Journal of the Taiwan Institute of Chemical Engineers 61 (2016) 276–286

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

# Synthesis and characterization of NaA zeolite nanoparticles from *Hordeum vulgare* L. husk for the separation of total petroleum hydrocarbon by an adsorption process

Akbar Esmaeili*, Betsabe Saremnia

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

ARTICLE INFO

*Article history:*
Received 9 July 2015
Revised 12 November 2015
Accepted 31 December 2015

*Keywords:*
NaA zeolite nanoparticles
Total petroleum hydrocarbon
Hydrothermal
*Hordeum vulgare*
Oil refinery

ABSTRACT

*Hordeum vulgare*, commonly known as barley, grows abundantly around an oil refinery in Bahregan, Bushehr, Iran. A mixture of hydrocarbons found in crude oil, total petroleum hydrocarbon (TPH), is one of the most common groups of persistent organic contaminants, and is found in the wastewater from the Bahregan oil refinery. The purpose of this study was to synthesize and characterize NaA zeolite nanoparticles (NaA-ZNPs) formed from *H. vulgare* husks using a hydrothermal method and research their effectiveness in removal of TPH from original oil waste by an adsorption process. The NaA-ZNPs were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and the Brunauer–Emmert–Teller (BET) theory. A pure phase of NaA-ZNP with a ratio of $Na_2O:SiO_2 = 6$ was synthesized in three days at room temperature. Adsorption of TPH was studied for both batch and continuous-flow processes. The parameters of time, pH, and adsorbent dosage were studied in the batch process, and flow rate and column height in the continuous process. The results were analyzed with GC–MS. The removal efficiency of the NaA-ZNPs was investigated using statistical test, one-way analysis of variance (ANOVA) SPSS 21 software. In the batch and continuous systems, the highest TPH removal efficiency under optimal conditions was 92.3% and 87.4%, respectively. The project results demonstrated a high potential for use of NaA-ZNPs in treatment or pretreatment of wastewater from oil refineries containing TPH.



## 1. Introduction

Petroleum pollution is a common problem in industrial areas throughout the world. TPH is of major interest, as the accumulation of the compounds found in TPH in different disposal pathways in the environment may lead to serious hazards to humans and other life forms [1]. The technologies widely used for the removal of organic compounds from wastewater include membrane filtration, biological treatment, and adsorption [2].

Zeolites are framework aluminosilicates with pore dimensions of molecular size generated by corner-sharing $Al^{3+}$ and $Si^{4+}$ oxygen tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphic replacement of $Si^{4+}$ by $Al^{3+}$ produces a negative charge in the lattice [3]. Due to this, they can function as molecular sieves and cation exchangers [4]. Compared with other zeolites, synthesized NaA zeolite displays a faster adsorption rate and higher adsorption capacity [3]. Nanometer-sized zeolites can be synthesized using hydrothermal methods that incorporate transparent aluminosilicate solutions in the presence of organic templates [5]. However, the use of organic templates has numerous disadvantages. They are nonrecyclable, expensive, and require calcinations, which results in the production of pollution [6].

Hydrothermal zeolite synthesis is a multiphase reaction–crystallization process, commonly including at least one liquid phase and amorphous and crystalline solid phases. The term *hydrothermal* is used here in a wide sense and includes zeolite crystallization from aqueous systems containing the necessary chemical components. Zeolites are metastable phases, and slight changes in the synthesis conditions can bring about a pollution of the desired product by the cocrystallization of other phases with a similar composition but with completely different properties [7].

The reduction of particle size in synthetic zeolites from micrometers to nanometers has led to fundamental changes in the

*Abbreviations:* BET, Brunauer–Emmert–Teller; FT-IR, Fourier transform infrared spectroscopy; GC–MS, gas chromatography–mass spectroscopy; NaA-ZNPs, NaA zeolite nanoparticles; ANOVA, one-way analysis of variance; SEM, scanning electron microscopy; TPH, total petroleum hydrocarbon; XRF, X-ray fluorescence; XRD, X-ray diffraction.

* Corresponding author. Tel.: +98 912 148 4813; fax: +98 21 88787204.
*E-mail address:* akbaresmaeili@yahoo.com, akbaresmaeili@iau.ac.ir (A. Esmaeili).

http://dx.doi.org/10.1016/j.jtice.2015.12.031
1876-1070/

properties of these materials and improved their performance in catalyst applications and in removal processes [8]. However, significant difference in adsorption uptake between micrometer- and nanometer-sized zeolite A samples has been observed [9].

Today, consumer demand and tough environmental laws have made green technology and environmentally friendly chemical processes more popular. A primary byproduct of *Hordeum vulgare* processing is its waste biomass, which along with other sources of urban biomass (sugarcane leaves, tree leaves, corn, and rice husk) is a source of energy through combustion. Burning *H. vulgare* husks leads to the formation of the ash that contains $SiO_2$; depending on such conditions as the type of furnace, moisture content of the atmosphere, climate, and geographic location the amount of $SiO_2$ in the ash derived from combustion of *H. vulgare* husks can vary from 85% to 98%. Small amounts of alkalis and alkaline earth oxides, such as $Na_2O$, CaO, and MgO, are also present in the ash. Therefore, *H. vulgare* husk offers a cheap source of $SiO_2$ for preparing valuable materials such as zeolites, helping to reduce costs and improve cost-effectiveness in their synthesis [10]. The main aim of this project was to synthesize NaA-ZNPs from *H. vulgare* and investigate the possibility of using them to remove TPH in oil-refinery waste.

## 2. Experimental

### 2.1. Ash preparation from H. vulgare

*H. vulgare* plants were harvested and rinsed with distilled water in order to wash off any particles or dust. The plants were then washed in a 1 M solution of hydrochloric acid dried for 6 h at 700 °C until a white ash was obtained.

### 2.2. Extracting silica from H. vulgare ash

To extract its silica content, the ash was mixed with sodium hydroxide and refluxed at 90 °C. The mixture was filtered and the residue on the filter paper was mixed with 60 ml of deionized water, refluxed at 90 °C, and then filtered again. After this step concentrated hydrochloric acid was added to the solution to reach pH 7 and the solution heated for 24 h at 25 °C to form a gel. The resulting gel was washed thoroughly with distilled water and filtered through Whatman filter paper to be free of chloride. The absence of chloride in the product was determined with silver nitrate (Merck, Germany). The resulting substance was dried for 12 h at 110 °C [11].

### 2.3. Synthesis of NaA-ZNPs

To synthesize the NaA-ZNPs employing a hydrothermal crystallization method, the molar composition $x Na_2O{:}0.55Al_2O_3{:}SiO_2{:}150H_2O$ was used to determine the optimum $Na_2O/SiO_2$ ratio for synthesis of NaA-ZNPs. The gel composition of the NaA-ZNPs was prepared based on XRF analysis of the extracted silica source. NaOH (7.79 g) was dissolved in $H_2O$ (2 mol) and then divided into two equal parts. Following this, 1.26 g of the silica source obtained from *H. vulgare* ash was completely dissolved in one part of the NaOH solution. An aluminate solution was prepared by mixing 13.6 g of an alumina source (sodium aluminate 98%, Merck) with the other part of the NaOH solution. After the solution had become clear, the silicate solution was slowly stirred into the aluminate solution resulting in a clear, homogenous solution. Crystallization was performed in a polypropylene reactor by maintaining an ambient temperature of 25 °C under continuous stirring at 250 rpm. The time and alkalinity conditions were varied as shown in Table 1 [12]. The NaA-ZNPs were then separated by centrifugation (17000 rpm, 30 min) and washed several times with distilled water until the pH value dropped to 8.5. The products were dried in an oven at 110 °C for 24 h. Scheme 1 provides a graphic overview of the synthesis of NaA-ZNPs from *H. vulgare*.

**Table 1**
NaA-ZNP synthesis conditions at room temperature (25 °C).

| Run | Time (d) | $Na_2O{:}SiO_2$ ratio |
|---|---|---|
| 1 | 3 | 0.9 |
| 2 | 3 | 6.0 |
| 3 | 3 | 9.0 |
| 4 | 2 | 6.0 |
| 5 | 1 | 6.0 |

### 2.4. Batch experiments on the adsorption process

Among the various factors, contact time, solution pH, adsorbent dosage, column height, and flow rate can be considered as the most important parameters influencing the biosorption process. *Contact time:* with longer contact time, the rate of adsorption decreased; this was a result of a saturation stage being attained due to the accumulation of the pollutant at the adsorption sites with a concomitant decrease in total adsorbent surface area and increased diffusion pathway. *Solution pH:* it has been reported that electrostatic repulsion between the pollutant and the biomass surface and the competition of hydronium ions for adsorption sites decreases at higher pH; hence, the metal uptake increases. In some studies, the metal uptake has increased as pH was raised until an optimum pH was reached, following which the uptake decreased with further increases in pH. High dosages of the biomass would obviously lead to more binding to the biomass, but could also result in more sorption site interaction. *Adsorbent dosage:* researchers have reported that increasing adsorbent dosage leads to increasing surface area at the adsorption sites, resulting in greater TPH removal.

#### 2.4.1. Contact time

To study the effect of time on particle size, adsorbent was added to an industrial wastewater sample at a neutral pH and ambient temperature. The reactor was placed on a shaker at 300 rpm and specimens of the effluent were taken at intervals over a period of 5–80 min. The effluent samples were centrifuged to separate the adsorbent and analyzed with GC–MS.

#### 2.4.2. Adsorbent dosage

To determine the proper adsorbent dosage for effective removal of oil contaminants, varying amounts were added to wastewater at a neutral pH. The samples were stirred at room temperature on a shaker for 20 min and isolated by centrifugation, and the solution was analyzed by GC–MS.

#### 2.4.3. pH assay

Solution pH is an important factor in adsorption. This parameter 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 adsorption process. To investigate this factor, solutions containing hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) were added to the wastewater to adjust the pH in the range of 3–11 in two-unit increments, and then the adsorbent was added to each sample and the reactor placed on the shaker at 25 °C. After removal of the adsorbent from the wastewater by centrifuge, each sample was subjected to GC–MS analysis.