



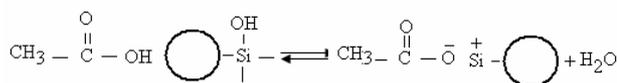
## STUDY OF THE ADSORPTION OF ACETIC ACID ON SILICA GEL IN AQUEOUS SOLUTION

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Received October 15, 2012

Adsorption of organic molecules on silica gel surfaces is widely used in a number of technological applications such as heterogeneous catalysis. A key step is the understanding of the nature of the adsorption on such surfaces, which is the specific aim of our study of the adsorption of acetic acid on silica gel. The adsorption of acetic acid on silica gel was studied under various conditions such as temperature, contact time, adsorbant dose and concentration of adsorbate. Batch adsorption experiments were conducted and the result showed that the adsorption was dependent on all these parameters. The adsorption process obeys the Langmuir and Freundlich adsorption isotherms. By these adsorption isotherms, thermodynamics adsorption parameters such as change in Gibb's free energy, enthalpy, entropy and kinetics adsorption parameters such as rate constant of adsorption were calculated.



### INTRODUCTION

The chemical and adsorption properties of silica surfaces have been extensively studied for many decades because of their use as adsorbents and carriers in gas and liquid chromatography and as support for catalysts.<sup>1-4</sup> There are hydroxyl groups on a silica gel surface therefore along with the hydrogen bonding with surface hydroxyl groups or oxygen ions, organic acids can interact with surface.<sup>5,6</sup> Removal methods of organic compounds in industrial discharges may be traditionally divided into three main categories: physical, chemical, and biological processes. Among them, physical adsorption is generally considered to be the most efficient method for quickly lowering the concentration of dissolved organic compounds in the solution. Acetic acid is an organic acid which is

an important compound in biochemistry, nature and industry. In many cases is necessary to isolate it from the environment.

Interest in the surface chemistry of carboxylic acids on transition metal surfaces and transition metal oxide surfaces partly stems from the fact that the associate species are important either as reaction intermediates or as product in catalytic oxidation reactions. See for example.<sup>7-10</sup> Several workers have reported on the potential use of TiO<sub>2</sub>,<sup>11,12</sup> silicas,<sup>13</sup> ion-exchange resins in non-aqueous conditions,<sup>14</sup> Au/Pd(1 1 1) alloy surfaces<sup>15</sup> and smooth Pt electrodes,<sup>16</sup> as good substrates for the removal of acetic acid from aqueous solutions. In this research work, is studied the adsorption of acetic acid in aqueous solution on silica gel as a model system. The purpose of this work was to study the adsorption properties of commercial

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silica gel with respect to acetic acid from aqueous solution. Batch experiments were conducted to investigate the effects of adsorbent dose, contact time, adsorbate concentration and temperature on the adsorption of acetic acid on the Silica gel. Langmuir and Freundlich isotherm models were used to illustrate the experimental isotherms models and isotherms constants.

## MATERIALS AND METHODS

Commercial KSKG Silica gel with a particle size 0.063-0.2 mm was used as adsorbent. Its specific surface area,  $s$ , determined by the thermal desorption of nitrogen equaled  $340 \text{ m}^2/\text{g}$ . The adsorbent treated preliminary at  $400^\circ\text{C}$  for 6 h. All experiments were carried out by the samples containing 50 cc of different initial concentration (0.15- 0.4 M) of acetic acid in the range of  $22\text{-}70^\circ\text{C}$  temperature. 3.5 g of the adsorbent was transferred into various 250 mL Erlenmeyer flask and acetic acid solution by fixed concentration was added and mixed using a stirrer- magnet for 20 min. Then the solution was filtered its concentration was determined by titration with 0.1 M solution of NaOH. The amount of equilibrium adsorption,  $q_e$  (mg/g), was calculated by:

$$q_e = \frac{C_0 - C_e}{W} V$$

where  $C_0$  and  $C_e$  (mg/L) are the liquid-phase concentrations of acetic acid at initial and equilibrium, respectively.  $V$  (l) is the volume of the solution and  $W$  (g) is the mass of dry adsorbent used.<sup>17</sup>

## EFFECT OF ADSORBATE CONCENTRATION

Several stock solutions with concentration (0.15-0.4 M) were prepared. Each solution was added to 3.5 g of the adsorbent in different 250 ml flasks and agitated using a mechanical agitator for 20 min each. At the end of the time, the contents of the flasks were filtered and analyzed. The results are shown in Fig. 1.

## EFFECT OF ADSORBENT DOSE

50 mL each of the acetic acid solutions were added to various amount of the adsorbent (0.5-6.0 g) in different 250 mL flasks, flasks were agitated for 1hr on a mechanical stirrer. The content of the flask was filtered and analyzed. The results are presented in Fig. 2.

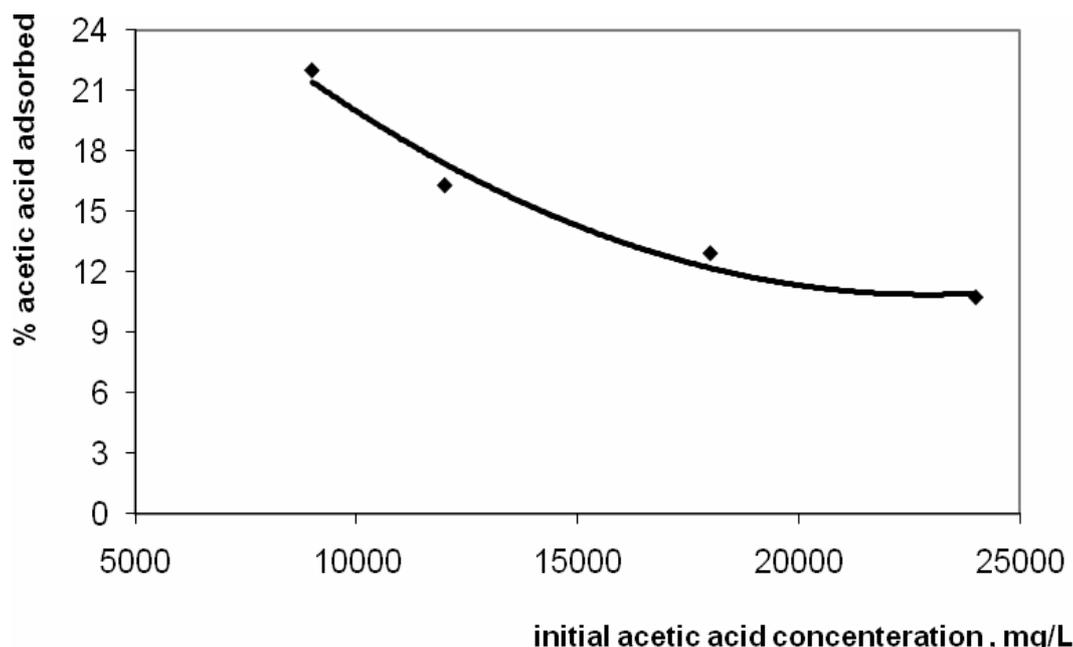


Fig. 1 – Influence of initial acetic acid concentration on adsorption of acetic acid on silica gel.

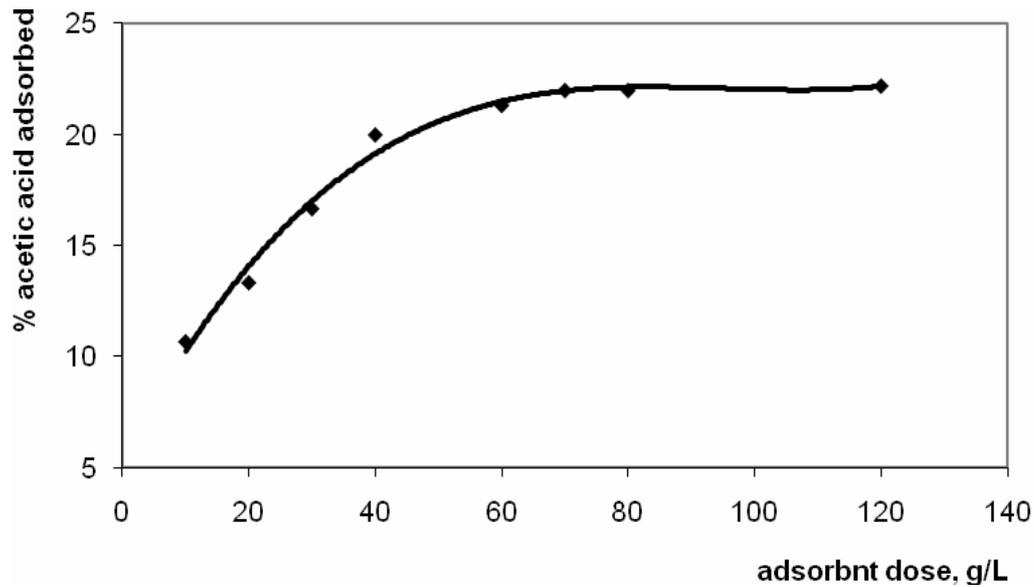


Fig. 2 – Influence of adsorbent dose on adsorption of acetic acid on silica gel.

#### EFFECT OF CONTACT TIME

50 mL each of stock solution of acetic acid was transferred into different 250 cm<sup>3</sup> Erlenmeyer flask, corked and labeled. 3.5 g each of the adsorbent was weighed into the different labeled flasks and agitated in a shaker for different contact times (0.5, 1, 1.5, 3, 5 and 10 minutes). After the mentioned time, the content of each flask was filtered. The equilibrium concentration of the acetic acid in each of the filtrate was determined. The results obtained are shown in Fig. 3.

#### EFFECT OF TEMPERATURE

50 mL each of stock solution was transferred into various 250 cm<sup>3</sup> flask containing 3.5 g each of the adsorbent, corked and labeled for different temperatures 22, 35, 55, 70°C respectively. The mixture was heated and shaken to the appropriate temperature in a water bath. At the right temperature, the content of the each of the flask was removed, filtered and analyzed. The results obtained are shown in Fig. 4.

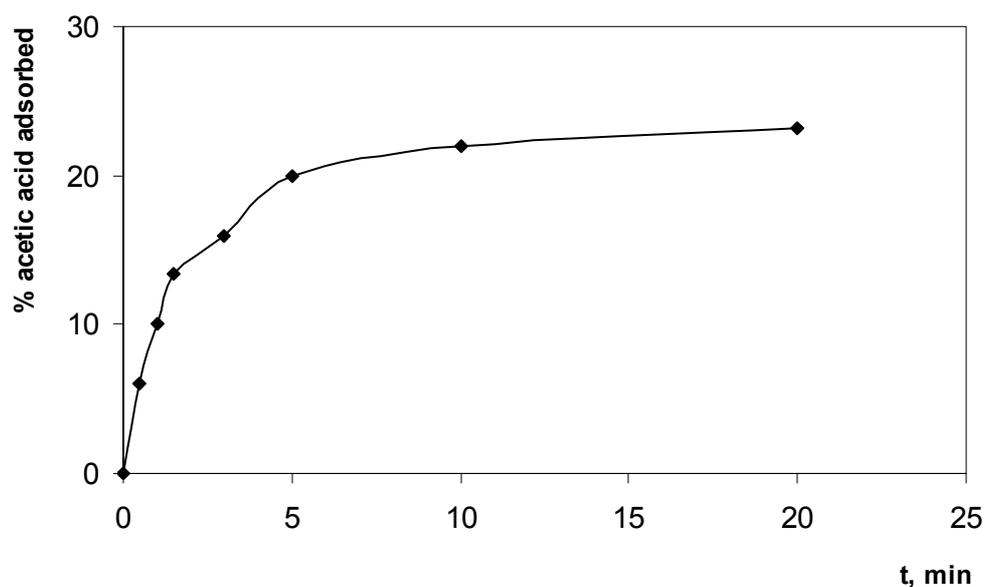


Fig. 3 – Influence of contact time on adsorption of acetic acid acid on silica gel.

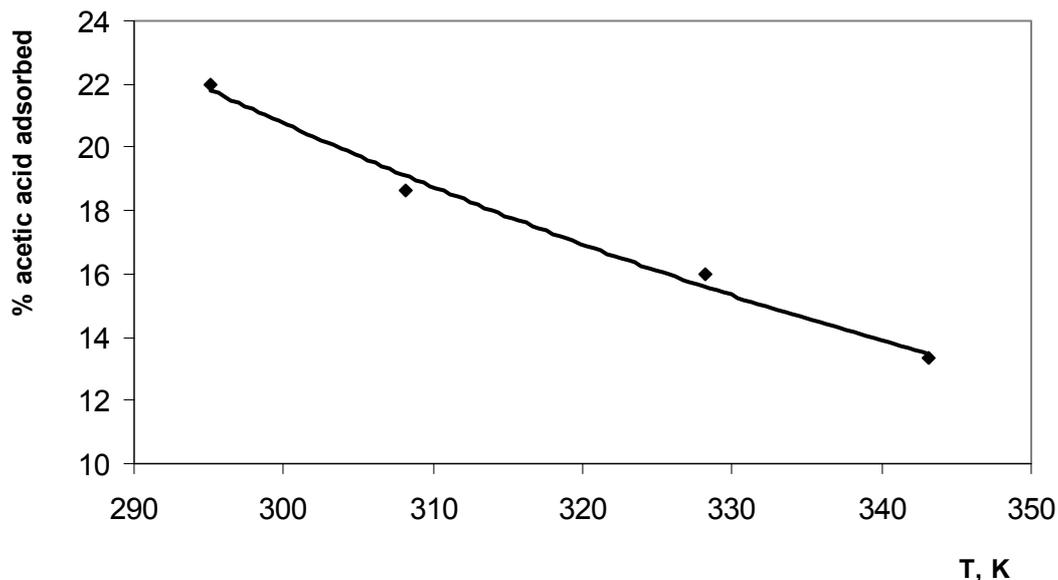


Fig. 4 – Influence of temperature on adsorption of acetic acid on silica gel.

## RESULTS AND DISCUSSION

The concentration-dependent data for the adsorption of acetic acid is presented in Fig. 1. This decrease in % adsorption of acetic acid is due to lesser availability of the adsorption site. Moreover, this can be explained by the fact that more adsorption sites were being covered as the acetic acid concentration increases. The effect of the adsorbent dose on the removal of acetic acid from aqueous solution was investigated by varying the dose of the adsorbent from 0.5–6 g. It is expected that an increase in the dose of adsorbent should yield a corresponding increase in the amount of acetic acid adsorbed on the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dose of the adsorbent.<sup>18,19</sup> From Fig. 2 this trend was inconsistent and therefore suggests that the use of silica gel as adsorbent partly depends on its dose in aqueous solution. Further increase of adsorbent dose did not cause any significant change because equilibrium was achieved between solution and solid phase.

The result obtained from time-dependent experiments for the adsorption of acetic acid on silica gel was presented in Fig. 3. As the contact time was increased, the amount of acetic acid removed also increased. The data showed acetic acid removal from aqueous solution increases initially until equilibrium was attained and then was constant. In according to Fig. 3, the observable time for maximum adsorption is between 7-10 minutes.

The effect of temperature on the removal of acetic acid from aqueous solution was investigated by varying the temperature of adsorption between 22°C and 70°C (Fig. 4). The data showed that with increasing temperature the amount of acetic acid adsorbed on the surface of the adsorbent decreases. The attractive forces between the adsorbent and the adsorbate ion may have been weakened making the adsorption to decrease. At high temperature, the thickness of the boundary layer is expected to decrease due to the increased tendency of the ions to escape from the surface of the adsorbent to the solution phase hence there is bound to be weak adsorption interactions between the adsorbent and the adsorbate.

## ADSORPTION ISOTHERMS

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. In this manner, the Langmuir, the Freundlich isotherm equations were used to interpret the experimental data. Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, *i.e.*, the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms onto surface.<sup>20</sup> The linearized form of the Langmuir adsorption isotherm equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

The Langmuir constants, which are  $q_m$  and  $K_L$  values, can be calculated from the plot  $Ce/qe$  versus  $Ce$ . Isotherm models constants and correlation coefficients for acetic acid adsorption on silica gel listed in Table 1.

The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogeneous surface is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where  $C_e$  is the equilibrium concentration of the solute (mg/L) and  $q_e$  is the equilibrium adsorption capacity (mg/g). The Freundlich isotherm constants  $K_F$  and  $1/n$  can be calculated from the plot of  $\ln q_e$  versus  $\ln C_e$ . The slope ( $1/n$ ) measures the surface heterogeneity. Heterogeneity becomes more prevalent as  $1/n$  gets closer to zero. The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 1. The correlation coefficient shows that the adsorption process could be described by the both Langmuir and Freundlich model equation. The Langmuir constants ( $q_m$  and  $K_L$ ) values were fit the experimental data.

### THERMODYNAMIC STUDIES

Thermodynamic parameters such as change in Gibb's free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were determined using the following equations:<sup>21,22</sup>

$$\ln \left( \frac{q_e m}{C_e} \right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where  $m$  is the adsorbent dose (mg/L),  $C_e$  is the equilibrium concentration (mg/l) of the malonic

acid in solution,  $R$  is the gas constant (8.314 J/mol/K) and  $T$  is the temperature (K).  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are changes in Gibb's free energy (J/mol), enthalpy (J/mol), entropy (J/mol/K), respectively. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slopes ( $-\Delta H^\circ / R$ ) and the intercepts ( $\Delta S^\circ / R$ ) of the plots of  $\ln \left( \frac{q_e m}{C_e} \right)$  vs.  $1/T$ .

The values of thermodynamic parameters are presented in Table 2. The negative values of  $\Delta G^\circ$  indicate that the adsorption process is feasible and spontaneous in nature. The decrease in the values of  $\Delta G^\circ$ , with the increase of temperature, demonstrated that the adsorption was benefited by the high temperature. The negative value of  $\Delta H^\circ$  suggest the exothermic nature of adsorption and the positive value of  $\Delta S^\circ$  described the randomness at the adsorbent-solution interface increased during the adsorption.

### SORPTION KINETICS

Sorption kinetics was studied for adsorption of acetic acid on silica gel of initial concentration 0.15 mol/l. The rate constant of adsorption was determined from the pseudo-second order rate expression:<sup>23</sup>

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where  $k_2$  is the rate constant of adsorption (g/mg/min),  $q_e$  and  $q_t$  are the amount of malonic acid adsorbed at equilibrium and at time  $t$  (mg/g) respectively. The values of  $k_2$  and  $q_e^{cal}$  were calculated from the intercepts ( $1/k_2 q_e^2$ ) and the slopes ( $1/q_e$ ) of the plots of  $t/q_e$  vs.  $t$ , respectively, reported in Table 3. The results show that the values of  $q_e^{cal}$  and  $q_e^{exp}$  are almost equal and regression correlation coefficient ( $R^2$ ) is close to unity which confirm that adsorption of acetic acid on silica gel follows pseudo-second order kinetic model.

Table 1

Isotherm models constants and correlation coefficients for acetic acid adsorption on silica gel

T, K	Freundlich			Langmuir		
	$K_F$ , mg/g	$n$ , mg/l	$R^2$	$K_L$ , l/mg	$q_m$ , mg/g	$R^2$
295.15	3.28	3.72	0.97	0.000191	9.34	0.99

Table 2

Thermodynamic parameters for acetic acid adsorption on silica gel

		$\Delta G^\circ$ , kJ/mol			
$\Delta S^\circ$ , kJ/mol.K <sup>-1</sup>	$\Delta H^\circ$ , kJ/mol	295.15	308.15	328.15	343.15
0.0072	-10.21	-12.33	-12.43	-12.57	-12.68

Table 3

Kinetic parameters for acetic acid adsorption on silica gel

Pseudo – second order			
$q_e^{exp}$ , mg/g	$q_e^{cal}$ , mg/g	$K_2$ , g/mg.min	$R^2$
5.66	6.71	0.091	0.99

## CONCLUSIONS

The adsorption of acetic acid on silica gel (5.66 mg/g) occurs because of donor-acceptor interactions. In this research work, Silica gel to compeer others adsorbents such as silicas, Au/Pd (1 1 1) alloy surfaces and smooth Pt electrodes has advantages such as readily available, good adsorption capacity and high adsorption rate. The study indicates that removal of acetic acid from aqueous solutions depends on the solution adsorbent dose, contact time, initial acetic acid concentration and temperature. The adsorption process obeys both Langmuir and Freundlich adsorption isotherms. The thermodynamic study shows that the adsorption process was exothermic and spontaneous in nature. The adsorption of acetic acid on the silica gel followed reversible second-order rate kinetics. The adsorption is relatively quick and the process is very efficient especially for water containing low concentrations of acetic acid.

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