

Effect of Chemical Activation of Natural Clay by FRRIC Chloride on Adsorption of Nitrobenzene

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Abstract: Natural clays have a high capacity of adsorption after activation. These materials are used to treatment of organics dyes solutions, uses minerals oils and degradation of non biodegradability compounds such us nitrobenzene, chlorobenzene, phenol... etc.

The aim of this work is the effect of chemical activation of natural clay by ferric chloride (FeCl_3) on adsorption of nitrobenzene onto theses new prepared activated clays.

The equilibrium was reached at the end of 4 hours. The adsorption isotherm was well described by the Dubinin-Radushkevich model. The high efficiency of treatment by activated clay is 79.62 %, was obtained at the optimum conditions of activation: activation temperature $T_a = 15^\circ\text{C}$, activation mass ratio (quantity of FeCl_3 /quantity of natural clay) $R_m = 0.3$, activation time $t_a = 15$ min and activation ferric chloride concentration $C = 15$ g/L.

Keywords: Activated clay, Adsorption, Natural clay, Nitrobenzene, Optimization

Date of Submission: 16-08-2018

Date of acceptance: 03-09-2018

I. INTRODUCTION

Wastewaters containing nitrobenzene is a serious environmental problem and these liquids cannot simply be released into the environment without treatment.

Nitrobenzene is present in the effluent from industries engaged in the manufacture of variety of chemicals such as dyes, plastic, pesticides, explosives, pharmaceuticals and intermediates in chemical synthesis industries for years. After use, nitrobenzene in solution is generally discharged to waste treatment plants where a larger proportion of it cannot be removed and finally is discharged into the aquatic environment, which tends to persist in the environment and poses a potential toxic threat to ecological and human health [1, 2].

Therefore, a variety of possible treatment technologies such as ozonation, Fenton process, advanced oxidation process and adsorption have been taken into account for purification of nitrobenzene contaminated water [3, 4, 5, 6, 7].

It is well known that clay minerals can be used to decolorize oils because of its high adsorptive capacity [8]. In other to enhance this adsorptive property, acid activation of clay is the most commonly used technique. This area of clay modification has received enormous interest from various researchers [9, 10].

This paper aims at studying the degradation of nitrobenzene from aqueous solutions by adsorption onto activated clay. It is necessary to product activated clay by chemical activation of natural clay by ferric chloride. Influencing parameters such as time, temperature and amounts of ferric chloride and natural clay are evaluated to characterize the effect of kind of chemical activation on degradation of nitrobenzene by adsorption onto these new prepared materials.

Kinetic study and adsorption isotherm of nitrobenzene by activated clay were presented in this works.

II. MATERIALS AND METHODS

2.1. Materials

2.1.1. Adsorbate (nitrobenzene)

Analytical grade nitrobenzene from ACROS (reference: 12842-0010) was used in the experiments. Aqueous solutions of nitrobenzene were prepared using bi-distilled water.

The initial pH of background solution was adjusted by introducing appropriate amounts of base (NaOH 2M) solutions.

Table 1 presents the principal physico-chemical properties of nitrobenzene.

Table1. Principal physico-chemicals properties of nitrobenzene (ACROS 12842-0010)

Molecular formula	C ₆ H ₅ NO ₂
Physical state	Liquid
Molecular mass (g/mol)	123.0
Fusion point (°C)	5.7
Boiling point at 1 atm (°C)	211.0
Solubility in water at 20°C (g/L)	1.9
Density at 20°C	1.2

2.1.2. Adsorbents (Natural Clay: NC and Activated Clay: AC)

Starting material natural clay was collected from Elhamma-Gabes (south of Tunisia). The preparation of the adsorbent was as followed: 1000g of natural clay were washed for 24 h with bi-distilled water on a shaker at 1000 rpm, dried at 80°C for 24h, crushed and sieved[7].

After these steps, obtained material is activated by metallic solution (ferric chloride) [11, 12].

On introduce in a reactor of 1 L capacity:

-500 mL of bi-distilled water;

-A masses of NC (m_{NC}) and ferric chloride (m_{FeCl_3}). These amounts are added as the ratio R_m (m_{FeCl_3}/m_{NC}): $0.15 \leq R_m \leq 1$ (w/w).

The mixture is put in agitation at 1000 rpm, at temperature T_a ($15 \leq T_a \leq 75$ °C) and for times t_a ($15 \text{ min} \leq t_a \leq 4 \text{ h}$).

pH and conductivity (χ) of natural clay and activated clay solutions (1 g/L) were analyzed by pH-meter (HANNA instruments) and conduct-meter (ino LAB) of laboratory respectively.

Apparent density (ρ) of two materials was analyzed by pycnometric method (NFT 51063 Method B).

The chemical composition and principal physico-chemicals properties of the materials are presented respectively in table 2 and table 3.

Table2. Chemical composition of NC and AC (Analyzed by Inductively Coupled Plasma)

<i>Element</i>	<i>Masses composition (%)</i>	
	NC	AC
Al ₂ O ₃	28.55	30.74
SiO ₂	50.43	47.95
FeO ₃	5.94	6.93
MgO	1.13	1.11
CaO	4.04	2.21
Na ₂ O	1.67	0.6
MnO	0.019	0.022
ZnO	0.011	0.013
Humidity	8.18	10.4

Table3. Principal physico-chemicals properties of NC and AC

<i>Properties</i>	<i>Material</i>	
	NC	AC
Apparent density ρ (kg/L)	1.9	2.4
pH	7.74	2.77
Conductivity χ (μ S/cm)	167.65	38.26

2.2. Methods

2.2.1. Adsorption studies

Adsorption studies were conducted in a routine manner by batch technique. For batch experiments a variable amount ($50 \leq m_{AC} \leq 600$ mg) of AC were placed into 250 mL flasks containing 100 mL solution with different initial concentrations (35 - 246 mg/L) of nitrobenzene solution. The flasks were shaken on a shaker at 280 rpm with a constant shaking rate for the time needed to reach equilibrium from the preliminary kinetic investigation (4 hours) then the sample was filtered on filters micro-pores of diameter 0.45 μ m and the nitrobenzene concentration was determined. The studies were performed at a constant temperature of 298K to be representative of environmentally relevant conditions and at pH = 8[7].

The amount of nitrobenzene adsorbed per volume unit of solution onto AC is determined by the difference between the initial concentration (C_0) and the equilibrium concentration (C_e).

The amounts of nitrobenzene adsorbed per gram of AC, q_e (mg/g), and efficiency of adsorption onto AC, at equilibrium, were calculated respectively from equations (1) and (2).

$$q_e = \frac{(C_0 - C_e)V}{m_{AC}} \tag{1}$$

$$\eta(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

The amount of nitrobenzene adsorbed per gram of AC at time (t), q_t (mg/g), was calculated by equation (3).

$$q_t = \frac{(C_0 - C_t)V}{m_{AC}} \tag{3}$$

Where C_t represents the instantaneous nitrobenzene concentration (mg/L) and V is the volume of nitrobenzene solution (mL).

2.2.2. Analytical method

The concentration of nitrobenzene was determined by high performance liquid chromatography (Agilent 1100) equipped with Ultra Violet detection at a wavelength of 261 nm, using a hypersil column G1316A (4 × 125 mm). The injection volume was 20 µL and the mobile phase was a mixture of acetonitril – water (80% v: 20% v) with a rate of 1 mL/min. Under these conditions, the retention time of nitrobenzene in the column was 1.69 min.

III. RESULTS AND DISCUSSION

3.1. Effect of activation time on adsorption of nitrobenzene

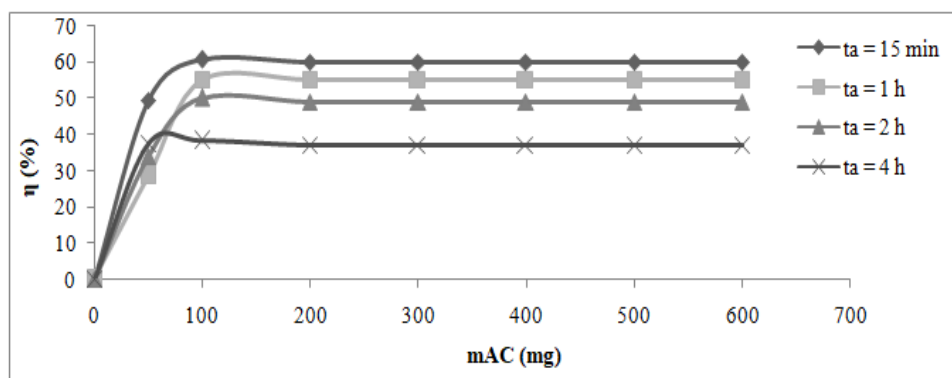


Figure1. Effect of activation time on adsorption of nitrobenzene by activated clays

Figure1. Effect of activation time on adsorption of nitrobenzene by activated clays

Conditions of adsorption: $C_0 = 246$ mg/L; pH = 8; N = 280 rpm; $t_{eq} = 4$ h; T = 25°C

The above Figure shows the effect of activation time on adsorption of nitrobenzene by different activated clays. It is observed that the degradation efficiencies of nitrobenzene increases with the decrease in activation time for all the adsorbent used herein. For the degradation of nitrobenzene, all activated clays present similar evolution of the retention capacities versus doses.

The evolution of high degradation efficiency (η_h) versus activation time at dose of 100 mg of AC is represented in table 4.

According to table 4, the optimum value of activation time of natural clay is 0.25h (15 min).

Table4. High adsorption efficiency of nitrobenzene by activated clays at different activation time at dose of 100 mg

ta (h)	η_h (%)
0.25	60.61
1	55.17
2	50
4	38.19

3.2. Effect of activation mass ratio on adsorption of nitrobenzene

The effect of ferric chloride-natural clay ratio on activation was studied at 25°C, with 15 g/L FeCl₃, for 15 min. The results are shown in fig. 2.

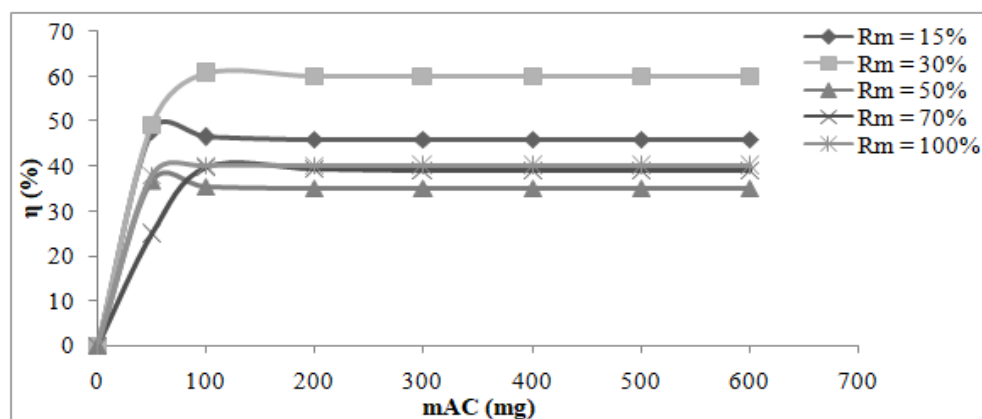


Figure2. Effect of activation ratio on adsorption of nitrobenzene by activated clays

Conditions of adsorption: C₀ = 246 mg/L; pH = 8; N = 280 rpm; t_{eq} = 4 h; T = 25°C

When the ratio was increased from 15 to 30% w/w, degradation performance of nitrobenzene increased from 46.5 to 60.61% at 100 mg of activated clay, an increase of about 14.11% implying a great effect on beneficiation of natural clay obtained at the expense of increased of pores due to formation of H⁺ clay. The kind of clays was an acid character which increases his activity [13].

Efficiency of degradation of nitrobenzene by different activated clay decreases when activation ratio increases from 50 to 100%.

The evolution of high degradation efficiency (η_h) versus activation ratio at doses of 50 mg and 100 mg of AC is represented in table 5.

According to table 5, the optimum value of activation ratio of natural clay is 30%.

Table5. High adsorption efficiency of nitrobenzene by activated clays at different activation ratio of FeCl₃/Natural clay

R _m (%)	m _{AC} (mg)	η _h (%)
15	50	47.75
50		36.74
30	100	60.61
70		39.85
100		40.15

3.3. Effect of activation temperature on adsorption of nitrobenzene

The effect of temperature on activation of natural clay was investigated with 15 g/L FeCl₃, 0.3 ferric chloride-natural clay ratio (w/w) for 15 min. The results are shown in fig. 3.

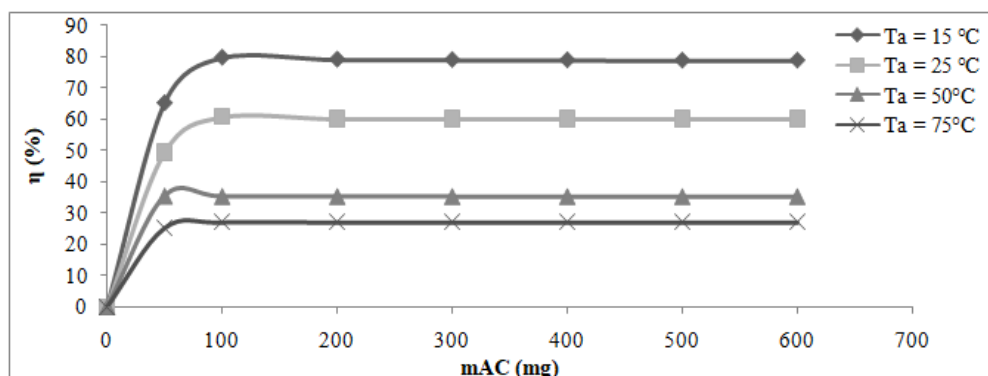


Figure3. Effect of activation temperature on adsorption of nitrobenzene by activated clays

Conditions of adsorption: $C_0 = 246 \text{ mg/L}$; $\text{pH} = 8$; $N = 280 \text{ rpm}$; $t_{\text{eq}} = 4 \text{ h}$; $T = 25^\circ\text{C}$

The above figure shows that activation of natural clay by ferric chloride was improved by decreasing temperature. This was probably due to increased speed of the molecules in the system which enhanced contact between clay surface and ferric chloride [14].

When the temperature was decreased from 25 to 15°C, degradation performance of nitrobenzene increased from 60.61 to 79.62% at 100 mg of activated clay, an increase of about 19.01% implying a great effect on beneficiation of natural clay obtained at the expense of increased of pores due to reactivity of ferric chloride in presence of hydrogen peroxide including in steps of preparation of activated clays [15, 16].

The attack reaction of natural clay by ferric chloride has endothermic character.

The evolution of high degradation efficiency (η_h) versus activation temperature at doses of 50 mg and 100 mg of AC is represented in table 6.

According to table 6, the optimum value of activation temperature of natural clay is 15°C.

Table6. High adsorption efficiency of nitrobenzene by activated clays at different activation temperature

Ta (°C)	m _{AC} (mg)	η_h (%)
15	100	79.62
25	100	60.61
50	50	35.26
75	100	26.85

Finally, the optimums conditions of activation of natural clay of Elhamma-Gabes by ferric chloride are:

- activation time $t_a = 15 \text{ min}$;
- activation ratio (FeCl_3/NC) $R_m = 0.3 \text{ (w/w)}$;
- activation temperature $T_a = 15^\circ\text{C}$.

3.4. Kinetic study of adsorption of nitrobenzene by activated clay

3.4.1. Effect of initial concentration of nitrobenzene

As illustrated by fig. 4, the amount adsorbed increases with the concentration of solution. When the initial nitrobenzene concentration was increased from 61.5 to 246 mg/L, the adsorption uptake of activated clay increased. The effect of contact time on the removal of nitrobenzene at initial concentrations 61.5 to 246 mg/L showed rapid adsorption of nitrobenzene in the first 60 min because the adsorption takes place primarily at easily accessible surface sites [1, 13]. And a hydrophobic interaction between adsorbent and organic compounds may be attributed to the rapid adsorption rate [1]. The adsorption rate decreased gradually and the adsorption reached equilibrium in about 4 hours for all the initial concentrations used.

The high efficiency of degradation of nitrobenzene is 32.79%, 44.8% and 60.61% at concentrations 61.5, 123 and 246 mg/L respectively.

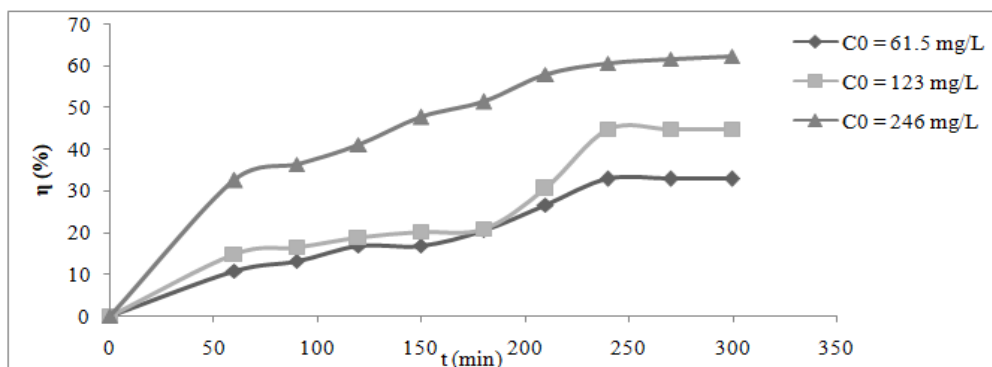


Figure4. Effect of initial concentration of nitrobenzene on adsorption by activated clay
Conditions: $t_a=15 \text{ min}$; $R_m=0.3(\text{w/w})$; $T_a=T = 25^\circ\text{C}$; $m_{\text{AC}} =100 \text{ mg}$; $\text{pH} = 8$; $N = 280 \text{ rpm}$

Figure4. Effect of initial concentration of nitrobenzene on adsorption by activated clay **Conditions: $t_a=15 \text{ min}$; $R_m=0.3(\text{w/w})$; $T_a=T = 25^\circ\text{C}$; $m_{\text{AC}} =100 \text{ mg}$; $\text{pH} = 8$; $N = 280 \text{ rpm}$**

3.4.2. Kinetic models

Several kinetic models (diffusion on homogeneous surface, diffusion pores, heterogeneous model of diffusion and model of Elovich) are tested on our experimental results in order to describe the mechanism of the process of adsorption of nitrobenzene by activated clay. The pseudo-first-order Lagergren equation is given as [17]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Where q_e and q_t are determined by equations (1) and (3), respectively and k_1 is the rate of constant of pseudo-first-order adsorption process (min^{-1}). The slope and intercept of plots of $\ln(q_e - q_t)$ versus t were used to determine the first-order rate constant k_1 and q_e .

The pseudo-second-order kinetic model by Ho and McKay [18], with the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where k_2 is the rate of constant of pseudo-second-order adsorption process (g/mg min). If the pseudo-second-order is applicable, the plot of t/q_t versus t gives a linear relationship, and then k_2 and q_e can be calculated from the slope and intercept of the line.

The Elovich equation [19] is tested with the linear form:

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

Where α is the initial sorption rate constant (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorptions (g/mg). The constant can be obtained from the slope and intercept of the plot of q_t versus $\ln(t)$.

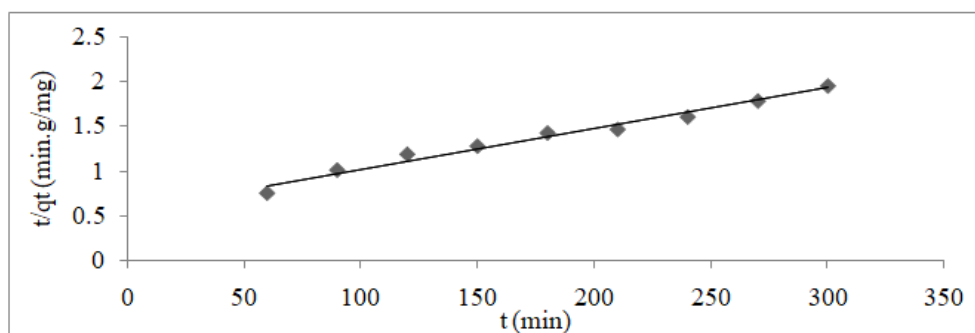


Figure5. Kinetic of the pseudo-second-order adsorption process of nitrobenzene by AC

The intra-particle diffusion model was tested. The model is illustrated by equation (7) [20]:

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

Where k_{int} ($\text{mg/g min}^{1/2}$), and C (mg/g) are the intra particle rate constant, and constant of model respectively. The factor of correlation R^2 of for equations and constants the kinetics of each model are presented in table 7.

Table7. Constants of the kinetic models of adsorption of nitrobenzene by activated clay

Model	Constant of model and correlation coefficient	
Lagergren	k_1 (min^{-1})	0.017
	q_e (mg/g)	340.360
	R^2	0.917
Pseudo-second-order	k_2 (g/mg min)	$3.73 \cdot 10^{-5}$
	q_e (mg/g)	217.4
	R^2	0.979
Elovich	α (mg/g min)	3.8
	β (g/mg)	0.019
	R^2	0.968
Layer diffuses	K_{int} ($\text{mg/g min}^{1/2}$)	8.584
	C (mg/g)	11.131
	R^2	0.976

We can conclude that the retention of nitrobenzene by activated clay is better represented by second-order kinetic (fig. 5) with extreme high values of correlation coefficient (table 7). But it can be also represented by a diffusion intra particle model.

3.5. Isotherm of adsorption

The adsorption isotherm is the variation at equilibrium of the quantity (q_e) of compound adsorbed on a solid according to concentration of adsorbate (C_e) in the liquid in contact, at a constant temperature $q_e = f(C_e)$. To determine the type and the nature of the adsorption isotherm of nitrobenzene by activated clay, we varied the initial concentration of nitrobenzene from 35 to 246 mg/L. The adsorption isotherm is illustrated in fig. 6.

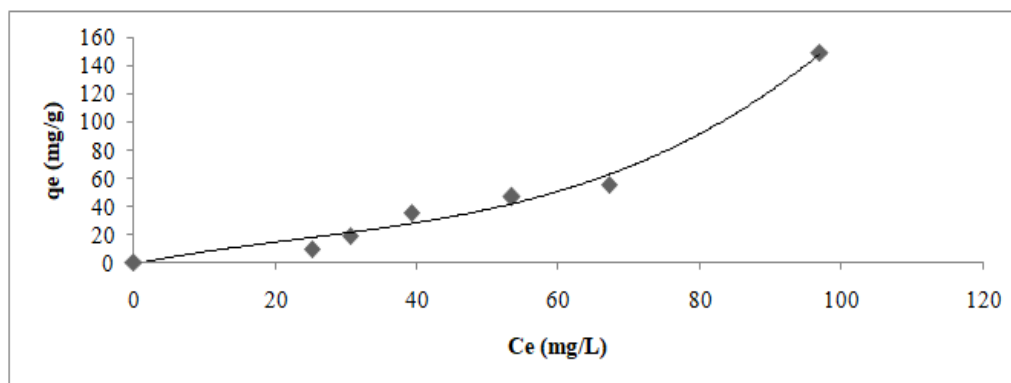


Figure 6. Adsorption isotherm of nitrobenzene by activated clay. Conditions: $t_a=15$ min; $R_m=0.3$ (w/w); $T_a=T = 25^\circ\text{C}$; $35 \leq C_0 \leq 246$ mg/L, $m_{AC} = 100$ mg; $\text{pH} = 8$; $N = 280$ rpm

According to the fig. 6, the amount adsorbed increase with increasing initial concentration of nitrobenzene (table 8). This isotherm is type III. This type shows a presence of hydrophobic interactions between nitrobenzene and activated clay and an isotherm with transition from mono-layer to multi-layer [21, 22].

Efficiency of degradation of nitrobenzene (η) by this technical at different initial concentration is represented in table 8.

In order to describe the adsorption isotherm, three important mathematic models of isotherm are selected in this study, Freundlich, Dubinin-Radushkevich and Temkin [22, 23, 24].

Table 8. Efficiency of degradation of nitrobenzene by activated clay at different initial concentration

C_0 (mg/L)	η (%)
246	60.61
123	45.43
100	46.57
75	47.69
50	38.68
35	28.02

The Freundlich model can be expressed by this equation:
$$\text{Ln}q_e = \text{Ln}k_F + \frac{1}{n_F} \text{Ln}C_e$$

(8)

Where K_F and n_F are the Freundlich adsorption constants.

Dubinin-Radushkevich (D-R) isotherm was used to fit with the experimental data, and it can be represented as:

$$\text{Ln}q_e = \text{Ln}q_m - 2BRTL \ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

Where q_m is the maximum adsorption capacity (mg/g) and B is the D-R adsorption constant.

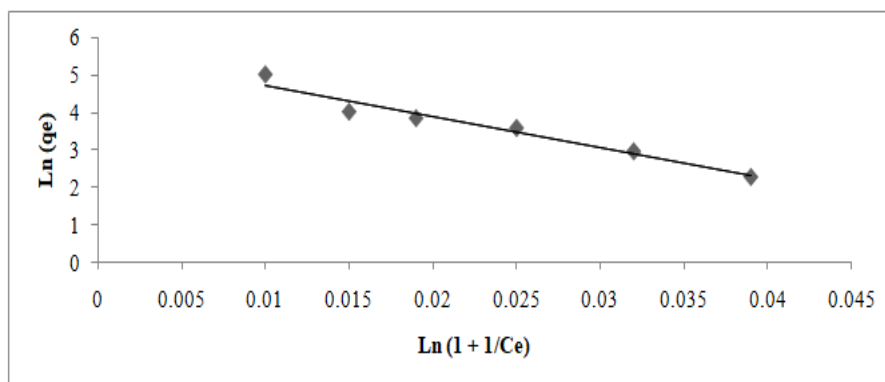


Figure7. Linear D-R model of adsorption isotherm for nitrobenzene on activated clay

The Temkin isotherm equation is given as: $q_e = B \ln A + B \ln C_e$ (10)

Where A and B are the Temkin adsorption constants.

Correlation coefficients and parameter values for the three isotherms were presented in table9.

Table9. Values of the used isotherm parameters

Isotherm model	Parameter	Correlation coefficient R^2
Freundlich	$n_F = 0.56$ $K_F = 0.037$	0.947
D-R	$B = 0.017 \text{ mol/J}$ $q_m = 261.64 \text{ mg/g}$	0.954
Temkin	$A = 0.038$ $B = 89.09 \text{ mg/g}$	0.803

Based on the correlation coefficient (table 9), the applicability of the isotherms was compared. The experimental results indicate that the adsorption of nitrobenzene onto activated clay followed Dubinin-Radushkevich (D-R) isotherm model (fig. 7). The theoretical value of the maximum adsorption capacity of activated clay at equilibrium $q_m = 261.64 \text{ mg/g}$ is lightly superior that experimental value which is of **195.86 mg/g**.

IV. CONCLUSION

Activated clay was produced from activated natural clay using ferric chloride as a chemical activation agent. The adsorption behavior of the produced activated clay was tested with nitrobenzene in aqueous solutions. The optimums conditions of activation of natural clay by this technical are: activation time $t_a = 15 \text{ min}$, activation ratio (FeCl_3/NC) $R_m = 0.3 \text{ (w/w)}$ and activation temperature $T_a = 15^\circ\text{C}$.

The adsorption of nitrobenzene by activated clays reached equilibrium in 4 hours. The kinetics of retention is better represented by a second order kinetic. The experimental results show an isotherm of type III and fit to the Dubinin-Radushkevich model.

We found that with a initial concentration of nitrobenzene of 246 mg/L , a temperature of 298 K , a mixing velocity of 280 rpm , a dose of $0.1 \text{ g adsorbent/100 mL}$ of solution (1 g/L) and $\text{pH} = 8$, the efficiency of retention reached 79.62% .

The removal of nitrobenzene by activated clay is much better that by natural clay only because efficiency of treatment increased from 37.5% (conditions: $C_0 = 246 \text{ mg/L}$, $t_{eq} = 8 \text{ hours}$, $\text{pH} = 8$ and dose of natural clay 1 g/L) with natural clay only [7] to 79.62% with activated clay (conditions: $C_0 = 246 \text{ mg/L}$, $t_{eq} = 4 \text{ hours}$, $\text{pH} = 8$ and dose of activated clay 1 g/L).

ACKNOWLEDGMENTS

The authors acknowledge GCT and FSG of Gabes for supporting this research. The authors acknowledge also, Chabbi. Asma, Kardamine. Manel, Elmasboub. Leila, Hmidi. Afef, Lhiaui Mouna and Bellazreg Houda for performing some of the experimental work.

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Imed Elmir, « Effect Of Chemical Activation Of Natural Clay By Ferric Chloride On Adsorption Of Nitrobenzene.» *IOSR Journal of Engineering (IOSRJEN)*, vol. 08, no. 8, 2018, pp. 62-70.