

# Kinetic Study on Adsorption of Fatty Hydroxamic Acids by Natural Clays

Basel M. Jafar<sup>1</sup>, Imad Hamadneh<sup>2</sup>, Fawwaz I. Khalili<sup>2</sup>, Ammar H. Al-Dujaili<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, King Khalid University, Abha-Bisha, Saudi Arabia

<sup>2</sup>Department of Chemistry, Faculty of Science, University of Jordan, 11942 Amman, Jordan

Received 12 February, 2015; Accepted 17 May 2015

## Abstract

Five fatty hydroxamic acids (FHAs) were synthesized by refluxing of vegetable oils, namely corn, olive, palm, soybean, and sunflower oil with hydroxylamine hydrochloride. The FHAs were synthesized by three different methods depending on the form of the fatty acids used, i.e., free fatty acid, methyl and ethyl fatty ester or raw oil. The efficiency of FHAs synthesized from methyl and ethyl ester was very high, because it gives good yield and pure product. These acids were characterized using the complex formation test of hydroxamic acid group with zinc(I), copper(II) and iron(III), elemental analysis, and Fourier transform infrared (FTIR) spectroscopy. The adsorption of these five FHAs onto bentonite (BT) and kaolinite (KT) clays was investigated using a series of batch adsorption experiments. The present study primarily focuses on the adsorption kinetics to modify BT and KT clays. Four adsorption kinetic models were tested for the adsorption of FHAs onto BT and KT clay surfaces. In order to investigate the mechanism of these five fatty hydroxamic acids adsorption, characteristic constants of adsorption were determined using a pseudo-first order equation of Lagergren, a pseudo-second order equation, Elovich equation and intraparticle diffusion model.

© 2015 Jordan Journal of Earth and Environmental Sciences. All rights reserved

**Keywords:** Vegetable oils; Fatty hydroxamic acids; Adsorption; Kinetics; Clay mineral

## 1. Introduction

Hydroxamic acid (HA), or (N-hydroxycarboxylic amides), has the general chemical formula R-CO-NHOH. It is regarded as a derivative of both hydroxylamine and carboxylic acids (Miller et al., 2002). The term FHA comes when (HA) is prepared from fatty acids. A Fatty acid (FA) is a carboxylic acid with a long unbranched aliphatic chain, which is either saturated or unsaturated. FAs are usually derived from triglycerides. When they are not attached to other molecules, they are known as free fatty acids. The FA can be defined by its source (animals or plants), or by its carbon number as a short chain (fewer than six), medium (6-12), long (longer than 12), or very long (longer than 22) (Clifford and Gessner, 1973).

In recent decades, hydroxamic acid derivatives have been widely applied as growth factors, food additives, neurotoxic drugs for anti HIV drugs, antibiotics, antimalarial drugs, antibacterial agents, cell division factor, rare earth mineral collectors and chelators (Kurzak et al., 1992), and enzyme inhibitors (Dankwardtet. al., 2001). Hydroxamic acids complexes have been used for analytical chemistry as reagents for gravimetric and spectrometric metal determination (Agrawal and Patel, 1980; Agrawal et al., 2000). Besides their ability to form a complex with metal ions, long-chain hydroxamic acids, by modification of the terminal OH group, are of a considerable interest as an efficient surfactant in the detergent industry (Masuyama et al., 1987).

Several studies were carried out on the synthesis of hydroxamic acids from acids and esters with hydroxylamine (Jahangirian et al., 2011; Al-Mulla et al., 2009; Holmes et al., 2001). Many researchers synthesized fatty hydroxamic acids from palm oil using immobilized lipase as the catalyst (Dedy et al., 2005; Vaysse et al., 1997). Hoidy et al. (2010) reported the synthesis of fatty hydroxamic acid using the reflux method for preparation of fatty hydroxamic acids from different oils including palm olein, palm stearin and corn oil with hydroxylamine hydrochloride

Bentonite is a clay deposit consisting essentially of smectite minerals. Smectites are unique by their extreme small crystal size and variation in the internal chemical composition, and structural characteristics (Rauf and Tahir, 2000). Bentonite is a 2:1 type of clay, which means that it is composed of units of two silica tetrahedral sheets with a central alumina octahedral sheet. All tips of tetrahedron points in the same direction and toward the center unit (Murray, 2007).

Kaolinite is a clay mineral with the chemical composition  $Al_2Si_2O_5(OH)_4$ , with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral (Srivastava et al., 2005). Kaolinite has a 1:1 layer structure, with the basic unit consisting of a tetrahedral sheet of  $SiO_4$  and an octahedral sheet with  $Al^{3+}$  as the octahedral cation. The repeating layers of the mineral are hydrogen bonded together (Trevino and Coles, 2003).

\* Corresponding author. e-mail: ah.aldujaili1946@gmail.com

The permanent negative charge in the crystal structures of some minerals (BT and KT as examples), make them suitable for surface modification by long chain and short chain organic surfactants (Li and Bowman, 2001; Li et. al., 2002). These modifications enable those clay minerals to be used as an adsorbent for removing organic and inorganic pollutants from aqueous solution. In addition, this organomodification make clay minerals compatible with polymers to synthesis the most promising materials, i.e., clay-polymer nanocomposites (Pavlidon and Pappaspyrides, 2008).

In the present study, the synthesis and characterization of fatty hydroxamic acid (FHA) derived from the reaction of hydroxylamin with five different oils, namely corn, olive, palm, soybean, and sunflower oil. The synthesized fatty hydroxamic acids were employed to modify BT and KTclays to form ten kinds of organic-modified clays, i.e., CornFHA/BT, OliveFHA/BT, PalmFHA/BT, SoybeanFHA/Bt, SunflowerFHA/BT, CornFHA/KT, OliveFHA/KT, PalmFHA/KT, SoybeanFHA/Kt, andSunflowerFHA/KT. The present paper primarily focuses on the adsorption kinetics of BT and KTclays. Four adsorption kinetic models were tested for the adsorption of FHAs onto BT and KTclay surfaces. In order to investigate the mechanism of these five fatty hydroxamic acids adsorption, characteristic constants of adsorption were determined using a pseudo-first order equation of Lagergren, a pseudo-second order equation, Elovich equation and interparticular diffusion model.

## 2. Materials and methods

### 2.1. Materials

Corn, olive, palm, soybean and sunflower vegetable oils were purchased from Universal Modern Industries Company (UMIC), Jordan. All chemicals used in this study were provided by Sigma-Aldrich Chemicals Company, where their purity is higher than 99% and used without further purification.

Samples of Jordanian BT and KT from the Azraq region in northeast of Jordan were obtained from Natural Resources Authority (NRA, Amman, Jordan). The crushed and milled samples were washed several times with deionised water with a constant stirring to remove soluble inorganic salts and any adhering materials, and then dried in a drying oven to constant weight at 110°C. The samples were sieved and fractions of 45 µm and below were collected.

### 2.2. Instrumentation

FT-IR spectra were recorded using Thermo Nicolet NEXUS 670 FT-IR spectrophotometer using KBr disc. The infrared spectrum was recorded in the wave-number range 400 - 4000 cm<sup>-1</sup>.

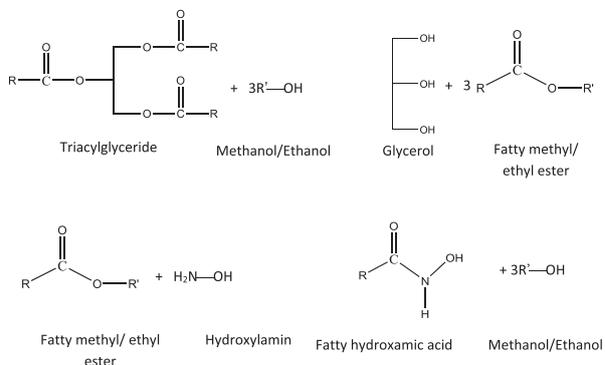
Scanning electron microscope (SEM) technique has been used to obtain information on the morphology and size of the sample by scanning electron microscopy (SEM). The morphology was studied using FEI inspect F50 scanning electron microscope operated at accelerating voltages of 2 kV with magnification of 15000 X. The particles were glued to a metallic sample holder using a carbon double-side tape and then coated with platinum to prevent the charging effect.

Ultra violet visible (UV-VIS) spectrophotometer type Cary 100 Varian spectrophotometer was used to identify the  $\lambda_{max}$  of FHA/Fe (III) complex and measuring the absorption intensity for all samples.

The chemical composition of BT and KT samples was performed using X-ray fluorescence (XRF) spectrometer (Philips PW 2400).

### 2.3. Synthesis of (FHAs)

The FHAs was prepared by three different methods depending on the form of fatty acids used, i.e., free fatty acid, methyl and ethyl fatty ester or raw oil. The FHA, prepared from methyl and ethyl ester, was found to be the best, because it gave a good yield and a pure product. The following procedure was used: The methyl and ethyl fatty ester were prepared using transesterification reaction method which was carried out by mixing methoxide/ethoxide with warmed palm oil as an example with continuous stirring for 6h (Ma and Hanna, 1999). Then, the product was separated and dissolved in hexane with hydroxylamine hydrochloride by reflux at the boiling point of hexane for 10 h, using a thermostated round bottom flask, equipped with a water cooled condenser, and a mechanical stirrer. The product was first dissolved in hot hexane, and separated from the bottom layer using a separating funnel. The hexane phase was cooled in an ice bath for 4 h to obtain FHA, then filtrated and washed by hexane three times. The products was recrystallized from hexane; finally, it was dried in vacuum desiccators over phosphorous pentoxide (Haron et. al., 1994). The reaction is shown in Scheme 1:



**Scheme 1.** The Reaction Equations of Triacylglyceride with Hydroxylamine

### 2.4. Adsorption of FHAs by Bentonite and Koalinite clays

Batch adsorption was carried out using Pyrex glass vessels. An accurate mass ( $0.5g \pm 0.1$  mg) of BT or KTclay measured to the nearest 0.0001g was shaken with 100 mL solutions of FHA prepared by dissolving 0.5 g of each of FHA in 100 mL of 70% ethanol at 25°C. For adsorption, a kinetics set of experiments was carried out by taking aliquot of the solution by pipette after different times 1, 3, 6, 12, 18, 24 and 48 h. The solution was then filtered using 0.45µm micro filter. One milliliter from this solution was reacted with 10 mL of FeCl<sub>3</sub> solution in 70% ethanol to give a colored solution. All of the samples were analyzed by UV-VIS spectrophotometer at wavelength 520 nm to measure the concentration of free FHA. The calibration curve, at this wave length, was established as a function of FHA concentration. The reproducibility of the data varied in the range of 1.5%.

The FHA uptake capacity was calculated by the simple concentration difference method. The FHA uptake (mg FHA adsorbed/g adsorbent) was calculated from the mass balance equation (1) as follows:

$$q_e = \frac{(C_i - C_{eq})V}{m} \quad (1)$$

where  $C_i$  is the initial concentration (mg/L);  $C_{eq}$  is the equilibrium concentration (mg/L) of the FHA in the aqueous phase;  $V$  is the volume of solution (L) and  $m$  is the mass of the adsorbent (g).

The removal efficiency (% Removal) (%R) values were calculated as a percentage using equation (2):

$$\%R = \frac{(C_i - C_{eq})}{C_i} \times 100(2) \quad (2)$$

### 3. Results and Discussion

#### 3.1. Characterization of Materials

The average molar mass of corn, olive, palm, soybean and sunflower vegetable oils was calculated by back titration technique and the calculated values were 560, 510, 435, 480 and 545 g/mol, respectively. A qualitative analysis of hydroxamic acid group on FHAs was carried out by observing the colored complex formed after methanolic solution of the FHAs reacted with iron(III), copper (II) and zinc (II) in the dilute hydrochloric acid solution. The colors of complexes of FHAs with iron(III), copper (II) and zinc (II) were green, dark red and pale yellow, respectively (Haron et. al., 1994).

The results of the elemental analysis showed that the nitrogen contents in the FHAs synthesized from the corn, olive, palm, soybean and sunflower oil were 6.41, 5.68, 4.93, 5.39 and 6.11%, respectively.

The chemical composition of BT and KT samples, as determined by XRF technique (wt%), are listed in Table 1. The loss on ignition (L.O.I.) values indicates the loading of mineral by the organic compounds.

**Table 1.** The chemical composition of bentonite and kaolinite samples (%)

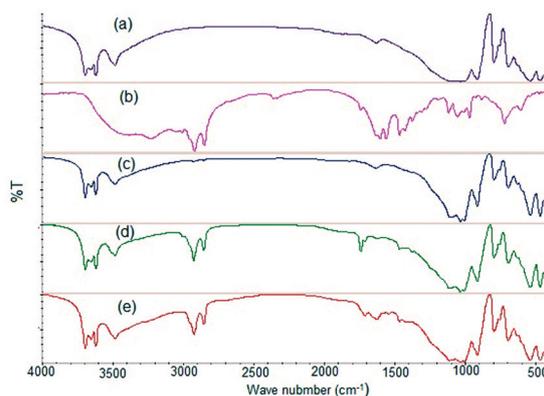
Constituents	Adsorbents	
	Bentonite	Kaolinite
SiO <sub>2</sub>	54.59	47.62
Al <sub>2</sub> O <sub>3</sub>	21.97	27.89
Fe <sub>2</sub> O <sub>3</sub>	2.09	6.11
CaO	4.17	0.49
TiO <sub>2</sub>	0.31	0.72
Na <sub>2</sub> O	3.42	0.84
MgO	1.01	1.01
K <sub>2</sub> O	2.35	2.34
L.O.I.	9.56	12.10

The results of FTIR spectrum of the FHA, synthesized from palm oil as a representative example (Figure 1b), show the characteristic absorption bands of hydroxamic acid at 3426 and 3264 cm<sup>-1</sup>, corresponding to N-H and OH stretching, respectively. These absorption bands are typical bands for amide (Vaysse et. al., 1997). Absorption bands at 2854 and

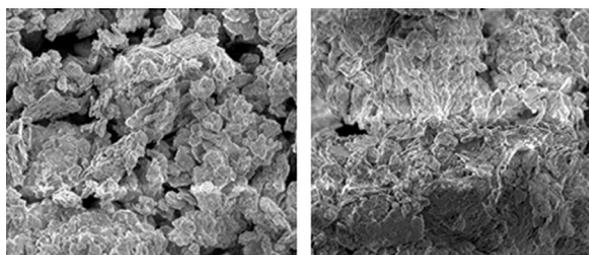
2917 cm<sup>-1</sup>, which correspond to C-H stretching of alkyl chain, at 1641 cm<sup>-1</sup> which correspond to C=O for secondary amide and at 1044 and 1113 cm<sup>-1</sup> which correspond to C-N stretching, respectively.

The characterization bands of raw BT (Figure 1a) that appear at 3434-3625 cm<sup>-1</sup> as a broad band is assigned to OH stretching vibrations, which may arise from the isomorphous substitution in the tetra and octahedral layers in bentonite (Wilson, 1994). On the other hand, the characteristic IR bands of Al and Mg bound water molecules appear at 1642 cm<sup>-1</sup>. The band at 1039 is assigned to the asymmetric stretching vibration of Si-O-Si of BT. It can be seen from the spectrum of raw KT (Figure 1c) that the absorption bands of OH within the crystal structure appear at 3621-3698 cm<sup>-1</sup>. The band at 1631 cm<sup>-1</sup> corresponds to the OH deformation of water, because the OH stretching band at 3467 cm<sup>-1</sup> suggests the presence of some interlamellar water (Gadsden, 1975). After the BT and KT were treated with FHAs, a pair of strong bands at 3434 cm<sup>-1</sup> and 3625 cm<sup>-1</sup> for BT and the bands at 3467 and 3654 cm<sup>-1</sup> for KT were observed which can be assigned to the symmetric and asymmetric stretching vibrations of the methylene groups (CH<sub>2</sub>-) and their bending vibrations are between 1384 and 1470 cm<sup>-1</sup>, (Figures 1d, e) which support the intercalation of FHAs molecules between the silica layers, but these stretching bands are not observed in the raw BT and KT.

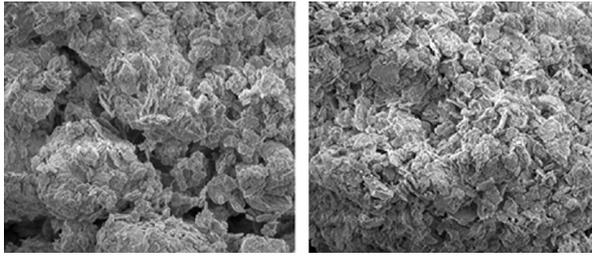
The surface morphology of the raw and modified BT and KT was studied by using scanning electron microscopy (SEM). Figures 2 and 3 give a clear picture of the surface morphology of the samples. They show the porous nature of the surfaces. BT exhibits sieve like structure. In both micrographs of the modified clays it can be noted that the modifier has coated most of the pores and edges.



**Figure 1.** FTIR for (a) Unmodified BT, (b) PalmFHA, (c) Unmodified KT, (d) PalmFHA/BT, and (e) PalmFHA/KT



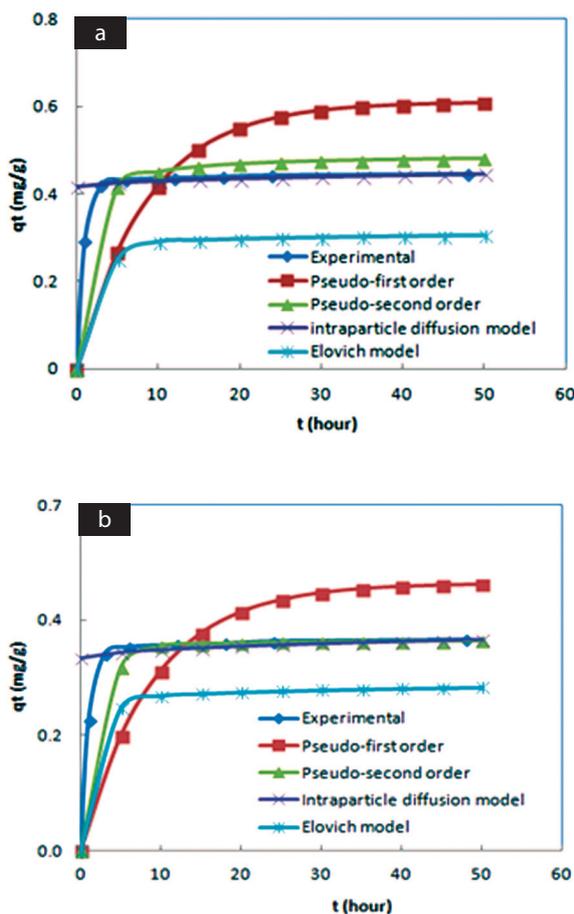
**Figure 2.** SEM Micrographs of (left) Unmodified BT and (right) PalmFHA/BT



**Figure 3.** SEM Micrographs of (left) Unmodified KT and (right) PalmFHA/KT

### 3.2. Kinetic models applied to the sorption of FHAs onto bentonite and kaolinite

Figure 4 shows the contact time curves for the adsorption of FHAs onto BT and KT. The adsorption equilibrium was reached after 8-10 h, depending on the FHAs type. Adsorption, first, followed a linear rising in which instantaneous extremely fast uptakes take place, and, then, a stationary state was observed. The fast initial uptake was due to the accumulation of FHAs on the surfaces of BT and KT adsorbents which is a rapid step (Al-Khalisy et. al., 2010). For all systems and in all subsequent investigations, a shaking time of 12 h was conveniently adopted followed by the standing overnight in the thermostatic bath.



**Figure 4.** Different adsorption kinetic models fit for adsorption of CornFHA on BT (a) and on KT (b) at 25°C

In order to investigate the mechanism of adsorption and the potential rate of controlling steps, such as mass transport and chemical reaction processes, kinetic models were used to test the experimental data. The four adsorption kinetic models included the pseudo-first order equation, the pseudo-second order equation, Elovich equation and the intraparticle diffusion model.

#### 3.2.1. Pseudo-First Order Rate Equation of Lagergren

The pseudo-first order equation of Lagergren (1898) is generally expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

where  $q_{e, \text{calcd.}}$  and  $q_t$  are the amount of FHA adsorbed per unit weight (mg/g) of adsorbent at equilibrium and at any time  $t$ , respectively and  $k_1$  the rate constant of pseudo-first order sorption ( $\text{min}^{-1}$ ).

#### 3.2.2. Pseudo-second order rate equation

If the rate of adsorption is a second order mechanism, the pseudo-second order kinetic rate equation is expressed as (Ho and McKay, 1999):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where  $k_2$  is the rate constant of pseudo-second order sorption ( $\text{g/mg min}$ ).

The constants  $q_{e, \text{calcd.}}$  and  $k_2$  values were calculated from the slopes and intercepts of  $t/q_t$  versus  $t$  plots. The value of  $h_i$ , which is the initial FHAs adsorption rate ( $\text{mg/g.min}$ ) (Chion and Li, 2003), was calculated using the  $k_2$  rate constant obtained from pseudo-second order kinetic data and expressed as equation (5):

$$h_i = k_2 q_{e, \text{calcd.}}^2 \quad (5)$$

According to Tables 2 and 3, the correlation coefficients ( $R^2$ ) of the pseudo second-order kinetic model for the linear plots are higher than 0.99 for all systems. These values are higher than the  $R^2$  values of the pseudo-first order kinetic model (maximum value 0.9265). The calculated adsorption amount ( $q_{e, \text{calcd.}}$ ) for the pseudo second-order kinetic model is close to the experimental one ( $q_{e, \text{exp.}}$ ) (The values were calculated from Langmuir isotherm), but  $q_{e, \text{calcd.}}$  for the pseudo-first order kinetic model are generally not supported by  $q_{e, \text{exp.}}$ . According to the correlation coefficient constant ( $R^2$ ) and the experimental adsorption amount ( $q_{e, \text{exp.}}$ ), it could be said that the experimental data exhibit a good compliance with the pseudo-second order equation for FHAs removal.

#### 3.2.3. The Elovich equation

The Elovich equation is given as follows (McKay et. al., 1999; Low, 1960):

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha \cdot \beta) + \left(\frac{1}{\beta}\right) \ln(t) \quad (6)$$

where  $\alpha$  is the initial adsorption rate ( $\text{mg/g.h}$ ) and  $\beta$  is the desorption constant ( $\text{g/mg}$ ).

The constants  $\alpha$  and  $\beta$  can be obtained from the slope and intercept of a straight line plot of  $q_t$  versus  $\ln t$  and are listed in Tables 2 and 3.

**Table 2.** Pseudo-First Order, Pseudo-Second Order, Elovich, and Intraparticle Diffusion Model Constants and Correlation Coefficients for FHAs Adsorption onto BT

Kinetic model	Constants	Adsorbents				
		CornFHA/BT	OliveFHA/BT	PalmFHA/BT	SoybeanFHA/BT	SunflowerFHA/BT
	$q_{e,exp}$ (mg/g)	0.453	0.448	0.511	0.486	0.445
Pseudo-first order	$q_{e,calcd}$ (mg/g)	0.081	0.028	0.595	0.220	0.004
	$k_1$ (h <sup>-1</sup> )	0.116	0.112	0.115	0.122	0.115
	R <sup>2</sup>	0.9255	0.9212	0.9265	0.9122	0.9233
Pseudo-second order	$q_{e,calcd}$ (mg/g)	0.439	0.438	0.481	0.451	0.436
	$k_2$ (g/mg.h)	0.308	0.263	0.239	0.241	0.254
	$h_i$ (mg/g.h)	0.059	0.051	0.239	0.049	0.048
	R <sup>2</sup>	0.9965	0.9968	0.9998	0.9984	0.9971
Elovich equation	(mg/g.h)	6.686	6.225	7.642	7.042	5.872
	(g/mg)	0.218	0.178	0.219	0.225	0.136
	R <sup>2</sup>	0.7771	0.8144	0.7839	0.7631	0.8648
Intraparticle diffusion	$k_{id}$ (mg/g.h <sup>0.5</sup> )	0.188	0.196	0.139	0.177	0.205
	R <sup>2</sup>	0.9184	0.9468	0.9184	0.9262	0.9184

**Table 3.** Pseudo-First-Order, Pseudo-Second-Order, Elovich, and Intraparticle Diffusion Model Constants and Correlation Coefficients for FHAs Adsorption onto KT

Kinetic model	Constants	Adsorbents				
		CornFHA/BT	OliveFHA/BT	PalmFHA/BT	SoybeanFHA/BT	SunflowerFHA/BT
	$q_{e,exp}$ (mg/g)	0.476	0.46	1.061	0.501	0.444
Pseudo-first order	$q_{e,calcd}$ (mg/g)	0.084	0.029	0.589	0.232	0.041
	$k_1$ (h <sup>-1</sup> )	0.112	0.107	0.101	0.107	0.118
	R <sup>2</sup>	0.9213	0.9131	0.9015	0.9134	0.9217
Pseudo-second order	$q_{e,calcd}$ (mg/g)	0.403	0.381	0.901	0.421	0.376
	$k_2$ (g/mg.h)	0.751	0.821	0.118	0.672	0.769
	$h_i$ (mg/g.h)	0.122	0.119	0.145	0.119	0.108
	R <sup>2</sup>	0.9998	0.9999	0.9998	0.9998	0.9941
Elovich equation	(mg/g.h)	6.562	10.781	10.059	11.962	5.546
	(g/mg)	0.159	0.153	0.143	0.168	0.187
	R <sup>2</sup>	0.8806	0.8686	0.8985	0.8716	0.7854
Intraparticle diffusion	$k_{id}$ (mg/g.h <sup>0.5</sup> )	0.118	0.124	0.135	0.116	0.216
	R <sup>2</sup>	0.9418	0.9403	0.9633	0.9403	0.9184

The Elovich equation was also applied to the adsorption of FHAs by BT and KT. The linearization of the equation giving the rate of reaction allows obtaining the initial adsorption rate  $a$  (mg/g.h) from the intercept of a straight line plot of  $q_t$  versus  $\ln t$ . However, the experimental initial adsorption rates were substantially higher than the predicted initial adsorption rates ( $h$ ) which have no physical sense.

Elovich equation was commonly used in the kinetics of chemisorption of gases on solids (Low, 1960). This equation has been rarely applied to liquid-state adsorption. If the adsorption of FHAs onto BT and KT is predominantly chemisorption, the Elovich equation may be used to describe the kinetics of these adsorption systems. It seems that the adsorption of FHAs onto BT and KT might be physical in nature, which explains the behavior of the studied systems.

### 3.2.4. The intraparticle diffusion

The intraparticle diffusion model, proposed by Weber and Morris, has been widely applied to the analysis of adsorption kinetics (Wu et. al., 2009) and can be defined as shown in equation (7) (Hameed et. al., 2009; Greluk and Hubicki, 2009):

$$q_t = k_{id}t^{1/2} + C \quad (7)$$

The intraparticle diffusion model, proposed by Weber and Morris, has been widely applied to the analysis of adsorption kinetics (Wu et. al., 2009) and can be defined as shown in equation (7) (Hameed et. al., 2009; Greluk and Hubicki, 2009):

where  $k_{id}$  (mg/g min<sup>1/2</sup>) is the Weber and Morris intraparticle diffusion rate constant and C is a value of intercept constant of the plot that provide information about thickness of the boundary layer (mg/g). The intraparticle diffusion constant ( $k_{id}$ ) was calculated from the slope of the straight line part of the plot of  $q_t$  versus  $t^{1/2}$ .

The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism; the kinetic results were then analyzed by using the intraparticle diffusion model. According to Greluk and Hubicki (Greluk and Hubicki, 2009), the plot of uptake  $q_t$  versus the square root of time ( $t^{1/2}$ ) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step (Wu et. al., 2009; Hameed et. al., 2009; El-Sikaily et. al., 2007). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not the only rate-controlling factor, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously (Greluk and Hubicki, 2009). As indicated by the fact that the linear plot does not pass through the origin, suggesting that the intraparticle diffusion is not the only rate-limiting step for FHAs adsorption.

The fitted parameters of adsorption kinetics for the five fatty hydroxamic acid at 25 (Tables 2 and 3) were calculated from the non-linear regressions of the integrated equations (3), (4), (6) and (7). The profiles of the fitted curves of the experimental kinetics of that fatty hydroxamic acid were displayed in Figures 4-8.

It can be deduced from the data in Tables 2 and 3 that in BT and KT modifications, the FHAs adsorption capacity,  $q_e$  is in the order:

PalmFHA>SoybeanFHA>CornFHA>OliveFHA>SunflowerFHA

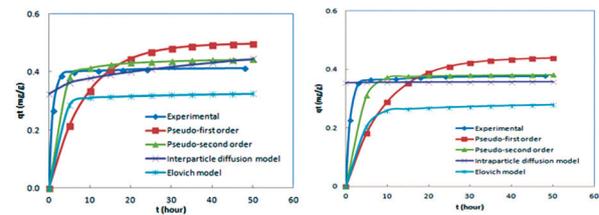


Figure 5. Different adsorption kinetic models fit for adsorption of OliveFHA on BT (left) and on KT (right) at 25°C

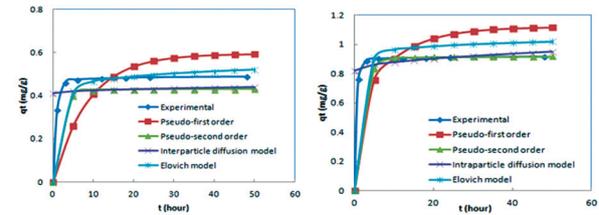


Figure 6. Different adsorption kinetic models fit for adsorption of PalmFHA on BT (left) and on KT (right) at 25°C

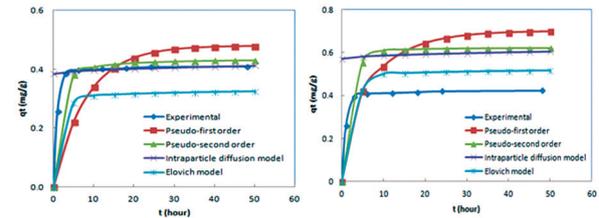


Figure 7. Different adsorption kinetic models fit for adsorption of SoybeanFHA on BT (left) and on KT (right) at 25°C

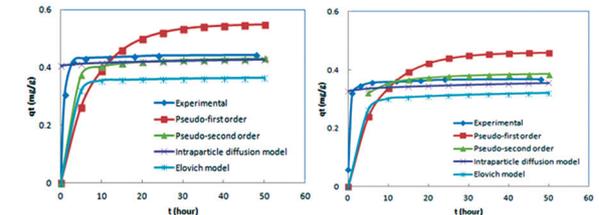


Figure 8. Different adsorption kinetic models fit for adsorption of SunflowerFHA on BT (left) and on KT (right) at 25°C

## 4. Conclusions

In the present study, BT and KT clays were tested as adsorbents for the removal of FHAs prepared from corn, olive, palm, soybean and sunflower vegetable oils from aqueous solution. The kinetics of adsorption of FHAs onto BT and KT was tested using four different kinetic models, namely pseudo-first order kinetic, pseudo-second order kinetic, Elovich equation and intraparticle diffusion model. All findings presented in the present study suggest that FHAS systems cannot be described by a pseudo-first order reaction and the Elovich equation. The pseudo-first order kinetic model does not give theoretical  $q_{e,calcd}$  values that agree with the experimental  $q_{e,exp}$  values, and the correlation coefficients  $R^2$  values were less than 0.94. For all of the systems examined, the pseudo-second order kinetic model provided the best correlation coefficients  $R^2$  of the experimental data (higher than 0.99) and the calculated value of adsorption capacity ( $q_{e,calcd}$ ) agreed well with the experimental ones ( $q_{e,exp}$ ), thus suggesting that the adsorption of FHAs follows the pseudo-

second order kinetic model. Intraparticle diffusion also be taken into account, but it was observed that intraparticle diffusion is not a rate-limiting step.

## References

- [1] Agrawal, Y. K., and Patel, S.A., 1980. Hydroxamic acids: Reagents for the solvent extraction and spectrophotometric determination of metals, *Reviews in Analytical Chemistry*, 4: 237-276.
- [2] Agrawal, Y.K., Shrivastav, P, and Meno S.K., 2000. Solvent extraction separation of uranium (VI) with crown ether, *Separation and Purification Technology*, 200: 177-183.
- [3] Al-Khalisy, R. S., Al-Haidary A.M.A.,and Al-Dujaili, A. H., 2010. Aqueous phase adsorption of cephalixin onto bentonite and activated carbon, *Separation and Purification Technology*, 45: 1286-1294.
- [4] Al-Mulla, E.A.,Yunus, W.M., Nor, A.I., and Rahman, M.Z., 2009. Synthesis and characterization of N,N'-carbonyl difattyamides from palm oil, *Journal of Oleo Science*, 58: 467-471.
- [5] Chion, M.S., and Li, H.Y., 2003. Adsorption behaviour of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere*, 50: 95-105.
- [6] Clifford, A.H., and Gessuer, G.H., 1973. *The Encyclopedia of Chemistry*, 3rd ed., Van No strand Reinhold Company, New York.
- [7] Dankwardt, S.M., Martin, R.L., Chan, C.S., Van Wart, H.E., Walker, K.A.M., Delaet, N.G., and Robinson, L.A., 2011. Amino acid derived sulfonamide hydroxamates as inhibitors of procollagen-proteinase: Solid-phase synthesis of ornithine analogues, *Bioorganic Medicinal Chemistry Letters*, II: 1465-1468.
- [8] Dedy, S.,Yunus, W.M.,Haron, J.,Mahiran, B., and Sidik S., 2005. Enzymatic synthesis of fatty hydroxamic acids from palm oil, *Journal of Oleo Science*, 54: 33-38.
- [9] El-Sikaily, A., El Nemr, A., Khaled, A.,and Abdelwehab, O., 2007. Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon, *Journal of Hazardous Materials*, 148: 216-228.
- [10] Gadsden, J. A., 1975. *Infrared Spectra of Minerals and Related Inorganic Compounds*, Butterworth, London.
- [11] Greluk, M., and Hubicki, Z., 2009. Sorption of SPADNS azo dye on polystyrene anion exchangers: Equilibrium and kinetic studies, *Journal of Hazardous Materials*, 172: 289-527.
- [12] Hameed, B.H., Salman, J.M., and Ahmad, A.L., 2009. Adsorption isotherm and kinetic modeling of 2, 4-D pesticide on activated carbon derived from date Stones, *Journal of Hazardous Materials*, 163: 121-126.
- [13] Haron, M. J., Yunus, W.M., Desa, M. Z., Kassim, A., 1994. Synthesis and properties of poly(hydroxamic acid) from crosslink poly (methacrylate), *Talanta*, 41: 805-807.
- [14] Ho, Y.S., and McKay, G., 1999. Pseudo-second order model for sorption processes, *Process Biochemistry*, 34: 451-465.
- [15] Hoidy, W.H., Ahmad, M.B., Al-Mulla, E.A.J., Yunus W.M.Z.W., and Ibrahim N. B., 2010. Synthesis and Characterization of fatty Hydroxamic Acids from Triacylglycerides, *Journal of Oleo Science*, 59: 15-19.
- [16] Holmes, J., Mast, K., Marcotte, P., Elmore, I., Li, J., Pease, L., Glaser, K., Morgan, D., Michaelides, M., and Davidsen, S., 2001. Discovery of hydroxamic acid inhibitors of tumor necrosis factor- $\alpha$  converting enzyme, *Bioorganic Medicinal Chemistry Letters*, 11: 2907-2910.
- [17] Jahangirian, H., Haron, M. J., Silong, S., and Yusof, N. A., 2011. Preparation of fatty hydroxamic acid from canola oil, *Asian Journal of Chemistry*, 23: 3371-3374.
- [18] Kurzak, B., Kozłowski, A., and Farkas F., 1992. Hydroxamic acid and amino hydroxamic acids and their complexes with metal ions, *Coordination Chemistry Reviews*, 114: 169-200.
- [19] Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens Handlingar* 24: 1-39.
- [20] Li, Z., Alessi, D., Zhang, P., and Bowman, R.S., 2002. Organo-illite as a low permeability sorbent to retard migration of anionic contaminants, *Journal of Environmental Engineering*, 128: 538-587.
- [21] Li, Z., Bowman, R.S., 2001. Retention of inorganic oxyanions by organo-kaolinite, *Water Research*, 35: 3771-3776.
- [22] Low, M.J.D., 1960. Kinetics of chemisorption of gases on solids, *Chemical Reviews*, 60: 267-312.
- [23] Ma, F., Hanna, M.A., 1999. Biodiesel production: a review, *Bioresource Technology*, 70: 1-15.
- [24] Masuyama, A., Akiyama, K.I., Okahara, M., 1987. Surface active hydroxamic acids. I. preparation and properties of long-chain alkyl oligo (oxyethylenehydroxamic acids), *Journal of the American Oil Chemists' Society*, 64: 764-768.
- [25] McKay, G., Ho, Y.S., and Ng, J.C.Y., 1999. Biosorption of copper from waste waters: a review, *Separation and Purification Methods*, 28: 87-125.
- [26] Miller, J.D., Wang, X., and Li, M., 2002. Selective flotation of phosphate minerals with hydroxamate collectors, *U.S. Pat.*, 17.
- [27] Murray, H., 2007. *Applied Clay Mineralogy*. 1st Ed., Elsevier, Amsterdam, pp. 275-301.
- [28] Pavlidon, S., and Papaspyrides C.D., 2008. A review on polymer-layered silica nanocomposites, *Progress in Polymer Science*, 33: 1119-98.
- [29] Rauf, N., and Tahir, S., 2000. Adsorption onto Bentonite from Aqueous Solutions, *Journal of Thermodynamics*, 32: 651-658.
- [30] Servat, F., Montet, D., Pinao, M., Galzy, P., Arnaud, A., Ledon, H., Marcou, L., and Graillea, J., 1990. Synthesis of fatty hydroxamic acids catalyzed by the lipase of *Mucor Miehei*, *Journal of the American Oil Chemists' Society*, 67: 646-649.
- [31] Sparks, D.L., 1986. Kinetics of reaction in pure and mixed systems, In: *Soil Physical Chemistry*, Edited by Sparks, D. L., CRC Press, and Boca Raton, Florida.
- [32] Srivastava, P., Singh, B., and Angove, M., 2005. Competitive adsorption behavior of heavy metals on kaolinite, *Chemical Journal of Colloid Interface Science*, 290: 28-38.
- [33] Trevino, J., and Coles, C., 2003. Kaolinite properties, structure and influence of metal retention on pH, *Applied Clay Science*, 23: 133-139.
- [34] Vaysse, L., Dubreucq, E., Pirat, J. L., and Galzy, P., 1997. Fatty hydroxamic acid biosynthesis in aqueous medium in the presence of the lipase-acyltransferase from *Candida parapsilosis*, *Journal of Biotechnology*, 53: 41-46.
- [35] Wilson, M. J., 1994. *Clay Mineralogy Spectroscopic and Determinative Methods*. Chapman and Hall, UK.
- [36] Wu, F. C., Tseng, R. L., and Juang, R. S., 2009. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics, *Chemical Engineering Journal*. 153: 1-8.