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Kinetic Studies of the Adsorption of Two Major Textile Dyes Dyeing Indigo and Red Cibacrone on Activated Carbon and Anion Resin in an Aqueous

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***Abstract*— today, the majority of synthetic dyes used in the field of textile finishing are very reactive azo dyes soluble in water and vat dyes. The use of such dyes produces a significant amount of visible and undesirable colored effluents to human health and the environment.**

In this work, we made a first step in processing a colorful pattern with a series of reactive azo dyes and vat environment are represented by the red cibacrone and indigo, used in the textile industry and this, by the technique of adsorption on different materials such as anionic resin A500 (AR A500), cationic resin (C300), crude and refined cellulose, powdered activated carbon (PAC) and calcium chloride. Following the optimization performed on different materials cited, the results obtained on powdered activated carbon and anionic resin A500 are the most important. The adsorption rate is 80 % and 92 % respectively for the torque indigo/activated carbon and red cibacrone/anionic resin A500.

Keywords—textile finishing; red cibacrone; indigo; adsorption; adsorbent materials; fading rate.

I. INTRODUCTION

Currently, the industry of dyeing and textile finishing [1], [2] uses a very large amount of synthetic dyes, among which we find the vat dyes and azo reagents. They are very soluble in water compared to other. The use of such dyes produces a large visible and undesirable for humans and the environment because of their toxicity [3], [4] and difficulty of biodegradability [5], [6] colored effluents. This requires treatment. Generally the elimination of dyes [7], [8] from textile effluents has essential problems during treatment and following their chemical complexity and diversity [9] due to their formulation. Therefore they reduce the effectiveness of the treatment method used.

Primarily, there are several conventional techniques for wastewater treatment and textile effluents. Among these we find adsorption processes [8], coagulation/flocculation [10], [11] and membrane [12] etc. The choice of treatment method of colored water depends mainly on the chemical nature of the dye to be eliminated. The ultrafiltration and adsorption techniques are commonly used [13], [14], [15], [16] for the treatment of this colored solutions type.

The technique requires adsorption using various organic adsorbents, minerals and/or inorganic. In our case we used a variety of materials, namely, anionic resins [17] and cationic [18], celluloses raw and refined [19], powdered activated carbon [20] and calcium chloride.

II. MATERIALS AND METHODS

A. Features dyes studied

The Table 1 shows the physico-chemical characteristics of dyes operated (indigo and red cibacrone).

	Indigo	**Red cibacrone**
Empirical formula	$C_{16}H_{10}N_2O_2$	$C_{25}H_{16}O_7N_7S_2Na_2Cl_2$
Molar mass (g.mol^{-1})	246	541
Solubility in water	insoluble	soluble
Utility	textile	textile
Vapor	low	low
λmax	660	550

B. Adsorbent materials used

1) *Original synthetic polymeric adsorbents*

a) *Anion resin A500*

The anionic resin A500 is a product marketed by the company of Shanxi Xinhua Chemical Co. Ltq., purity of 95%, are clear spherical beads having a chemical structure R-$N(CH_3)_2(C_2H_4OH)^+$, a total exchange capacity that equals 1.15 eq/l.min and a density of 0.65 to 0.75 g/l.

b) *Cationic resin C300*

The cationic resin C300 is a product also marketed by company of Zhengzhou City Jintai Water Treatment Raw Material Co. Ltd., purity of 90%, are clear spherical beads having a chemical structure R-SO_3^- and the total exchange capacity is about 2.2 eq/l. min. In both resins, R represents a cross linked macromolecular group.

2) *Original and natural absorbent polymers*

The cellulose exploited in this study is the "Kraft cellulose" was provided by the firm "Cellulose-Morocco, Sidi Yahia El Gharb". This material is in the form of crude and refined pulp [19] with a gross formula: $(C_6H_{10}O_5)_n$.

3) *The artificial origin of the adsorbent polymer*

a) Powdered activated carbon

The powdered activated carbon used is a commercial product that was provided by Merck, it is vegetable powder form. It has a particle size less than 80 microns, its physicochemical characteristics have been given as following: specific surface area of 831 m^2/g, pH = 1.84, diameter of the pores varies from 40 to 50 Å and the density of 1.71.

4) *Mineral adsorbents*

a) *Calcium chloride*

The calcium chloride used in this work is a calcium salt ($CaCl_2$), having a molar mass equal to 110.984g/mol and which was provided by the Company Shouguang Jinlei Chemical Co. Ltd..

5) *Optimization method for measuring the adsorption*

During this study a part, we optimized different adsorbents (anionic resin, cationic resin, crude and refined cellulose, powdered activated carbon and calcium chloride) in order to determine the proper adsorbent for each dye studied, and on the other hand, we investigated the influence of various parameters (weight of the support, pH, temperature and adsorption time) and the amount on adsorption kinetics. To do this, we took model solutions (the colored indigo and red cibacrone water) mass concentration of 20 mg/l on which we added 0.1g of each adsorbent. The mixture was put into a beaker and allowed to stir using a magnetic stirrer for two hours. During this stage, we carried out the measurement of the amount of adsorption of couples indigo/PAC and red cibacrone/AR A500 during each 20 min.

The pH of each mixture was adjusted by adding either NaOH or HCl, which was measured using a pH meter type Schott Titro Line (TE96). The determined concentration of model solutions dyes was performed by a UV-spectrometer JENWAY 6405 category.

III. Results and Discussion

Experimental results show that the percentage retention of dyes increases with the increase of the mass of adsorbent.

1) *Study of dyes adsorption*

a) *Study of quality adsorbents*

In order to optimize the dyes adsorption studied, we used different materials namely synthetic polymers (anionic resin A500 and cationic resin C300), natural polymers (cellulose refined and crude), artificial polymer (powdered activated carbon) and minerals (calcium chloride).

The Table 2 and 3 respectively include the rate of discoloration (RD) of the colored patterns on the various adsorbents used solutions.

Table 2: Adsorption of indigo dye on different adsorbents.

	RD after 24h	***RD after 48h***	***RD after 72h***
Anion resin AR A500	36%	72%	74%
Cationic resin C300	3.5%	3.8%	3.9%
Crude cellulose	1.4%	1.9%	1.9%
Refined cellulose	1.5%	2%	2%
Powdered activated carbon	76%	79%	80%
Calcium chloride	2.5%	2.8%	2.8%

Table 3: Adsorption of cibacrone red dye on different adsorbents.

	RD after 24h	***RD after 48h***	***RD after 72h***
Anion resin AR A500	30%	60%	92%
Cationic resin C300	3.5%	5%	5%
Crude cellulose	1%	1%	1.4%
Refined cellulose	0.5%	1%	1%
Powdered activated carbon	0.5%	2.8%	3.3%
Calcium chloride	1.2%	2%	2%

The results obtained in these tables, we note that:

The powdered activated carbon (PAC) is a good adsorbent for indigo dye. While the anionic resin A500 proves a good adsorbent for red cibacrone, both adsorbents give a very high increasing rate of adsorption time of discoloration.

The values of RD dyes treated by other adsorbents (cationic resin C300, crude and refined cellulose and calcium chloride) were stabilized from 24 hours in the vicinity of might understand values between 0.5% and 3.9%.

According to the optimization of the quality adsorbents, we can conclude that the indigo dye is better adsorbed by the activated carbon powder that red cibacrone by anionic resin AR A500.

2) *Influence of parameters on the adsorption*

a) *Study of the influence of the mass on the adsorption*

The figures 1 and 2 shows respectively the variations of the amount of adsorption of dyes indigo and red cibacrone according to two values of mass (0.1g and 0.2g) of powdered activated carbon and anion resin AR A500 for a contact time of 2 hours.

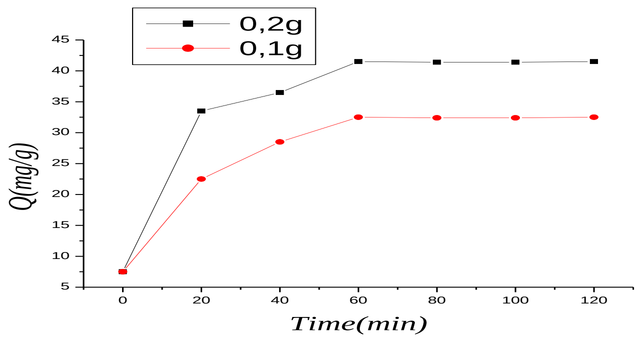


Figure 1: Influence of the mass of the PAC on the amount of adsorption of indigo with time.

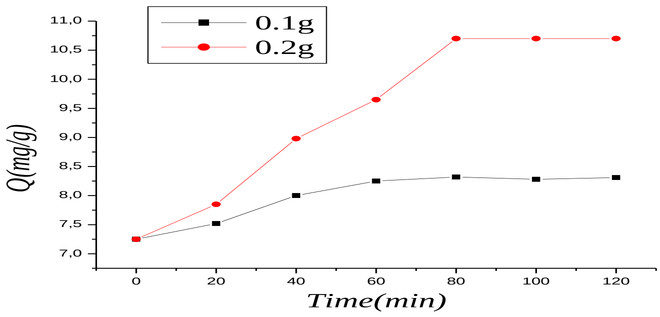


Figure 2: Influence of the mass of RA A500 on the adsorption amount of red cibacrone with time.

From the curves shown in figures 1 and 2, we find that there is a gradual increase in the amount of adsorption for two couples indigo/PAC and red cibacrone/RAA500 depending on the time of touch adsorbate/adsorbent mass when the adsorbent used increases.

The increase of dye adsorption performance was studied well observed when using a mass of 0.2g of each adsorbent. This improvement could be justified by the increase in specific sites found in the adsorbent surface.

b) Study of the influence of pH on the adsorption of dyes

In this study, we followed the influence of pH on the adsorption of these two materials power. The pH is therefore a very important factor in any study, because it influences the structure of both adsorbent and adsorbate and the mechanism of adsorption. This factor may depend on the source of water to be treated and their treatment method (coagulation, flocculation, oxidation, complexation, adsorption, etc.). So it is wise to know the effectiveness of adsorption at different pH values.

The figures 3 and 4 successively show the effect of pH on the adsorption amount of indigo on the PAC and red cibacrone on the RA A500.

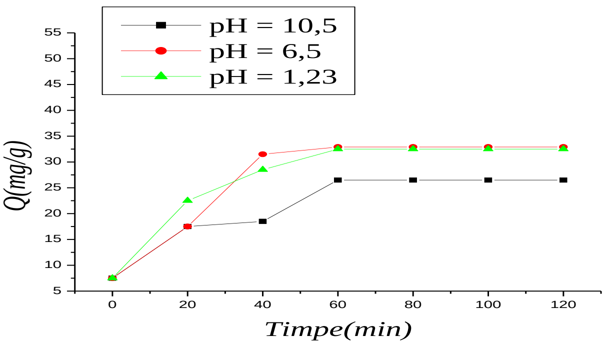


Figure 3: Effect of pH on the adsorption of torque indigo/CAP.

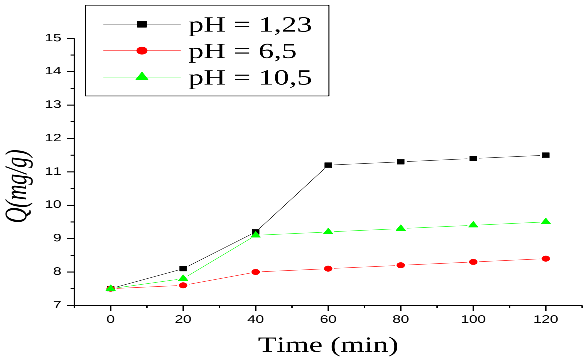


Figure 4: Effect of pH on the adsorption of red cibacrone/RA A500.

From the curves of figures 3 and 4, we observe that the adsorption for torque indigo/PAC is important both in acidic and near neutral environment. By against, at the torque cibacrone red/RAA500, the influence of pH is clearly important in acid medium. Increasing the amount of adsorption in an acidic medium for recorded couples could reveal both the adsorbent and adsorbate structure. Indeed, the acidity would enable specific adsorption sites on the surface of the adsorbent for the PAC and RA A500 and release more preferably the functional group of the RA A500 resin.

c) Influence of temperature on the dyes adsorption

The figures 5 and 6 show the influence of temperature on the adsorption amount of torques indigo/PAC and cibacrone red/RA A500.

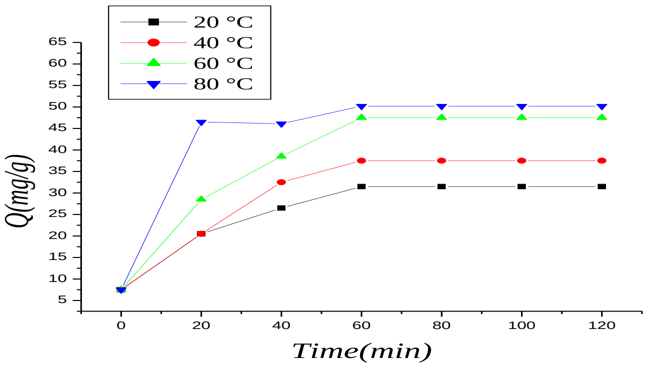


Figure 5: Effect of temperature on the adsorption of torque indigo/PAC.

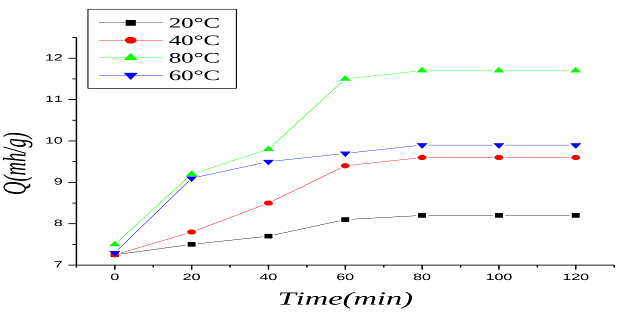


Figure 6: Effect of temperature on the adsorption of red torque cibacrone/RA A500.

This study shows that the adsorption amount is gradually larger as the temperature increases on the one hand, and on the other hand, the amount of adsorption obtained stabilizes after 60 min stirring.

3) Kinetic Study of adsorption of dyes (indigo and red cibacrone)

a) Adsorption kinetics

The retention kinetics describes the reaction rate for determining the time between ignition on the adsorbent and the adsorbate to reach equilibrium. This is an important step in any study of adsorption.

According to the optimization results of the adsorption of each dye, we are interested in studying the effect of powdered activated carbon for indigo and RA A500 anionic resin for red cibacrone. To do this, we followed the kinetics of adsorption for an initial concentration of 20mg/l for dyes exploited, with masses of 0.1g for powdered activated carbon and RA A500 anionic resin.
The figures 7 and 8 successively represent the kinetics of adsorption of indigo in to the activated carbon powder and red cibacrone RA A500 anionic resin.

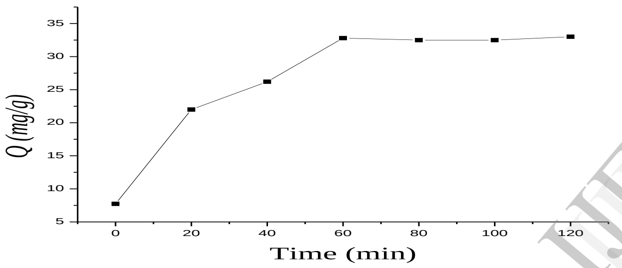


Figure 7: Adsorption kinetics of indigo on the CAP.

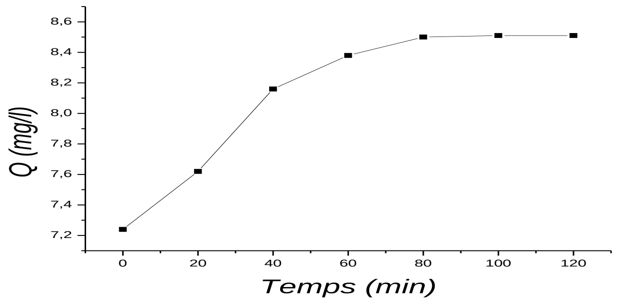


Figure 8: Adsorption kinetics of red cibacrone RA A500 anionic resin.

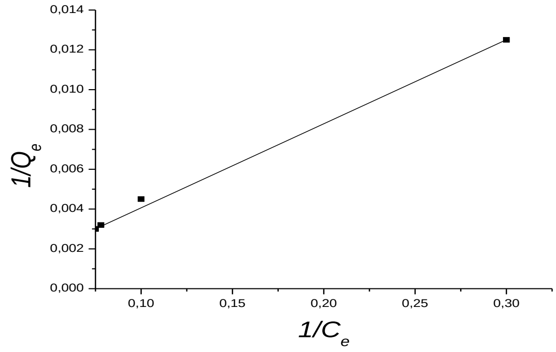
The figures 7 and 8 show that indigo was set on powdered activated carbon for a period of 60 min and 90 min in the case of red cibacrone RA A500. These results can be explained by the saturation of active sites of the substrates.

b) Adsorption isotherms

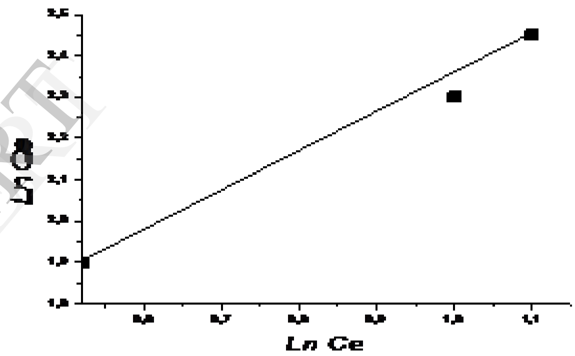
The most known adsorption kinetics of adsorption isotherms were given by Langmuir [21], [22], [23], [24] and Freundlich [25], [26]. They play an important role in determining the maximum capacity and identifying the type of adsorption that can occur before. The Langmuir isotherm has been given by the following equation: $Q_e = Q_0aC_e/1+ aC_e$ and by the Freundlich equation: $Q_e = KfC_e^{1/n}$. These are represented by $1/Qe = f(1/Ce)=1/(Q_0)$ LnQe and

$LnQe = f(LnCe) = LnK_f + 1/(nLnCe)$.

The figures 9 and 10 after successively elucidating Freundlich and Langmuir isotherms for torques indigo/CAP and red cibacrone/RA A500:

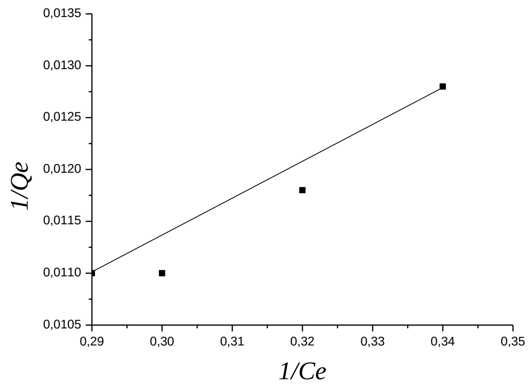


(a)

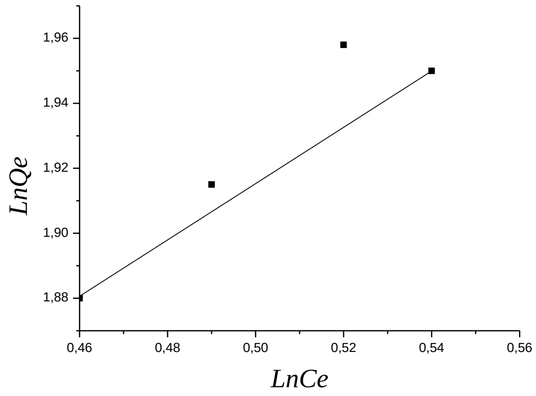


(b)

Figure 9: Langmuir isotherms (a) and Freundlich (b) of torque indigo/CAP.



(a)



(b)

Figure 10: Langmuir isotherms (a) and Freundlich (b) torque red cibacrone/RA A500.

According to the Langmuir and Freundlich isotherms, we determined the main parameters of two adsorption models shown in Table 4.

Table 4: Key parameters characterizing the two adsorption of torques indigo/CAP and red cibacrone/RA A500 models.

	Langmuir	***Of***	***equation***	***Freundlich***	***of***	***Equation***
	Q_0 (mg/g)	a	R^2	k	n	R^2
Indigo/PAC	10	0.397	0.9967	3.872	0.972	0.9877
Red cibacrone/ RA A500	2500	97.5	0.9606	4.246	0.999	0.9393

The results recorded in this table confirm those obtained previously in figures 9 and 10. Regarding the factor (n), in all cases, it is less than 1, as a confirming favorable adsorption. The values of the coefficients of correlation R^2 expressing the degree of linearization show that the Langmuir model describes well the experimental values.

IV. CONCLUSION

This work aims at studying the retention of two families of textile dyes (indigo and red cibacrone) different static regime adsorbents. The study has shown in particular the influence of certain parameters (pH, time, adsorbent mass and temperature) on the retention of this indigo and red cibacrone adsorbate. The experimental results of adsorption kinetics on powdered activated carbon (PAC) and the RAA500 resin are respectively 60 min, 70 min and 90 min. As for the value of the activated carbon powder and resin RA A500 necessary fading model solutions is 0.2g. The adsorption isotherms of activated carbon powder and the anionic resin RA A500 rather follow the Langmuir model than Freundlich. The indigo-based and red colored solutions cibacrone adsorb better in an acid medium.

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