Removal of total petroleum hydrocarbons from oil refinery waste using granulated NaA zeolite nanoparticles modified with hexadecyltrimethylammonium bromide

<table>
<thead>
<tr>
<th><strong>Journal:</strong></th>
<th>Canadian Journal of Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manuscript ID:</strong></td>
<td>cjc-2015-0390.R1</td>
</tr>
<tr>
<td><strong>Manuscript Type:</strong></td>
<td>Article</td>
</tr>
<tr>
<td><strong>Date Submitted by the Author:</strong></td>
<td>01-Sep-2015</td>
</tr>
<tr>
<td><strong>Complete List of Authors:</strong></td>
<td>Esmaeili, Akbar; Chemical Engineering, Saremnia, Betsabe; Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, PO Box 19585/936, Tehran, Iran, Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, PO Box 19585/936, Tehran, Iran, Sohrabi, Mohammad-Reza; Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, PO Box 19585/936, Tehran, Iran., Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, PO Box 19585/936, Tehran, Iran.</td>
</tr>
<tr>
<td><strong>Keyword:</strong></td>
<td>Granulated NaA-ZNPs, hexadecyltrimethylammonium bromide (CTAB), adsorption</td>
</tr>
</tbody>
</table>
Title of manuscript

Removal of total petroleum hydrocarbons from oil refinery waste using granulated NaA zeolite nanoparticles modified with hexadecyltrimethylammonium bromide

Running title

TPHs removal by HCTAB for oil refinery wastewater

Names of authors

Betsabe Saremnia, Akbar Esmaeili*, Mohammad-Reza Sohrabi

Addresses of authors

Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, PO Box 19585/936, Tehran, Iran.

Address for correspondence

Department of Chemical Engineering, North Tehran Branch, Islamic Azad University

PO Box 19585/936, Tehran, Iran.


Email: akbaresmaeili@yahoo.com; akbaresmaeili@iau.ac.ir

Number of text pages: 14

Table: 01

Figures: 03

Word count: 4086
Removal of total petroleum hydrocarbons from oil refinery waste using granulated NaA zeolite nanoparticles modified with hexadecyltrimethylammonium bromide

Betsabe Saremnia, Akbar Esmaeili*, Mohammad-Reza Sohrabi

Department of Chemical Engineering, North Tehran Branch, Islamic Azad University, PO Box 19585/936, Tehran, Iran

*Corresponding author: akbaresmaeili@yahoo.com; tel: +98-912-148-4813; fax: +98-21-88787204

Abstract

Petroleum pollution is a common problem in industrial areas to such an extent that it poses a global threat. The wastes of oil refineries contain a wide variety of hydrocarbons. The aim of this study was to investigate the possibility to removal of total petroleum hydrocarbons (TPH) from Behregan oil refinery, Bushehr, Iran, by granulated nanozeolite NaA particles (NaA-ZNPs) modified with cationic surfactants. Synthesized NaA-ZNPs with a silica source extracted from Hordeum vulgare were granulated by an alginate granulation method and were modified by the cationic surfactant hexadecyltrimethylammonium bromide (CTAB). The CTAB-modified granulated NaA-ZNPs were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and the Brunauer-Emmett-Teller (BET) theory. Adsorption of TPH was studied using both a batch process and a continuous-flow process in a fixed-bed column. The effect of various parameters, including time, pH, adsorbent dosage, flow rate, and column height investigated, and the results were analyzed by Gas chromatography-mass spectrocop (GC-MS). The efficiency of the CTAB-modified granulated NaA-ZNPs was evaluated with one-way analysis of variance (ANOVA) software SPSS 21. The highest TPH removal efficiency for batch processing (92.3%) was achieved at
adsorbent dosage 0.5 mg, pH=7, and 20 min contact time; the highest TPH removal efficiency for continuous processing (87.4%) was achieved at 15 cm column height and 17.26 mL min$^{-1}$ flow rate. The results indicated the potential of CTAB-modified granulated NaA-ZNPs for absorbing TPH in treating oil-refinery waste.

**Keywords:** granulated NaA-ZNPs, hexadecyltrimethylammonium bromide (CTAB), adsorption, total petroleum hydrocarbons (TPH)

1. Introduction

Various industries, including oil refineries and other petrochemical complexes, generate wastewater that can include aromatic compounds, hydrocarbons, oil, grease, and other hazardous organic materials $^1$. In recent years it has been observed that adsorption processes are a good way to absorb contaminants. However, due to the high price of many adsorbents, efforts have been made to identify and use low-cost natural or synthetic adsorbents. Zeolites fall in this category $^2$. Zeolites are porous crystalline aluminosilicates with high surface areas and molecular sieving properties. These hydrated aluminosilicates are structured in three-dimensional lattices that are composed of SiO$_4$ and AlO$_4$. Zeolites are generally divided into two categories: natural and synthetic $^3$. Synthetic zeolites, by reason of high purity, formation of a specific type rather than a mixture of several types, easy of synthesis on a commercial scale, and controllable pore size, offer a considerable advantage over to their natural forms $^4$. Zeolite synthesis is achieved by hydrothermal crystallization of an active solution of hydrated aluminosilicate or gel in an alkaline environment. A suitable alkaline environment can be created with alkali hydroxides, alkaline-earth hydroxides, organic bases, and combined bases $^5$.

It should be noted that synthesized ZNPs cannot be used in their original size for many industries because of high-pressure drops in the reactor. Granulating ZNPs may reduce some of
the technical problems such as loss ZNPs from the powder, formation of lumps, alteration of flow properties, dangers in handling, low surface-to-volume ratio, low porosity, and high-pressure drops. Overall, size enlargement of the ZNPs, particularly in the form of granules, would be essential to broaden their industrial applications as adsorbents and catalysts.

Zeolites have a permanent negative charge on their surface; thus, it is possible to modify them with a cationic surfactant for better stability and absorption of other compounds (anionites and nonpolar organic materials). At low concentrations of surfactant, cations are retained by ion exchange, which leads to the formation of a monolayer on the external surface of the zeolite. The retained surfactant adds a hydrophobic surface to the zeolite, thus making it suitable for retaining organic compounds. This use of surface-modified zeolites can be performed at a low price and with high pollutant removal. The main objective of this project was to investigate the possibility of removal of TPH using granulated modified with NaA-ZNPs by the cationic surfactant CTAB. Scheme 1 provides an overview of the process of producing granulated NaA-ZNPs modified by CTAB to investigate their use in removal of TPH from industrial wastewater.

2. Material and methods

2.1. Materials

Wastewater containing TPH (pH 3.6) was provided from an oil refinery in Bahregan, Bushehr, Iran. Sodium hydroxide, sodium aluminate, hydrochloric acid, sodium alginate, barium chloride, CTAB, clay, and acetone were purchased from Merck of Germany. Deionized water was used throughout this work. H. vulgare was purchased from Sobhan Darou (Iran). Acetic acid, HCl and H₂SO₄ and CHCL₃ were purchased from Sigma Chemical Co. (St. Louis, MO, USA).

2.2. Synthesis of NaA-ZNPs
For the synthesis of NaA-ZNPs, the following molar composition was used:

\[ xNa_2O : 0.55Al_2O_3 : SiO_2 : 150H_2O \]

A sodium hydroxide solution was prepared and divided into two parts. An alumina source (sodium aluminate, 98%, Merck) was added to the first portion, and silica extracted from *H. vulgare* was added in the second portion. Crystallinity was achieved in an oil bath at ambient temperature (25 °C) in a polypropylene reactor, varying the time and alkalinity conditions (Table 1). After centrifuging (2000 rpm) each sample, the resulting NaA-ZNPs were washed with deionized water for several times and dried at 110 °C.

### 2.3. Preparation of NaA-ZNP granules

NaA-ZNPs with an appropriate amount of clay were suspended in distilled water, and sodium alginate was added to it. The slurry was mixed with a magnetic stirrer while being heated to 90 °C. The solution was left to motionless for 1 h until any trapped air bubbles were released. The lump of sodium alginate was separated by centrifugation at 2500 rpm.

Using a peristaltic pump, the slurry was sent through a tube and with a needle at the end. Air passed around the needle caused spherical droplets to form as the slurry was expressed through the needle and dripped into a tank filled with continuously stirred barium chloride solution. This mixture was slowly stirred for 2 h and then repeatedly washed with distilled water. The resulting granules were immersed in acetone for 1 h and dried at the ambient temperature for 24 h. In order to use the nanozeolite it is necessary that the alginate content be burned and removed. To this purpose, the nanozeolite granules were heated in a furnace at 500 °C.

### 2.4. Surface modification of absorbents

CTAB cationic surfactant was used to modify the surface of the granulated NaA-ZNPs. Sodium zeolite was mixed with the surfactant solution in a polyethylene container. The container was shaken slowly for 48 h. The samples were then filtered and washed with a large amount of
distilled water, with care taken not to create foam by shaking the outlet water of the filter. The resulting adsorbent was then dried in ambient temperature and stored in a watertight polyethylene bottle in a refrigerator.

2.5. TPH adsorption tests

2.5.1. Batch studies

2.5.1.1. Effect of time

To study the effect of time in the batch process, adsorbent was added to oil-refinery waste with a neutral pH and at ambient temperature, and the reactor was placed on a shaker. At different intervals over a period of 5–80 min, specimens of the effluent were taken and centrifuged to separate the adsorbent, and then analyzed by GC-MS.

2.5.1.2. Effect of adsorbent dosage

To determine the proper amount of sorbent for removing oil contaminants, 0.25–1.25 g of adsorbent in increments of 0.25 g were added to 10 mL of tepid wastewater with a neutral pH=3. The samples were stirred on a shaker for 20 min and isolated by centrifugation, then analyzed by GC-MS.

2.5.1.3. Effect of pH

Solution pH is an important factor in absorption. This parameter may alter the chemical properties affecting the affinity of sorbent materials for their targets. Solution pH affects the degree of ionization and the formation of different types of pollutants and consequently leads to changes in reaction kinetics and equilibrium properties during the absorption processes. In this study, hydrochloric acid solution and sodium hydroxide were added to the wastewater to adjust the pH within the range of 3–11 in increments of two units. For each pH, 0.5 g adsorbent was added to 10 ml of effluent. The samples were placed on a shaker for 20 min at 300 rpm at room
temperature (25 °C). After removal of the adsorbent from the wastewater by centrifuge, the samples were analyzed by GC-MS.

2.5.2. Continuous studies

To determine the conditions under which the adsorbent to provided the lowest concentration of pollutants in post-treatment wastewater, a column with a 3-cm internal diameter and 20-cm length was used as a fixed-bed reactor with ascending flow. The column was sealed at the top and bottom with fiberglass to prevent escape of the NaA-ZNPs granules. Column height and the input flow rate were examined. Figure 1a provides a schematic diagram of the NaA-ZNP granulation process and Figure 1b provides a schematic diagram of the columns used in this study.

To evaluate the effect of column height on absorption, an adsorbent mass of 5 g was introduced to heights of 5, 15, and 20 cm. Column height was adjusted by placing glass bullets in the column. For each column height, distilled water was pumped into the column for 10 min. Following this, an inlet hose was connected to a waste tank containing wastewater with pH adjusted to 3. The wastewater was fed into the column at the rate of 17.26 mL min$^{-1}$ and allowed to flow out into an outlet tank. After 20 min, a sample of the treated wastewater was taken and centrifuged at 2500 rpm for 10 min to separate the adsorbent particles. The sample for each column height was analyzed by GC-MS.

To evaluate the effect of flow rate, a peristaltic pump was used to provide flow rates of 7.4, 12.3, and 17.26 mL min$^{-1}$. The formulae for the assessment of the percentage of TPH removed at varying flow rates were as follows: $Y = (X_i/X_0) \times 100$; removal percentage $= Y - 100$; $X_0$ and $X_i$ are the ppm values of the initial and final volumes of TPH, respectively.$^{10}$

2.6. Analysis GC/MS
Analysis was performed using a Hewlett-Packard 5973, USA, with a HP-5 MS column (30 m × 0.25 mm, film thickness 0.25 µm). The column temperature was kept at 60°C for 3 min and programmed to 220°C for 5 min. The flow rate of Helium as carrier gas with 1 ml.min⁻¹. MS were taken at 70 eV. Identification of the constituents of each oil was made by comparison of their mass spectra and retention indices (RI) with those given in the literature and those authentic samples.

2.7. Statistical test

One-way analysis of variance (ANOVA) was used to evaluate the differences among five variables affecting the process. All statistical analyses were carried out using SPSS 21. Statistical significance was expressed at $F$ and $P$ value < 0.05.

3. Results and discussion

3.1. Characterization of synthesized NaA-ZNPs

Although 5 different tests for the synthesis of NaA-ZNPs were performed, due to lack of successful synthesis, only the results of a powder sample synthesized for 3 days using a ratio of $\text{Na}_2\text{O}/\text{SiO}_2 = 6$ were investigated (Table 1). Figure 2a shows the XRD (Philips PW3040, Germany) patterns for NaA-ZNPs and granulated NaA-ZNPs. Comparative analysis of the nanopowder XRD pattern of the sample synthesized with standard patterns indicates that the NaA zeolite phase was synthesized with high purity and without interference.

The crystal size of the NaA-ZNPs obtained was analyzed using the Scherrer equation and found to be in the range of 10–30 nm; the particle size was in the range of 20–100 nm. The $\text{Na}_2\text{O}/\text{SiO}_2$ ratio has an effect on the kinetics of formation of zeolite. Increasing the ratio from 0.9 to 6 allowed the formation of crystalline zeolite in 3 days. An increase in the ratio from 6 to 9 changed the synthesized zeolite phase into a NaP1 phase. To investigate the effect of time on the synthesis of NaA-ZNPs, periods of 1, 2, and 3 days were selected for synthesis. Based on the
XRD results, the best time period for synthesis of NaA-ZNPs with this method for a silica source derived from *H. vulgare* ash was 3 days, and the best Na$_2$O/SiO$_2$ ratio was 6. Valtchev and colleagues also found that the best time for synthesis of nanozeolite NaA using a sodium silicate source and without using organic additives with this method was 3 days at room temperature, with an Na$_2$O/SiO$_2$ ratio of 6.

### 3.2. Characterization of granulated NaA-ZNPs

The XRD pattern of granulated NaA-ZNPs can be seen in Figure 2a. The pattern shows that the overlapping amorphous solid phase led to sharp increases in the underlying lines that covered the peak of the zeolite phase. But it remained part of the zeolite structure, so the sample could be used for surface modification and absorption. SEM (KYKY-EM3200, China) image of the granular samples is shown in Figures 2b and 2c. The NaA-ZNP crystals embedded within the granules increase the size to 300–500 nm.

BET (Sorptometer 1042, Italy) nitrogen adsorption analysis of the NaA-ZNPs and granules is shown in Figures 2d and 2e. Based on this analysis, the specific surface area of the NaA-ZNPs is equal to 210.729 m$^2$/g and of the granules is 90.870 m$^2$/g, which indicates that the absorption capacity of nanozeolite decreases under granulation. But it should be noted that surfactant adsorption occurs only on the external surface area and is affected by the size of the surfactant molecules, absorbing capacity of the adsorbents, and the surfactant cation exchange capacity on the external surface of the granules. As other researchers have discussed, the reduced particle size of nanozeolites and subsequent larger surface area in relation to volume, as well as the lower Si:Al ratio of synthesized nanozeolite, can be considered as the main reasons for the improvement in absorbency.

### 3.3. Characterization of CTAB-modified granulated NaA-ZNPs
Vibrations that are related to the Al$_2$O$_4$ and SiO$_4$ tetrahedral connection manifested no significant changes by changing the structure of the sample. Vibrations related to the tetrahedral connection and structure are sensitive to the tetrahedral structure and individual connections in secondary structural units.

Generally, three types of peak absorption in the FT-IR spectrum (thermo scientific Nicolet 8700 FTIR spectrometer) can be observed in any type of aluminosilicate: an H$_2$O absorption peak at 3431 and 1643 cm$^{-1}$ indicates that it is related to the H–O–H bending vibration for protonation -OH. The Al$_2$O$_4$ and SiO$_4$ tetrahedral structural unit’s peaks at 991 and 1150 cm$^{-1}$ are related to Al–O and Si–O asymmetric stretching, and peaks at 562 and 732 cm$^{-1}$ are related to Al–O and Si–O symmetric stretching. The peak at 610 cm$^{-1}$ of the external connections is associated with dual ring stretching of the secondary structural units (Figures 2f and 2g). This result was unexpected since modification of the CTAB-modified NaA should ideally increase the basal spacing of the NaA-ZNP interlayer, which implies more adsorption sites are accessible. One cause the smaller surface area of CTAB-modified granulated NaA-ZNPs may be the introduction of the large surfactant molecules into the clay interlayer. As researchers have reported previously, the internal pore spaces may be occupied mainly by long-chained surfactants, leading to a decrease in the specific surface area of the CTAB-modified NaA zeolite compared with the NaA-ZNPs. This implies that adsorption is occurring primarily on the external surface of the adsorbent, thus the corresponding low surface area obtained.

3.4. Removal of TPH with batch processing

3.4.1. Effect of contact time
Figure 3a (F-value = 3.172) shows that the rate of adsorption of TPH onto the adsorbent was initially rapid and then slowed down. This could be explained by the fact that a large number of empty adsorption sites are available during the initial stage of sorption, allowing contaminants to be adsorbed quickly onto the adsorbent. Other researchers have reported the same result using different adsorbents. The maximum amount of adsorption (87.5%) occurred in 20 min; after this time fewer remaining vacant sites were available, so the rate and efficiency of adsorption was reduced.

3.4.2. Effect of adsorbent dosage

The results showed that the percentage of TPH removal increases with increasing adsorbent dosage. This is due to the increased surface activity caused by increasing the amount of absorbent, thus affording more vacant sites for uptake of contaminants. The maximum amount of TPH removal (92.3%) occurred with 500 mg of adsorbent, which indicates that the largest number of available adsorption sites are formed at this dosage (Figure 3b; F-value = 0.025). When the absorbent dose was increased from 500 mg to 1000 mg, the absorption rate became almost constant and then declined sharply. Other researchers have reported similar results for organic pollutant removal.

3.4.3. Effect of pH

The pH is one of the most important parameters affecting the TPH adsorption capacity of oil-refinery waste. As can be seen in Figure 3c, the maximum adsorption capacity achieved was 92.3%, which was observed at pH=7. Due to the negative surface charge of the adsorbent caused by increasing the acidity of the solution, the $\text{H}_3\text{O}^+$ will have a greater effect. Due to the small size of $\text{H}_3\text{O}^+$ ions and their high mobility, the ions easily enter the holes in the zeolites and are replaced with the exchangeable ions in adsorbent. Thus, by increasing the
concentration of \( H_3O^+ \), reduction in absorption can be seen. Other researchers have reported that the existence of \( OH^- \) ions at higher pH affects adsorption adversely \(^{16-17}\). Increasing pH decreases the efficiency and absorption capacity and insoluble hydroxide complexes are formed \(^{18}\). Since the structure of zeolite is damaged at pH > 11, higher pHs were not tested in this study (F-value = 0.041).

3.5. Removal of TPH in a continuous system

Using a continuous system of absorption on a laboratory scale can serve as an introduction to the use of adsorbents on industrial and semi-industrial scales. In this part of the study, TPH removal with a nanogranular absorbent in a fixed-bed reactor was studied. Important parameters affecting the adsorption in the continuous process are (a) the height of the column, and (b) the wastewater flow rate.

3.5.1. Effect of column height

In the continuous process, the percentage of TPH removal was raised by increasing the bed height, due to the availability of more binding sites for sorption. The adsorbent forms a monolayer on the zeolite, so the number of active positions will depend on the available area. Numerous similar observations have been made by researchers for different types of zeolite, with smaller bed heights corresponding to less absorption \(^{19}\). The maximum adsorption of 87.4% was achieved with a bed height of 15 cm (Figure 3d; F-value = 0.880).

3.5.2. Effect of flow rate

Figure 3e is adsorption improved with increasing flow rate. Because of the kinetics of adsorption, the greatest adsorption takes place in the shortest time. When internal mass transfer limits control the process, low flow rates are more effective, but when external mass transfer limits control the process, high flow rates increase the mass transfer. Most research to date has
shown different results, indicating that an increase in flow rate allows more solute ions to come in contact with the adsorbent, making it less dependent on the availability of adsorbate. Based on the results of the bed-height testing, the 15-cm column height was used in evaluating the effect of flow rate. A flow rate of 17.26 mL min$^{-1}$ provided the best efficiency, yielding 87.4% adsorption (Figure 3e; F-value = 188.595). In optimum conditions (pH 7, 20 min contact time, adsorbent dosage 500 g, bed height 15 cm, flow rate 17.26 mL min$^{-1}$), removal of 87.4% of TPH from wastewater was achieved. In summary, it is possible to make efficient use of natural sources for synthesis of strong adsorbents for eliminating petroleum pollutants such as TPH from the environment. Figure 3f shows the data of the ANOVA test on all five parameters investigated in processing the Behregan oil-refinery wastewater to remove TPH. Figure 3g shows GC-MS data for all five parameters during process for TPH of treatment wastewater. The decrease in peak areas confirms the ability of CTAB-modified granulated NaA-ZNPs to remove oil-refinery waste.

4. Conclusion

NaA-type zeolite nanoparticles synthesized under optimal conditions of crystallization time and Na$_2$O/SiO$_2$ ratio were investigated in detail. After determining the optimal parameters, NaA zeolite nanoparticles 20–100 nm in size were synthesized in 3 days using a hydrothermal method without organic additives and then modified into granules using the cationic surfactant CTAB. The NaA-ZNP granules were then tested for their ability to absorb and remove TPH from oil-refinery wastewater. The batch and continuous processing in a fixed-bed reactor were used to conduct the experiments, and GC-MS spectrum analyses confirmed the removal of TPH. Statistical analysis of the experimental data were been performed with an ANOVA test. Under optimal values of the process parameters (pH=7, contact time 20 min, adsorbent dosage 500 g,
bed height 15 cm, flow rate 17.26 mL min\(^{-1}\)) 87.4\% TPH removal was achieved in a continuous-flow system.

**List of abbreviations**

Total petroleum hydrocarbons (TPH), hexadecyltrimethylammonium bromide (CTAB), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), Fourier transform infrared spectroscopy (FT-IR), gas chromatography-mass spectroscopy (GC-MS), X-ray diffraction (XRD), NaA zeolite nanoparticles (NaA-ZNPs)

**References**

Scheme 1. Investigation into the possibility of removal of TPH using granulated NaA-ZNPs modified by the cationic surfactant CTAB.

Figure captions:

Figure 1a. Schematic of granulation process: (A) NaA zeolite, alginate, clay suspension; (B) peristaltic pump; (C) air pump; (D) 0.1 M BaCl₂ solution; (1b) Schematic of continuous fixed-bed adsorption process (FT = feed tank; P = pump; GB = glass beads; NaA-ZNPs = NaA zeolite nanoparticles; A, B, and C = 5 cm; O = outlet).

Figure 2a. XRD pattern of (a) synthesized NaA nanozeolite; (b) granulated NaA nanozeolite; (2b) SEM image of final synthesized granulated NaA-ZNPs; (c) SEM image of final granulated NaA-ZNPs; (2d) BET test result of NaA nanozeolite; (2e) BET test result of granulated NaA nanozeolite; (2f) IR spectra of zeolite modified with a cationic surfactant; (2g) IR spectra of zeolite NaA.

Figure 3a. Data of ANOVA test for the effect of contact time on the removal of TPH in (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 80 min (adsorbent dosage 200 mg, effluent volume 50 ml, pH 7); (3b) Data of ANOVA test for the effect of adsorbent dosage on the removal of TPH: (a) 250 mg, (b) 500 mg, (c) 750 mg, (d) 1000 mg, (e) 1250 mg (contact time 20 min, effluent volume 50 ml, pH 7); (3c) Data of ANOVA test for the effect of pH on the removal of TPH: (a) pH 3, (b) pH 5, (c) pH 7, (d) pH 9, (e) pH=11 (adsorbent dosage 500 mg, contact time 20 min, wastewater volume 50 ml). (3d) Data of ANOVA test for the effect of column height on the removal of TPH: (a) height 5 cm, (b) height 10 cm, (c) height 15 cm (adsorbent dosage 500 mg, contact time 20 min, wastewater volume 50 ml, pH 7); (3e) Data of ANOVA test for the effect of flow rate on the removal of TPH: (a) flow rate = 7.4 mL min⁻¹, (b) flow rate 12.5 mL min⁻¹, (c) flow rate 17.26 mL min⁻¹ (adsorbent dosage 500 mg, contact time 20 min, effluent volume 50 ml, pH 7). (3f) Data of
ANOVA test of five parameters during processing of oil-refinery waste containing TPH; (3g) Data of GC-MS for five parameters during processing of oil-refinery waste containing TPH.

Table Captions:

Table 1. NaA-ZNP synthesis conditions at 25 °C.
Table 1. NaA-ZNP synthesis conditions at 25 °C.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (days)</th>
<th>Na₂O:SiO₂ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>
Scheme 1.
**Figure 1a.** Schematic of granulation process: (A) NaA zeolite, alginate, clay suspension; (B) peristaltic pump; (C) air pump; (D) 0.1 M BaCl$_2$ solution.
Figure 1b. Schematic of continuous fixed-bed adsorption process (FT = feed tank; P = pump; GB = glass beads; NaA-ZNPs = NaA zeolite nanoparticles; A, B, and C = 5 cm; O = outlet).
Figure 2a. XRD pattern of (a) synthesized NaA nanozeolite; (b) granulated NaA nanozeolite.
Figure 2b. SEM image of final synthesized granulated NaA-ZNPs.
Figure 2c. SEM image of final granulated NaA-ZNPs.
Figure 2d. BET test result of NaA nanozeolite.
Figure 2e. BET test result of granulated NaA nanozeolite.
Figure 2f: IR spectra of zeolite modified with a cationic surfactant.
Figure 2g: IR spectra of zeolite NaA.

https://mc06.manuscriptcentral.com/cjc-pubs
Figure 3a. Data of ANOVA test for the effect of contact time on the removal of TPH in (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 80 min (adsorbent dosage 200 mg, effluent volume 50 ml, pH 7).
Figure 3b. Data of ANOVA test for the effect of adsorbent dosage on the removal of TPH: (a) 250 mg, (b) 500 mg, © 750 mg, (d) 1000 mg, (e) 1250 mg (contact time 20min, effluent volume 50 ml, pH 7).
Figure 3c. Data of ANOVA test for the effect of pH on the removal of TPH: (a) pH 3, (b) pH 5, (c) pH 7, (d) pH 9, (e) pH=11 (adsorbent dosage 500mg, contact time 20 min, wastewater volume 50ml).
Figure 3d. Data of ANOVA test for the effect of column height on the removal of TPH: (a) height 5 cm, (b) height 10 cm, (c) height 15 cm (adsorbent dosage 500 mg, contact time 20 min, wastewater volume 50ml, pH 7).
Figure 3e. Data of ANOVA test for the effect of flow rate on the removal of TPH: (a) flow rate = 7.4 mL min\(^{-1}\), (b) flow rate 12.5 mL min\(^{-1}\), (c) flow rate 17.26 mL min\(^{-1}\) (adsorbent dosage 500 mg, contact time 20 min, effluent volume 50 ml, pH 7).
Figure 3f. Data of ANOVA test of five parameters during processing of oil-refinery waste containing TPH.
Figure 3g. Data of GC-MS for five parameters during processing of oil-refinery waste containing TPH.
Figure 1a.
Figure 2c.
Figure 2d.
Figure 2e.
Figure 2f.
Figure 2g.
Figure 3a.
Figure 3b.
Figure 3c.
Figure 3d.
Figure 3e.
Figure 3g.