Potential of granulated modified nanozeolites Y for MTBE removal from aqueous solutions: Kinetic and isotherm studies

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Adsorption of methyl tert–butyl ether (MTBE) from aqueous solutions by granulated modified nanozeolites Y was investigated. Nanozeolite Y powders were converted into granulated zeolites and subsequently modified with two cationic surfactants (20 mmol/dm^3), to be used as adsorbent. Granulated nanozeolites were characterized by BET surface area analysis, elemental analysis and X-ray diffractometer. Hexadecyltrimethylammonium (HDTMA-Cl) modified granulated zeolite had more effective performance than N-cetylpyridinium bromide (CPB) modified granulated zeolite. The most conventional adsorption isotherms and kinetic models were applied to describe MTBE adsorption and reaction dynamic, respectively. The equilibrium sorption data fitted the Langmuir 2 isotherm model and the kinetic study was followed the pseudo-second-order model. The maximum adsorption capacities for HDTMA-Cl modified zeolite and CPB modified granulated zeolite were 333.33 and 142.8 mg/g, respectively as calculated by the Langmuir model. This study demonstrated that the removal of mtbe by granulated modified nanozeolites Y is a promising technique.

Keywords: Methyl tert–butyl ether (MTBE), Nanozeolites, Granulation, Modification, Adsorption isotherm, Adsorption kinetic.

INTRODUCTION

Methyl tert–butyl ether (commonly referred to as MTBE) is the most common anti-knocking agent used to promote combustion efficiency[1]. From a drinking-water perspective, one of the most important aspects of MTBE is its objectionable taste and odor. Due to its high water solubility, low Henry's law constant, and slow biodegradability, MTBE is the relatively stable and resistant compound in the environment[2]. However, with the widespread use of MTBE, it has become one of the most frequently detected underground water pollutants[3,4]. MTBE concentrations in water supplies may be reduced by air stripping, photocatalytic degradation, filtration, advance oxidation, and adsorption5. Among the MTBE removal processes, adsorption is believed to be the most economic and feasible method for water treatment. In addition, absence of undesirable byproducts in drinking water is the advantage of using adsorption processes[6].

Zeolites are crystalline materials and their structure consists of hydrated aluminosilicates of metals from group I and group II elements. Structurally the zeolites are framework aluminosilicates which are based on an infinitely extending three-dimensional network of $(AlO_4)^{-5}$ and $(SiO_4)^{-4}$ tetrahedral units linked to each other by sharing all of the oxygen. This framework causes negative structural charges and a high cation exchange capacity (CEC). These characteristics have made the zeolites excellent adsorbent materials. Zeolites are divided into two main classes, namely, mineral such as clinoptilolite and mordenite and the synthetic zeolite such as zeolite A, X and Y. Synthetic zeolite Y exhibits a structure similar to naturally occurring faujasite types which has a 3-dimensional pore structure. The pore diameter of

zeolite Y is 7.4Å since the aperture is defined by a 12 member oxygen ring, and leads into a larger cavity of diameter 12Å. The cavity is surrounded by ten sodalite cages connected on their hexagonal faces[7].

Nanozeolites particles have higher available surface area than the typical zeolites. This availability decreases the diffusion path length and on the other hand, it can increase the adsorption feasibility[8].

In order to utilize nanozeolites particles as water treatment media in various industrial applications, granulation of nanozeolites with a glue-like media (sodium alginate) and consequently removal of this binder media by calcination is highly desired. This method is a suitable shaping process which would be able to assemble these powders into stable aggregates without losing their original characteristics[9–11].

There have been various attempts to improve the surface quality and characteristics of the zeolites by modifying them with different techniques[12]. Modification of zeolites and altering their surface chemistry using cationic surfactants make the modified zeolites suitable for the adsorption of anions and organic materials such as petroleum monoaromatics including benzene, toluene, ethylbenzene, and xylenes[13] and MTBE[14].

In this study, a synthetic type nanozeolite Y was granulated by a simple and novel method for the preparation of uniform nanozeolite microspheres by utilizing sodium alginate as an external template. Then the granulated nanozeolites were modified by two cationic surfactants, HDTMA-Cl and CPB. The structural characteristics of the adsorbents were studied. The adsorption process of MTBE by the mentioned adsorbents was investigated. Finally, the kinetics and isotherms for MTBE adsorp-

tion onto the granulated modified nanozeolites Y were studied in single solutions.

EXPERIMENTAL SECTION

Chemicals and Materials

All the chemicals used in this study were of analytical grade. MTBE ($C_5H_{12}O$; w=88.15), with >99% purity (HPLC grade), supplied by Merck Company, was used as adsorbate. The MTBE solutions were prepared by deionized water and all adsorption experiments were carried out at room temperature (20°C) in batch mode at constant pH of 7.1. Deionized water was used everywhere in this work. Sodium alginate was purchased from Sigma-Aldrich and used as an external template in the granulation of nanozeolites. Two types of cationic surfactants, HDTMA-Cl and CPB were used for the modification of zeolites. Both surfactants used in this research were obtained from Merck Company. Prior to any test, all of the instruments used in this study were washed by hot tap water, dichloromethane and deionized water respectively, and then dried at 100°C for 45 min. The adsorbent used in this study, nanozeolites Y powder (50–100 nm), was obtained from Neutrino Company.

Preparation of Synthetic Solution

A stock solution of MTBE ($1g/dm^3$) was prepared by pouring pure MTBE ($1.350 cm^3$) into the distilled water ($1000 cm^3$), and the solution was used for further experimental solution preparation. The concentrations, ranging from 1 to 200 mg/dm^3, were prepared by stock solution. The pH solution was adjusted using 0.1M HCl or 0.1M NaOH before mixing the adsorbent and the MTBE solution.

Adsorbents Preparation

In this step for the use of nanozeolite Y powder for the adsorption of MTBE, we used a novel shaping process developed by our group that named granulation[11,15]. In this regard sodium alginate has been used as an external template and to increase the mechanical resistance of granules a binder material such as clay was added to nanozeolite powder. In this method for the preparation of granulated nanozeolite Y initially two grams of nanozeolite powder were blended with clay (20 wt %) that poured in 5 cm^3 of distilled water and 15 min were subjected to intense ultrasonic waves (135 kHz). And for the preparation of a 2% by weight of sodium alginate gel, 2 g of sodium alginate added to 98 g of water and then was well stirred (150 rpm).

In the next stage, the mixture of nanozeolite and clay was added to sodium alginate gel. This slurry-like mixture was mixed with a magnetic agitator (150 rpm). For the formation of granules, the above mentioned slurry consisting of zeolite, sodium alginate, clay and water was poured into a 0.1 M solution of barium chloride and after 2 h was washed with distilled water, dried at room temperature, and then through calcinations process the alginate was completely volatized out and left behind spherical granules. The influence of different temperatures and the duration of calcinations was investigated. But finally from the comparison of XRD patterns between the granulated nanozeolites and nanozeolite powder we chose the best calcination condition of 600°C temperature and 5 h duration of calcinations. After the calcination process the granules were sieved to the size of 250–420 μm in order to have a rational comparison of granules chosen for further experimental tests.

Instruments

The granulated nanozeolites were characterized by BET surface area analysis (Micromeritics Gemini, 2360), X-ray fluorescence (XRF) (Oxford, ED2000) and X-ray diffractometer (XRD, model: XD-5A, Shimadzu). For surface morphology investigation of the zeolites, scanning electron microscopy (SEM, model: XL-30, Philips) was used. Finally, the produced granules were sieved to 0.25–0.42 mm (ASTM sieve size no. 35-60). MTBE concentration in water was measured using a Varian Gas Chromatograph with a flame ionization detector and Combipal Headspace auto-sampler system (CP-3800, Varian, Australia). For the determination of the solution pH, a Metrohm pH meter (827 pH lab, Switzerland) was used. To shake the mixtures a reciprocating shaker was utilized.

Modification of Adsorbents

The granulated nanozeolite Y were treated using HDTMA-Cl (GMN-Y#1) and CPB (GMN-Y#2) solutions with the initial concentration of 20 $mmol/dm^3$ that were desirable concentrations according to our recently work[14]. In this regard, 5 g of the granulated zeolite was added to a 125 cm^3 polyethylene bottle with 100 cm^3 of HDTMA-Cl or CPB solutions. Then the bottles were stirred in a reciprocating shaker (20.0±0.5°C; 150 rpm) for two days. The obtained granulated modified nanozeolites Y complex was separated from the mixture by vacuum filtration and washed out several times with deionized water. The modified zeolites were dried in ambient air for two days and stored for further use.

Concentrations and Adsorption Procedure

The ability of GMN-Y for the removal of MTBE from aqueous solutions was carried out by a batch technique at room temperature (20.0±0.5 °C). The container was a 125 cm^3 Teflon-sealed screw cap amber glass with 100 cm^3 solution containing, 1, 10, 20, 50, 100 and 200 mg/dm^3 of MTBE. Then 5 g/dm^3 of each previously prepared adsorbent (i.e. GMN-Y#1 and GMN-Y#2) was added to the solution and the bottles were shaken on a reciprocating shaker (150 rpm) for 24 h (the time that was found to be sufficient to reach the adsorption equilibrium based on our previous works). After 10 minutes of sedimentation, the supernatants were put into 10 cm^3 headspace vials. The concentrations of MTBE in the supernatant solutions before and after adsorption were analyzed using a VARIAN gas chromatograph with a flame ionization detector and a combipal headspace auto sampler system. All adsorption tests were doubled run and the averages are reported. Blank samples were also carried out using the same conditions except for the presence of the adsorbent. The experimental blanks showed no significant losses of MTBE due to volatilization and adsorption to bottle walls. The adsorption capacity of MTBE at equilibrium conditions was determined as

below:

$$q_e = \frac{(C_{in} - C_t) \times V}{W}$$ (1)

Where:

q_e is the MTBE adsorption capacity (milligrams of MTBE per gram of adsorbent), C_{in} and C_t are the initial and equilibrium concentrations of MTBE, respectively (milligrams per dm^3), V is the solution volume (dm^3) and W is the dry weight of the adsorbent (gram).

Adsorption Isotherm Studies

Adsorption isotherm experiments were carried out in 125 cm^3 sealed amber bottles at room temperature on a reciprocating shaker (150rpm) for 24h to reach adsorption equilibrium. The two adsorbents (GMN-Y#1 and GMN-Y#2) with a constant mass of 0.5 g were mixed with 100 cm^3 of MTBE solutions by different concentrations of 1, 10, 20, 50, 100 and 200 ppm. After the 10 minutes sedimentation, samples of 5 cm^3 were collected from the supernatant and were analyzed for residual MTBE concentration.

Adsorption Kinetic Studies

Adsorption kinetics study was done in order to test the relationship between contact time and MTBE adsorption. This step was performed by shaking 0.5 g of each adsorbent into 100 cm^3 of MTBE solution (50, 100 and 200 mg/dm^3). The mixture was constantly stirred by a reciprocating shaker at a speed of 150 rpm for 1 to 24 h. The residual concentration of MTBE in the supernatants was analyzed finally.

RESULTS AND DISCUSSION

Adsorbent Characterization

The chemical composition of nanozeolite Y was SiO$_2$ 43.35%, Al$_2$O$_3$ 18.14%, Na$_2$O 9.65%, TiO$_2$ 1.08% and LOI 23.56%. Fig. 1 and 2 depict the XRD patterns of
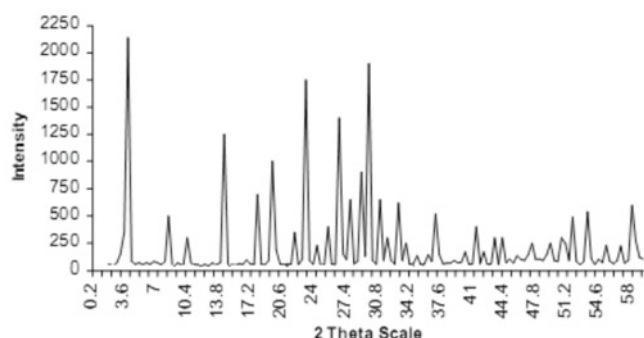

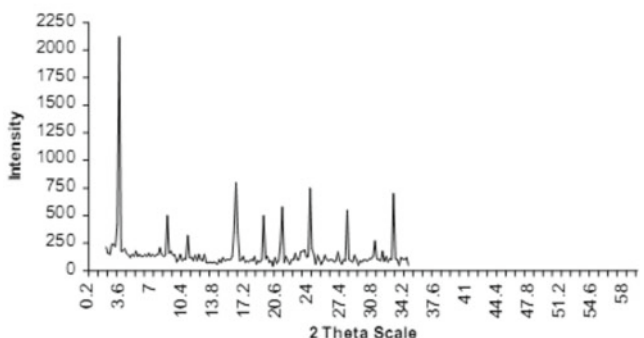
Figure 1. XRD pattern of nanozeolite Y

Figure 2. XRD patterns of granulated nanozeolites Y

nanozeolite Y and produced granules at different temperatures of calcination. The SEM images of nanozeolite Y and produced granules are illustrated in Fig. 3 and 4. Fig. 5 shows the SEM image of the surfactant modified granulated nanozeolite Y. The BET surface area of nanozeolite Y and granulated nanozeolite Y is 705.6 and 370.8 m^2/g, respectively.
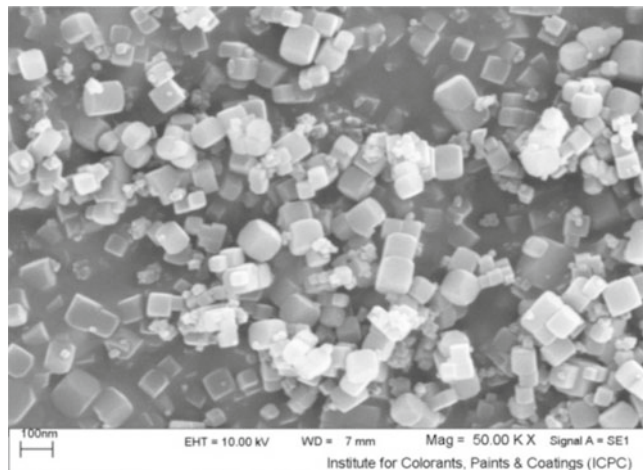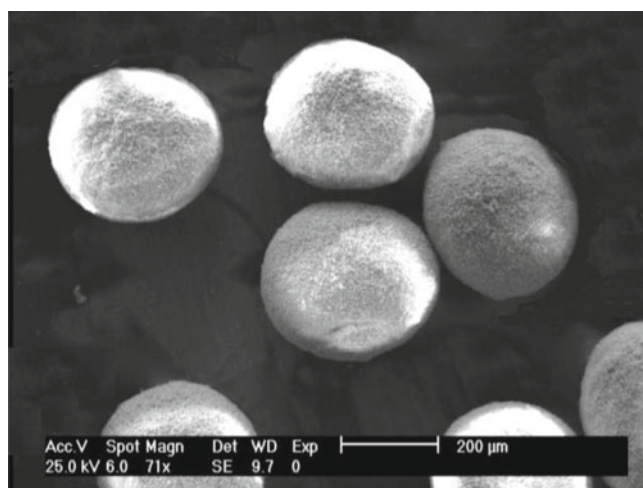

Figure 3. SEM image of nanozeolite Y

Figure 4. SEM image of granulated nanozeolite Y
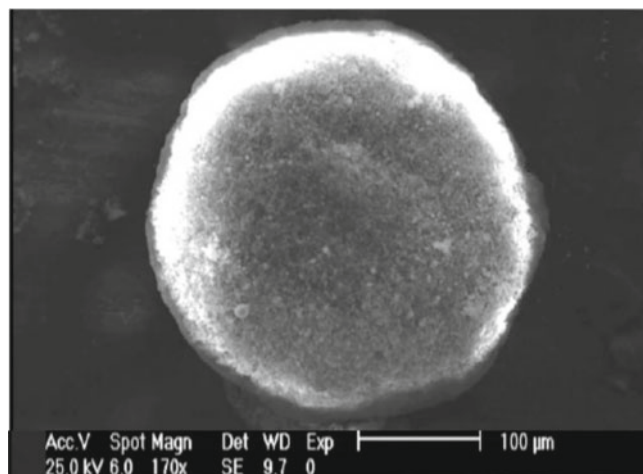

Figure 5. SEM image of surfactant modified granulated nanozeolite Y

Adsorption Capacity

The results of MTBE adsorption capacity with two types of adsorbent (GMN-Y#1 and GMN-Y#2) are illustrated in Fig. 6. The adsorbents dry weight was 0.5 g.
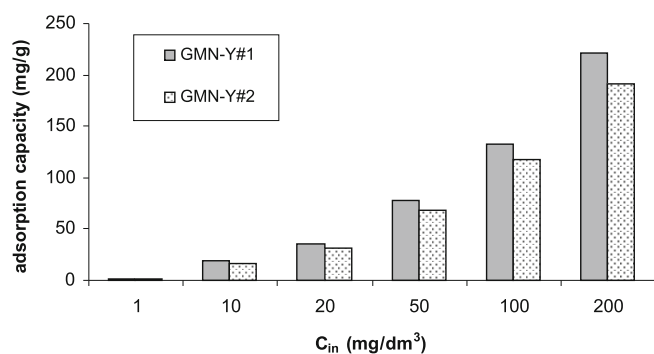
Figure 6. Adsorption capacity of MTBE by GMN-Y#1 and GMN-Y#2

According to the obtained results (Fig. 6), it is obvious that GMN-Y#1 is more effective than GMN-Y#2 in any concentration. On the other hand, the results showed that the adsorption capacity of MTBE was highly concentration dependent. In different concentrations of MTBE, the parameter of adsorption capacity increased with the MTBE concentration. The molecules of MTBE at higher concentrations play as a driving force and overcome the mass transfer resistance between the aqueous and solid phases. Therefore, the maximum adsorption capacity of GMN- Y took place at higher concentrations of MTBE.

Adsorption Isotherms

Isotherms help to determine the maximum adsorptive capacity of the material and to evaluate the mechanism of performance of the adsorption system. In addition, it allows an evaluation how an adsorption system can be improved. Therefore, an Isotherm study is essential in improving the use of adsorbent. Several isotherm equations have been published in the literature. The Langmuir, Freundlich and Temkin models are the most widely employed isotherms for modeling the adsorption in single-solute systems. In this study, seven most frequently employed isotherm models, namely, Langmuir[1–4], Fruendlich, Temkin and Dubinin–Radushkevich (D–R) were used for the analysis of the obtained data. The linear forms and Parameters of seven used isotherms are listed in Table 1.

Langmuir Model

The Langmuir isotherm assumes that adsorption takes places at specific homogenous surfaces of the adsorbent. Moreover, the Langmuir isotherm represents a single coating layer of the adsorbate on the adsorbent surface[20]. The Langmuir isotherm can be linearized as four different types of isotherms as shown in table 1. The isotherm constants in the linear equations can be calculated from the slope and intercept of the plots between the mentioned expressions (table 1). The obtained values of the Langmuir isotherm parameters are given in Table 2. The results show that the Langmuir correlation coefficients (R^2) are in the range of 0.914 to 0.999. And the values of R^2 were in the order of Langmuir 2 > Langmuir 1 > Langmuir 3 and Langmuir 4. Therefore R^2 values indicate that Langmuir 2 fits all of the experimental data better than other Langmuir isotherms (Fig. 7). It has been found that GMN-Y#1 shows better adsorption capacity (mg/g) than GMN-Y#2. As calculated by the Langmuir 2 model, the maximum adsorption capacity for GMN-Y#1 and GMN-Y#2 is 333.33 and 142.8 (mg/g), respectively.

On the other hand, the essential characteristic of Langmuir isotherm can be obtained from a dimensionless constant called equilibrium factor (R_L). Which R_L can be defined by following equation:
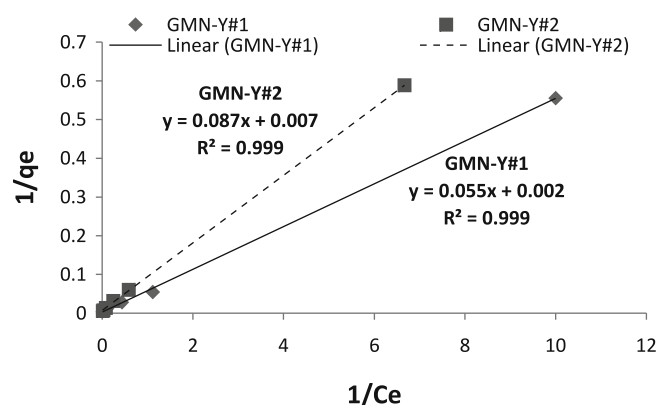

Figure 7. Application of Langmuir 2 model to MTBE adsorption onto GMN-Y#1 and GMN- Y#2

Table 1. Isotherms and their linear expressions

Isotherm	Linear equation	Plot	Parameters	Reference
Langmuir 1	$\dfrac{C_e}{q_e} = \left(\dfrac{1}{K_L q_m}\right) + \left(\dfrac{1}{q_m}\right)C_e$	C_e/q_e vs. C_e	q_m= 1/slope, K_L =1/(intercept ×q_m)	16
Langmuir 2	$\dfrac{1}{q_e} = \dfrac{1}{Q_m} + \left(\dfrac{1}{K_L Q_m}\right)\dfrac{1}{C_e}$	1/ C_e vs. 1/q_e	q_m = 1/intercept, K_L = intercept/slope	16
Langmuir 3	$q_e = Q_m - \left(\dfrac{1}{K_L}\right)\dfrac{q_e}{C_e}$	q_e/C_e vs. q_e	q_m = intercept, K_L = 1/slope	16
Langmuir 4	$\dfrac{q_e}{C_e} = K_L Q_m - K_L q_e$	q_e vs. q_e /C_e	K_L = slope, q_m=intercept/slope	16
Freundlich	$\log(qe) = \log(K_f) + \left(\dfrac{1}{n}\right)\log(C_e)$	log (q_e) vs. log (C_e)	K_f = exp (intercept), 1/n = slope	17
Temkin	$q_e = B_T \ln A_T + B_T \ln Ce$	q_e vs. ln (C_e)	B_T= slope, ln A_T=intercept/ B_T	18
Dubinin-Radushkevich	$\ln q_e = \ln Q_m - \left(\dfrac{RT}{E}\right)^2 [\ln(\dfrac{C_S}{C_e})]^2$	ln q_e vs. [ln(C_s/C_e)]²	E= slope, q_m= intercept	19

Table 2. Isotherm parameters obtained from the four linear forms of Langmuir model

Isotherm model	adsorbent	Langmuir isotherm parameters								
		q_m (mg/g)	$K_L \times 10^3$ (dm^3/mg)	R^2	R_L					
					MTBE initial concentration (mg/dm^3)					
					1	10	20	50	100	200
Langmuir 1	GMN-Y#1	250.0	0.05	0.996	0.952	0.666	0.500	0.285	0.166	0.091
	GMN-Y#2	99.19	0.04	0.994	0.961	0.714	0.555	0.333	0.200	0.111
Langmuir 2	GMN-Y#1	333.33	0.036	0.999	0.965	0.735	0.581	0.357	0.217	0.122
	GMN-Y#2	142.8	0.08	0.999	0.926	0.555	0.384	0.200	0.111	0.058
Langmuir 3	GMN-Y#1	18.55	12.65	0.914	0.073	0.007	0.007	0.004	0.0008	0.0004
	GMN-Y#2	10.23	21.27	0.939	0.045	0.004	0.002	0.001	0.0004	0.0002
Langmuir 4	GMN-Y#1	19.17	11.58	0.914	0.080	0.008	0.004	0.002	0.0008	0.0004
	GMN-Y#2	10.45	19.69	0.939	0.048	0.005	0.002	0.001	0.0005	0.0003

$$R_L = \frac{1}{1 + (K_L C_i)} \qquad (2)$$

Where:

C_i is the initial concentration of adsorbate (mg/dm^3) and K_L is the Langmuir constant (dm^3/mg). The R_L value indicates the isotherm shape. The R_L value in the range from zero to one, indicates a favorable adsorption condition[21]. As mentioned in Table 2, the equilibrium factor values for the Langmuir isotherm models are in the range of 0.002 to 0.965. The R_L values indicate that adsorption processes of MTBE by GMN-Y are favorable. Similar results were obtained for MTBE and even the BTEX compounds uptake from water using surfactant modified natural zeolites in our previously works[13,14].

Freundlich Model

Freundlich model is an empirical method that is suitable for the description of an adsorption process in heterogeneous systems. On the other hand, the Freundlich model represents a multilayer adsorption on the heterogeneous surface. The Freundlich isotherm constants (1/n and K_F) can be calculated by plotting log (q_e) versus log (C_e) (Table 1). Parameter 1/n is the heterogeneity factor that shows the adorability of the adsorption process. KF (mg/g(dm^3/mg)1/n) is the Freundlich constant or adsorption coefficient[15]. For other materials it was found that the Freundlich kinetic is the best model of describing the kinetic data for MTBE removal from water[22]. The parameters of the Freundlich isotherm are presented in Table 3. As the results show, the Freundlich correlation coefficients (R^2) for adsorption of MTBE by GMN-Y#1 and GMN-Y#2 are 0.959 and 0.976, respectively. But in comparison with the Langmuir model, the Freundlich isotherm model is not fitted very well by this study's data. It means that, because the R^2 obtained from the Langmuir isotherm is better than the Freundlich isotherm, the absorption process of MTBE on GMN-Y is chemical and makes a monolayer of MTBE molecules on adsorbents surface. Moreover, if the value of 1/n become below one, the Freundlich model reduces to the normal Langmuir isotherm[23]. Because 1/n values of this study are less than one (table 3), we can conclude that the Langmuir model is a stronger isotherm than the Freundlich model.

Temkin Model

The Temkin isotherm model express that the adsorption heat of all the molecules in the layer declines linearly with coverage due to adsorbent-adsorbate interactions[18]. The Temkin isotherm parameters (B_T and A_T) can be calculated by plotting q_e versus ln (C_e) (Table 1). Parameter B_T (J/mol) is the temkin isotherm constant related to the heat of sorption and A_T (dm^3/mg) is the equilibrium binding constant, corresponding to the maximum binding energy. The results of this model are represented in table 3. According to the results, the correlation coefficients of the Temkin isotherm model are lower than the Langmuir and even the Freundlich models. Therefore, the adsorption process of MTBE on GMN-Y does not fit the Temkin Model.

Dubinin–Radushkevich Model

Another isotherm equation that was also used to test the experimental data was the Dubinin–Radushkevich (D–R) equation. It does not assume a constant sorption potential or a homogeneous surface[24]. The Dubinin–Radushkevich parameters (E and qs) can be calculated by plotting ln qe versus [ln (Cs/Ce)]^2 (Table 1). Parameter E (KJ/mol) is the mean free energy of sorption per adsorbate molecule and q_s (mg/g) is the maximum adsorption capacity. Depending on the obtained results from the linear regression of Dubinin–Radushkevich isotherm (table 3), the correlation coefficients of this method are even less than the other above discussed isotherm models. Therefore, this method does not fit the experimental data.

Adsorption Kinetics

Prediction of the contamination removal rate from aqueous solutions is very important and interesting in order to design an adsorption treatment plant. Kinetic

Table 3. Isotherm parameters obtained from Freundlich, Temkin and Dubinin–Radushkevich models

adsorbent	Isotherm model										
	Freundlich				Temkin				Dubinin–Radushkevich		
	K_F (dm^3/g)	1/n	R^2		B_T (J/mol)	A_T (dm^3/mg)	R^2		q_m (mg/g)	E (KJ/mol)	R^2
GMN-Y#1	3.183	0.704	0.959		32.67	3.337	0.868		6.183	0.715	0.690
GMN-Y#2	2.622	0.730	0.976		28.96	2.137	0.841		6.295	1.312	0.858

Table 4. Kinetics and their linear expressions

Kinetic model	Linear equation	Plot	Parameters	Reference
Pseudo first-order	$\log(q_e - q_t) = \log(q_e) - \dfrac{k_1}{2.303}t$	$\log(q_e - q_t)$ vs. t	k_1 = slope, q_e = intercept	24, 25
Pseudo second-order	$\dfrac{t}{q_t} = \left(\dfrac{1}{k_2 q_e^2}\right) + \left(\dfrac{1}{q_e}\right)t$	t/q_t vs. t	$1/q_e$ = Slope, $1/(k_2 q_e^2)$ = Intercept	25, 26
Elovich	$q_e = \left(\dfrac{1}{\beta}\right)\ln(\alpha\beta) + \left(\dfrac{1}{\beta}\right)\ln t$	q_t vs. ln(t)	$1/\beta$ = Slope, $1/\beta \times \ln(\alpha\beta)$ = Intercept	24
Intraparticle Diffusion	$q_t = K_{dif}\,t^{0.5} + C$	q_t vs. ?t	C = Intercept, K_{dif} = Slope	25

Adsorbent	Initial MTBE (mg/dm^3)	Pseudo first-order			Pseudo second-order		
		q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2(g/mg.min)	R^2
	50	2.449	0.001	0.905	90.90	0.005	0.997
GMN-Y#1	100	2.862	0.001	0.828	142.85	0.006	0.999
	200	3.009	0.002	0.903	250	0.005	0.998
	50	2.535	0.002	0.909	76.923	0.005	0.999
GMN-Y#2	100	2.928	0.003	0.756	125	0.005	0.997
	200	3.154	0.001	0.869	200	0.004	0.997

Table 5. Comparison of pseudo first- and second-order kinetics parameters for different GMN-Y and initial concentrations

studies are useful for the prediction of adsorption reaction rate, modeling and designing the processes. Therefore, four most commonly used kinetic methods: pseudo first-order; pseudo second-order; Intraparticle Diffusion and Elovich were used to represent the experimental data. The linear forms and Parameters of four employed kinetic methods are listed in Table 4. The effect of contact time was carried out by ranging from 1 to 24 hours in order to perform the kinetic study. And three different initial concentrations of MTBE used, which were 50, 100 and 200 mg/dm^3. The solution pH was kept constant at 7.1 during experiments.

Pseudo First-Order Model

Pseudo first-order kinetics is the one of the earliest methods of describing the adsorption rate based on the adsorption capacity. The Pseudo first-order parameters (k_1 and q_e) can be calculated by plotting log ($q_e - q_t$) versus t, as shown in table 4. Parameter k_1 (1/min) is the first-order adsorption rate constant and q_e (mg/g) is the maximum adsorption capacity at equilibrium. Table 5 shows the Pseudo first-order kinetic parameters corresponding to MTBE removal by granulated modified nanozeolites Y. The obtained values of R^2 for the Pseudo first-order kinetics (Table 5) show that this model was not fit to the experimental data.

Pseudo Second-Order Model

The pseudo second- order method was explained by Ho[27] and its adsorption mechanism is relative to chemical adsorption. The characteristics of Pseudo second-order kinetic are mentioned in Table 4 and the results are summarized in Table 5. According to the results, the correlation coefficients for both of adsorbents were greater than 0.997 (Fig. 8 and Fig. 9). Therefore, the second-order equation provided a good fitting to the experimented data in contrast to the pseudo first-order model.
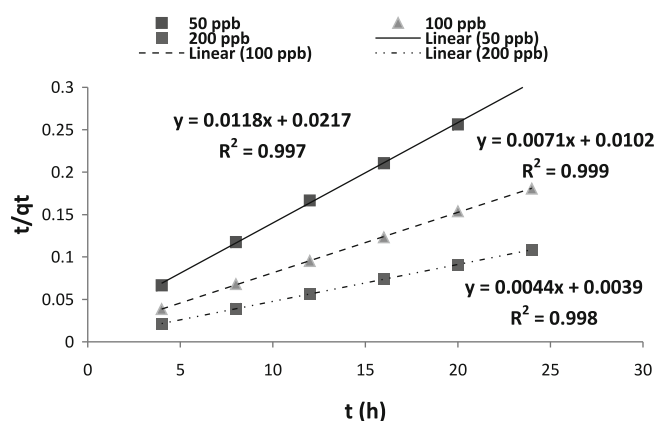
Figure 8. Pseudo second-order adsorption kinetics of MTBE on GMN-Y#1
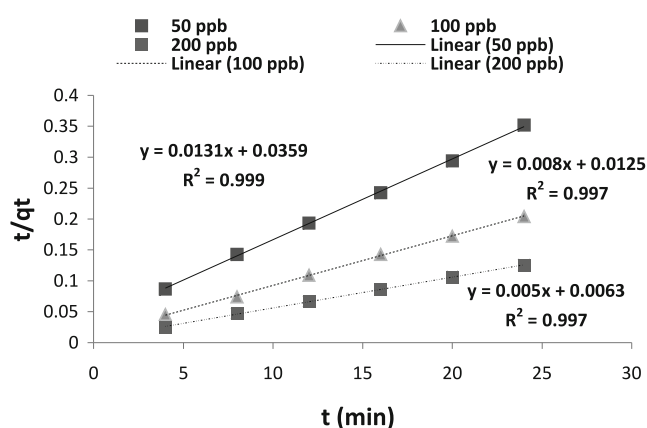
Figure 9. Pseudo second-order adsorption kinetics of MTBE on GMN-Y#2

Elovich Model

Another rate equation that also used to test the experimental data was the Elovich Model, which is based on the adsorption capacity. The Elovich model is useful to describe adsorption processes without the desorption of adsorbate[28]. The constants of the Elovich kinetic (A and B) can be obtained from the intercept and the slope of the straight line (Table 4). The R^2 values obtained

Table 6. The parameters of Elovich and Intraparticle Diffusion kinetic methods using different GMN-Y and initial concentrations

Adsorbent	Initial MTBE (mg/dm^3)	Elovich			Intraparticle Diffusion		
		α (mg/g.min)	B (g/mg)	R^2	C (mg/g)	K_{dif} (mg/g.min$^{0.5}$)	R^2
GMN-Y#1	50	6.604	0.093	0.991	53.07	4.074	0.882
	100	7.957	0.062	0.965	95.77	5.943	0.808
	200	12.81	0.059	0.994	181.0	6.404	0.890
GMN-Y#2	50	4.783	0.077	0.982	38.37	4.585	0.846
	100	7.336	0.065	0.910	82.09	5.683	0.760
	200	9.917	0.053	0.991	145.0	7.241	0.888

by the Elovich model (Table 6) were higher than that obtained from the first-order kinetics. But the R^2 values of the Elovich model are comparable to that obtained from the pseudo second-order model.

Intraparticle Diffusion Model

The Weber and Morris sorption kinetic model that is the most widely applied intraparticle diffusion equation[25], was employed to analyzing the sorption kinetics. According to the R^2 values (Table 6), experimental data are not following the Intraparticle Diffusion kinetics.

CONCLUSION

Granulated modified nanozeolite Y was used for removal of MTBE. In order to investigate the effect of adsorbents modification, granulated nanozeolites were modified by two cationic surfactants namely HDTMA-Cl and CPB. HDTMA-Cl modified granulated nanozeolite showed a better adsorption capacity for MTBE than CPB modified samples. Isotherm Studies were performed at initial concentrations with the range of of 1 to 200 mg/dm^3. the adsorption capacity (mg/g) of GMN- Y increased with the initial concentration of MTBE solutions. It means that, maximum adsorption capacity of GMN- Y took place at higher concentrations of MTBE, which the Langmuir parameters can prove.

The adsorption isotherms of MTBE on GMN-Y were well described by the Langmuir 2 adsorption equation. The RL values obtained from the Langmuir isotherms expressed that adsorption processes of MTBE on GMN-Y were favorable. The adsorption kinetics for MTBE removal from water followed the pseudo-second-order kinetic method. The obtained data from the Langmuir isotherm and the pseudo-second-order kinetic models represent that the absorption process of MTBE on GMN-Y is chemical and makes a monolayer of MTBE molecules on the adsorbents surface. The monolayer adsorption capacity by GMN-Y#1and GMN-Y#2 was 333.33 and 142.8 (mg/g) respectively, which is comparable with the adsorption capacity of other sorbents previously studied in other works.

NOMENCLATURE

A_T — Temkin constant (dm^3/g)
B_T — constant related to heat of adsorption (mg/dm^3)
C_e — equilibrium concentration in solution (mg/dm^3)
C_s — saturation concentration in solution(mmol/dm^3)
C_t — equilibrium concentration in solution at time t (mg/dm^3)
k_1 — pseudo first-order rate constant (1/min)
k_2 — pseudo second-order rate constant (g/mg min)
K_{dif} — intraparticle diffusion rate constant (mg/g min$^{0.5}$)
K_f — Freundlich isotherm constants (dm^3/g)
K_L — Langmuir isotherm constants (dm^3/mg)
n — adsorption intensity
q_e — equilibrium adsorbent concentration on adsorbent (mg/g)
q_m — maximum monolayer capacity (mg/g)
q_t — adsorbed metal concentration at time t (mg/g)
R^2 — correlation coefficients
R_L — Langmuir equilibrium factor
α — initial adsorption rate (mg/g.min)
β — desorption constant (g/mg)

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