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By Ibtissam Maghri, Fatiha Amegrissi, Mohamed Elkouali, Abdelkbir Kenz , Omar Tanane, Mohamed Talbi & M. Salouhi

Hassan II Mohamedia-Casablanca University, Morocco

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Ibtissam Maghri [α], Fatiha Amegrissi [σ], Mohamed Elkouali [ρ], Abdelkbir Kenz [ω], Omar Tanane [¥], Mohamed Talbi [§] & M. Salouhi [χ]

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I. Introduction

Water pollution is beginning to take alarming proportions for both terrestrial waters and seacoast. Several physicochemical methods have been proposed to treat contaminated waters. At the high cost of certain techniques, it seems appropriate to direct the activities of the national scientific research in the field of environment, to the development of economic techniques. Among these techniques, there is adsorption on activated carbon. This treatment was effective but in most cases expensive [1]. Severalworkers have reported on the potential use of maritime and agricultural by–products as good substrates for the removal of dyes from aqueous solutions and wastewaters such as bacteria [2], sawdust [3], algae [4], shells [5], clay minerals [6,7], china [8], bauxite [9], bagasse [10], molasses [11] and coconut [12]. This process attempts to put into use of waste to treat waste and become even more efficient because these maritime and agricultural by products are readily available and often pose waste disposal problems. Hence, they are available at little or no cost. This makes the process of treating wastewaters with maritime and agricultural by–product adsorbents more cost effective than the use of conventional adsorbents like activated carbon.

This work aims to study elimination of methylene blue using as adsorbent two materials: Corn stalks and Mytilus Edulis shells.

II. Theoretical and Experimental Part

a) Adsorption parameters

In order to optimize process conditions for adsorption of methylene blue on Corn Stalks and Mytilus Edulis shells, we studied the influence of some factors which may be involved in the process of this phenomenon such as concentration of adsorbate, adsorbent dosage and granulometry.

b) Modeling of adsorption isotherms

Freundlich model (van Bemmelen, 1988 [13] Freundlich, 1909 [14]) is the most commonly used. We consider that it applies to many cases, especially in the case of multilayer adsorption with possible interactions between the adsorbed molecules [15]:

$$q_e = K_F . C_e$$

The most common form used is the plot in logarithmic scale variations qe according to Ce:

$$\text{Log } q_e = \log K_F + \log C_e$$

The constant n (adimentionelle) gives an indication of the intensity of adsorption. It is generally accepted that:

- $0.1<n<0.5$ characteristic of a good adsorption.
- $0.5<n<1$ characteristic of a moderate adsorption.
- $n>1$ characteristic of a weak adsorption.

Langmuir model is based on assumptions well known. The initial assumptions are that the solid adsorbent has a limited adsorption capacity (qm), all active sites are identical, they can only complex solute molecule (monolayer adsorption) and there are no interactions between adsorbed molecules. This model can be expressed by equation (1):

$$q_e/q_m = \theta = KL . C_e / (1 + K \ \ C) \quad (1)$$

Author α: Laboratory of analytical chemistry and physico chemistry of materials, faculty of sciences, Casablanca, Morocco.
E-mail : maghri.ibtissam@gmail.com
E-mails : m.elkouali@gmail.com [ρ], a.kenz@voila.fr [ω], o.tanane@gmail.com [¥]
Author §: Laboratoire des Sciences et d'ingénieur des Bio-systemes, EMI, Agdal-Rabat, Morocco. E-mail : maarifcentre@yahoo.fr

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K_L, equilibrium constant of Langmuir, θ, recovery rate The development of equation (1) leads to the linear form of Langmuir isotherm. The ratio RL = 1 / (1 + KL.C0), unitless magnitude, indicates that:

- The adsorption more favorable if R_L tends to 0.
- Adsorption much worse if R_L tends to 1.

Figure 2 : Principal equilibrum models.

Isotherms	Non linear expression	Linear expression
Langmuir	$q_e/q_m = \theta = K_L.C_e / (1 + K_L.C_e)$	$1/q_e = 1/(C_e. K_L.q_m) + 1/q_m$
Freundlich	$q_e = K_F.C_e.n$	$\text{Log}(q_e) = \log(K_F) + n \log(C_e)$

III. Results and Discussions

a) Adsorbate concentration effect

The figure 1 shows the adsorption kinetics of methylene blue onto Mytilus Edulis (A) and Corn Stalks (B) at different initial concentrations. We notify a decrease in the residual concentration. After sixty minutes, it reaches a constant value whatever the initial concentration; this shows that the equilibrium time is independent of the initial concentration of the dye.

b) Effect of adsorbent dosage

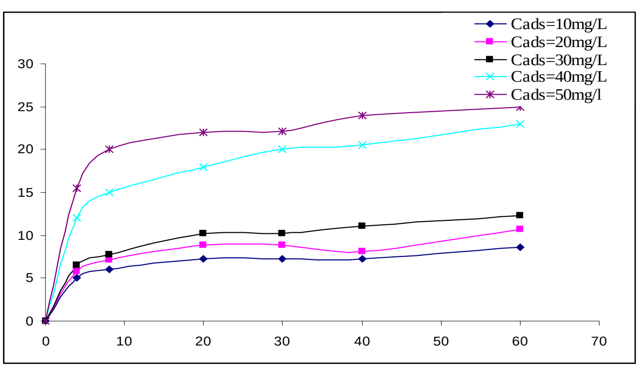
The adsorption kinetics of methylene blue with three different masses of adsorbents is shown in figure 2. From these results, the biosorption is important for a mass of 4g.l-1 of adsorbent.

c) Adsorbent particle size effect

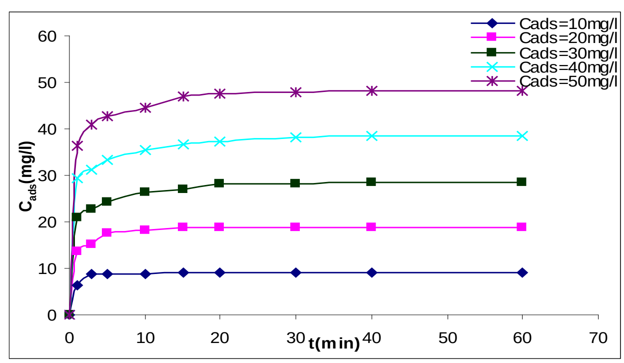
In this study we used different size fractions. The adsorption kinetics of methylene blue is shown in 3. The adsorption capacity is better for a size range between 0.08 and 0.2mm for Corn Stalks and for a size range 0,056mm for Mytilus Edulis Shells because the adsorption depends on the external surface of the adsorbent material increases with the fineness of its particles.

d) Modeling adsorption isotherms

The experimental isotherms of adsorption equilibrium and maximum adsorption capacity have been validated in detail by the Langmuir model (Corn stalks (Table 2), Mytilus Edulis shells (Table 3)) and Freundlich model (Corn Stalks (Table 4), Mytilus Edulis (Table 5)). The isotherms obtained were L-type according to the classification of Giles [16], which promotes a monolayer adsorption and the interaction between the adsorbate and the adsorbent is important.

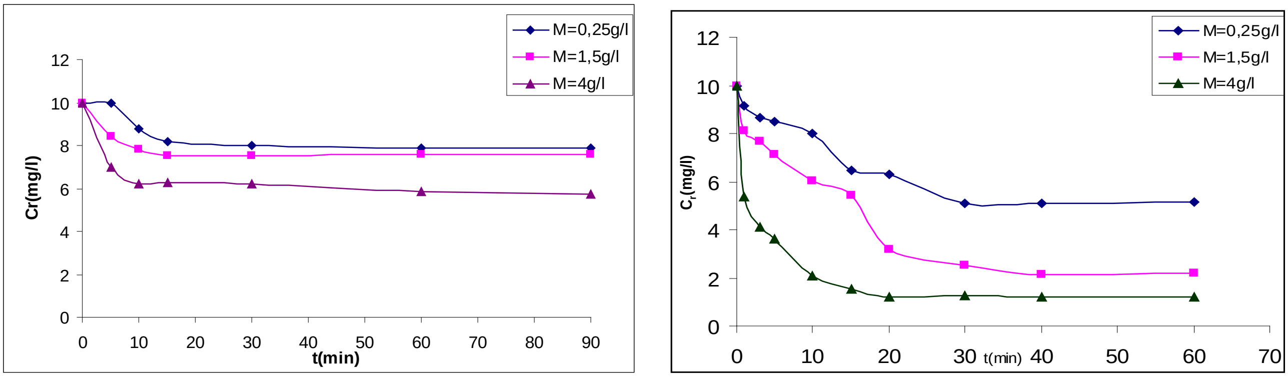


(A) Mytilus edulis shells



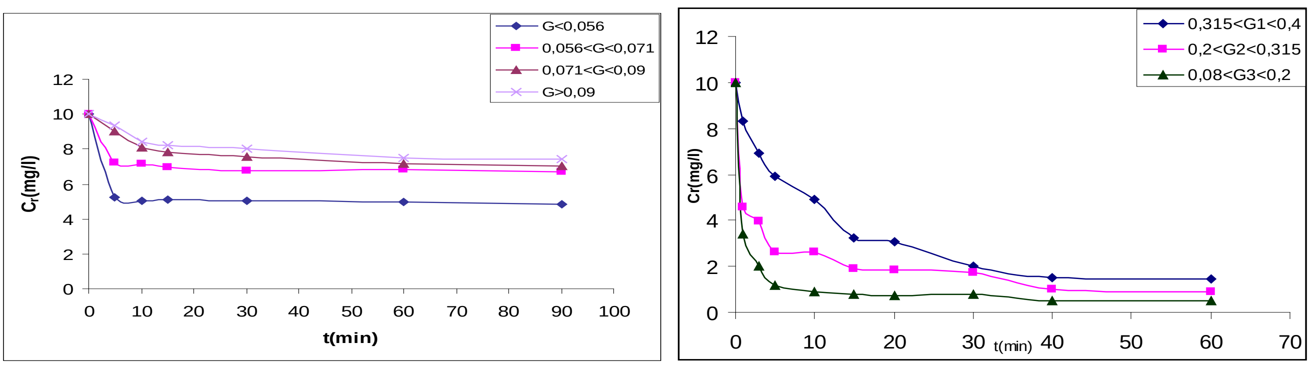
(B) Corn Stalks

Figure 1 : Effect of Methylene Blue concentration, pH = 6,8; g <0,056 mm; adsorbent dosage 4 g.l-1; ambient temperature.



(A) Mytilus edulis shells (B) Corn Stalks

Figure 2 : Effect of adsorbent dosage, pH = 6,8; initial concentration 10 mg.l 1; G <0,056 mm; ambient temperature.



(A) Mytilus edulis shells (B) Corn Stalks

Figure 3 : Effect of adsorbent particle size, pH = 6,8; initial concentration 10 mg.l-1; adsorbent dosage 4 g.l-1 ; ambient temperature.

Table 2 : Parameters of Langmuir adsorption of methylene blue onto Corn Stalks.

C_0 (mg.l^{-1})	K_L(l.mg^{-1})	q_m (mg.g^{-1})	r^2	R_L
20	0,023	500	0,9858	0,684
40	0,1429	58,479	0,9718	0,149
50	0,313	29,154	0,9692	0,050

Table 3 : Parameters of Langmuir adsorption of methylene blue onto Mytilus Edulis Shells.

C_0 (mg.l^{-1})	K_L(l.mg^{-1})	q_m (mg.g^{-1})	r^2	R_L
20	0,149	95,23	0,8271	0,251
40	0,91	5,66	0,8316	0,027
50	0,81	3,43	0,9083	0,024

Table 4 : Parameters of Freundlich adsorption of methylene blue onto Corn Stalks.

C_0 (mg.l^{-1})	K_F (mg$^{(1-n)}$l ^{n}g^{-1})	n	r^2	q_m(mg.g^{-1})
20	2,867	0,901	0,985	42,624
40	2,50	0,617	0,9706	24,336
50	3,389	0,134	0,889	5,866

Table 5 : Parameters of Freundlich adsorption of methylene blue onto Mytilus Edulis Shells.

C_0 (mg.l^{-1})	K_F (mg$^{(1-n)}$l ^{n}g^{-1})	n	r^2	q_m(mg.g^{-1})
20	1,258	0,4586	0,8057	40,969
40	2,474	0,5245	0,844	17,12
50	1,845	0,4867	0,9758	12,38

The results show that the maximum adsorption capacity (q_m) obtained from Langmuir model decreases with increasing the concentration value of the Methylene Blue (C_0). It reaches its maximum value at C_0 = 20 mg. l^{-1}. The adsorption is favorable (R_L tends to 0) and moderate (0.5< n <1).

The low values of maximum adsorption capacities obtained from the Freundlich model, confirm that the molecule of Methylene Blue is not strongly adsorbed inside the pores because of its size.

IV. Conclusion

This review highlighted the capacities of Corn Stalks and Mytilus Edulis shells to pretreat raw wastewaters. The extent of dye removal increased with decrease in the initial concentration of dye and particle size of the adsorbents and also increased with increase in contact time and the adsorbents doses used. The equilibrium adsorption is practically achieved in 60 min. Adsorption data were modelled using the Freundlich and Langmuir adsorption isotherms. The adsorption capacities of Corn stalks and Mytilus Edulis shells reaches a maximum at C0=20 mg.l-1. We can say that Mytilus Edulis shells adsorb dyes better than Corn stalks with a high maximum adsorption capacity in comparison with corn stalks. The results indicate that both Corn stalks and Mytilus Edulis shells could be employed as low-cost alternative to commercial activated carbon in methylene blue wastewater treatment.

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