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Iranian natural zeolite particle modification: Green synthesis, characterization, and oil spill remediation

Maryam Khandan, Shohreh Saffarzadeh-Matin*, Anvar Shalmashi

Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

HIGHLIGHTS

- Iranian NZ was mainly comprising of clinoptiolite and cristobalite framework
- Solventless synthesis with stearic acid was employed for the NZ modification.
- Composite particles were produced with tunable hydrophobic/ hydrophilic properties.
- The modified particles showed some oil removal properties.

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ABSTRACT

In the present work, Iranian natural zeolite particles (NZ) as an abundant and low-cost resource were modified by chemical covalent attachments of commercially available stearic acid (SA) with tunable hydrophobic/hydrophilic properties. The versatile, simple, and green technique of mechanogriding was performed for the hydrophobic derivatisation of NZ. The NZ and as-prepared modified particles were thoroughly characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET), Barret-Joyner-Halenda (BJH), and static water contact angle (WCA) measurements. TG-DTA results revealed the high thermal stability of the modified sample up to 490 °C. The flake-like structures of functionalized NZ were discrete and no longer aggregated due to modification. The absorbing function of the modified NZ was evaluated by its removal of oil from a stable crude oil emulsion in water.

1. Introduction

Natural zeolites (NZ) are crystalline hydrated aluminosilicates with a porous structure whose pores are occupied by water, alkali and alkaline earth cations. Due to their special physio-chemical properties, zeoliterich rocks have opened new horizons in pharmaceutical and veterinarian industries [1]. The key factors inducing the positive, beneficial effects of NZ are its high cation-exchange ability, the molecular sieve, and high absorption properties [2,3]. The latter characteristics have triggered their inclusive applications in water and wastewater treatment, oil spill remediation, water-soluble dyes, toxic ion removal from aqueous solutions, etc. [4-7]. The adsorption capacity of each kind of zeolite is dependent on its detailed chemical/ structural characteristics, namely Si/Al ratio, type, location, and number of cations. A variety of chemical treatments, including acid/base treatment and surfactant impregnation, have commonly been used for ion exchange and changing hydrophilic/ hydrophobic properties to improve the adsorption of various ions or organics in the zeolite structure [4,8-11]. Dealumination, which influences the micropore volumes, occurs during the acid treatment and leads to increased porosity and an absorbent specific surface area [5]. We have the ability to functionalize zeolite systems with long-chain organic molecules and turn them into systems capable of exchanging and absorbing other organic molecules. Complexes formed in this way can absorb hydrophobic compounds or facilitate obtaining stable aqueous suspensions of hydrophobic systems [12]. Hydrophobic modification of these materials is usually implemented by surfactants such as long chain quaternary amines, for example, hexadecyltrimethylammonium chloride [13,4].

One of the main drawbacks of using surfactant modified zeolite with balanced hydrophilic/hydrophobic properties in wastewater treatments is microbial toxicity caused by desorption (leaching) of the surfactant into the water. In a recent review, the toxicity of surfactants used in natural zeolite modification towards microorganisms has been investigated [15]. In the present study, natural zeolite from the Semnan region (southeast Semnan, central Alborz Mountains, Iran) was first characterized thoroughly as an abundant, low cost, and versatile resource. It was then chemically modified with SA through a solventless method for the first time. Lastly, the absorbing property of the functional NZ was assessed in the removal of oil from a stable crude oil emulsion in water. Chemical oxygen demand (COD) of wastewater before and after treatments were measured as an indication of successful oil spill remediation [16].

Surface modification of hydroxyl groups in the presence of organic solvents is usually carried out by the solution impregnation technique accompanied by exhaustive work-up and purification procedures [17-19]. To the best of our knowledge, there is currently no report of solventless covalent attachment of SA to natural zeolite particles.

Alternatively, hydrophobic modification of NZ particles with tuneable amphiphilic properties has been studied because it could potentially be a promising matrix for industrial use in various multiphase mediums such as multiphase reactions, molecular sieves, gas separation, dehydration of organic materials, etc. the ability to fine tune the hydrophilic-hydrophobic balance in natural zeolite particles could also provide for deliberate dispersion and their adhesion in composite materials if applied as fillers [20].

2. Materials and methods

2.1. Materials

The following analytical grade chemicals were used without further modification. Natural zeolite (NZ) was purchased from the Semnan Gostar Co. (Semnan region, Iran). SA and tween 80 were obtained from the Merck Chemical Co. (Germany). Crude oil was purchased from the Iranian Oil Co. All other reagents and solvents were of the highest available purity and used as purchased. Deionized water was also used throughout. All the analyses and experiments were carried out in triplicate and the results were averaged.

2.2. Natural zeolite modification

2.2.1. NZ pretreatment

The pure NZ sample was first crushed with a mill to obtain a fine powder, then washed once with distilled water and then again with hot acetone using a Soxhlet apparatus, and finally the sample was dried in an oven at 100 °C for 4 h. The dried powder was used for hydrophobic modification.

2.2.2. Hydrophobic modification of NZ with SA

Hydrophobic modification of NZ was carried out through a mechanochemical synthesis after grinding. In a typical procedure, an accurately defined ratio of SA/ NZ was ground using a pestle and mortar to prepare a homogeneous powder with no discrete white solids. Grinding continued until a uniform powder was achieved. The resulted powder was then heated in an autoclave at 160 °C for 8 h in a sealed container with opening the tap and mixing in time intervals of 1 h after cooling to about 100 °C. The physisorbed SA was removed by washing thoroughly with hot acetone using a Soxhlet extractor and then the solvent was recycled via rotary evaporation (Rotavapor® R-100, Buchi, Germany) for further use. The produced dark grey powder was filtered and further dried in an oven at 80 °C for 2 h. We referred to this sample as modified SA(a)-NZ throughout this paper, in which "a" means the initial SA/NZ ratio.

2.2.3. Characterization techniques

Various techniques were used to characterize the NZ and modified samples. Surface morphology was observed using a TESCAN WEGA3-SB FESEM. To evaluate the crystalline structure and composition of the NZ, X-ray Diffraction (XRD) was applied (Philips diffractometer, PW1730, Netherland) and peak characterization was carried out using X'pert High Score Plus 3.0 software. The operating conditions were: Cu K α radiation, 40kV, 30 mA, 2 θ range from 10-80°, and scanning speed 0.05° (2 θ) s⁻¹.

The average crystal dimension was calculated using Debye-Scherrer's equation (Eq. (1)).

$$d = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where d is the mean size of the ordered domains (crystal size), λ is the wavelength of the incident X-ray (nm), *K* is the dimensionless shape factor with a typical value of 0.9, β is the line broadening at half of the maximum intensity (FWHM) in radians, θ is the value of the Bragg angle [21,22].

The structural parameters of pure and modified samples were determined using the low temperature (77 K) nitrogen adsorption/desorption method (BEL, Belsorp Mini II, Japan). Sample outgassing was carried out (Bel Prep Vac II) at 393 K under vacuum for 5 h. The Fourier transform infrared spectroscopy (FT-IR) was applied to investigate SA grafting on the surface of the NZ using a Perkin-Elmer (Spectrum-1) over 4000-400 cm⁻¹. The water contact angle of the NZ and modified samples were measured and compared by the sessile drop method using a goniometer (OCA20, Data Physics, Germany). In a typical procedure, 200 mg of SA-NZ was compressed into a thin pellet under pressure > 0.1 MPa, 2 μ l of double distilled water was placed on the pellet surface. The equilibrium sessile drop contact angles were determined by averaging four sets of the steady-state angles. The thermal stability of NZ and modified samples were investigated through TG-DTA curves recorded by a simultaneous thermal analyzer (STA504, Bahr, Germany) at a constant heating rate of 20 °C.min⁻¹ and a temperature range of 50-820 °C.

2.3. SA(a)-NZ application in spill oil remediation

2.3.1. Preparation of stable crude oil suspension in water

To prepare a spiked water suspension similar to the wastewater produced in the petroleum industry, 1 mL of crude oil was added to 20 mL of distilled water containing 0.25 mL of tween 80. The mixture was then sonicated for about 20 min with the power of 100 W until a uniform suspension was produced. The final suspension was diluted to 50 mL for further use. The COD of the latter sample was 14300 mg.L⁻¹.

2.3.2. Oil spill remediation procedure

Ten mg of the solid absorbent (both unmodified and modified NZs in separate vials) was added to 3 mL of the crude oil suspension, shacked well and left for 30 min. The mixture was centrifuged at 10000 rpm for 10 min. After settling the mixture, a volume of suspension was pipetted at a distance of 5 mm from the surface of the sample to conduct the COD analysis.

3. Results and discussion

3.1. Synthesis of hydrophobic modified NZ

In this study mechanogrinding (described in the experimental section), was applied for the hydrophobic modification of NZ by SA. Mechanogrinding is commonly induced using either a pestle and mortar

or ball milling and is performed as a mechanical activation process for solvent-free synthesis of various nanoparticles. It has several advantages , namely high atom economy, a lack of solvent, and a reduction of by-products, which have encouraged researchers worldwide to develop various innovative synthetic routes [23]. In the present study, hydrophobic modification reactions were performed in sealed containers by opening the tap and mixing the reaction mixture at time intervals of 1 h after cooling the container from 160 °C (reaction temperature) to about 100 °C. This method facilitated the removal of the water molecules produced during the esterification reaction between the NZ and SA, while avoiding SA evaporation.

3.2. Characterization of the solid structure

3.2.1. FT-IR observation

FT-IR was employed to affirm the successful functionalization of NZ with SA. As it is clearly shown in Fig. 1, significant features observed in the IR spectrum of the SA-NZ were the disappearance of the carbonyl stretching vibration of SA around 1700 cm⁻¹ and a peak at 1435 cm⁻¹, which was attributed to a coupling of acidic CO stretching and OH bending modes of carboxylic acid. The latter indicated a successful esterification reaction between MO-H (M: Si, Al) of surface silanols and SA [6]. Absorption peaks of -CH stretching vibration at 2925 and 2867 cm⁻¹ (the C-H asymmetric and symmetric stretching vibrations of -CH₂ groups,



Fig. 1. FT-IR spectra of (a) raw NZ (b) SA(0.3)-NZ, (c), SA(0.5)-NZ and (d) SA.

respectively) evidenced the octadecyl content in the SA-NZ [20]. There were no significant frequency shifts in C-H stretching of SA-NZ compared with the peaks of SA (Fig. 1(d)), indicating that the hydrophobic alkyl chains of SA were not perturbed to any significant extent by an interaction with the surface [24].

A broad stretching vibration peak at 3600-2700 cm⁻¹ was detectable for both NZ and SA-NZ, which was attributed to the presence of water and disturbed hydroxyls (less accessible silanols groups of the SA molecules), its intensity did not decrease upon modification [25].

In the tetrahedrons of the NZ framework, vibration bands of Si-O-Si, Si-O-Al, and Si-O as well as Al-O bridges appeared in 1200-400 cm⁻¹ [26]. The bands in the range of 3700-1600 cm⁻¹ were attributed to vibrations of absorbed water in the clinoptilolite framework [25,26]. In this latter region there are three intense bands at 1629, 3427, and 3629 cm⁻¹, each assigned to OH stretching vibration modes of adsorbed water in the zeolite, intermolecular hydrogen bonding in zeolite structure, and Si-OH-Al bridges, respectively [27,28]. Strong absorbance at 1093 and 796 cm⁻¹ were assigned to the asymmetric and symmetric stretching vibration of Si-O-Si groups. The most intense peaks appeared at 1093 and 1043 cm⁻¹ [29] and are attributed to external tetrahedral asymmetric stretching of Si-O-Si and Si-O-Al. Based on the Al/Si ratio in the formula, the position of these bands can be used for identification of the type of natural zeolite [30,31]. The presence of a 1043 cm⁻¹ band confirmed a lower Si/Al ratio of clinoptilolite. Comparing the FT-IR spectrums of both the pure and modified samples also confirmed that the modification treatment did not alter the Al/Si ratio, and no dealumination occurred in the NZ framework despite the high temperature during the modification process.

As a function of the degree of surface modification, an increase in the number of stearate groups resulted in a decrease in the intensity of O-H stretching vibrations of free silanol (Figs. 1(a), 1(b) and 1(c)). Both a narrow band at 3629 cm⁻¹ and an increase in the intensity of C-H stretching vibrations (2920 and 2852 cm⁻¹) verified this phenomenon. The vibration of the O-H band at 3427 and 3629 cm⁻¹ were assigned to the less accessible silanol groups and the free silanol groups, respectively, during the modification process. The free silanol band at 3629 cm⁻¹ was no longer detected after higher hydrophobic functionalization of the samples. However, this does not inhibit water adsorption as the intensity of the band at 3730-2900 cm⁻¹ was still detectable [32].

3.2.2. XRD investigation

XRD pattern of *zure* NZ and modified NZ are depicted in Fig. 2. The XRD pattern of NZ (Fig. 2(a)) exhibited an obvious crystalline structure, and the pattern is identified by the characteristic peaks of different NZs namely clinoptilolite, cristobalite and sodium aluminum silicon oxide. The three major reflections referring to the clinoptilolite structure at 22.34, 22.46 and 22.75° confirmed that 36 wt% of the NZ was composed of clinoptilolite with a chemical formula of $[KNa_2Ca_2(Si_{29}Al_7)O_{72}.24H_2O]$ [33,34]. According to the related literature, the other major components were cristobalite [SiO₂] [35] and sodium aluminum silicon oxide [Al_{1.15}Na_{1.15}O₄Si_{0.85}] [36] with 42 and 20 wt%, respectively. The chemical composition of the parental material, based on XRD findings, were in complete accordance with the FT-IR spectrum of the NZ and modified samples. In this study, the mineral compositions classified by XRD and FT-IR findings were mostly NZ; this differed from previous reports conducted on NZ from the Semnan region, which has been characterized as purely clinoptiolite [4,7].

Basically, the modification process did not altered the crystal structure of NZ in the modified sample compared with pure NZ (Figs. 2(a) and 2(b)). Characteristic reflections of SA were at 11.18, 21.68(100%), and 24.23° as shown in Fig. 2(c), which is in complete accordance with other reports [37]. The average crystal size of



Fig. 2. XRD patterns of the (a) NZ, (b) SA(0.5)-NZ and (c) SA.

zeolite particles calculated by the Xpert software, based on Debye-Scherrer's equation (Eq. (1)), was 30.8 nm. As shown in Fig. 2(b) characteristic peaks of SA also appeared in the XRD pattern of SA-NZ. This indicates that the crystal structure of stearate moiety attached to the NZ surface was preserved during the modification reaction. XRD along with FT-IR results confirmed that in contrast to surfactant displacement, the number and type of cations in the mineral structure were restored upon SA modification. Cations in the zeolite structure could be further exchanged for other purposes, e.g., various inserted cations may run catalytic reactions in a multiphase environment because of the hydrophobic/ hydrophilic character of the prepared structure.

3.2.3. TG-DTA analysis

Thermal behavior of the NZ and modified samples were investigated by thermal gravimetric (TG) analysis. A TG-DTA diagram of the NZ with a heating rate of 20 °C min⁻¹ and in the heating range of 50 to 820 °C are depicted in Fig. 3. About 12.25% of the NZ weight was lost in a three-step reduction manner as a result of the thermal treatment, which is in accordance with other reports [5,28,31]. The NZ weight loss was attributed to the dehydration and dehydroxylation of NZ. The first observed weight loss was close to a rapid weight loss from 100 to 300 °C, the second step was a moderate weight loss from 400 to 670 °C, and the third was a very slow weight loss from 720 to 820 °C. The DTA curve showed an endothermic peak from 50 to 100 °C, followed by another steep endothermic slope from 400 to 690 °C. The appearance of the last endothermic slope in the DTA curve of NZ was observed at 720 °C. Each endothermic peak represents a chemical change in the NZ subjected to the thermal treatment. According to Perraki and Orfanoudaki [31] weight losses at 25-100 °C and 100-200 °C were respectively attributed to releasing hygroscopic water and loosely bonded water (water residing in channels and cavities of the framework). According to Korkuna [28], there are two forms of water in silica minerals, intact molecules which in the clinoptilolite structure are released below 100 °C, and water from dehydration of OH groups (structural water) which is removed at T > 400 °C. Structural water in clinoptilolite is released after exceeding 360 °C. Generally, in this study the first endothermic change corresponded to the release of the

intact and loosely bonded water molecules. The second and third endothermic changes were, respectively, dehydrogenations of more and less accessible hydroxyl groups, which lined up completely with the first and the second weight loss in the TGA diagram of NZ. The TG-DTA curve of SA0.7-NZ is illustrated in Fig. 4. The extra endothermic peak in the DTA curve in Fig. 4 started at 490 °C, compared with the DTA curve of NZ (Fig. 3) assigned to the release of grafted SA from the NZ surface. The latter indicated the high stability of the modified flake-like particles, which could be beneficial in high-temperature applications. Comparing the weight loss of the two TGA diagrams confirmed 14.67 wt% and 12.25 wt% for the modified (Fig. 4) and raw NZ (Fig. 3). The excess weight loss for the modified NZ, approximately 2.42 wt%, was assigned to the stearate moiety in its surface.



Fig. 3. TGA-DTA curve of raw NZ.



Fig. 4. TG-DTA curve of SA0.7-NZ.

3.2.4. SEM observation

SEM images of pure NZ are shown in Fig. 5. According to the SEM images, NZ had a flake-like crystal configuration with an irregular surface. As expected, NZ exhibited low porosity due to the presence of the other silica compositions (cristobalite and sodium aluminum silicon oxide). The SEM image of modified NZ (Fig. 6) also demonstrated preservation of the flake crystal structure after modification. The major difference was that the flake-like structures were discrete and no longer aggregated. It is believed that the presence of stearate moiety on the surface of the NZ caused a uniformity in the physical forces between flakes. This means that if the flake-like particles were completely hydrophilic or hydrophobic they would have formed as agglomerates. This fact has also been observed in the case of highly hydrophobic silica particles [32]. However, in the present study the presence of hydrophilic mesopore/ micropores within the zeolite structure (which are not accessible even by N₂ molecules [5]) prevents SA from modifing the superhydrophobic surface.



Fig. 5. SEM images of the NZ before modification.



Fig. 6. SEM images of SA modified NZ : SA(0.5)-NZ.

3.2.5. Water contact angle (WCA)

The WCA of various NZ surfaces was dependent to the hydrophobization degree. As shown in Fig. 7, although the relationship between the initial SA/NZ ratio and the WCA of the modified samples was not linear, the WCA of the modified samples increased as the SA/NZ ratio increased until it reached a nearly plateau value of about 80°. Increasing the SA further did not lead to more chemical-modification and the additional SA remained physisorbed, which has been washed away following the soxhlet procedure.

Another interesting observation during WCA analysis of the modified samples was their swelling behaviour upon water absorbance a few seconds after placing water droplet on the pellet surfaces (Fig. 8). This swelling could be explained by a balance between hydrophobic/ hydrophilic characteristics of the modified samples. As evidenced by BET and SEM results, modification of the NZ had taken placed on the external surface of the flake-like structures, while the hydroxyl groups



Fig. 7. WCA of the modifed SA(a)-NZ samples with different initial SA/NZ ratios (a).



Fig. 8. Swelling behavior of (a) SA0.7-NZ and (b) after a few minutes.

inside the internal surface of structures (not accessible for SA moieties) remained intact and therefore were hydrophilic. According to IUPAC description, the external surface is usually regarded as an envelope surrounding the discrete particles or agglomerates, including all the distinctions, the surface of cracks, and the internal surface comprised of the walls of all cracks, pores and cavities [38].

3.3. Characterization of the porous structure

3.3.1. Low pressure nitrogen adsorption/desorption isotherm

The nitrogen adsorption at boiling temperature (77 K) technique was used to determine the NZ, SA(0.3)-NZ, and SA(0.7)-NZ surface area and to characterize their porous texture. According to IUPAC classification [38], the adsorption-desorption isotherm of the pure and modified samples (shown in Fig. 9) were classified as a type IV isotherm. The shape of the hysteresis loops of the pure and modified NZs indicated a type H₃ loop, which did not exhibit any limiting adsorption at high



Fig. 9. Nitrogen adsorption/desorption isotherms of NZ, SA(0.3)-NZ and SA(0.7)-NZ.

 P/P_{0} . This type of loop was observed with aggregates of plate-like particles with slit-shaped pores, correspondent to clinoptilolite-rich NZ [28]. The structure proposed by the hysteresis loop shape was in complete accordance with the SEM images of the pure and modified NZs (Figs. 5 and 6).

BET, BJH, and t-plot methods were used for quantitative morphological characterization of the NZ, SA(0.3)-NZ, and SA(0.7)-NZ samples.

3.3.2. Specific surface area (SSA) and pore shape

According to IUPAC recommendations [39], the BET method was used for SSA calculations of NZ, SA(0.3)-NZ and SA(0.7)-NZ samples (Table 1). However, for comparsion purposes, SSA of the latter samples were also calculated by the BJH method (Table 1). SSA of NZ calculated by BET and BJH were 30.24 and 33.37 m^2 .g⁻¹, respectively. The main reason for this difference

has been attributed to the different assumptions and equations used by each techniques. The basic assumptions of the BET theory for calculating the average pore diameter of a porous structure is that it is a finely divided solid consisting of uniform cylindrical pores, and correspondent equations and approximations have been introduced and applied over the years. In reality the BET method neither provides an average pore diameter nor pore size distribution. The BJH procedure assumes capillary condensation of the liquid nitrogen within the pores and from the relative pressures, and from the amount of nitrogen taken up at a given relative pressure of the sorption isotherm calculates the pore size distribution. So, either the adsorption or the desorption branch of isotherms lead to different pore size distributions [40,41].

Low surface area values were also reported for clinoptilolite rich zeolite structures by other researchers [11,28,42-44]. Therefore, the specific surface area (S_{BET}) for the modified samples was dramatically reduced from 30.24 m².g⁻¹ to 10.12 and 12.04 m².g⁻¹ for 0.3 and 0.7 initial SA/FS ratios, respectively. These results confirmed that the modification process occurred in the vicinity of the slit-shaped pores, leading to a decrease of the specific surface area of the modified NZ to about one-third of the specific surface area of the pure NZ. It is believed that the modification process caused the blocking of the slit-like pores and channels in the NZ structure, which reduced total pore volume from ~0.1 to ~0.06 cm³.g⁻¹ for the modified samples.

As can be seen in Table 1, the mean pore diameter (MPD) of the modified NZ has increased, compared to the unmodified NZ (Entry 5). According to the basic assumption in BET theory, a porous structure has been considered as a finely divided solid consisting of uniform

Table 1. Parameters of the unmodified NZ and the porous NZ modified by using the N_2 adsorption/desorption isotherm.

Entry	Parameter	Method					
		BET			BJH		
		SA(0.7)-NZ	SA(0.3)-NZ	NZ	SA(0.7)-NZ SA(0.3)-NZ NZ		
1	SSA [m ² /g]	12.04	10.13	30.24	17.50 14.83 33.39		
2	SSA/(SSANZ)	0.40	0.33	1			
3	SPV [cm ³ /g]	0.0650	0.0666	0.1075	0.0684 0.0694 0.1095		
4	SPV/(SPVNZ)	0.61	0.62	1			
5	MPD* [nm]	21.60	26.31	14.21	15.63 18.71 13.11		
* 0 1 1	11 E (2)						

* Calculated by Eq. (2).

open-ended cylindrical pores [40,41]. Following this assumption, the average pore diameter was calculated using Eq. (2) [45].

Mean pore diameter(MPD)[nm] =

$$\frac{4V}{S} = \frac{n4\pi r_{mean}^2 l}{n2\pi r_{mean} l} = 2r_{mean}$$
(2)

where V is the specific pore volume (SPV), S is the specific surface area (SSA), n is the number of pores, rmean is the mean pore radius, and l is the length of the cylindrical pore (assuming the same length for all pores). Thus, with SPV and SSA determined by the BET method and applying Eq. (2), the calculated MPD seemed to have increased. The same trend was observed using SPV and SSA values obtained by the BJH method (Table 1).

According to the data in Table 1, the calculated MPD increased after the modification process. A more thorough review of Table 1 data revealed that both SPV and SSA of the modified sample, respectively, appearing in the numerator and nominator of Eq. (2) decreased. But it seems that after modification the decline of SSA was much higher than the decline of SPV in the BET method results (Entries 2 and 4, respectively).

Barret *et al.* showed that in many absorbents the pores did not have a Gaussian or Maxwellian distribution [46]. This means that pores in a porous material have a discrete radius value trend. This could be observed and confirmed by dV_p/dr_p vs. r_p diagram plotted using the BJH method (Fig. 10).

Therefore, from mathematical point of view calculating the theoretical MPD is no longer realistic



Fig. 10. Pore size distribution (PSD) of NZ samples determined by BJH method: Natural zeolite (NZ), SA(0.3)-NZ and SA(0.7)-NZ.

and reliable by the simple Eq. (2). If we still assume the presence of open-ended cylindrical pores with a discrete radius and length, one could rewrite Eq. (3) in which r_i refers to the radius of pore *i*, l_i is the length of cylindrical pore *i*, and $r_1 < r_2 < r_3 < ... < r_n$.

$$MPD [nm] = \frac{4V}{S} = \frac{4\pi (r_1^2 l_1 + r_2^2 l_2 + r_3^2 l_{3+} \dots + r_n^2 l_n)}{2\pi (r_1 l_1 + r_2 l_2 + r_3 l_3 + \dots + r_n l_n)}$$
(3)
$$= 2\frac{(r_1^2 l_1 + r_2^2 l_2 + r_3^2 l_{3+} \dots + r_n^2 l_n)}{(r_1 l_1 + r_2 l_2 + r_3 l_3 + \dots + r_n l_n)}$$

Modification of NZ using a large molecule like SA will block most of the pores with small radiuses. These pores contributed largely to the total surface area but less so to the total pore volume of the modified substance; additionally, modification has also straitened large pores, which caused SPV reduction. Therefore, as the modification process went on, the small radiuses pores (the first phrases in the numerator and denominator of Eq. (3)) were gradually removed from Eq. (3). This led to a sharp depletion of the SSA and relatively less decrease in SPV, leading to a larger MPD (Entry 5 in Table 1). A similar observation has been reported by other researches [41].

3.3.3. Pore size distribution (PSD)

From the various methods for obtaining a PSD diagram, including the BJH, HK and DFT method [41,47,48], the BJH method was used in the present study. PSD and a meso/macro combination of pore volume were obtained from the adsorption branch [39] of the N₂ physisorption isotherm based on IUPAC recommendations [49] (Fig. 10), in which r_p was the representative of a cylindrical pore radius [46]. PSD results revealed that the unmodified and modified NZ did not have an uniform pore size distribution (PSD) compared to other clinoptiolite rich samples [50]. The most abundant pore diameter of pure NZ was about 16 nm. Two distinguishable drops in the PSD diagrams were also detected around pore diameters of 5 and 16 nm for both the SA (0.3)-NZ and SA(0.7)-NZ modified samples, this originated from the presence of a large fraction of mesopores ($2 < r_p < 50 \text{ nm}$) [49] and macropores ($r_p > 50$ nm) ranging from 10-100 nm. There were no considerable differences between the PSD of the two modified samples. It was suggested that by grafting the modifier (SA) to the walls of former pores (16 nm

pores or pores with higher width), a great number of 5 nm pores were appeared in the both modified samples.

The modified samples also appeared to have a wide distribution of mesopores, with the majority of the pores distributed from 20-60 nm.

3.3.4. Porosity size assessment

Among the different techniques, the t-plot method was used (Fig. 11) to calculate the microporous and mesoporous volume of the porous materials [51, 52]. T-plots of pure NZ, SA(0.3)-NZ and SA(0.7)-NZ revealed no microporosity, as all had the same zero intercept [53]. An upward deviation from the linearity corresponding to the capillary condensation in the t-plots of the unmodifed and modified samples also confirmed the mesoporosity of the samples [40]. Thus, all the volumes of the porous samples were attributed to the existence of pores with meso and macro diameters, which is in accordance with other clinoptilolite rich materials [28]. Modification had its effects on straitening former meso and macropores, which resulted in increasing the abundancy of 5 and 16 nm pores compared to the NZ pores. According to the references [40,54], this can be easily observed by the increased deviation from linear behavior in t-curves of the 0.3 and 0.7 modified samples.

3.4. Partitioning of modified samples in water and oil/ water mixture

Partitioning of raw and modified samples was investigated in water and the oil/water mixture. As



Fig. 11. *t*-Plots of NZ, SA(0.3)-NZ and SA(0.7)-NZ.

shown in Fig.12 (upper row), NZ rapidly immersed in a water medium while the modified samples, depending on the modification degree, were partitioned between two phases. For higher modified samples (0.5-0.7 SA/ NZ ratio), almost all the powder floated on the top of the water surface.

With the addition of oil (cottonseed oil) to the prior mixtures (Fig. 12, bottom row), almost all of the samples withdrew into the upper organic phase due to the presence of stearate moieties. Increasing the SA/NZ ratio in the modified samples increased particles moving into the oil phase causing the aqueous phase turbidity to decrese. For SA0.7-NZ, the oil phase was completely turbid, while the water phase remained clear. However, regarding the hydrophobic/hydrophilic characteristics of the modified sample, they remained mostly in the interface of the oil/water medium.

3.5. COD removal

The environmentally acceptable disposal of oily wastewater is a current challenge to the petroleum industry. Therefore, more research activities have been conducted on acquiring various treatment techniques for oily wastewater. According to IUPAC, terminology COD is a measure of the amount of oxygen divided by the volume of the system required to oxidize the organic (and inorganic) matter in wastewater using a chemically oxidizing agent. In practice, it is usually expressed in milligrams O_2 per liter [55]. COD is the most popular representative test for establishing



Fig. 12. Partitioning behavior of raw NZ and hydrophobic modified NZs (top: in water, bottom: in water/oil mixture).

organic materials in wastewater [16,56].

COD removal from the spiked aqueous oil suspension was attempted using SA0.7-NZ following a procedure described in the experimental section. As expected, the COD of the aqueous oil suspension was reduced from 14300 to 1280 mg/L. It was expected that the organic modifier on the surface of the NZ would facilitate the absorption of organic compounds suspended in the water. However, it is worth to mention that the critical process parameters for COD removal, such as temperature and adsorbent amount, were not optimized in the present study and this could be an objective of future studies.

4. Conclusions

In this research, a sample of Iranian natural zeolite was thoroughly characterized by different techniques and identified as crystobalite (40 wt%), clinoptilolite (36 wt%) and sodium aluminium silicium oxide (20 wt%), and classified as mostly natural zeolite. A new solventless and green method for hydrophobic modification of NZ was implemented using SA as a modifier, the NZ structure remained intact during the modification. Modified samples were also characterized by various techniques and the results confirmed both successful graftings of stearate moieties to the NZ surface and their high stability at as high as 450 °C temperature. The modified samples were successfully used for COD removal from oil-contaminated wastewater.

Specific swelling behavior of the modified samples once exposed to water molecules makes them the best possible candidate for hydrophobically modified membranes in future works. The hydrophilic/ hydrophobic character of the modified samples makes them potentially proper candidates as support for phase transfer catalysts. The modified structures may possibly work as carriers of water-soluble agents into the organic phase. Possessing discrete hydrophobic modified flake-like structures, they may potentially be used as cheap fillers due to their hydrophobic/ hydrophilic character and good dispersion property throughout organic solutions.

Following the success of the present study, green modification of various structures bearing hydroxyl groups, such as mesoporous silica fumed silica or silica aerosols, is under investigation by our research group.

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