DEGRADATION DE NITROBENZENE PAR ADSORPTION SUR ARGILE NATURELLE COUPLEE D'UNE OXYDATION PAR LE REACTIF DE FENTON

DEGRADATION OF NITROBENZENE BY ADSORPTION ONTO NATURAL CLAY COUPLED WITH OXIDATION BY FENTON SYSTEM

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RESUME

Le nitrobenzène est un intermédiaire de synthèse important utilisé pour la production industrielle des colorants, des matières plastiques, des pesticides, des explosifs et des produits pharmaceutiques. Il est présent sous forme des traces dans les effluents liquides issues de ces industries et constitue donc une pollution potentielle pouvant dégrader la faune et la flore, d'où la nécessité de trouvé des techniques de traitement afin de minimiser les concentrations résiduelles de ce produit toxique dans les effluents avant rejets dans l'environnement. L'objectif de ce travail est l'étude de traitement des solutions aqueuses de nitrobenzène par adsorption on batch sur argile naturelle couplée d'une oxydation avec le réactif de Fenton. L'équilibre d'adsorption a été obtenu après 20 minutes et la cinétique d'adsorption est de type pseudo second ordre. L'isotherme d'adsorption suit la loi de Dubinin-Radushkevich. Le rendement maximal de traitement de cet effluent par cette technique est de 66,51%.

MOTS CLES: Nitrobenzène, adsorption, argile naturelle, oxydation, Réactif de Fenton.

ABSTRACT

Nitrobenzene is an important chemical which used in the manufacture of many products such as dyes, plastics, pesticides, explosives, pharmaceuticals products, etc. It is very toxic even present as traces in industrial waste liquids effluents. It may constitute a potential pollution source of faun and flare. It is necessary to investigate technical treatment in aim to reduce the residual concentration of nitrobenzene in environment. In this work the removal of nitrobenzene from synthesized aqueous solutions was carried out by adsorption onto natural clay in presence of Fenton's reagent at batch processes. The equilibrium was reached at the end of 20 minutes. The adsorption isotherm was well described by the Dubinin-Radushkevich model. The high efficiency of treatment by this technical is 66.51 %, was obtained at the optimum conditions: initial concentration of nitrobenzene (C_0 = 246 mg/l), dose of natural clay (D_{NC} = 0.6 g/L), concentration of hydrogen peroxide ($[H_2O_2]$ = 5µmol/L) and concentration of ferrous ion ($[Fe^{2+}]$ = 50µmol/L).

KEYWORDS: Nitrobenzene, adsorption, natural clay, oxidation, Fenton's reagent.

1 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 environmental, 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 [3-6].

Particularly, advanced oxidation processes are used for the treatment of pharmaceutical wastewater [7], dyes and pigments [8] and sulfate ion [9]. This paper aims at studying the degradation of nitrobenzene from aqueous solutions by adsorption on natural clay coupled with Fenton's reagent (H2O2/ Fe2+). As a first step in the study, it is necessary to quantify the equilibrium time during adsorption in presence of Fenton's reagent. In turn, adsorption isotherm is conducted at batch experiments at ambient temperature (298K). Influencing parameters such as pH, initial concentration of nitrobenzene, molar ratio between the amount of hydrogen peroxide and ferrous ions ([H2O2] / [Fe2+]) and doses of natural clay are evaluated to characterize the degradation of nitrobenzene by this technical.

2   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 acid (HCl 2M) and base (NaOH 2M) solutions.

Table 01 presents the principal physic-chemicals properties of nitrobenzene.

Table 01: Principal physic-chemicals properties of nitrobenzene (ACROS 12842-0010)

Molecular formula	$C_6H_5NO_2$
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   Adsorbent (Natural Clay: NC)

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.

The chemical composition of the adsorbent was presented in table 02.

Table 02: Chemical composition of natural clay (Analyzed by Inductively Coupled Plasma)

Element	Masses composition (%)
Al_2O_3	28.55
SiO_2	50.43
FeO_3	5.94
MgO	1.13
CaO	4.04
Na_2O	1.67
MnO	0.019
ZnO	0.011
Humidity	8.18

2.1.3   Fenton system (H_2O_2/ Fe^{2+})

The Fenton process was reported by Fenton [10] already over a hundred years ago for maleic acid oxidation:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH$$
(R1)

The rate constant for the reaction of ferrous ion with hydrogen peroxide is high and Fe (II) oxidized to Fe (III) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. Hydrogen peroxide decomposes catalytically by Fe (III) and generates again hydroxyl radicals according to the reactions [10]:

$$Fe^{3+} + H_2O_2 \longrightarrow H^+ + Fe\text{-}OOH^{2+}$$
(R2)

$$Fe\text{-}OOH^{2+} \longrightarrow \cdot OOH + Fe^{2+}$$
(R3)

$$Fe^{2+} + \cdot OOH \longrightarrow Fe^{3+} + OOH^-$$
(R4)

$$Fe^{3+} + \cdot OOH \longrightarrow Fe^{2+} + O_2 + H^+$$
(R5)

$$H_2O_2 + \cdot OH \longrightarrow H_2O + \cdot OOH$$
(R6)
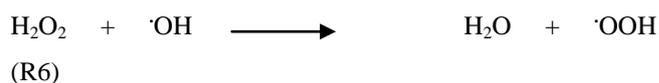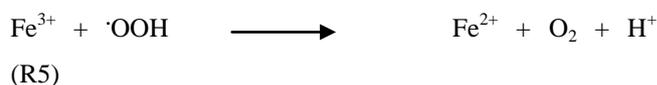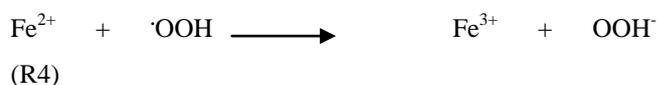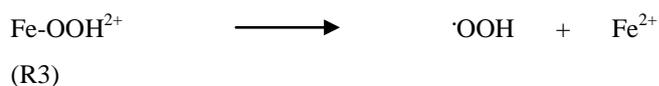
The hydroxyl radicals produced in the above reactions has very high oxidation potential (E^0 = +2.8 V).

The ferrous ion in Fenton's reagent can be replaced with the ferric ion [11].

The chemicals used such as hydrogen peroxide (with purity

of 30% v H_2O_2) and hepta-hydrated ferrous sulfate ($FeSO_4.7H_2O$) were all of commercial grade respectively PROLABO and PANREAC.

2.2   Methods

2.2.1   *Chemical adsorption experiments*

Effect of parameters such as the time of contact (t), the pH, the initial concentration of nitrobenzene (C_0), the dose of natural clay (D_{NC}) and the molar ratio (r = [H_2O_2]/[Fe^{2+}]), were studies. In order to obtain the optimum of each parameter, we vary this last, and to leave all the other constant ones.

2.2.1.1   Preliminary kinetic study

A preliminary kinetic investigation was made at certain operating conditions in order to determine the equilibrium time of adsorption.

The study consists to put in a flask of 250 mL, a volume of 100 mL of a solution of nitrobenzene (C_0 = 246 mg/L) with 0.6 g of NC and amount of Fenton's reagent (R = 1%). The mixture is putter in agitation at 280 rpm and 298K then we follow the variations of the concentration of the liquid phase with the time. The amount of nitrobenzene adsorbed per gram of NC at time (t), qt (mg/g), was calculated equation 1.

$$q_t = \frac{(C_0 - C_t)V}{m_{NC}}$$

(Eq 1)

Where C_0 and Ct represent the initial and instantaneous nitrobenzene concentrations (mg/L), respectively; V is the volume of nitrobenzene solution (mL) and m_{NC} is the amount of adsorbent (g).

2.2.1.2   Adsorption studies

Adsorption studies were conducted in a routine manner by batch technique. For batch experiments a fixed amount (0.6 g) of NC were placed into 250 mL flasks containing 100 mL solution with different initial concentrations (20 - 450 mg/L) of nitrobenzene solution. The flasks were shacked on a shaker at 280 rpm with a constant shaking rate for the time needed to reach equilibrium from the preliminary kinetic investigation then the sample was filtered on filters micro-pores of diameter 0.45 μm and the nitrobenzene concentration was determined. The studies were performed at a constant temperature of 298K to be representative of environmentally relevant conditions.

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

The amount of nitrobenzene adsorbed per gram of NC at equilibrium, q_e (mg/g), was calculated from equation 2.

$$q_e = \frac{(C_0 - C_e)V}{m_{NC}}$$

(Eq2)

The adsorbent dosage (D_{NC}) was changed in the range of 0.5 – 8 g/L.

The initial nitrobenzene concentrations were varied from 20 to 450 mg/L.

The molar ratios between molar concentrations of H_2O_2 and Fe^{2+} were varied from 1 to 30%: first at constant concentration of hydrogen peroxide ([H_2O_2] = 1μmol/L) and second at constant concentration of ferrous ion ([Fe^{2+}] = 50μmol/L).

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 acitonitril – 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.

3   RESULTS AND DISCUSSION

3.1   Preliminary kinetic investigation

Figure 01 shows the preliminary curve for the degradation of nitrobenzene by adsorption onto NC in the presence of Fenton's reagent.
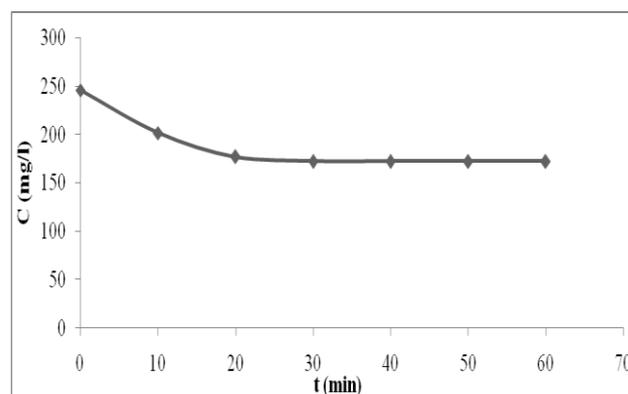

Figure 01: Contacting time effect on the retention of nitrobenzene; Conditions: Co = 246 mg/L, pH = 8, DNC = 6 g/L, r = 1%, N = 280 rpm, T = 298K

According to this figure we notice that equilibrium is reached at the end of 20 minutes. The results obtained show the existence of two phases: The first is rapid and the

second is low. This relates to the great availability of the free active sites of the adsorbent where realized instantaneous reaction between nitrobenzene and Fenton's reagent at the beginning of the experiment and which becomes weak with time.

3.2 Effect of initial concentration of nitrobenzene

As illustrated by figure 02, 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 natural clay in the presence of Fenton's reagent 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 10 min because the adsorption takes place primarily at easily accessible surface sites. 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 30 min for all the initial concentrations used.

The high efficiency of degradation of nitrobenzene is 33.58, 37.64 and 66.51% at concentrations 61.5, 123 and 246 mg/L respectively.
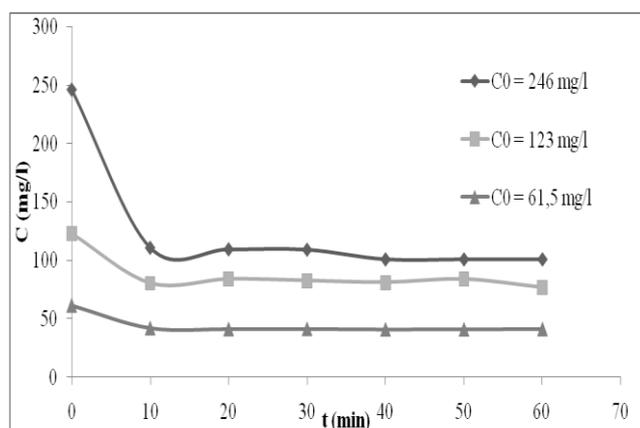

Figure 02: Effect of initial concentration of nitrobenzene on adsorption by natural clay with Fenton's reagent; Conditions: DNC = 6 g/L, pH = 8, r = 10%, N = 280 rpm, T = 298K

3.3 Kinetic study

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 chemical adsorption of nitrobenzene by natural clay in presence of Fenton's reagent. The pseudo-first-order Lagergren equation is given as [12]:

$$Ln(q_e - q_t) = Lnq_e - k_1 t$$

(Eq3)

Where q_t and q_e are determined by (Eq1) and (Eq2), respectively, and k1 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 [13], with the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(Eq4)

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 [14] is tested with the linear form:

$$q_t = \frac{1}{\beta} Ln(\alpha\beta) + \frac{1}{\beta} Ln(t)$$

(Eq5)

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).
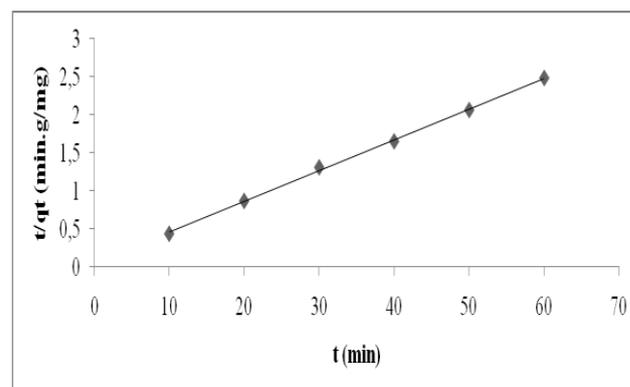

Figure 03: Kinetic of the pseudo-second-order adsorption process of nitrobenzene

The intra-particle diffusion model was tested. The model is illustrated by equation 6 [15]:

$$q_t = C + k_{int} t^{1/2}$$

(Eq6)

Where k_{int} is the intra particle rate constant (mg/g min$^{1/2}$) .

The factor of correlation R^2 of for equations as well as constants the kinetics of each model are presented on table 03.

Table 03: Constants of the kinetic models of adsorption of nitrobenzene

Model		
Lagergren	$k_1 (min^{-1})$	0.043
	$q_e (mg/g)$	1.983
	R^2	0.24
Pseudo-second-order	$k_2 (g/mg\ min)$	**0.028**
	$q_e (mg/g)$	**25**
	R^2	**0.999**
Elovich	$\alpha (mg/g\ min)$	$8.86\ 10^7$
	$\beta (g/mg)$	0.821
	R^2	0.773
Layer diffuses	$K_{int} (mg/g\ min^{1/2})$	0.435
	R^2	0.818

We can conclude that the retention of nitrobenzene by natural clay in presence of Fenton's reagent is better represented by second-order kinetic (figure 03) with extreme high values of correlation coefficient (> 0.99). These results indicate a chemical reaction in the pores of natural clay [16].

3.4   Effect of pH

In order to determine the effect of pH on adsorption capacity of natural clay in presence of Fenton's reagent, solutions were prepared at different pH values ranging from 2.0 to 12.0. The effect of pH on the degradation of nitrobenzene by adsorption onto natural clay coupled with Fenton's reagent at an initial concentration of 246 mg/l is illustrated in figure 04. Obviously, the amount of adsorbed nitrobenzene (q_e) is increased by increasing of pH from 2.0 to 8.0, maximum at a pH value of 8.0, and then dropped with further increase in the pH value of solutions of nitrobenzene (pH > 8.0), because the pH could greatly influence on adsorption of nitrobenzene by natural clay [17] and formation of hydroxyl radicals [18]. The adsorption mechanisms can be contributed by hydrophobic interaction at the interface between nitrobenzene and natural clay [17].
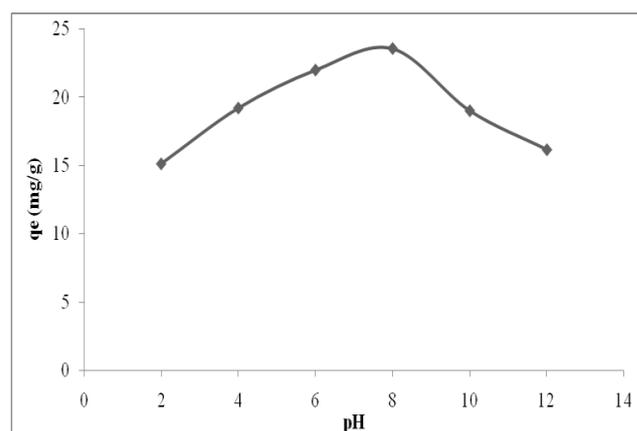

Figure 04: Effect of pH on retention of nitrobenzene on adsorption by natural clay in presence of Fenton's reagent; Conditions: Co=246 mg/L, DNC= 6 g/L, t=20 min, r=2%, N=280 rpm, T=298K

When the pH of aqueous solutions of nitrobenzene is relatively low, the adsorption capacity of natural clay is feeble [17] and a reduced concentration of HO_2^- radicals is not conductive to the formation of $.OH$ radicals [18]. The maximum capacity of degradation of nitrobenzene is obtained at pH = 8 because adsorption of this composes is favorite at this value [17] and hydrogen peroxide is more prone to decompose into HO_2^- radicals, that can accelerate the rate of formation of $^.OH$ radicals resulted from catalytic decomposition of H_2O_2 by Fe^{2+} to speed up oxidation rate in pores of natural clay. When the pH of nitrobenzene solutions is excessively high, the concentration of OH^- is high and the excess of this ion can react on HO_2^- radicals to form relatively inactive O_2^- ions [18], as shown by the following reaction:

$$HO_2^- + OH^- \longrightarrow O_2^- + H_2O \qquad (R7)$$

There by the $^.OH$ chain reaction is terminated to reduce the number of $^.OH$ radicals formed to pose a negative impact on the oxidation of nitrobenzene into the pores of natural clay.

3.5   Effect of molar ratio (r)

The use of H_2O_2/ Fe^{2+} as an oxidant for wastewater treatment is attractive due to the fact that: (1) iron is a highly abundant and non-toxic element, and (2) hydrogen peroxide is easy to handle and environmentally benign [19].

Thus, the Fenton process is very effective for $.OH$ radicals generation. However, it involves consumption of one molecule of Fe^{2+} for each $^.OH$ radical produced, demanding a high concentration of Fe^{2+} [19].

Therefore the study of effect of amount of hydrogen peroxide and ferrous ion is investigated. The effect of molar ratio (r) on the degradation of nitrobenzene by adsorption onto natural clay coupled with Fenton's reagent at an initial

concentration of 246 mg/l is illustrated in figure 05.
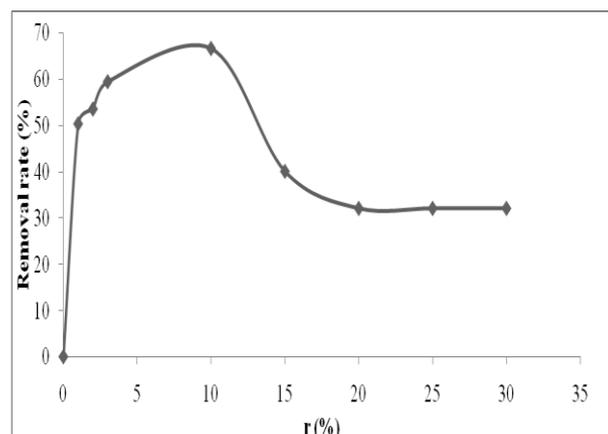
Figure 05: Effect of molar ratio on efficiency for treating nitrobenzene by adsorption onto natural clay in presence of Fenton's reagent; Conditions: Co=246 mg/L, [Fe^{2+}]=50 µmol/L, DNC=6 g/L, t=20 min, pH=8, N=280 rpm, T=298K

It can be seen from figure 05 that with an increasing amount of added H_2O_2 at lower molar ratios (r) the nitrobenzene removal rate was increased continuously. When the H_2O_2/ Fe^{2+} molar ratio increased from 0.01 to 0.1 the nitrobenzene removal rate increased from 50.24% to 66.51%, because ferrous ions functioned as a promoter for decomposition of hydrogen peroxide to form $^{.}OH$ free radicals to oxide nitrobenzene in the pores of natural clay. With a continuously increasing amount of added hydrogen peroxide, the amount of $^{.}OH$ radicals also increased to effectively enhance the oxidative degradation of nitrobenzene after adsorption in the natural clay. When the H_2O_2/ Fe^{2+} molar ratio exceeded 0.1, the removal of nitrobenzene dropped, because excess hydrogen peroxide could react upon $^{.}OH$ radicals to consume some $^{.}OH$ radicals, and HO_2^- ions formed during dissociation of hydrogen peroxide could also on $^{.}OH$ radicals as shown below:

$$HO_2^- + \, ^{.}OH \longrightarrow OH^- + \, ^{.}HO_2 \qquad (R8)$$

At these conditions, the optimum molar ratio of treatment is r = 10%.

Therefore excess amount of hydrogen peroxide could lead decrease of $^{.}OH$ radicals in pores of natural clay to negatively affect of degradation of nitrobenzene solutions, leading to reduced treatment efficiency at 35%.

3.6   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 natural clay in presence of Fenton's reagent, we varied the initial concentration of nitrobenzene from 20 to 455 mg/L at experimental optimum conditions (pH = 8, r = 10% and DNC = 6 g/L). The adsorption isotherm is illustrated in figure 06.
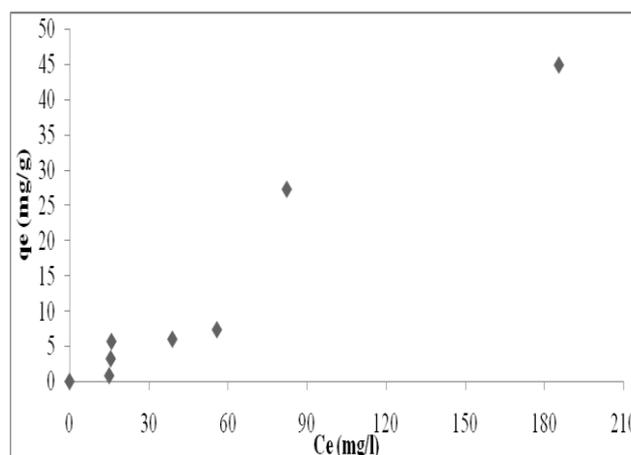

Figure 06: Adsorption isotherm of nitrobenzene by natural clay in presence of Fenton's reagent

Conditions: 20≤C0 ≤455 mg/L, r=10%, DNC=6 g/L, t=20 min, pH=8, N=280 rpm, T=298K

According to the figure 06, the amount adsorbed increase with increasing initial concentration of nitrobenzene (table 4). This type shows a presence of high interaction intermolecular, interactions are feeble between nitrobenzene and natural clay and an isotherm with monolayer [17, 20]. The adsorption mechanism of nitrobenzene by natural clay in presence of Fenton's reagent is explained by preponderance of hydrogen bonding and Van Dar Waals forces [22].

Efficiency of degradation of nitrobenzene (η) by this technical at different initial concentration is represented in table 04.

In order to describe the adsorption isotherm, three important mathematic models of isotherm are selected in this study, Freundlich, Dubinin-Radushkevich and Temkin [16, 21, 23].

Table 04: Efficiency of degradation of nitrobenzene at different initial concentration

C$_0$ (mg/L)	η (%)
455	59.21
246	66.51
100	44.11

75	48.00
50	68.22
20	24.80
C_0 (mg/L)	η (%)
455	59.21
246	66.51

The Freundlich model can be expressed by this equation:

$$Lnq_e = Lnk_F + \frac{1}{n_F} LnC_e$$

(Eq7)

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:

$$Lnq_e = Lnq_m - 2BRTLn(1 + \frac{1}{C_e})$$

(Eq 8)

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

The Temkin isotherm equation is given as:

$$q_e = BLnA + BLnC_e$$

(Eq 9)

Where A and B are the Temkin adsorption constants.

Correlation coefficients and parameter values for the three isotherms were presented in table 05.

Table 05: Values of the used isotherm parameters

Isotherm model	Parameter	Correlation coefficient R^2
Freundlich	$n_F = 0.78$ $K_F = 0.061$	0.788
D-R	**B = 0.013 mol/J** **$q_m = 40.69$ mg/g**	**0.911**
Temkin	A = 0.059 B = 15.8 mg/g	0.801

Based on the correlation coefficient, the applicability of the isotherms was compared. The experimental results indicate that the adsorption of nitrobenzene onto natural clay in presence of Fenton's reagent followed Dubinin-Radushkevich (D-R) isotherm model. The theoretical value of the maximum adsorption capacity at equilibrium **qm = 40.69 mg/g** is lightly inferior that experimental value which is of **44.9 mg/g**.

4. CONCLUSION

The degradation of nitrobenzene from aqueous solution by adsorption onto natural clay coupled with oxidation by Fenton's reagent was investigated under different conditions in batch process. The chemical adsorption of nitrobenzene reached equilibrium in 20 minutes. The kinetics of retention is better represented by a second order kinetic. The experimental results show an isotherm of type V 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 report of 0.6 g adsorbent/100 mL of solution (6 g/L), pH = 8 and a molar ratio H_2O_2/Fe^{2+} (r = 10%), the efficiency of retention reached 66.51%.

The degradation of nitrobenzene by this technical is much better that by natural clay only because efficiency of treatment increased from 37.5% (conditions: C_0 = 246 mg/L, t = 8 h, pH = 8 and D_{NC} = 1g/L) with natural clay only [17] to 66.51% in presence of Fenton's reagent (conditions: C_0 = 246 mg/L, t = 20 min, pH = 8, D_{NC} = 6 g/L and r = 10%).

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