REMOVAL OF CIBACET BLUE (CB) BY ADSORPTION ONTO AN ALGERIAN RED SLAG

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ABSTRACT

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This study is based on the implementation of a composite material with absorbent properties for the elimination of organic pollutants. In our case we used the slag (red slag) from the region of Bechar, (South-East of Algeria). Characterization using DRX and Fourier transforms infrared spectrometer (FT-IR), shows that, we were able to prepare adsorbents with very interesting structural and mechanical properties. The effectiveness of obtained adsorbents was evaluated in the removal of Cibacet Blue (CB) dye using the adsorption process. Kinetic results with an elimination rate of 83 % show that, the time to equilibrium is influenced by experimental conditions such us, contact time, pH, initial concentration, temperature and adsorbent mass. Pseudo-first order model represent very well our experimental results with adjustment coefficients (R^2) close to 1. Modeling of adsorption isotherms of the CB dye on the red slag shows that both models of Langmuir and Freundlich can present our results with acceptable adjustment coefficients ($R^2 > 0.995$).

Keywords: red slag, adsorption, Cibacet, adsorption isotherms, thermodynamics.

INTRODUCTION

Water which is a common heritage for all humanity, can significantly affect individual and collective health, agriculture, industry and domestic life…etc. There is no access to the production of wealth without access to water. In some countries such as Algeria, water pollution remains one of the major concerns because of limited, conventional processes to ensure a satisfactory treatment of polluted water. For that, it is necessary to design global and sustainable solutions through an original process for the treatment of any polluted water (Abel, 2012).

Algerian industrial effluents are part of the most poorly treated wastewater and are characterized by strong colorations, strong variations of pH and high chemical oxygen demands (COD) (Rana et al., 2004). In order to treat these effluents, several processes are

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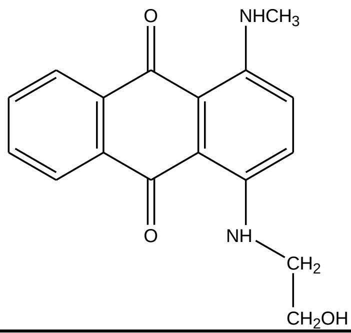
used based on the type of water to be treated. Adsorption is one of the most used processes because of its ease of use and the efficiency for the elimination of organic and/or inorganic pollutants from water. Elimination efficiency of such process is directly related to the nature of used adsorbent that can be of biological, mineral or organic origin. Several adsorbents showed better efficiency for the elimination of pollutants such us, activated carbon, pillared clay…etc. But the very high costs of these adsorbents push the researchers from around the world to find other natural adsorbents (Chavan, 2011). In this perspective, we are interested developing an original and innovative process for the adsorption of industrial effluents (dyes) using locally available red slag (from Algeria) which can be considered as a new adsorbent for the treatment of water contaminated by textile dye. The dye used is "Cibacet Blue (CB)"; it is an anthraquinone dye. Its chemical name is 1-methylamino-4-(beta-hydroxyethylamino) anthraquinone. It has been used as a dye for nylon, cellulose, polyester, and acrylate fibers. It has also been used to dye the exterior of the thermoplastics and in semi-permanent formulations for hair dye at concentrations less than 1%.

MATERIALS AND METHODS

Characteristics of adsorbate

Table 1 summarizes the properties of Cibacet Blue (CB) dye.

Table 1. Main characteristics of blue cibacet (CB) dye.

Dye	Cibacet Blue (CB)
Structure	
Chemical formula	$C_{17}H_{16}N_2O_3$
Molar mass (g /mol)	296.325
Maximum wave length λmax (nm)	630
melting point	332° C
Soluble in	Acetone, ethanol, benzene, linseed oil

Characterization of adsorbent (red slag)

The following methods are used to characterize adsorbent: The FTIR spectroscopy is used to confirm the slag components based on the chemical functional groups. The crystalline structure of Red slag was obtained by X-ray diffraction (XRD) recorded on (BRUKER D2 PHASER) powder diffractometer (Cu Ka radiation, k = 1.5418 Å).

The isoelectric point was determined by preparing series of NaCl solutions (0.1N) at different initial pH ranging from 3 to 12. pH was adjusted by addition of HCl (0.1N) and NaOH (0.1N) (Zermane et al., 2005). To each solution, 0.1 g of adsorbent (red slag) was added, and the solutions were stirred for 48 hours. The samples were filtered and pH was measured. PZC was determined by drawing the curve presenting the difference between the initial and final pH in function of the initial pH. (Elqada et al., 2006) (Ghazi Mokri et al., 2015).

Application of Cibacet Blue in adsorption

The Cibacet Blue (CB) dye was chosen as an organic pollutant. To carry out the adsorption kinetics using red slag, the protocol given by (Chennouf et al., 2015) was followed. Adsorption tests were performed in series of reagent bottles at constant temperature of 25°C, by mixing 0.05 g of red slag with 50 mL of CB aqueous solution (0.04 g/l). pH of the obtained solution is 6.5 which is the nature pH. All kinetic adsorption experiments were conducted at this pH. In order to determine the maximum adsorption, adsorption isotherms were carried out by adding different quantities of sorbent (from 0.01 to 0.1 g) to 50 mL of the CB solutions. The experimental results are expressed as percentage adsorption capacity which is defined as follows:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

Where C_O is the initial concentration of adsorbent in (mg/l), C_t is the adsorbent concentration at time t in (mg / l). (Santhi et al., 2009) and Qt is the adsorption capacity:

$$Qt = \frac{C_0 - C_t}{m} \cdot V \qquad (2)$$

Where V is the volume of the adsorbed solution (ml), *m* is the mass of the adsorbent (mg) (Faling et al., 2016).

RESULTS AND DISCUSSION

Characterization results

The natural slag of Bechar, (south-East of Algeria) has very interesting properties in water treatment by adsorption even in its raw state (See figure 1).

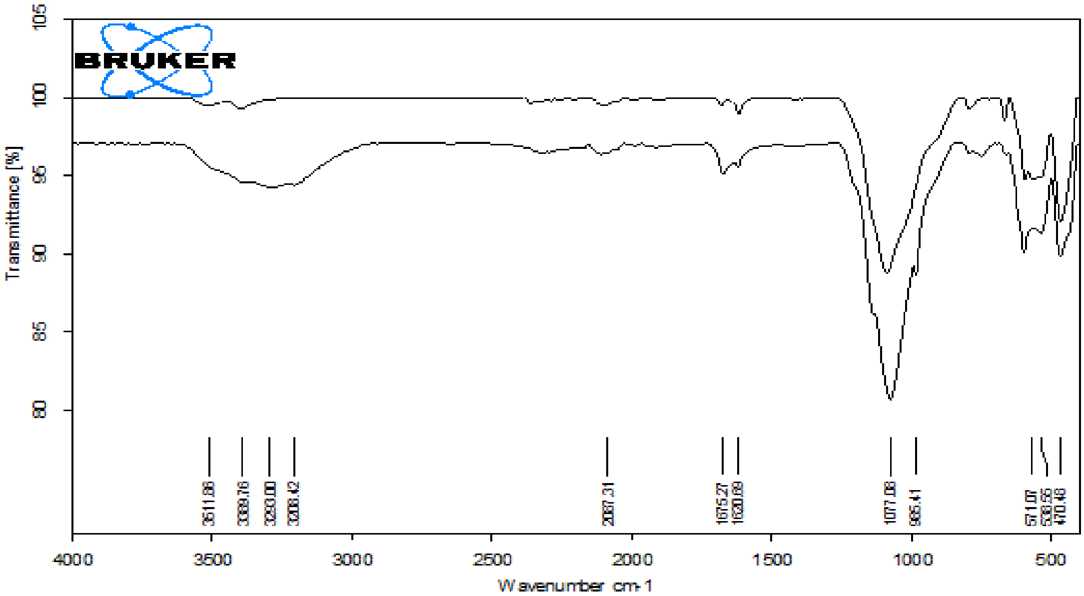


Figure 1. Infrared Spectrum of the slag: (a) before adsorption, (b) after adsorption.

Figure 2 shows the red slag Infrared spectrum. According to maximums peaks, the components of the slag were confirmed. Compared to the literature, the adsorbent has a montmarillonitic character (Kacha et al., 1997), with a report of SiO_2 / Al_2O_3 = 2.23 (See Table 2).

Table 2. The chemical composition of slag.

Component%	**SiO_2**	**Al_2O_3**	**SO_3**	**MgO**	**CaO**	**Fe_2O_3**
Red slag	**62.7**	**28**	**0.8**	**1**	**1.5**	**6**

Slag consists of different rock fragments, including small pieces of coal, but in small quantities and also different heavy minerals. In addition, the investigated slag includes fragments of rock or minerals very identical at slightly different proportions (Table 3).

Table 3. Result of mineralogical and petrographic analysis of the slag.

Minerals and fragments	(%)
Calcite	1%
Coal Fragments	3%
Fragments of black schist	10%
Fragments of red schist	35%
White sandstone	15%
psammite I	33%
Wind sand	3%
Total	100%

Figure 2 presents the X-ray diffraction of used Red slag.it can be seen from the diagram that the adsorbent is composed of number of peaks which indicate the complex nature of the material.

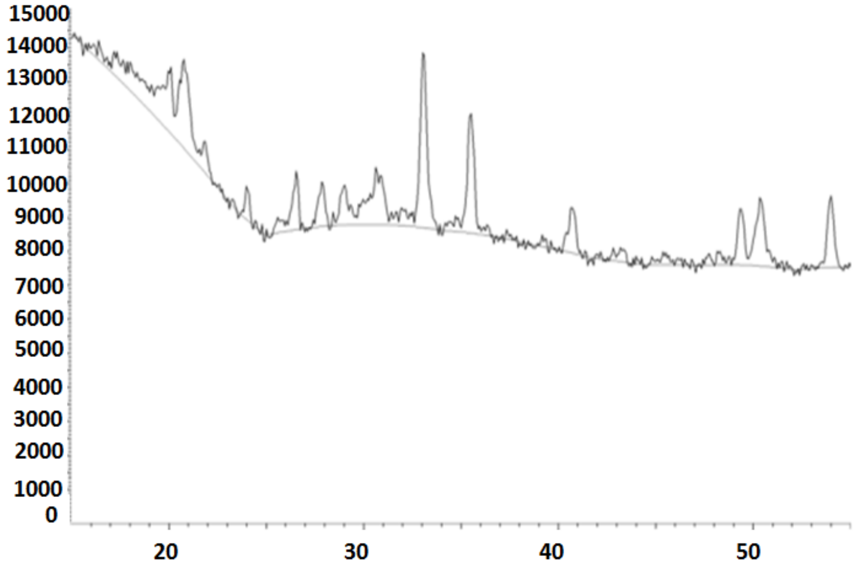


Figure 2. DRX diagram of the slag.

The physical characteristics of used adsorbent are summarized in Table 4. These characteristics show that the used adsorbent has significant physical properties with extragranular porosity exceeding 30%.

Table 4. The physical characteristics of slag.

Parameter	Slag
Fineness module	4.52
Effective diameter d_{10} (mm)	0.16
Coefficient of uniformity (CU)	2.95
Specific air of the material cm^{-1}(As)	19.4
Density abs ρ (kg/m3)	1.90
Porosity (ε) (%)	38.81

The PZC values allow to determine the acidic or basic nature of the Red slag and to know, according to the pH of the solution, its net surface charge. Results given by the figure 3, show that the red slag has a surface of acid functional groups with a PZC = 6.8.

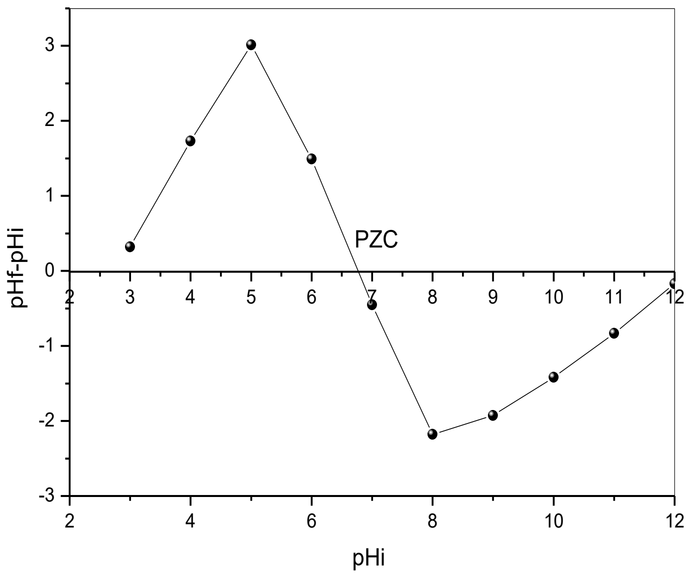


Figure 3. Zero point of charge of red slag curve (PZC).

Kinetic adsorption

A kinetic adsorption curve of the CB by the red slag is presented as the adsorbed amount and the percentage of adsorption capacity (Santhi et al., 2009) relative to time (see figure 4). It is noted that the kinetic adsorption of CB is composed of two phases: a very fast phase in the time ranging from 1 to 35 min, followed by a very slow phase which represents the state of equilibrium (percentage of elimination R=77%) for an interval from 35 to 60 min. This can be explained by the fact that the adsorption sites are open and easily accessible at the beginning, so the CB molecules interact easily with these sites.

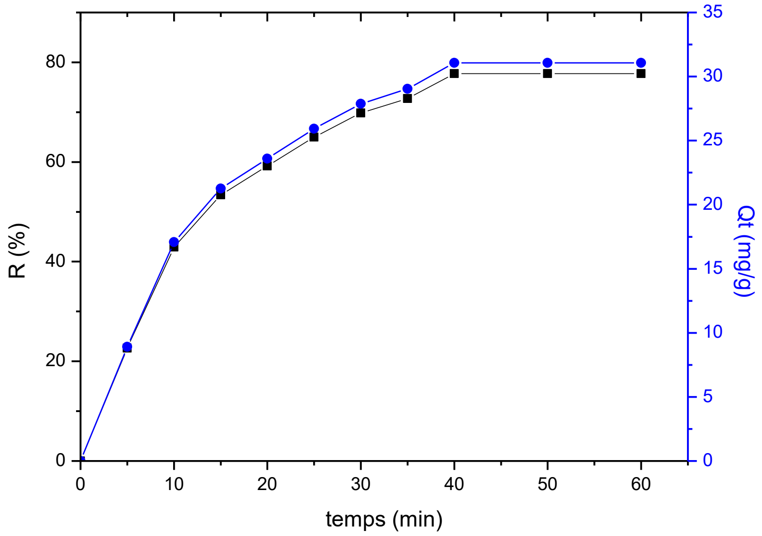


Figure 4. CB dye adsorption kinetics (m = 1 g / l, [CB] = 40 mg / l, T = 25 ° C., V = 250 rpm, d_p = <0.53 µm).

In this section, the parameters influencing the kinetic adsorption of CB by red slag are studied. These parameters are given as follows:

- **Effect of initial dye concentration**

The evolution of the adsorbed amount of CB by the red slag as a function of the contact time at different initial concentrations of CB (5 to 100 mg / l) is represented by figure 5.

The figure shows that the equilibrium time and the adsorption capacity are strongly dependent of the initial concentration.

When the initial dye concentration increases the available adsorption sites are increasingly occupied till saturation. At this time, the adsorption becomes difficult leading to the decrease of adsorption efficiency. In other word, at low dye concentrations, the available adsorption sites are easily occupied, which implies very high adsorption efficiency (Miyah et al., 2015) (Abdallah et al., 2016).

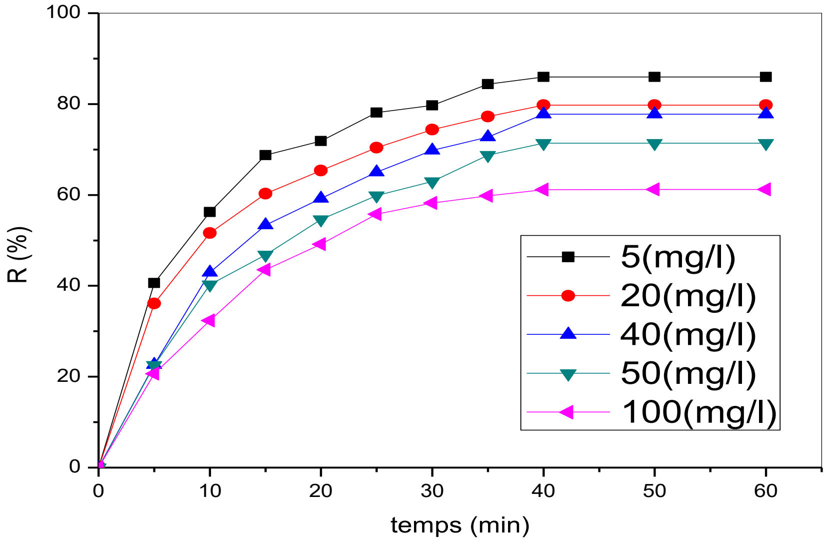


Figure 5. Effect of contact time on CB dye removal (m = 1g / l, T = 25 ° C, V = 250 rpm, d_p = <0.53 µm).

- **Effect of pH**

The elimination of pollutant from simulated aqueous solution by adsorption is extremely influenced by the pH medium of the solution which can strongly affects the nature of the adsorbent surface charge, the ionization of the adsorbate extent and the adsorption rate. The adsorption process is affected by pH change (Khattria & Singh, 2009).

The adsorption of CB increases with the increasing pH of the solution. According to data presented in figure 6, the best value of adsorption capacity, Q_e = 29.2 mg/g, was recorded at pH 3. And this can be explained by the very high interaction between the sites of red slag and CB molecules. The slag is positively-charged and the CB in its molecular state is negatively–charged. Consequently, the interaction between them is highly polarized due to charge difference.

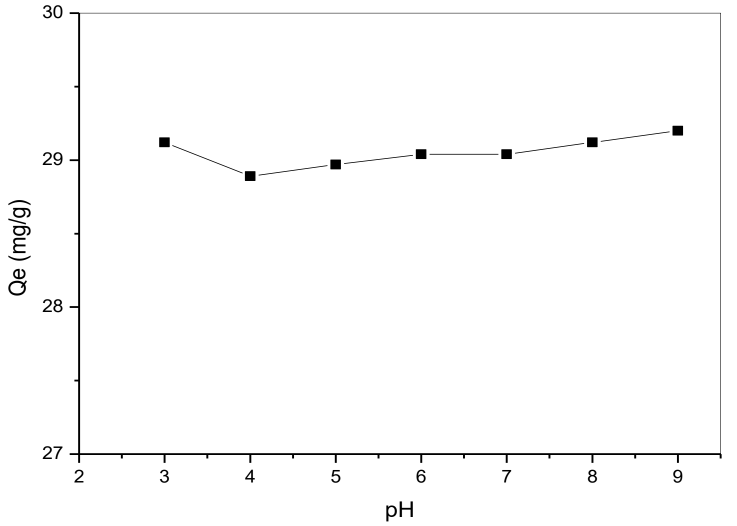


Figure 6. Effect of pH on the adsorption capacity of CB dye.

- **Effect of stirring rate on adsorption of CB dye**

The evolution of the adsorption amount of CB by red slag as function of the stirring speed is presented in Figure 7. The figure illustrates that the optimal stirring speed for the adsorption dye is reached starting to 250 rpm. This is due to the good dispersion of the used adsorbent in the solutions, leading to better contact rate adsorabent-adsorbate (Annouar & Soufiane, 2005).

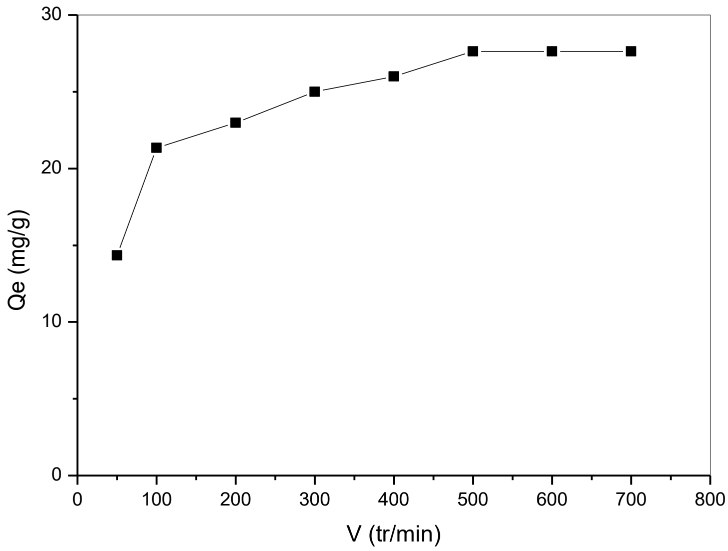


Figure 7. Effect of stirring on the adsorption capacity ([CB]= 40 mg / l, m = 1 g / l, d_p = <53 µm, T = 20 ° C and pH = 6.50, time = 20 min).

- **Effect of size of the adsorbent particles**

The effect of size of the red slag on the kinetic adsorption of CB was studied by varying this parameter from 50 to 2500 µm. the obtained results are given in figure 8. It shows that the rate of adsorption is directly related to the size of adsorbent. The increase of dp (pore diameter) leads to decrease the adsorption amount of CB by red slag. This can be explained by the fact that the more the slag is small, the larger is the contact surface. (Cheknane et al., 2012).

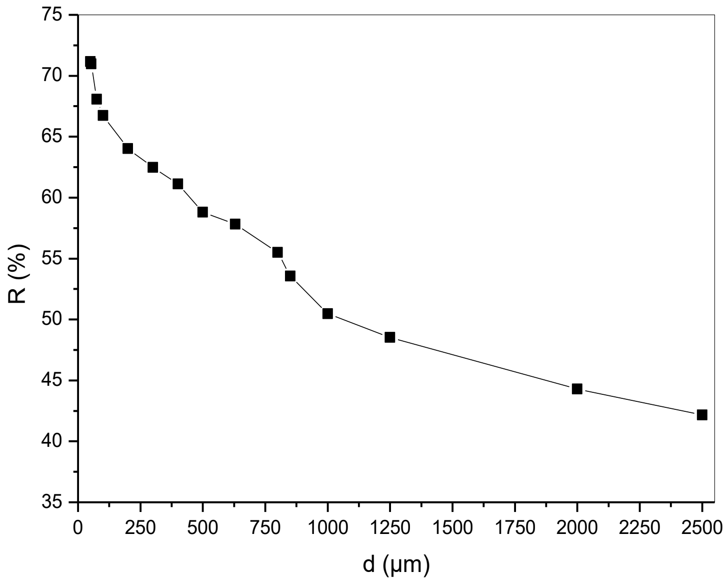


Figure 8. Effect of pore diameter on adsorption capacity. ([CB] = 40 mg / l, m = 1 g / l, T = 20 ° C and pH = 6.50, v = 250 rpm).

Order of kinetic adsorption

In order to investigate the mechanism of CB, the two models of the chemical reaction were applied to the experimental data. The pseudo-first- and pseudo-second-order models were used to specify the adsorption mechanism (Baliti et al., 2014) (Li et al., 2009).

$$q = q_e(1 - e^{-k1t}) \quad \text{(Eq.1)}$$

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad \text{(Eq.2)}$$

Where q_e and q (mg g^{-1}) are the amount of dye adsorbed at equilibrium and time t (min), k_1 (min^{-1}) is the pseudo-first rate constant and k_2 (g $mg^{-1}min^{-1}$) is the pseudo-second-order model (Talal, 2014) (Zermane et al., 2013).

The corresponding constant rates k_1 and the correlation coefficients (R^2) values are summarized in Table 5. The obtained results showed that the pseudo-first order model (R^2 = 0.996) gave the best correlation than the second one (R^2 = 0.991).

Table 5. Kinetic parameters evaluated for CB adsorption onto slag.

Model	Parameters	values
Pseudo first order	K_1 (min^{-1})	0.070
	$Q_{e.cal}$(mg/g)	31.873
	$Q_{e.exp}$ (mg/g)	31.060
	R^2	0.996
Pseudo second order	K_2(g/mg.min)	0.001
	$Q_{e.cal}$ (mg/g)	40.116
	$Q_{e.exp}$ (mg/g)	31.060
	R^2	0.991

Adsorption isotherms

Adsorption isotherms of CB by red slag are presented in figure 9. It is showed that the evolution of the adsorption capacities relative to residual concentrations of dye (Senturk et al., 2010) and show also a high affinity of red slag towards CB molecules with an adsorption capacity close to 60 mg/g. Modeling results show clearly that the obtained equilibrium isotherm is in close agreement with Langmuir equation (Langmuir, 1918), as the correlation coefficient (R^2) values reach 0.988. In our case, isotherm constants were calculated using non-linear regression (Hamad et al., 2018).

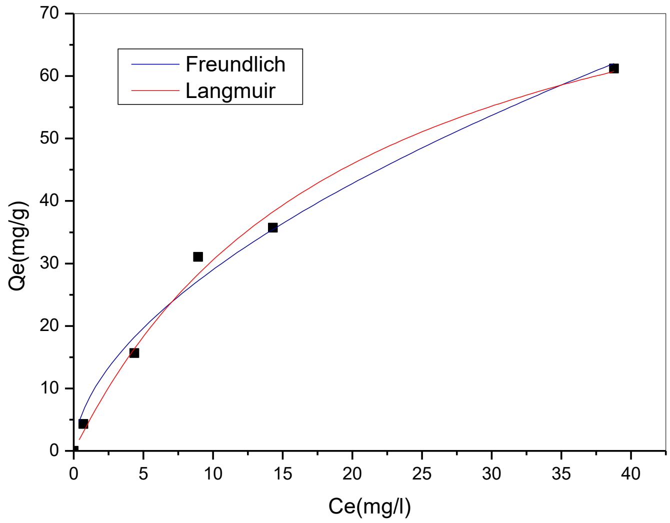


Figure 9. Langmuir and Freundlich isotherms for the adsorption of CB by the slag.

Thermodynamic parameters of adsorption

Thermodynamic parameters of the adsorption of CB by red slag such as, enthalpy (ΔH°), entropy (ΔS °) and free energy (ΔG °) of activation (Table 6), were determined at different temperature (from 10 to 40°C) (Saman et al., 2007) using the following equations (Dawood & Sen, 2012.), (Yu & Luo, 2014):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{(Eq3)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{(Eq4)}$$

Where Kd = Qe / Ce is the distribution coefficient, T is solution temperature in Kelvin (K). R is the constant of the perfect gases (R = 8.314J / mol.K).

Table 6. Isotherms parameters of the adsorption process of the CB by slag.

Models	Parameters	values
Langmuir isotherm	K_L (min^{-1})	0.049
	$Q_{e.cal}$(mg/g)	92.417
	R^2	0.988
Freundlich isotherm	K_F(g/mg.min)	7.954
	n_F	0.560
	R^2	0.980

The obtained results relative to the thermodynamic study (See table 7) show that Gibbs free energy change is negative and decreases when temperature increases, which indicates the spontaneous process in our case (Ahmad & Kumar, 2010).

Table 7. Thermodynamic parameters of the adsorption process of the CB by slag.

T(°C)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol.K)
10	-2.072	93.032	336.059
20	-5.433		
30	-7.113		
40	-12.154		

The positive values of ΔH°, implies that the process of the adsorption is endothermic and a higher temperatures facilitate the uptake of CB molecules by adsorption by red slag.

The positive value of ΔS° indicates that the molecules of the CB remain less ordered on the interface solids / solution during the process of adsorption (Colak et al., 2009).

CONCLUSION

In This study, the adsorption process of Cibacet blue (CB) by red slag was investigated. The results show that the percentage of elimination (which can reached 80%) is strongly influenced by the operational conditions such as, contact time, pH, initial dye concentration and size of adsorbent. In addition, the temperature has a favorable effect on the percentage of dye removal, suggesting that the adsorption of CB on slag was a spontaneous endothermic process. The Modeling of adsorption kinetics reveals that the pseudo-second-order model offers a better correlation of the kinetic data with an adjustment coefficient higher than 0.995. Isotherms were best described using the Langmuir model with R^2 of 0.99, which indicates that the CB dye molecules are adsorbed in monolayers and without any interactions among them. The obtained results reveal that the red slag is a potential low cost adsorbent that can be used effectively for the treatment of effluents from the textile industry.

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