Preparation and Characterization of Tertiary Amine Functionalized MCM-41 for the Removal of Nitrate from Aqueous Solution

by

Siti Nadirah binti Abdul Rahman
(13818)

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or person.

(SITI NADIRAH BINTI ABDUL RAHMAN)

ABSTRACT

Nitrate is known as one of the major pollutants in water. The presence of nitrate in water together with phosphates, pesticides and heavy metals create public health and environment hazards because it enhanced the growth of algae and causes depletion of dissolved oxygen. Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption, thus making it difficult to be removed from water. Scientists and technologists have been doing numerous researches to invent the best nitrate removal processes. Among them, adsorption methods are favorable due to its simple application and economical operation because sludge production and disposal issues are at minimal. Amine functionalized mesoporous silica represents one of the potential adsorbents offering an opportunity to remove nitrate ions from aqueous solutions. Some successful studies have been done by applying primary amine-functionalized mesoporous silica, APTMS MCM-41 as adsorbents and 40% percentage removal was achieved. The aim of this research project is to study the nitrate removal efficiency by using tertiary amine functionalized, AEPTMS MCM-41 as adsorbents at different percentage loading of tertiary aminosilanes group. The preparation of the samples was done by using co-condensation method. The experimental work was carried out by mixing the functionalized samples with nitrate solution at different initial nitrate concentrations and time duration in order to perform kinetics and isotherms study. Absorbance of the final nitrate solution was analyzed by using UV-Vis spectroscopy. Based on the results obtained, the percentage removal of nitrate from sodium nitrate solution increases with increasing loading of tertiary aminosilanes group in the samples. Kinetic study showed that the kinetic data follows Pseudo-second order model while for isotherm study, the isotherm data of MCM-41 loaded with 10% and 20% AEPTMS fitted well by using Langmuir isotherm model while the pure MCM-41 fitted by Freundlich isotherm model. Sample characterization by using FTIR spectroscopy proved the presence of aminosilane group (N-H) in the sample.

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CHAPTER 1

PROJECT BACKGROUND

1.1 Background of Study

Nitrate is essential for life especially in environmental sector because crop plants require nitrates from soil in order to satisfy their nutrient requirements.However, when its concentration reaches excessive levels, it can be harmful to biological consequences for the living organisms [1]. The most common technologies used for reduction or removal of nitrate are reverse osmosis, ion exchange and electrodialysis. These technologies have their own strengths and drawbackssuch as expensive, less effective, generate additional by-products as well as nitrate concentrated waste streams that pose disposal problems due to high saline concentration [2]. The disposal of sludge from the waste streams is expensive andwillcreate environmental issues.

Adsorption process is generally considered better in water treatment because of its convenience, simple design and east to operate. Furthermore, the process can remove or minimize different types of organic and inorganic pollutants from water or wastewater and thus it has a wider applicability in water pollution control [2]. Various kinds of adsorption materials have been used for the removal of heavy metals such as activated carbon, peat, saw-dust, activated alumina, risk husk carbon, orange peel, red mud blast furnace sludge and fly ash [3]. However, these materials have their own limitations that encourage researchers to create better adsorbents such as developing surface modified mesoporous materials.

Mesoporous materials gained so much interest since their discovery because they exhibit a number of desirable physical properties such as stable, narrow pore sizes [4], high surface area and pore volume, high thermal stability and ease of surface modifications [5]. Recently, surface functionalization of ordered mesoporous silica obtained by surfactant promoted alkoxysilane auto-assembly methods [6] has gained intense attention due to its controllable pore sizes and pore arrangements [5].

1.2 Problem Statement

United States Environmental Protection Agency (EPA) has set an enforceable regulation for nitrate, called Maximum Contaminant Level (MCL) at 10 mg/L or 10 ppm [7]. Nitrate is considered as a health hazard because of its conversion to nitrite. Once ingested, conversion of nitrate to nitrite takes place in the saliva of people of all age groups including the gastrointestinal tract ofinfants [8].A study conducted in Iowa, USA revealed that many private wells suffer from nitrate contamination in which about 18.3% of Iowa's private and rural wells have nitrate concentrations exceeding the EPA health advisory level [9].Doctors at the State University of Iowa Medical Center have encountered many babies suffering from diarrhea and other symptoms consistent with methemoglobinemia. After some tests are conducted to determine the cause, it was found that all of these infants were being fed with water from the private wells in Iowa [9].

For nitrate removal, adsorption is the most promising method due to its advantages as compared to the other nitrate removal methods [10]. Although amine functionalized MCM-41 has been reported as an adsorbent, the nitrate removal efficiency still need to be enhanced. The development of tertiary amine functionalized MCM-41 as an adsorbent for nitrate removal remains a new task. The previous researches only focused on the adsorption study of primary amine functionalized MCM-41 which uses APTMS as silica source. The adsorption capacity of this material was 46.5mg NO_3-/ g adsorbent [2]. The presence of more nitrogen in tertiary amine functionalized MCM-41 is predicted to increase the adsorption capability. The successful development of this new type of tertiary amine-functionalized MCM-41 could replace the existing adsorbents and give a major impact to nitrate removal industry.

1.3 Objective

The objectives of the present research are:

1. To synthesize 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) functionalized MCM-41absorbents via co-condensation method.
2. To characterize the adsorbents using Brunauer – Emmett – Teller (BET) surface analyzer and Fourier transform infrared (FTIR) spectroscopy method.
3. To study the nitrate adsorption behavior of the resultant adsorbent by conducting kinetics and isotherms studies.

1.4 Scope of Study

The scope of study in this research involves the synthesis of tertiary amine functionalized MCM-41 by using co-condensation method. Three samples will be prepared including pure MCM-41, 10% loaded AEPTMS MCM-41 and 20% loaded AEPTMS MCM-41. Cetryltrimethylammonium bromide (CTAB) surfactant, tetraethoxysilane (TEOS), sodium hydroxide (NaOH), de-ionized water (H_2O) and 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) will be used to synthesize the adsorbents. The synthesized adsorbents will be characterized by using varieties of analytical tools such as Brunauer – Emmett – Teller (BET) surface analyzer and Fourier transform infrared (FTIR) spectroscopy method. Nitrate removal studies will be conducted to determine the adsorbent with highest percentage of nitrate removal. The resultant adsorbent will undergo kinetics studies in order to investigate the behavior of adsorption with time as well as isotherm studies to determine the effect of adsorbent concentration on the removal of nitrate.

1.5 Relevancy of Project

This project is considered important and relevant since it relates to the environmental health and safety. It is raised due to the concern on water and soil pollution by nitrate that may affect the ecosystem. Apart from other nitrate removal methods and adsorbents already implemented, adsorption method by using tertiary amine functionalized MCM-41 is predicted to be another solution for this problem and its effectiveness will be further studied in this project.

1.6 Feasibility of Project

This project is feasible as it only deals with one type of adsorbent with the chemicals and equipments readily available in the laboratory. It is highly assured that this project can be completed within the allocated time with the acquiring materials and chemicals needed. This project will be successfully executed with the help and guidance from supervisor, technicians and graduate assistants.

CHAPTER 2
LITERATURE REVIEW

2.1 Effects of Nitrate

Nitrogen is a major constituent of the earth's atmosphere and occurs in many forms such as elemental nitrogen, nitrate and ammonia. Natural reactions of atmospheric forms of nitrogen with rainwater result in the formation of nitrate and ammonium ions [9].The best known use of nitrates is as inorganic fertilizer. Nitrates formed when microorganisms break down the fertilizers, decaying plants, manures or other organic residues [1]. The increasing use of artificial fertilizers, disposal of wastes, and changes in land use are the main factors that contribute to the progressive increase in nitrate levels in groundwater supplies over the last 20 years [11].

Due to its high stability and solubility, nitrate is imposing a serious threat to drinking water supplies and enhancing eutrophication. The main effects of eutrophication are algal blooms (rapid increase of algae), hypoxia (reduced dissolved oxygen content of a body of water), increase in poisoned, decline or loss of species biodiversity and some phytoplankton species may produce toxins that cause several symptoms such as diarrhea, memory loss, paralysis and can causes death for some cases[11].

Infants below six months who drink water containing nitrate in excess of MCL could become seriously ill and, if untreated, may die [7]. The syndrome is called methemoglobinemia or baby blue syndrome [1]. Food is another major sources of nitrate especially vegetables. Ingestion of up to 250 mg/day of nitrate has been reported for people whose diets consist mainly of food from vegetable sources [8].The other concern about nitrate is its carcinogenic effects. This causes diverse kinds of cancers and outbreaks of infectious diseases in human such as gastrointestinal cancer and diabetes.

Nitrate and nitrite themselves are not carcinogenic, but nitrite formed from dietary nitrate might react with dietary amines to form carcinogenic nitrosamines.There is also some evidence that nitrate reduces blood pressure [12].

2.2 Existing methods in Nitrate Removal

Varieties of traditional and conventional methods have been studied and applied in the process of removing nitrate. The high solubility and stability of nitrate makes it difficult to be removed from water. Therefore, treatment of nitrate is usually costly and complicated. The conventional methods for nitrogen removal from wastewater are biological processes (denitrification, nitrification, bacterial assimilation, harvesting of algae, oxidation ponds), chemical processes (breakpoint chlorination, chemical coagulation), physical operation (ammonia stripping, electrodialysis, filtration) and land application (irrigation rapid infiltration, overland flow) [13].

Chemical denitrification uses metals such as platinum, palladium, tin and copper to chemically reduce nitrate to other forms but they usually require a low pH and need addition of hydrogen gas or another strong reductant with better performance [14]. As a result, full-scale treatment systems based on these catalysts are not yet used for drinking water applications. The process of nitrate reduction in groundwater does not proceed to innocuous gases but the majority of the nitrogen transform into ammonia which poses other water-quality challenges that may necessitate further treatment [14]. The maximum reported efficiency of this method is 60-70% which is the lowest out of the five options [2].

Biological denitrification occurs naturally when certain bacteria use nitrate as terminal electron acceptor in the respiratory process in the absence of oxygen [15]. The efficiency can reach 99% and medium operational cost is required [2]. The most significant drawbacks of biological systems are that they require start-up time after prolonged periods of closure (such as in response to seasonal water demand), require more operator support than nonbiological systems and less mature in marketplace compared to ion exchange systems [14].

Beside of conventional methods, the alternatives methods used for removing nitrate are ion exchange, reverse osmosis and adsorption. Ion exchange method operates in the same manner as a common water softener and can easily remove approximately 90% of the nitrates [16]. Despite the high efficiency, ion exchange is fairly high in capital and operating costs with undesirable high residual constituents such as chlorides and bicarbonates in the treated water which must be removed prior to consumption [17].

Reverse osmosis uses semipermeable membrane that is selective about what it allows to pass through and what it prevents from passing [16]. More than 95% efficiency can be achieved from this technology. The main disadvantage of reverse osmosis is the high cost needed for energy input, thereby limiting its applications to mainly specialized industrial applications [17].

Adsorption is the process of collecting soluble substances in a solution by using suitable interface or materials. Compared to the other methods, adsorption is the most promising method because of convenience, ease of operation, simplicity of design and economical operation resulting in less sludge production and disposal problems. Numerous materials have been studied for the removal of nitrate such as carbon based sorbents, clay sorbents, agricultural wastes as sorbents, industrial wastes as sorbents, biosorbents and miscellaneous adsorbents [2]. Mesoporous silica as one of the miscellaneous types of adsorbents is preferable for removal of nitrate due its high surface area, open pore structure, appropriate surface functionalization and proved to be high-capacity adsorbent for nitrate anions in water [18]. The common types of adsorbents used and their adsorption capacities are provided in Table 1.

Table 1: Type of adsorbents and their adsorption capacity [2]

Type	Adsorbents	Adsorption capacity
Carbon-based sorbents	H_2SO_4 treated carbon cloth	2.03 mmol/g
	Powdered activated carbon	10 mmol/g
	Carbon nanotubes	25 mmol/g
Natural sorbents	Modified clay	12.83-14.76 mg/g
	Modified Zeolite	0.6-0.74 mmol/g
	Modified Sepiolite	453 mmol/kg
Agricultural wastes sorbents	Sugarcane bagasse	1.41 mmol/g
	Rice hull	1.32 mmol/g
	Modified wheat residue	2.08 mmol/g
Industrial wastes sorbents	Original red mud	1.859 mmol/g
	Activated red mud	5.858 mmol/g
Biosorbents	Bamboo charcoal	0.104 mmol/g
	Chitosan beads	90.7 mg/g
	Cross-linked and quaternized Chinese reed	7.55 mg/g
Miscellaneous sorbents	Nano-alumina	4 mg/g
	Cement paste	43.6 L/kg
	Layered double hydroxides	20-35 mg/g
	Ammonium functionalized MCM-41	46.5 mg/g

2.3 MCM-41

Recently, nanotechnology and mesoporous silica materials have gained attention in the industry because ofthe promising advantages that these materials can provide.Typical characteristics of mesoporous materials are large surface area and pore volume, well-ordered, uniform and adjustable poresizesbetween 2 and 50 nm [4]. They can be used in different fields, such as separation techniques, adsorption, catalysis, drug delivery [19], sensors, or photonics. Mesoporoussilicas are inorganic materialssynthesized in the presence of surfactants astemplates for the polycondensation of silica species, originating from different sourcesof silica (sodium silicate, alkoxydeslikeTEOS and tetramethylortosilicate, TMOS) [20].

The superstructure of mesoporous silica family is designated MCMs which is an acronym for Mobil's Composition of Matter and are respectively MCM-41 (hexagonal), MCM-48 (cubic) as well as MCM-50 (lamellar). MCM-41 is the most studied member mesoporous materials since it combines a myriad of attractive properties including highly ordered pore systems with tunable pore diameters (in the range 2-10 nm), large pore volumes, high hydrocarbon sorption capacities, high BET surface areas and thermal stability, as well as a high density of surface silanols [21]. The hexagonal structure of MCM-41 is shown in Figure 1.

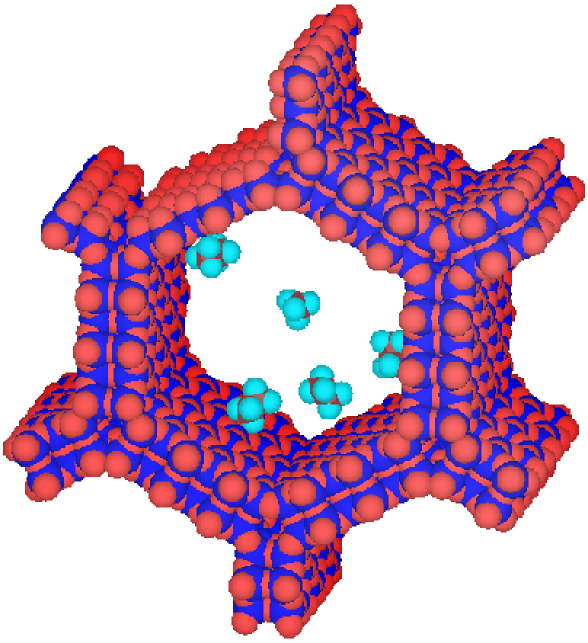


Figure 1: Structure of MCM-41 [22]

2.4 Amine functionalized MCM-41

Generally, there are two methods widely adopted for functionalization, namely direct co-condensation method and a post-grafting method. The direct co-condensation method is more plausible because it mightavoid several shortcomings in the post-grafting method suchas reduction of pore sizes, pore blocking at the aperture and difficulties in controlled loadings and distributions of theactive sites [23]. Preparation of amino-functionalized mesoporousby reaction of mesoporous silica withorganosilanes is called post grafting method. However, the final material by this method, likely consists ofmultiple types of amines. Some are isolated amines but themajorities are hydrogen-bonded to each other. To create truly well-defined functionalized site in the materials, functionalized amine should be isolated [23].

Co-condensation is a synthesis method in preparing a series of new mesoporous silica materials with MCM-41 type of structure containing a homogeneous layer of organic functional groups inside the pores under low surfactant concentration condition [24]. The method uses organoalkoxysilane precursor as structure-directing reactants. Figure 2 shows the organoalkoxysilane precursors with different functional groups used for co-condensation reactions that contain a common trimethoxysilyl or triethoxysilyl terminal group. Functionalized MCM-41 using primary amine source (APTMS) has been reported and its performance in nitrate removal is only 20.1% [10]. In the present project, MCM-41 functionalized with tertiary amine source (AEPTMS) will be used as the adsorbent for removal of nitrate. It is expected that the percentage removal will be higher compared to APTMS due to the higher amounts of nitrogen presence in the structure.

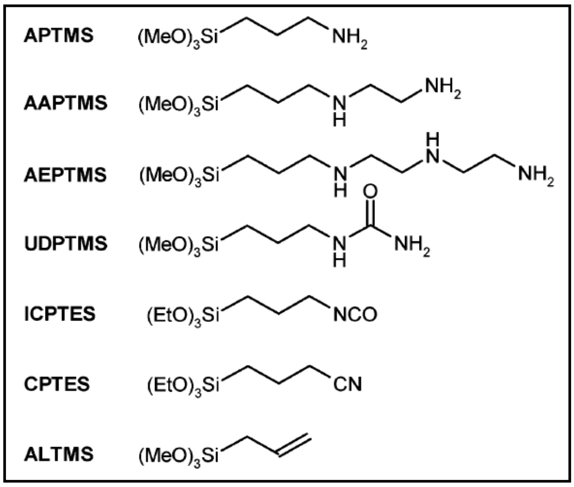


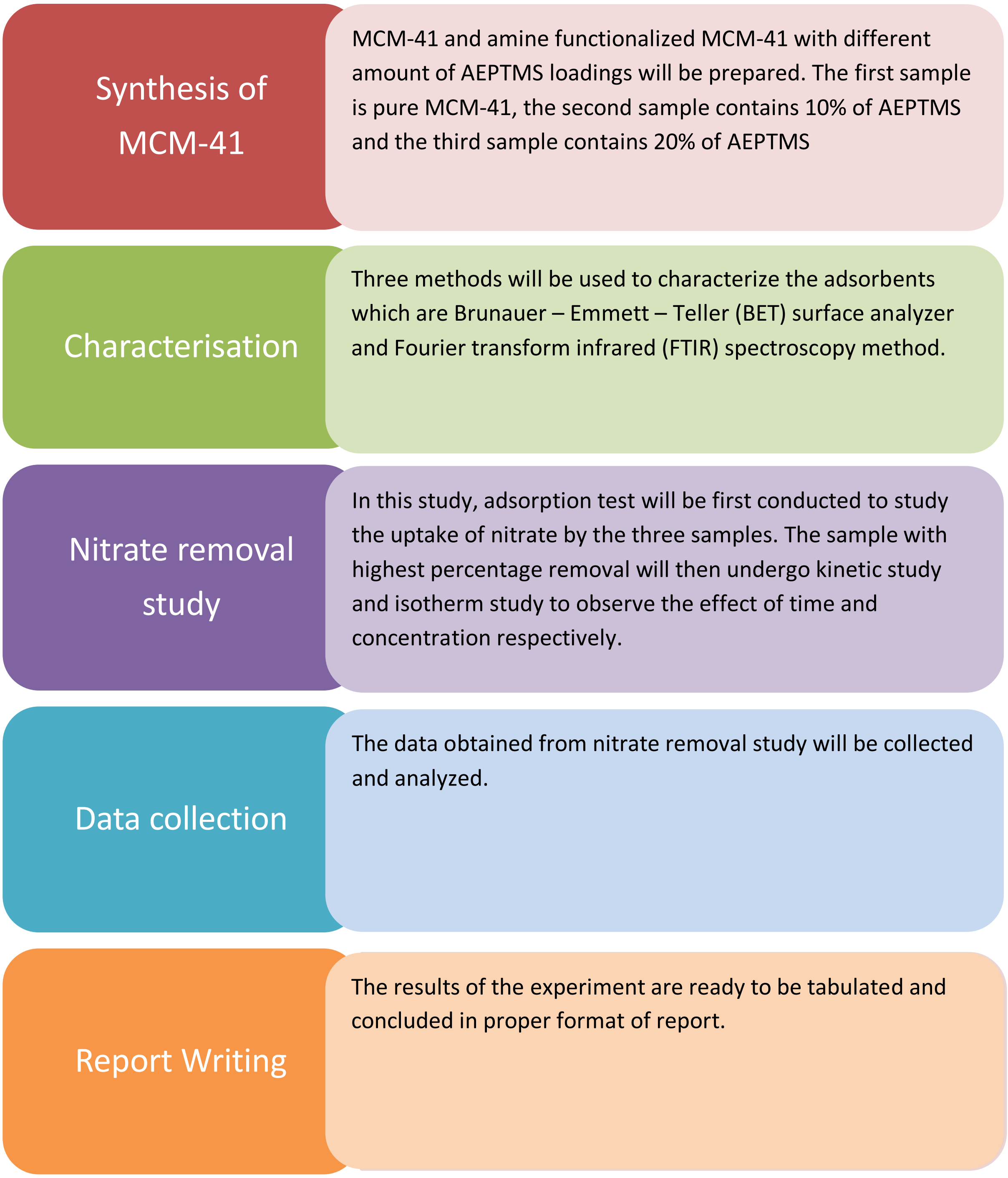
Figure 2: Organoalkoxysilane precursors used as structure-directing reactant for co-condensation method [24]

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

Figure 3 shows the flow diagram of this research project.



Synthesis of MCM-41	MCM-41 and amine functionalized MCM-41 with different amount of AEPTMS loadings will be prepared. The first sample is pure MCM-41, the second sample contains 10% of AEPTMS and the third sample contains 20% of AEPTMS
Characterisation	Three methods will be used to characterize the adsorbents which are Brunauer – Emmett – Teller (BET) surface analyzer and Fourier transform infrared (FTIR) spectroscopy method.
Nitrate removal study	In this study, adsorption test will be first conducted to study the uptake of nitrate by the three samples. The sample with highest percentage removal will then undergo kinetic study and isotherm study to observe the effect of time and concentration respectively.
Data collection	The data obtained from nitrate removal study will be collected and analyzed.
Report Writing	The results of the experiment are ready to be tabulated and concluded in proper format of report.

Figure 3: Project flow diagram

3.2 Synthesis of MCM-41

The experimental procedures for the synthesis of MCM-41 and tertiary amine functionalized MCM-41were done as follows [24]:

1. The reaction mixtures for the three samples were prepared based on the molar ratio of CTAB:TEOS:AEPTMS:NaOH:H_2O (1:8.16:1.05:2.55:4857). The amounts of reactants for all samples are simplified in Table 1. For the synthesis of MCM-41 as reference sample, the molar ratio of the reaction mixture was CTAB:TEOS:AEPTMS:NaOH:H_2O (1:9.20:0 :2.55:4857).
2. Firstly, the mixture of CTAB, NaOH and H_2O was heated at 80^oC for 30 min. Then, TEOS and AEPTMS were added sequentially and rapidly.
3. The reaction temperature was maintained at 80^oC for 2 h.

Figure 4: Bubble formed after the solutions were mixed and heated

4. After 2 h, the products were isolated by a hot filtration, washed with copious amount of water and methanol, and dried under vacuum at temperature of 60^oC .

Figure 5: Vacuum filtration

5. An acid extraction was performed in a methanol (100mL) mixture of concentrated hydrochloric acid (1 mL) and the product materials (1 g) at 60^oC for 6 hours.

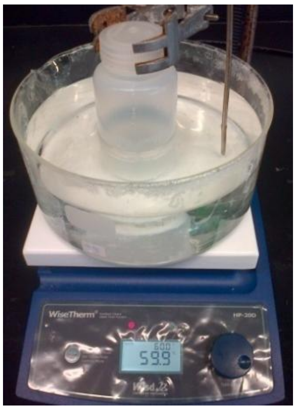


Figure 6: Acid extraction

6. Finally, the resulting surfactant-removed solid products were filtered and washed with water and methanol and then dried under vacuum. Table 2 shows the reaction mixtures of samples that have been synthesized.

Figure 7: Resultant sample (pure MCM-41)

Table 2: Reaction mixtures for samples preparation

Sample	A (Pure MCM-41)	B (10% AEPTMS MCM-41)	C (20% AEPTMS MCM-41)
Cetryltrimethylammonium bromide (CTAB)	2 g (5.49 mmol)	2 g (5.49 mmol)	2 g (5.49 mmol)
Tetraethoxysilane (TEOS)	10.53 g (50.55 mmol)	9.34 g (44.8 mmol)	8.452 g (40.44 mmol)
3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (AEPTMS)	-	1.526 g (5.75 mmol)	2.683 g (10.11 mmol)
Sodium Hydroxide (NaOH)	7 mL (2 M, 14 mmol)	7 mL (2 M, 14 mmol)	7 mL (2 M, 14 mmol)
De-ionized water (H_2O)	480 g (26.67 mol)	480 g (26.67 mol)	480 g (26.67 mol)

3.3 Characterization

3.3.1 Brunauer – Emmett – Teller (BET)

BET is one of the most widely used methods to determine the specific surface area of an adsorbent. This method was performed based on the adsorption of gas on a surface. The amount of gas adsorbed at a given pressure allows to determine the surface area [25]. Nitrogen sorption measurement and BET surface area analysis was performed using BELSORP physisorption analyzer. The specific surface area, S_{BET}, was determined from the linear partof the BET plot (P/P0 = 0.05–1.00).

3.3.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is a method used to identify the functional groups in the sample [27]. Spectra were recorded with Perkin Elmer equipment between 400 and 4000 cm^{-1}using KBr method [27]. Infrared spectra was obtained by first collecting an interferogram of a sample signal using an interferometer, and then performed a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FTIR Spectrometer collected and digitized the interferogram, performed the FT function, and displayed the spectrum [28].

3.4 Nitrate Removal Test

3.4.1 Adsorption study [29]

The uptake of nitrate using the three adsorbents synthesized in the present work was carried out as follows [29]:

1. 25 mL of 1 mM sodium nitrate ($NaNO_3$) solution (i.e. 61.98 mg/L) was added to 0.05 g of the samples in conical flask to conduct a batch equilibration study.
2. The mixture wasshaked by hand for one or two minutes before mixing on a shaker for 24 hours.
3. After 24-hour equilibration, the solid and solution phases were separated by centrifugation.
4. 15 mL of each solution were collected in clean vials for nitrate analysis.
5. The percentage removal of anions at equilibrium was calculated using equation 1 as follows [29]:

$$R = \frac{(C_i - C_e)}{C_i} \text{ x } 100 \text{...} \quad (1)$$

where R = percentage of nitrate removal (%),
Ci = initial concentration of nitrate in solution (mg/L),
Ce = final (equilibrium) concentration of nitrate in solution (mg/L)

6. The nitrate adsorption capacity of the samples at equilibrium was calculated using equation 2 as follows [10]:

$$q_e = (C_i - C_e) \text{x} \frac{V}{m} \text{...} (2)$$

Where q_e= adsorption capacity (mg NO^{-3}/g adsorbent)
V = volume of solution (L)
m = mass of adsorbent (g)

3.4.2 Kinetics Study[29]

Kinetics study was conducted to determine kinetics of nitrate removal by the resultant adsorbent with the best capability of removing nitrate. The trend of nitrate adsorption as a function of contact time was analyzed from the result. The experimental data was fitted to pseudo-first order model using equation 4 and pseudo-second order model using equation 5 as follows [29]:

$$\log(q_e - q_t) = \log q_e - k_1 t \text{..................................(4)}$$

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \text{.. (5)}$$

Where k_1 = rate constant of pseudo-first order (min-1),

k_2 = rate constant of pseudo-second order (g/mg min),

q_t=amount of nitrate adsorbed at time t (mg/g),

q_e= amount of nitrate absorbed at equilibrium (mg/g),

t=time (min)

The procedure for kinetics studies were performed as follows [29]:

1. 0.05 g of adsorbent was mixed with 25 mL of nitrate solution at concentration of 1mM in centrifuge tube.
2. The suspension was mixed for 1 hour, 2 hours, 4 hours and 20 hours on a shaker.
3. The tube was centrifuged and 15 mL of the solution was collected in clean vials for nitrate analysis.

3.4.3 Isotherms Study[29]

Isotherm study was conducted to indicate the distribution of nitrate between solution and adsorbent at the equilibrium state of the adsorption process. Langmuir and Freundlich models were used to study the adsorption behavior of nitrate. Langmuir isotherm was based on the assumptions that adsorption takes place at the specific homogeneous sites within the adsorbent, there was no significant interaction among adsorbed species, and the adsorbent was saturated after the formation of one layer of adsorbate on the surface of adsorbent. The Langmuir isotherm equation can be written in equation 3 as follows [29]:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \text{...} (3)$$

Where Ce = equilibrium concentration of the remaining solution (mg/l),

q_e= amount of the solute adsorbed per mass unit of adsorbent at equilibrium (mg/g),

b = Langmuir constant (l/mg),

q_{max} = amount of adsorbate per mass of adsorbent at complete monolayer coverage (mg/g)

Freundlich isotherm model was used to describe the non-ideal adsorption of heterogeneous system and reversible adsorption. The isotherm can be expressed by the equation 4 as follows [29]:

$$q_e = K_F C_e^{1/n} \text{...} (4)$$

which can be linearized to give the equation 5as follows [29]:

$$\log q_e = \log K_F + \frac{1}{n} log C_e \text{..} (5)$$

Where $K_F$and n are Freudhlich adsorption isotherm.

The procedures for adsorption isotherms study were performed as follows [29]:

1. 0.05 g of adsorbent was mixed with 25 mL of 0.2, 0.4, 0.6, 0.8 and 1.0 mM of nitrate solution into centrifuge tubes to conduct batch equilibration study.
2. The solutions were mixed for 24 hours in shaker.
3. The tubes were centrifuged to separate solid and liquid phases.
4. 15 mL of each solutions were collected in clean vials for nitrate analysis.

3.5 Equipment and Chemicals Used

3.5.1 Equipment and apparatus

1. Oven
2. Hot plate stirrer
3. Vacuum filtration
4. Centrifuge
5. BELSORP physisoption analyzer
6. FTIR Spectrometer

3.5.2 Chemicals

1. Cetryltrimethylammonium bromide (CTAB)
2. Tetraethoxysilane (TEOS)
3. 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS)
4. Sodium Hydroxide (NaOH)
5. De-ionized water (H_2O)
6. Methanol (CH_4)
7. Hydrochloric acid (HCl)
8. Sodium Nitrate ($NaNO_3$)

3.6 Key Milestones

Figure 8 shows the key milestones of FYP II.

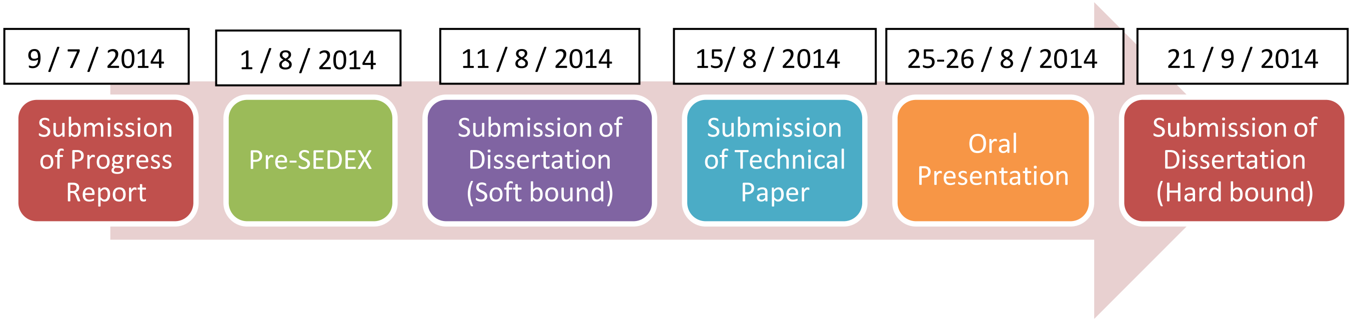


Figure 8: Key Milestones

3.7 Activities Gantt Chart

Table 3 shows the activities Gantt Chart of FYP II for this project.

Table 3: Gantt Chart of FYP I

No	**Detail/Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
1.	Project work continues	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦					
2.	Preparation and submission of Progress Report								🟦							
3.	Pre-EDX											🟦				
4.	Submission of Draft Report												🟦			
5.	Submission of Dissertation (Soft bound)													🟦		
6.	Submission of Technical Paper													🟦		
7.	Oral presentation														🟦	
8.	Submission of Dissertation (Hard bound)															🟦

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation

4.1.1 FTIR Spectroscopy

FTIR spectra for pure MCM-41, 10% loaded AEPTMS MCM-41 and 20% loaded AEPTMS MCM-41 is shown in Figure 9. For all spectra, strong adsorption bands near 1200-1000 cm^{-1} and 3500-3400 cm^{-1} were observed,attributed to Si—O—Si asymmetric stretching vibrations and SiOH groups, respectively. As compared to pure MCM-41, the spectrum of 10% loaded and 20% loaded AEPTMS MCM-41 showed a distinguished vibration band denoting the presence of aminosilanes group (N—H) around 1500-1400 cm^{-1}.

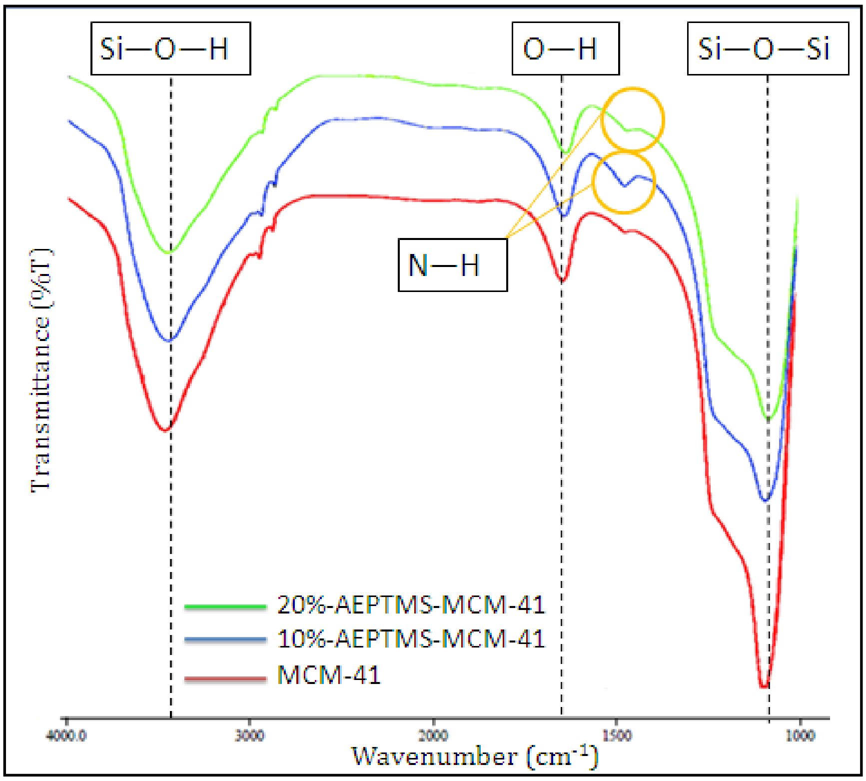


Figure 9: FTIR spectra for synthesized adsorbents

4.1.2 BET Surface Area Analysis

Table 4: Result BET surface area analysis

Adsorbent	BET surface area (m^2/g)	Pore diameter (nm)	Total pore volume (cm^3/g)
MCM-41	401.67	2.7802	0.2792
10-AEPTMS-MCM-41	288.96	3.4869	0.2519
20-AEPTMS-MCM-41	147.57	3.2388	0.1195

BET surface area analysis was performed and the results of the analysis are tabulated in Table 4. For all analyzed adsorbents, pure MCM-41 displayed the highest BET surface areas and total pore volumes compared to amino functionalized materials. Adsorbents loaded with AEPTMS exhibits lower surface areas and total pore volumes. The textural parameters of the amine-functionalized MCM-41 decreased mainly attributed to the occupation of the pore framework by the terminal organic functional groups protruding into the internal surface of the pores [18].

4.2NO_3^- Removal Study

Nitrate removal test has been carried out to test the adsorption capability of pure MCM-41, 10% loaded AEPTMS MCM-41 and 20% loaded AEPTMS MCM-41 towards nitrate solution. The test was done in a bath shaker for different adsorption duration. UV-Vis spectrophotometer was used for the analysis of the concentration of the solution after nitrate removal. Table 5 tabulates the results of adsorption test for the three synthesized adsorbents. C_i is the concentration of nitrate solution before adsorbent is added andC_t is the concentration of the solution after the adsorption test is carried out at specified durations.

Table 5: Results of Adsorption Test

Pure MCM-41			10-AEPTMS- MCM-41			20-AEPTMS- MCM-41		
C_i (mM)	T (hr)	C_t (mM)	C_i (mM)	T (hr)	C_t (mM)	C_i (mM)	T (hr)	C_t (mM)
0.2	24	0.2	0.2	24	0.2	0.2	24	0.2
0.4	24	0.4	0.4	24	0.3	0.4	24	0.3
0.6	24	0.6	0.6	24	0.3	0.6	24	0.2
0.8	24	0.6	0.8	24	0.4	0.8	24	0.3
1.0	24	0.5	1.0	24	0.3	1.0	24	0.2
1.0	1	1.0	1.0	1	0.6	1.0	1	0.5
1.0	2	0.9	1.0	2	0.6	1.0	2	0.5
1.0	4	0.9	1.0	4	0.6	1.0	4	0.4
1.0	20	0.6	1.0	20	0.5	1.0	20	0.2

Table 6 shows the percentage nitrate removal obtained using the adsorbents synthesized in the present work. From the results shown in Table 5, the highest percentage nitrate removal was obtained by using MCM-41 loaded with 20% AEPTMS followed by MCM-41 loaded with 10%AEPTMS and pure MCM-41. The highest adsorption capacity achieved was 24.8 mg NO_3^-/g adsorbent by the 20-AEPTMS-MCM41.

Table 6: Nitrate adsorption at equilibrium

Sample	Nitrate removal (%)	q_e(mg NO^{-3}/g adsorbent)
Pure	50	15.5
10% loaded	70	21.7
20% loaded	80	24.8

The values of percentage removal obtained from this present work are compared with the values obtained by different adsorbents reported in the literature review. The comparison showed significant deviation of percentage removal values for pure MCM-41 between this work and Moaaz K. Seliem (2013). This is assumed to be caused by the different adsorbent synthesis methods. However, the work by SafiaHamoudi (2007) gave 71% nitrate removal by MCM-48 which can be relate to MCM-41 since they have the same pore volumes and only differs in configurations. Based on RabihSaad (2008), the percentage removal by APTMS MCM-41 was 40%.

Table 7: NO_3^-adsorption test comparison with the literature studies

Adsorbent	R (%)	References
MCM-41	20	Moaaz K. Seliem, 2013
MCM-48	71	SafiaHamoudi, 2007
APTMS MCM-41	40	RabihSaad, 2008
MCM-41	50	This work
10-AEPTMS-MCM-41	70	This work
20-AEPTMS-MCM-41	80	This work

4.3 Kinetic Study

The adsorption capacity of the samples as a function of contact time at initial concentration of 1.0 mM is given in Figure 10. As seen, the amount of nitrate adsorbed by all samples increase as the time increase. For pure MCM-41, there is no nitrate uptake during the first hour and then the amount adsorbed increases gradually with time. However, this sample showed the lowest value of q_t during the range of studied time compared to the samples loaded with AEPTMS. Slow nitrate uptake was observed for 10% loaded AEPTMS MCM-41 during the initial stage rapid increment was found after 20hours. For 20% loaded AEPTMS MCM-41, the value of q_t at the beginning of the test was slightly more than MCM-41 loaded with 10% AEPTMS and increased rapidly until it achieved equilibrium at 20 hours. Since this sample reached equilibrium the earliest and gave the highest value of q, it can be concluded that the other two samples achieved equilibrium more or less the same as their adsorption amount at 24 hours.

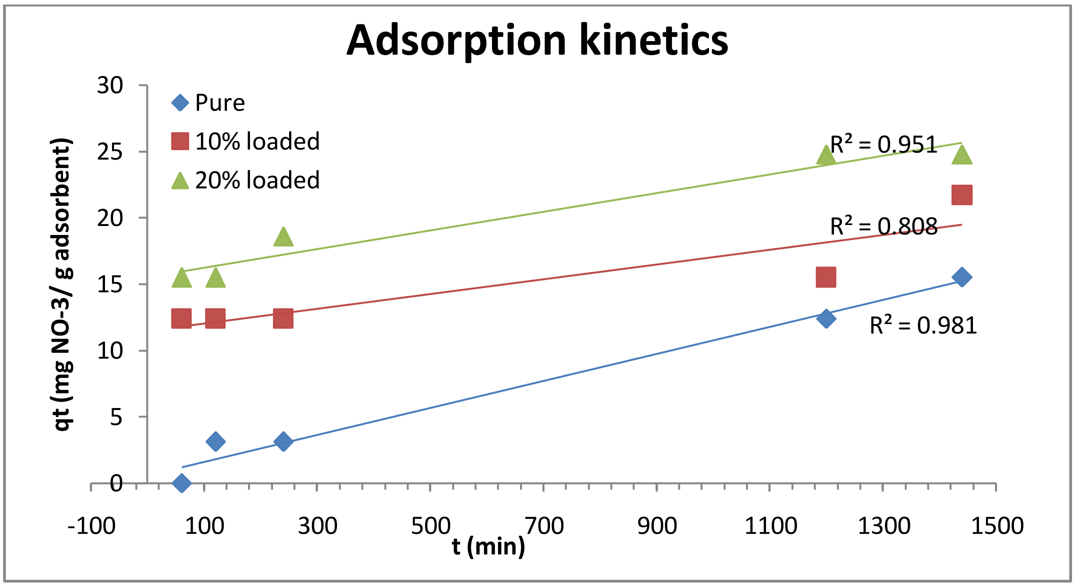


Figure 10: Plot of nitrate uptake by adsorbents against time

4.3.1 Kinetic Modeling

The experimental data obtained from the adsorption study was fitted with pseudo-first and pseudo-second order models where k_1 and k_2 are the rate constants. Based on the previous studies, low rate constant value indicates high adsorption efficiency [10,29]. Using pseudo-first order model, the profiles are depicted in Figure 11. There was a good agreement of the experimental data with correlation coefficients of 0.978. As clearly evidenced from the figure, the plots for pure MCM-41 and 10% loaded AEPTMS MCM-41 failed to describe the experimental kinetic data and makes the pseudo-first order kinetic model inadequate to describe the adsorption kinetics.

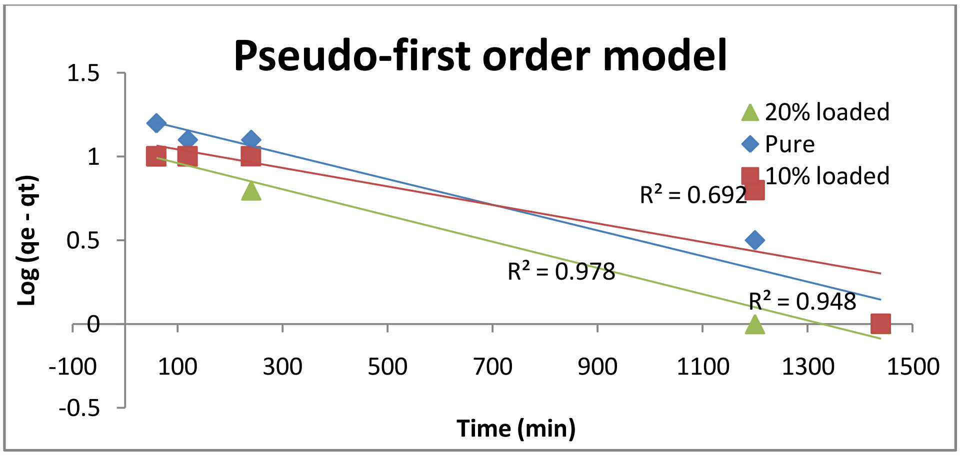


Figure 11: Pseudo-first order adsorption kinetic model

Figure 12 shows the application of pseudo-second order kinetic model indicated a good agreement of the experimental data with correlation coefficient up to 0.999 that suggests a pretty strong relationship between the parameters and proves that the process follows pseudo-second order kinetic model. The calculated nitrate uptakes at equilibrium, rate constants and the corresponding correlation coefficients for this model are tabulated in Table 8. According to this model, the value of the rate constant for 20% loaded AEPTMS MCM-41 is the highest followed by 10% loaded AEPTMS and pure MCM-41.

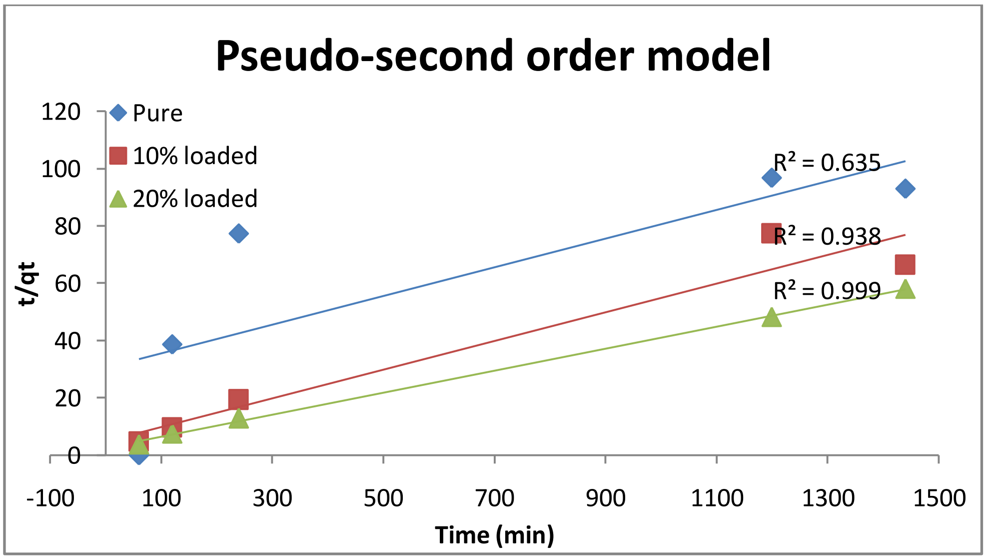


Figure 12: Pseudo-second order adsorption kinetic model

Table 8: Kinetics parameters for pseudo-second order kinetic model

Samples	q_e (mg/g)	k_2 (g/mg min)	Correlation coefficient, R^2
Pure	15.5	0.0042	0.635
10% loaded	21.7	0.0021	0.938
20% loaded	24.8	0.0016	0.999

4.4 Isotherm Study

Adsorption isotherm study is conducted to explain the adsorptive behavior of the samples at various initial concentrations. The test was carried out at the same time duration which is 24 hours. The trend of nitrate uptake by the three samples against initial is plotted in Figure 13. It is clearly showed that the removal of nitrate is increasing linearly with increasing initial concentration. However, there was no removal occurred when the concentration of the solution is 0.2 mM for all samples. For pure MCM-41, zero percentage removal was recorded when initial concentration of less than 0.8 mM is used. With the presence of AEPTMS in the samples, the nitrate uptake started to occur in solution concentration as low as 0.3 to 0.4 mM.

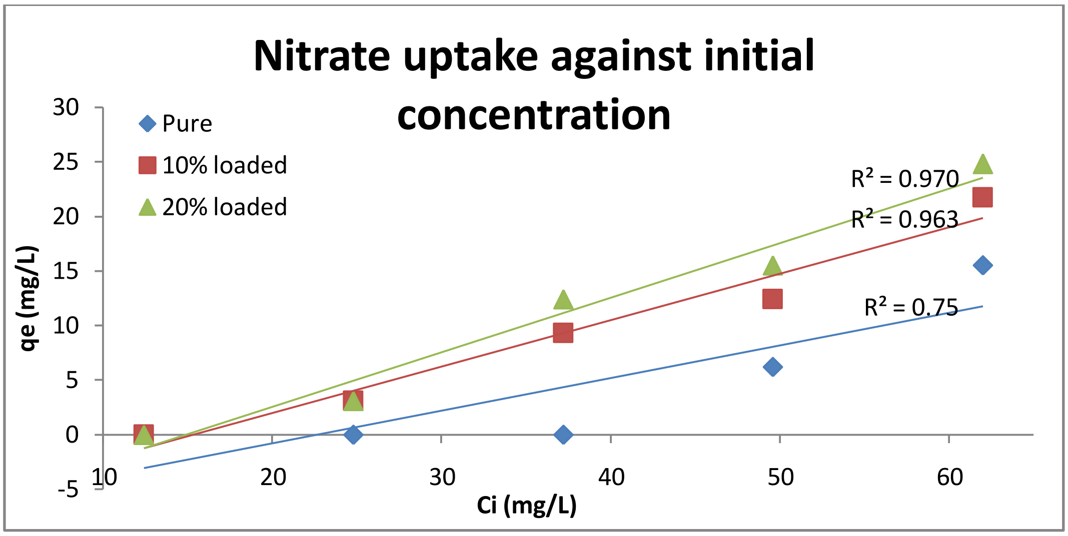


Figure 13: Plot of nitrate uptake by adsorbents against initial concentration

The experimental data was fitted to Langmuir and Freundlich isotherms. Figure 14 and 15 show Langmuir isotherm and Freundlich isotherm plots. Based on these plots, the isotherm data of MCM-41 loaded with 10% and 20% AEPTMS fits the Langmuir equation with correlation of 0.828 and 0.996 respectively. On the other hand, pure MCM-41 did not show linearity with correlation coefficients of 0.2. Langmuir isotherm parameters for the three samples were calculated and tabulated in Table 9. q_{max} is defined as the amount of adsorbate per mass unit adsorbent at complete monolayer coverage (mg/g) and the 20-AEPTMS-MCM-41 shows the highest q_{max}value.

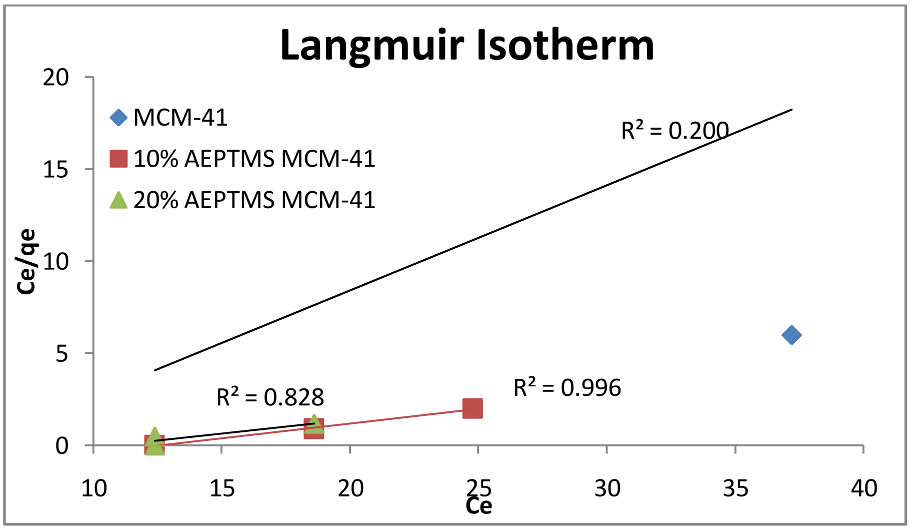


Figure 14: Langmuir plots for nitrate uptake.

Table 9: Langmuir parameters of studied samples

Sample	q_{max} (mg/g)	b (l/mg)	R^2
Pure	1.754	0.190	0.200
10% loaded	6.211	0.079	0.996
20% loaded	6.536	0.093	0.828

By fitting to Langmuir isotherm, the essential characteristic of this isotherm called equilibrium parameter, $R_L$of the two samples can be determined. The nature of adsorption process can be classified as either unfavorable ($R_L > 1$), linear ($R_L= 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values calculated for 10% loaded and 20% loaded AEPTMS MCM-41 ranges from 0.1 to 0.5 indicating that the adsorption process by these samples at the studied concentrations is favorable.R_L is a dimensionless constant and can be calculated by using the following the equation [6] as follows [29]:

$$R_L = \frac{1}{1+bC_i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[6]$$

Where R_L = equilibrium parameter,

b = Langmuir constant,
Ci= initial concentration

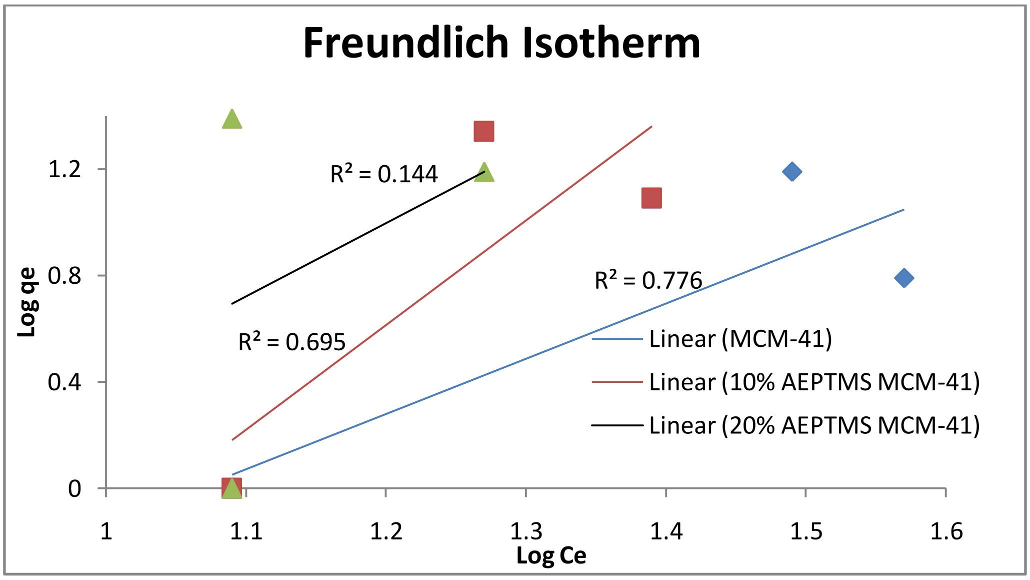


Figure 15: Freundlich plot for nitrate uptake

Table 10: Freundlich parameters of studied samplethe adsorbent synthesized in the present work.

Sample	n	K_F	R^2
Pure	0.482	0.00618	0.776
10% loaded	0.254	0.00008	0.695
20% loaded	0.364	0.00499	0.144

For Freundlich isotherm, only pure MCM-41 data can be considered to fit the isotherm with correlation coefficient, R^2 of 0.78 while the R^2 values were very low for samples loaded with 10% and 20% of AEPTMS. Table 10 shows the Freundlich parameters of the adsorbents. K_F is Freundlich constant related to adsorption capacity and n is the energy or intensity of adsorption. The n value for pure MCM-41 is less than 1.0, thus adsorption of nitrate indicates cooperative adsorption instead of normal Freundlich adsorption. The value of K_F is rather low which means the adsorption favorability by this sample is low.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1Conclusion

As a conclusion, this project is important as it involves the removal of nitrate from aqueous solutions which has been one of the main environmental issues. The presence of excess nitrate in water, soil and air may become pollutant and harmful to flora, fauna as well as human beings. The existing nitrate removal technologies and adsorbents available in the industry have their own drawbacks and the studies to find the most effective adsorbents and technologies are being carried out. Tertiary amine functionalized MCM-41 is believed to be one of the possible candidates for nitrate adsorbents and shall be proved in this research project. The experimental work involves synthesis of the samples and nitrate removal studies that include adsorption test, kinetics and isotherms studies.

Based on the results of the nitrate removal studies, it is proven that the presence of AEPTMS in the sample helped to increase the efficiency of nitrate uptake. 20% loaded AEPTMS MCM-41 showed the highest percentage removal which is 80% with adsorption capacity of 24.8 mg of nitrate per g of adsorbent. 10% loaded AEPTMS MCM-41 showed second best performance with 70% removal and 21.7 mg/g nitrate capacity whilst pure MCM-41 also gave good nitrate adsorption capability with 50% removal and 15.5 mg/g nitrate adsorption capacity. The experimental data was successfully fitted to pseudo-second order kinetic model with correlation coefficient achieving 1.0. Langmuir and Freundlich isotherms cannot be used to interpret and study the adsorption behavior of these samples towards nitrate. However, the data showed excellent expected linearity plot of nitrate uptakes against initial concentration. Characterisation study using FTIR Spectrometer showed the presence of aminosilance group in the sample (N-H). This proved that the presence of nitrate elements in AEPTMS as well as the sample has improved the nitrate adsorption efficiency.

5.2 Recommendation

Two experimental works or projects can be recommended that are related to this present study. First, a study can be performed to observe the effect of solution temperature on percentage removal. This study will come out with a trend of nitrate removal percentage at different aqueous solution temperature. Second study that can be proposed is to identify the most optimum loading of AEPTMS percentage on the sample to achieve maximum nitrate removal capacity. The results from the present work showed that 70% percentage removal was obtained for 20% AEPTMS loading and it is predicted that at higher amount of loading (50% for example) of AEPTMS could resulted in higher nitrate removal,

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APPENDIX

ADSORPTION STUDY

Percentage removal at equilibrium, $R = \frac{(C_i - C_e)}{C_i}$ x 100

Amount of nitrate adsorbed at equilibrium, $q_e = (C_i - C_e)x \frac{V}{m}$

Distribution coefficient, $K_d = \frac{(C_i - C_e)}{C_i}$ x $\frac{V}{m}$

V = 25 mL m = 0.05 g

Pure MCM-41:

C_i = 62 mg/L

C_e = 0.0005 mol/L x 62000mg/mol = 31 mg/L

Thus, $R = \frac{(62-31)}{62}$ x 100 = 50%

$q_e = (62 - 31)x \frac{0.025}{0.05}$ = 15.5 mg NO^{-3}/g adsorbent

$K_d = \frac{(62-31)}{62}$ x $\frac{25}{0.05}$ = 250 mL/g

10% loaded AEPTMS MCM-41:

C_i = 62 mg/L

C_e = 0.0003mol/L x 62 g/mol = 18.6 mg/L

Thus, $R = \frac{(62-18.6)}{62}$ x 100 = 70%

$q_e = (62 - 18.6)x \frac{0.025}{0.05}$ = 21.7 mg NO^{-3}/g adsorbent

$K_d = \frac{(62-18.6)}{62}$ x $\frac{25}{0.05}$ = 350 mL/g

20% loaded AEPTMS MCM-41:

C_i = 62 mg/L

C_e = 0.0002mol/L x 62000 mg/mol = 12.4 mg/L

Thus, $R = \frac{(62-12.4)}{62}$ x 100 = 80%

$q_e = (62 - 12.4)x \frac{0.025}{0.05}$ = 24.8 mg NO^{-3}/g adsorbent

$K_d = \frac{(62-12.4)}{62}$ x $\frac{25}{0.05}$ = 400 mL/g

KINETIC STUDY

Amount of nitrate adsorbed at time t, $q_t = (C_i - C_t) \text{ x } \frac{V}{m}$

C_i = 62 mg/L   V = 0.025 L   m = 0.05 g

Pure MCM-41:

C_t = 0.001 mol/L x 62000 mg/mol = 62 mg/L

Thus, $q_t = (62 - 62) \text{ x } \frac{0.025}{0.05} = 0$

Time (min)	q_t(mg NO^{-3}/ g adsorbent)		
	Pure MCM-41	10% AEPTMS MCM-41	20% AEPTMS MCM-41
60	0.0	12.4	15.5
120	3.1	12.4	15.5
240	3.1	12.4	18.6
1200	12.4	15.5	24.8
1440	15.5	21.7	24.8

Kinetic Modelling

Pseudo-first order:

$$\log(q_e - q_t) = \log q_e - k_1 t$$

Pure: q_e= 15.5 mg NO^{-3}/g adsorbent

10% loaded AEPTMS MCM-41: q_e= 21.7 mg NO^{-3}/g adsorbent

20% loaded AEPTMS MCM-41: q_e= 24.8 mg NO^{-3}/g adsorbent

Time (min)	q_t(mg NO^{-3}/g adsorbent)			Log (q_e– q_t)		
	Pure	10%	20%	Pure	10%	20%
60	0.0	12.4	15.5	1.2	1.0	1.0
120	3.1	12.4	15.5	1.1	1.0	1.0
240	3.1	12.4	18.6	1.1	1.0	0.8
1200	12.4	15.5	24.8	0.5	0.8	0.0
1440	15.5	21.7	24.8	0.0	0.0	0.0

Based on pseudo-second order model,

Samples	q_e (mg/g)	k_2 (g/mg min)	R^2
Pure	15.5	0.00077	0.692
10% loaded AEPTMS	21.7	0.00055	0.948
20% loaded AEPTMS	24.8	0.00078	0.978

Pseudo-second order:

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e}$$

Pure: q_e= 15.5 mg NO^{-3}/g adsorbent

10% loaded AEPTMS MCM-41: q_e= 21.7 mg NO^{-3}/g adsorbent

20% loaded AEPTMS MCM-41: q_e= 24.8 mg NO^{-3}/g adsorbent

Time (min)	q_t(mg NO^{-3}/g adsorbent)			t/q_t		
	Pure	10%	20%	Pure	10%	20%
60	0.0	12.4	15.5	0.0	4.8	3.9
120	3.1	12.4	15.5	38.7	9.7	7.7
240	3.1	12.4	18.6	77.4	19.4	12.9
1200	12.4	15.5	24.8	96.8	77.4	48.4
1440	15.5	21.7	24.8	93.0	66.4	58.1

Based on pseudo-second order model,

Samples	q_e (mg/g)	k_2 (g/mg min)	R^2
Pure	15.5	0.0042	0.635
10% loaded AEPTMS	21.7	0.0021	0.938
20% loaded AEPTMS	24.8	0.0016	0.999

For Pure MCM-41,

$k_2 = \frac{1}{20^2} = 0.0042$

ISOTHERM STUDY

Initial concentration, Ci (mg/L)	qe (mg/g)		
	Pure	10% loaded	20% loaded
12.4	0	0.0	0
24.8	0	3.1	3.1
37.2	0	9.3	12.4
49.6	6.2	12.4	15.5
62.0	15.5	21.7	24.8

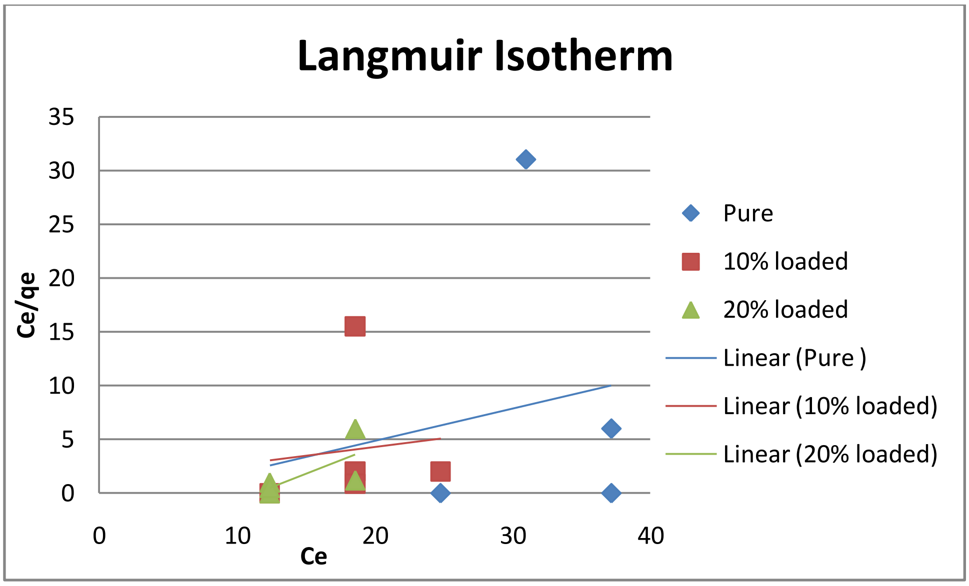
Langmuir Isotherm

$$\frac{C_e}{q_e} = \frac{1}{b\,q_{max}} + \frac{C_e}{q_{max}}$$

Initial concentration, Ci (mg/L)	Pure		10% loaded		20% loaded	
	Ce	Ce/qe	Ce	Ce/qe	Ce	Ce/qe
12.4	12.4	0.0	12.4	0.0	12.4	0.0
24.8	24.8	0.0	18.6	15.5	18.6	6.0
37.2	37.2	0.0	18.6	2.0	12.4	1.0
49.6	37.2	6.0	24.8	2.0	18.6	1.2
62.0	31.0	31.0	18.6	0.9	12.4	0.5

Slope = $\frac{1}{q_{max}}$

Y-intercept = $\frac{1}{b\,q_{max}}$



Sample	q_{max} (mg/g)	b (l/mg)	R^2
Pure	3.34	-0.262	0.053
10% loaded	6.21	0.149	0.012
20% loaded	2.00	-0.088	0.489

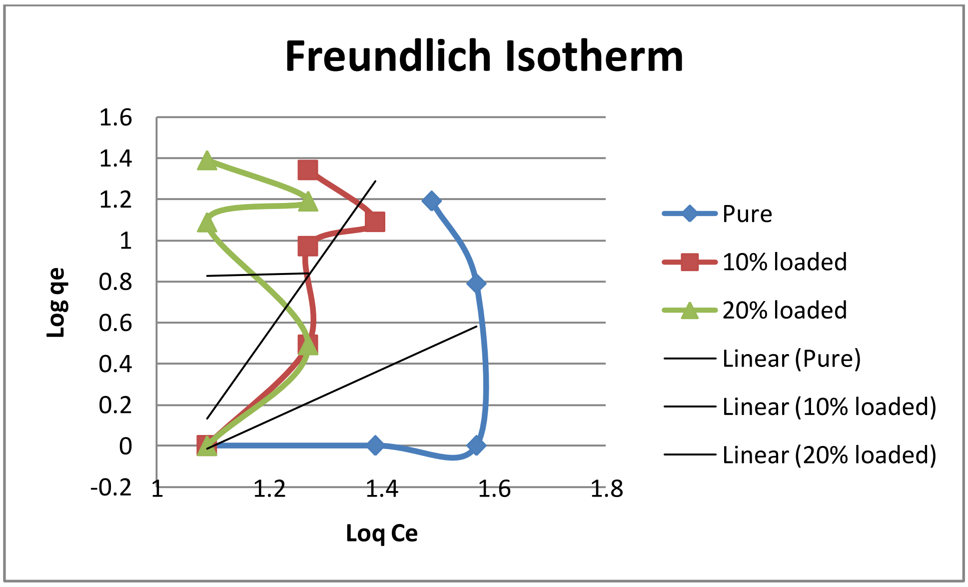
Freundlich Isotherm

$$\log q_e = \log K_F + \frac{1}{n} log C_e$$

Initial concentration, Ci (mg/L)	Pure		10% loaded		20% loaded	
	Log Ce	Log qe	Log Ce	Log qe	Log Ce	Log qe
12.4	1.09	0.00	1.09	0.00	1.09	0.00
24.8	1.39	0.00	1.27	0.49	1.27	0.49
37.2	1.57	0.00	1.27	0.97	1.09	1.09
49.6	1.57	0.79	1.39	1.09	1.27	1.19
62.0	1.49	1.19	1.27	1.34	1.09	1.39

Slope = $\frac{1}{n}$

Y-intercept = $\log K_F$



Sample	K_F (mg/g)	n	R^2
Pure	0.04300	0.807	0.195
10% loaded	0.00009	0.260	0.600
20% loaded	5.55904	13.513	0.000