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Bio sorption of textile dyes from aqueous solution onto three different pine barks: kinetics and isotherm studies

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Abstract - *The main objective of the present study is to evaluate the sorption capacities of some natural raw materials of vegetable origin for the treatment of the sewage coming from the textile industry. The selected barks are: maritime pine (MP), pine pinion (PP) and Aleppo pine (AP) bark. The effectiveness of these barks was evaluated in the removal of three dye; rhodamine B (RhB), Green Malachite (GM) and Methyl Orange (MO). Initially, the effects of some parameters such as the nature of the adsorbents, the nature of the dyes and the pH were studied. Obtained results reveals that the speed sorption is strongly influencing by the pH medium and the comparative study shows that the adsorption is favourable in the acidic medium with a sorbed amount of (Q=40mg/g) for rhodamine B. The results of the biosorption kinetics reveal that the GM molecules are better biosorbed (Q=48 mg/g) than those of RhB (Q=46 mg/g) and methyl orange (Q=18mg/g), with an equilibrium time of 6 hours. The results of the biosorption isotherms show clearly that the maritime pine bark is the most effective biosorbents with sorbed amount of (QRhB=200mg/g) and (QMO=88mg/g) followed by pignon pine (PP) with (Q_{RhB}=184mg/g) and (Q_{MO}=56mg/g) and finally Aleppo pine (AP) bark with (Q_{RhB}=131mg/g) and (Qmo=46mg/g). All obtained isotherms are modeled using the Langmuir and Freundlich models. According to the adjustment coefficient values R^2, corresponding isotherms are well represented by Freundlich model.*

Résumé - *L'objectif du présent travail de mémoire est la valorisation des matériaux naturels d'origine végétal (écorce du pin maritime, du pignon de pin et du pin d'alep) pour le traitement des eaux usées issus de l'industrie de textiles. Au premier temps nous nous somme focaliser à étudier les différentes paramètres influençant l'adsorption à savoir: la nature des adsorbants, la nature des adsorbats et l'effet du pH. Les résultats obtenus montrent globalement que la vitesse d'adsorption est fortement influencée par le pH du milieu et l'étude comparative montre que l'adsorption est favorable dans le milieu acide avec des quantités adsorbées (Q=40mg/g) pour le RhB. Les résultats de la cinétique d'adsorption révèlent que les molécules de VM sont mieux adsorbées (Q=48mg/g) que les molécules de RhB (Q=46mg/g) et de méthyle orange MO (Q=18mg/g) , le temps de contact de 6h est suffisant pour atteindre le temps de pseudo-équilibre. Les résultats des isothermes d'adsorption montrent clairement que l'écorce de pin maritime (PM) est le plus efficace avec une quantité absorbée de (Q_{RhB}=200mg/g) et (Q_{MO}=88mg/g) suivie du pignon de pin avec (Q_{RhB}=184mg/g) et (Q_{MO}=56mg/g) et enfin de l'écorce de pin d'Alep (AP) avec (Q_{RhB}=131mg/g) et (Q_{MO}=46mg/g). Toutes les isothermes obtenues ont été modélisées en utilisant le modèle de Langmuir et de Freundlich. Selon les valeurs du coefficient d'ajustement R^2, les isothermes correspondantes sont bien représentées par le modèle de Freundlich.*

Mots clés: Ecorce - Pin maritime - Pignon de pin - Pin d'alep - Adsorption - Colorants.

1. INTRODUCTION

In recent years, many industries have used synthetic dyes to dye their products, including textiles. Annually, more than 07 tons of these dyes are produced globally. It is estimated that 10 to 15 % of these chemical compounds are derived from the textile industry effluents. Most dyes are considered dangerous to environmental conditions such as light, temperature, microbial attack and oxidizing agents. Moreover, their very visible presence in aquatic systems, even low concentrations, reduces light penetration and has a detrimental effect on photosynthesis.

Therefore, the decontamination of water polluted with chemicals is necessary both to protect the environment and for future rational use. Among the techniques which are used to eliminate these dyes, adsorption is one of the most used. In this context, activated carbon is the most commonly used adsorbent, but it is very expensive and also requires regeneration. This limits its use in developing countries. The research was then oriented towards treatment methods using cheaper natural materials [1].

In this way, we are interested for natural materials of plant origin such as pine bark. Several studies have focused for this kind of research, G. Antorena [2], Dubos [3], Gengrault Derveaux [4], A.E. Leitch, P.B. Armstrong and K.H. Chu, '*Characteristics of dye adsorption by pre-treated pine bark adsorbent*', International Journal of Environmental Studies, Vol. 63, N°1, pp. 59 - 66, 2006 [5], G. Vazquez *et al* [6], R. Alnoso [7].

The objective of the present study is therefore to valorize certain natural raw materials of plant origin for the treatment of wastewater from textile industry. The barks selected were: maritime pin (MP), pine pinion (PP) and Aleppo pine (AP) bark. The effectiveness of these barks was tested for the removal of three dyes; Rhodamine B (RhB), Green Malachite (GM) and Methyl Orange (MO).

2. METHODS AND MATERIALS

2.1 Used sorbents

In this study we have used three of vegetable biosorbents: maritime pine bark (MP), pinion pine bark (PP), Aleppo pine (AP) bark. These adsorbents were prepared using the method given by Gengrault *et al.* [4]. Pieces of crude bark was washed with distilled water and dried in an oven at 80 °C for 24 h and then ground with a mill pestle and sieved with a sieve of 0.315 mm.

2.2 Used pollutants

To examine and study the capacity and affinity owned pine bark in the sorption of organic micro-pollutants, we selected three commercial water-soluble dyes widely used in textile and tanning industries. These products are Rhodamine B (RhB), the Malachite Green (MG) and the methyl orange (MO).

2.3 Bio sorption kinetics

In this part we are interested to determine the time of pseudo-equilibrium bio sorption of (RhB, VM and MO) onto pine bark. The bio sorption trials were conducted at room temperature, using an E. Buhler GMBH type shaker on which are placed several vials of capacity 250 ml. For each solute, we treated the same volumes of solution (50 ml) contained 50 mg/l of pollutant and 50 mg of the sorbent. At intervals of time ranging from 5 min to 24 hours, samples are taken and filtered through membranes. Quantifications are carried out through measures of absorbance UV-visible spectrophotometry at appropriate wavelengths (for RhB, GM and MO).

2.4 Sorption isotherms

Experiments are performed in a closed reactor in a series of small flasks (capacity of 250 ml). The process consists to mixing biosorbent masses ranging from 5 to 50 mg with the same volume of adsorbate (50 ml). The experiments were performed at a fixed initial concentration (50 mg/l). The study was performed at room temperature (25 ± 1 °C) at least a 6 hours contact time. This time is considered sufficient to achieve the sorbent-sorbate equilibrium. Beyond this contact time, all samples were filtered on membranes (porosity 0.45 μm) and then analyzed by UV-visible to the maximum suitable wavelength (for RhB, MO and GM).

3. RESULTS AND DISCUSSION

3.1 Bio sorption kinetics

3.1.1 Effect of contact time

In this kinetic study, we followed the results of the biosorption kinetics of the three adsorbents (PM, PP, PA) on the three sorbates (GM, RhB, MO) under the following operating conditions:

-Initial concentration of dye: 50 mg/l
-Adsorbent mass: 50 mg
-Initial pH: 5

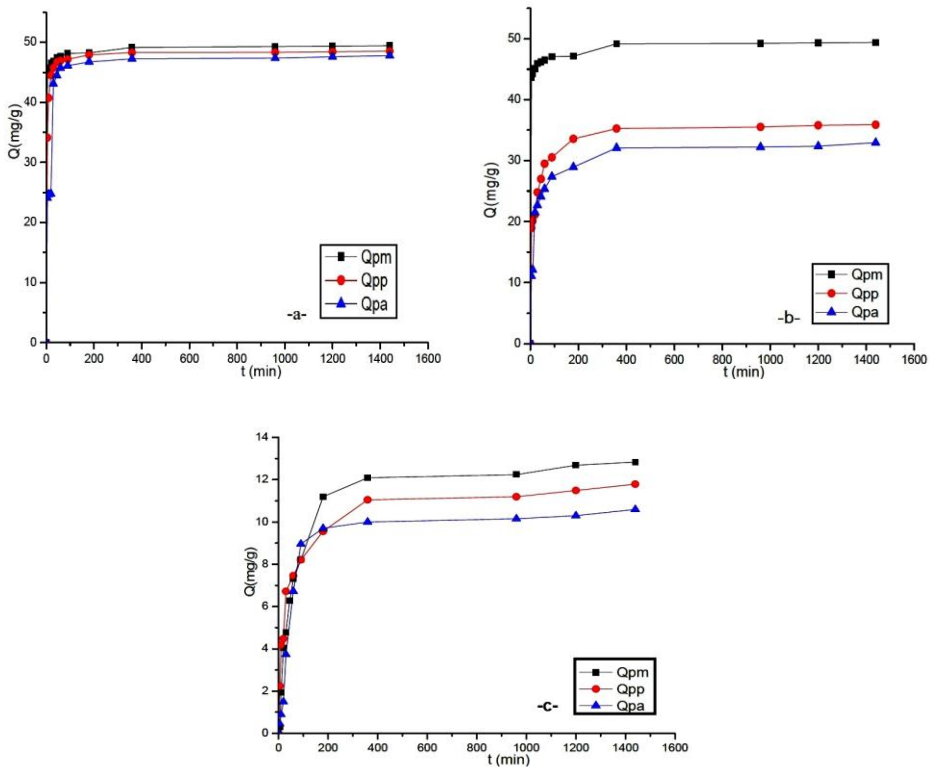

Fig. 1: Kinetic bio sorption on the three adsorbents bark (PM, PP, PA): -**a**-GM, -**b**- RhB, -**c**- MO

Obtained results (figure 1), shows in general that the shape of these curves is classified kinetic curves and which may imposed two distinguished steps:

The first zone characterized by strong sorption of the sorbate in the first minutes of contact sorbate / sorbent obtained at an initial concentration of 50 mg/l. The startup speed of the adsorption can be interpreted by the fact of the number active sites available on the surface of the sorbent materials at the beginning of sorption.

The second zone is in the form of stationary state where the sorption kinetics become very slow. At the end of this kinetic study we consider a 6 h time is sufficient to achieve the time pseudo-balance. We opted for this time of 6 h for all the rest of our study.

3.1.2 Effect of the nature of the biosorbent

In order to compare the sorption performance of the three targeted sorbents (maritime pine bark, Pinion Pine, eppo Pine) we have chosen to work with three types of Malachite Green dye, Rhodamine B and methyl orange. The following operating conditions were kept constant: (pH=5, initial pollutant concentration = 50 mg/l. The corresponding results are shown in the following figures 2.

In view of these histograms we note that the adsorbed quantities of RhB are $Q_{(PM)} \geq$ 48 mg/g, $Q_{(PP)} \geq$ 35 mg/g, $Q_{(PA)} \geq$ 32mg/g respectively. The comparative study between the three sorbates shows that the sorbed amounts follow the present sequence: $\text{GM} > \text{Rhb} > \text{MO}$.

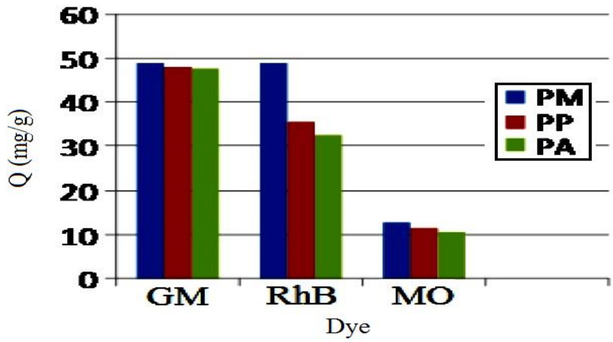

Fig. 2: Effect of the adsorbent nature

3.1.3 Effect of pH

To study the pH effect of the three biosorbents onto the elimination of RhB dye, several experiments were performed by varying the pH of the medium in the range of 3-12; the following parameters were kept constant:

- Initial concentration: 50 mg/l
- Mass of sorbent = 50 mg

Figure 3 shows the effect of pH on the GM adsorption onto the three selected biosorbents. By this figure we can clearly observe that for all used sorbents, maximum removal is obtained at value of pH = 5 (Q=41mg/g) for maritime pine bark followed by pine pinion (Q=39mg/g) and then Aleppo pine bark (Q=34mg/g).

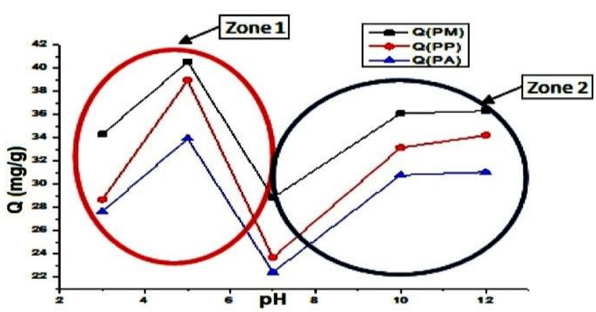

Fig. 3: Effect of the medium pH on the sorption of GM onto the three employed sorbents

Then we observe also a decrease in sorption capacity to a value of. This may be explained as follow:

The increase of the sorbed amounts obtained in the pH range (3-5) can be also explained by the highly negative charged surface of the three used bio sorbents and the cationic form of RhB.

3.2 Bio sorption isotherms

The adsorption isotherms are obtained by the graphical representation of $Q_e = f(C_e)$ {Q_e and C_e are respectively the amount of dye adsorbed and the equilibrium concentration of this dye}. The results are shown in the figures 4.

According to the classification Giles, the obtained curves show that the three used biosorbent isotherms are of type S, which indicates that the sorbed molecules promote the subsequent sorption to others.

This phenomenon can be explained by the cooperative sorption due to attractions between molecules of the solute by Van Der Waals forces).

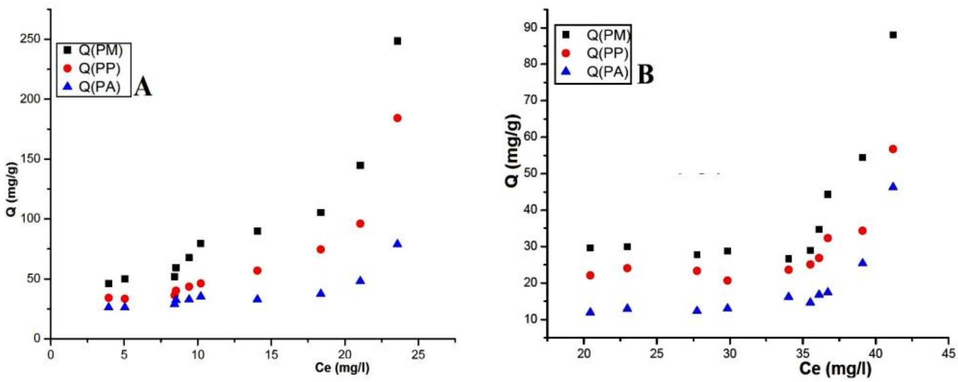

Fig. 4: Bio sorption isotherms on the three adsorbents bark (PM, PP, PA): **A**) RhB, **B**) MO

3.3 Modeling of bio sorption isotherms

Sorption isotherms were analyzed by the Langmuir {Eq.(1)} and Freundlich models {Eq.(2)} using non-linear regression technique:

$$q_e = K_F C_e^n \tag{1}$$

$$q_e = q_m \frac{k_L C_e}{1 + k_L C_e} \tag{2}$$

where q_e (mg/g) and C_e (mg/l), are respectively, the dye concentration adsorbed and in solution, q_{max} (mg/g), K_L (mg/g) are the Langmuir constants related to the sorption capacity and energy, respectively, K_F is the Freudlich constant (mg/l l_{3n}/g).

Non-linear regression analyses were performed using Origin 7.5 software running on a Windows XP platform.

Obtained results show clearly that the better fits were obtained using the freundlich model. Values of the Freundlich constants (n, K_f) and correlation coefficients (R^2)

given in **Table 1** indicate presence of the dyes (RhB), (GM) and (MO) onto the different used sorbent as a multilayer, and also confirm the heterogeneous nature of the used sorbent surface.

Table 1: Results of modelling of bio sorption isotherms

		Freundlich			Langmuir		
		K	n	R^2	Q_{max}	K_1	R^2
RhB	PM	3.82	1.24	0.82	523433	1.49	0.79
	PP	1.57	1.43	0.79	241195	6.59	0.74
	PA	7.82	0.63	0.65	353224	2.21	0.59
MO	PM	-	3.59	0.58	42206	2.13	0.40
	PP	-	2.40	0.48	84016	7.07	0.37
	PA	0.20	1.42	0.46	113035	11.09	0.36

3. CONCLUSION

This work aimed to study the sorption using pine bark (maritine, sprocket, Alep) for the elimination of three dyes rhodamine B (RhB), Green Malachite (GN) and Methyl Orange (MO). The different obtained results allowed the following conclusions.

The experimental results for the sorption kinetics of different dyes onto the three used sorbents show that a time of about six hours is sufficient to reach the state of pseudo-balance. The experimental results relating to the influence of pH show that the best results are obtained for acidic medium ($pH \leq 5$).

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