

Isotherms, Kinetic Study of Adsorption of Acetic Acid on Marl Calcareous in Aqueous

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Abstract: The main applications of adsorption methods are among other surface treatment, water use for sewage and compensate for the consumption of fresh water, and soil remediation, where the activated carbon adsorption underpins most used, but with the advent of competition in the market and the downward trend in prices, several media were used because of their natural abundance, their low cost, etc. The research focused on the adsorption of acetic acid on marl calcareous. Studies in "batch" method were used to determine the contact time (0, 5 hours for a removal efficiency of 75% at a concentration of 0, 2 mol/l substrate). However, this contact time may vary under the influence of parameters such as: temperature, concentration of adsorbate in solution, time, mass of adsorbent and pH revealed a significant improvement in the capacity and the rate of adsorption of acetic acid on the support. In addition, the adsorption of this compound is well described by kinetic models of Langmuir and Freundlich.

Keywords: organic molecule, acetic acid, temperature, pH, kinetic model, and marl calcareous.

1. Introduction

The intensive use of organic molecule in everyday life has created problems both in the environment and in food [1,2]. It is important to mention that environmental pollution is due to the discharge of effluents from textile industries and in power, the toxicity is due to the incorporation of several organic molecules [3]. To remedy this situation, several decontamination methods have been developed, we include for example: adsorption [4, 5], ion exchange [6,7], flocculation-coagulation [8], etc. In this work, we present the results for the adsorption of acetic acid on limestone marl powder. To do this, we determined successively, the contact time, the influence of parameters such as temperature, concentration of adsorbate in solution pH and initial substrate concentration. This study is necessary to understand the mechanisms governing the adsorption.

2. Materials and Methods

Measures the concentration of the organic molecule solutions at different reaction times were followed by the chemical method of assay. The experiments were conducted in "batch method" (in a single flask 50 ml) at room temperature (25 °C). It should be noted that the temperature control was done by simply reading the thermometer. Also to ensure good dispersion of solid particles of marl calcareous, we adopted the value of 10 g/l (0,5 g/50ml) for the solid/liquid ratio.

Adsorption isotherm:

To investigate the adsorption capacity of our samples, we applied the models of Langmuir and Freundlich.

3. Results and Discussions

3.1. Characterization of marl calcareous:

From Table 1, we can conclude that the marl calcareous shows a percentage of CaO in the range of 41.95%. This rate is linked to the presence of calcite. We also note the high

rate of organic matter 36.09%. Therefore, we have low oxides Fe₂O₃, Al₂O₃, MgO and K₂O. The diffract-gram shows also that our soil is rich in calcite.

Table 1: Results of analysis of marl calcareous fluorescence X

Compound	%
SiO ₂	12,68
Al ₂ O ₃	3,73
Fe ₂ O ₃	2,10
CaO	41,95
MgO	0,79
SO ₃	0,03
K ₂ O	0,64
Na ₂ O	0,14
P ₂ O ₅	0,11
Cl	0,00
Loss of-fire	36,09
total	98,27

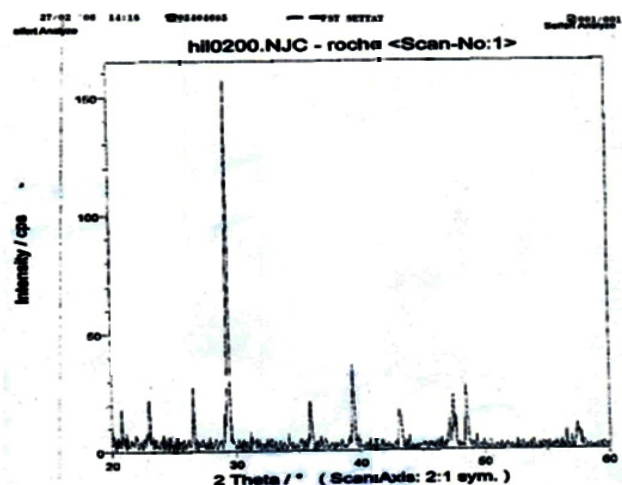


Figure 1: X-ray diffract-gram of the marl calcareous

3.2. Influence of contact time

The study of the adsorption of acetic acid on the powdered marl calcareous, obviously involves the determination of the

contact time, which corresponds to the adsorption equilibrium or a saturation condition of the support by the substrate. In this case, the experimental procedure followed is simple "batch method", is to be contacted separately 0,2 mol/l acetic acid with 10 g/l of marl calcareous powder. Analysis by chemical assay method will determine the residual concentrations of the substrate, when samples taken at different reaction times.

The determination of equilibrium time, led to the establishment of adsorption isotherm that are essential for the calculation of the maximum adsorption capacity and identification of the type of adsorption to occur in mono or multilayer. The results from Figure 2 showed that the contact time obtained is 0,5 hour and corresponds to a removal of the organic molecular interesting 75%. Moreover, the extension of the time until (5 hours) does not lead to a further improvement. This fully justifies the inclusion of this contact time for other adsorption experiments.

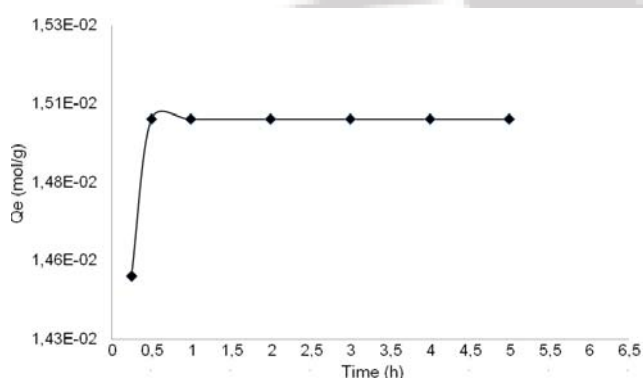


Figure 2: Influence of contact time on the adsorption

This result was obtained by the relation:

$$Q = \frac{(C_0 - C_t) * V}{m}$$

- Q: adsorption capacity of the support (mg/g).
- C0: initial concentration of the organic molecule (mg/l) at t=0.
- Ct: Concentration of the organic molecule (mg/g) at the time t of the adsorption process.
- V: Volume of solution substrate (l).
- m: Mass of support (g).

Other factors such as the initial concentration, temperature, pH, and the adsorbent mass can influence the adsorption capacity. [9] In addition, it finds its application in various adsorption models used.

3.3. Influence of the initial concentration and temperature:

Examination of Figure 3 shows the influence of the initial concentration on the adsorption capacity of the organic molecule (the mass of the support being fixed). It is found that it increases at the same time as increasing the initial concentration.

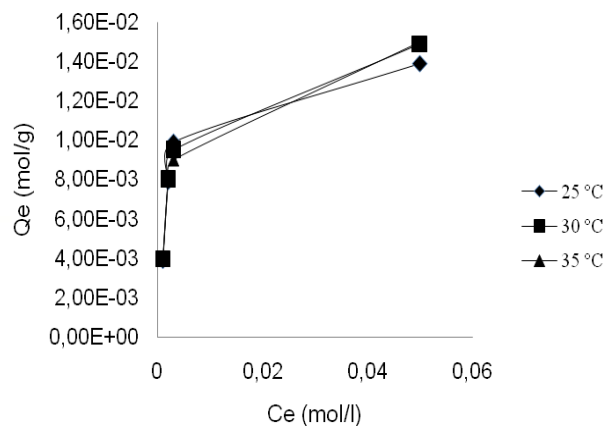


Figure 3: Influence of temperature and initial substrate concentration on the adsorption

But for temperature, the experimental results show a strong retention at high temperatures and shows that this parameter affects this process positively by high energy contribution, to grow attraction forces localized at the interfaces of liquids and solids [10]. So it is interesting to note that the contribution of heating plays a direct role in the kinetics of retention of this organic molecular. This means that the retention process could be endothermic ($\Delta H > 0$) and in these conditions lead to chemisorptions [11].

3.4. Influence of pH

This stage (Figure 4), we find that the adsorption is highly dependent on pH for limestone marl, where we find: Increasing adsorption varies proportionally with the increase of pH.

The maximum of adsorption is obtained at pH= 6. The adsorption is better for $pH > 4, 5$.

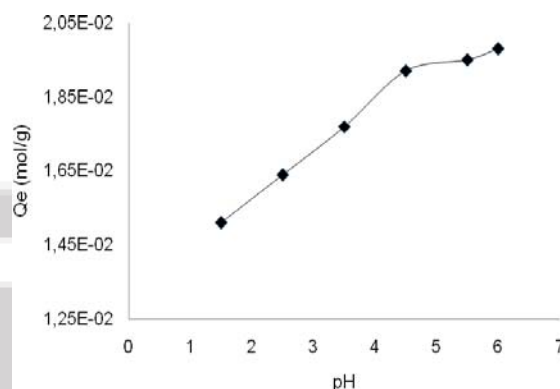


Figure 4: Influence of pH on the adsorption

Probably the form of acetic acid is stable in basic medium; the anionic form of acetic acid (acetate) is stable and subsequently promotes the adsorption.

3.5. Influence of the mass of adsorbent:

The curve in Figure 5 shows the variation of the amount adsorbed by the mass of adsorbents used at an ambient temperature of 25 °C.

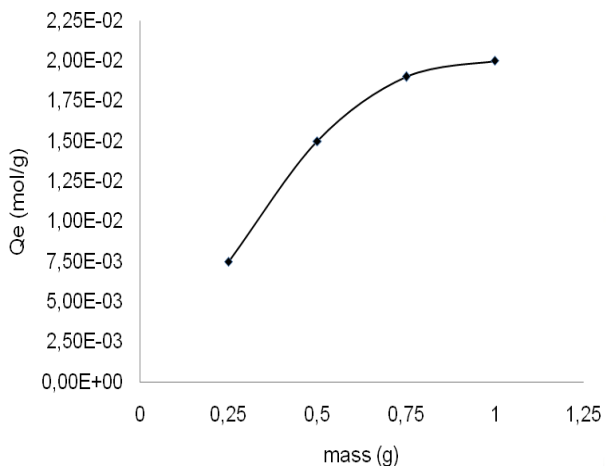


Figure 5: Effect of adsorbent mass on the adsorption

Indeed, we observe that the amount adsorbed acetic acid increases with increasing mass of marl calcareous. Therefore, the optimum mass is 1 g.

3.6. Study of adsorption isotherms:

The adsorption isotherms play an important role in determining the maximum capacity and identification of the type of adsorption. They are first obtained by the knowledge of the contact time and then the graphical representation of $Q_e = f(C_e)$ where Q_e and C_e are, respectively, the amount of the organic molecule adsorbed per gram of adsorbent and concentration the balance of the organic molecule respectively. The experimental results show that the isotherm is of type L, which corresponds to the classification of Gilles [12]. This indicates a growth of adsorption when the concentration of the adsorbate increases, and these curves can be mathematically described by the Langmuir equation and Freundlich (see below). As the number of sites occupied by solute molecules increases, the adsorption of new molecules become difficult. The molecules are arranged in a monolayer on the solid surface. The shape obtained shows that the adsorption process of the organic molecule may occur in monolayer. Due to their simplicity, the kinetic models, the most commonly used are those of Langmuir and Freundlich.

- Langmuir isotherm: represented by the following equation:

$$Q_e = \frac{Q_0 a C_e}{1 + a C_e}$$

Q_e : Quantity adsorbed at equilibrium per unit weight of the adsorbent (mg/g).

Q_0 : adsorption capacity at saturation (mg/g) and correspond to the formation of a monolayer.

a : adsorption coefficient.

The linearization of the Langmuir equation to determine the parameters a and Q_0 .

Representing:

$$\frac{1}{Q_e} = \frac{1+aC_e}{Q_0 a C_e} = \frac{1}{Q_0 a C_e} + \frac{1}{Q_0}$$

Representing:

$$\frac{1}{Q_e} = f\left(\frac{1}{C_e}\right)$$

and we can deduce:

- Q_0 from the intercept.
- a from the slope.
- Isotherm of Freundlich: it can be described by the following equation:

$$Q_e = K_f C_e^{1/n}$$

K_f and $1/n$ are respectively the adsorption capacity in mg/g and a constant indicating the intensity of the adsorption:

$$\ln Q_e = f(\ln(C_e))$$

The linear form of this equation allows the determination of K_f and $1/n$

Representing:

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e$$

The results showed in Figures 5 and 6 that the adsorption of acetic acid on marl calcareous follows two linear models of Langmuir and Freundlich.

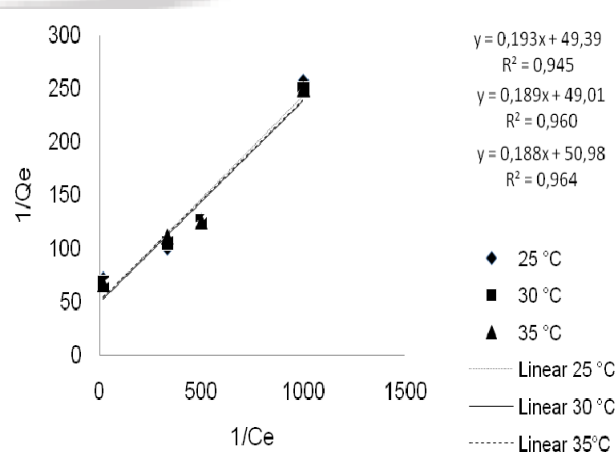


Figure 6: Adsorption isotherm of Langmuir at different temperature

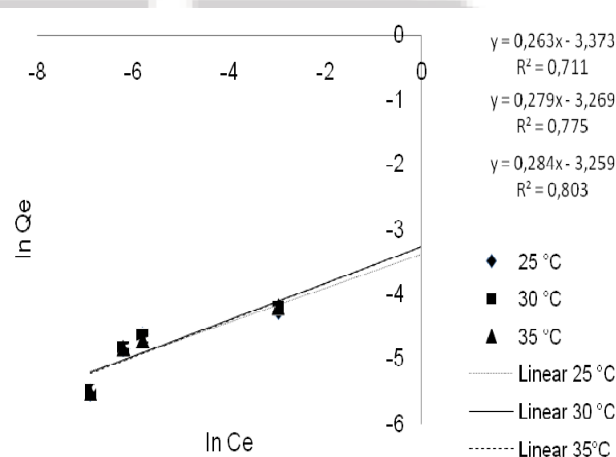


Figure 7: Adsorption isotherm of Freundlich at different temperature

The following table 3 resumes the different correlation coefficients obtained by figure 6 and 7:

Table 3: Correlation coefficient for isotherm of Langmuir and Freundlich

Isotherm	Langmuir			Freundlich		
	Temperature (°C)	25	30	35	25	30
R ²	0,945	0,960	0,964	0,711	0,775	0,803

We can conclude that the adsorption of acetic acid on marl calcareous follows the Langmuir model with a correlation coefficient of 0,964 at a temperature of 35 °C.

3.7. The specific surface area:

The specific surface area of an adsorbent is based on measurements of the adsorption capacity for a given solute. The adsorbate must have an acceptable surface. Just donations determine the value of the adsorption capacity of the monolayer from the adsorption isotherm. Knowledge of the maximum amount of adsorption (mg/g or mol/g) following the equation Langmuir, leading to the determination of the surface σ by the equation:

$$\sigma = Q_0 * s * N$$

Where N is Avogadro's number

$s = 21 \text{ \AA}^2$ is the area occupied by a molecule of acetic acid. The specific surface areas obtained at different temperatures are summarized below in Table 2:

Table 2: Specific surface at different time

Temperature	25°C	30°C	35°C
$\sigma \text{ (m}^2\text{/g)}$	1757	1885	1896

Based on these results, the acetic acid adsorption on marl calcareous has the best performance at a temperature of 35 °C with a maximum surface area of 1896 m²/g [13].

3.8. Adsorption Kinetics

For the adsorption kinetics of acetic acid on both types of clay was studied by adjusting the experimental data with two kinetic models, namely pseudo-first order and pseudo-second order.

The form of the equation linéairisée pseudo-first-order [16] is generally expressed as:

$$\ln(q_e - qt) = \ln q_e - k_1 t$$

Where q_e and qt is the amount of solute adsorbed at equilibrium and at time t , respectively (mg.g-1), k_1 is the adsorption rate constant (min-1). The values of k_1 and q_e result of the slope and intercept of the plot $\ln(q_e - qt)$ versus t .

Linearised form of the equation of the second order is pseudo-[16]:

$$t/qt = 1/K_2 q_e^2 + t/q_e$$

Where k_2 is the constant rate of adsorption (mg.g-1.min-1). The equilibrium adsorption capacity, q_e and pseudo-second-order rate constant, k_2 the result from the slope and intercept

of the curve t / qt versus t . Table4 shows the parameters from the pseudo-second order kinetic model:

Table 4: Parameters of pseudo first order and second order model

C mol.l-1	qe,exp (mg.g-1)	pseudo first order			pseudo second order			
		qe,cal (mg.g-1)	k1 (min-1)	R ²	qe,cal (mg.g-1)	k2 (min-1) (mg g-1 min-1)	R ²	
0,2	0,015	0,015018	0,3388	0,2348	0,0150	20908,38	4,7125	1,00

Based on these results, the adsorption of acetic acid on marl calcareous is best described by the pseudo-second order model with a correlation coefficient of 1,00.

4. Conclusion

The results obtained in this work have shown that acetic acid (0,2 mol/l) adsorbs well on marl calcareous with a contact time of 0,5 hour, which corresponds to 75% adsorption where the Langmuir kinetic model correctly describes the adsorption process for marl calcareous.

The effect of the initial concentration and temperature had a positive influence on the ability and retention kinetics of acetic acid on marl calcareous. pH also has a positive impact on the kinetics of adsorption of the organic molecule. The marl calcareous has a specific surface of 1896 m²/g. Adsorption on marl calcareous is best described by the pseudo-second order model

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