Removal of organic pollutants using pyrolyzed carbons produced from olive and sugar industry byproducts

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1. INTRODUCTION

The olive oil production is one of the main economic pillars of the countries of the Mediterranean basin. Nevertheless, the last few years the cultivation of olive trees (*Olea europaea L*) has also been expanded in more countries globally (Otero 2021). Parallel to this abundant production of table olives and oil, huge amounts of wastes and byproducts are also being generated. Those residues constitute a severe environmental issue, due to their high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Al-Shaweesh et al., 2018).

Additionally, another widely used product all over the world is sugar, with an annual production of 160 million tons. During this huge production a wide amount of wastes (e.g. molasses) is also generated with adverse effects in the ecosystems (e.g. leads to death of aquatic organisms due to the adsorption of the available oxygen) (Anastopoulos et al., 2017).

Till now various waste treatment techniques have been tested. Among them, the removal of pollutants via activated carbons' (ACs) adsorption is considered one of the most appropriate and efficient solution (Lewoyehu, 2021). The aim of this work is to investigate the possibility for the preparation of new, efficient adsorptive materials, eliminating agro-industrial by-products that their free discharge can harm the environment and to use these materials for wastewater treatment.

2. EXPERIMENTAL

Four samples were tested with different ratios of the precursors (Olive stone, Molasses, Zeolite): 80/20% Z-OS (D1), 80/10/10% Z-OS-M (D2), 90/5/5% Z-OS-M (D3) w/w/w, and 50/50 % OS-M w/w. Olive stones were first washed thoroughly with distilled water to remove impurities. In second step, they were dried at 110 ◦C for 24 h and then they were crushed and sieved up to 200 μm. Molasses and zeolite, in the form of clinoptilolite, were purchased from trade. Carbonization of the mixtures occurred at 800oC for 30 minutes, under nitrogen flow into a horizontal furnace. The carbonization of pure clinoptilolite (CZ) was tested as well as a reference sample.

The adsorption capacity of the prepared bio-sorbents was tested using the cationic methylene blue dye (MB). FT-IR analysis of the adsorbents took place using an FTIR model Cary 630 (Agilent Technologies). Moreover, the kinetic analysis of MB adsorption onto ACs was examined using four kinetic models, i.e. pseudo-first order, pseudo-second order, elovich and intraparticle diffusion model.

3. RESULTS AND DISCUSSION

The weight loss percentage of the materials occurring after the carbonization process, is shown in Fig. 1. The results show that the increase in weight loss follows the order: OS-M>D1≥D2>D3≥CZ. It is observed that less zeolite content or higher content in molasses leads to higher weight losses. This happens due to the increase in cellulose, hemicellulose and lignin (agro-food by-products) in the samples reducing simultaneously the mineral content (zeolite)

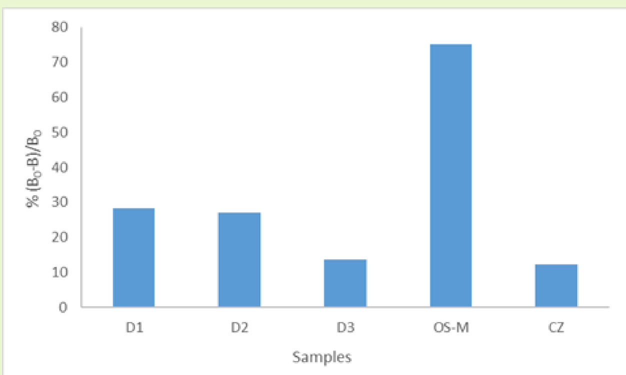

Fig. 1: Percentage of weight loss for each sample after carbonization.

The adsorption capacity of the samples can be observed in Fig. 2. In general, the results show that the increase in MB adsorption follows the order: D1>D2>OS-M>D3>CZ. This leads to the observation that the mixtures with smaller content in zeolite present higher adsorption capacity. Nevertheless, the total absence of zeolite from the material, e.g., OS-M means that it can totally adsorb MB dye but in greater time.

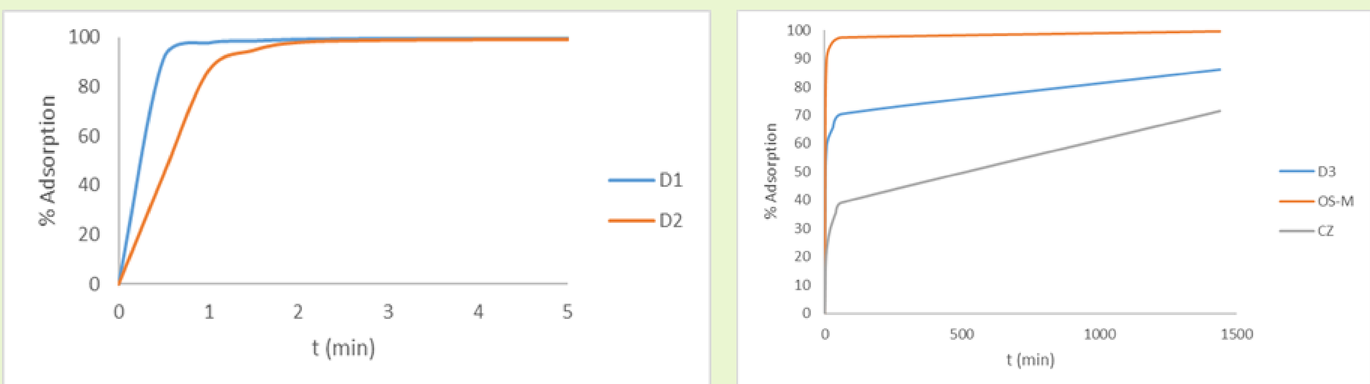

Fig. 2: Percentage of MB adsorption on different materials, carbonized at 800ºC, versus time, at a ratio of 10g adsorbent L^{-1} adsorbate.

Different kinetic models (pseudo-first, pseudo-second order, elovich and intraparticle diffusion) were applied to MB adsorption data. It was found that all the samples follow the pseudo-second order indicating that chemical adsorption is the prevailing mechanism.

The mathematical expression of the best fitted model follows:

Pseudo-second order: $\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_t}$

where $q_{e.\,exp}$ (mg/g) and $q_{e.\,cal}$ (mg/g) are the experimental and theoretical calculated adsorbed amount of MB in equilibrium per gram of adsorbent, k_2 (g mg^{-1} min^{-1}) is the constants of the model (Ioannou et al. 2013).

Table 1. : Kinetic parameters of pseudo-second order model for MB adsorption from aqueous solution on different materials carbonized at 800ºC.

	Pseudo-second order			
	$q_{e.\,exp}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	$q_{e.\,cal}$ (mg/g)	R^2
D1	2.983	19.802	3.003	1
D2	2.982	1.561	3.222	0.997
D3	2.772	0.174	2.776	1
OS-M	2.957	0.703	2.992	1
CZ	2.536	0.085	2.543	0.999

The FTIR spectra of the materials are shown in Fig. 3. The broad bands between 3270 and 3285 cm-1, observed in samples that have adsorbed MB, correspond to stretching vibration of bonded and non-bonded –O-H groups. Moreover, the peaks at 1623-1626 cm^{-1} may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. This can be confirmed as well by Benzekri et al., 2018 who mentions that the peaks at 1641 cm^{-1} are indicative of the stretching vibration of the carbonyl CO or the aromatic (C−C) ring stretching. The bands at 1017-1043cm^{-1}, which observed more intense at samples' D1 and D2 spectra, are assigned to -C-H bending "in plane" vibrations (Galletti et al., 2015).

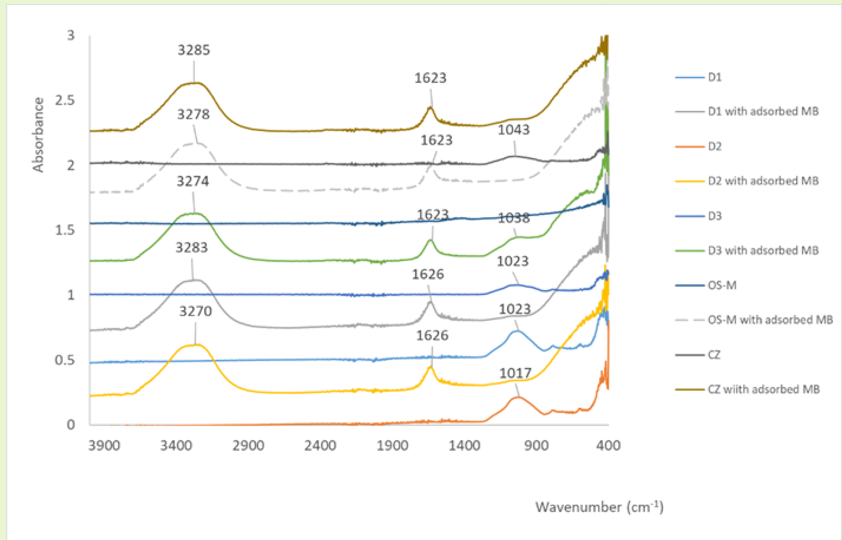

Fig. 3:FTIR spectra for carbonized biomass before and after methylene blue adsorption.

4. CONCLUSIONS

1. The adsorption capacity of the materials follows the order: D1>D2>OS-M>D3>CZ. The 80/20% w./w. zeolite/olive stone and the 80/10/10% w./w. zeolite/olive stone/molasses materials show the higher adsorption in shorter time compared to all the other adsorbents.
2. According to FTIR analysis, the peak appeared at 1626 cm^{-1} shows the presence of C=C stretching "in plane" vibrations of the aromatic ring indicating the adsorption of MB to adsorbents
3. The kinetic model that describes better the MB adsorption data on carbonaceous materials is pseudo-second order model indicating that chemical adsorption is the prevailing mechanism
4. ACs resulting from the combination of those two food industry by-products and zeolite can be deemed as efficient and low-cost materials for purification and wastewater treatment.

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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης