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

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Abstract

Olive oil production belongs to the branches of industry that produce large quantities of by-products. 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. In the present study, samples of olive stone (OL) and clinoptilolite (CL) are prepared in proportions of 100% w./w. OL., 50-50% w./w. OL.-CL. and 20-80% w./w. OL.-CL. The samples are chemically activated with HCL acid at 3 and 6M. The adsorption of methylene blue dye (MB) is studied. Four kinetic models are applied to the experimental adsorption data: pseudo-first order, pseudo-second order, Elovich and Intraparticle diffusion model. The results show that the increase in MB adsorption 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. Adsorbents activated with HCL 6M present higher MB adsorption percentages in shorter time compared to the adsorbents activated with HCL 3M. The implementation of different kinetic models has shown that MB experimental adsorption data on olive stone (100% OL. w./w.) either activated with HCL 3 or 6 M follows pseudo second order kinetic model while MB adsorption data on mixtures of CL and OL follows initially intraparticle diffusion and then pseudo second order kinetic models. In conclusion, chemically activated olive stones alone or in combination with minerals can be used as filters for the purification of water from organic compounds reducing the by-product amounts released to the environment.

Keywords: olive stone, zeolite, kinetic models, adsorption

Introduction

Industries, such as textile, paper and plastics, use a substantial amount of dyes and water to color their products. As a result, considerable amounts of synthetic dyes as effluents are discharged annually into the environment [1,2]. Methylene blue (MB) is a cationic dye that is used extremely for dying cotton, wool and silk. Therefore, many methods such as chemical coagulation, ion exchange, electrolysis, biological treatments and adsorption [3] have been developed for dye removal from wastewater. Among these methods, adsorption through activated adsorbents is highly effective, cheap and eco-friendly for the removal of dyes and pigments as well as other organic and inorganic polluters [4,5].

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 [6].

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 chemically activated with HCL acid at 3 and 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.

Materials and Methods

New adsorptive materials were prepared from the chemical modification of olive by-products and zeolites appropriate for dye removal. Different proportions of olive stone (OL) and clinoptilolite (CL) were mixed (100%OL., 50%OL.+50%CL., 20%OL.+80%CL. w./w.) in powder form and were activated with HCL acid at different concentrations (3 and 6 M). Then, the samples were placed in an orbital shaker for 24 h at 24°C. They were filtered and washed several times with distilled water until the filtrate pH remained neutral (~7). After that, the samples were dried in an oven at 110°C for 24 h.

0.14 g of each adsorbent were mixed with 14mL of dye and placed in test tubes in a proportion of 10g of adsorbent/L of dye. Then, the samples were stirred and centrifuged for 5 min at 5000 rpm. The absorbance of each sample was measured in the VIS spectrophotometer (λ = 664 nm). The adsorbed amount (q_t) of the adsorbate onto the adsorbent was determined from the difference between the initial amount of adsorbate (q_o) in the solution and the measured amount of the adsorbate, expressed as %, i.e. $(q_t/q_o)\cdot 100$. The above procedure was repeated three times for each sample. The initial dye concentration was equal to 0.035g/L.

Different kinetic models were used to investigate the mechanism of adsorption [7]. The pseudo-first order kinetic model is given by the following equation:

$$\log(q_e - q_t) = logq_e - \frac{K_L}{2.303}t$$

where q_e and q_t are the amounts, mg, of dye adsorbed per unit mass of adsorbent at equilibrium and at time, t, respectively and K_L is the equilibrium rate constant of pseudo-first order adsorption ($mgg^{-1}min^{-1}$). The slope of the plot of $\log(q_e-q_t)$ versus t was used to determine K_L and the intercept q_e.

The pseudo-second order kinetic model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_{se}q_e^2} + \frac{t}{q_e}$$

where K_{se} is the equilibrium rate constant of pseudo-second order adsorption ($gmg^{-1}min^{-1}$). The slope of the plot of t/q_t versus t was used to determine q_e and the intercept K_{se}.

Elovich equation can be expressed by the following equation:

$$q_t = \frac{1}{p}\ln(mp) + \frac{1}{p}lnt$$

where m ($mgg^{-1}min^{-1}$) is the initial sorption rate and the parameter p (mgg^{-1}) is related to the extent of surface coverage and activation energy for chemisorption. The slope of the plot of q_t versus lnt was used to determine p and the intercept m.

When the diffusion is the prevailing mechanism then the intraparticle diffusion model can be defined as follows:

$$q_t = K_D t^{0,5} + C$$

where K_D ($mgg^{-1}min^{-0.5}$) is the intraparticle diffusion rate and C is a constant

Results and Discussions

The adsorption of MB on chemically modified olive stone and clinoptilolite is shown in Fig.1.

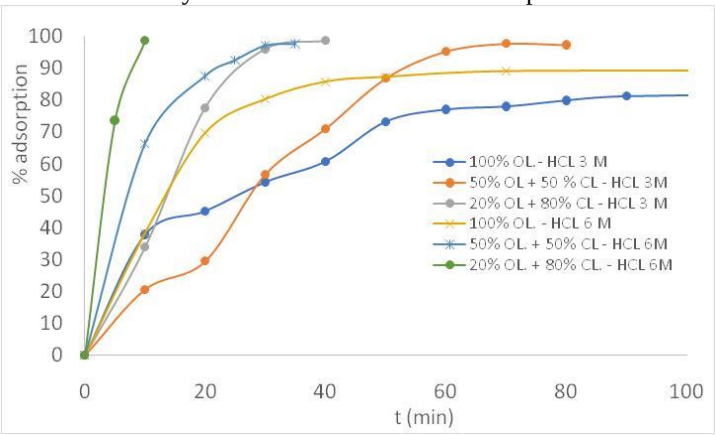


Fig. 1 Percentage of methylene blue adsorption from its aqueous solutions on different mixtures of olive stones and zeolites activated with HCL acid at 3 and 6M versus time, t, at a ratio of 10 g adsorbent L^{-1} adsorbate. The adsorption MB ability measured for the first 100 min.

The adsorption capacity of methylene blue follows the order: 20%OL.+80%CL. > 50%OL.+50%CL. >

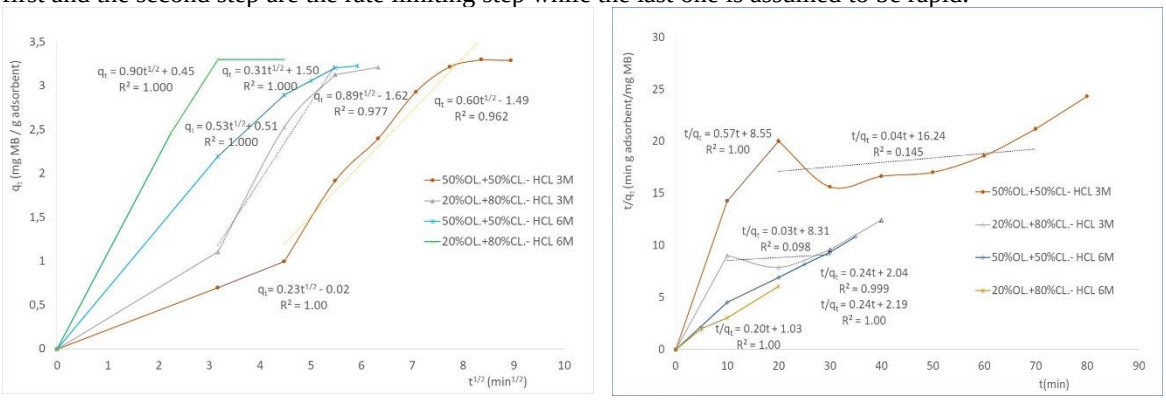
100%OL. w./w., respectively for both acid concentrations 3 or 6 M. It is observed that the mixtures of olive stone with zeolite, i.e. clinoptilolite present higher adsorption than the chemically activated raw materials alone. Comparing the adsorption capacity of the adsorbents activated at 3 and 6 M, 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. Generally, the increase in the amount of zeolite in the mixture leads to higher adsorption ability of the materials. The adsorption curves for all the materials reach equilibrium after a certain time, which differ among them.

Moreover, the maximum adsorption of MB on the materials and the adsorption time are presented in table 1. The 100% OL. material activated with HCL at 3 and 6M reached at equilibrium after 86.5 and 17.2 h as it seems to table 1. 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.

Table 1: Maximum percentage of MB adsorption

HCL conc.	Materials	% maximum MB adsorption	t(min)
	100%OL.	93.9%	5190
3M	50%OL.+50%CL.	97.3%	80
	20%OL.+80%CL	98.7%	40
	100%OL.	90.6%	1030
6M	50%OL.+50%CL.	97.6%	35
	20%OL.+80%CL	98.7%	10

Different kinetic models (pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion) were applied to MB adsorption data indicating that the adsorption process follows different mechanisms in the mixtures of olive stone and clinoptilolite compared to olive stone alone. The adsorbents, which consist of olive stone and clinoptilolite, present either the same or different mechanism of adsorption. It is necessary to examine the adsorption process into stages [8]. Adsorbate molecules may be moved from the the bulk liquid to the liquid film surrounding the adsorbent. 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 step are the rate limiting step while the last one is assumed to be rapid.



(a) (b)

Fig.2(a) Application of Intraparticle diffusion model and **(b)** pseudo-second order kinetic 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

According to literature [8] the initial portion (from the origin up to the first experimental point), A region is due to external mass transfer and then two linear regions follow representing the intraparticle diffusion. 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 2). Comparing the correlation coefficient factors after the application of intraparticle diffusion model to the experimental data,

it seems that Intraparticle diffusion model 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.

Table 2: 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

Figure 2(b) shows the application of pseudo-second order kinetic model to MB adsorption data. It seems 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. Pseudo-first order kinetic model and Elovich model present low correlation coefficient values for all regions and are not presented in the paper.

Table 3 summarizes the results of the kinetic parameters of the two models, i.e. pseudo-second order, intraparticle diffusion that fit well to MB adsorption data for the B and C region. The correlation coefficient values, R^2, are near unity.

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

Materials (w./w.)	Pseudo-second order						Intraparticle Diffusion			
	B region			C region			B region		C region	
	K_{SE}[a]	q_E[a]	R^2	K_{SE}[a]	q_E[a]	R^2	K_D[a]	R^2	K_D[a]	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

[a] K_D, K_{SE} and q_E are expressed in $mgg^{-1}min^{-1/2}$, $gmin^{-1}mg^{-1}$, mgg^{-1}, respectively

The adsorption data of MB dye on olive stone (100%w./w.) at two different concentrations of 3 and 6M are presented to Fig. 4. It seems that the experimental adsorption data fit well to the pseudo-second order kinetic model indicating that the the overall rate of dye adsorption is controlled by the chemisorption process. The kinetic parameters of the pseudo-second order model are: $K_{SE} = 0.17x10^{-1}$ $gmin^{-1}mg^{-1}$ and q_E = 3.23 mgg^{-1} for 100% olive stone activated with HCL 3M and $K_{SE} = 0.46x10^{-1}gmin^{-1}mg^{-1}$ and q_E = 3.23 mgg^{-1} for 100% olive stone activated with HCL 6M. All the other kinetic models, i.e. intraparticle diffusion model, pseudo-first order and Elovich model, show correlation coefficient factors less than unity indicating that they cannot describe well MB adsorption data on olive stones.

The sorption data of MB on olive stone samples activated either with 3 or 6 M HCL acid follows pseudo second order kinetic model showing that the chemical sorption of methylene blue onto OL is prevalent. In the other hand, the sorption data of MB on mixtures of olive stone and zeolite activated either with 3 or 6 M HCL follows intraparticle diffusion kinetic model and pseudo second order kinetic model indicating that both physical and chemical adsorption of MB onto mixtures take place. Other studies have shown similar results [9,10].

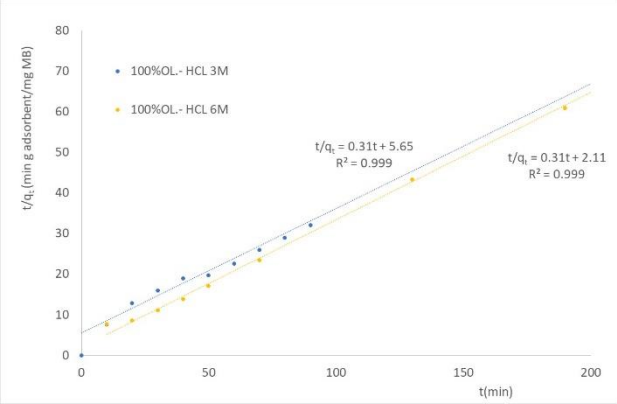


Fig.4 Application of pseudo-second order kinetic model to the experimental adsorption data of methylene blue dye (MB) on chemically modified olive stones (OL) at two different concentrations 3 and 6M.

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
- Adsorbents consisting of both activated food by-products and zeolites combine unique low-cost abilities and are promising materials in water purifiers as filters.

References

1. Feng, Y., Yang, F., Wang, Y., Ma, L., Wu, Y., Kerr, P.G, Yang, L.: Basic dye adsorption onto an agro-based waste material – Sesame hull (*Sesamum indicum L.*). Bioresource Technology. 102, 10280–10285 (2011)
2. Youcef, L.D., Belaroui, L.S., López-Galindo, A.: Adsorption of a cationic methylene blue dye on an Algerian palygorskite. Applied Clay Science. 179, 105145 (2019)
3. Gupta, V.K., Mittal, A., Krishnan, L., Gajbe, V.: Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. Separation and Purification Technology. 40(1), 87–96 (2004)
4. Acemioğlu, B.: Batch kinetic study of sorption of methylene blue by perlite. Chemical Engineering Journal 106(1), 73–81 (2005)
5. Jawad, AH, Razuan, R, Appaturi, JN, Wilson, L.D.: Adsorption and mechanism study for methylene blue dye removal with carbonized watermelon (*Citrullus lanatus*) rind prepared via one-step liquid phase H_2SO_4 activation. Surfaces and Interfaces. 16, 76-84 (2019)
6. Corral-Bobadilla, M., Lostado-Lorza, R., Somovilla-Gómez, F., Escribano-Garcíab, R.: Effective use of activated carbon from olive stone waste in thebiosorption removal of Fe(III) ions from aqueous solutions. Journal of Cleaner Production. 294, 126332 (2021)
7. Bello, M. O., Abdus-Salam, N., Adekola, F.A., Pal, U.: Isotherm and kinetic studies of adsorption of methylene blue using activated carbon from ackee apple pods. Chemical Data Collections. 31, 100607 (2021)
8. Ioannou, Z., Simitzis, J.: Adsorption kinetics of phenol and 3-nitrophnol from aqueous solutions on conventional and novel carbons. Journal of Hazardous Materials. 171, 954-964 (2009)

9. Marrakchi, F., Hameed, B.H., Bouaziz, M.: Mesoporous and high-surface-area activated carbon from defatted olive cake by-products of olive mills for the adsorption kinetics and isotherm of methylene blue and acid blue. Journal of Environmental Chemical Engineering. 8(5), 104199 (2020)
10. Al-Ghouti, M. A., Sweleh, A. O.: Optimizing textile dye removal by activated carbon prepared from olive stones. Environmental Technology & Innovation. 16, 100488 (2019)