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REMOVAL OF ACETIC ACID FROM DILUTE AQUEOUS SOLUTIONS USING ZEOLITE 13X

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Abstract: In this study, acetic acid adsorption equilibrium and kinetics of 13X synthetic zeolite from aqueous solutions at 25, 35 and 45 °C were investigated. 13X particles (particle diameter in the range of 75–150 μm) were contacted with different initial acetic acid cocentrations in aqueous phases (0.2–3 wt. %) at constant temperature in a batch reactor. Acetic acid concentrations of the liquid samples taken from the adsorption mixtures at specific time intervals were measured by titration with NaOH solution and the time required for the system to reach equilibrium and acetic acid amounts adsorbed at equilibrium were determined. The experimental adsorption kinetics data was best represented by the pseudo-second order model and the model parameters were calculated. The experimental equilibrium data was fitted to the Sips model and the model parameters were calculated. Adsorption thermodynamic parameters (standard Gibbs free energy change, enthalpy change, and entropy change of adsorption) were determined. The acetic acid-saturated adsorbent was regenerated by two methods in order to evaluate its reusability. Adsorption of acetic acid on 13X led to appearance of new bands in at 1390, 1472 and 1593 cm^{-1} in the transmittance infrared spectrum which were assigned to the acetate ions. Regeneration of the acetic acid-saturated 13X in deionized water at 45 °C led to loss in intensities of these bands indicating dissolution of the weakly adsorbed species associated with these bands. After heating at 300 °C, the bands at 1472 and 1593 cm^{-1} disappeared whereas 1390 cm^{-1} band remained and a very weak shoulder band appeared at 1720 cm^{-1}.

Keywords: Synthetic zeolite, acetic acid, adsorption, equilibrium, kinetics, modelling.

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INTRODUCTION

Acetic acid is one of the most important chemicals in the chemical industry and belongs to the top 50 chemicals in amount produced (1). Acetic acid is used in the manufacture of vinyl acetate, acetic anhydride, acetate esters, monochloroacetic acid, and as a solvent in the production of dimethyl terephthalate and terephthalic acid (2). Worldwide acetic acid production between 2009 and 2014 had grown by an average of 3–4% per year, while world acetic acid capacity had grown by an average of 4% per year. In 2010 world capacity exceeded 12 million tons/year (2). On an industrial scale acetic acid is produced via the petrochemical route: Carbonylation of methanol, liquid-phase oxidation of hydrocarbons, and oxidation of acetaldehyde (3). By 2012 *ca.* 90% of acetic acid is manufactured by low-pressure methanol carbonylation technologies (2). In this process, methanol and carbon monoxide are reacted in the liquid phase, with some water to keep the catalyst in solution. After the reaction, a distillation column is employed to remove methanol, water and carbon monoxide (4).

Gradual depletion of petroleum reserves, increasing prices of petrochemical feedstocks as well as environmental concerns have led to a search for alternative carboxylic acid production methods such as fermentation of biomass, forestry residues, municipal wastes, and other byproducts (5, 6). The acetic acid produced by fermentation is in dilute aqueous solutions, usually lower than 5 wt. % (7), so that its purification involves separation of acetic acid from a large quantity of water. The cost of such separation accounts more than half of the total production cost (8).

The increasing demand for acetic acid has led to an increase in the acetic acid amount in the industrial wastewaters. Acids in wastewater are classified as priority pollutants and they must be recycled, diluted or treated chemically and then degraded biologically. European countries require neutralization or biological degradation of these waste streams (2).

Acetic acid concentrations in the waste streams and fermentation broths are usually lower than 5 wt. % (9-12). Separation of carboxylic acids from aqueous solution is necessary in petrochemical manufacture, fermentation, and the environmentally and economically important recovery from waste streams (13). The selection of an acetic acid separation method depends on the economics. The conventional industrial method of carboxylic acid separation from the fermentation broth is precipitation using calcium hydroxide. However this separation process requires large amounts of sulfuric acid and generates solid waste in the form of calcium sulfate. Conventional distillation is energy-intensive due to the small differences in the volatilities of water and acetic acid. This separation process is economically viable provided that the acetic acid is highly concentrated (1, 14, 15) at concentrations exceeding 70 wt. % (3).

For separation of acetic acid from the dilute solutions, various other methods have been investigated in recent years including solvent extraction (16), reactive extraction (10, 17-20), pervaporation (14, 21-34) and electrodialysis (35-38). However most of these methods have drawbacks such as high capital costs, low efficiency, complexity of operation, high chemical and energy consumption as well as adverse environmental impact (39, 40).

Adsorptive separations can provide a viable option for separation of acetic acid from the dilute aqueous solutions (41). The adsorption process allows flexibility in terms of both design and operation. After adsorption, the adsorbent should be easily regenerated, thereby resulting in significant cost savings. Activated carbons (15, 41-48), basic polymeric adsorbents (42, 45, 49-51), ion exchangers (17, 52), silica gel (53), clays (54, 55), and carbon nanotubes (56) were investigated as adsorbents for removal of acetic acid from the dilute aqueous solutions. Synthetic zeolites (55, 57-60) and metal organic frameworks (61) are other adsorbents tested recently for the adsorptive separation of acetic acid/water.

Pervaporation has attracted increasing attention as an effective and energy-efficient technique for the separation of azeotrope or close-boiling liquid mixtures (62-65). Zeolite membranes have advantages over polymer membranes due to their better chemical and thermal stability. In general, hydrophilic zeolite membranes have been used for dehydration of organic solvents (66-68), while hydrophobic zeolite membranes have been used for separation of organics from water (14, 27, 66, 69, 70). Zeolite membranes have examined for separation of acetic acid-water mixtures by pervaporation (14, 22, 26, 29, 34).

An energy-efficient cyclic process has been patented for the simultaneous removal and recovery of acetic acid from water by concentration swing adsorption based on activated carbon adsorbent. In this process the more adsorbable component is acetic acid, the less adsorbable component is water, and the desorbent liquid is acetone (15).

The design and optimization of such a cyclic adsorptive separation process require determination of the adsorption equilibrium and kinetic parameters. Furthermore, the ideal adsorbent should have high adsorption capacity and selectivity, and be low-cost, easy to handle, environmentally neutral, non-toxic, and easy to regenerate.

In the present study equilibrium and kinetics of adsorption of acetic acid on 13X was studied. Several adsorption equilibrium and kinetic models were used to correlate the experimental data. From the adsorption equilibrium studies at 25, 35 and 45°C, the thermodynamic parameters were determined. Two different regeneration methods were employed in order to test the reusability of the adsorbent.

MATERIALS AND METHODS

Materials

Commercial synthetic zeolite 13X (Sigma-Aldrich, 3.2 mm pellets, Si/Al=1.2) was used as the adsorbent in the present study. The extrudates were ground in a mortar and sieved to particle diameter of 75–150 μm. Prior to the adsorption of acetic acid, these particles were activated in a static oven at 320 °C for 24 hours.

Experimental procedure

The stock solution of acetic acid (Carlo Erba, glacial, %99.5–100.5) was prepared by using distilled water. The solutions which were used in the adsorption kinetic and equilibrium experiments with the initial acetic acid concentrations in the range of 0.03–0.54 mol/L (0.17–3.25 wt. %) were prepared by diluting the stock solution. Two grams of 13X were contacted with 100 mL of acetic acid solutions of different initial concentrations in a thermostatic water bath at 25, 35 and 45°C at a shaking speed of 150 rpm. The samples which were taken from the supernatant at specific times were titrated with 0.05 M aqueous NaOH solution in order to determine the acetic acid concentration in the solution. The amount of acetic acid adsorbed was calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \qquad \text{(Eq. 1)}$$

where q_t is the amount of acetic acid adsorbed at the specified time, C_o is the initial acetic acid concentration of the solution, C_t is the acetic acid concentration in the solution at the specified time, V is the volume of the solution, and m is the adsorbent mass.

Regeneration of the adsorbent is a critical step as it influences the overall economy of the process. In order to test regenerability of the adsorbent, the 13X particles were saturated with acetic acid, then washed with distilled water and dried in a static oven at 60 °C overnight. One gram of these particles was then contacted with 50 mL of distilled water in the thermostatic water bath at 45 °C. The samples which were taken at specific time intervals were titrated with a NaOH solution in order to determine the amount of acetic acid desorbed. As another regeneration method, the acetic acid-saturated 13X particles were kept in a static oven at 300 °C for 24 hours and were used in acetic acid adsorption at 25 °C again.

Adsorption Kinetics

During adsorption of acetic acid molecules in 13X, the acid molecules were first transferred from the bulk solution to the external film surrounding the adsorbent particle (through the interparticle pores), then through the external film and through the intraparticle pores. Then sorption occured at the adsorption sites by chemisorption or ion exchange or physisorption. The rate of sorption might be controlled by the slowest mass transfer step.

In order to investigate the mechanism of adsorption of acetic acid in the 13X particles, the pseudo-first-order (71), pseudo-second-order (72) and intraparticle diffusion (73) models were employed. The model equations are given in Table 1.

Table 1: Adsorption kinetic models employed to the experimental kinetic data for acetic acid adsorption in 13X.

Model	**Equation**	**Eqn. number**
Pseudo first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	(Eq. 2)
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	(Eq. 3)
Intraparticle diffusion	$q_t = k_i \sqrt{t} + c$	(Eq. 4)

In these equations q_t and q_e are the amounts of acetic acid adsorbed at time t and equilibrium, respectively, k_1 is the pseudo-first-order rate constant for the adsorption process, k_2 is the pseudo-second-order rate constant for the adsorption process, k_i is the intraparticle diffusion constant, and c is the thickness of the boundary layer formed between the adsorbate molecules and the adsorbent surface.

The goodness of fit was evaluated based on the linearity of the $\log(q_\mathrm{e}\text{-}q_\mathrm{t})$ versus t, t/q_t versus t and q_t versus $t^{0.5}$ plots for the pseudo first-order, pseudo second-order and intraparticle diffusion models, respectively.

Adsorption Equilibrium

Adsorption equilibrium isotherm describes how the adsorbate molecules distribute between the liquid and the solid phases at equilibrium.

Two-parameter (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich models), and three-parameter (Redlich–Peterson, Toth, Sips models) adsorption equilibrium models were employed to describe the acetic acid adsorption kinetics in 13X in the present study. The model equations are given in Table 2.

Table 2: Adsorption equilibrium models

Model	**Equation**	**Eq. no.**
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	(Eq. 5)
Freundlich	$q_e = K_F C_e^{1/n_F}$	(Eq. 6)
Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	(Eq. 7)
Dubinin-Radushkevich (D-R)	$q_e = q_{mDR} \exp(-K_{DR} \varepsilon^2)$	(Eq. 8)
Redlich-Peterson (R-P)	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^g}$	(Eq. 9)
Sips (Langmuir–Freundlich)	$q_e = \frac{q_m (a_s C_e)^{1/n_s}}{1 + (a_s C_e)^{1/n_s}}$	(Eq. 101)
Toth	$q_e = \frac{q_m a_T C_e}{\left[1 + (a_T C_e)^{n_T}\right]^{1/n_T}}$	(Eq. 11)

In these equations, C_e is the concentration of acetic acid in solution at equilibrium, q_m is the saturation adsorption capacity, q_{mDR} is the D–R model constant related to the degree of adsorption by the adsorbent under the optimized experimental conditions, K_L is the Langmuir model adsorption equilibrium constant related to the adsorption energy, K_F is the Freundlich model constant related to the adsorption capacity, n_F is the Freundlich model constant related to the adsorption intensity, b is the Temkin model constant related to heat of adsorption, K_T is the Temkin model equilibrium binding constant corresponding to the maximum binding energy, K_{DR} is the Dubinin-Radushkevich model adsorption equilibrium constant related to the adsorption energy, ε is the Polanyi potential, K_{RP} is the Redlich-Peterson model adsorption equilibrium constant, a_{RP} is the Redlich-Peterson model affinity consant, g is the Redlich-Peterson model exponent (Redlich-Peterson model reduces to the Langmuir isotherm for g=1), a_s is the Sips model affinity consant, n_s is the Sips model parameter characterizing the system heterogeneity, a_T is the Toth model affinity consant, n_T is the Toth model parameter characterizing the system heterogeneity, R is the gas constant, and T is the absolute temperature.

The equations for the adsorption equilibrium models given in Table 2 were fitted to the experimental data using the Generalized Reduced Gradient (GRG) nonlinear regression algorithm of Excel Solver. The model parameters minimizing the sum of the squares of the errors (*SSE*) were calculated. The *SSE* values for the model fittings were calculated as follows:

$$SSE = \sum \left(q_{e,\mathrm{model}} - q_{e,\mathrm{exp}}\right)^2 \quad \text{(Eq. 12)}$$

where $q_{e,model}$ and $q_{e,exp}$ are the calculated and experimentally measured adsorbate concentrations at equilibrium, respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

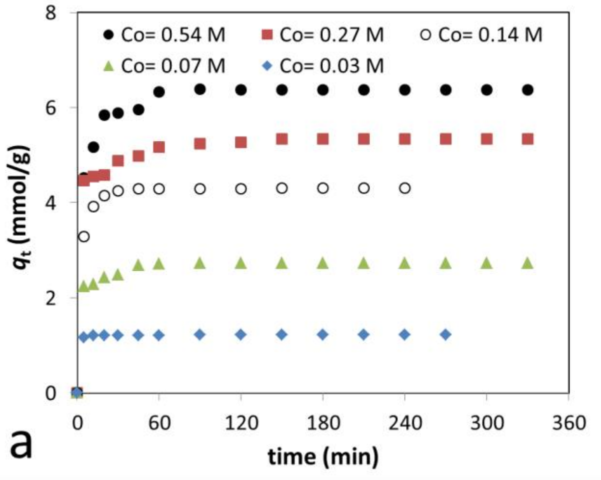
The 13X zeolite was characterized before and after activation, acetic acid adsorption, regeneration in deionized water at 45 °C and heating at 300 °C successive to the saturation with acetic acid by used transmittance FTIR spectroscopy. The samples were prepared using the standard KBr pellet method (sample/KBr weight ratio of 1/200). The sample-KBr mixtures were ground together in an agate mortar and pelletized under 10 tons pressure by a hydraulic press. The spectra were recorded in the region of 400–4000 cm^{-1} at room temperature after 128 scans at 2 cm^{-1} resolution using a spectrometer (Spectrum II, Perkin Elmer). For all the spectra, the baseline correction was performed.

RESULTS and DISCUSSION

Adsorption Kinetics

From the experimental adsorption kinetics data shown in Figure 1, it was concluded that the equilibrium has been reached within the first 240 minutes. The acetic acid removal efficiency (%) is calculated by following equation:

$$\%\,removal\ efficiency = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{(Eq. 13)}$$



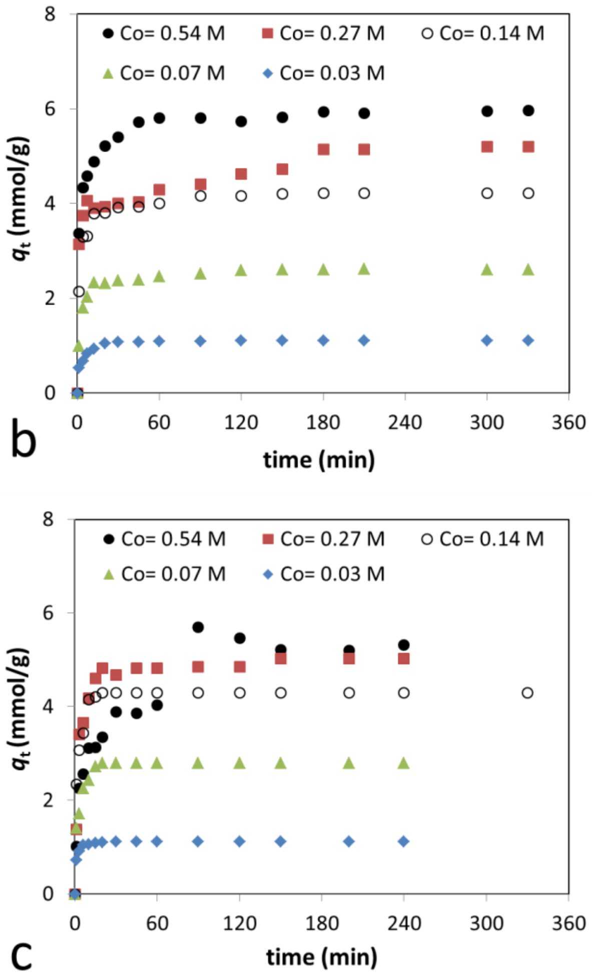


Figure 1: Variation of the amount of acetic acid adsorbed in 13X with time for different initial acetic acid concentratons at (a) 25°C, (b) 35°C and (c) 45°C.

The acetic acid removal efficiency of the 13X zeolite decreased with the initial acetic acid concentrations but was not affected remarkably by the adsorption temperature as seen in Figure 2.

The values of the kinetic parameters (q_e, k_1, k_2, k_i, and c) and the regression coefficients (r^2) were determined from the intercepts and slopes of the linear plots using the corresponding kinetic model equations in Table 1.

The regression coefficients (r^2) calculated form the pseudo-first and pseudo-second order models are given in Table 3. The correlation coefficients calculated for the pseudo-second order kinetic model fitting are significantly higher than those obtained for the pseudo-first order kinetic model for the whole acetic acid concentrations and temperatures indicating that the experimental adsorption kinetic data can be represented by the pseudo-second-order kinetic model. This revealed that the adsorption rate is controlled by a chemical reaction between the 13X surface and acetic acid molecules involving valency forces through sharing or exchange of electrons between sorbent and sorbate (72).

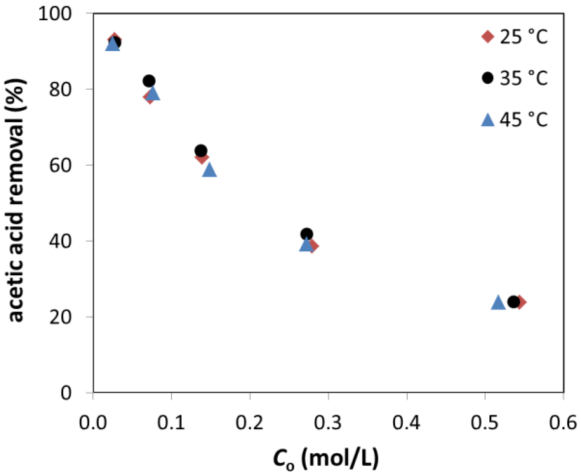


Figure 2: Variation of the acetic acid removal efficiency with the initial acetic acid concentration at 25, 35 and 45°C.

Table 3: Comparison of the regression coefficients for linearized pseudo-first and pseudo-second order kinetic models at various initial concentrations and temperatures.

	25°C		**35°C**		**45°C**	
C_o (mol/L)	**Pseudo-first order**	**Pseudo-second order**	**Pseudo-first order**	**Pseudo-second order**	**Pseudo-first order**	**Pseudo-second order**
0.54	0.875	1.000	0.830	1.000	0.754	0.993
0.27	0.826	1.000	0.904	0.997	0.552	1.000
0.14	0.954	1.000	0.885	0.999	0.956	1.000
0.07	0.920	1.000	0.908	0.999	0.967	0.999
0.03	0.507	1.000	0.878	1.000	0.925	1.000

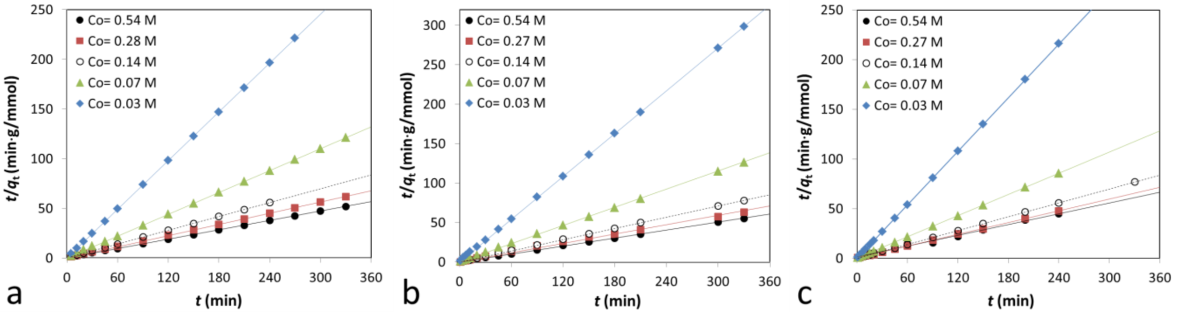


Figure 3: t/q_t versus t plots for adsorption at (a) 25°C, (b) 35°C and (c) 45°C.

The values q_e and k_2 calculated from the linear plots of t/q_t versus t shown in Figure 3 are presented in Table 4. The calculated q_e values obtained from this model were in excellent agreement with the experimental ones. The model represented the experimental data fairly well in the whole concentration and temperature range of interest in the present study.

The pseudo-second order kinetic rate constant (k_2) values were found to decrease while the equilibrium adsorption capacities (q_e) increased with the increasing initial acetic acid concentration. The equilibrium sorption capacity (q_e) did not change significantly with the temperature at the low initial acetic acid concentrations while it decreased with the increasing temperature at the higher initial acetic acid concentrations. This suggested that the acetic acid adsorption in 13X zeolite is favored at low temperatures and high initial acetic acid concentrations.

Table 4: Pseudo second-order model parameters.

T (°C)	C_o (mol/L)	k_2 (g/mmol·min)	q_e (mmol/g)
25	0.54	0.079	6.42
	0.28	0.073	5.39
	0.14	0.259	4.33
	0.07	0.235	2.74
	0.03	3.281	1.22
35	0.54	0.066	5.99
	0.27	0.023	5.27
	0.14	0.112	4.25
	0.07	0.145	2.63
	0.03	0.577	1.11
45	0.52	0.019	5.54
	0.27	0.087	5.06
	0.15	0.479	4.30
	0.08	0.430	2.81
	0.03	2.783	1.11

From the q_t versus $t^{0.5}$ plots drawn according to the intraparticle diffusion model (for 35°C shown in Figure 4), it was found that all the plots exhibited three linear regions involved in adsorption of acetic acid in 13X zeolite. The initial linear region where the adsorbed amount of acetic acid increased rapidly corresponds to the adsorption on the external surface of the 13X particles. The linear regions at later times where the adsorption occurs at a gradual rate represent adsorption of the adsorbate molecules in the adsorbent particles (in mesopores between the zeolite crystals and within the crystals) (73).

None of these plots passed through the origin (*c* is not equal to zero) implying that the intraparticle diffusion was not the only rate-controlling step in the adsorption of acetic acid in 13X (73). The k_i and *c* values calculated respectively from the slopes and intercepts of the linear portions together with the regression coefficients (r^2) for adsorption at 35°C are given in Table 5. The k_i values (rate of adsorption) at the later period of the adsorption were lower than those at the beginning of the adsorption due to decrease in the mass transfer rate due to the low acetic acid concentration left in the solution, i.e. lower driving force. The values of *c* decreased with the decreasing initial acetic acid concentration.

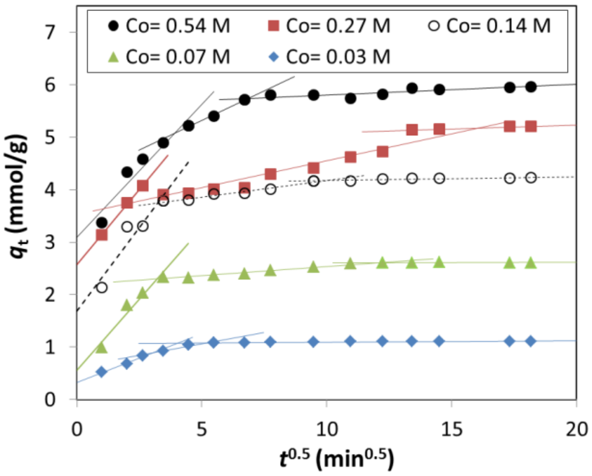


Figure 4: q_t versus $t^{0.5}$ plots for the acetic acid adsorption at 35 °C.

Table 5: Intraparticle diffusion control model parameters for the acetic acid adsorption at 35°C.

C_o (mol/L)	r^2	k_i (mmol/g·min$^{0.5}$)	c
	1st linear region		
0.54	0.911	0.373	3.414
0.27	0.997	0.573	2.570
0.14	0.892	0.635	1.684
0.07	0.952	0.541	0.554
0.03	0.978	0.185	0.329
	2nd linear region		
0.54	0.992	0.225	4.192
0.27	0.878	0.102	3.530
0.14	0.957	0.062	3.546
0.07	0.971	0.035	2.182
0.03	0.949	0.088	0.618
	3rd linear region		
0.54	0.771	0.020	5.600
0.27	0.989	0.015	4.937
0.14	0.767	0.007	4.106
0.07	0.109	0.001	2.602
0.03	0.650	0.003	1.057

Adsorption Equilibrium

The values of the model parameters and *SSE* for the adsorption equilibrium models are given in Table 6. Considering these *SSE* values given in Table 6, it is evident that the experimental equilibrium data can be represented better by the three-parameter models (R-P, Sips and Toth models) than by the two-parameter models (Langmuir, Freundlich, Temkin and D-R models). The *SSE* values for the Sips model were the lowest among those for the equilibrium models fitted. Thus it was concluded that the experimental adsorption equilibrium data can be represented best with the Sips model.

Table 6: Adsorption equilibrium model parametres and *SSE* values for the fitted equilibrium models.

Model	Parameter	25°C	35°C	45°C
Langmuir	q_m	6.319	5.916	5.402
	K_L	47.316	61.926	73.708
	SSE	0.750	0.343	0.217
Freundlich	K_F	8.30	7.89	7.15
	n_F	3.82	3.99	4.33
	SSE	0.43	0.77	0.93
Temkin	b	2.567	2.723	3.157
	K_T	1533.3	1520.1	1999.5
	SSE	0.201	0.071	0.179
Dubinin-Radushkevich	q_{mDR}	6.265		
	K_{DR}	0.0069		
	SSE	0.334	0.031	0.291
Redlich-Peterson	K_{RP}	1154.7	702.6	654.6
	a_{RP}	150.6	102.7	108.8
	g	0.811	0.876	0.912
	SSE	0.106	0.042	0.093
Sips	q_m	8.68	6.92	5.97
	a_s	15.91	37.98	56.93
	n_s	1.90	1.53	1.41
	SSE	0.061	0.012	0.022
Toth	q_m	11.112	7.485	6.222
	a_T	507.0	186.3	175.1
	n_T	0.311	0.491	0.580
	SSE	0.068	0.015	0.038

Fitting of the Sips model to the experimental adsorption isotherms at 25, 35 and 45°C are shown in Figure 5. It can also be seen that the amount of acetic acid adsorbed at equilibrium decreased with the increasing adsorption temperature.

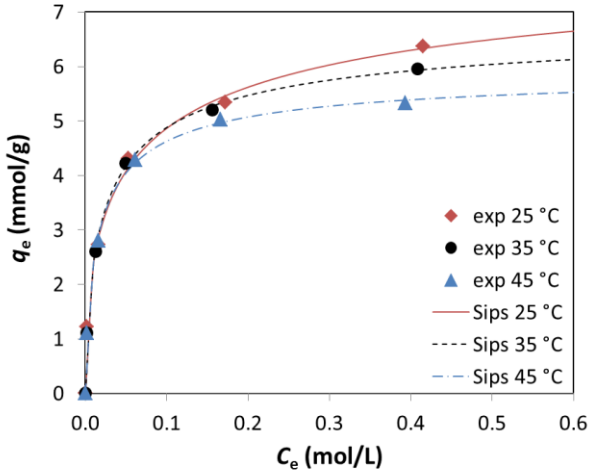


Figure 5: Experimental adsorption equilibrium data and the Sips model fittings.

The Sips model parameter characterizing the system's heterogeneity (74) was found to decrease with the increasing temperature suggesting that the system is "apparently" less heterogeneous at higher temperatures. However, this does not point to what is the source of the heterogeneity, whether it is the adsorbent structural property, the adsorbent energetical property or the sorbate property (74).

The temperature dependence of the Sips model adsorption affinity constant (a_s) has the following form (74):

$$a_s = a_{s\infty} \exp(Q/RT) \qquad \text{(Eq. 14)}$$

where $a_{s\infty}$ is the affinity constant at infinite temperature and Q is the adsorption heat.

From the linear plot of lna_s versus $1/T$ (Figure 6) (r^2=0.965), the adsorption heat (Q) and $a_{s\infty}$were calculated as 50.40 kJ/mol and 1.16×10^{10} L/mol, respectively. The calculated Q corresponds to the isosteric heat at the fractional loading of 0.5 (74).

Zhang and co-workers stated that the experimental acetic acid adsorption isotherms for 13X pellets (Si/Al<3) can be represented by the Freundlich model and determined the model parameters as K_F=1.20 mmol/g and n_F=2.66 at 25°C. The amount of acetic acid adsorbed increased with the initial acetic acid concentration and temperature (endothermic adsorption). The monolayer acetic acid adsorption capacity of was calculated as 6.38, 6.75 and 7.11 mmol/g at 25, 35 and 45°C, respectively, by the Langmuir model (60). The same research group had found that the adsorbed amount of acetic acid decreased with increasing temperature, indicating that acetic acid adsorption on UiO-66 was exothermic. The monolayer acetic acid adsorption capacity of the MOF was calculated as 4.50 and 4.73 at 25 and 45°C, respectively (61). The monolayer acetic acid adsorption capacity of 13X used in the present study at 25°C (6.32

mmol/g) was shown to be in good agreement with that reported for the 13X pellets (Si/Al<3) (6.38 mmol/g) (60), and higher than those of 330 resin (0.53 mmol/g) (75), activated carbon (0.92 mmol/g) (48), multiwall carbon nanotube (0.09 mmol/g) (56) and UiO-66 (4.50 mmol/g) (61).

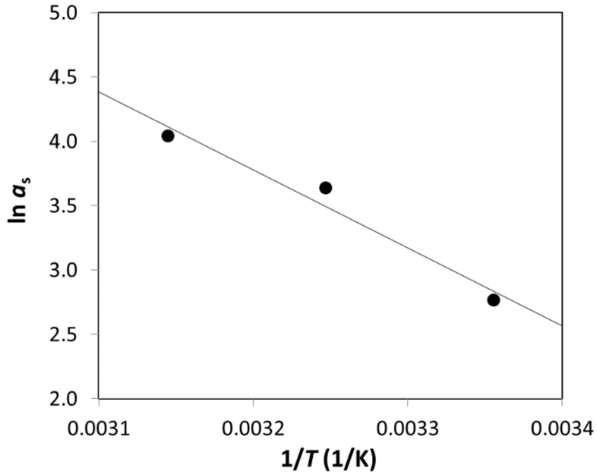


Figure 6: Temperature dependence of the Sips model parameter a_s.

Langmuir model constant, K_L, indicates the affinity for the binding of acetic acid. A dimensionless constant, commonly known as dimensionless separation factor (R_L) can be represented as (76):

$$R_L = \frac{1}{1+K_L C_o} \quad \text{(Eq. 15)}$$

The R_L value indicates whether the adsorption is unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$) (77). In the present study, the R_L values were found to vary within the range of 0.026–0.434 indicating the favorable adsorption. The R_L values decreased as the temperature and initial acetic acid concentration increased (Figure 7).

Although it was found in the present study that the experimental adsorption equilibrium data can be represented by the Sips model better, the monolayer adsorption capacity (q_m) calculated from the Langmuir model fitting was used to calculate the specific surface area (S) of the 13X as follows:

$$S = A_a N_A q_m \quad \text{(Eq. 16)}$$

where N_A is Avogadro's number and A_a is the cross-sectional area of the adsorbate molecule. Assuming that the acid molecules are adsorbed vertically, with the alipatic chain up and the carboxyl group down attached to the adsorbent surface, the cross-sectional area of a straight-chain acid was taken to be about 21×10^{-20} m^2 (78). From the monolayer adsorption capacities were calculated from the Langmuir model fitting, the average specific surface area of the 13X was calculated as 745 m^2/g. This value fell in the range of the reported BET surface areas (500–800 m^2/g) measured with N_2 adsorption data at -196 °C for X and Y type zeolites (79).

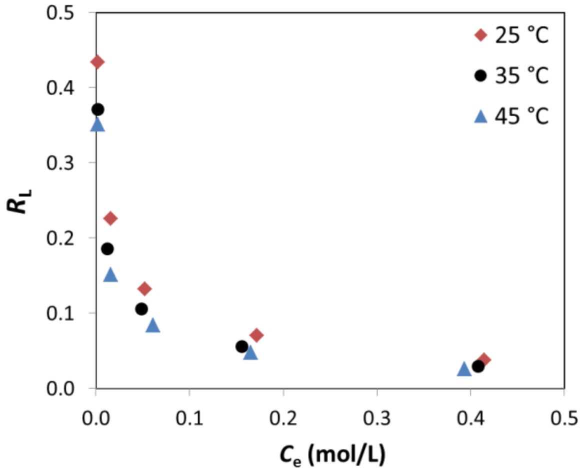


Figure 7: Separation factor as a function of the initial acetic acid concentration and temperature.

The Dubinin–Radushkevich (D-R) model, given in Table 2 by Eqn.(8), is a semi-empirical model which is originally developed for sub-critical vapors in microporous solids, where the adsorption process follows a pore filling mechanism onto an energetically non-uniform surface (80). D–R model is rarely applied to liquid-phase adsorption due to the complexities associated with other factors such as pH and ionic equilibria inherent in these systems. Additionally, the solute-solvent interactions often render the bulk solution non-ideal. However the model was applied to adsorption from liquid phase using 13X zeolite in the literature (81-84). In this model the Polanyi potential (ε) is expressed by the equation below;

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \qquad \text{(Eq. 17)}$$

The experimental data and the D-R model fittings plotted using the model parameters given in Table 6 were shown in Figure 8. Even though only one value of the characteristic energy was used in the fitting of the experimental data at three temperatures, the fit is very good (r^2=0.993) demonstrating the effectiveness of this model in describing the experimental data for acetic acid adsorption in 13X.

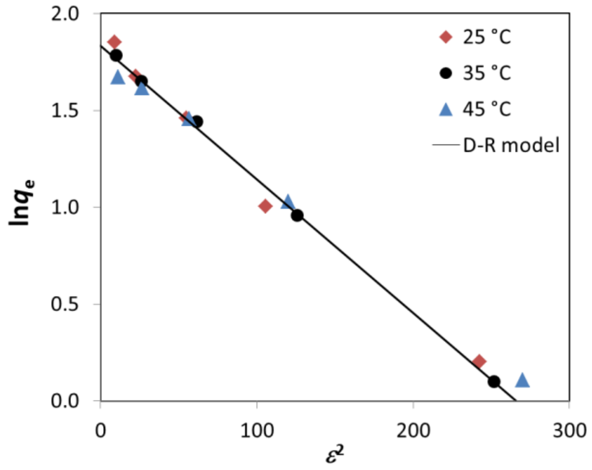


Figure 8: Experimental characteristic curve and the D-R model fitting.

The D-R model adsorption equilibrium constant K_{DR} is related to the mean free energy of transfer of one mole of solute from infinity in solution to the adsorbent surface as:

$$E = \frac{1}{\sqrt{2K_{DR}}} \qquad \text{(Eq. 2)}$$

This parameter gives information about the adsorption mechanism: If the magnitude of E is between 8 and 16 kJ/mol the adsorption process follows by ion exchange, while the value below 8 kJ/mol the adsorption process is of a physical nature (85). In the present study the calculated value of E (8.51 kJ/mol) is slightly above 8 kJ/mol suggesting that the removal of acetic acid by 13X occurred by both physisorption and ion exchange mechanisms.

The micropore volume of 13X pellets was calculated as 0.359 cm^3/g using the saturation adsorption capacity corresponding to the D-R maximum pore volume (calculated from q_{mDR}). This value is in good agreement with the pore volume of NaX (Si/Al=1.25) determined from the adsorption of different types of molecules including water, gases and hydrocarbon (0.25–0.36 cm^3/g) in the literature (86).

Adsorption Thermodynamics

The change in the standard Gibbs free energy of adsorption (ΔG°) can be expressed as:

$$\Delta G^{o} = -RT\ln K = -RT\ln(55.5K') \qquad \text{(Eq. 3)}$$

where K is the dimensionless equilibrium constant and 55.5 is the activity of water in solution. K' was determined from C_e versus C_e/q_e plots. Temperature dependence of the dimensionless adsorption equilibrium constant is given by the van’t Hoff equation,

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad \text{(Eq. 4)}$$

where ΔH° is the standard enthalpy of adsorption and ΔS° is the standard entropy of adsorption. The values of ΔH° and ΔS° were calculated from the slope and intercept of the van't Hoff plot shown in Figure 9, respectively. The values of ΔG°, ΔH° and ΔS° are given in Table 7.

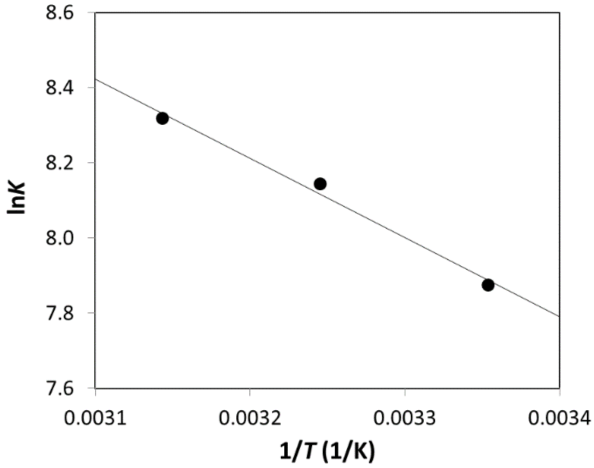


Figure 9: van't Hoff plot(ln *K* versus 1/*T*)

Table 7: Thermodynamic parameters.

T (°C)	Δ*G*° (kJ/mol)	Δ*H*° (kJ/mol)	Δ*S*° (J/mol/K)
25	-19.52		
35	-20.86		
45	-22.00		

The negative ΔG° values indicated spontaneous adsorption of acetic acid on 13X zeolite. The values of ΔG° decreased from -19.52 to -22.00 kJ/mol with increase in temperature from 25°C to 45 °C indicating that the sorption of acetic acid was favorable at high temperatures. The positive ΔH° values designated that the sorption of acetic acid in 13X was endothermic. However, as previously stated and shown in Figure 5, the amount of acetic acid adsorbed at equilibrium decreased with the increasing temperature. The reason for this is that in the low acetic acid concentration range in which the dimensionless adsorption equilibrium constant (K') was calculated the amount of acetic acid adsorbed at equilibrium increased with temperature. This indicates that the interaction between the acetic acid molecules and the 13X surface increased with temperature in the low acetic acid concentration range, while weaker interaction between the acetic acid and adsorbent than that between water and the adsorbent at high acetic acid concentration range (87). The positive values of entropy change (ΔS°) implied the increased randomness (degree of freedom of the system) at the solid-solute interface during adsorption, which may be caused by the restricted mobility of acetic acid on the surface of 13X particles compared with that of aqueous solution (88).

Regeneration of the Adsorbent

In order to determine the reusability of the 13X adsorbent, a consecutive adsorption–desorption cycle was conducted. In the present study the 13X zeolite saturated with acetic acid (88) was regenerated using two different methods: shaking with distilled water at 45 °C (1 g of solid/100 mL of water) and heating to 300 °C under static aereal atmosphere. The acetic acid-saturated 13X did not desorb the acetic acid in distilled water at 45 °C as seen in Figure 10. From Figure 11, it can be seen that the acetic acid adsorption capacity of the 13X particles at 25 °C after being regenerated at 300 °C has dropped to about half of that of the fresh 13X.

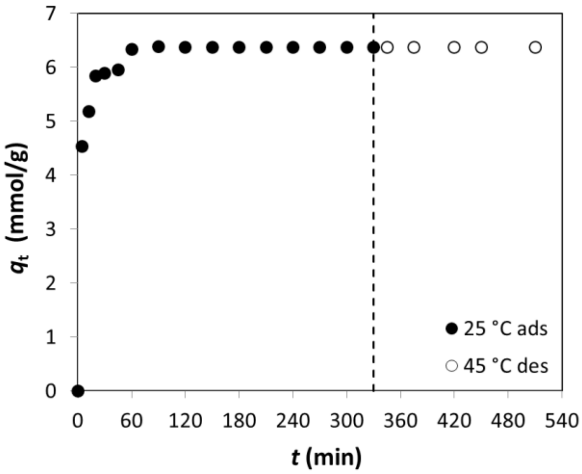


Figure 10: Desorption kinetics of acetic acid at 45°C in distilled water after the acetic acid adsorption at 25°C.

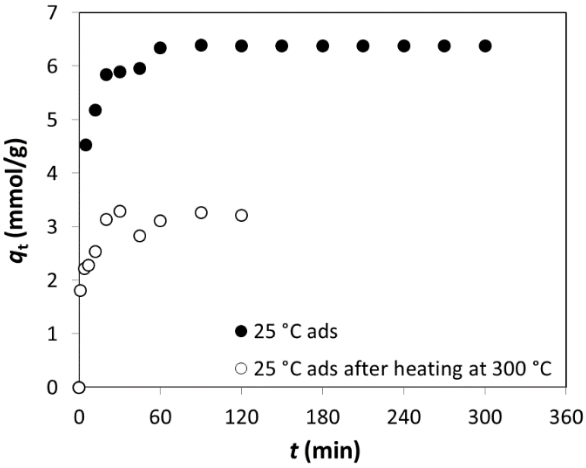


Figure 11: Acetic acid adsorption kinetics for the fresh and heated (at 300°C) 13X after being saturated with acetic acid.

For regeneration of the acetic acid loaded activated carbons and macroreticular styrene-divinylbenzene adsorbents, methanol, methyl acetate, and acetone were suggested as suitable regeneration solvents (49). Lv and co-workers regenerated acetic acid-loaded ion exchange resin with 2 to 4 % NaOH solution efficiently without harming the resin (75). In another study, a metal-organic framework (UiO-66) was washed with deionized water and ethanol, and reused in acetic acid adsorption. After three adsorption-desorption cycles, the adsorption capacity of UiO-66 decreased by 7% without any deformation in the structure of UiO-66 (61). Ethanol was suggested as an adsorption-competitive solvent for the regeneration of the high-silica ZSM-5 powder (58). In fixed-bed separation process by concentration swing adsorption where activated carbon was used as the adsorbent the bed was rinsed with acetone to displace acetic acid and water from the bed (15). However, these regeneration processes increase the operational cost and cause environmental pollution as they require use of chemicals. Acetic acid decomposes to form CO_2 and methane or to form ketene and water above 440 °C (89, 90). However this temperature may harm the adsorbent concerning the regeneration temperature given by the producer (91).

Fourier Transform Infrared Spectroscopy (FTIR)

The strongest band in the spectrum of 13X was detected at 966 cm^{-1} with a shoulder at 1072 cm^{-1}. These bands are due to the asymmetric T–O stretching vibrations (T: tetrahedral Si or Al atoms). The band at 467 cm^{-1} corresponds to the O–T–O angular deformation (T–O bending) vibrations. The bands at 697 and 746 cm^{-1} are due to symmetric O–T–O stretching vibrations and are attributed to internal tetrahedral stretch and external linkage symmetric stretch, respectively. 568 cm^{-1} band corresponds to the vibrations of the double rings (D6R rings). The bands at 966, 697 and 467 cm^{-1} are due to internal vibrations of the TO_4 tetrahedron which is the primary unit of structure and which are not sensitive to structural variations. The bands at 1072, 746 and 568 cm^{-1} are sensitive to the linkages between tetrahedra (external linkages) and the topology and mode of arrangement of the secondary units of structure. The band at 1656 cm^{-1} is due to the angular deformation of H–O–H bonds (H–O–H bending mode of water molecule) (86).

No significant changes neither in frequency nor in absorbance of the bands in the 400–1200 cm^{-1} region was observed after the activation of 13X at 320 °C (Figure 12A, spectrum b). The changes in bands in the the O–H stretching region are discussed below.

Upon adsorption of acetic acid from the solution with the initial acid concentration of 0.54 M at 25 °C resulted in a shift of the 966 cm^{-1} band to 1059 cm^{-1} and 1072 cm^{-1} band to 1156 cm^{-1} (Figure 12A, spectrum c). The frequency of 966 cm^{-1} band varies linearly with the number of aluminum atoms in the framework tetrahedral sites (86). Thus the shift of 966 cm^{-1} band to a higher frequency after the acetic acid adsorption indicated a decrease in the number of aluminum atoms in the framework tetrahedral sites. Dealumination of zeolites is partially due to action of proton. In acidic to neutral solutions, the protons in the solution can be adsorbed to the neutral and negative surface groups and thereby protonate them (proton binding). The formation of the

≡Al-OH_2^+ surface complexes increases aluminum dissolution and consequently increases Al^{3+} hydrolysis (92).

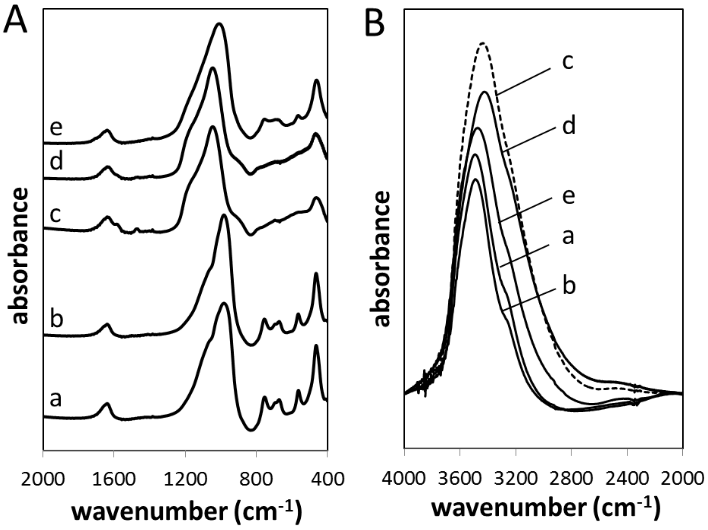


Figure 12: Absorbance IR spectra of 13X (A) 400–2000 cm^{-1} region and (B) 2000–4000 cm^{-1} region. (a) before activation, (b) after activation, (c) after acetic acid adsorption at 25°C (C_o=0.54 M), (d) after desorption in deionized water at 45°C and (e) after heating at 300°C subsequent to the adsorption.

Upon acetic acid adsorption, the bands at 467 cm^{-1} and 697 cm^{-1} lost intensity and the bands at 568 and 746 cm^{-1} disappeared. As mentioned above, the bands at 997, 697 and 467 cm^{-1} are due to internal vibrations of the primary building units (TO_4 tetrahedra) and are not sensitive to structural variations while the bands at 746 and 568 cm^{-1} are sensitive to the linkages between tetrahedra (external linkages). Thus it may be concluded that aluminum removal from the framework sites upon acid adsorption led to changes in the external vibrations (secondary structure, linkages between the tetrahedral units) but did not change the internal tetrahedral vibrations significantly. The perturbations observed can be associated to T–O bond length, T–O–T and O–T–O angles (93, 94). The disappearance of the band at 568 cm^{-1} suggested that the external linkages were broken as a result of aluminum removal, *i.e.* that aluminum removal left "holes" in the framework. Moreover, the formation of holes or the replacement of Al atoms by H atoms involves changes in the frequencies and new bands or shoulders probably occur (95). These perturbations created a new shoulder band at 900 cm^{-1}.

Adsorption of acetic acid on 13X led to appearance of new bands in at 1390, 1472 and 1593 cm^{-1}. The intensities of these bands were low since the acetic acid adsorption was performed in a dilute acidic solution with low sorbent/solution ratio (2 g of sorbent/100 mL of solution). The bands in the region of 1550–1610 cm^{-1} and 1300–1420 cm^{-1} were assigned to carboxylate (carboxylic acid salt) while those in the 1700–1725 cm^{-1} region to carboxylic acid (96). The weak band at 1390 cm^{-1} can be attributed to asymmetric deformation vibration of CH_3. The band at

1472 cm^{-1} and the shoulder at 1593 cm^{-1} may be assigned to the symmetric C–O stretching and asymmetric stretching vibrations of the COO$^-$ group, respectively (97, 98).

Regeneration of the acetic acid-saturated 13X in deionized water at 45°C was led to loss in intensities of the bands at 1390, 1472 and 1593 cm^{-1} (Figure 12A, spectrum d) indicating dissolution of the weakly adsorbed species were associated with these bands. Any significant change was observed in the intensity or frequency of the bands in the 400–1400 cm^{-1} spectral region.

In the spectra which were taken after heating at 300 °C (Figure 12A, spectrum e), the intensities of the 467 and 697 cm^{-1} bands increased almost to their values in the spectrum for activated 13X and the bands at 568 and 746 cm^{-1} reappeared in the spectrum. The main asymmetric stretching band at 1059 cm^{-1} was hifted back to 994 cm^{-1} and the asymmetric stretching band (detected as a shoulder in the spectrum of 13X at 1072 cm^{-1}) disappeared. These indicated the reconstruction of the secondary building units. The bands at 1472 and 1593 cm^{-1} were disappeared whereas 1390 cm^{-1} band was remained and a very weak shoulder band was appeared at 1720 cm^{-1}. In the literature the band at 1720 cm^{-1} was detected in the spectrum of acetic acid dissolved in CCl_4 and assigned to the stretching vibrations of the C=O group (97, 99).

Evacuation of acetic acid vapor adsorbed NaHY at 200 °C led to a decrease in the intensity of the typical bands of acetic acid (1690 and 1280 cm^{-1}) and appearance of a doublet at 1580-1610 cm^{-1} and a band at 1480 cm^{-1}. These new bands were similar to those in the spectrum of sodium acetate. Evacuation at 300 °C resulted in a diminishing of the bands of unreacted acetic acid molecules, without any decrease of the intensity of acetate ion bands. This suggested that acetate ions formed in NaHY were stable until 300 °C (99).

O-H stretching region

In the O–H stretching region, a broad band in the 3000–3800 cm^{-1} region with maximum at 3506 cm^{-1} and with a shoulder at 3288 cm^{-1} were detected in the spectra of 13X before activation (Figure 12B, spectrum a). The intensities of 3506 and 3288 cm^{-1} bands decreased slightly after the activation (Figure 12B, spectrum b). However after the activation since 13X was exposed to atmosphere during the preparation of the KBr pellets thereby adsorbed water vapor, it was not possible to resolve the peaks in the O–H stretching region due to presence of water clusters giving the broad band superimposing the O–H bands if present.

The bands in this region are attributed to the O–H bond stretching of the surface hydroxyl groups or O–H stretching mode of the water molecules (100). Surface hydroxyl groups in zeolites originate from several sources: Acidic O–H groups due to framework Al and other trivalent ions such as B, Ga, Fe, etc.; silanol groups (Si–OH) on the external surface and in the "nests" (defect sites); O–H groups attached to di- or tri-valent cations due to hydrolysis; O–H groups from "dangling Al"; O–H groups associated with non-framework aluminum species and O–H groups of adsorbed water. The O–H groups attached on the charge balancing ions formed via hydrolysis can also be observed (101). The theoretical structure of X-type zeolite does not include any O–H groups. However cation deficient form of NaX may exhibit properties associated with hydroxyl groups due to partial hydrolysis of the Na^+ cations and replacement by hydronium ions (86).

For the activated NaX, presence of various bands in the 3000-3800 cm^{-1} range of the spectra was explained by the presence of several types of hydroxyl groups. The band at 3645 cm^{-1} was assigned to free acidic O–H groups bridging Al and Si atoms, pointing towards the supercages (102, 103), while other types of acidic hydroxyls gave bands in the 3200-3600 cm^{-1} range (103). These bands were related to cation deficiencies of NaX due to the fact that exchangeable cations (*e.g.* Na^+) were partially hydrolyzed during the preparation or the subsequent washing treatment (104).

However in order to resolve the various O–H groups, the adsorbed water must be removed so the sample must be activated *in situ*. In the present study NaX was in fully hydrated state since the acetic acid adsorption was studied in the aqueous solutions.

Zeolites always adsorb water when they are exposed to the atmosphere due to their hydrophilic properties. The adsorbed water in zeolites can be present in the forms of free water, loosely coordinated water, tightly coordinated water and even water clusters (105). Infrared spectroscopic studies of water adsorption in faujasites revealed the existence of different structures of adsorption complexes depending on the water loading (106-110). The water-bending vibration at 1640 cm^{-1} indicates the presence of adsorbed water in zeolites. Due to the hydrogen bonding of water with O–H groups, the bands in the hydroxyl spectral region (3000–4000 cm^{-1}) are generally structureless and broad (101). Beta and co-workers reported a broad band at about 3400–3500 cm^{-1} with a shoulder at about 3180–3250 cm^{-1} in the diffuse reflectance infrared Fourier transform (DRIFT) spectra of the hydrated faujasites (including NaX). The latter was assigned to the collective in-phase O–H stretching vibrations of hydrogen bonded aggregates consisting of a central water molecule and its nearest and higher neighbors. The band at about 3400–3500 cm^{-1} was assigned to O-H stretchings of water molecules which are hydrogen bonded to framework oxygen (107).

The intensity and width of the 3506 cm^{-1} band increased remarkably after the acetic acid adsorption (Figure 12B, spectrum c). Intensity of this band decreased after the rinsing in water without change in the width (Figure 12B, spectrum d). The intensity further declined and the band has become less broadened upon heating at 300 °C (Figure 12B, spectrum e). The band at 3506 cm^{-1} shifted to 3458 cm^{-1} after the acetic acid adsorption, to 3446 cm^{-1} after rinsing at

45 °C in water and to 3493 cm^{-1} after heating to 300 °C. Upon acetic acid adsorption, a weak band appeared at 2461 cm^{-1} and remained in the spectra after the rinsing of the acetic acid-saturated 13X in distilled water and heating at 300 °C. A characteristic broad feature in the range 3300–2500 cm^{-1}, that overlaps the C–H stretching region, and with a secondary absorption close to 2600 cm^{-1}, is observed for the hydrogen-bonded O–H of most carboxylic acids. Other bands that are associated with the C–O and O–H components of the carboxylic acid tend to be less pronounced, and sometimes may be overlapped with other fingerprint absorptions of the molecule. These are located in the ranges 1320–1210 cm^{-1} (C–O stretch) and 960–850 cm^{-1} (hydrogen-bonded O–H out-of-plane bending) (96).

Formation of acetate ions in NaHY was explained by the following reaction (99):

$$\text{zeol–OH} + \text{HOOC–CH}_3 \rightarrow \text{zeol–OH}_2^+ + {}^-\text{OOC–CH}_3 \rightarrow \text{zeol}^+ + {}^-\text{OOC–CH}_3 + \text{H}_2\text{O}$$

Upon the adsorption of acetic acid vapor on NaHY at 200 °C resulted in the removal of first 3640 cm^{-1} band (high frequency band, typical of Si–O1H–Al situated inside supercages) and then 3550 cm^{-1} band (low frequency band, typical of Si–O3H–Al situated inside hexagonal prisms). However in the same study interaction of acetic acid vapor with Na$^+$ ions in NaY did not result in any important variation of the spectrum of the acetic acid solution suggesting molecular adsorption of acetic acid in NaY. For NaY which usually does not contain Si–OH–Al groups, the acetate ions were actually not formed. A small number of acetate ions formed in NaY was related to the presence of very small amounts of extra framework Al species and/or a very small amount of Si–OH–Al formed by the hydrolysis of NaY (99).

The shift of the 3506 cm^{-1} band to lower wavenumbers upon acetic acid adsorption and to higher wavenumbers upon heating at 300 °C can be explained by the increased and decreased strength of the water or acetic acid–framework oxygen hydrogen bonds, respectively. Beta and co-workers observed a correlation between the position of the broad band at about 3400–3500 cm^{-1} (assigned to O–H stretchings of water molecules hydrogen bonded to framework oxygen) and the basicity of framework oxygen atoms of NaX. The frequency of this band decreased with decreasing water loading suggesting formation of more strongly bonded water-cation clusters as a significant number of water molecules was removed (107).

The surface of the framework of 13X is essentially oxygen atoms, whereas Si and Al are buried or recessed in the tetrahedra of oxygen atoms. They therefore are not fully exposed and cannot be readily accessed by adsorbate molecules. Also, the anionic oxygen atoms are more abundant and are much more polarizable than the Al and Si cations (79). In 13X, the framework oxygen atoms which bear the negative charge of the lattice are considered as the structural basic sites. Basic sites on oxide surfaces may be constituted by surface OH_s^- or O_s^{2-} anions. Acids which contain H-X functions are expected to undergo H-bonding interactions with basic surface sites (111):

$$O_s^{2-} + H–X \leftrightarrows O_s^{2-}\cdots H–X$$

For weak interactions, the H-bond characteristics are the same as in the case of basic probe molecules interacting with Brønsted acid sites. Therefore, frequency shifts of the H-X stretching mode in the H-bonded complex relative to the free acid molecule must be induced and line broadening and intensity enhancements must also occur (111).

Thermogravimetric and IR spectroscopic studies of acetic acid adsorbed on faujasite-type zeolites for the characterization of the strength and catalytic behavior of base centres have been reported in the literature (97, 112, 113). Przystajko and co-workers determined distributions of base strengths using indicator techniques and infrared spectroscopic studies of acetic acid vapor adsorbed on faujasite-type zeolites. The infrared spectra in the region of wavenumbers below 1200 cm^{-1} were also examined since removal of aluminum from the lattice is reflected by a shift of the bands in this region towards higher frequencies. The aluminum atoms removed from the lattice and present as extralattice aluminum can be present in the form of species contributing to sample basicity. It was shown that the lattice $(AlO_4)^-$ tetrahedra or oxide anions of these tetrahedral (Lewis type basicity) played the role of base sites in the sodium forms of X and Y type zeolites (112).

In the present study, the bands detected in the 1200–1800 cm^{-1} after the acetic acid adsorption indicated that adsorption of acetic acid in 13X resulted in formation of acetic acid ions (acetate, CH_3COO^-). For 13X which usually does not contain Si–OH–Al groups, formation of the acetate ions was not expected (99). However it was reported that NaX does not contain a total exchange cation equivalency due to partial hydrolysis of the Na^+ cations and replacement by hydronium ions. This cation deficient form of NaX may exhibit properties associated with hydroxyl groups (86). Thus the formation of the acetate ions in 13X in the present study can be related to presence of extraframework Al species and/or Si–OH–Al formed by the hydrolysis of 13X (99). However it was not possible to follow the changes in the bands in the O–H stretching and H–O–H bending regions upon the adsorption/desorption treatments performed since presence of water in 13X complicated interpretation of the bands in these regions. The broad band in the O–H stretching region of the hydrated 13X completely blanked out the spectral region.

In the literature Zhang and co-workers did not reported obvious changes in the SEM micrographs and XRD patterns after interaction of 5 g of 13X zeolite ($SiO_2/Al_2O_3<3$, in pellet and powder forms) with 100 mL of aqueous acetic acid solutions with the initial concentrations of 0.076–0.901 mol/L. The results verified that the 13X was stable when exposed to dilute acetic acid solution (60). Considering the lower initial concentrations of the acetic acid solutions (0.028-0.544 mol/L) and lower adsorbent/solution ratio (2 g/100 mL) in the present study it is expected that the 13X has chemical stability in the dilute acetic acid solutions.

CONCLUSION

It was shown that the kinetics of adsorption of acetic acid from diluted acetic acid solutions might be represented by the pseudo-second order model and the model parameters were determined. The adsorbed amount of acetic acid at equilibrium was decreased with the increasing adsorption temperature. The adsorption equilibrium data was best described by the Sips model and the model parameters were determined. The Sips model parameter characterizing the system heterogeneity was found to decrease with the increased temperature. From the temperature dependence of the Sips model adsorption affinity constant the isosteric heat at the fractional loading of 0.5 was calculated as 50.40 kJ/mol. The monolayer acetic acid adsorption capacity of 13X at 25 °C was calculated as 6.32 mmol/g. The dimensionless separation factor values were found to vary within the range of 0.026–0.434 indicating the favorable adsorption. The negative ΔG° values indicated spontaneous adsorption of acetic acid on 13X zeolite. The positive ΔH° values designated that the sorption of acetic acid in 13X was endothermic. However, as previously stated, the amount of acetic acid adsorbed at equilibrium decreased with the increasing temperature. The reason for that in the low acetic acid concentration range in which the dimensionless adsorption equilibrium constant was calculated the amount of acetic acid adsorbed at equilibrium increased with temperature. The positive values of entropy change was implied the increased randomness (degree of freedom of the system) at the solid-solute interface during adsorption. FTIR studies were revealed that the acetic acid adsorption was resulted in formation of acetate ions. It was not possible desorb all the species formed by rinsing the acid-saturated 13X in distilled water at 45°C or by heating at 300°C in air although removal of some species was observed by FTIR spectroscopy.

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