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Kinetic Study Of Adsorption Of Azo Dye (Evans Blue) On Titanuim Dioxide In Aqueous Medium

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***Abstract*— Today pollution of aquatic water has become one of the most serious environmental problems. Thanks to their structure, semi conductors like ZnO or TiO_2 have been widely used in the decontamination process of water when they were coupled with UV light. In this work, we studied the retention of Evans blue onto TiO_2 as support. Studies led in batch "method" showed on almost total elimination of the dye. The influence of some parameters like initial concentration of dye and salts was also studied and showed a significant improvement of the speed and the adsorption capacity;. Moreover, this process was well described by several kinetic models such as Langmuir and Freundlich.**

Keywords—Evans blue, dyes, environmental, adsorption, water.

I. INTRODUCTION

Pollution of the environment resulting from an accelerated industrialization around the world becomes today a significant problem. This is due to an intensive use of organic materials (phytosanitary products and dyes) and also inorganic materials (metals and non metals). For dyes, particularly, those which have been synthesized, contamination of the aqueous medium are linked to the discharge of effluents (often heavily colored) from the textile industry. What could generate an important nuisance like the systematic destructions of fauna and flora and even human health throughout food and drinking water.To deal with this situation, governments of the countries concerned, as well as the international organizations, have used stringent regulation to reduce these pollutants at their lowest concentrations and why not, to their total elimination. Hence, the development in the past of several processes such as: the ion exchanges [1-2], filtration [3], biodegradation [4-6], adsorption over numerous supports [7-10] and recently photochemical methods, particularly the advanced oxidation process (called also AOPs) [11-15].

The adsorption, although this process was less efficient than the latter (it leads to a transfer of pollution to one phase to another rather than its destruction), continue to be used actually because of its simple implementation and also its low cost. Then, this technique needs to be well developed both experimentally and in terms of treatment of the obtained results. This has allowed for example the determination of some parameters like: adsorption heat, various equilibrium constants adsorbent-adsorbat, type of interactions (with support complexation for example) [16]

In this work, we present results for the adsorption of azo dye (Evans blue) in absence of light onto a particular support which has been used so far in photocatalysis: TiO_2 in powder. Determination of maximum capacity, effect of salts and adsorption kinetic will be investigated. Besides, some isotherm models will be investigated in order to know which will give the better description of the process and these are: Langmuir and Freundlich.

Nomenclature

Q_{ads}: Adsorption capacity of the support at time t (mg/g).
C_0: Initial concentration (mg/l) at t=0.
C_t: Dye concentration (mg /l) at time t of the adsorption process.
$m_{adsorbent}$: Mass of the catalyst (g).
C_e: concentration at equilibrium (mg L^{-1})
Q_e : quantity of adsorbed Evans blue on equilibrium ($mg.g^{-1}$).
Q_{max} : maximum capacity of adsorption to saturation ($mg.g^{-1}$).
k_f :Constant of Freundlich relation
n :Coefficient of the Freundlich equation.

MATERIALS AND METHODS

II.1.Material

The titanium dioxide 100% anatase, its specific surface is 320 m^2 g^{-1}, Evans blue (EB), was furnished from sigma-aldrich and used without further purification its structure solution is depicted in figure 1. All solutions of dye were prepared from bidistilled water and filtered on a Millipore filter: 0,45µm.

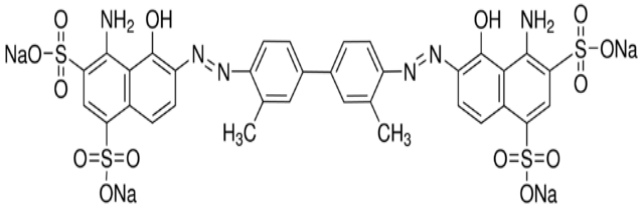

Fig.1. Structure of Evans blue

II.2. Analysis

The spectral evolution and measurements of the absorbency of all solutions at different times were monitored by UV/Visible spectrometer type "UnicamHelios-αspectronic". HANNA pH meter was used for measurement of pH solutions.

II.3. Experiments

The adsorption of the EB on TiO_2 was carried out in a simple pyrex vessel with a capacity of 200 ml with an agitator under velocity of 500 turns/min and at ambient temperature (22°C ± 2).Mixing was made with a magnetic stirrer. The absorbance of all samples was measured against a calibration curve at λ_{max} equal to 604nm.

RESULTS AND DISCUSSION

3.1. Spectrophotometric Properties of Evans blue

The spectrum of Evans blue (10mg/l), obtained at natural pH (6.3), shows the existence of three bands having variable intensities and located successively at 230 nm,320 nm and 604 nm for an optical path of 1 cm, (figure 2).

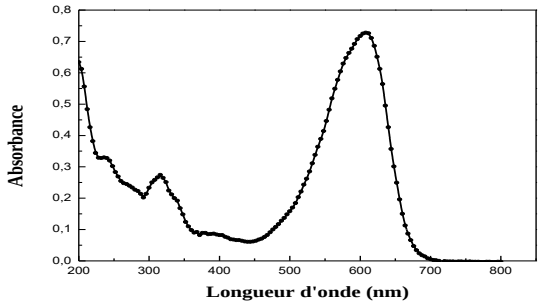

Fig.2.UV /Visible spectrum of the EB (10 mg/l, pH=6.3)

3.2. Contact time

The study of adsorption of EB into TiO_2 powder, obviously involves determining the contact time which corresponds to the equilibrium establishment or a state of saturation of the support by the substrate. It consists to put in contact, 10 ppm of Evans blue and 1g/l of TiO_2 powder until we reach this state of saturation. The results obtained at the end of these experiment showed that this contacting time is 30 minutes and corresponds to an almost total elimination of dyes; 95%. It has been obtained from the following relation (1) (Figure 3):

$$q_{ads} = \frac{(C_o - C_t)}{m_{adsorbant}} V \qquad (1)$$

Where: q_t= quantity of the EB absorbed at instant t
C_0= initial concentration
C_t= concentration at instant t
m= masse of the support

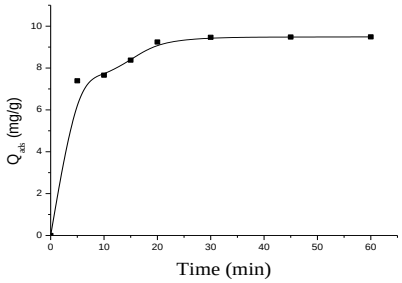

Fig.3. Adsorption kinetics of Evans blue on the TiO_2; r = 1g/l , T° = 22°C ; pH =6.3. V_{ag} = 500 turns / minute

Determination of the equilibrium time is important for calculating the maximum adsorption capacity and the establishment of adsorption isotherm which are essential for the identification of adsorption type occuring in single or multilayer form. Other factors such as initial concentration and salts may influence the adsorption capacity [17].

3.3.Effect of parameters on the adsorption

3.3.1. Effect of the initial concentration

The examination of figure 4 shows the influence of the initial concentration of the substrate. We note that its increasing, led also to a sensitive increase of the absorbed quantity of EB for the same mass of TiO_2. Then, this could be due to a great availability of free sites of adsorption. Therefore and in this case, we observed a series of superimposed monolayer curves, having same equilibrium time: 30 minutes in all cases.

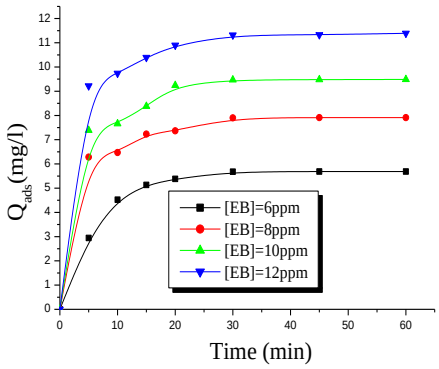

Fig.4. Adsorption kinetics of Evans blue on the TiO_2,; r = 1g/l , T° = 22°C ; pH =6.3,V_{ag} = 500 turns / minute [EB] = 10ppm, Influence of initial concentration of EB

3.3.2. Effect of salts

It is well known that natural contaminated water, contains some ions at variable concentrations. There are for example: NO^-_3, SO^{2-}_4, Cl^-, $NaHCO_3$, CO^{2-}_3, Ca^{2+}… In order to understand their impact of these ions on the retention process, experiments were performed by mixing at each substrate solution and at fixed concentration (10 ppm), salts of monovalent cations (NaCl, Na_2SO_4 and $NaHCO_3$) and bivalent cations ($CaCl_24H_2O$, $BaCl_22H_2O$), at given concentrations. It should be mentioned that before to undergo to this investigation, some experiments have been carried out in absence of the support TiO_2, in

order to verify if any reaction could occur in that mixing. It was observed in presence of salt like NaCl , $BaCl_2 2H_2O$ and Na_2SO_4 and for concentrations ranging from 10^{-1} to 10^{-4} M, no reaction was observed. Same results were observed too in the presence of salt such: $NaHCO_3$ and $CaCl_2$ 4 H_2O but of low concentration (< 10^{-4} M) Indeed, for concentration greater than 10^{-4}M, a decolorization of the dye was constated. In these conditions and on the basis of this result, experiments were conducted on mixtures of these salts and the dye (10 ppm) for a reaction time of 60 minutes. No significant effect was observed in the retention process due to an absence of competitivity between substrate and salts for the sites of the catalyst (Figures 5a and 5b). .

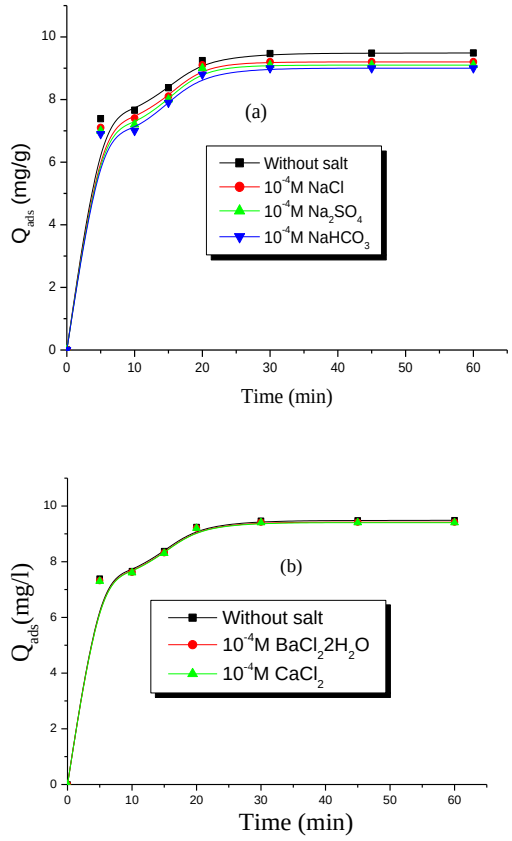

Figure.5. Effect of salts [10^{-4}M] on the adsorption of Evans blue [EB] =10ppm on TiO_2;a)[EB] =10ppm; T= 22°C, r = 1 g / l, pH=6.3;Vag=500 rev /min. **b)** Effect of bivalent salts[10^{-4}M]; T= 22°C, r = 1 g / l, pH=6.3;Vag=500 rev /min

3.3.2. Linearization processes

Experimental results were treated by various linearized equations issued from known models such as: Langmuir and Freundlich, This has conducted to the purpose of some useful parameters. Thus, for the:

-For Langmuir model, the linearization allowed the determination of the maximal capacity (noted Q_{max}) with a good correlation coefficient (0,98). We observed also an identical value with those obtained experimentally (table2). This, shows that adsorption of the dye occurred in monolayer form, which is however, an ideal model by taking into account the type of the texture of this support and where the upper limit exists for this model ((→1 where C→∞).

-for Frendlich, linearization allows also determination of maximal capacity (Q_{max}) but with a good correlation coefficient 1 and consequently a good fitting.. Thus, this model described correctly the adsorption process of EB onto TiO_2 .

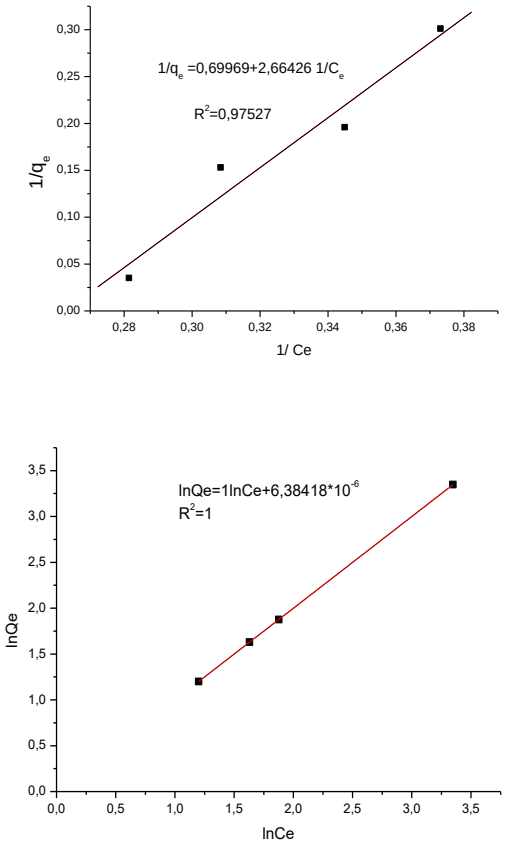

Fig.6.linearization of isotherms adsorption for various models which have been studied:
a) Langmuir; b) Freudlich;

Table 1. Parameters characterizing each model adsorption on TiO_2.

Models	q_m (mg/g)	a (L/mg)	n et k_f (mg/g).(L/g)^n	R^2
Langmuir	1.42	1.87	/	0.97527
Freundlich	/	/	n=1 k_f=25.5367	1

4. CONCLUSION

The results obtained in this work have shown that:

-The Evans blue (10ppm) is well adsorbed onto TiO_2 to a rate percent equal to 95% and for a contacting time of 60 minutes.

-The effect of salts did not affect the capacity and kinetics adsorption, meaning a total absence of competition between dye and salts for the sites of the catalyst.

- The process was described by some isotherm adsorptions and led to appreciable fitting, mainly, in the following order: Freundlich > Langmuir.

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