

Equilibrium and kinetic studies for the sorption of 3-methoxybenzaldehyde on activated kaolinites

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Abstract

The sorption of 3-methoxybenzaldehyde on activated kaolinites has been investigated at different temperatures. Two types of activation tests were performed. The sorption equilibrium was studied by sorption isotherms in the temperature range 303–333 K for natural (untreated), thermally and acid activated kaolinites. It was shown that the isotherm shapes were not affected by temperature and activation types of kaolinite. The absorbance data at 312 nm were fitted reasonably well with the Langmuir and Freundlich isotherm models and the model parameters were determined for different temperatures. Thermodynamic quantities such as Gibbs free energy (ΔG), the enthalpy (ΔH) and the entropy change of sorption (ΔS) were determined for natural, thermally and acid activated kaolinites. It was shown that the sorption processes were an endothermic reactions, controlled by physical mechanisms and spontaneously. Adsorption capacity of acid activated kaolinite for 3-methoxybenzaldehyde was higher compared to that of natural and thermally activated kaolinites at various temperatures. The adsorption and desorption rate constants (k_a and k_d) were obtained separately by applying a geometric approach to the first order Langmuir model. This method provided good conformity between the K from Langmuir parameters and K_{geo} (k_a/k_d) from geometric approach.

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1. Introduction

Substituted benzaldehyde compounds used largely as intermediates to synthesize medicine and pesticides. 3-methoxybenzaldehyde is an important chemical and chemical intermediate in the pharmaceutical and perfumery industry [1,2]. Because they are commonly disposed into environmental after processing, it is important to investigate their environmental behaviour in terms of environmental pollution. There are a few studies are reported by Brasquet et al. [3], Fontanesi et al. [4], Weinstock et al. [5], Lichtenberger et al. [6]. There are many methods for the removal of organic pollutants such as adsorption, ion exchange, membrane processes, chemical oxidation, chemical precipita-

tion, solvent extraction and biological degradation. Adsorption is the most popular method in which activated carbon or ion exchange resins are generally applied. Researches have been interested in low-cost adsorbents such as silica gel and clay [7]. One type of clay minerals is kaolinite. Kaolinite has a wide variety of applications in industry. It is used as an extender in water-based paints and ink, insecticide, formulation of medicine and cosmetics, and as a functional additive in polymers and is a major component of ceramics [8,9]. Kaolinite is an inexpensive additive that can improve the properties of the material in which it dispersed provided that a stable dispersion is formed.

Kaolinite is a 1:1 dioctahedral aluminosilicate that has two different basal cleavage faces [10]. One basal face consists of a tetrahedral siloxane surface of very inert –Si–O–Si– links. The other basal surface consists of an octahedral gibbsite ($\text{Al}(\text{OH})_3$) sheet. Both of these surfaces are theoretically electrically neutral. At the edges of a 1:1 layer, the structure is disrupted and broken bonds occur, which are accommodated as OH groups. These edges are estimated to occupy approximately 10% of the whole kaolinite surface [11–13]. The kaolinite surface has a

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Nomenclature

$A_{a,d}$	frequency factor of adsorption and desorption
A_0, A	initial absorbance, final absorbance
C_e	equilibrium concentration of the fluid phase
C_i	initial concentration of 3-methoxybenzaldehyde (mol/L)
$E_{a,d}$	activation energy of adsorption and desorption (kJ mol^{-1})
ΔG	Gibbs free energy of sorption (kJ mol^{-1})
ΔH	enthalpy change of sorption (kJ mol^{-1})
ΔS	entropy change of sorption ($\text{kJ mol}^{-1} \text{K}^{-1}$)
k_a, k_d	adsorption rate constant, desorption rate constant (min^{-1})
k_0	initial adsorption rate (min^{-1})
K	sorption equilibrium constant (from Langmuir)
K_f	Freundlich constant (g^{-1})
K_{geo}	sorption equilibrium constant (from geometric approach, k_a/k_d)
m	amount of kaolinite (g)
n	Freundlich constant
Q	equilibrium concentration of the adsorbate in the adsorbing phase (g^{-1})
Q_0	maximum concentration retained by the adsorbent (g^{-1})
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
t	time (min)
t_{ie}	initial equilibrium time (min)
T	absolute temperature (K)
<i>Greek letters</i>	
θ	coverage fraction
θ_e	equilibrium coverage fraction

complex chemistry due to the existence of these different sites on the basal faces and edges.

Kaolinite has a low CEC of the range 3–15 mequiv./100 g and therefore it is not expected to be an ion-exchanger on high order [14]. The small number of exchange sites is located on the surface of kaolinite and it has no interlayer exchange sites [15].

As kaolinite is one of the most important clay minerals and the wide industrial application of kaolinite depends on the ability to modify its properties for other uses. The methods used to modify kaolinite surfaces include acid activation and thermal treatment [16–18].

Treatment of clay minerals with concentrated inorganic acids usually at high temperature is known as acid activation. Acid treatments of clay minerals are an important control over mineral weathering and genesis [19,20]. Such treatments can often replace exchangeable cations with H^+ ions and release Al and other cations out of both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact [21]. The ion exchange capacity of clay minerals is attributed to structural defects, broken bonds and structural hydroxyl transfers. The treatment of the kaolinite with acid results in replacement of a large number

of different cations with H^+ ions as reported by Bhattacharyya and Sen Gupta [22]. Also acid treatment of kaolinite has been shown to create enhanced mesoporosity with important textural and structural changes [23].

Thermal treatment causes the crystalline structure of kaolinite to transform to amorphous metakaolin [24]. The loss of water molecules, which caused the structural changes of kaolinite with increasing temperature, will affect the specific surface area and adsorption capacity of kaolinite [25]. Several studies were reported on thermal activation by Suraj et al. [24], Tekin et al. [25], Sabah et al. [26], Kara et al. [27] and Tekin et al. [28].

Clays contain both Bronsted and Lewis acid sites associated, respectively, with the interlamellar region and the edge sites. When clay is heated ($\sim 373 \text{ K}$), most of the interlamellar water is removed leaving only “one layer” of water and Bronsted acidity increases markedly [29] to that of a very strong acid. The clay interlayer structure collapses if the temperature is raised to 473–573 K with the residual water being driven out and the Lewis acidity increases at the expense of the Bronsted acidity. Further heating (calcination at $\sim 700 \text{ K}$) results in complete dehydroxylation of the aluminosilicate lattice, while retaining the Lewis acidity [22].

The aim of the present investigation is to study the sorption mechanism of 3-methoxybenzaldehyde on natural, thermally activated and acid activated kaolinites and determination of the equilibrium and kinetic parameters. Towards this aim, the sorption isotherms at different temperatures, Langmuir and Freundlich model parameters and thermodynamic parameters were determined. The adsorption and desorption rate constants and the other kinetic constants were determined separately by geometric approach.

2. Materials and methods

2.1. Materials

3-Methoxybenzaldehyde purchased from Fluka Chemika was used all the sorption studies. The kaolinite sample KS 1 (Ukraine) was obtained from Eczacıbaşı Co. in Turkey. The chemical constituent of the kaolinite was analysed by XRF and given in Table 1. All solutions were prepared with 99.5% ethyl alcohol from Merck, at room temperature.

Table 1
The chemical composition (%) of kaolinite KS 1 (Ukraine)

SiO_2	48.39
Al_2O_3	35.99
Fe_2O_3	0.43
TiO_2	0.58
CaO	0.24
MgO	0.09
Na_2O	0.03
K_2O	1.74
LoI^a	12.39
Others ^b	0.12

^a Loss of ignition at 1025 °C.

^b P_2O_5 , Cr_2O_3 , Mn_3O_4 , ZrO_2 , HfO_2 , PbO , ZnO , BaO , SrO , SnO_2 , and CuO .

2.1.1. Preparation and characterization of samples

The thermal activation, 30 g of natural kaolinite was placed in a furnace (SFL, Seven Furnaces Limited) at 873 K for a period of 24 h. Then the sample was sieved 325 mesh sieve (0.045 mm) and then put into placed in a desiccator. Selected calcination temperature in this study (873 K) is enough to ensure thermal activation. The studied temperature is generally in line with the reported literature [24,25,28,30]. Bhattacharyya and Sen Gupta [22] reported that further heating (calcination at ~700 K) results in complete dehydroxylation of the aluminosilicate lattice, while retaining the Lewis acidity.

The acid treatment was carried out using a pyrex glass reactor with reflux condenser. The reactor was placed onto Chiltern Hotplate Magnetic Stirrer HS 31. 30 g natural kaolinite was slowly added to 250 mL 3 M HCl solution, stirred and maintained at boiling temperature (approximately 378 K) during 5 h. After treatment, the reaction products were filtered and 15 times washed with distilled water to remove traces of acid. After each washing Cl^- ions were detected with silver acetate solution and then the sample was centrifuged with MSE MISTRAL 2000 at 4500 rpm for 5 min. The final sample was centrifuged and kept at 393 K in an oven (Philip Harris Ltd.) to remove some of the moisture for 24 h for complete drying. The sample was milled passing 325 mesh sieve (0.045 mm) to eliminate the formation of lumps produced during drying and then saved in a desiccator [19–21,25,31].

Specific surface areas (BET) and pore-size distributions of the original and activated kaolinite samples were determined using a Quantachrome NOVA 2200 series volumetric gas adsorption instrument. The determinations were based on measurements of the corresponding nitrogen adsorption isotherms at 77 K. Before measurements were started, moisture and gases such as nitrogen, oxygen that were adsorbed on the solid surface or held in the open pores were removed under reduced pressure at 423 K for 5 h.

X-ray diffractograms of the original and activated kaolinite samples were obtained by XRD analysis (Phillips PW 1830-40). For FTIR analysis (Bio-Rad FTS 135) of the samples, KBr pellet method was used. Effect of temperature on the morphology of the original and activated kaolinite samples were evaluated by DTA-TGA analysis (Rigaku Thermoflex TG 8110).

2.2. Methods

In order to increase the surface area and provide physico-chemical changes in the structure of kaolinite, two types of activation tests were performed. Cation exchange capacities (CEC) of these kaolinites were determined via methylene blue test (ANSI/ASTM C837-76). Equilibrium and kinetic studies were performed with natural (untreated), thermally activated and acid activated kaolinites. Adsorption studies were performed by the batch technique to obtain equilibrium data. The batch technique was selected because of its simplicity. For the equilibrium studies; batch sorption test of 3-methoxybenzaldehyde on the natural, thermally and acid activated kaolinites were performed by weighing 0.01 g samples into glass flasks fitted with stoppers and adding 10 mL of 3-methoxybenzaldehyde solutions.

The initial concentrations of 3-methoxybenzaldehyde solution, C_i were 0.15×10^{-4} , 0.25×10^{-4} , 0.35×10^{-4} M. All flasks were put in a incubator at fixed temperatures (303, 318 and 333 K) and shaking for up to 180 min to reach the equilibrium conditions. Concentrations of the 3-methoxybenzaldehyde, C_e , were determined with the aid of a UV–vis spectrophotometer (LKB Biochrom Ultrospec 4050 model spectrophotometer). The measurements were made at the maximum wavelength of 3-methoxybenzaldehyde (at 312 nm). A flask containing 10 mL of 3-methoxybenzaldehyde (no kaolinites) were used as a control sample and the initial absorbance value (A_0) were determined with these samples at 312 nm. For the sorption kinetic studies of 3-methoxybenzaldehyde on the natural, heat- and acid-activated kaolinites were performed by weighing 0.01 g samples into glass flasks and adding 10 mL of 3-methoxybenzaldehyde solutions. The initial concentrations of 3-methoxybenzaldehyde solution, C_i were 0.15×10^{-4} , 0.25×10^{-4} and 0.35×10^{-4} M and the changes of absorbance at 312 nm were determined at 5, 10, 20, 40, 60, 80, 100, 120, 140 and 180 min during the sorption process at three different temperatures (303, 318 and 333 K).

2.2.1. Equilibrium models

The sorption isotherms express the relationships between equilibrium concentrations of the adsorbate in the adsorbing phase (Q) and fluid phase (C_e) at a fixed temperature. The linear form of Langmuir [32] model can be expressed as

$$\frac{1}{Q} = \frac{1}{Q_0} + \frac{1}{Q_0 K C_e} \quad (1)$$

where C_e is equilibrium concentration, Q_0 the maximum concentration retained by the adsorbent and K is the equilibrium constant.

The linear form of Freundlich model [33] can be expressed as

$$\ln Q = \ln K_f + n \ln C_e \quad (2)$$

where K_f and n are Freundlich constants, K_f is a Freundlich affinity parameter for a hetero-disperse system and n is related to the magnitude of the sorption driving force and to the energy distribution of the sorption sites [34].

In this study, the dimensionless forms of isotherms are studied. The dimensionless study is preferred by some researchers due to its simplicity and accuracy. The dimensionless forms of isotherms are reported by Carabasa et al. [35], Gökmen and Serpen [36], Veglio et al. [37], Chang et al. [38], Coles and Yong [39]. Where C_e ; (A/A_0) represents the liquid phase absorbance at 312 nm and Q ; $([(A_0 - A)/A_0]/m)$ represents the solid phase absorbance at 312 nm, where m is the amount of kaolinite and A is a measure of the amount of 3-methoxybenzaldehyde solutions at equilibrium.

2.2.2. Thermodynamic and kinetic parameters

Thermodynamic parameters such as Gibbs free energy (ΔG), the enthalpy change (ΔH) and entropy change (ΔS) for the sorption of 3-methoxybenzaldehyde on natural, thermally and acid activated kaolinites are calculated using the following equations.

ΔG is calculated using the following equation [7,40]:

$$\Delta G = -RT \ln K \quad (3)$$

where K is the equilibrium constant (from Langmuir model), T the absolute temperature and R is the universal gas constant. The relation between K and the thermodynamic parameters of ΔH and ΔS can be described by Van't Hoff correlation in the following equation.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

In this study a geometric approach described by Kuan et al. [41] was applied to determine adsorption and desorption constants, separately. Fig. 9 is the typical plots θ versus time (t) relationship resulting from a conventional kinetic experiment. The curves can be divided into a fore fast reaction interval and a latter slow reaction interval. A linear regression analysis of data collected from the early stage will yield a slope k_0 , namely initial adsorption rate and the intercept of linearization of data in the late stage gives the equilibrium coverage fraction (θ_e). Initial equilibrium time t_{ie} , k_a and k_d can be expressed as [36,41]:

$$t_{ie} = \frac{\theta_e}{k_0} \quad (5)$$

$$k_a = \frac{2k_0}{C} \quad (6)$$

$$k_d = \frac{2(1 - k_0 t_{ie})}{t_{ie}} \quad (7)$$

The activation energies of the adsorption and desorption can be calculated according to the linear form of Arrhenius equation

$$\ln k_a = \ln A_a - \frac{E_a}{RT} \quad (8)$$

$$\ln k_d = \ln A_d - \frac{E_d}{RT} \quad (9)$$

where E_a and E_d represent the activation energy of the adsorption and desorption, respectively. A_a and A_d are the frequency factors, R the universal gas constant and T is the absolute temperature.

3. Results and discussion

3.1. Characterization of the samples

Nitrogen adsorption isotherms of natural clay and thermally and acid activated samples are shown in Fig. 1. The specific surface areas of the samples were calculated from nitrogen adsorption isotherms by the BET method mainly for comparative purposes. Acid activation markedly affected N_2 adsorption characteristics of the kaolinite. However, the general shape of the isotherm stayed at the same, after acid activation relatively increased the nitrogen uptake, while thermal activation of the kaolinite decreased the nitrogen uptake as seen in Fig. 1.

The BET surface areas of the samples are also determined. The acid activation causes formation of smaller pores in solid particles resulting higher surface area ($29.6 \text{ m}^2/\text{g}$) relative to

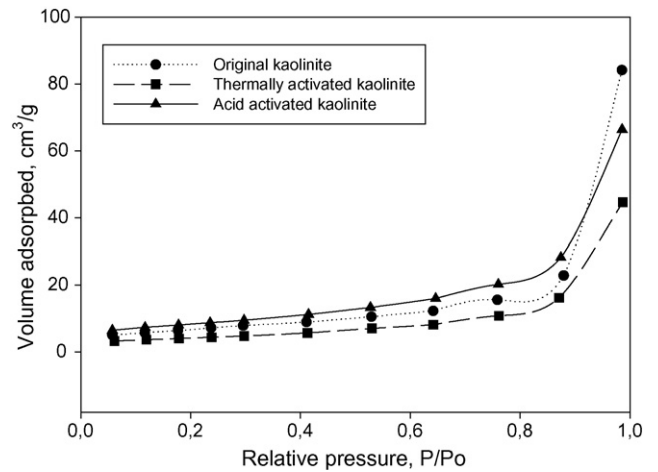


Fig. 1. Nitrogen adsorption isotherms of the original and activated kaolinite samples.

original and thermal activated kaolinite (24.95 and $14.98 \text{ m}^2/\text{g}$, respectively). The decrease in the specific surface area of the thermal activated kaolinite may be a result of removal of the most of the micropores and the folding of structure due to heating the samples as stated by Tekin et al. [25]. For a textural characterization of any porous solid, the concept of surface area does not give a visual picture of it. Pore size and pore size distributions are necessary if the material is to be fully characterised. The pore size distribution in the mesopore region was obtained by applying the method of BJH [42] to the desorption branch of the isotherms of nitrogen at 77 K , assuming the pores to be cylindrical in shape. Fig. 2 compares the change of pore size distribution for original and activated kaolinite samples. The pore size distribution plots indicate that for the samples calcined at $600 \text{ }^\circ\text{C}$ the dv/dr ratio (ratio of the change in volume to change in radius) decreases slightly when compared to the raw sample. On acid activation, dv/dr ratio tends to increase. Generally it can be described that the distribution of particles with smaller pore radius decreases in the case of calcined samples whereas as their acid activated forms show a reverse trend [24]. The samples have almost mesopores of which

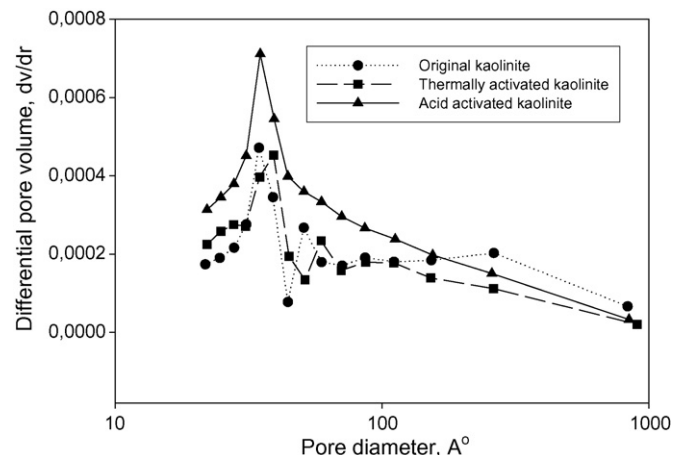


Fig. 2. Pore size distributions of the original and activated kaolinite samples.

kaolinite exhibited maxima in differential pore volumes at about 34.5 Å in pore diameter, for thermally activated kaolinite it was 39 Å.

X-ray diffractograms of the original and activated kaolinites were shown in Fig. 3. Patterns of the original kaolinite and its acid activated form were similar and indicating that there are no serious changes taking place in the clay structure due to acid activation. Calcining the kaolinite to 600 °C (873 K), all the peaks in the diffractogram due to kaolinite disappear indicating

its transformation to amorphous metakaolinite. Similar results were found by Suraj et al. [24].

The FTIR spectra of the original and activated kaolinite samples are shown in Fig. 4. In original and acid activated samples there are characteristic peaks of kaolinite, the O–H stretching (3700–3620 cm^{-1}), the Si–O stretching (at about 1000 cm^{-1}), the O–H bending (940–910 cm^{-1}) and the SiO₂ bending (550–400 cm^{-1}). As can be seen from FTIR spectrum after calcination at 600 °C, the structure of kaolinite is changing

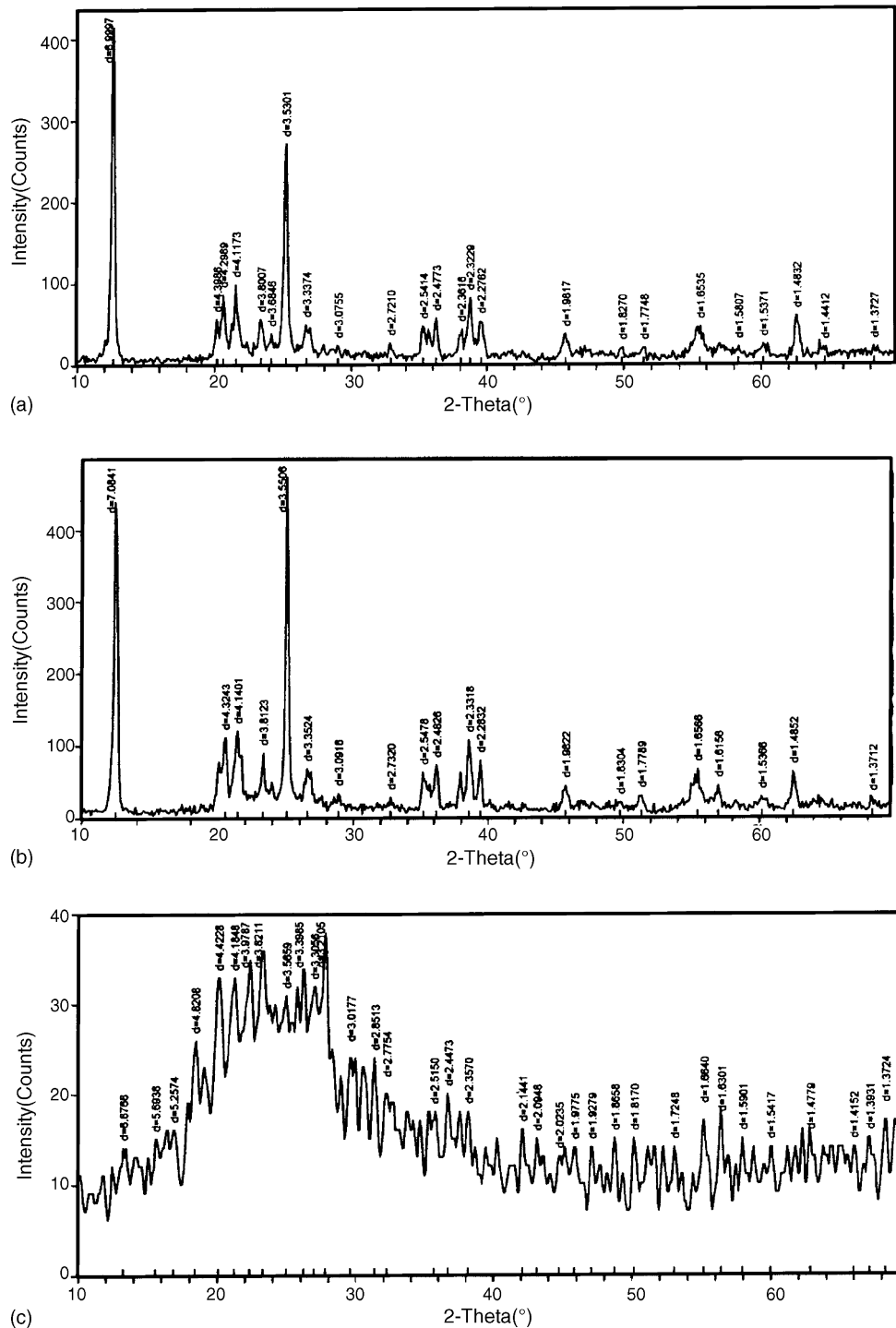


Fig. 3. X-ray diffraction patterns of the kaolinite samples (a) original, (b) acid activated, and (c) thermally activated.

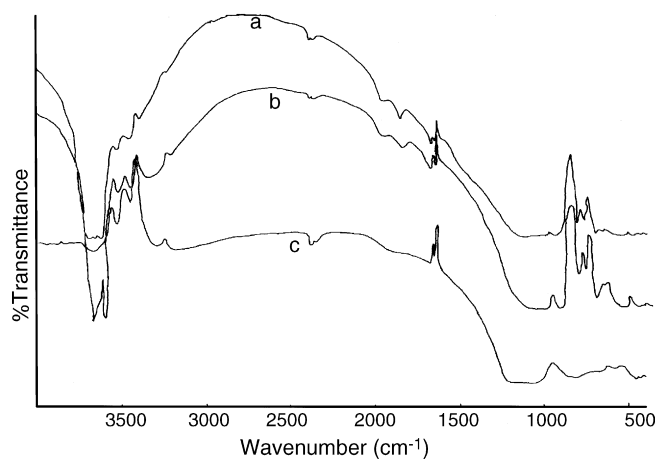


Fig. 4. FTIR spectrums of the kaolinite samples (a) original, (b) acid activated, and (c) thermally activated.

as reported by Tekin et al. [25,28]. This change was supported by thermal analysis of the original and activated kaolinite samples (Fig. 5).

In order to assess the exchangeability of the clay samples, the cation exchange capacity (CEC) measurements were carried out. CEC of the thermally activated, natural and acid activated kaolinites were found as 5, 8.5 and 9 mequiv./100 g, respectively. The observed decrease in CEC of the thermally activated kaolinite is indicative of the reduced number of exchangeable sites caused during the dehydroxylation process. Furthermore, it is clear that the sample heated to 600 °C has the least CEC due to collapse the structure while acid activated kaolinite shows an increase depending on H⁺ ions. But, as expected, a reverse trend has been noticed for the acid activated kaolinite. Similar results are reported by Suraj et al. [24].

3.2. Adsorption efficiency

The adsorption efficiency of 3-methoxybenzaldehyde on the kaolinite samples were evaluated by determining the following percentage decrease of the absorbance at 312 nm of the 3-methoxybenzaldehyde solutions using the following equation as previously expressed by Carabasa et al. [35] and Gökmen and Serpen [36]:

$$\text{adsorption efficiency(\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (10)$$

where A_0 is the initial absorbance at 312 nm and A is the final absorbance at 312 nm. The adsorption efficiency of 3-methoxybenzaldehyde on the original and activated kaolinites at various temperatures were shown in Fig. 6. Adsorption efficiency for acid activated kaolinite reached at about 80% while it was at about 70 and 60% for thermally and original kaolinite, respectively at 303 K (Fig. 6). It can be seen that the adsorption efficiency increases with increasing temperature which is typical for the adsorption of most organics from their solutions as reported by Tekin et al. [25]. The effect of temperature is fairly common and increasing the temperature must increase the mobility of the solute. Also, it was explained that the endother-

mic adsorption enthalpy. Similar results have been reported by references [14,36,43,44]. It was found that the adsorption efficiency with acid activated kaolinite was greater than thermally activated kaolinite and natural kaolinite, respectively. It was expected, because the acid activation causes formation of smaller pores in solid particles resulting higher surface area relative to original and thermal activated kaolinite. As demonstrated [22] acid activation and thermally treatment increases the adsorbent capacity to a good extent.

3.3. Equilibrium studies

The analysis of the isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. Fig. 7 shows the plots of Q versus of C_e for the adsorption isotherms of 3-methoxybenzaldehyde on the original and activated kaolinites at various temperatures. These curves are convex upward throughout are designated as favourable type [45]. The sorption properties of kaolinite are merely determined by the nature of its surface and edges. Kaolinite has a variable charge that can be related to the reactions between ionisable surface groups located at the edges or at the gibbsite basal plane and the ions present in aqueous solution [46]. This study showed that the silanol groups (Si–OH) at the crystal edges of kaolinite contribute exclusively to the negative charge, through formation of SiO surface complexes. Also, the aluminol groups at the edges are amphoteric, resulting in the formation of the surface complexes AlOH_2^+ and AlO^- [24,47]. Bhattacharyya and Sen Gupta [22] noted that clays contain both Bronsted and Lewis acid sites associated, respectively, with the interlamellar region and the edge sites. Further heating (calcination at ~700 K) results in complete dehydroxylation of the aluminosilicate lattice, while retaining the Lewis acidity. Therefore, it can be said that the polar functional groups of 3-methoxybenzaldehyde such as –CHO and –OCH₃ interact with Bronsted sites at the interlamellar region and Lewis acid sites at the edge for original kaolinite. This interaction can be occurred with Lewis acid sites at the edge and interlamellar region for thermally activated kaolinite. Similar results are reported by Castellini et al. [48] for the adsorption of hexametaphosphate on kaolinite. Enhanced mesoporosity for acid activated kaolinite is also affected on the interaction between the functional groups of 3-methoxybenzaldehyde and surface and edge sites.

The sorption data for the natural, thermally and acid activated kaolinites were fitted to linear form of the Langmuir model Eq. (1) The intercept of lines at $1/Q$ axis give $1/Q_0$ and the slope of lines give $1/KQ_0$. The maximum sorption capacities (Q_0), the sorption equilibrium constants (K) and correlation coefficients (r^2) for natural, thermally and acid activated kaolinites are given in Table 2. The sorption equilibrium constants (K) were observed to increase with increasing temperature, but the maximum sorption capacities (Q_0) were decreased with temperatures. It can be explained that the fundamental process for adsorption of 3-methoxybenzaldehyde on the kaolinites is more complex than hydrophobic theory suggests. It is commonly observed

that organic chemicals with polar functional groups such as $-OH$ and $-CHO$ sorb nonlinearly. Some investigator explain that, for polar organic compounds, hydrogen bonding and electron donor–acceptor processes involving free radicals have a prominent role in polar organic compound–clay interaction [49,50].

Although sorption data are often modelled using linear isotherms such as Langmuir isotherm, researchers have also used nonlinear Freundlich isotherm to fit experimental data while studying sorption to soil [51–56]. The fitting of the experimen-

tal data to the linear form of the Freundlich model Eq. (2) were performed K_f and n are determined from the intercept and the slope of the plot $\ln Q$ versus $\ln C_e$, respectively. In each case the Freundlich parameters K_f and n were decreased with increasing temperature (Table 2). K_f varied from 1.6510 to 6.7423 g^{-1} and n from 0.2465 to 0.6565 for the sorption processes. These results agree with the studies of Jin et al. [1]. In case of $n=1$ indicates linear adsorption and equal adsorption energies for all sites. However $n < 1$ shows that the marginal adsorption energy decreases with increasing surface concentration. The n values of

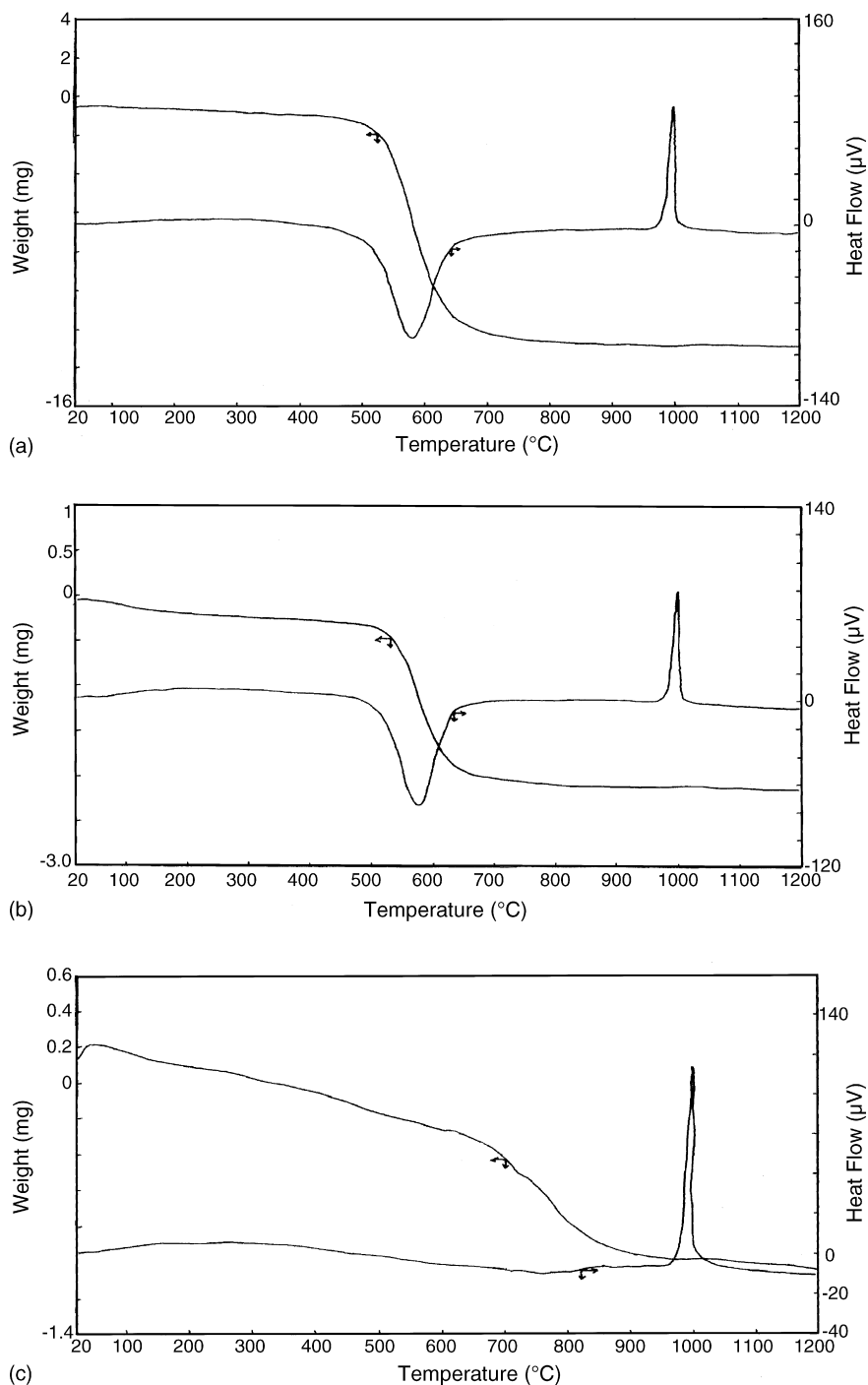


Fig. 5. Thermoanalytical curves patterns of the kaolinite samples (a) original, (b) acid activated, and (c) thermally activated.

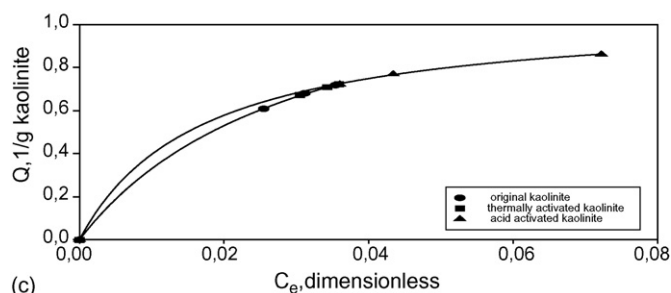
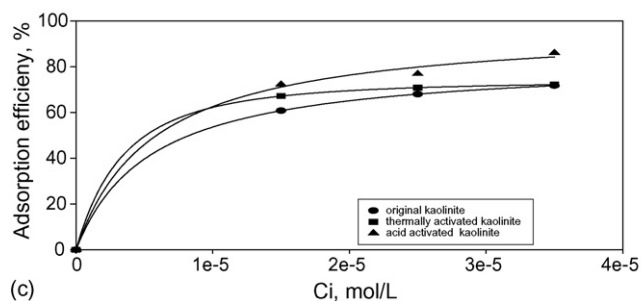
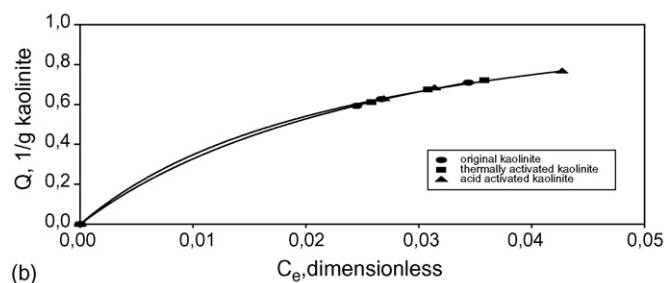
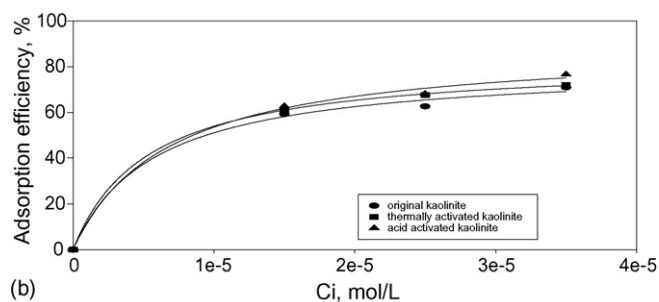
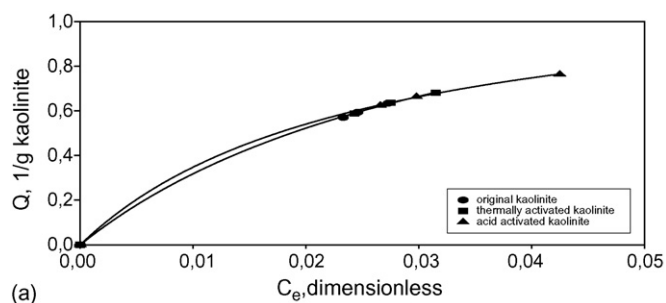
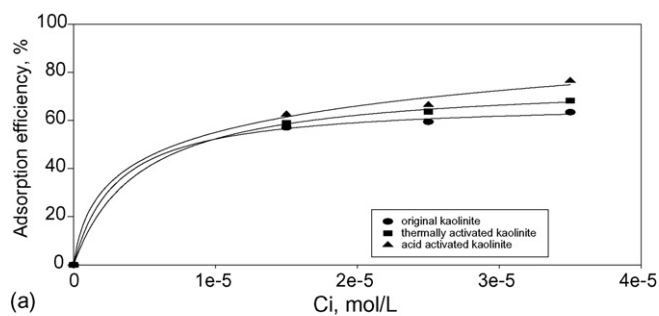


Fig. 6. The adsorption efficiency of 3-methoxybenzaldehyde on the original and activated kaolinites at various temperatures: (a) 303 K, (b) 318 K, and (c) 333 K (equilibrium time 3 h).

Fig. 7. The adsorption isotherms of 3-methoxybenzaldehyde on the original and activated kaolinites at various temperatures: (a) 303 K, (b) 318 K, and (c) 333 K (equilibrium time 3 h).

acid activated kaolinite were lower than the thermally activated and natural kaolinites. It can be explained that is the advantage to the formation of hydrogen bond, hence leads to enhanced sorption. For both isotherm model equations consistently resulted in correlation coefficients close to unity. This indicates that the isotherm data are empirically consistent with the Freundlich and Langmuir models.

3.4. Thermodynamic studies

The type of sorption may be determined through such thermodynamic quantities as Gibbs free energy (ΔG), the enthalpy change (ΔH) and entropy change (ΔS) for the sorption of 3-methoxybenzaldehyde on natural, thermally and acid activated kaolinites are given in Table 3. ΔG is calculated using Eq. (3). ΔH and ΔS were calculated from the slope and intercept of

Table 2
Langmuir and Freundlich parameters at different temperatures for natural, thermally and acid activated kaolinites

Adsorbent	T (K)	Langmuir			Freundlich		
		Q_0 (g ⁻¹ kaolinite)	K	r^2	K_f (g ⁻¹ kaolinite)	n	r^2
Natural kaolinite	303	1.7544	20.6522	0.9992	6.7423	0.6565	0.9988
	318	1.5625	25.6000	0.9504	4.1666	0.5250	0.9968
	333	1.3514	32.0346	0.9984	3.9563	0.5099	0.9960
Thermally activated kaolinite	303	1.4925	26.9076	0.9982	4.9313	0.5712	0.9966
	318	1.3158	33.3333	0.9457	3.8102	0.4991	0.9952
	333	1.2346	39.1304	0.9998	3.0904	0.4370	0.9994
Acid activated kaolinite	303	1.2195	39.6135	0.9978	2.9209	0.4238	0.9952
	318	1.1363	49.4382	0.9725	1.9472	0.3054	0.9903
	333	1.0638	59.1195	0.9979	1.6510	0.2465	0.9900

Table 3
Thermodynamic parameters for the sorption processes of 3-methoxybenzaldehyde on natural, thermally and acid activated kaolinites

Adsorbent	T (K)	K	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	r^2
Natural kaolinite	303	20.6522	-7.6272	12.2623	0.0656	0.9984
	318	25.6000	-8.5729			
	333	32.0346	-9.5981			
Thermally activated kaolinite	303	26.9076	-8.2940	10.4881	0.0620	0.9969
	318	33.3333	-9.2708			
	333	39.1304	-10.1520			
Acid activated kaolinite	303	39.6135	-9.2684	11.2056	0.0676	0.9990
	318	49.4382	-10.3129			
	333	59.1195	-11.2945			

Van't Hoff plots given in Eq. (4), respectively (Fig. 8). As evident from Table 3, the enthalpy of sorption for each kaolinite samples is lower than 40 kJ mol⁻¹ indicating that the sorption processes were controlled by physical mechanism rather than chemical mechanism. This result shows that the interaction between kaolinite and 3-methoxybenzaldehyde is mainly electrostatic (Coulombic interactions). The heat of physical adsorption involves relatively weak intermolecular forces such as van der Waals and mainly electrostatic interaction as well as hydrogen bond. In addition, the positive values of ΔH indicated the endothermic nature of sorption of 3-methoxybenzaldehyde on natural, thermally and acid activated kaolinites. In general, exothermic heats requisite for an adsorption process (unless adsorption is very weak) to compensate for losses in entropy. However, there are many papers in the literature concerning the adsorption heats with positive values [14,36,43,44,57]. The negative values of Gibbs free energy of sorption (ΔG) indicated that the sorption of 3-methoxybenzaldehyde on the kaolinite surfaces were spontaneous. The value of ΔG decreases with increase in temperature shows that the reaction is easier at high temperature. The reorientation or restructuring of water around solute or surface is very unfavourable in terms of entropy since it disturbs the existing water structure and imposes a new and less ordered structure on the surrounding water molecules. As a result of adsorption 3-methoxybenzaldehyde onto kaolinite surface the number of the water molecules surrounding 3-methoxybenzaldehyde molecules change and thus the degree of the freedom of the water molecules increases. Therefore the positive values of ΔS suggest the increased randomness at the solid-solution interface during the sorption of 3-methoxybenzaldehyde on kaolinites [25,28]. The sorption process is composed of two contributions enthalpic and

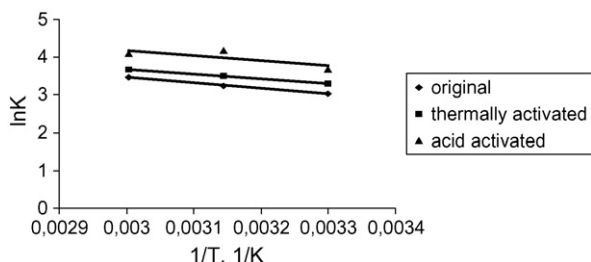


Fig. 8. Van't Hoff plots of the original and activated kaolinite samples.

entropic, which characterize whether the reaction is spontaneous [27]. Examination of Table 3 reveals that ΔH is rather larger compared to the total sorption energy. However, the entropic contributions are even smaller than the Gibbs free energy of sorption. Therefore, it is easily to say that the sorption of 3-methoxybenzaldehyde on the kaolinites are enthalpic governed. In addition, there is no large change in value of any of the thermodynamic parameters for all the tested kaolinites, suggesting that thermodynamic processes involved in the kaolinite 3-methoxybenzaldehyde interaction are more or less uniform in nature.

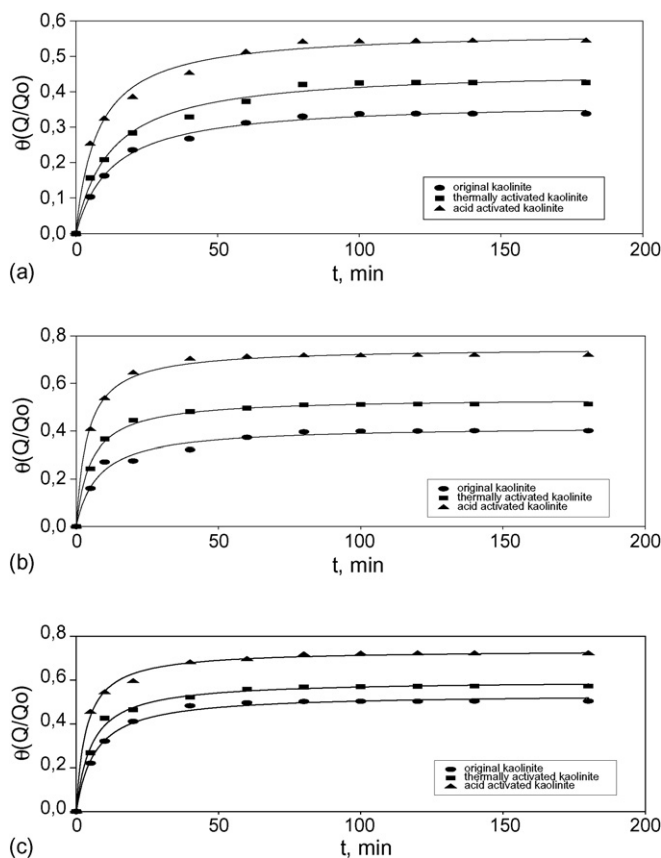


Fig. 9. The typical example of geometric approach of the kinetic data to obtain k_0 , t_{0e} , and θ_e (0.25.10⁻⁴ M 3-methoxybenzaldehyde/original and activated kaolinites at various temperatures): (a) 303 K, (b) 318 K, and (c) 333 K.

Table 4

The kinetic parameters of 3-methoxybenzaldehyde sorption onto natural (N-K), thermally activated (T-K) and acid activated (A-K) kaolinites as determined by geometric approach

C_i ($\times 10^{-4}$ M)	T (K)	θ_e	k_0 (min^{-1})	t_{ie} (min)	k_a (min^{-1})	k_d (min^{-1})	r^2
0.15	303 (N-K)	0.3251	0.0226	14.3835	1.9401	0.0938	0.9906
	303 (T-K)	0.3943	0.0343	11.5034	2.8211	0.1053	0.9989
	303 (A-K)	0.5125	0.0760	6.7403	5.6955	0.1446	0.9939
	318 (N-K)	0.3792	0.0267	14.1779	2.1833	0.0876	0.9961
	318 (T-K)	0.4938	0.0643	7.6823	4.9828	0.1318	0.9976
	318 (A-K)	0.7092	0.0989	7.1650	7.3591	0.0812	0.9963
	333 (N-K)	0.4509	0.0304	14.8188	2.3865	0.0741	0.9959
	333 (T-K)	0.5442	0.0709	7.6787	4.6473	0.1187	0.9825
	333 (A-K)	0.6793	0.1039	6.5354	5.7585	0.0981	0.9846
0.25	303 (N-K)	0.3386	0.0180	18.8102	1.4635	0.0703	0.9935
	303 (T-K)	0.4264	0.0201	21.2096	1.4621	0.0541	0.9860
	303 (A-K)	0.5445	0.0391	13.9339	2.6226	0.0654	0.9817
	318 (N-K)	0.4007	0.0311	12.8882	2.3289	0.0930	0.9759
	318 (T-K)	0.5133	0.0626	8.2062	4.0617	0.1186	0.9977
	318 (A-K)	0.7205	0.1047	6.8821	6.6683	0.0812	0.9975
	333 (N-K)	0.5032	0.0489	10.2839	3.1266	0.0966	0.9981
	333 (T-K)	0.5740	0.0685	8.3828	3.9926	0.1016	0.9922
	333 (A-K)	0.7233	0.1143	6.3308	5.2649	0.0874	0.9864
0.35	303 (N-K)	0.3612	0.0402	8.9786	2.9472	0.1423	0.9913
	303 (T-K)	0.4569	0.0608	7.5198	3.8577	0.1444	0.9974
	303 (A-K)	0.6262	0.0792	7.9022	3.7291	0.0946	0.9950
	318 (N-K)	0.4255	0.0534	7.9743	3.1023	0.1441	0.9836
	318 (T-K)	0.5331	0.0700	7.6145	3.6751	0.1226	0.9952
	318 (A-K)	0.8272	0.1211	6.8307	5.6721	0.0506	0.9894
	333 (N-K)	0.5309	0.0621	8.5534	3.5067	0.1097	0.9896
	333 (T-K)	0.5846	0.0764	7.6567	4.2536	0.1085	0.9915
	333 (A-K)	0.8098	0.1385	5.8476	3.8361	0.0651	0.9753

3.5. Sorption kinetics

The data (θ versus t) were fitted to a growth model exponential association $\theta = a(b - e^{-ct})$, where a , b and c are constants which were calculated by using the software package programme of Curve Expert Version 1.3. The derivative of the growth model function at $t = 0$, ($d\theta/dt = ac$) yielded the initial sorption rate (k_0). The initial equilibrium time (t_{ie}) was the calculated using Eq. (5). The initial equilibrium times of the adsorption for natural, thermally and acid activated kaolinites were about 14.0574, 13.4109 and 9.5255 minutes at 303 K, respectively for all concentrations of the solution and tend to decrease as the adsorption temperature increases. The equilibrium coverage fraction (θ_e) was also obtained from the intercept of the linearized data in the later stage (Fig. 9). The equilibrium coverage fraction of the adsorption for natural, thermally and acid activated kaolinites were about 0.3416, 0.4259 and 0.5611 at 303 K, respectively, for all concentrations of the solution and tend to increase as the adsorption temperature increases. Based on the calculations using the geometric approach, the values of k_0 , t_{ie} , θ_e , k_a and k_d for the natural, thermally and acid activated kaolinites are given in Table 4. Since the k_a (Eq. (6)) and k_d (Eq. (7)) were separately determined, the activation energy of adsorption and desorption can be calculated according to the linear forms of Arrhenius Eqs. ((8) and (9)) (Table 5). The adsorption and desorption rate constants depend both on temperature and concentration of the solution. However, the activation energies of adsorption and desorption should be

the same for each concentrations of the solutions. Here, the averaged activation energies of the adsorption (E_a) and desorption (E_d) and frequency factors ($A_{a,d}$) for natural, thermally and acid activated kaolinite at the range of the temperatures were shown in Table 5.

The results reveal that equilibrium constants obtained by geometric kinetic calculation (K_{geo}) are consistent with that (K) obtained by fitting the Langmuir equation to experimental data of equilibrium adsorption (Table 6). This proves that this approach can be applied to 3-methoxybenzaldehyde adsorption and desorption kinetic constants are reasonable. This geometric approach belonging to first-order kinetic model has been demonstrated to be applicable to 3-methoxybenzaldehyde ions onto the kaolinites. The criterion of good conformity is that the adsorption behaviour must follow the monolayer adsorption type. Kithome et al. [58] reported that first-order kinetic

Table 5

The averaged activation energies and frequency factors of the adsorption and desorption for natural, thermally and acid activated kaolinites at the range of temperatures

	E_a (kJ mol^{-1})	A_a	E_d (kJ mol^{-1})	A_d
Natural kaolinite	15.8121	2177.8026	8.9400	2.5292
Thermally activated kaolinite	15.0752	45558.0880	10.7660	3.9895
Acid activated kaolinite	10.6429	4386.7972	8.1101	1.6671

Table 6

The conformity of the K (from Langmuir) and K_{geo} (from geometric approach, k_a/k_d) for natural, thermally and acid activated kaolinites

Adsorbent	T (K)	K (from Langmuir)	K_{geo} (k_a/k_d)
Natural kaolinite	303	20.6522	20.7375
	318	25.6000	23.8314
	333	32.0346	32.1798
Thermally activated kaolinite	303	26.9176	26.8441
	318	33.3333	34.0097
	333	39.1304	39.2175
Acid activated kaolinite	303	39.6135	39.6362
	318	64.9682	64.9493
	333	59.1295	59.2885

model can be applied extensively to cation and anion sorption in soils. Boyd et al. [59] also demonstrated this equation can describe both film diffusion-controlled reaction and chemically controlled reaction for isotopic exchange conditions. Helfferich [60] stated that other reactions known to be diffusion controlled can also be described using second-order chemical reactions through a mathematical coincidence. Therefore, other information must then be used to determine the rate-limiting mechanism but the overall kinetic constant is enough to describe the change of adsorption reaction with time.

The geometric method for directly determining both adsorption and desorption kinetic constants was used in this study. As a consequence, it was shown that this method provided good conformity between the K from Langmuir parameters and K_{geo} (k_a/k_d) from geometric approach (Table 6).

4. Conclusions

In the sorption studies conducted on natural, thermally and acid activated kaolinites resulted in the following salient points.

- (1) The sorption of 3-methoxybenzaldehyde on the natural, thermally and acid activated kaolinites were an endothermic processes, controlled by physical mechanisms, enthalpic governed and spontaneously. The adsorption efficiency with acid activated kaolinite was greater than thermally activated and natural kaolinite, respectively.
- (2) The adsorption and desorption rate constants (k_a and k_d) were obtained separately by applying a geometric approach. The initial equilibrium times of the adsorption for acid-activated kaolinites were shorter than the natural and thermally activated kaolinites at all the temperature studied and tend to decrease as the adsorption temperature increases. The equilibrium coverage fraction of the adsorption for acid-activated kaolinites were bigger than the equilibrium coverage fraction of the adsorption for natural and thermally activated kaolinites at all the temperature studied and tend to increase as the adsorption temperature increases. It is clearly showed that acid activated kaolinite is more suitable for the sorption of 3-methoxybenzaldehyde and the method of geometric approach can be successfully applied to kinetic

sorption studies of 3-methoxybenzaldehyde on these kaolinites.

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