



Utility of Crosslinking a Lignocellulosic Waste Polymer for Fast and Efficient Adsorption of Bimacid Red ETL dye

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Abstract. A novel quaternized cross-linked lignocellulosic waste-sebacoyl-trietanolamine (QSB) polymer with excellent adsorption performance for Bimacid Red ETL dye was synthesized by a one-step reaction. Kinetic, thermodynamic, and adsorption isotherm studies were conducted to evaluate the sorption process of Bimacid Red ETL dye on the synthesized material. The experiments have demonstrated that the adsorbent/adsorbate system studied followed very fast kinetics so that the equilibrium is reached after 20 minutes of contact time. In addition, the process is controlled by the pseudo-second-order model, and the isotherm is satisfactorily described by the Langmuir mathematical model. Furthermore, the thermodynamic study revealed that the adsorption process is spontaneous and exothermic. Under ideal conditions, the as-prepared material showed a maximum dye removal capacity of 200 mg/g for the Bimacid Red ETL dye. The present work contributes to the development of chemically functionalized lignocellulosic waste materials for application in environmental protection.

Keywords. Lignocellulosic; cross-linked; adsorption; Kinetic; thermodynamic.

INTRODUCTION

Nowadays, water is considered a rare wealth that it is essential to protect. The increase in industrial activities is causing increasing pressure on the planet's freshwater reserves. These activities generate a wide variety of chemicals in the water cycle. Dyes are organic compounds used in many industries such as paper mills, cosmetics, food processing, textiles, and pharmaceutical products, as well as in medical diagnoses (Doğan and Alkan, 2003;

Annadurai et al., 2002). Their elimination represents one of the main problems in the treatment process of liquid discharges. Several types are very toxic and difficult to biodegrade (Damodar et al., 2007).

The elimination of these pollutants, therefore, proves to be a real necessity which has led to the development of a very specific research axis which is the treatment of water and the recovery of industrial residues. The conventional processes, by way of illustration, ion exchange (Ates and Un, 2013), membrane filtration (Sharifpour et al., 2018), and electrochemical (Fernández-Sánchez and Costa-García, 2000), etc., reach their limits in the depollution of water because they remain less efficient and very expensive. For our study, we were interested in an innovative process that provides an effective solution to adsorption. Indeed, it is one of the simplest, most effective, and most economical methods (Mohan and Chander, 2006). These characteristics have been reinforced by the highlighting of the potential of the valorization of natural materials that are quite abundant and practically less expensive to be used as adsorbents alternative to activated carbons, the cost of which is a limiting factor that makes their regenerations and reuses delicate operations (Malik, 2003). The linear polymer presented in this study is a biopolymer derived from a waste of the wood industry to serve as a support for anchoring dendrons prepared by copolymerization of multifunctional monomers. The choice of pretreated sawdust as a linear polymer is due to its specific properties: abundance, non-toxicity, biodegradability, and the ease of chemical functionalization through its hydroxyl groups in its lignocellulosic matrix. Thus, the cross-linking of this biopolymer by dendrons could lead to innovative materials possessing new characteristics such as the strong sorption capacity for dyes and heavy metals with very rapid elimination kinetics.

MATERIALS AND METHODS

Preparation of quaternized sawdust (QSB)

To a stirred suspension at ambient temperature containing 15 g of SB-ONa and 10 g of triethanolamine in 200 mL of toluene, 10 g of sebacoyl chloride is added dropwise and then the reaction mixture is refluxed for 4 hours. After cooling, a large excess of methyl iodide (10 mL) is added and the reaction mixture was left to stir for two additional hours.

The mixture is then filtered and the solid material obtained is washed thoroughly with distilled water and then with acetone. The dark brown solid material was dried in the oven for 24 hours at a temperature of approximately 70°C. The preparation of soda sawdust (SB-ONa) was carried out by alkaline treatment of the raw sawdust with an 18% weight sodium hydroxide solution.

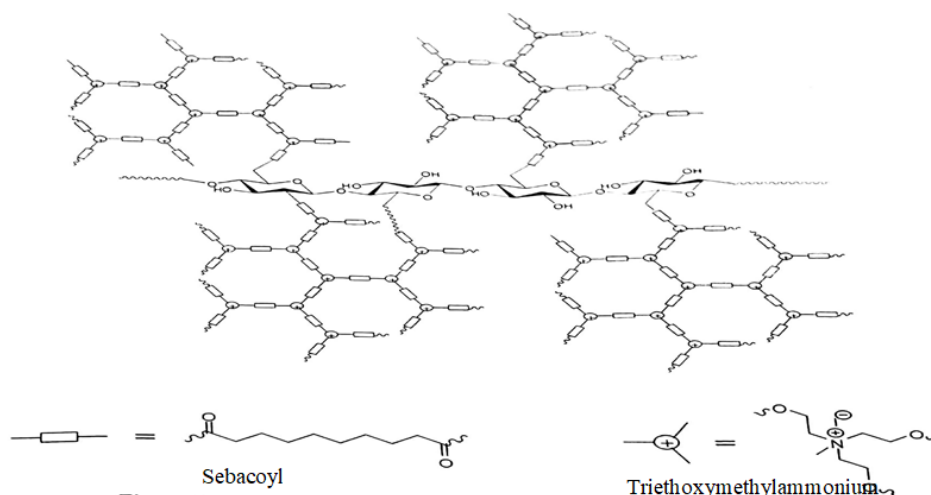


Fig.1. Simplified molecular structure of the dendronized polymer (QSB).

Dye studied

The dye used in this study was supplied by the SOITEX textile industry of Tlemcen, known under the trade name Bimacid Red ETL (BR.ETL).

Study of the Elimination of RB.ETL on QSB

The dye stock solution (BR.ETL) was prepared by dissolving 1 g of the dye in 1000 mL of distilled water and test solutions of desired concentrations were obtained by further dilution with distilled water. To determine the adsorption equilibrium time, volumes of 25 ml were taken from the solution of the BR.ETL of arbitrarily selected concentrations of 20 mg/l is successively contacted with 25 mg of QSB. The whole is stirred at times ranging from 1 to 60 minutes. The study of the initial concentration effect (adsorption isotherm) of dye BR.ETL is carried out with different concentrations varying between 20 and 500 mg/l for a solid-liquid ratio of 1 g /l (50 ml of solution + 50 mg of QSB) for 60 min of stirring (contact time) at ambient temperature. The effect of temperature on the removal process has been studied at three temperatures 25, 40, and 50 °C. The influence of the ionic strength on the adsorption capacity of the dyes is very useful to estimate the effectiveness of the adsorbent in the water discharged by the textile industries. This study consists in examining the influence of the concentration of NaCl (varying from 1 to 5 M), on the adsorption process of the dye BR.ETL (20mg/l) with the QSB material (50mg) for a contact time of 60 minutes. Under these conditions, the UV-visible spectrum of this dye has not undergone any variation as a whole (λ_{max}). The residual dye concentration is analyzed by a UV-Visible spectrophotometer type - DPTIZEN 3220UV- regularized over a maximum wavelength of 500 nm, determined experimentally by scanning the wavelength range ranging from 400 to 800 nm.

RESULTS AND DISCUSSION

Adsorption kinetics

The sorption rate of BR.ETL by QSB is deduced by the following Equation (1):

$$R\% = \frac{(C_i - C_e)}{C_i} \cdot 100 \quad (1)$$

Where C_0 (mg/L) is the initial concentration of the adsorbate; C_e (mg/L) is the residual concentration of the adsorbate at equilibrium.

Figure 2 shows the sorption process for the BR.ETL dye is very fast. Indeed, not less than 98.25% of the dye is sequestered onto the surface of QSB material within the first 5 minutes of contact time. The removal process is so spontaneous that the equilibrium is reached after

20 minutes of contact time with a total removal of 100%. The rapid adsorption indicates the presence of abundant sorption sites at each dendron. These results also suggest that the removal process is probably governed by strong ionic interactions between the positively charged amine groups (quaternary amine) on the QSB material surface and the negative charge of the dye (BR.ETL). Similar results were reported by M. Bendjelloul et al. (2017) for the removal of acid dyes by a dendritic polymer.

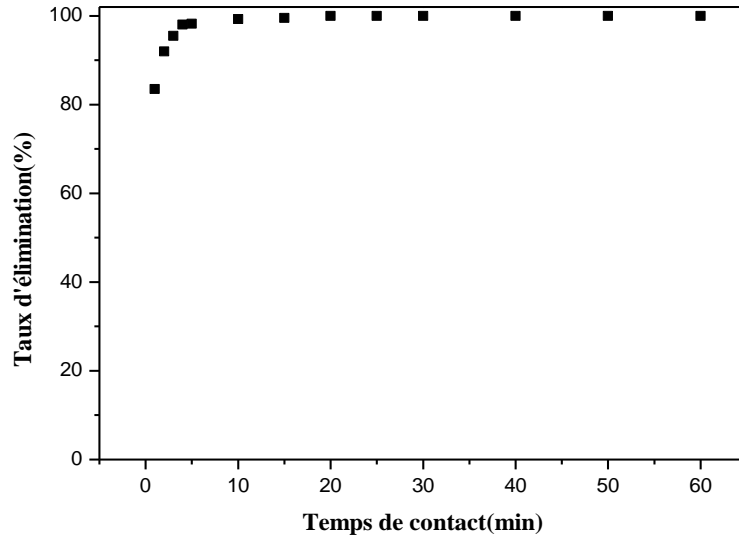


Fig.2. Effect of contact time on the sorption rate of BR.ETL dye by QSB.

To model the adsorption kinetics of solutes on a solid surface, several models describing the diffusion of solutes on the surface and in the pores of the particles have been developed. Among the models of adsorption kinetics, there are two widely used models the pseudo-first-order and pseudo-second-order models.

The pseudo-first-order model expression is given by Lagergren (1898) in equation (2):

$$\text{Log}(q_e - q_t) = \text{Log}q_e - \frac{K_1}{2.303}t \quad (2)$$

Where, t: contact time (min) and k_1 is the rate constant in min^{-1} .

The values of k_1 and q_e are determined by extrapolating the plot of $\log(q_e - q_t)$ versus time t (Figure 3 a).

The pseudo-second-order model is given by Ho and McKay (1999) in equation (3):

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (3)$$

With: k_2 : adsorption rate constant of the pseudo-second-order in $(\text{g}/\text{mg min})$; q_e : adsorbed quantity at equilibrium in (mg/g) , q_t : adsorbed quantity at time t in (mg/g) ; t: contact time in (min).

The parameters of this kinetic model q_e and k_2 are determined experimentally from the slope $1/q_e$ and the intercept $1/k_2 q_e^2$ of the plot $t/q_t = f(t)$. The results obtained are shown in figure 3 b.

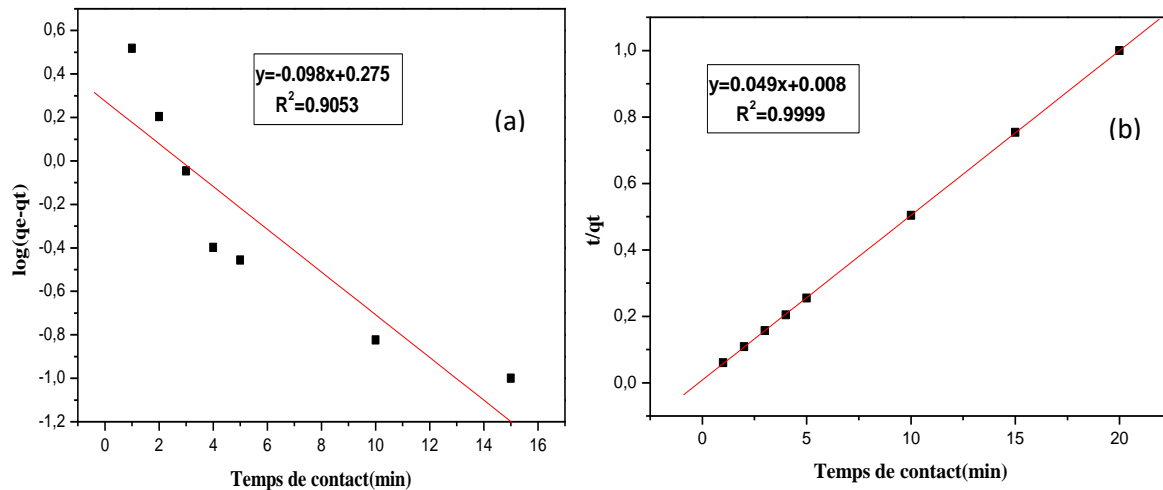


Fig.3. Pseudo-first-order (a) and pseudo-second-order kinetics (b) of BR.ETL removal by (a) QSB.

The parameters of the two kinetic models of McKay and Ho and Lagergren are shown in table 1.

Table 1. Comparison of experimental and calculated values of first and second-order kinetic parameters of BR.ETL on QSB.

Colorant	$q_{e, exp}$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
		k_1 (min^{-1})	$q_{e, cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e, cal}$ (mg/g)	R^2
BR.ETL	20	0.225	1.883	0.9053	0.3	20.40	0.9999

According to the analysis of the kinetic results grouped in table 1, it turned out that: For the variation of Log ($q_e - q_t$) as a function of time t (Fig. 3a) is not revealed to be very linear and the regression coefficient obtained is no longer satisfactory ($R^2=0.9053$), thus the experimental amount adsorbed at the equilibrium of BR.ETL by QSB is different from the calculated one.

On the other hand, the variation of t/q_t as a function of t turns out to be linear as indicated very clearly in figure 3b, a perfect correlation of which is observed between the experimental data and the kinetic model of the pseudo-second-order. The regression analysis gives a satisfactory value for the regression coefficient R^2 , close to unity ($R^2=0.999$). Furthermore, the calculated sorption capacity overlaps with the experimental value of 20mg /l with a very small deviation, less than 1% (Table 1). Given this comparison, we, therefore, conclude that the pseudo-second-order model is reliable for determining the order of the adsorption kinetics of BR.ETL by the QSB material. Many studies have shown that the adsorption kinetics of many dyes on various polymer-based adsorbents is well described by the pseudo-second-order model. For example, Renault et al. (2008) found that pseudo-second-order was the best model to describe the adsorption kinetics of AB 25dye on a cross-linked starch-based ion exchange resin.

Sorption isotherm

The experimental study of adsorption reactions corresponding to a state of equilibrium is often presented by an isotherm governed by a mathematical model representing the variation of the quantity of solute adsorbed per unit mass of adsorbent q_e (mg/g) as a function of the

concentration of the solute adsorbate in solution C_e (mg/L), at a constant temperature The amount of adsorbate expressed in mg, fixed on one gram of material (mg/g), is given by the following relation 4:

$$q_e = \frac{x}{m} = \frac{(C_i - C_e)V}{m} \quad (4)$$

With: C_i : initial concentration of the solute (mg/L); C_e : residual concentration of the solute at equilibrium in the solution (mg/L); m : mass of the solid (g); V : the volume of the solution (L). Figure 4 represents the variation of the adsorbed quantities of BR.ETL by one gram of QSB (q_e) as a function of the concentration C_e , at equilibrium.

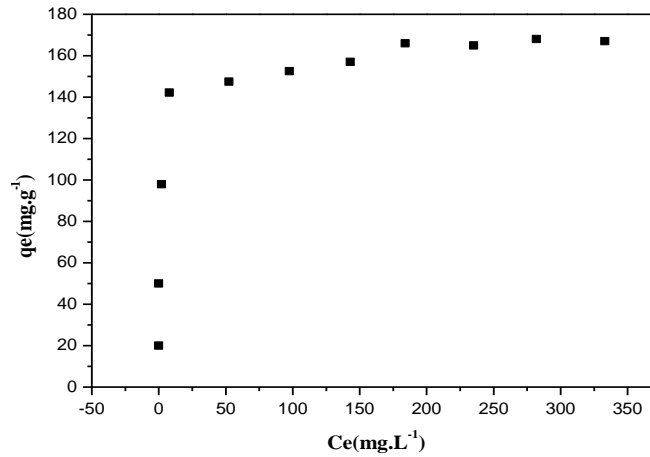


Fig.4. Sorption isotherm for BR.ETL onto QSB.

The curve obtained shows that the adsorption isotherm of BR.ETL by QSB is of type I of the classification of Giles et al. (1974). This type of isotherm indicates a sufficient flexibility of adsorbate to be attached to the surface of the adsorbent. The saturation of the adsorption sites occurs progressively until a saturation plateau is reached. Because of their simplicity, the most commonly used isotherm models are those of Langmuir (Eq.5) and Freundlich (Eq.6), to determine the adequacy or not of our experimental results.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \quad (5)$$

By plotting C_e/q_e as a function of C_e , we obtain a linear line with slope $1/q_{max}$ and ordinate at the origin $1/(q_{max} \cdot b)$.

$$\text{Log} \frac{x}{m} = \frac{1}{n} \cdot \text{Log} C_e + \text{Log} K_F \quad (6)$$

By plotting the $\text{Log} (x/m) = f(\text{Log} C_e)$ curve, the values of the Freundlich constants K and n can be determined.

The representations of the isotherm results according to the Freundlich and Langmuir models are shown in figures 5 (a) and (b).

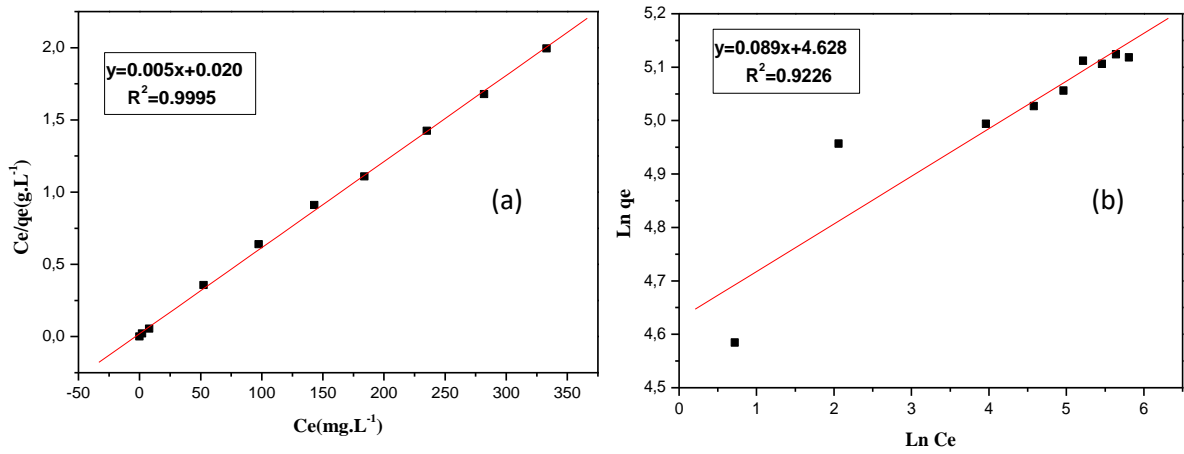


Fig.5. Langmuir (a) and Freundlich (b) isotherm of the adsorption of BR.ETL by QSB.

From the graphical representation of each model (Fig. 5 (a) and (b)) and the table below (2), it is evident that the sorption process of BR.ETL dye by QSB material is described in a favorable way by the Langmuir isotherm with an excellent linear regression coefficient R^2 which is very close to unity. This reflects the homogeneous nature of the surface of this material. The value of the correlation coefficient $R^2=0.9226$ of the Freundlich model is lower than that of Langmuir. Therefore and according to Langmuir's theory, the case of the formation of more than one adsorption monolayer on the surface may be possible and the sites are homogeneous with equivalent binding energies. The adsorbent material has an excellent affinity for the dye BR.ETL is confirmed by the value of the maximum sorption capacity of about 200mg/g.

Table 2. Langmuir and Freundlich isotherm constants for the sorption of BR.ETL by QSB.

Colorant	Langmuir Constants			Freundlich Constants		
	Q_{max} (mg/g)	b (L/ mg)	R^2	K_F (L/g)	N	R^2
BR.ETL	200	0.25	0.9995	102.30	11.235	9.226

Temperature effect

The study of the temperature effect allowed us to determine the thermodynamic parameters (ΔG° , ΔH° , and ΔS°) by combining the Gibbs thermodynamic relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and the Vant'Hoff equation :

$$\ln K_d = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} \quad (7)$$

Where, K_d : Sorption distribution constant which is defined as the ratio of the amount of fixed dye q_e (mg/g) to the amount of dye remaining in solution (mg/cm³); R: Constant of perfect gases 8.31447 J/mol K; T: Temperature of the adsorption isotherm in °K.

Table 3. Thermodynamic parameters for BR.ETL sorption onto QSB.

Colorant	ΔH° (KJ/mol)	ΔS° (J/ K mol)	ΔG° (KJ/mol)		
			298 K	313 K	323 K
BR.ETL	-37.0293	-38.7661	- 25.476	- 24.895	- 24.507

From the data in table 3, it can be seen that the negative value of ΔH° (-37.0293 KJ/mol) indicates that the sorption process is exothermic and therefore less favorable at high temperatures with a small decrease in the amount of dye adsorption. It is accepted that

binding strengths ranging from -80 to 400 KJ/mol (Zhu et al., 2010) are generally for chemisorption while binding strengths between -20 and 0 KJ/mol are for physisorption. On this basis, the adsorption of BR.ETL dye by the QSB material is characterized as a physical adsorption process enhanced by chemical interactions. The negative value of ΔG° at each temperature indicates a favorable and spontaneous adsorption process of BR.ETL dye by QSB material. This means that the adsorbate-adsorbent attractive forces are strong enough to establish without the input of an external energy source. Therefore, the sorption process is thermodynamically favorable at room temperature and feasible at higher temperatures. The negative value of entropy ΔS° (-38.7661 J/mol k) indicates the increase in randomness of molecules (increase in disorder) at the solid/liquid interface during the adsorption process.

Influence of ionic strength on BR.ETL adsorption process on QSB

The experimental results presented in figure 6 show that the influence of the salt is practically insignificant on the maximum adsorption capacity. In fact, the increase in the ionic strength up to 5M does not affect the removal rate of the dye ($R = 100\%$). Similar studies have been reported by Karcher et al. (2001) on the effect of inorganic salts on the adsorption of reactive dyes by anion exchange resins. These results confirm the efficiency and the performance of the synthesized adsorbent material QSB used in this study.

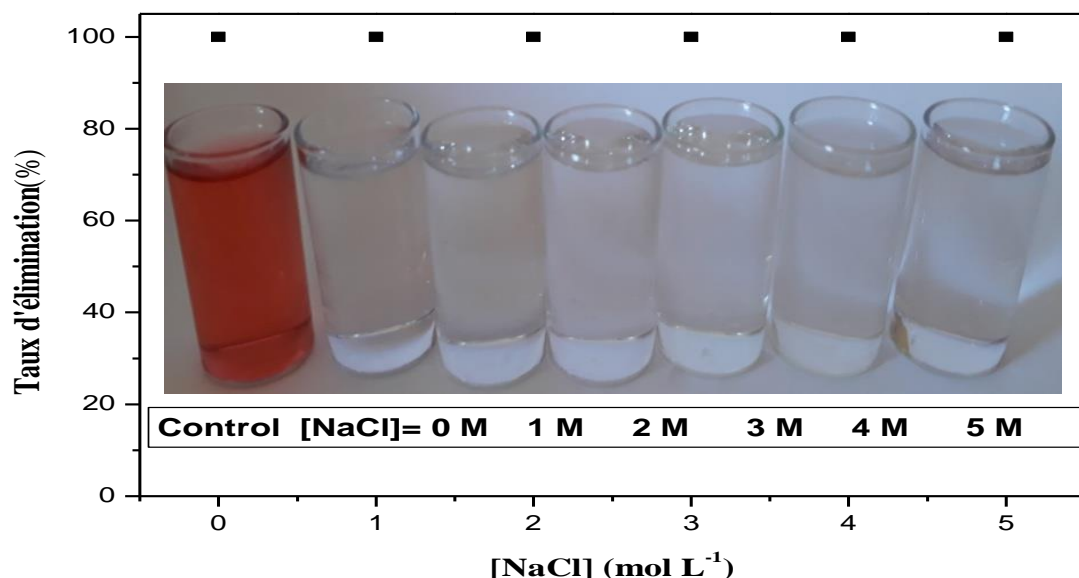


Fig.6. Effect of ionic strength on the removal efficiency of BR.ETL dye by QSB.

CONCLUSION

In summary, a new type of dendronized polymer can be synthesized by a one-pot reaction from a lignocellulosic waste of the timber industry. The as-prepared adsorbent material has a strong affinity for industrial Bimacid Red.ETL dye performs efficiently through a uniform and fast sorption process. The QSB material can adsorb BR.ETL efficiently with a maximum sorption capacity of 200 mg/g. Thermodynamic parameters indicated the exothermic and spontaneous nature of the adsorption process. This work also demonstrated that the sorption capacity achieved by QSB adsorbent material remained unaffected when the ionic strength of the solution was increased five-fold from 1 to 5 M. Finally, this study shows the importance of crosslinking strategies in designing powerful adsorbent materials for water treatment by a cost-effective single-pot chemical modification of a low-value lignocellulosic by-product.

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