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## Characterization of Dyes Adsorption on Carbonized Sewage Sludge.

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### ABSTRACT

In the present work, activated carbon was prepared and characterized in laboratory. Batch experiments were performed to test its adsorption affinity for Eriochrome Black T and Rhodamine b dyes. Kinetics and isotherms adsorption were evaluated and several models were used to describe the experimental data. The obtained results show that the prepared activated carbon is basic and is more efficient to remove the Eriochrome Black T. The calculated rate adsorption constants are about  $0.0327 \text{ mg}^{-1} \cdot \text{g} \cdot \text{mn}^{-1}$  for Eriochrome Black T removal and 0.0036 for Rhodamine b removal. For low concentrations, the adsorption isotherms are better described by Langmuir equation.

**Keywords:** carbon, sewage sludge, adsorption, Eriochrome Black T, Rhodamine b.

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## INTRODUCTION

Dyes are considered as major constituents of the wastewater discharged from many industries, like dyeing, textile, leather, paint and plastic industry [1]. Their removal from waste water becomes environmentally important. Among the various chemical and physical methods used in pollutants removal, adsorption seems to be efficient process [2]. The choice of the adsorbent is the first important step in waste water treatment. Activated carbons are usually used because they are cheap in production and possess a great adsorption capacity, which is in a relation to their porous structure [3]. They are obtained from materials with high carbon content. Sewage sludge is a major by-product generated in conventional sewage treatment plants. Due to the presence of high volatile carbon, several researchers have used sewage sludge for the production of activated carbon to find substitute for commercially available activated one [4]. In the present study, the carbonized sludge-based adsorbent has been tested for the removal of two dyes in aqueous solutions.

## MATERIAL AND METHODS

### Preparation and characterization of activated carbon from sewage sludge

The activated carbon is prepared from the sewage sludge collected from Sidi Merouane sewage treatment station, located in the North-Est of Algeria. The sewage sludge sample was dried at 105 °C for 24 hours, crushed and sieved to a uniform size. Then, carbonized at 550 °C in a muffle furnace. The thermal decomposition of the material serves to eliminate much of the non-carbon elements through their release as gaseous volatile products. It also leads to the grouping together of the freed atoms of elementary carbon as elementary graphitic crystallites which assume an irregular arrangement [5]. The point of zero charge (PZC) of the obtained activated carbon was determined by titration method. The estimation of its surface functional groups was performed qualitatively by Fourier Transform Infra-Red spectroscopy and quantitatively by neutralization method using NaOH and HCl solutions.

### Dyes sorption experiments

The two dyes used in this study are Eriochrome Black T ( $C_{20}H_{12}N_3NaO_7S$ ) as an azo dye and Rhodamine b ( $C_{28}H_{31}ClN_2O_3$ ) as a cationic dye. Their chemical structures are shown in Figure 1.

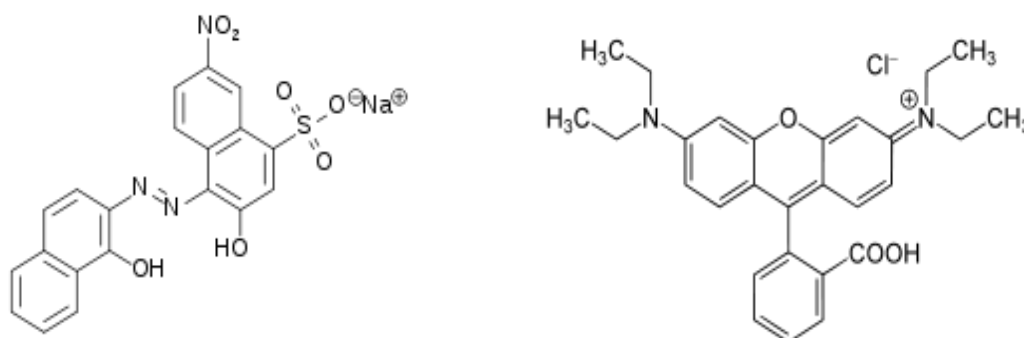


Figure 1: Structures of dyes: Eriochrome Black T; Rhodamine b

All chemicals reagents used in this study were of analytical grade. All solutions were prepared with distilled water. The stock solutions of dyes were prepared by dissolving commercial products. The adsorption experiments were performed in batch system. The effects of activated carbon dose, time and dyes concentrations were evaluated. In all experiments, the dyes analyses were performed in solutions obtained after centrifugation and filtration through 0.45  $\mu$ m membrane. The adsorption progress was measured directly by using UV-Visible SCHIMADZU 1650 PC spectrophotometer at wavelengths 533.9 for EriochromeT and 553.7 for Rhodamine b. The removal efficiencies were calculated from the differences between the initial and the final concentrations.

## RESULTS AND DISCUSSION

### Carbon characterization

The PZC of the prepared activated carbon is about 8.47. The total acid and basic functions are estimated to about  $6.810^{-3}$  and  $1.810^{-3}$  equivalent respectively. In the IR spectrum presented in Figure 2, the bands observed at  $3440.8\text{cm}^{-1}$ ,  $1635.5\text{cm}^{-1}$  are assigned to hydroxyl group; those observed at  $1134.1\text{cm}^{-1}$  and  $1045.3\text{cm}^{-1}$  are related to either Si-O-C or Si-O-Si structures [6]. The bands at 798.9 and 879.5 can be attributed to the presence of iron oxyhydroxides.

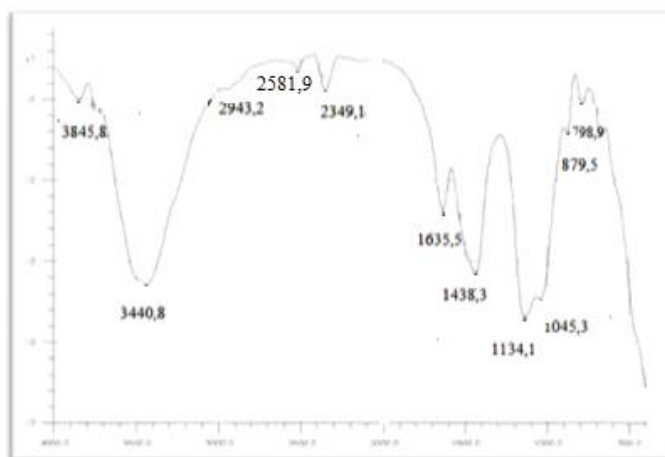


Figure 2: IR Spectrum of the prepared activated carbon

### Dyes adsorption

#### Effect of activated carbon dose

As shown in Figures 3 and 4, the increase of the activated carbon dose induces an increase in the two dyes uptake. For the initial dyes concentration tested, the increase is more important in the case of Eriochrome Black T. For a dose of 2g/L, the removal rate is about 73% and 56% for Eriochrome Black T and Rhodamine b respectively. The increase of the adsorbent dose to 5g/L, induces dyes removal higher than 90%.

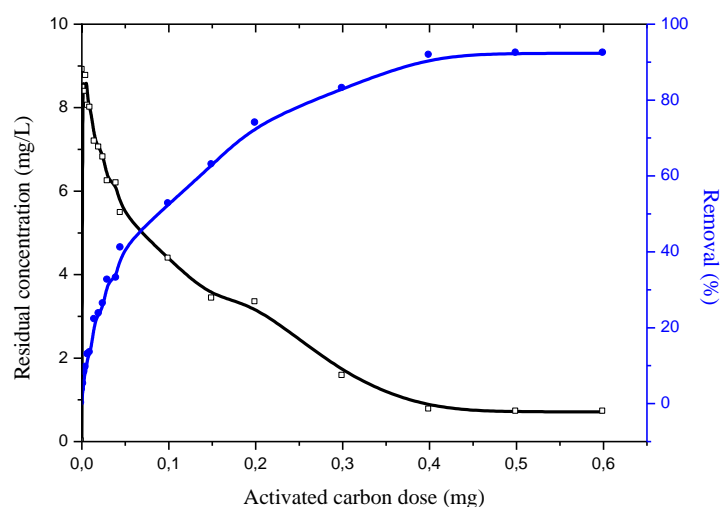
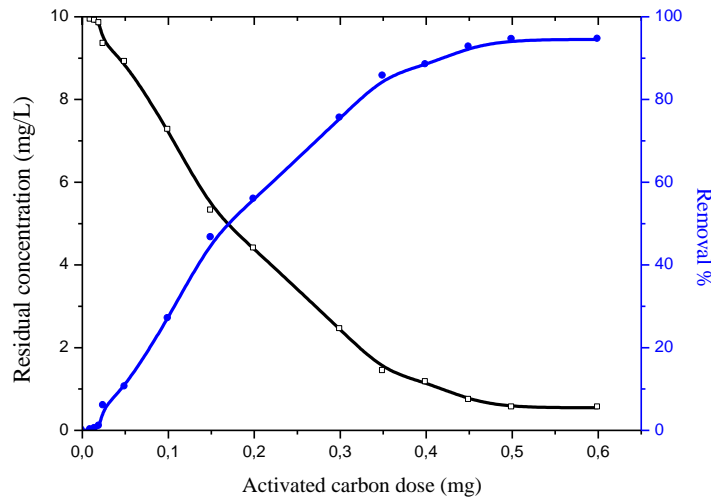


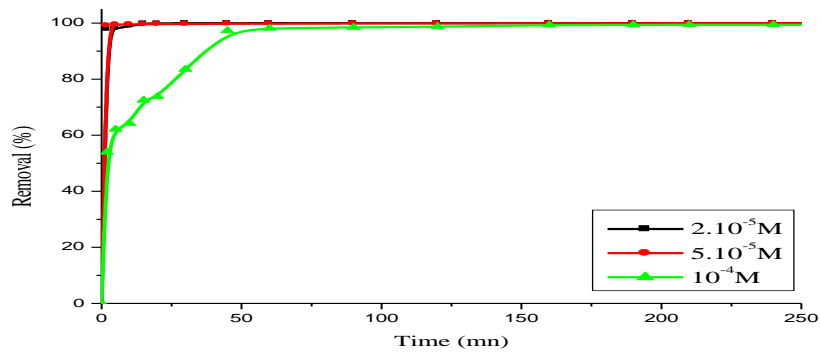
Figure 3: Eriochrome Black T adsorption -Effect of the activated carbon dose ( $C_0: 2.10^{-5}\text{M}$ ;  $t:1\text{h}$ )



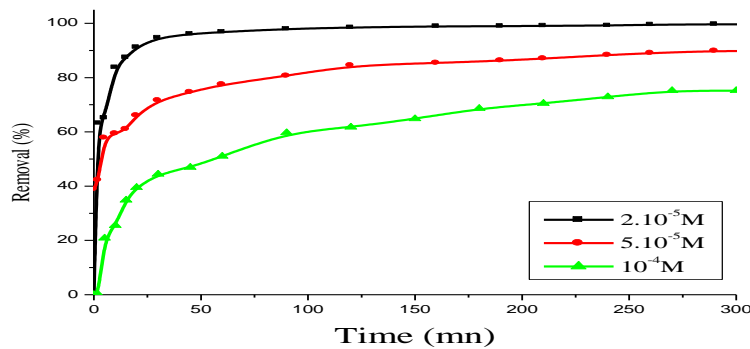
**Figure 4: Rhodamine b adsorption -Effect of the activated carbon dose**  
( $C_0: 2.10^{-5}M$ ;  $t:1h$ )

**Adsorption kinetics**

The evolution of each dye adsorption with time was studied at various concentrations. The obtained results presented in Figures 5 and 6, show that the rate of the Eriochrome Black T removal is very fast for the two lower concentrations. For a concentration of 50mg/L, the maximum removal is reached for an equilibrium time of 60minutes. In the case of Rhodamine b, the adsorption capacity increases rapidly then slowly. The equilibrium time is in a relation to the dye concentration.



**Figure 5: Eriochrome Blake T adsorption - Effect of contact time**  
(Activated carbon dose: 5g/L)



**Figure 6: Rhodamine b adsorption - Effect of contact time**  
(Activated carbon dose: 5g/L).

To determine the possible rate-controlling step of the adsorption mechanism, kinetic modeling is used. In the present study, four kinetics models are used to characterize the experimental data: the pseudo-first order, the pseudo-second order, Elovich and intraparticules diffusion. The obtained results are presented in Figures 7, 8 and 9. The calculated parameters for a concentration of  $10^{-4}M$  are presented in Table 1.

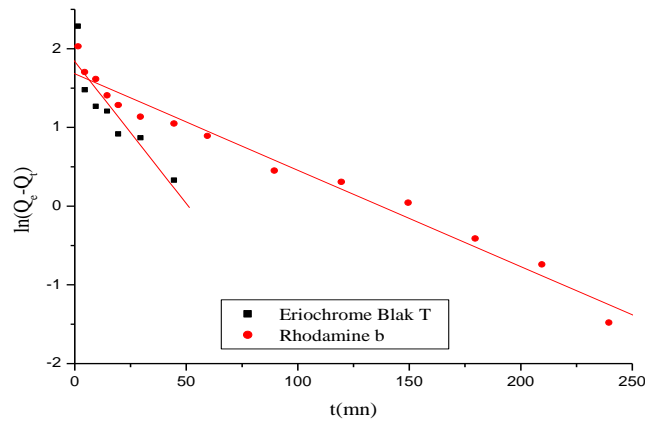


Figure 7: Pseudo-first order plots for dyes adsorption

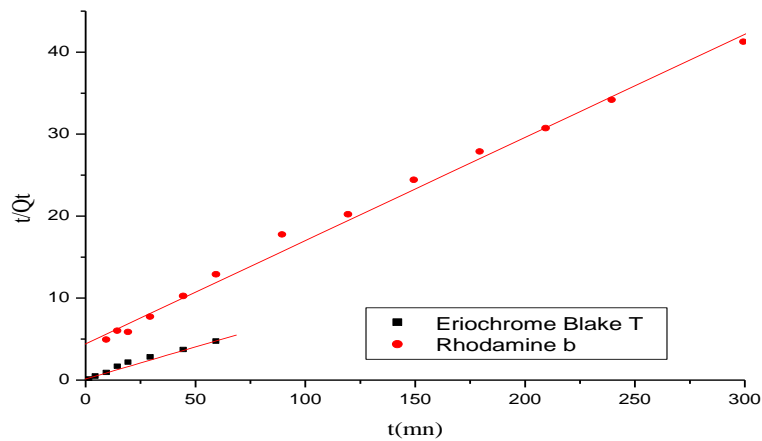


Figure 8: Pseudo-second order plots for dyes adsorption

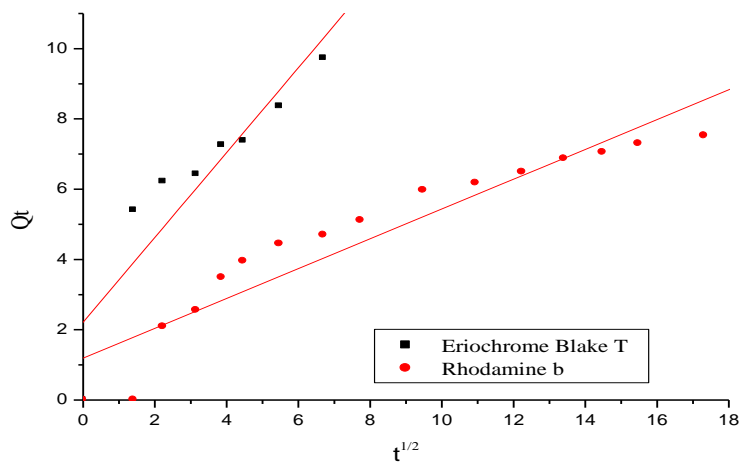


Figure 9: Diffusion plots for dyes adsorption

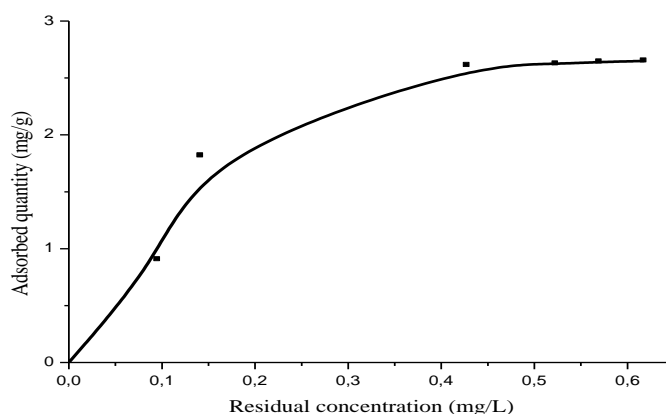
According to the correlation coefficients, the experimental data of Eriochrome Black T adsorption are successfully described by respectively the second order and diffusion models. However, those of the Rhodamine adsorption can be best described by both the first order and the second order models.

**Table 1: Kinetic parameters for the removal of dyes ( $C_0:10^{-4}M$ )**

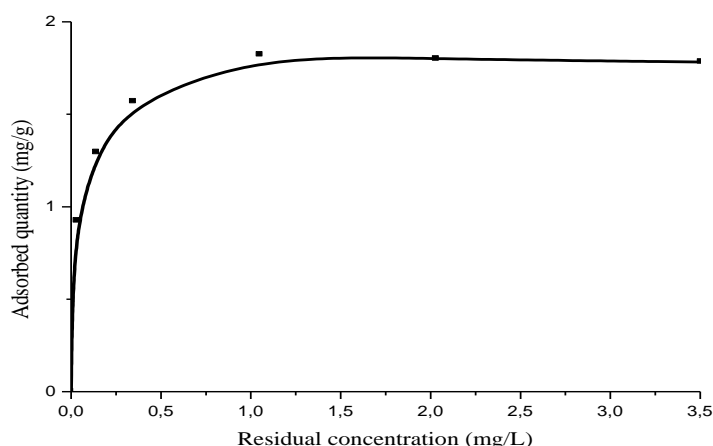
Dye	Model	$R^2$	K	$Q_e(mg/g)$
Eriochrome Black T	First order	0.906	0.0515	1.195
	Second order	0.987	0.0327	9.676
	Diffusion	0.986	0.7779	-
Rhodamine b	First order	0.986	0.0125	5.375
	Second order	0.997	0.0036	7.944
	Diffusion	0.945	0.4241	-

**Adsorption isotherms**

The removal of the two dyes increases with the increase of their initial concentrations. At high concentrations, a linear increase of the dyes uptake is observed (data not shown). Only the first step has been taken into consideration (Figure 10; 11). The two dyes are characterized by different adsorption evolution. Saturation is observed at a residual concentration of 1mg/L in the case of Eriochrome T and 0.4mg/L in the case of Rhodamine b.



**Figure 10: Eriochrome Blake T adsorption - Effect of concentration**  
(Activated carbone dose: 5g/L, t: 4h)



**Figure 11: Rhodamine b adsorption - Effect of concentration**  
(Activated carbone dose: 5g/L, t: 4h)

Several models are used to describe the relationship between adsorption capacity and equilibrium concentration in solution. The application of Langmuir and Freundlich equations to our experimental data for low concentrations gives the results shown in Figures 12 and 13.

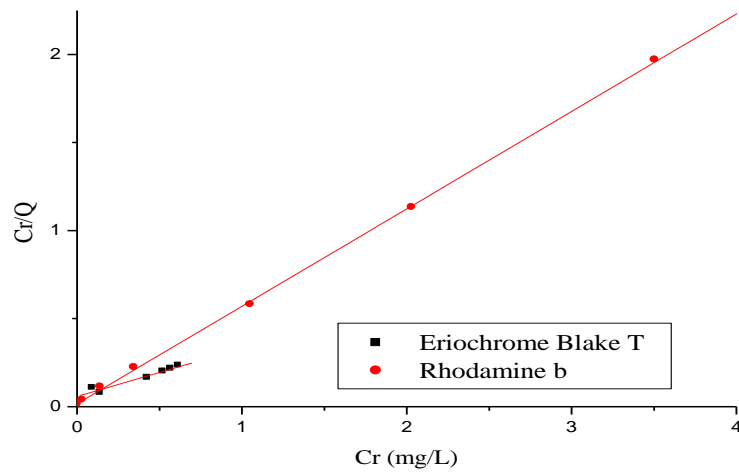


Figure 12: Langmuir plots for dyes adsorption

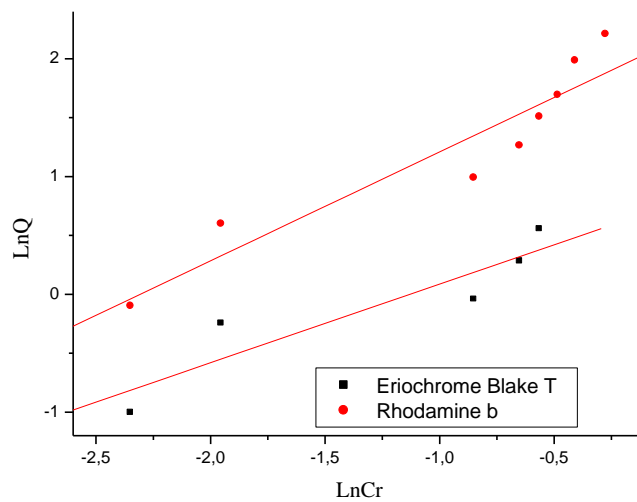


Figure 13: Freundlich plots for dyes adsorption

The calculated parameters are presented in Table 2. The obtained correlation coefficients values indicate that the Langmuir model is more suitable for describing the experimental data for the two dyes. The highest adsorption capacity for monolayer adsorption is greater for Eriochrome T adsorption. This can be in a relation to the surface nature of the prepared carbon which is mainly basic.

Table 2: Isotherm parameters of dyes removal by carbon

Dye	Model	R <sup>2</sup>	Q <sub>max</sub>	n
Eriochrome Black T	Langmuir	0.974	3.69	-
	Freundlich	0.922	-	2.127

**CONCLUSION**

The results of the present study show that the activated carbon prepared by carbonization of sewage sludge is basic. It has more efficiency for removing Eriochrome Black T than Rhodamine b. For low concentrations, the two dyes are sorbed as a monolayer.



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