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Abstract

The investigation aimed at improving the palm oil β -carotene adsorption capacity of smectite clay. With mixtures of Fe (II) / clay mass percentage of 0.1, 0.15 and 0.2 %, the beaching capacity of clay increased from 41 % to 45.2, 52.5, and 56.7% respectively. The optimum processing parameters applied were 90 °C for temperature, 0.04 for adsorbent/oil mass ratio, and 60 min for contact time. The suggested mechanism indicated that the fixation of β -carotene onto Clay-Fe(II) sites was controlled by weak Van der Waals bonds with a rate constant of 0.0048 m g⁻¹.min indicating the higher speed of interactions compared to that of raw clay (0.0040 m g⁻¹), that turns out as a benefit to the easy recyclability of the adsorbent. For both adsorbents, Clay-Fe (II) and raw clay, the intra-particle diffusion kinetic model best fit with R² values of 0.9721 and 0.9743 respectively.

Keywords: *Smectite clay, Lewis acid, palm oil, β -carotene, bleaching capacity, kinetic and mechanism*

1.0 INTRODUCTION

Palm oil is a vegetable oil that can be either used directly for consumption or as a raw material in the manufacture for many industrial and cosmetic products (Nde-Aga et al., 2007; Ojewuni et al., 2021). As produced palm oil contains phospholipids, hydroxides, trace of metals, pigments (carotenoids and chlorophylls) and oxidizing by-products that limit its conservation and applications (Nguetkam et al., 2008; Ribeiro et al., 2008). The orange-red color due to the relatively high β -carotene content is always considered as a flaw for most applications (Hamad et al., 2009; Porhdorf et al., 2016). For this reason, discoloration is one of the main steps of the refining process of palm oil; it is generally carried out by adsorption thanks to some typical adsorbents such as zeolites, silica, alumina and clays to only listed that. Extensive results so far put emphasis on the effect of experimental parameters on bleaching capacity such as concentration of the activators, ambient temperature, activation time and on the kinetic study of adsorption process (Nguetkam et al., 2008; Djoufac et al., 2007; Huseyin et al., 2007; Sabah et al., 2007; Tong et al., 2009; Didi et al., 2009; Kurtulbas et al., 2021; Tawfik et al., 2021).

To enhance the bleaching capacity of clay, mineral acids and bases as well as thermal treatment are often used with satisfactory results (Hymore et al., 1996; Shaked et al., 1998; Djoufac et al., 2007; Nguetkam et al., 2008; Tong et al., 2009; Mustapha et al., 2013; Porhdorf et al., 2016; Testaye et al., 2017; Alastair et al., 2018; Nde et al., 2019; Baptiste et al., 2020). However, when dealing with heating or reaction with Brönsted acids or bases to activate clays, the destruction of clay lattice is awkward as the recyclability and durability of the obtained adsorbents are concerned (Shaked et al., 1998). Previous works reported successful decomposition of β -carotene by metal salts such as those of Fe (III), Cu (II) or Al (III) (Shaked et al., 1998).

Similarly, great improvement in bleaching palm oil capacity of clays was achieved by previous activation of clays with sulphuric acid and then addition of Fe (III) chloride or Cu (II) sulphate (Hymore et al., 1996). It can be pointed out that current data on this interesting aspect of clay activation with these metal salts are limited. Moreover, these activators are actually Lewis acids, and such might surely have different mechanism and tendency to meddle with clays in comparison to that of Brönsted acids that are already widely discussed in the literature. Therefore, the present work is one more contribution that discusses the use of Lewis acids to activate clays destined for the bleaching of palm oil. Likewise, it targeted the complete study in terms of mechanism and kinetic adsorption of clay activated by Fe (II) sulfate. The choice of clay and iron was motivated by their availability in our area and their not harmfulness for consumption application of the oil to be bleached.

2.0 EXPERIMENTAL

2.1 Materials and Chemical Reagents

The smectite clay used in this work comes from the locality of Bana (West, Cameroon). A previous work (Mache et al., 2015) on this material has shown that its basic mineral is a

Ca-montmorillonite associated with kaolinite, hematite, anatase, micas and k-feldspars. The physical characteristics, chemical and mineralogical compositions of the material are given in table1.

Table 1: Characteristics of the clay material wet sieved at 63 μm

Physical characteristics												
Color (code Munsell)	5Y8/4: pale yellow											
BET Specific area (m^2/g)	64.8											
Micropores Surface (m^2/g)	28.2											
Non-micropores surface (m^2/g)	40.8											
CEC (m $\acute{\text{e}}$ q/100g)	56-60											
pH	4.2											
SiO ₂ /Al ₂ O	2.28											
Fraction $\leq 2\mu\text{m}$ (%)	9.5											
$2\mu\text{m} < \text{Fraction} \leq 63 \mu\text{m}$ (%)	90.5											
Chemical Composition												
Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI	T
Wt.%	50.94	22.39	5.52	0.01	0.05	1.85	0.70	0.02	2.31	0.26	16.15	100
Mineralogical Composition												
Mineral	Mont	Mica	Kao	Qtz	An	K-feldspars		Hematite				
Wt.%	70.5	9.0	7.2	1.5	2.1	0.8		7.3				

Mont: Montmorillonite, Kao: kaolinite, An: Anatase, Qtz: Quartz

The crude Palm oil is local oil purchased from Master Foods Co. (Cameroon). The oil was stored in the dark chamber at low temperature to avoid any degradation of the pigments. All chemicals and reagents used are of analytical grade, and have been used without any further treatment: Iron (II) sulfate heptahydrate (FeSO₄.7H₂O), Sulfuric acid (H₂SO₄) 98%) from PROLABO ANALAR, 1-10-Phenanthroline monohydrate (C₁₂H₈N₂.H₂O) 99.5%) from E MERCK Typanalysis, Trisodium Citrate dihydrate (Na₃C₆H₅O₇.2H₂O) 99% from E.MERCK Typanalysis, Hydroxylammonium chloride (NH₃OH.Cl) 99% from Riedel-De-Haen Typanalye , Acetone (H₃CCOCH₃ 99% from PROLABO, pure anhydrous Disodium carbonate (Na₂CO₃) from LABOSI, Bariyum dichloride dihydrate (BaCl₂.2H₂O 98%) from PROBUS and Helianthine as a colored indicator.

2.2 Instrumentation

The main experimental device of this study is a thermostatic reactor Thermocryostat type MGW LAUDA RM6 ($T_{\max}=100$) presented in Figure 1. A UV-visible FT-IR spectrophotometer type HACH 2500 Odyssey was used to confirm the fixation of Fe (II) onto smectite clay surface. A P. SELECTA type centrifuge type was used to separate the solid phase of each solution from its liquid phase. The pH of the Fe(II) solutions were measured using an Electronic pH-meter type SHOTT GERÄTE CG81 equipped with a calomel electrode SCHOTT GERÄTE type B180N and a glass electrode SCHOTT GERÄTE type N 15.

2.3 Clay, Sampling and Activation with Fe (II) Ions

A clay sample was wet sieved with 63 μm mesh and dried at 105°C in oven to a powder. One part of this clay powder was directly used as adsorbent denoted as “Clay” and the other activated with Fe (II) ions. For this, 1000 ppm solution was prepared using Fe (II) sulphate heptahydrate ($\text{Fe} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$) and from thence, aliquot solutions (40, 80, 90, 100, 125, 150, 200, 300, 400 and 450 ppm) were obtained by dilution. For each solution, 100 mL were introduced into the thermostatic reactor at $26 \pm 1^\circ\text{C}$ and the pH was adjusted to 3 by adding 2-3 drops of 25% trisodium citrate or 0.1N sulphuric acid solutions respectively to increase or to decrease the pH value of the Fe(II) solution. This value of pH is for an acid environment to avoid hydroxides formation, and was fixed according to the iron trace titration described by Douglas et al. (1969). Then, 1 g of clay powder was added and the mixture was stirred for 90 min before centrifugation to separate from the filtrate the solid activated clay, the latter was denoted Clay-Fe (II) adsorbent.

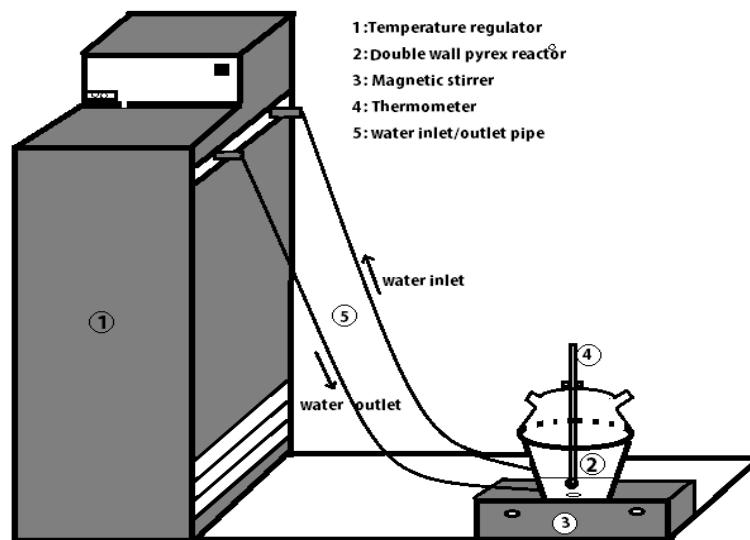
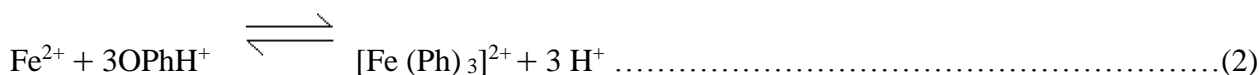


Figure 1: Experimental device

The filtrate was titrated to measure the amount of the remaining unadsorbed Fe(II) ions in order to evaluate the amount of Fe(II) ions fixed onto the clay (Q_{ads}) and the results are shown in Table

2 For this purpose, 1 mL of 10% hydroxyammonium hydrochloride solution and 2 mL of the 0.5% orthophenanthroline solution were mixed with 5 mL of the solution to be analysed and the pH was adjusted to 3 as described above. In such a slightly acidic environment, orthophenanthroline (O-Ph) which is a weak base protonizes and releases orthophenanthroline ion (OphH⁺) that formed an orange colour complex with the Fe(II) ions easily following equations (1) & (2) respectively.



Phenanthroline ion Orange-red Fe(II)-complex

This complex was analysed by UV-visible spectrophotometry, type HACH 2500 Odyssey apparatus. The absorbance (A) was then measured at the wavelength λ varying from 370 to 800 nm for a 5 ppm solution of complex. Figure 2a presents the absorption spectrum whereas Figure 2b shows the curve of $A = f(C)$. Where A is the absorbance corresponding to the concentration C of complex solution. The calibration straight line obtained was used to calculate the amount of remaining unadsorbed Fe(II) ions at equilibrium (Q_r), and then Q_{ads} is deduced according to the Equation 3 (Kammegne et al., 2017; Tchanang et al., 2022).

$$Q_{\text{ads}} = \frac{(Q_0 - Q_r)}{m} \dots\dots\dots(3)$$

Where Q₀ is the initial quantity of Fe (II) ions and m the considered mass of adsorbent. Q₀ and Q_r are calculated using Equations 4 & 5 respectively.

$$Q_0 = C_0 V \dots\dots\dots(4)$$

$$Q_r = C_r V \dots\dots\dots(5)$$

Where C₀, C_r and V are the initial concentration, the concentration after contact with clay (ppm) and the volume (L) of the Fe(II) solution. C_r is obtained by using the calibration curve of Figure

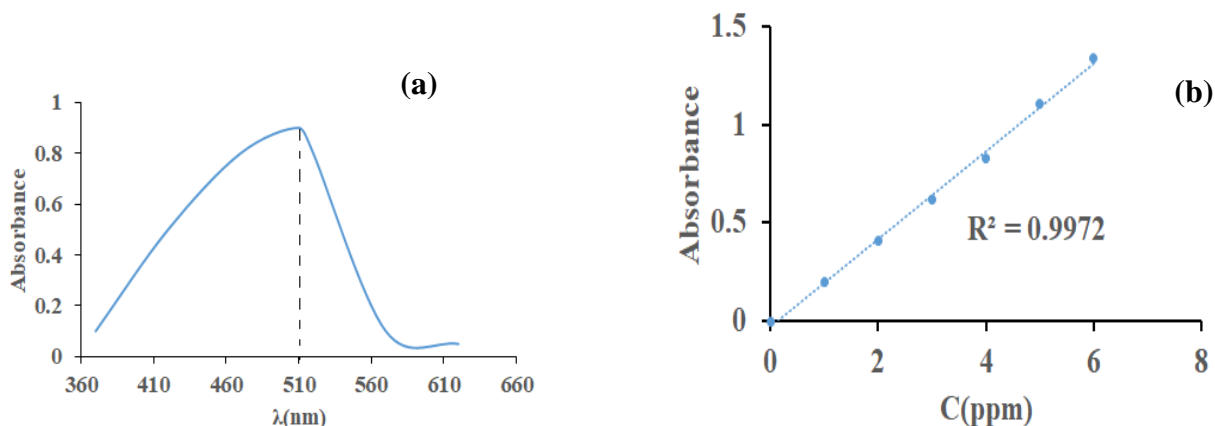


Figure 2: (a) Absorbance spectrum

(b) Calibration line of the Orange-red Fe (II)-complex

Table 2: The overall mass percentage of Fe (II) fixed onto the Smectite clay

Initial mass (mg) of Fe(II) ions in 100 mL of solution(Q_0)	Remaining mass (mg) of Fe(II) ions in solution (Q_r)	Mass of Fe(II) ions (mg) fixed onto 1g of clay	Mass percentage of fixed Fe(II) ions (%) onto clay
0	0	0	0
4	3.05	0.95	0.095
8	6.58	1.52	0.151
9	6.96	2.04	0.204
10	7.93	2.07	0.207
12.5	10.38	2.12	0.212
15	12.87	2.13	0.213
20	17.85	2.15	0.215
30	27.74	2.26	0.226
40	37.65	2.35	0.235
45	42.53	2.37	0.246

2.4 Bleaching of Palm Oil

2.4.1 Experiments

For each of the two adsorbents Clay and Clay-Fe (II), experiments were performed in a thermostatically controlled reactor (Figure1), stirring at 100 rpm at the varied temperatures of 80,

90 and 95°C. The mixture of palm oil and adsorbent with an adsorbent/oil mass ratio ranging from 0.01 to 0.05.

To access the bleaching capacity of the adsorbent, the adsorbent and oil mixture was filtered under vacuum using Whatman paper N°1; the bleaching capacity was then measured thanks to a UV-vis spectrophotometer calibrated at the maximum absorption wavelength of 450 nm taking acetone as the reference solution. 450 nm is the optimal value of the Wavelength obtained by diluting 0.05 g of palm oil in 5 mL of acetone (98%), and the absorbance values were measured at wavelengths ranging from 370 to 700 nm. The plot $A = f(\lambda)$ given by Figure 3 indicated that needed value (450nm). The bleaching capacity (BC) of the adsorbent were calculated using Equation 4 (Nwabanne et al., 2004; Nguetkam et al., 2008; Kammegne et al., 2017).

$$BC (\%) = \frac{(A_0 - A_t) \times 100}{A_0} \dots\dots\dots(6)$$

Where A_0 and A_t are respectively the absorbance of initial palm oil and that of the oil after contact with adsorbent during the time t .

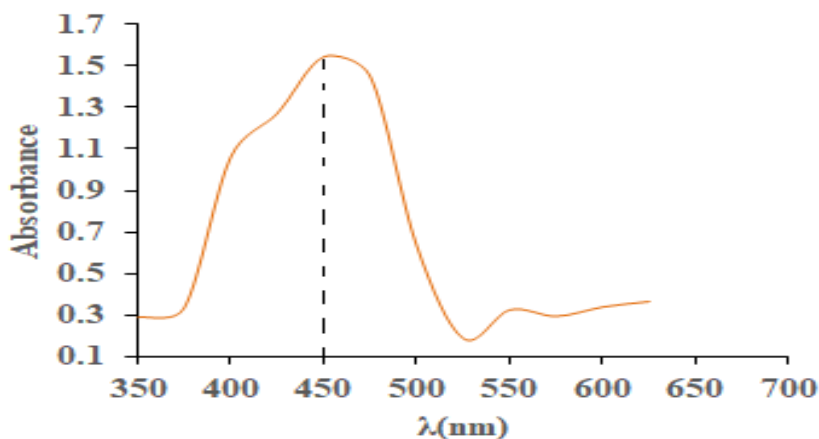


Figure 3: Absorption spectrum of β -carotene

The effect of some processing parameters on the bleaching capacity was investigated: firstly, the effect of the quantity of Fe (II) fixed onto clay, the adsorbent/oil mass ratio ranging from 0.01 to 0.05. For the adsorbent/oil mass ratio of 0.04 (e.i 0.2 g of adsorbent for 5g of oil) that gave good results, the bleaching temperature was changed at 80, 90 and 95°C.

2.4.2 Kinetic Study

The contact time from 0 to 150 min with 10 min increment was applied for each of the two adsorbents Clay and Clay-Fe at the adsorbent/oil mass ratio of 0.04 and the temperature of 90°C.

The relative amounts of β -carotene adsorbed at equilibrium (Q_e) and at time t (Q_t) were calculated using Equations 7 & 8.

$$Q_e = \frac{A_0 - A_e}{A_0 m} \dots\dots\dots(7)$$

$$Q_t = \frac{A_0 - A_t}{A_0 m} \dots\dots\dots(8)$$

Where A_0 , A_e and A_t are the absorbance of the crude, the decolorized oil at equilibrium and decolorized oil at time t respectively and m is the mass of adsorbent used. Three different kinetic models were used for a better understanding of the adsorption mechanism and its characteristics.

Pseudo-1st Order Kinetic Model

The pseudo-1st order kinetic modeling is given by Equation 9 (Ahmad et al., 2009; Nwabanne et al., 2018).

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \dots\dots\dots(9)$$

K_1 (min^{-1}) is the kinetic constant of the 1st order, t (min) is the time; Q_e and Q_t (mg / g) represent the amounts of β -carotene adsorbed at equilibrium and at time t respectively. By considering Equations 7 & 8, Equation 9 can be rewritten as a function of absorbances and leads to Equation 10.

$$\ln \frac{(A_t - A_e)}{(A_0 - A_e)} = -K_1 t \dots\dots\dots(10)$$

Pseudo-2nd Order Kinetic Model

The pseudo-2nd order kinetic modeling is given by Equation 11 (Nwabanne et al., 2018)

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \dots\dots\dots(11)$$

Where K_2 ($\text{mg}^{-1}\text{g}\cdot\text{min}$) is the 2nd order kinetic constant. Equation 11 can be rewritten as a function of absorbances as:

$$\frac{t}{A_0 - A_t} = \frac{A_0 m}{K_2 (A_0 - A_e)^2} + \frac{t}{(A_0 - A_e)} \dots\dots\dots(11)$$

By setting $K = k_2/A_0 m$ ($\text{mg}^{-1}\cdot\text{min}$) into Equation 11 we have:

$$\frac{t}{A_0 - A_t} = \frac{1}{K(A_0 - A_\infty)^2} + \frac{t}{(A_0 - A_\infty)} \dots\dots\dots(12)$$

Intraparticle diffusion kinetic model

The Weber–Morris intraparticle diffusion model is expressed as:

$$Q_t = K_{id}t^{1/2} + \gamma \dots\dots\dots(13)$$

Where k_{id} (mg/gmin^{0.5}) is the intra-particle diffusion rate constant and γ (mg/g) is associated to the boundary layer thickness. If intra-particle diffusion is the limiting step of adsorption process, the plot Q_t against $t^{1/2}$ is a straight line. According to the Weber–Morris model, it is essential that the plot goes through the origin if intraparticle diffusion is the only rate-limiting step (Ludmila et al., 2020). As a function of absorbances, a new expression of intraparticle diffusion model is given by Equation 14.

$$A_0 - A_t = A_0 m K_{id} t^{1/2} + A_0 m \gamma \dots\dots\dots(14)$$

By setting $K'_{id} = A_0 m K_{id}$ (in mg/min^{0.5}) and $\gamma' = A_0 m \gamma$ (in mg) Equation14 becomes:

$$A_0 - A_t = K'_{id} t^{1/2} + \gamma' \dots\dots\dots(15)$$

3.0 RESULTS AND DISCUSSION

3.1 Quantity of Iron (II) Fixed onto Clay

Table 2 gives the quantity (Q_{ads}) deduced from the spectrometry determination of remaining iron (II) Q_r after clay activation, comparison to the initial value Q_0 . It shows that the quantity of Fe (II) adsorbed increases with the initial quantity Q_0 , then reaches an equilibrium. In fact, when the surface of the clay is not yet saturated, it continues to fix more and more ions until it reached a limit. That steady state is due to the fact that the surface of the clay is completely covered with Fe (II) ions, thus creating an electrostatic repulsion on the other ions which seek to attach themselves (Silva et al., 2013) [28]. According to the previous Q_{ads} values in the Table 2, 0.1; 0.15, 0.2 and 0.25% were considered to investigate the effect of the mass percentage of fixed Fe (II) on the

bleaching capacity of the activated smectites clay.

3.2 Structure of the Activated Clay by Fe (II)

Figure 4 presents the FTIR spectra of the two adsorbents used, Clay and Clay-Fe (II). It can be evidenced from the figure that bands allocated to non Fe-related bonds are superimposable for the both adsorbents: the band at 1624 cm^{-1} and the broad band around 3408 cm^{-1} due to the stretching and bending vibration of H-O-H. Finally, the band at 3621 cm^{-1} corresponds to stretching vibrations of Al-Al-OH or Al-Mg-OH. But the difference occurred for the bands related to the Si-O-Fe groups between 400 and 600 cm^{-1} and to Fe-OH groups between 880 and 1100 cm^{-1} (Maguie et al., 2017) [29]. The latter bands exhibited higher absorbance for Clay-Fe (II), indicating that the fixation of Fe(II) onto clay has just provoked the rise of the Fe-related bands intensity. This is a clear demonstration that the structure of the clay was not really altered during the activation, in comparison to Brönsted acid activation which generally destroys the clay lattice due to protonation followed by the leaching of silanol and aluminol groups as demonstrated in literature (Madejová et al., 1998; Djoufac et al., 2007; Nguetkam et al., 2008) This is a proof that the fixation of iron onto clay is a surface phenomenon; it is then found to be very interesting as the recyclability and durability of the activated clay adsorbent are concerned. In other terms, the Clay lattice is maintained after activation, thereby the fixation of Fe(II) as Lewis-acid.

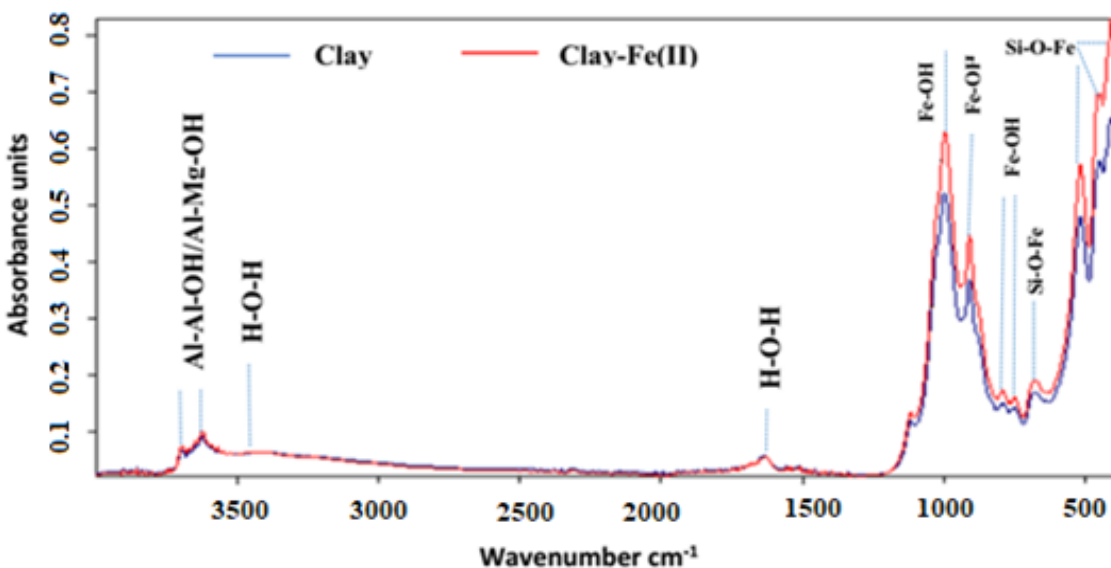


Figure 4: FTIR Spectra of adsorbents: raw clay (Clay) and Clay activated with iron (II) sulphate heptahydrate (Clay-Fe (II)).

3.3 Bleaching Capacity of Clay

3.3.1. Effect of Fe(II) Adsorption onto Clay and Mechanism

Figure 5 shows the progress of bleaching capacity with the amount of Fe(II) ions adsorbed onto

the clay. There is a slight increase up to 0.1% (1 mg of Fe (II)/g of clay) then a speedy increase up to 0.2% (2 mg of Fe(II) /g of clay) where a level up tendency is observed. The increase of bleaching capacity can be attributed to the presence of Fe (II) ions which are actually Lewis acid with empty quantum cases that are active sites on clay surfaces (James et al., 2008; Gu et al., 2020). This suggests that an increase of the amount of Fe (II) adsorbed onto the clay is a comprehensive way to raise the number of active sites ready to react with carotene as non-ionic molecules with double bond chains. In agreement with the mechanism described by Jahouac-rabia et al. (Jahouac-rabia et al., 2009).

Figures. 6a & 6b were set up to demonstrate how carotene molecule is adsorbed on clay and Clay-Fe(II) respectively. In general, there is transfer of electrons to adsorbent's quantum cases that are from aluminium and silicon (Helen et al., 2016) for Clay (Figure 6a) and also from iron for Clay-Fe(II). In the latter case, the quantum cases may have resulted from the reorganization of the d-orbitals electrons after the electrons exchange with silanol from clay (Figure 6b). In this environment, electrons from non-ionic molecules containing multiple combined bonds such as β -carotene are obviously transferred to the available quantum cases. This mechanism described that the fixation of iron onto clay is a surface phenomenon, it has not altered the clay structure. This is in accordance with FTIR analysis result discussed above that exhibited bands in Clay and Clay-Fe(II) at the same frequencies with the only difference at the level of the higher intensity of peaks related to iron bonds in the case of Clay-Fe (II).

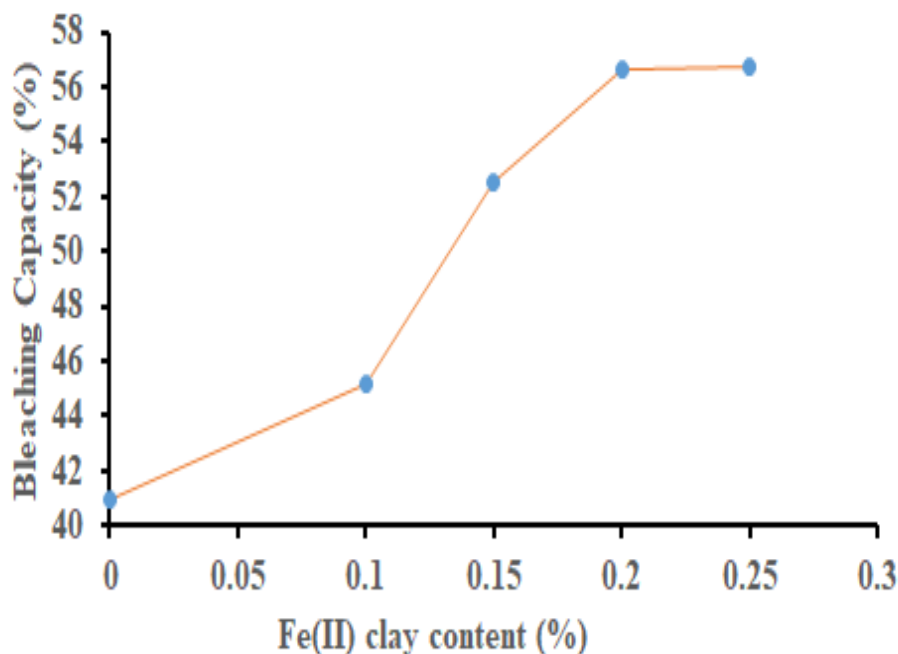


Figure 5: Influence of the adsorbed Fe (II) clay content on the elimination of β -carotene

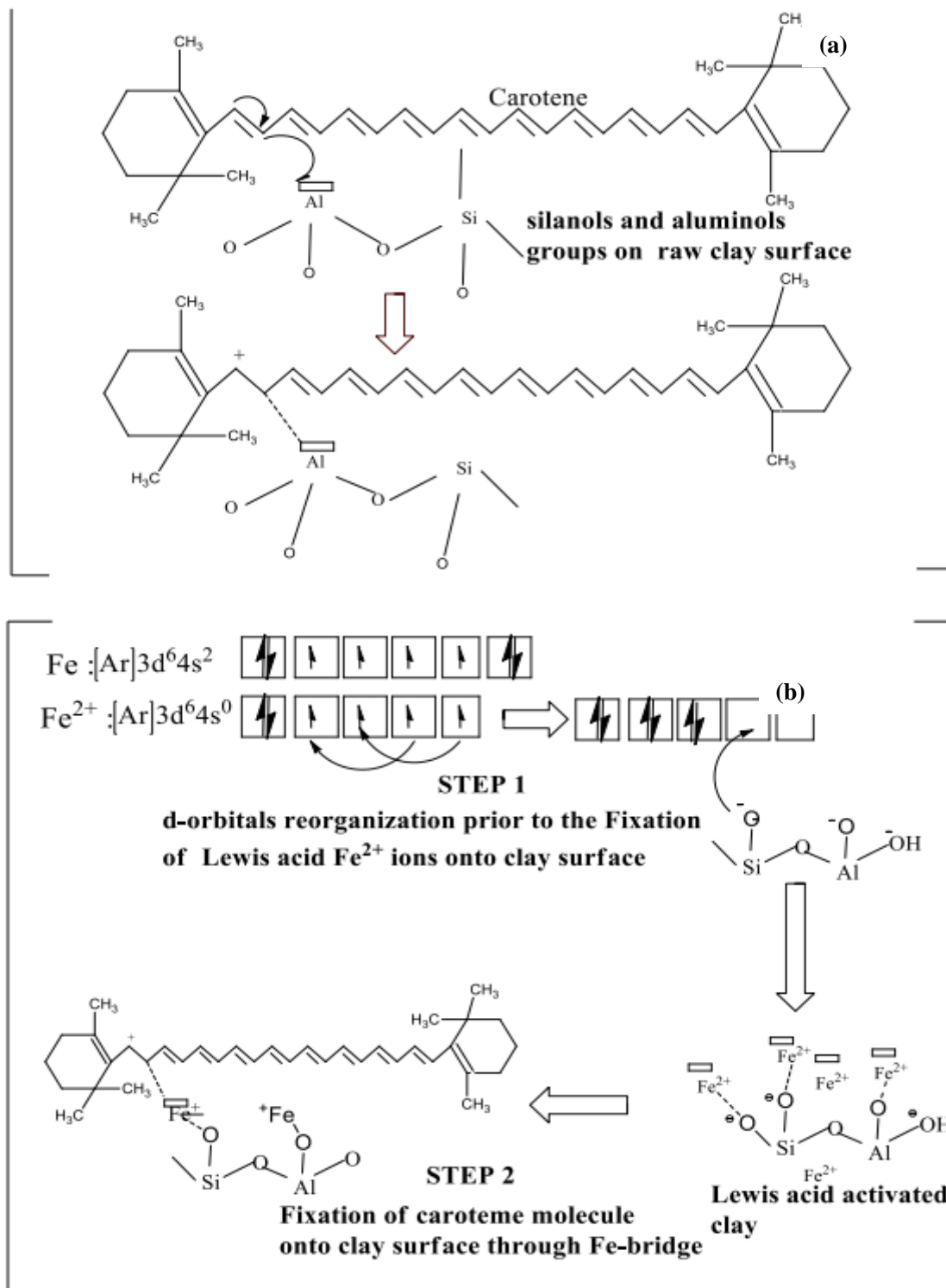


Figure. 6: Mechanism of the adsorption of β -carotene on (a) clay sites, (b) Clay-Fe(II) sites

3.3.2. Effect of Adsorbent Dosage on the Bleaching Capacity

Figure 7 shows an increase of the bleaching capacity with the mass of adsorbent for the two adsorbents Clay and Clay-Fe(II). Also, the rate of increase has a constant slope up to 0.2 g, and beyond has a bearing tendency indicating a maximum value with no significant change. Moreover, bleaching capacity values remain greater for Clay- Fe(II) than for Clay. These observations are in agreement with the adsorption mechanism of the bleaching process, thereby, it is mainly controlled by the availability of active sites for adsorption. Their number obviously increase with the mass of adsorbent evolving the adsorption process, but always reaches a steady-state due to the saturation. Saturation of sites is a frequent occurrence in adsorption, it has similarities with equilibrium state since both are pertaining to the stationary state of the process. It seems there is obstruction of the active sites that reduces the mobility and limits the binding of the adsorbate (Huseyin et al., 2007; Didi et al., 2009; Nwabanne et al., 2013; Kammegne et al., 2017). It also came out that Clay-Fe (II) was more efficient than Clay due to the cumulative effect of classical active sites and Lewis-acid active sites on the surface of Clay-Fe(II). As discussed above, the activation of clay by fixation of Fe(II) is also an adsorption process that is also limited by the saturation of sites despite its higher number for Clay-Fe(II). From this result it can be admitted that 0.2 g is the optimum mass for 5 g of oil corresponding to adsorbent/oil mass percentage of 4% for the two adsorbents.

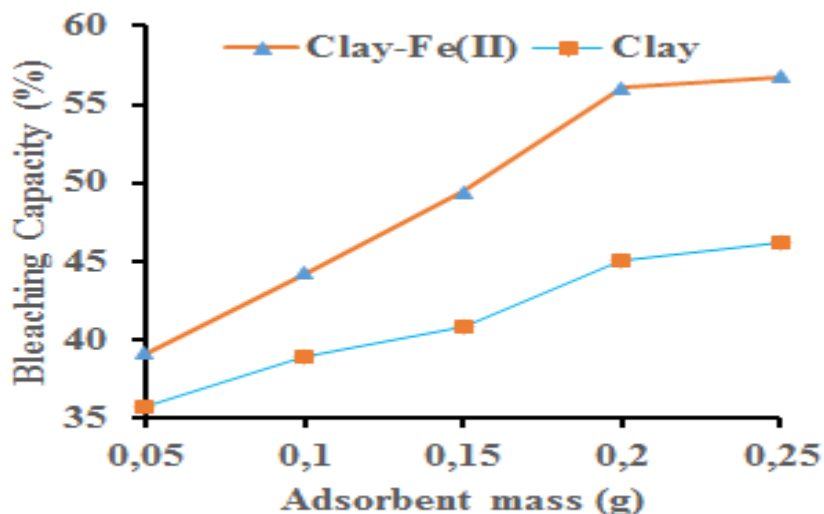


Figure 7: Influence of adsorbent dosage on the bleaching capacity of

3.3.3. Effect of Temperature

Figure 8 revealed that increase in temperature of the reactor begets more efficiency in bleaching capacity of the two adsorbents, Clay and Clay-Fe(II). The highest value at 90°C is around 57% for Clay-Fe(II) and 41% for obtained Clay, the latter was the maximum that can be handled in

aqueous environment avoiding evaporation. The increase in temperature reduces the adsorbate viscosity allowing the better dispersion of the adsorbent particles and therefore an increase in clay-oil interactions. Moreover, the promoting dependence of adsorption capacity of the to temperature is in good agreement with the activation of adsorption sites on clay as demonstrated in previous works (Alastair et al., 2018).

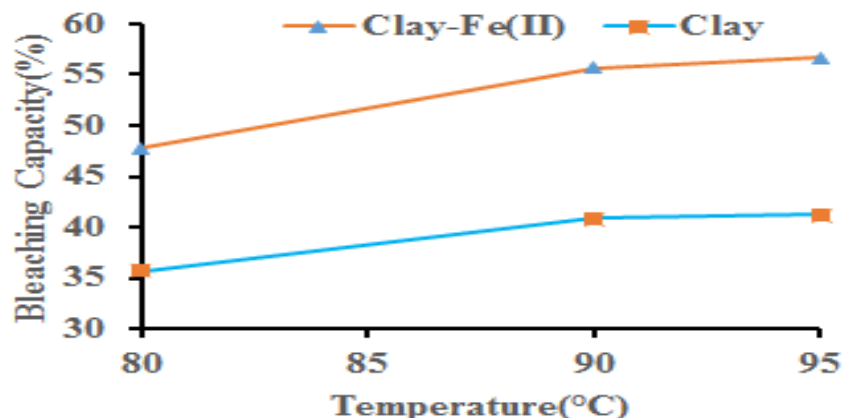


Figure 8: plot of the effect of temperature on the bleaching capacity of Clay and Clay-Fe(II).

3.3.4. Effect of Contact Time

It appears in Figure 9 that the bleaching capacity increases with the contact time up to around 60 min, then reaches a steady value which is 41% for Clay and 57% for Clay-Fe(II). These results are similar to those obtained by Ajemba & Unukwuli for the two cases, the equilibrium time for β -carotene elimination is around 60 min. Other authors found less time for equilibrium, the tendency in most common cases is ranging from 15 to 45 min (Ajemba & Unukwuli; 2012).

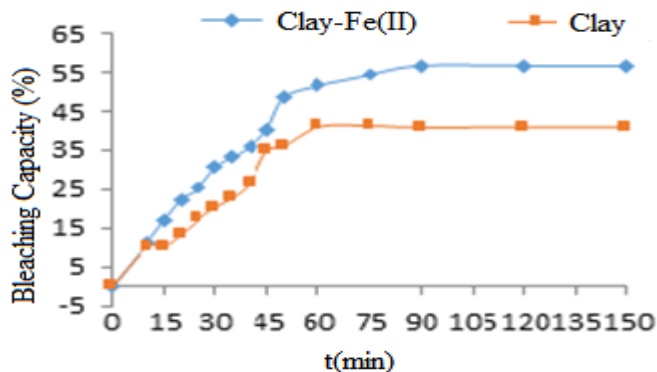


Figure 9: Bleaching capacity as a function of time.

Definitively, the activation of smectite clay by Fe(II), that has Lewis acid character is an adsorption mechanism with equilibrium concentration of 0.2%, that is 2 mg of Fe(II) per gram of clay. The bleaching capacity of this activated adsorbent (Clay-Fe(II)) in optima parameters (90°C of temperature, 45 min of contact time and 4% of adsorbent /oil mass ratio) is 57%. This value is greater than those of commercial smectites and in contrary less than those of bronsted acids activated smectites shown in table 4 (Nguetkam et al., 2008; Baptiste et al., 2020; Nwabanne et al., 2013; Nwabanne et al., 2018; Anyikwa et al., 2021). However, the use of Lewis acid in clay activation is advantageous because it maintains the clay lattice that is favourable to its reuse. The lower time of contact at the same temperature in comparison with others is also valuable to the use of Lewis.

Table 3: Bleaching capacity of Fe(II) activated clay for β -carotene rich-palm oil and those of other adsorbents

Adsorbent (s)	Optimal parameters (Temperature/contact time/Adsorbent/oil ratio)	Percentage of β-carotene retained	Other workers
Commercial smectites (Fulmont, FlorB80 and Enge)	95 °C /30-60min / 2%/crude palm oil	50%	Nguetkam et al., 2008 [3]
Bronsted acid Activated smectites clay	110-90°C/90-70min/2-3%/ crude palm oil	96-50%	JM Bike Bah et al., 2020 [20], Nwabanne et al., 2018 [24]
Fe(II) activated smectite	90°C/45min/4%/crude palm oil	57%	Present work
5M H ₂ SO ₄ kaolin clay	120°C/3%/30min/ crude palm oil	77.87%	Onyikwa et al., 2021 [35]
Polymeric resin (diaion HP-20)	30°C /25min/10%crude hybrid palm oil	80%	Ludmila et al., 2020 [25]
4N H ₂ SO ₄ activated smectite clay	95 °C /2.5 h / 2%/palm oil	90%	Nguetkam et al., 2008 [3]

Kinetic Models

For the sake of a better understanding of the kinetic from which adsorbent uptake rate can better be explained, facilitating the appreciation of the adsorption efficiency; Plots of three (03) different kinetic models are presented on Figures 10-12 and Table 3 summarizes the values of the correlation coefficient R^2 and constant rate respectively for pseudo first order, pseudo-second order and the intra-particle diffusion models. It can be deduced from these experimental parameters that the adsorption onto Clay does not well fit neither pseudo first order kinetic nor pseudo-second order whereas for Clay-Fe(II), the adsorption best fitted in pseudo-first order kinetic with $R^2 = 0.9527$ and $K = 0.0090 \text{ min}^{-1}$. Considering that the intra-particle diffusion is typically appropriate to ascertain the adsorption process, the linear line plots pass through origin for both Clay and Clay-Fe (II) adsorbents, indicating the rate-limiting step (Figure 12). It was finally shown that the adsorption of carotene onto a smectite clay activated with Fe (II) ions mostly fits well with pseudo-first order and intra-particle diffusion kinetic model regarding to their higher R^2 values which are 0.9527 and 0.9721 respectively compare to that of the pseudo-second order. A similar result has been reported by other authors concerning the adsorption of β -carotene onto acid activated bleaching earth (Nwabanne et al., 2018; Ludmila et al., 2020).

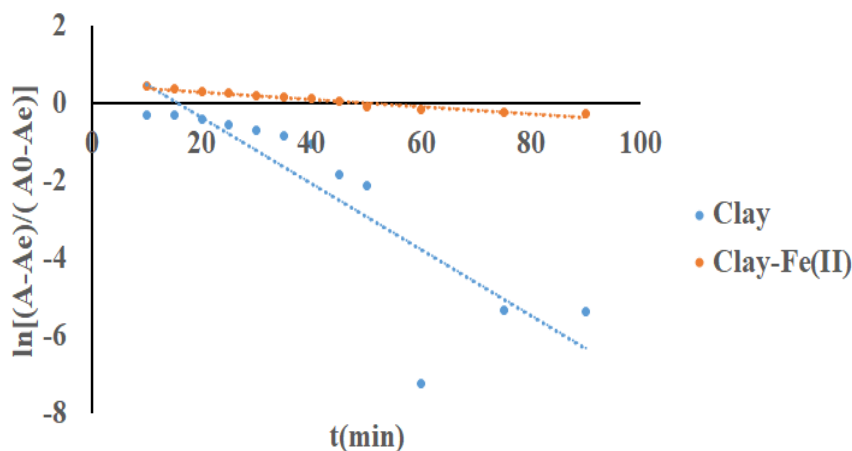


Figure 10: Plot of the pseudo-first order kinetic

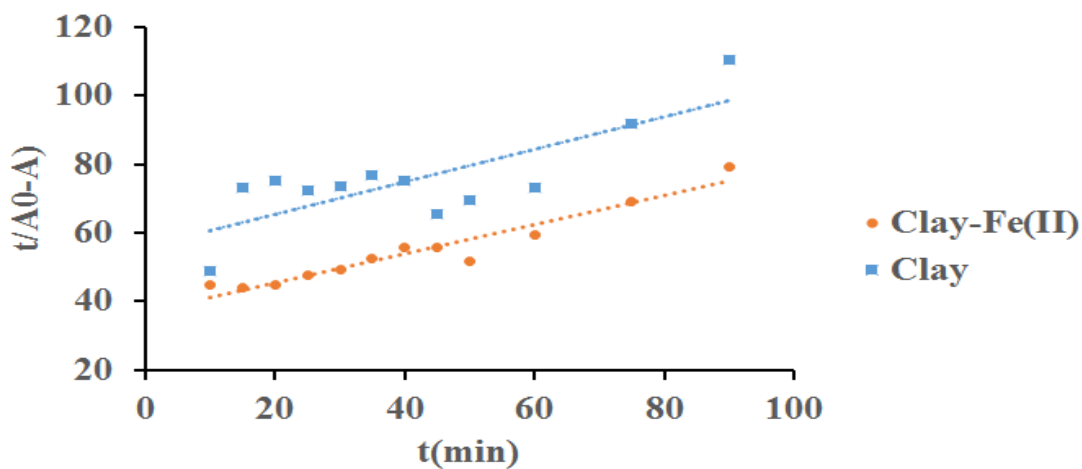


Figure 11: Plot of the pseudo-second order kinetic

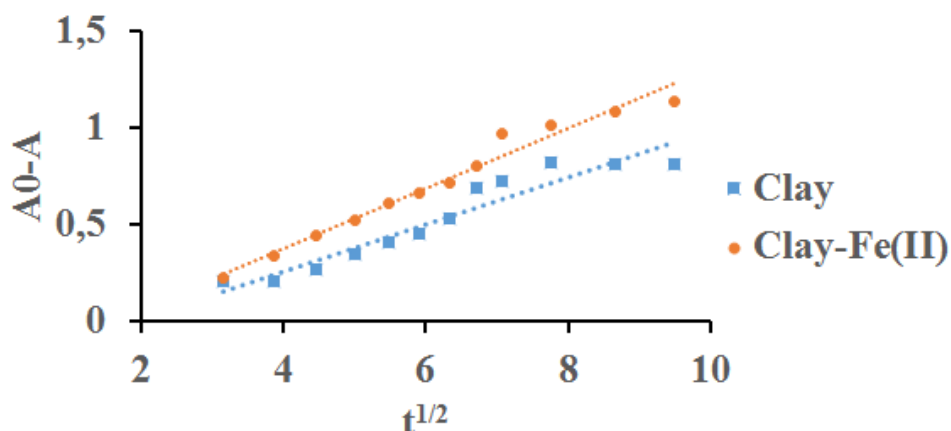


Figure 12: The plot of the intra-particle diffusion model of Clay and clay-Fe

Table 4: Values of the correlation coefficients R^2 and rate constants for the different kinetic models

Samples	Pseudo-First order		Pseudo-second order		Intraparticle diffusion	
	K_1 ($\text{min}^{-1/2}$)	R^2	K ($\text{g.mg}^{-1}.\text{min}^{-1}$)	R^2	K'_{id} ($\text{mg.min}^{-1/2}$)	R^2
Clay	0.0825	0.7384	0.0272	0.6212	0.1219	0.9243
Clay-Fe	0.0090	0.9527	0.0211	0.9280	0.1541	0.9721

CONCLUSION

The activation of clay with Fe (II) compounds is a successful method to ensure the conservation of the clay lattice in contrast with the activation with of bronsted acids. Thereby it is interesting as the durability and recyclability of the adsorbent are concerned. The fixation of Fe(II) ions onto the surface of the clay is done following the adsorption process that creates active sites on iron. The adsorption of β -carotene is then happened via these sites newly created sites making the bridge of iron between clay and adsorbate;

The pre-adsorption of Fe(II) on clay begot an increase of palm oil bleaching capacity from 41% to 57%. The adsorbent dosage, temperature and contact time had a great effect on the bleaching capacity especially with clay activated with Fe(II). In addition, each of the parameters exhibited a steady state which remains however the same for Clay and Clay-Fe(II). For the latter, the optimum processing parameters were 0.04 for adsorbent/oil mass ratio, 0.2% for Fe(II) clay content, 90°C and 60 min for bleaching temperature and contact time respectively. Pseudo-first order kinetics described efficiently the experimental data of bleaching process with Clay-Fe(II) and the intraparticle transport is the sole rate- limiting step as the plot goes through the origin.

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