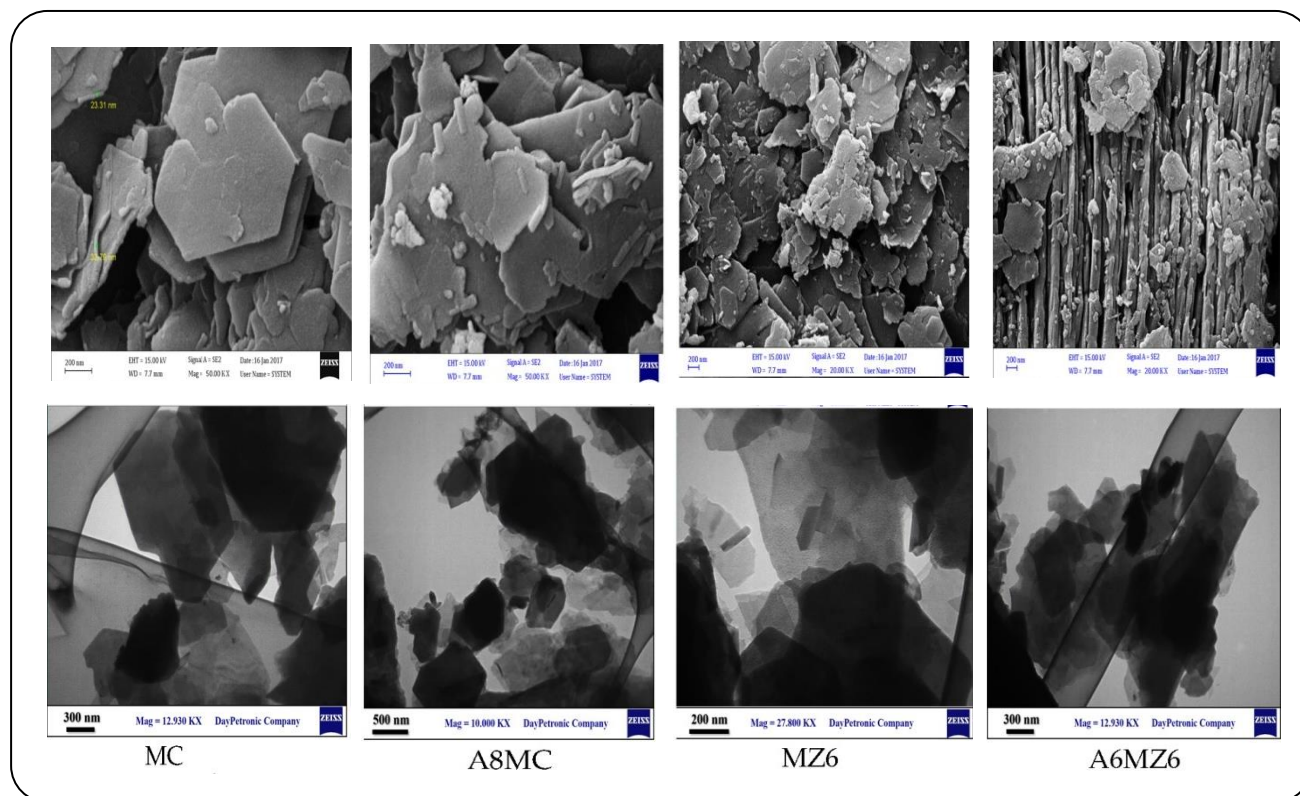


Fig. 2: FE-SEM & TEM images of samples MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub>.

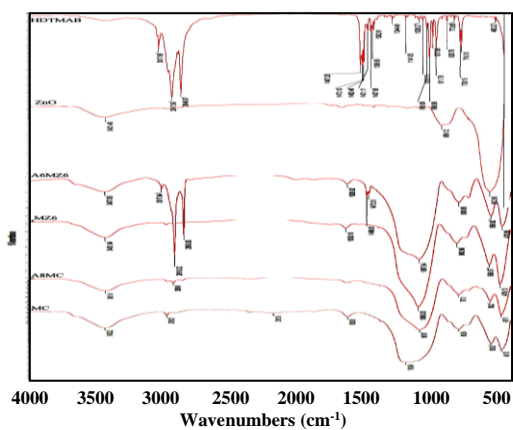


Fig. 3: FT-IR spectra of samples ZnO, HDTMAB, MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub>.

(8 to 10) may restrict the exchange of nitrate ion with hydroxide. But at pH 2, the most nitrate ion adsorption was observed, but with increase in pH up to 7, decrease in nitrate ion adsorption was observed with minimum change in adsorption at A<sub>6</sub>MZ<sub>6</sub> adsorbent. Therefore, maximum adsorption was reported to be around neutral pH, because it causes less pollution in the environment [42].

#### Effects of sorbents weight

Effects of adsorbent weight for samples MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> were investigated. With increase in the amount of adsorbents from 0.4 to 1.2 g, the adsorption of nitrate ion increased for all the adsorbents. This can show the dependence of adsorption on availability of binding sites for nitrate ion as shown in Fig. 5. Hence, increase of adsorbent weight leads to increase in nitrate ion adsorption and the peak of adsorption is observed with 1 g sorbents for both samples, but increase more than 1 g is not logical and it decreased nitrate ion removal because montmorillonite particles stick together.

#### Effects of contact time on adsorption

The effect of contact time on nitrate ion adsorption showed an increase in nitrate ion adsorption with an increase in contact time until equilibrium is reached. The best adsorption percentage for all the adsorbents was at 60 min, but on the other hand when it passes 60 min, the increase in adsorption is very small (Fig. 6). The initial nitrate ion concentration changes shown represent low ability to eliminate nitrate ion for MC and is not

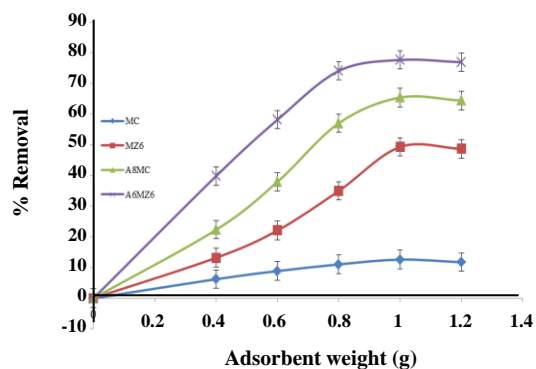


Fig. 4: Effect of adsorbent amount on nitrate ion adsorption, pH of solution 7, 25ml solution contain 120 mg nitrate ion, equilibration time 30 min, (SD= ±3).

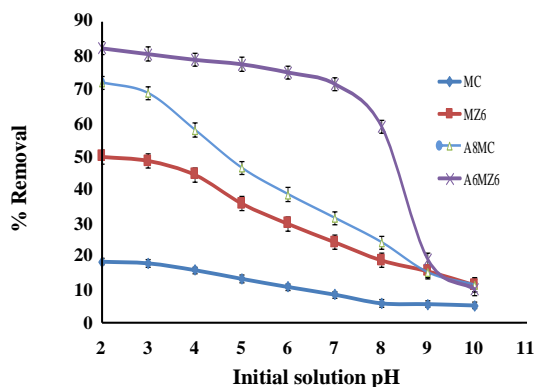


Fig. 5: Effect of aqueous phase pH on nitrate ion adsorption percentage by MC, MZ<sub>6</sub>, A<sub>8</sub>MC and A<sub>6</sub>MZ<sub>6</sub>, weight of adsorbent 1.0 g, 25 ml solution containing 120 mg nitrate ion, equilibration time of 30 min (SD= ±3).

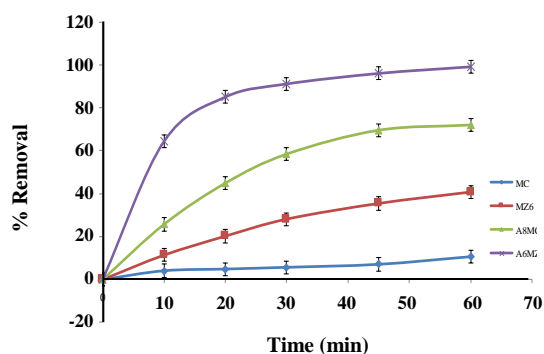


Fig. 6: Effect of contact time on nitrate ion adsorption percentage by different adsorbents, pH solution 7, 25 ml solution containing 120 mg nitrate ion, and weight of adsorbent at 1.0 g (SD= ±3).

a significant adsorbent. Modification of montmorillonites with ZnO nanoparticles (MZ<sub>6</sub>) improved the adsorption sites with the removal of nitrate ion. Loading HDTMAB surfactant on unmodified and modified montmorillonites with ZnO nanoparticles (A<sub>8</sub>MC and A<sub>6</sub>MZ<sub>6</sub>) in the bilayer coverage made inner and outer sites of adsorption nitrate ion to result in the best adsorption capacity for them.

#### Effect of ZnO lamination on montmorillonite

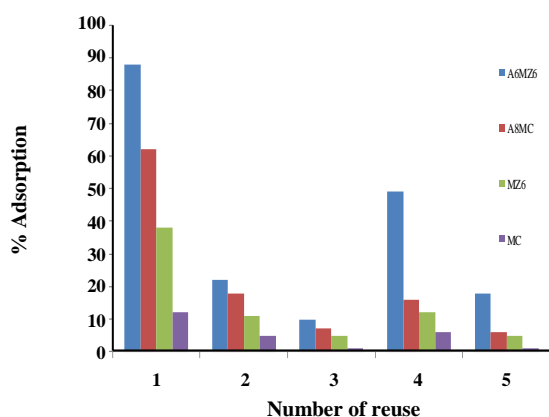
The effect of different amounts of ZnO lamination on montmorillonite for nitrate ion adsorption was investigated. The characterization and adsorption studies show that increase in ZnO lamination on montmorillonite causes increased in nitrate ion adsorption. The cause of choice MZ<sub>6</sub> adsorbent when compared with MZ<sub>8</sub> with an increased amount of ZnO on MC did not show an impressive change in nitrate ion adsorption, which is attributed to the aggregate and no distribution of ZnO on the surface of the silicates.

#### Effect of surfactant loading

The effect of HDTMAB loading concentrations (4-6-8% w/w) on nitrate ion adsorption is presented as supplementary data A<sub>8</sub>MC and A<sub>6</sub>MZ<sub>6</sub>. Nitrate ion adsorption percentage increases with the increase of HDTMAB loading in A<sub>8</sub>MC, but the highest HDTMAB loading (6% w/w) was observed in A<sub>6</sub>MZ<sub>6</sub>. Increase of nitrate ion adsorption capacity in A<sub>8</sub>MC with surfactant loading can be due to the formation of bilayer coverage on the modified montmorillonite. Since monolayer formation did not lead to charge reversal on the external surface of the silicates from negative to positive, A<sub>(4-8)</sub>MC and A<sub>(4-8)</sub>MZ<sub>6</sub> with monolayer coverage could not remove the negatively charged nitrate ion from aqueous solution by anionic exchange and electrostatic attraction. However, bilayer formation led to charge reversal on the external surface of the silicates from negative to positive and the positively charged head groups of surfactant were balanced by counter bromide ions. Therefore, A<sub>(4-8)</sub>MC and A<sub>(4-8)</sub>MZ<sub>6</sub> could remove the negatively charged nitrate ions from aqueous solution via anion exchange and electrostatic attraction. According to these studies, increase of the surfactant loading may lead to bilayer coverage and thereby a suitable adsorption. Therefore, two-layer surfactant can be loaded with a good removal of nitrate ion.

**Table 2: Number of reuse and maximum capacity adsorption (mg/g) with 1.0g adsorbents under optimum conditions, 25ml solution contain 120 mg nitrate ion, pH~7, t=30min.**

Maximum Adsorption(mg/g) →	MC	MZ <sub>6</sub>	A <sub>8</sub> MC	A <sub>6</sub> MZ <sub>6</sub>
Reuse condition ↓				
First	12	38	62	88
Second	5	12	18	22
Third	1	5	7	10
Acidic etchingFirst	6	12	16	49
Second	1	5	6	18



**Fig. 7: Number (1-3) is reuse with double distillation water and number (4-5) is after acidic washing, 1.0 g adsorbents, 25 mL solution containing 120 mg nitrate ion, pH~7, t=30 min.**

### Recovery study

After the third time wash with a solution of double distillation water, the montmorillonites were extracted for recycling. Montmorillonites were washed in acidic solutions and the pH was adjusted to 7 by leaching and it was added to a solution containing HDTMB surfactant; then it was vigorously stirred at 70°C for 24 h and was dried at 50°C for 3 days. Adsorption percentage of nitrate ion after 3 times wash for MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> was achieved as 8.33, 13.15, 11.29, and 11.36%. The adsorbents pass of three times is out of use and need to be recovered. The system is divided into acidic washing and need to add surfactant also over time after acidic washing, which leads to decrease in adsorption. The maximum capacity of adsorption (mg/g) for MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> was investigated to be 18, 55, 87 and 120 (mg/g), respectively (Fig. 7 and Table 2).

### Adsorption isotherm

The distribution of nitrate ions among MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> and solution at equilibrium state were studied using Freundlich and Langmuir isotherms which have been extensively used for the assessment of adsorption behavior in different solid-liquid systems. In Langmuir isotherm, the specific adsorption sites on the surface become saturated following the monolayer adsorption [46]. The Langmuir model is presented by Eq. (3):

$$C_e/q_e = 1/b \cdot Q_0 + C_e/Q_0 \quad (3)$$

Where  $q_e$  is the amount of nitrate ion adsorbed per unit weight of adsorbent (mg/g),  $C_e$  is the concentration of nitrate ion adsorbed in the liquid phase at equilibrium (mg/L),  $b$  is the Langmuir constant which is related to adsorption energy and capacity of adsorption (mg/L) and  $Q_0$  is the obtained concentrations corresponding to monolayer coverage. If  $C_e/q_e$  is plotted against  $C_e$ ,  $Q_0$  and  $b$  can be calculated from the intercept and slope of this plot. Additional, the important characteristics of the Langmuir isotherm can be explained separation factor  $R_L$  which, is calculated by Eq. (4):

$$R_L = \frac{1}{(1 + b/Q_0)} \quad (4)$$

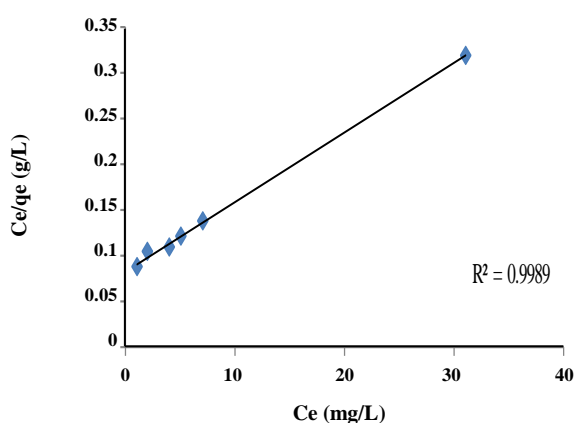
The  $R_L$  value assumes the nature and the feasibility of adsorption process which,  $R_L=1$  is Linear,  $0 < R_L < 1$  is favorable and  $R_L=0$  is Irreversible.

The Langmuir adsorption isotherm for the nitrate ion uptake by the best adsorbent (A<sub>6</sub>MZ<sub>6</sub>) is as shown in Fig. 8. The Freundlich isotherm was raised as the earliest empirical equation and proved to be consistent with the exponential distribution of active sites [46].



Table 3: The Langmuir and Freundlich isotherm parameters of this study.

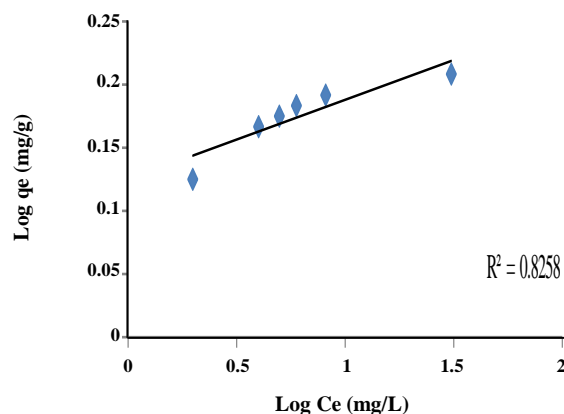
Isotherm	Parameter	MC	MZ <sub>6</sub>	A <sub>8</sub> MC	A <sub>6</sub> MZ <sub>6</sub>
Langmuir Freundlich	Q <sub>0</sub> (mg/g)	17.54	54.04	86.95	119.04
	b (L/mg)	0.031	0.083	0.15	0.321
	R <sub>L</sub>	0.651	0.182	0.071	0.025
	R <sup>2</sup>	0.9307	0.9954	0.9939	0.9989
	n	1.39	2.83	2.58	1.579
	K	10.98	12.28	14.1	17.39
	R <sup>2</sup>	0.8168	0.8686	0.8668	0.8258

Fig. 8: Langmuir isotherm for nitrate ion removal by A<sub>6</sub>MZ<sub>6</sub>.

The Freundlich isotherm shows that reactions occur in several sorption sites and the binding surface energy decreases exponentially with the rise of the amount of adsorbed solute. Freundlich isotherm is presented by Eq. (5):

$$\text{Log } q_e = \text{log } k + 1/n \text{ log } C_e \quad (5)$$

Coefficients  $k$  and  $n$  can be calculated by plotting  $\text{Log } q_e$  versus  $\text{Log } C_e$ , if a straight line is obtained. The Freundlich isotherms for nitrate ion adsorption by A<sub>6</sub>MZ<sub>6</sub> are as shown in Fig. 9. Higher correlation coefficients show that the nitrate ion adsorption can be explained by Langmuir isotherm. Correlation coefficients and isotherm constants were obtained by Freundlich and Langmuir equations (Table 3). The values of Q<sub>0</sub> for nitrate ion removal by A<sub>6</sub>MZ<sub>6</sub> were calculated at 119.04 mg/g. In this study, A<sub>6</sub>MZ<sub>6</sub>, which refers to good adsorption capacities for nitrate ion adsorption, is compared based on adsorption capacities derived from the Langmuir adsorption model. In other studies for nitrate ion removal,

Fig. 9: Freundlich isotherm for nitrate ion removal by A<sub>6</sub>MZ<sub>6</sub>.

organoclay such as zeolite, clinoptilolite, and montmorillonite (deposit of different mines) prepared using HDTMA used and reported [35].

#### Adsorption kinetics

Adsorption kinetics of nitrate ion onto MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub> were investigated. For better understanding of adsorption kinetics and mechanisms, the data were analyzed using the Lagergren pseudo-first-order and Lagergren pseudo-second-order kinetic models. In the pseudo-first order process, the Lagergren equation can be obtained as shown in Equation 6 [46]:

$$dq_t/dt = k_1 (q_e - q_t) \quad (6)$$

Integration of Equation 5 with the conditions ( $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$ ) led to Eq. (7):

$$\text{Ln}(q_e - q_t) = \text{Ln}(q_e) - k_1 t \quad (7)$$

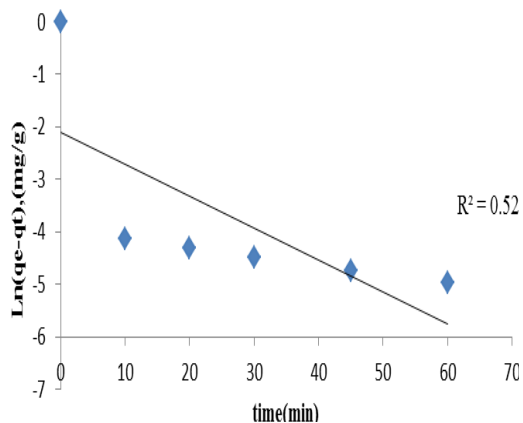


Fig. 10: Pseudo-first order model for nitrate ion removal by  $A_6MZ_6$ .

Where  $q_t$  (mg/g) is the amount of nitrate ion adsorbed on the adsorbent at time  $t$ ;  $q_e$ , which is the equilibrium sorption uptake, is extrapolated from the experimental data at time  $t = \infty$ ; and  $k_1$  (1/min) shows the rate constant of the first-order adsorption. The pseudo-first order model for nitrate ion adsorption  $A_6MZ_6$  is as shown in Fig. 10. The pseudo-second order process can be written as Equation 8:

$$t/q_t = 1/k_2 (q_e)^2 + t/q_e \quad (8)$$

Where  $q_e$  (mg/g) is the nitrate ion concentration at equilibrium and  $q_t$  (mg/g) is the nitrate ion concentration at time,  $t$ . Thus, the rate constants of second-order adsorption,  $k_2$  (g/mg/min) and  $q_e$ , can be calculated by plotting  $t/q_t$  versus  $t$ . The pseudo-second order model for nitrate ion adsorption onto  $A_6MZ_6$  is as shown in Fig. 11. Furthermore, the rate constants for nitrate ion removal and kinetic parameters were calculated as shown in Table 4. The pseudo-second order mechanisms for MC,  $MZ_6$ ,  $A_8MC$ , and  $A_6MZ_6$ , respectively are in line with the correlation coefficients of 0.9964, 0.9991, 0.9964, and 0.9917. According to the results,  $q_e$  (mg/g) and  $k_2$  (g/mg.min) values for  $A_6MZ_6$  were found to be much higher as compared to MC,  $MZ_6$ , and  $A_8MC$  (Table 4). The synthetic organoclay showed high adsorption of nitrate ion as predicted by  $A_6MZ_6$ .

#### Maximum capacity of nitrate ion sorption

The maximum capacity of the montmorillonite modified adsorbents was compared to other materials

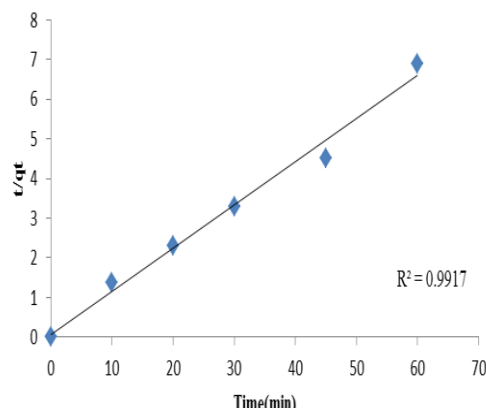


Fig. 11: Pseudo-second order model for nitrate ion removal  $A_6MZ_6$ .

(Table 5). The obtained experimental results proved to be very promising, because it increased nitrate ion sorption capacity from 17.24 (mg/g) for MC to 119.04 (mg/g) for  $A_6MZ_6$ . Surfactant modified montmorillonite has also been studied, but their results remained lower than the present study. This is clear, modified by ZnO and surfactant causing increased substitution and anion adsorption capacity. These findings show that surfactant-ZnO modified montmorillonite are suitable based materials for nitrate ion removal [47, 48].

## CONCLUSIONS

Montmorillonite has been loaded with ZnO nanoparticles and surfactant.

Different analytical techniques such as FT-IR, XRD, EDAX, TEM FE-SEM, and BET are used to characterize the adsorbents. Morphological studies performed in this study show the nano size particles of products. The presence of ZnO on montmorillonite ( $MZ_6$ ) led to increase in the lamination of surfactant on the adsorbent, such that in  $A_6MZ_6$ , 96.66% of 6% w/w surfactant is adsorbed and it shows the highest absorption. Montmorillonite with monolayer surfactant coverage was less efficient than the one with bilayer surfactant coverage in nitrate ion removal from aqueous solution. When compared with MC, the removal efficiency of  $A_6MZ_6$  was increased from 10.65 to 99.10% for 25 ml solution containing 120 mg nitrate ion. The adsorption and regeneration studies of nitrate ion showed that  $A_6MZ_6$  could be reused and regenerated with acidic solution.

Table 4: Kinetic parameter for nitrate ion removals by MC, MZ<sub>6</sub>, A<sub>8</sub>MC, and A<sub>6</sub>MZ<sub>6</sub>.

Kinetic	Parameter	MC	MZ <sub>6</sub>	A <sub>8</sub> MC	A <sub>6</sub> MZ <sub>6</sub>
pseudo-first	K <sub>1</sub> (mg/min <sup>1</sup> )	0.0395	0.0481	0.0631	0.067
	R <sup>2</sup>	0.7804	0.9669	0.7852	0.522
pseudo-second	q <sub>e</sub> (mg/g)	17.6	54.11	87.02	119.1
	K <sub>2</sub> (g mg/min)	0.0101	0.0104	0.0112	0.012
	R <sup>2</sup>	0.9964	0.9991	0.9964	0.9917

Table 5: Removal results of nitrate ion by different sorbents from the literature.

Adsorbents <sup>a</sup> Experimental value <sup>b</sup> Langmuir parameter q <sub>m</sub> )	Nitrate ion sorption capacity (mg/g)	Nitrate Concentration(mg/L)	Adsorbent weight (g)	Contact time (min)	References
A <sub>6</sub> MZ <sub>6</sub> <sup>a</sup>	119.04	120	1.0	30	This study
A <sub>8</sub> MC <sup>a</sup>	86.95	120	1.0	30	
MZ <sub>6</sub> <sup>a</sup>	54.05	120	1.0	30	
Mod. Pine sawdust <sup>a</sup>	31.55	30	0.4	1440	Keränen and Leiviska(2013)
Mod. Pine bark <sup>a</sup>	26.5	30	0.4	1440	
Mod. Spruce bark <sup>a</sup>	27.70	30	0.4	1440	
Mod. Birch bark <sup>a</sup>	28.03	30	0.4	1440	
Mod. Peat <sup>a</sup>	27.36	30	0.4	1440	
ETM method Wheat straw <sup>b</sup>	52.8	60	0.5	240	Xu et al. (2010b,2011)
Active carbon residue <sup>b</sup>	80	25	0.125	1440	Kilpimaa and Runtti(2014)
Organosilica modified <sup>b</sup>	11.75	61.98	0.05	1440	Seliem (2013)
Layered organosilica <sup>b</sup>	7.75	61.98	0.05	1440	

The auxiliary effect of zinc oxide on the adsorption and penetration of surfactant into the composite, based on observation in the infrared spectrum, showed that increasing the amount of cationic surfactant increases the absorption and storage capacity of nitrate ions in the adsorbent.

The adsorption data of nitrate ion can be explained by Langmuir isotherm and pseudo-second order kinetic model. The adsorbents showed different range capacity for nitrate ion adsorption and the maximum uptake capacity (Q<sub>max</sub>) from Langmuir equation for montmorillonite (17.24 mg/g) < montmorillonite by laminated ZnO (54.05 mg/g) < montmorillonite modified by surfactant (86.95 mg/g) < montmorillonite loaded by ZnO and surfactant (119.92 mg/g) was calculated.

Most of adsorption capacity is observed in A<sub>6</sub>MZ<sub>6</sub>. The 120 mg per gram of adsorbent was able to attract

ions in a solution of concentrated nitrate ion, nitrate concentration was reduced at the beginning. But after a short time of about 5 minutes desorption process to happen and stop at 120 mg was absorbed.

According to calculations, the separation factor, absorbed in the absorption process is irreversible. These calculations are consistent with the performance of absorbent recycling process, which confirmed the results of the isotherm is Langmuir.

A<sub>6</sub>MZ<sub>6</sub> in this study has high adsorption capacity, which could explore a new biocompatible and eco-friendly strategy for nitrate ion removal and could be used in aqueous solutions treatment process.

Based on the experimental results and the results of isotherm Langmuir, the conclusion is that the mechanism of pseudo second order. In the experimental results, the presence of surfactant on the montmorillonite adsorbent

was able to influence the uptake of nitrate ion. However, the proper interaction between surfactant and montmorillonite was not created and the amount of surfactant loading on the adsorbent was negligible. The addition of zinc oxide to the montmorillonite not only resulted in the absorption of nitric ion but also achieved a good interaction between zinc oxide and montmorillonite. Finally, when adsorbent was activated by zinc oxide and surfactant at the same time, the adsorbent encountered a significant increase in nitrate ion adsorption. As a result, both zinc oxide and surfactant were effective in the adsorption process, and with increasing concentration each of them, adsorption capacity increased. For this reason, both zinc oxide and surfactant have a direct effect on increasing the nitrate ion absorption. Therefore, the response kinetics of the function is proportional to the concentration of the two components of the composite, and in accordance with the prediction of the Langmuir isotherm of a pseudo second order.

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