

Adsorption of EDTA from Aqueous Solution Using HDTMA-Modified Zeolite

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Abstract: Adsorption of EDTA on HDTMA modified-Zeolite from aqueous solution has been investigated. Factors affecting the adsorption of EDTA on modified-Zeolite, such as contact time, temperature, pH, Zeolite dosage, stirring rate and initial concentration of EDTA were considered. The experimental results revealed that the EDTA adsorption rate increases with raising the initial concentration. The adsorption equilibrium could be reached in 55 min. Also, the studies illustrated that the adsorption process has a weak fitness with the Langmuir isotherm by $q_m=147.06 \text{ mgg}^{-1}$, $K_L=6.83 \text{ Lmg}^{-1}$ and $R_L^2=0.913$. But, the Freundlich isotherm was found to provide a good fit with the adsorption data with $K_f=159.8 \text{ mgg}^{-1}$, $n=0.754$ and $R_L^2=0.978$. The kinetic study determined an appropriate compliance of experimental data with the pseudo-second-order kinetic model and the significant phase might be chemisorption. Thermodynamic parameters (ΔG° , ΔH° , ΔS°) represented that the adsorption process was endothermic and spontaneous.

Key words: EDTA • HDTMA • Zeolite • Adsorption • Isotherm

INTRODUCTION

The act of using two various electron donors by a ligand to bond with a same metal is known as chelation [1]. Since the last years of 20th century, the presence of chelating agents such as ethylene diaminetetraacetic acid (EDTA) and diethylene triaminepenta acetic acid (DTPA) in aquatic ecosystems have been under examination [2]. These complex agents cause international concern due to weak biodegradability and affecting the metal displacement in the environment [3].

Resulting from the industries such as paper mills, pulp, nuclear reactors and food production, effluents contain EDTA and other chelating agents have been appeared in wastewater treatment plants and also in

surface waters. EDTA is characterized by varying concentrations from 10 to 500 μgL^{-1} in water sources [4]. Metal capturing ability of EDTA is a beneficial characteristic during respective industrial processes but after discharging the industrial wastewater effluents into the environment, this property is known as a negative aspect [4]. EDTA ligands with entrapped metals resist against natural precipitation and therefore remain soluble [5].

The environmental studies regarding to chelating agents mainly have focused on ligand performance in metal elimination from aqueous solutions and soil remediation [6, 7] while the side effects of ligands and their removal from liquid and soil media have not been considered properly [3].

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Different methods have been used for EDTA removal or degradation in aqueous solutions such as chemical degradation [4] TiO_2 photocatalysis [8] biodegradation [9] ion exchange [10] membrane filtration [11] and adsorption [12].

Most experiments focused on EDTA degradation have studied oxidant agents like hydrogen peroxide and ozone [3]. Degradation processes may lead to produce some intermediate chemicals which have chelating properties again or have other side effects on environment. Nevertheless, chemical degradation and TiO_2 photocatalysis are unusable to eliminate the metals and EDTA together because the EDTA may be stay in original form in solute ion after degradation process. Also, other approaches such as ion exchange and membrane filtration are not feasible in practical situations due to high costs respect with operation and maintenance [12]. Of these, adsorption process is usually identified as effective and also beneficial mechanism due to low-cost and readily available adsorbents which also can be regenerated easily [13, 14]. Among removal processes based on adsorption, activated carbon [15] zeolite [12] and molecular selective tools [16] have revealed noticeable results.

This study aimed to investigate EDTA adsorption from aqueous solution on Iranian zeolite that modified with Hexadecyltrimethylammonium (HDTMA). HDTMA is a cationic surfactant which has been used in same experiments for increasing the ability of zeolite to remove anions and organic contaminants from water [17, 18]. The kinetic studies by Lagergren pseudo-first-order, Ho pseudo-second-order, Elovich and intra-particle diffusion models are considered. Experimental data were analyzed with Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. Finally, the thermodynamic parameters (ΔG° , ΔH° , ΔS°) were obtained to indicate the effect of temperature on adsorption process.

MATERIALS AND METHODS

Materials: Used ZnCl_2 , NaCl, Acetic acid, Sodium acetate, $\text{Na}_2\text{H}_2\text{EDTA}$, NaOH, Xylenol orange and nitric acid were those from Merck® Company. Used hexadecyltrimethyl ammonium chloride (HDTMA-Cl: $\text{C}_{19}\text{H}_{42}\text{ClN}$) was prepared from Sigma-Aldrich® Company. All reagents were of analytical grade and also were used without further purification. Deionized water was used throughout the study.

Modification of Iranian Natural Zeolite by HDTMA

Cationic Surfactant: Raw clinoptilolite obtained from Semnan province mine via Farshid Zand Company (Tehran, Iran). Internal (Zeolitic) cation exchange capacity (CEC) of 0.917 mequiv/g and external (Nonzeolitic) cation exchange capacities (ECEC) ranged from 0.074 to 0.102 mequiv/kg were obtained based on modified method of Ming and Dixon [19].

Clinoptilolite Preparation: The aim of this step, was preparing Clinoptilolite for surfactant modification. Preparation consists of milling, sieving, washing, drying and cationic converting, respectively [17, 18]. ASTM sieves no. 70 and 80 (Pore sizes 210 and 185 μm , respectively) were used for obtaining grain size around 200 μm . Mud and dirt removal was performed by washing with tap water followed by submerging in deionized water at room temperature for 24 hours. Washed clinoptilolite then transferred to an oven adjusted in 250°C during 24 hours for removing readily degradable organics, based on KOH and Dixon method [20]. Converting to the cationic form is performed to saturating clinoptilolite adsorption sites with sodium ions [21]. So, after drying step, concentrate solution of pure Sodium Chloride (2M) was added to Clinoptilolite. Then, obtained mixture was blended (150rpm) up to 72 hours for converting the adsorbent to the cationic form. Based on Li and Kirk approach, cationic-converted-site Clinoptilolite should be washed several times with deionized water to get rid of free chloride ion interference [22]. Finally, the argentometric test was done to be sure of Chloride absent from clinoptilolite ambient water [23].

Clinoptilolite Modification: The surface modification of Clinoptilolite by a cationic surfactant prepares a hydrophobic situation in aqueous solution which is suitable for the nesting of organic molecules especially those with fewer polarity and higher molecular weight [24]. The modification can be performed by adsorption an appropriate surfactant on the surface of Clinoptilolite. Developing a monolayer structure of surfactant at the solid–liquid interface by powerful bonds is a well-known model to describe the adsorption of surfactants on a solid surface. The monolayer structure may be occurred when the concentration of surfactant is equal or less than the critical micelle concentration (CMC). Furthermore, the surfactant concentrations more than the CMC can be tend to form a bilayer of surfactant molecules on the

clinoptilolite surface [25]. In this experiment, the HDTMA-Cl ($C_{19}H_{42}ClN$) was applied to modify the natural clinoptilolite. As reported by Ghiaci *et al.*, (2004), the critical micelle concentration (CMC) of HDTMA is 1.8 mmol L^{-1} [23]. According to the previous experiments, the maximum removal efficiencies were reported when the Clinoptilolite was modified with the HDTMA concentrations higher than the CMC [17, 23]. Therefore, the HDTMA concentration of 5 mmol L^{-1} which can exceed the CMC was applied in this study to create a bilayer of HDTMA molecules on the clinoptilolite surface.

HDTMA solution (5 mmol L^{-1}) was prepared by dissolving an appropriate quantity of HDTMA concentrate (50% w/w) to deionized water. Then, HDTMA solution (5 mmol L^{-1}) was added to the Clinoptilolite prepared as method described in 2.2.1. The mixture was kept in blending condition (100 rpm) for 48 hours.

Then, the obtained mixture was filtered the solid phase was thoroughly by shaking in plenty amounts of deionized water until no foam observed in the supernatant. Finally, based on Torabian *et al.* [26] suggestions, the acquired modified Clinoptilolite was dried in ambient air and stored in tight polyethylene vessels.

Characterization: ED2000 XRF (Oxford®, England) was used for determining chemical composition of Clinoptilolite (Table 1). X-ray powder diffraction (XRD) data were collected on X-Pert MPD diffractometer (Philips®, Netherland) with Cu radiation in the range of 3 to 70° (2θ) at 40 kV and 30 mA (Fig. 1). FT-IR tests were applied to determine the functional groups on the clinoptilolite surface, before and after the modification process (Fig. 2).

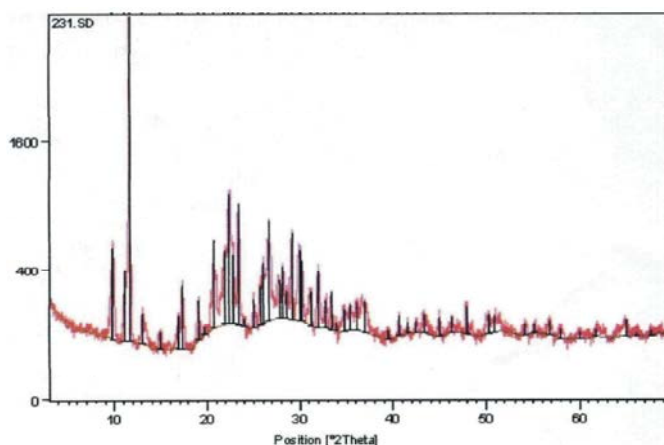


Fig. 1: XRD pattern for Iranian raw clinoptilolite

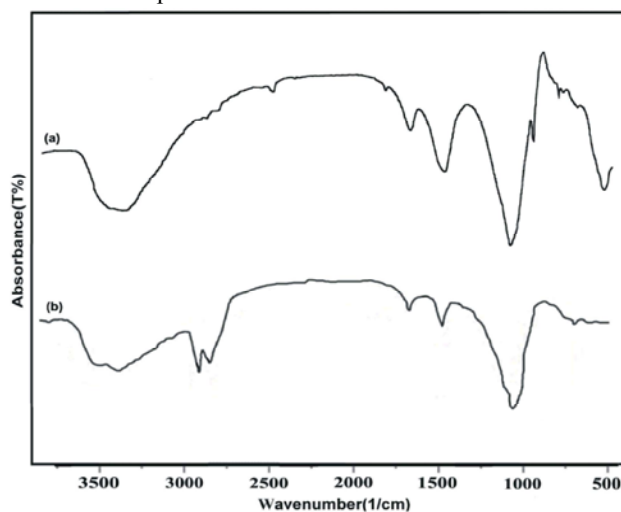


Fig. 2: FT-IR spectra of raw clinoptilolite (a) and clinoptilolite-HDTMA (b)

Table 1: Semi-quantitative XRF analysis results

Contents	Na ₂ O	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Sr	Zr	L.O.I
Proportion(%)	1.62	7.02	59.91	2.22	4.25	9.32	2.42	1.17	0.04	0.02	12.01

Analysis Methods: Determination of EDTA concentration was based on titration with Zinc Chloride (0.01 molL⁻¹) beside Xylenol Orange Indicator and Acetate buffer solution of pH 5.5 [15]. EDTA ligand can produce a complex with Zn²⁺ as follows (Eq. 1):



The endpoint of titration will reveal when Zn-XO (Chelating complex of Zinc and Xylenol Orange) be produced according to Eq. 2.



Equilibrium adsorption capacity of EDTA on modified-Clinoptilolite can be calculated based on Eq. 3.

$$q_e = \frac{(C_0 - C_t) \times V \times 291 \times 1000}{m} \quad (3)$$

where C_0 and C_t are EDTA concentrations (MolL⁻¹) at times 0 and t respectively, V is the volume (L) of EDTA solution, m is dosage (g) of modified-Clinoptilolite, 291 is molecular weight (gmol⁻¹) of EDTA and 1000 is converting factor (mg g⁻¹).

EDTA removal efficiency (RE) is calculated as follows:

$$RE = \left[\frac{(C_0 - C_t)}{C_0} \right] \times 100 \quad (4)$$

RESULTS AND DISCUSSIONS

Characterization: Table 1. shows the semi-quantitative XRF data of raw clinoptilolite and reveals that, SiO₂, CaO and Al₂O₃ are the prevalent constituents in raw Iranian clinoptilolite with weight percentages of 59.9, 9.32 and 7.02 respectively. Also, strontium and zirconium exist with the least amounts of 0.04 and 0.02, respectively. The ratio of silica to alumina content in clinoptilolite determines the thermal and chemical stability, the hydrophilic nature, the number and the capacity of the ion exchange in this material. Alteration the Si/Al ratio may affects the cation content and stability of the clinoptilolite. Increasing the Si/Al ratio is assigned to increase the siliceous nature of clinoptilolite which is regarding to improve the thermal stability.

In the Table 1, the report of major elements concentration is according the weight percentage of the oxides, recalculated to 100%. According to the results, the mass ratio of Si/Al was achieved 15.07 and the mass ratio of SiO₂/Al₂O₃ was 8.53. The L.O.I. (Loss on ignition) can be defined as the percentage of volatile components, mainly comprise the crystalline bound water and the organic carbon, releases from a sample when the sample temperature is elevated to 1000 °C. As depicted in Table 1, the L.O.I. for the Iranian clinoptilolite is obtained 12.01% which represented that 12.01% of the clinoptilolite comprised the volatile components [27].

Fig. 2 represents the FT-IR spectra of raw clinoptilolite and clinoptilolite-HDTMA. As shown in Fig. 2(a), the vibrations occurred at 3448 and 1637 were referred to the water molecules associated with Na and Ca in the channels and cages of the clinoptilolite structure [28]. Also, the other band appeared at 1023 cm⁻¹ arises from the asymmetric stretching vibration modes of internal Si-O and Al-O bonds in tetrahedral M-O₄ (M: Si and Al). The bonds revealed at 799 and 452 cm⁻¹ are attributed to the stretching vibration modes of O-M-O functional groups and the bending vibration modes of M-O bonds, respectively [29]. According to Fig. 2(b), the modification process using HDTMA was tend to appear new bonds at 2919 and 2850 cm⁻¹, assigned to the antisymmetric and symmetric C-H stretching vibrations modes of methylene groups, respectively. This confirms that the surface of the raw clinoptilolite was covered by the alkylammonium bromides and/or alkylammonium cations [30].

Effect of Clinoptilolite and HDTMA- Modified Clinoptilolite Dosage on Adsorption of EDTA: As can be inferred from Fig. 3, modifying the raw Clinoptilolite via HDTMA cationic surfactant has a noticeable impact on the equilibrium adsorption capacity (q_e). Equilibrium adsorption capacity (q_e) of EDTA was reported around 90 mgg⁻¹ for 0.1g (Raw clinoptilolite)/100ml and up to 270 mgg⁻¹ was obtained for surface modified Clinoptilolite in same dose.

An experiment performed by Ghadiri *et al.* [15] stated the significant effect of surface modification on improving the adsorption capacity of Clinoptilolite. According to their report, after Clinoptilolite modification by HDTMA, the equilibrium capacity for MTBE adsorption

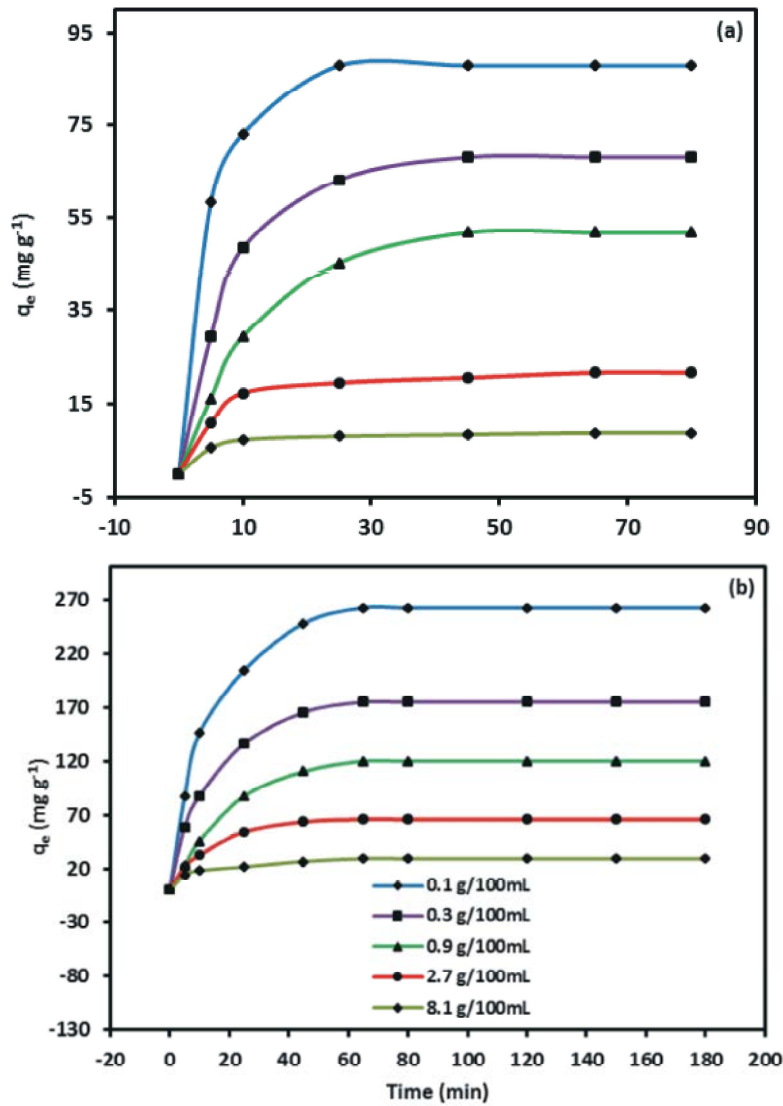


Fig. 3: Effect of clinoptilolite (a) and clinoptilolite-HDTMA (b) dosage on the EDTA adsorption (Mixing = 150 rpm, mesh = 70-80, EDTA = 0.01 mg/L, pH = 5.5, T = 25°C)

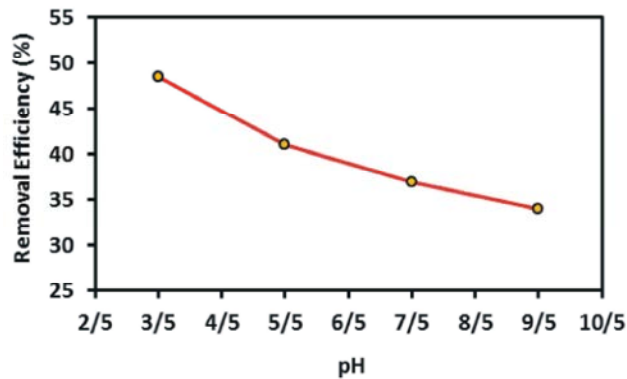


Fig. 4: Effect of pH on EDTA adsorption (clinoptilolite-HDTMA dosage = 0.9g/100 mL, Mixing = 150 rpm, mesh = 70-80, EDTA = 0.01 mg/L, T = 25°C)

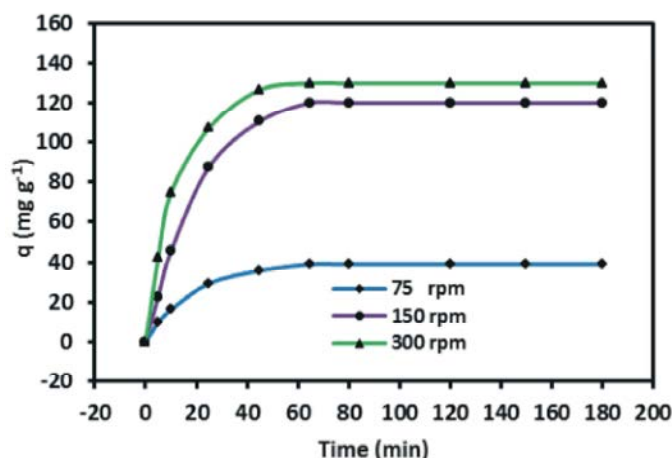


Fig. 5: Effect of agitation on EDTA adsorption (clinoptilolite-HDTMA dosage = 0.9 g/100mL, pH = 5.5, mesh = 70-80, EDTA = 0.01 mg/L, T = 25°C

was increased more than 8 times. Li *et al.* [22] reported the significant sorption of Benzene by HDTMA-Clinoptilolite. Their study showed that, the amount of Benzene adsorbed by raw Clinoptilolite is almost less than one tenth of those from modified Clinoptilolite. Increasing the adsorption capacity after surface modification by a cationic surfactant may be due to the alteration of Zeolite surface charges. Surfaces of the raw Clinoptilolite usually have negative charge which restrict the affinity for adsorption the anions or non-polar organics [17].

Effect of pH on Adsorption of EDTA: The effect of solution pH on EDTA adsorption was investigated at pH 3.5 – 9.5 and T = 298 K. As represented in Fig. 4, almost less than 35% of aqueous EDTA was adsorbed on HDTMA-modified-Clinoptilolite at pH 2. The adsorbed EDTA on modified Clinoptilolite increases with decreasing of pH from 9.5 to 3.5. Perhaps, One reason for this phenomenon is due to the competition between hydroxide (OH⁻) and H₂EDTA²⁻ ions for occupation of M-Clinoptilolite surface sites [31, 32].

Effect of Mixing Rate on Adsorption of EDTA: The agitation of EDTA in aqueous solution has important effect on adsorption process. As shown in Fig. 5, EDTA adsorption increases significantly in higher mixing rates (RPM). Fig. 5 also illustrates the noticeable difference between EDTA adsorption in 75 rpm and other mixing rates (150 and 300 rpm). One possible explanation for this discrepancy is relatively high density of clinoptilolite ($\rho=2.35 \text{ g cm}^{-3}$) that tends to higher settling affinity during low agitated hydraulic regimes which can be

explained with Stokes' law. Consequently, sedimentation of adsorbent in the bottom of vessel due to low stirring rate, which could be indicated by visual observation, decreased the effective contacts between aqueous EDTA and clinoptilolite and thus consumed much more time to reach the equilibrium [33]. As also revealed from Fig. 5, the mixing rate more than 150 rpm has not significant effect on EDTA adsorption. It seems that, after 150 rpm, clinoptilolite has reached to a completely mixed hydraulic regime and increasing the agitation from this well-dispersed mixture, does not tend to better adsorption condition [34].

Adsorption Kinetics: Modeling the EDTA uptake rate in aqueous solution is performed by adsorption kinetics. It can be inferred from Fig. 6 that the EDTA adsorption on modified-clinoptilolite increases with its initial concentration. As shown in Fig. 6, higher concentrations of initial EDTA related to higher rates of adsorption. It may be due to increase of mass-transfer between liquid bulk and solid surface. Also, increasing the diffusivity of EDTA in higher concentrations which can accelerate the adsorption rate is the other explanation [15]. The uptake of EDTA reaches to equilibrium within 55 min which was in agreement with those based on ion uptake by natural adsorbent [35, 36].

Compared to coconut shell activated carbon experiment that Zhu *et al.* reported [15] the modified-clinoptilolite has a shorter adsorption equilibrium time and lower adsorption capacity. Other adsorption experiment relied on clinoptilolite [22] indicates the same equilibrium time.

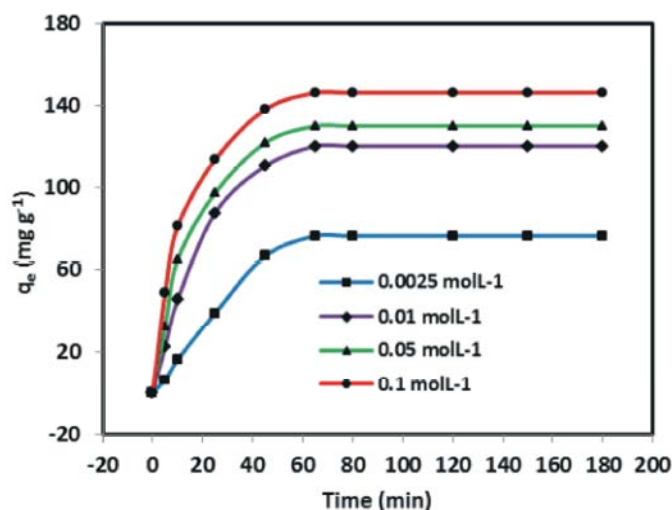


Fig. 6: Effect of EDTA initial concentration on EDTA adsorption (clinoptilolite-HDTMA dosage = 0.9g/100 mL, pH = 5.5, mesh = 70-80, Mixing = 150rpm, T= 25 °C)

Table 2: Equations of kinetic models in the EDTA adsorption

Kinetic models	Linear equations	Plot	Calculated coefficients
Lagergren pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$, (Eq. 5)	$\ln(q_e - q_t)$ vs. t	$q_e = e^{\text{intercept}}$, $k_1 = -\text{slope}$
Pseudo-second-order	$t/q_t = 1/k_2 q_e^2 + t/q_e$, $h = k_2 t$, (Eq. 6)	t/q_t vs. t	$k_2 = \text{slope}^2 / \text{intercept}$, $q_e = 1 / \text{slope}$
Elovich	$q_t = 1/\beta \cdot \ln(\alpha\beta) + 1/\beta \cdot \ln(t)$, (Eq. 7)	q_t vs. $\ln(t)$	$\alpha = e^{(\text{intercept} / \text{slope} - \ln(\beta))}$, $\beta = 1 / \text{slope}$
Intra-particle diffusion	$q_t = k_3 \cdot t^{1/2} + C$, (Eq. 8)	q_t vs. $t^{1/2}$	$k_3 = \text{slope}$

In order to evaluate the kinetics of EDTA adsorption, four kinetic models consist of Lagergren pseudo-first order (Table 2; Eq. 5), pseudo-second order (Table 2; Eq. 6), Elovich (Table 2; Eq. 7) and intra particle diffusion (Table 2; Eq. 8) was used. The mathematical equations of kinetics are shown in Table 2.

As can be found in Table 2, calculated coefficients necessary for plotting appropriate curves have been mentioned, where k is the rate constant, q_e and q_t are the sorption capacity (mg g^{-1}) at equilibrium and at time t (Min) and h is the initial sorption rate in pseudo-second-order model. Other parameters are defined in following sections.

The plots of $\ln(q_e - q_t)$ versus time are shown in Fig. 7. The Lagergren pseudo first order rate constant k_1 is calculated from the slope of Fig. 7 and based on respective mathematical relationship in Table 2. Kinetic calculated parameters are depicted in Table 3. The Lagergren correlation coefficients (R^2) were in the range of 0.951–0.998 that means an acceptable agreement with experimental data. The calculated q_e and k_1 are illustrated in Table 3.

As represents in Fig. 8, the pseudo-second order kinetic constants (k_2 and q_e) can be obtained from plot t/q_t vs. t and determining slope and intercept based upon Table 2. Values of k_2 , q_e , h and R^2 are observed in Table 3. The correlation coefficients of pseudo-second order were in the range of 0.961- 0.997 which reveals that experimental data are also in good agreement with this kinetic model. Consequently, it can be inferred that chemical process controls the adsorption rate [7, 15, 37, 38].

Elovich kinetic model has best agreement with processes dominated with chemical sorption especially in highly heterogeneous adsorbents [39]. In Elovich equation (Table 2; Eq. 7), α and β are adsorption rate ($\text{mg g}^{-1} \text{min}^{-2}$) and desorption constant ($\text{g mg}^{-1} \text{min}^{-1}$) respectively. β is related to activation energy for chemisorptions[7]. Table 2 indicates the calculation methods of α and β . The plots q_t vs. $\ln(t)$, as shown in Fig. 9, depicts the Elovich kinetic model in two distinct parts; before and after equilibrium. According to Fig. 9 and Table 3, except for the lowest concentration (0.0025molL^{-1} , $R^2=0.475$), there were suitable linear relationships for higher concentrations before reaching to equilibrium ($R^2>0.99$).

Table 3: Kinetic parameters fitted to experimental data based on different models

Kinetic Models and parameters	EDTA C_0 (molL ⁻¹)			
	0.0025	0.01	0.05	0.1
q_e (exp.)(mg.g ⁻¹)	76	120	129	146
Lagergren pseudo first order				
q_e (calc.) (mg.g ⁻¹)	85.96	127.09	129.77	135.69
k_1 (min ⁻¹)	0.447	0.0564	0.0605	0.0596
R ²	0.951	0.998	0.995	0.993
Pseudo second order				
q_e (calc.) (mg.g ⁻¹)	90.91	130.21	137.36	152.44
K_2 (g.mg ⁻¹ .min ⁻¹)	0.005	0.0068	0.0094	0.011
h (mg.g ⁻¹ .min ⁻¹)	41.841	116.60	178.76	165.74
R ²	0.9618	0.988	0.995	0.997
Elovich				
q_e (calc.) (mg.g ⁻¹)(t=55min)	80.24	118.07	129.54	145.76
α (g.mg ⁻¹ .min ⁻²)	5.43779	13.53	18.81	28.261
β (mg.g ⁻¹ .min ⁻¹)	0.0249	0.0249	0.0251	0.0251
R ²	0.475	0.996	0.995	0.997
Intra particle diffusion				
q_e (calc.) (mg.g ⁻¹)(t=55min)	62.89	119.70	137.87	162.12
k_3 (g.mg ⁻¹ .min ^{-1/2})	8.48	16.14	18.59	21.86
C	0	0	0	0
R ²	0.907	0.968	0.984	0.979

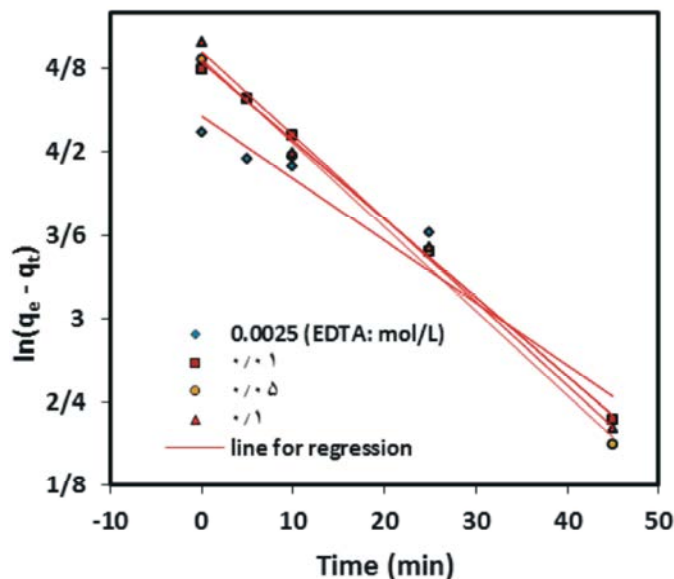


Fig. 7: Fitting of Lagergren pseudo-first order kinetic models for EDTA adsorption on clinoptilolite-HDTMA (T = 298 K)

Intra particle diffusion is a process probably governs adsorbate transport from the bulk of the solution into the solid-phase [40]. Adsorbate transportation from liquid to solid phase is often the main limiting step in adsorption processes. Based on the equation of intra particle diffusion (Table 2; Eq. 8), C is the intercept and k_3 is the intra particle diffusion rate constant (mg g⁻¹ h^{-1/2}) [40, 41].

Fig. 11 depicts the intra particle diffusion model and the plots of q_t vs. $t^{1/2}$ for EDTA in two obvious parts have been represented.

The first and second straight parts of Fig. 10 indicate macropore and micropore diffusion, respectively. Table 3 represents that the intra-particle diffusion rate constants (C) are zero in the study.

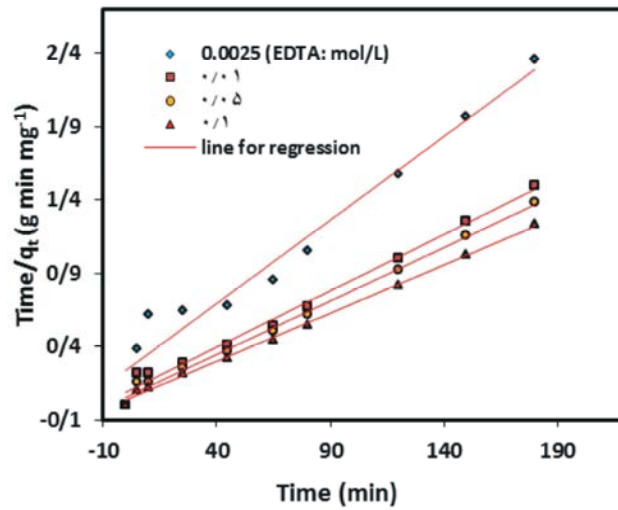


Fig. 8: Fitting of pseudo-second order kinetic models for EDTA adsorption on clinoptilolite-HDTMA (T = 298 K)

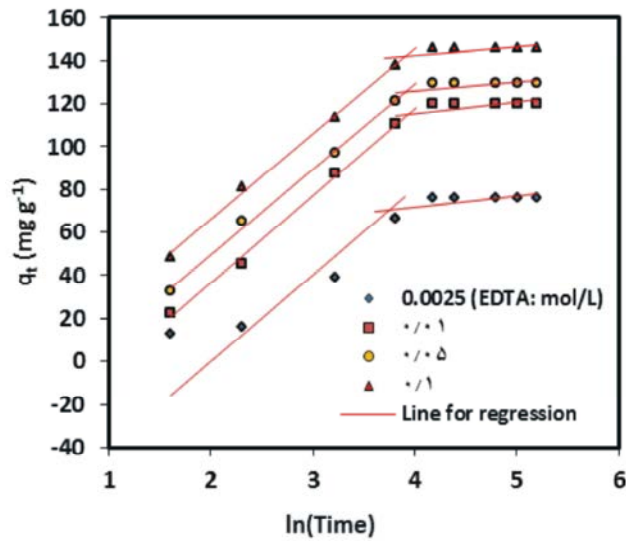


Fig. 9: Fitting of Elovich kinetic models for EDTA adsorption on clinoptilolite-HDTMA (T = 298 K)

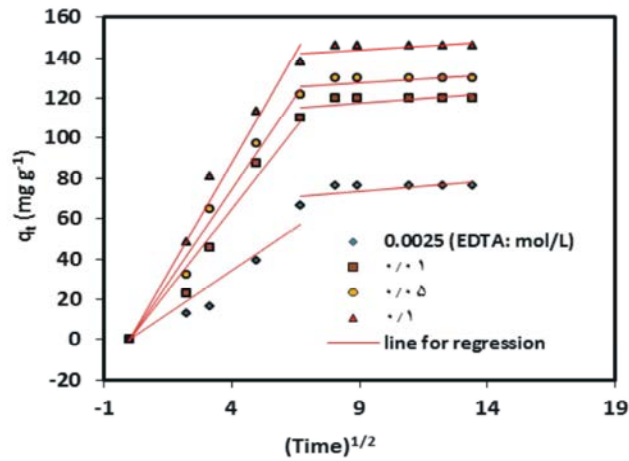


Fig. 10: Fitting of intra-particle diffusion kinetic models for EDTA adsorption on clinoptilolite-HDTMA (T = 298 K)

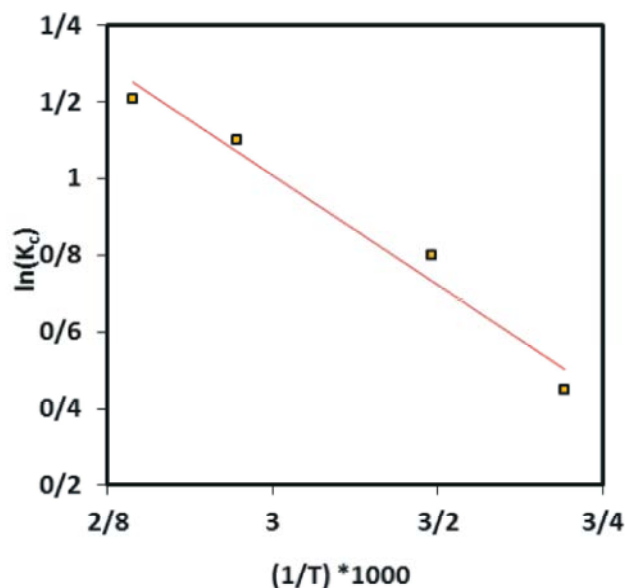


Fig. 11: Effect of temperature on the adsorption of EDTA by M-Zeolite (clinoptilolite-HDTMA dosage = 2.7 g/100mL, pH = 7.5, EDTA = 0.01mol⁻¹, T = 25 °C, Mixing rate =150 rpm)

Zero values of C indicate that adsorption process may be mainly controlled by intra-particle diffusion [42]. Regression correlation coefficients R^2 are in the range of 0.907 – 0.984 (Table 3). So, the experimental data are not properly fitted to Intra particle diffusion model.

Adsorption Isotherms: Three important isotherms including Dubinin [42], Langmuir [43] and Freundlich [44] Radushkevich (D-R) were used for analyzing adsorption data which are expressed as following equations:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (9)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (11)$$

where q_e is the amount of EDTA adsorbed on the adsorbent at equilibrium (mg g⁻¹), C_e describes the equilibrium EDTA concentration (mg L⁻¹), K_L is the Langmuir adsorption constant (Lmg⁻¹) and q_m denotes the maximum adsorption capacity corresponding to complete monolayer coverage. While K_F is the Freundlich constants related to the maximum sorption capacity (mg g⁻¹), also, n is the Freundlich constant attributed to the heterogeneity factor (m g⁻¹). ε is the Polanyi potential

(kJ² mol⁻²) which can be calculated from and β is a constant related to the mean energy of adsorption (mol² J⁻²).

$$\varepsilon = RT \cdot \ln(1 + \frac{1}{C_e})$$

Calculated constants of above isotherms have been presented in Table 4. According to Eq. 9, Langmuir isotherm curve can be illustrated by plotting C_e/q_e against C_e (Figure not shown). Table 4 indicates that correlation coefficient of Langmuir isotherm (R_L^2) is less than 0.92. So, adsorption isotherm derived from experimental data has not appropriate agreement with Langmuir isotherm. However, the results are in disagreement with those of Zhu *et al.*'s study [15].

The Freundlich logarithm form is normally written as Eq. 10, where K_F and n are Freundlich isotherm incorporating adsorption capacity (mg g⁻¹) and intensity, respectively. Freundlich isotherm can properly estimate the adsorption intensity of adsorbent towards the adsorbate. The values of K_F and n can be determined from the slope and intercept of the linear plots of $\ln(q_e)$ vs. $\ln(C_e)$, respectively (Figure not shown). Amounts of Freundlich constants are illustrated in Table 4 where correlation coefficient (R_F^2) is 0.978. The amount of n obtained from experimental data are in agreement with those of Zhu *et al* [15] but is noticeably less than Yan *et al.* [7] and Sakadevan *et al.* [7, 45].

Table 4: Isotherm constants for the adsorption of EDTA onto modified-Zeolite

T(K)	Langmuir			Fraundlich			Dubinin-Radushkevich			
	q_m (mgg ⁻¹)	K_L (Lmg ⁻¹)	R_L^2	n (mg ⁻¹)	K_F (mgg ⁻¹)	R_F^2	q_{max} (mgg ⁻¹)	β (mol ² Kj ⁻²)	E (kJmol ⁻¹)	R^2_{D-R}
298	147.06	6.83	0.913	0.754	159.81	0.978	173.99	0.095	2.29	0.805

Table 5: Thermodynamic parameters of EDTA adsorbed by modified-clinoptilolite

T(K)	ΔG° (kJmol ⁻¹)	ΔH° (kJmol ⁻¹)	ΔS° (Jmol ⁻¹ K ⁻¹)	R^2
298	-1.11	11.92	44.17	0.97
313	-2.08			
338	-3.09			
353	-3.55			

The adsorption data also were analyzed by Dubinin–Radushkevich (D–R) isotherm. Logarithm form of Dubinin–Radushkevich (D–R) isotherm is illustrated in Eq. 11. D-R isotherm is generally used in order to distinguish whether the adsorption has a physical or chemical basis. The amounts of q_{max} and b can be obtained from the intercept and slope of plotting $\ln(q_e)$ against ϵ^2 . Table 4 represents the amounts of D-R constants. Mean adsorption energy (E) is a useful parameter to obtain a better description of D-R isotherm. Mean adsorption energy (kJ mol⁻¹) is calculated as follows:

$$E = \sqrt{\frac{1}{2\beta}} \tag{12}$$

If the magnitude of E (From Eq. 12) be calculated less than 8 kJ mol⁻¹, the physical adsorption is dominated. However, the E amounts more than 8 kJ mol⁻¹ indicate that the adsorption proceeds chemically. As can be shown in Table 4, E value is 2.29 kJ mol⁻¹ which are so less than 8 kJ mol⁻¹ that reveals predomination of physical adsorption, although the D-R correlation coefficient (R^2_{D-R}) of 0.805 decreases the validity of judgment.

Finally, the EDTA adsorption with modified-Clinoptilolite may be explained by chemisorption process and Freundlich isotherm model has better fitness to experimental data than other isotherms.

Thermodynamic Parameters: Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) should be determined if the effect of temperature on adsorption process is considered. Change in free energy (ΔG°) can be obtained by following equation:

$$\Delta G^\circ = -RT \ln K_c \tag{13}$$

where R is the gas constant (8.3145 Jmol⁻¹K⁻¹), K_c (q_e/C_e) is equilibrium constant at various temperatures and T is the absolute temperature (K). Eq. 13 calculates ΔG° values attributed to obtained temperature as shown in Table 5.

Enthalpy (ΔH°) and entropy (ΔS°) can be calculated by a semi-logarithm equation defined as follows:

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{14}$$

As depicted in Fig. 11, Enthalpy (ΔH°) and entropy (ΔS°) can be determined by plotting $\ln(K_c)$ vs. $1/T$. So, (ΔH°) and (ΔS°) are obtained from slope and intercept of linear Eq. 14, respectively [46].

From Table 5, it represents that ΔG° has negative amounts attributed to various temperatures. So, it can be concluded that EDTA adsorption on modified-Clinoptilolite proceeds spontaneously.

Zhu *et al.* [15] found that obtained ΔG° is ranged from -0.79 to -8.40 kJ mol⁻¹ at 313-343 K. Also, Yan *et al.* [7] reported that the changes of free energy ΔG° at 298 K is -11.089 kJmol⁻¹. As shown in Table 5, ΔG° is -2.08 kJ mol⁻¹ at 313 K which has an appropriate agreement with findings of Yan *et al.* [7] and Zhu *et al.* [13]. However, the results are in disagreement with those of Emará *et al.* [34] which found that ΔG° is 1.0192 kJmol⁻¹ at 313 K during photodegradation of EDTA by mordenite-clinoptilolite modified with Fe.

With the raise in temperature, the ΔG° is decreased. This phenomenon recommends that the adsorption would be more advantageous at higher temperatures and is supported with other studies [7, 15, 34]. The positive value of ΔH° , as depicted in table 5, confirms the endothermic nature of adsorption. The sign of entropy (ΔS°) value is positive which indicates increased randomness during EDTA adsorption process [46].

CONCLUSIONS

In this study the adsorption of EDTA from aqueous solutions on HDTMA modified-Clinoptilolite has been investigated. The obtained results indicated that HDTMA-modified Clinoptilolite could be applied as an effective adsorbent for the treatment of water and wastewater containing EDTA complexes. Several conclusions have been drawn as follows:

- The impacts of diffusion on EDTA adsorption on modified-Clinoptilolite could be relatively ignored with a mixing speed over 150 rpm. In shaking rate less than 150 rpm, the adsorption capacity decreased dramatically may be due to Zeolite sedimentation because of its density and consequently tend to reduce the EDTA-Clinoptilolite effective contacts.
- The modified-Clinoptilolite represented a relatively noticeable adsorption capacity toward EDTA in aqueous medium. The amounts of the EDTA adsorbed at equilibrium (q_e), increase with temperature.
- Also, the EDTA adsorption on modified-Clinoptilolite increases with its initial concentration in the aqueous medium.
- The pseudo-second-order was the suitable kinetic model.
- Adsorbate transportation from liquid to solid phase was the rate-limiting step.
- EDTA adsorption equilibrium was achieved within 55 min.
- The isotherm analysis determined that the experimental data could be well illustrated by the Freundlich isotherm.
- The incorporating adsorption capacity (K_F) and intensity (n) were 159.8 mg g^{-1} and 0.754 respectively, at pH 7.5 and 298 K.
- The adsorption process was spontaneous and also endothermic.

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