Adsorption of methylene blue dye onto chemically activated olive stones and zeolites

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Introduction

In the Mediterranean area, the most widespread consumed product is olives and olive oil. Countries such as Spain, Italy, Turkey and Greece produce the largest amounts of olives and olive oil globally. The basic by-products produced are a solid residue known as olive press cake (OPC) and large amounts of liquid known as olive-mill wastewater (OMW). The various by-products of olive oil industry are not used and accumulate as waste. They are not easily biodegradable and needs to be detoxified before it can properly be used in agricultural and other industrial processes due to the high organic load especially phenols and a great variety of contaminants [1]. Olive stones are collected from by-products generated during the preparation of olive oil and can be used not only as sources of bioactive compounds but also as high-cost adsorbents for purification purposes [2,3,4,5].

In the present work, the development of new adsorptive materials is studied combing the properties of agro-food by-products and minerals. These adsorbents are derived from the lignocellulosic wastes of the olive industry and more specifically from olive stones (OL) in combination with clinoptilolite (CL), an abundant zeolite with low cost, either separately or in mixtures in different proportions (100%OL., 50%OL.+ 50%CL., 20%OL.+80%CL. w./w.), chemically activated with HCL acid at 3 or 6M. The MB adsorption ability of the materials is examined. Different kinetic models (pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion) are applied to MB adsorption data.

Results and Discussions

The adsorption capacity of methylene blue follows the order (Fig. 1): 20%OL.+80%CL. > 50%OL.+50%CL. > 100%OL. w./w., respectively for both acid concentrations 3 or 6 M. It is observed that the mixtures of olive stone with zeolite, i.e. clinoptilolite present higher adsorption than the chemically activated raw materials alone. Comparing the adsorption capacity of the adsorbents activated at 3 and 6 M, it seems that the adsorbents that are activated at 6M present higher adsorption capacity at shorter time than those which are activated at HCL 3M. The highest maximum MB adsorption is observed in 20% w./w. OL and 80% w./w. CL activated with HCL acid at 6M after 10 min while the lowest maximum MB adsorption is observed in 100% w./w. OL activated with 6M after 1030 min.

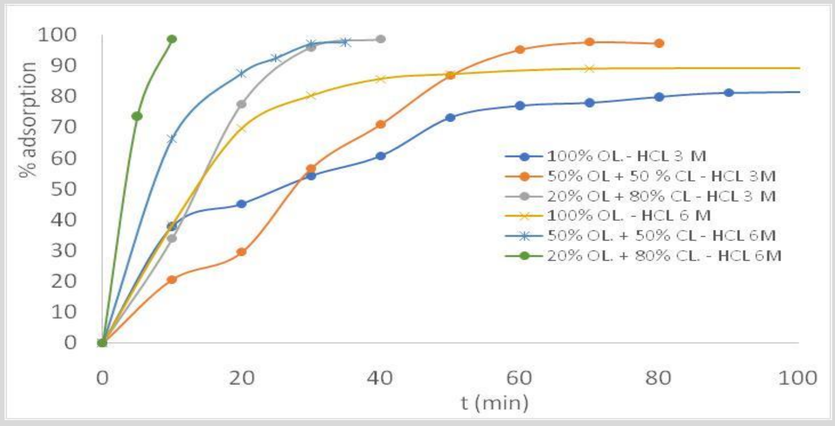
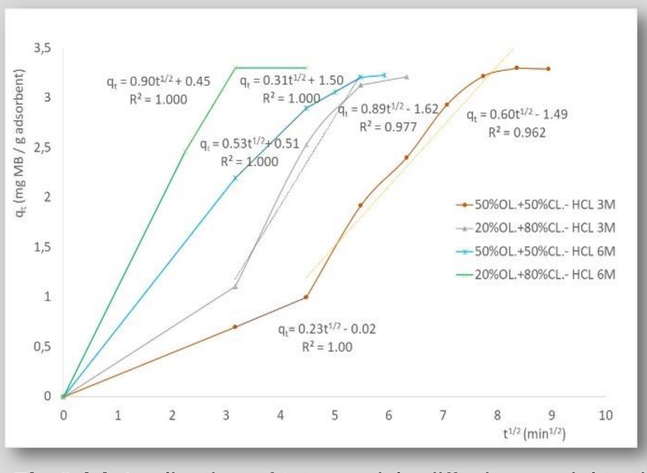


Fig. 1 Percentage of methylene blue adsorption from its aqueous solutions on different mixtures of olive stones and zeolites activated with HCL acid at 3 and 6M versus time, t, at a ratio of 10 g adsorbent L^{-1} adsorbate. The adsorption MB ability measured for the first 100 min.

Adsorbate molecules may be moved from the bulk liquid to the liquid film surrounding the adsorbent [6]. Then, they can a) diffuse through the solution to the external surface of the adsorbent (film mass transfer), b) diffuse within the pores or capillaries of the adsorbent internal structure to the sorption sites, c) be uptaken by the adsorbent leading to equilibrium. The first and the second steps are the rate limiting steps while the last one is assumed to be rapid.

Fig.2(a) shows the application of Intraparticle diffusion model to the experimental MB adsorption data and depicts the experimental curves which give the amount of adsorbate (MB) adsorbed per unit mass of adsorbent (mgg^{-1}) versus $t^{1/2}$. Four different regions can be distinguished (see Table 1).



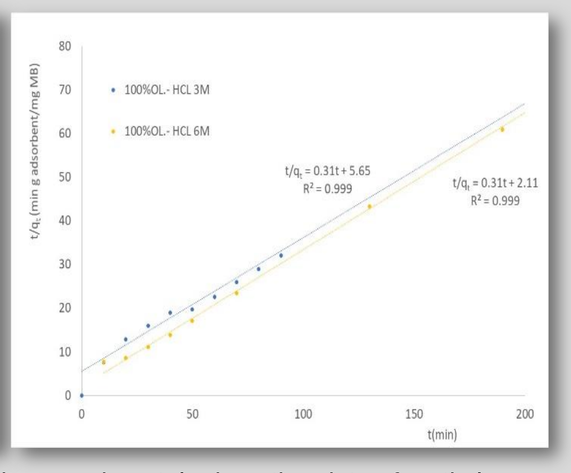


Fig.2 (a) Application of Intraparticle diffusion model to the experimental adsorption data of methylene blue dye (MB) on chemically modified mixtures of olive stones (OL) and clinoptilolite (CL) at HCL 3 and 6M, **(b)** Application of pseudo-second order kinetic model to the experimental adsorption data of methylene blue dye (MB) on chemically modified olive stones (OL) at two different concentrations 3 and 6M.

Table 1: The regions according to Fig.2a for the adsorption of MB on chemically activated mixtures of OL with CL.

Materials (w./w.)	Regions (t in min)			
	A	B	C	D
20%OL+80%CL, HCL 3M	0-10	10-30	-	30-40
50%OL+50%CL, HCL 3M	0-10	10-20	20-70	70-80
20%OL+80%CL, HCL 6M	0-5	5-10	-	10-20
50%OL+50%CL, HCL 6M	0-10	10-20	20-30	30-35

Comparing the correlation coefficient factors after the application of intraparticle diffusion model (see table 3) to the experimental data, it seems that it describes well the B region for all materials (R^2>0.98). As far as the C region may concern, mixtures of 50% w./w. OL with 50%w./w. of CL present high correlation coefficient factors for the application of Intraparticle diffusion model to the experimental adsorption data. The rate parameter for the diffusion in the B and C region is attributed to macropore diffusion and mesopore or transitional pore diffusion [8]. Above the C region is the D region for which the final equilibrium stage occurs. Moreover, the application of pseudo-second order kinetic model to MB adsorption data shows that pseudo-second order model fits well to the experimental data of the B region for 50-50% w./w. OL-CL, HCL 3M, 20-80% w./w. OL-CL, HCL 6M and 50-50% w./w. OL-CL, HCL 6M and of the C region only for the material 50-50% w./w. OL-CL activated with HCL 6M.

Table 3: Kinetic parameters of the two models (pseudo-second order, intraparticle diffusion model) based on the adsorption of MB from chemically activated mixtures of olive stones with clinoptilolite. K_D, K_{SE} and q_E are expressed in $mgg^{-1}min^{-1/2}$, $gmin^{-1}mg^{-1}$, mgg^{-1}, respectively

Materials (w./w.)	Pseudo-second order						Intraparticle Diffusion			
	B region			C region			B region		C region	
	K_{SE}	q_E	R^2	K_{SE}	q_E	R^2	K_D	R^2	K_D	R^2
20-80% OL-CL, HCL 3M	-	-	-	-	-	-	0.89	0.98	-	-
50-50% OL-CL, HCL 3M	$0.38x10^{-1}$	1.75	1.00	-	-	-	0.23	1.00	0.60	0.96
20-80% OL-CL, HCL 6M	$0.39x10^{-1}$	5.00	1.00	-	-	-	0.90	1.00	-	-
50-50% OL-CL, HCL 6M	$0.26x10^{-1}$	4.16	1.00	$0.28\ x10^{-1}$	4.16	0.99	0.53	1.00	0.31	1.00

The adsorption data of MB dye on olive stone (100%w./w.) at two different concentrations of 3 and 6M are presented to Fig. 2b. It seems that the pseudo-second order kinetic model fits well to the experimental adsorption data indicating that the overall rate of dye adsorption is controlled by the chemisorption process.

The other two kinetic models, i.e. pseudo-first order and Elovich models were applied to the experimental MB adsorption data but they were not fitted well to the experimental data (low correlation coefficient factors).

Conclusions

- The adsorption ability of methylene blue follows the order: 20%OL.+80%CL. (HCL 6M) > 20%OL.+80%CL. (HCL 3M) > 50%OL.+50%CL. (HCL 6M) > 50%OL.+50%CL. (HCL 3M) > 100%OL. (HCL 3M) ≈100%OL. (HCL 6M) w./w.
- The chemical activation of olive stone and zeolite with higher acid concentration leads to higher MB adsorption due to the increase in the pore structure of the material.
- The adsorption data of MB on olive stone (100% OL. w./w.) either activated with 3 or 6 M HCL follows pseudo second order kinetic model while the sorption data of MB on mixtures of clinoptilolite and olive stone follows intraparticle diffusion model and pseudo second order kinetic model indicating that both physical and chemical adsorption of MB onto mixtures take place

Reference

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