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

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Keywords: activated carbon, olive stone, molasses, methylene blue
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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 extraction of olive oil and can be used as sources of bioactive compounds and as low-cost adsorbents for wastewater treatment purposes. In addition, sugar industries belong as well in the total of food industries that are characterized by a wide global production and a huge by-product generation. In the present study, samples of olive stone (OS), molasses (M) and zeolite (CZ) are prepared in proportions of 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. The samples are carbonized at 800ºC in an inert atmosphere, into a horizontal furnace. The adsorption capacity of the samples was studied using the methylene blue (MB) dye. All materials were characterized using FTIR analysis. 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: D1>D2>OS-M>D3>Z. Consequently, samples containing zeolite in smaller proportions present higher MB adsorption percentages in shorter time. According to FTIR analysis, the peaks at 1623-1626 cm^{-1} may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. The implementation of different kinetic models has shown that MB adsorption data on all samples follow pseudo second order kinetic model indicating that chemisorption is the prevailing mechanism. In conclusion, such carbonaceous materials can be used as filters for the purification of wastewater from organic compounds, reducing the by-product amounts released to the environment.

Keywords: olive stone, molasses, zeolite, methylene blue adsorption, carbonization, FTIR analysis

INTRODUCTION

Environmental pollution nowadays is of great concern globally. Annually large amounts of diverse pollutants and toxic emissions are discharged in the atmosphere and in the ecosystems, terrestrial and aqueous, with disastrous consequences. Synthetic dyes, used extensively in a wide range of industrial activities (food, plastic, textile, paper, pharmaceutics, cosmetics), are one of the most common pollutants discharged in the environment (Lewoyehu, 2021).

The olive oil production is one of the main economic pillars of the countries of the Mediterranean basin, predominantly Spain, Italy, Greece, Portugal, Turkey, Tunisia and Morocco, with the first three being the leading producers in the European Union (EU). Nevertheless, the last few years the cultivation of olive trees (species *Olea europaea L*) has also been expanded in more countries globally (Otero 2021). According to the Food and Agriculture Organization of the United Nations, in 2018, in 41 different countries were cultivated 10.7 million hectares of olive trees with a total production of 21.6 million tons of olives (Contreras et al., 2020). 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. Sugar can be produced from sugarcane, sugar beet or other crops with high content in sugar. Sugar crystals are covered with molasses, giving them a brown-golden color, which is the color of raw sugar. The larger amount of raw sugar is used to produce bleached, refined sugar. During this production, wastes (e.g. molasses) are generated burdening the environment and leading to 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; Sahu, 2018).

Till now various waste treatment techniques, such as adsorption, coagulation, advanced oxidation, and membrane separation, have been tested. Among them, the removal of pollutants via activated carbon adsorption is considered one of the most appropriate and efficient solution (Lewoyehu, 2021). Materials such as activated or

pyrolyzed carbons can be produced using a wide range of ecofriendly and low-cost precursors, such as agro-industrial byproducts (e.g., olive stones, molasses). In this way, waste disposal can be diminished in two ways by using one technique.
The aim of this current 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. The preparation of the bio-sorbents aims to be eco-friendly with the total absence of chemical reagents. The final purpose of this research is to use these novel sorbents to adsorb toxic organic compounds from wastewater, such as synthetic dyes.

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 discoloring abilities of the carbonized materials to adsorb dyes, were also determined, using methylene blue as dye from an aqueous solution of 0.032g/L. More specifically 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 % adsorption (Fig. 2), i.e. $(q_t/q_o)\cdot 100$. The above procedure was repeated three times for each sample.
FT-IR spectra were determined for the carbonized biomass before and after MB adsorption. An Agilent Cary 630 FTIR spectroscope, equipped with an ATR accessory, was used with Microlab software. All measurements were performed on the same day in an ambient temperature equal to 25◦C. The spectra were measured in the region from 400 to 4000 cm^{-1}. The diamond ATR sensor was cleaned with ethyl alcohol or acetone before each sample measurements.

RESULTS AND DISCUSION

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). According to Hazza et al., 2015, activated carbon (AC) prepared at 800ºC from olive stones marked a yield percentage of 32%.

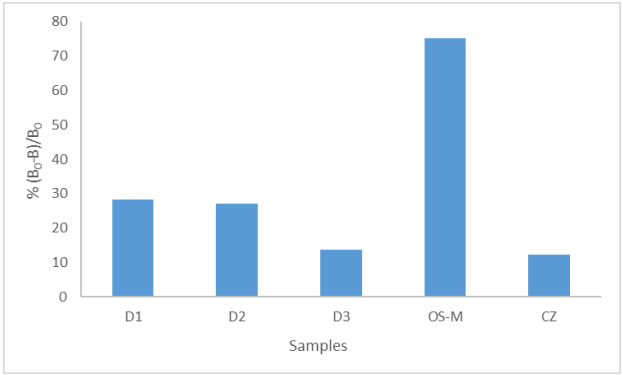

Fig.1 Percentage of weight loss for each sample after carbonization.

The adsorption capacity of the samples can be observed in Fig. 2. Materials D1 and D2 seem to have better adsorption characteristics. 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 adsorb totally MB dye but in greater time than the materials D1 and D2. According to literature activated carbons (ACs), prepared only by using olive stones as precursors, needed more than one hour to reach at equilibrium (Benzekri et al., 2018).

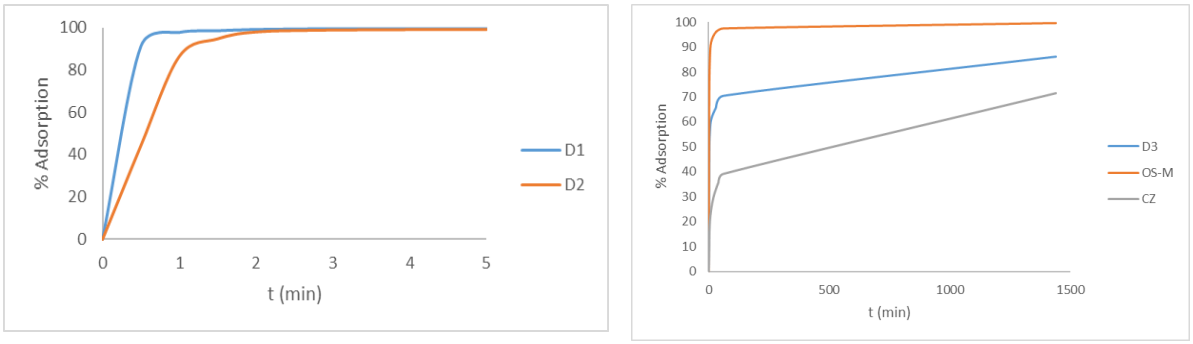

Fig. 2 Adsorption of methylene blue from aqueous solution on carbonaceous materials.

Kinetic Analysis

Different kinetic models were used to investigate the mechanism of adsorption (Bello et al. 2021). 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

Comparing the experimental ($q_{e,exp}$) and the calculated ($q_{e,cal}$) adsorbed amount of MB per unit mass of adsorbent at equilibrium and the coefficients of determination (R^2) during the application of all kinetic models in the experimental data, it is concluded that the MB adsorption data on all carbonized materials follow the pseudo-second order kinetic model (Table 1), indicating that chemical adsorption is the prevailing mechanism. This can also be confirmed by other studies, in which it was found that ACs prepared using olive stones followed the pseudo-second order kinetic model for the adsorption of MB from aqueous solutions (Hazza et al., 2015).

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

	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	1.000
D2	2.982	1.561	3.222	0.997
D3	2.772	0.174	2.776	1.000
OS-M	2.957	0.703	2.992	1.000
CZ	2.536	0.085	2.543	0.999

FTIR analysis

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).

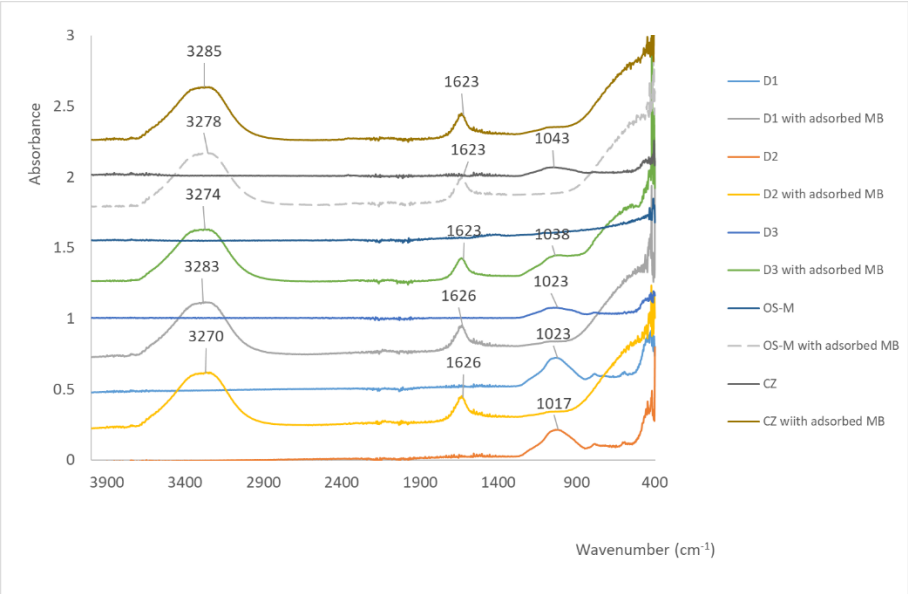

Fig. 3 FTIR spectra for carbonized biomass before and after methylene blue adsorption.

CONCLUSIONS

- 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.
- 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
- 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
- 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.

Acknowledgments

Support for this study was provided by the research program AGRICA II: AGrifood Research and Innovation Network of Excellence of the Aegean, ESPA 2014-2020, in the context of the call of the Operational Program "Competitiveness, Entrepreneurship and Innovation", Action "Support of Regional Excellence"

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