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REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS WITH NATURAL OLIVE POMACE MODIFIED WITH ULTRASOUNDS AND ACID

Removal of methylene blue (MB) from aqueous solution by raw olive pomace (ROP) which is a waste of industrial olive oil and olive pomace modified with ultrasounds and acid (MOP) has been investigated. It was found that the data for ROP and MOP were well fit to the Freundlich isotherm model (R^2 equal to 0.864 and 0.834, respectively). As a result; it was determined that raw olive pomace can be used for the removal of methylene blue dye (K_F = 10.08 mg/g(dm^3/mg)$^{1/n}$) and modified olive pomace had high adsorption capacity for MB (K_F = 73.08 mg/g(dm^3/mg)$^{1/n}$).

1. INTRODUCTION

Many dyestuff are commonly used in industrial fields such as textile, paper, leather, plastic, food, dye factories, etc. Since dyed wastewater sourced from these sectors has a toxic nature, it is risky in terms of human and environmental health. Moreover, this kind of coloured wastewater also causes aesthetic problems in the fields where it is discharged [1]. It not only breaks the natural aesthetic of the environment but also has poisonous effect for aquatic life. It reduces transparency of water, changes photosynthetic activity, affects aquatic life and food chain and might have carcinogenic and mutagenic effects. Recently, treatment techniques such as coagulation, Fenton process, electro-Fenton process, chemical or electrochemical precipitation, biological treatment processes, ozonation, adsorption [1, 2], etc. are involved in order to decrease the detrimental effects of these dyestuff. Among these methods, the Fenton process, electro-Fenton process, chemical and electrochemical precipitation produce chemical sludge containing toxic and heavy metal compounds. Disposal of this sludge seriously in-

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creases the cost of treatment. Ozonation is a process which requires high cost and qualified employee. Moreover, since ozone is not selective, it will be in a tendency to react with all pollutants in wastewater. This will increase the ozone need for adequate treatment efficiency and result in increase in the cost of treatment. Generally too little decolorization can be performed by biological processes [3]. Among current technologies, the most suitable technology for the removal of dyes and other pollutants from wastewater is adsorption [4]. The most important preference of adsorption process contrary to these mentioned methods is that it is a cheap and effective treatment method by using natural adsorbent materials [5]. As well as the fact that adsorption is an effective treatment method for the removal of pollutants from water, if the adsorbents used are environmentally friendly, cheap and easily available, then the economical aspect of adsorption is also revealed [6].

Recently, wastewater treatment with ultrasounds has become an attractive treatment technique [7] and an increase is observed in applications where ultrasounds are used. Especially the effect of ultrasound modification on the capacity of adsorption has been searched recently. The studies indicated that ultrasound modification increased the adsorption capacity [8]. Ultrasonication has an accelerating effect in chemical process due to acoustic cavitation. For ultrasonic frequencies lower than 100 kHz, ultrasonic radiation creates very strong hydromechanics shear forces. These forces increase and develop pores on the surface of the adsorbent material and expand the surface for adsorption. Thus they increase the adsorption capacity of the material [9].

Methylene blue was chosen as a target contaminant to characterize the adsorptive properties of olive pomace as it is a common cationic dye used in the medical, factories, textile and printing industries. In this study, raw olive pomace, which is cheap, abundantly available and does not include toxic materials, is used as an alternative treatment material after modification with ultrasounds and acid for the removal of methylene blue from aqueous solution. Pomace which is a waste material of olive oil industry can be used as an adsorbent for the removal of pollutants from aqueous solutions [10]. These materials might enhance the efficiency of adsorption after modification. In Mediterranean countries such as Greece, Italy, Lebanon, Portugal, Spain, Syria, Tunisia and Turkey, where olive oil industry is present [11], the usability of pomace which develops as an abundantly available industrial waste was searched with this new modification method.

2. MATERIALS AND METHODS

Materials. Solid waste (raw pomace) constituting of oil seed and pulp remaining from olive oil production was used as an adsorbent. Raw olive pomace samples were collected from olive oil production plants in Turkey as pressed and sunny dried disks. Experimental studies were performed by using raw olive pomace (ROP) and modified olive pomace (MOP). The main characteristics of ROP are given in Table 1. The scanning electron microscope (SEM) images of ROP and MOP are shown in Figs. 1a, b, respectively.

Table 1

Main characteristics of raw olive pomace

Parameter	Range	Parameter	Range
Moisture, %	52.3–71.6	Water soluble carbohydrates, g·kg^{-1}	12.0–158.0
pH, water	4.45–6.34	Water soluble phenols, g·kg^{-1}	6.0–22.7
Electrical conductivity, dS·m^{-1}	0.83–4.55	Phosphorus, g·kg^{-1}	0.8–2.0
Organic matter, g·kg^{-1}	837.6–968.2	Potassium, g·kg^{-1}	7.5–28.9
Lignin, g·kg^{-1}	320.0–554.3	Calcium, g·kg^{-1}	1.5–9.0
Cellulose, g·kg^{-1}	139.3–247.0	Magnesium, g·kg^{-1}	0.8–3.7
Hemicellulose, g·kg^{-1}	271.3–412.7	Sodium, g·kg^{-1}	0.6–1.4
Total organic carbon, g·kg^{-1}	492.5–538.0	İron, g·kg^{-1}	80–1445
Total nitrogen, g·kg^{-1}	6.8–17.9	Copper, g·kg^{-1}	11–27
C/N ratio	27.5–71.8	Manganese, g·kg^{-1}	6–35
Total oil, g·kg^{-1}	76.4–192.8	Zinc, g·kg^{-1}	12–35

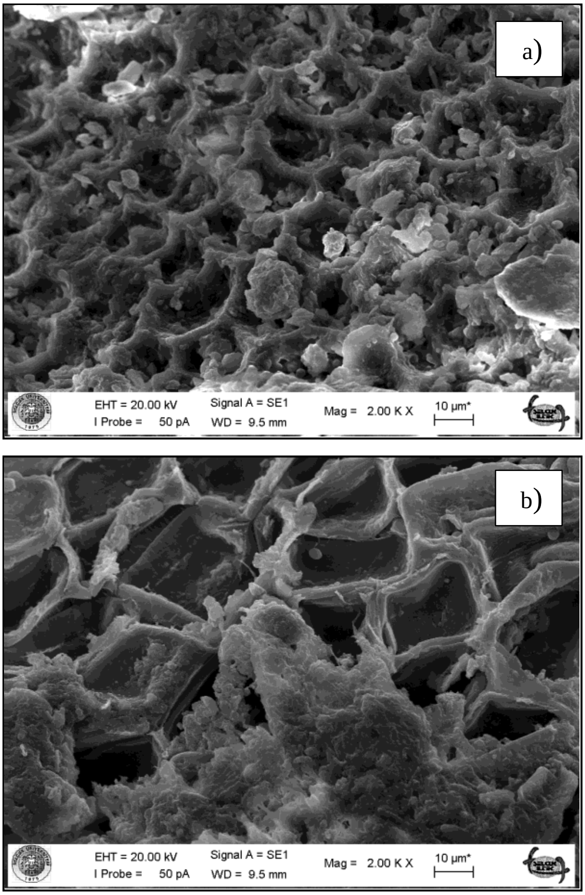

Fig. 1. SEM images of: a) ROP, b) MOP

The basic dye MB (basic blue 9, C.I. 52015, chemical formula, $C_{16}H_{18}C_lN_3S\cdot 3H_2O$, 373.90 g·mol^{-1}) was used as such without further purification to prepare the aqueous solution. It has a maximum visible absorbance at 662 nm. The chemical structure of MB (obtained from Carlo Erba) is shown in Fig. 2 [12].

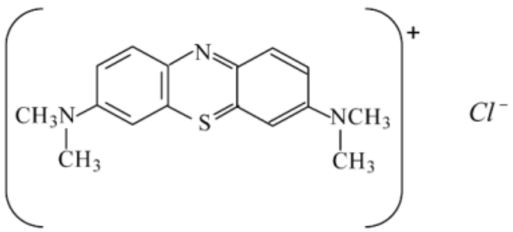

Fig. 2. Chemical structure of MB [12]

Experimental methods via ultrasound modification. Ultrasonic acid modification of raw olive pomace was performed by subjecting 200 mg/dm^3 of screened pomace to ultrasound in 500 cm^3 of 3 M H_2SO_4 solution for 2 h in ultrasonic water bath at 35 kHz frequency. In order to prevent settlement of pomace in the solution, it was mixed with a mechanical stirrer (Heidoplh Germany) for 2 h at low-speed. At the end of this period, the mixture was filtered, the material was washed with ultrapure water and then dried in a drying-oven (105 °C during 1 day). Since particle size of the material is important, it was screened through the same sieves with similar screen openings (0.25–0.4 mm) and made ready for use. For this modification, Kudos SK 1200 H ultrasonic water bath was used.

Adsorption. Methylene blue solutions were as prepared with ultra-distilled water (MP Minipure Destup). 1 g of accurately weighed of methylene blue was dissolved in ultra-distilled water to prepare the stock solution (1000 mg/dm^3). Experimental solutions of the desired concentration were obtained by successive dilutions. All chemicals used in this study were of analytical-laboratory grade, being purchased from Merck. In the dosage-time experiments, 200, 400, 600, and 800 mg/dm^3 of ROP and MOP were shaken with 250 cm^3 of MB solution (100 mg/dm^3) at desired pH and temperature at a fixed mixing speed of 250 rpm for 0–300 min. pH of the solution was adjusted to 6 with 0.1 M HCl or 0.1 M NaOH by using a Hach Lange HQ 30D pH-meter with a combined pH electrode. Adsorption was carried out in a batch system at 30 °C in the dosage-time experiments.

Pomace samples were screened through sieves between 0.25 and 0.4 mm, washed with distilled water and then used after drying at 105 °C in a drying oven (JSR JSOF-050). The experiments were performed using 250 cm^3 glass flasks with cooling and shaking incubator (JSR JSSI-300 C). After mixing processes, 0.45 μm membrane filters (Millipore

Corp., Bedford, Mass.) were used to separate the sample from the adsorbent. For measurements, a Thermo Scientific Aqua Mate Plus UV-VIS model spectrophotometer was used.

The adsorbed amount of MB at equilibrium, q_e (mg/g) was calculated by the following equation:

$$q_e = \frac{V\left(C_0 - C_e\right)}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium MB concentrations (mg/dm^3), respectively, V is the volume of solution (dm^3) and W is the dry weight of the added raw olive pomace (g) [13].

The Langmuir isotherm presupposes monolayer adsorption onto a surface containing a finite number of adsorption sites via uniform strategies of adsorption with no transmigration of the adsorbate taking place along the plane of the surface. The linear form of the Langmuir isotherm model represents the following equation [14]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{2}$$

where Q_0 (mg/g) and b (dm^3/mg) are the Langmuir constants relating to adsorption capacity and rate of adsorption, respectively, q_e is the amount of MB adsorbed at equilibrium (mg/g) and C_e is the liquid-phase equilibrium concentration (mg/dm^3) [14].

The Freundlich adsorption isotherm is expressed by the following equations obtained on the assumption that multilayer adsorption takes place on a heterogeneous adsorbent surface [15]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where q_e is the solid phase equilibrium concentration (mg/g), C_e is the liquid-phase equilibrium concentration (mg/dm^3), K_F and n are Freundlich constants with n giving an indication of the facility with which the adsorption process takes place. K_F (mg/g(dm^3/mg)$^{1/n}$) is the adsorption capacity of the adsorbent (i.e. the adsorption or distribution coefficient) and represents the quantity of dye adsorbed onto the olive pomace per unit of equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, $1/n$ closer to zero, the more heterogeneous surface is. $1/n < 1$ indicates a normal Langmuir isotherm, while $1/n > 1$ is indicative of cooperative adsorption [16].

3. RESULTS AND DISCUSSION

3.1. EFFECT OF CONTACT TIME AND ADSORBENT DOSAGES

The removal of MB with ROP and MOP was studied at various adsorbent dosages (200–800 mg/dm^3) of dye solution at a constant concentration (100 mg/dm^3), stirring speed (250 rpm), pH (6) and contact time up to 300 min.

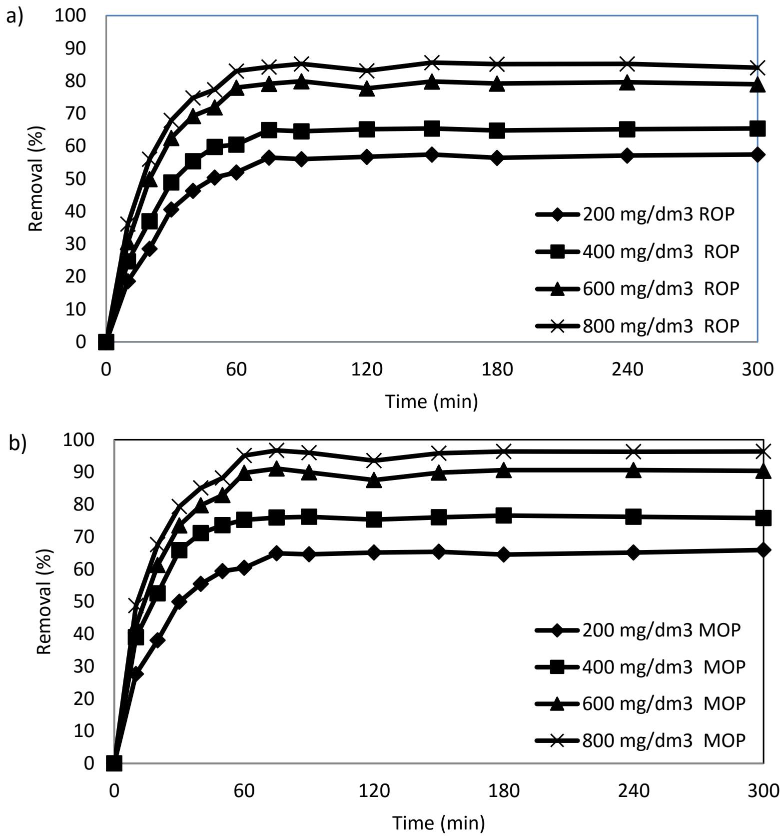

Fig. 3. Effect of time and dosage on the removal of MB (100 mg/dm^3, pH = 6) by using of a) ROP, b) MOP

The effect of time and dosage of ROP on the removal of MB from aqueous solution is shown in Fig. 3a. An increase in the efficiency upon time was observed and the adsorption equilibrium was obtained after 75 min. The equilibrium removal efficiencies at the ROP dosages of 200, 400, 600, and 800 mg/dm^3 were 56.5, 64.9, 79.1, 84.3, respectively. ROP was effective for the removal of MB and increase in the ROP dosage also increased available bonding sites on the surface of pomace and dye removal efficiency was increased due to binding of ions to more sites. These results correspond with those by Banat et al. [17].

A combination of olive pomace after solvent extraction and charcoal produced from the solid waste of olive oil press industry was used as an adsorbent for the removal of MB from aqueous solutions. Batch tests showed that up to 80% of dye was removed when the dye concentration was 10 mg/cm^3 and the sorbent concentration was 45 mg/cm^3. An increase in the olive pomace concentration resulted in better dye removal [17]. As can be seen in Fig. 3b, MOP was more effective for the removal of MB and increase in the amount of MOP also increased the removal efficiency. In the removal experiments carried out by using MOP in dosages of 200, 400, 600, and 800 mg/dm^3, the equilibrium removal efficiencies determined after 75 min of experiment were 64.9, 75.9, 91.1, 96.7, respectively. Ultrasonic acid modification increased the removal efficiency by using MOP as a result of opening sites on the surface of the adsorbent for the adsorption. Ultrasonic radiation generates very strong hydromechanical shear forces in the liquid medium at the frequencies of 20 kHz. These forces extend the adsorption surface by increasing the pores on the surface of the adsorbent material. Thus, the adsorption capacity of the material is enhanced via ultrasonication [8, 9].

3.2. EFFECT OF TEMPERATURE

Upon increasing temperature the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles increases, as a result of the reduced viscosity of the solution. In addition, the equilibrium capacity of the adsorbent for a particular adsorbate is also temperature dependent [18]. Temperature dependences of the removal efficiency of MB using ROP and MOP are shown in in Fig. 4.

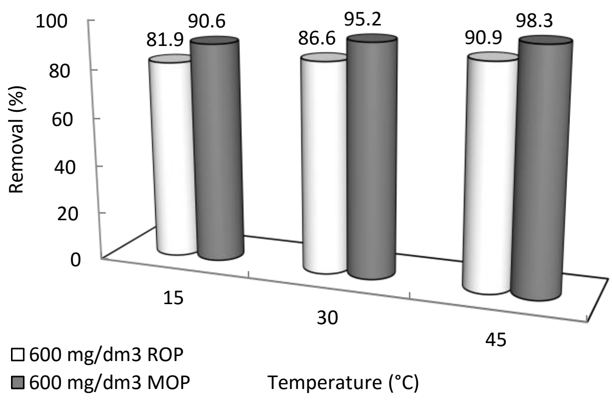

Fig. 4. Effect of temperature on the removal of MB (100 mg/dm^3, pH = 6) by using ROP and MOP

In a study carried out using graphite powder for the removal of MB, it was found that an increase in temperature resulted in an increase in the adsorption efficiency [19]. In the experiments carried out with ROP, increase in temperature only slightly increased the removal efficiency. This might be due to an increase in the chemical potential of dye molecules penetrating the surface of the pomace. The removal efficiencies for ROP were: 81.9% at 15 °C, 86.6%, at 30 °C, and 90.9% at 45 °C. The removal efficiencies for MOP were 90.6% at 15 °C, 95.2% at 30 °C, and 98.3% at 45 °C. Due to weak temperature effect, the temperature of 30 °C was found optimum for further experiments.

3.3. EFFECT OF pH

The studies indicated that pH has a significant effect on the adsorption capacity [19]. The adsorption efficiencies determined at various pH are shown in Fig. 5. In the experiments carried out with ROP, the removal efficiencies were: 65.5% for pH 3, 79.1% for pH 6, 86.6% for pH 9 and 89.9% for pH 12. The removal efficiencies for MOP were: 72.7% for pH 3, 91.1% for pH 6, 95.2% pH 9 as, and 99.3% for pH 12. In a similar study, it was found that increase in pH increased negative charge at the surface and therefore an increase was observed in the adsorption capacity [19]. Increase in pH resulted in negative charging of the pomace surface with OH^- ions and removal efficiency of cationic MB was enhanced.

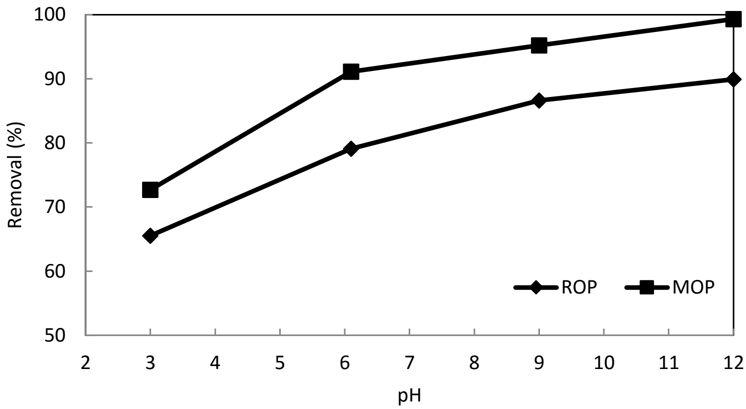

Fig. 5. Effect of pH on the removal efficiency of MB by using ROP and MOP (adsorbent dosage = 600 mg/dm^3, 30 °C, 250 rpm)

3.4. EFFECT OF STIRRING SPEED

The dependence of removal efficiency on the stirring speed was examined at 30 °C for 75 min, with ROP and MOP dosage of 600 mg/dm^3, the dye concentration of 100 mg/dm^3 at 200 , 250 and 300 rpm. The results are shown in in Fig. 6.

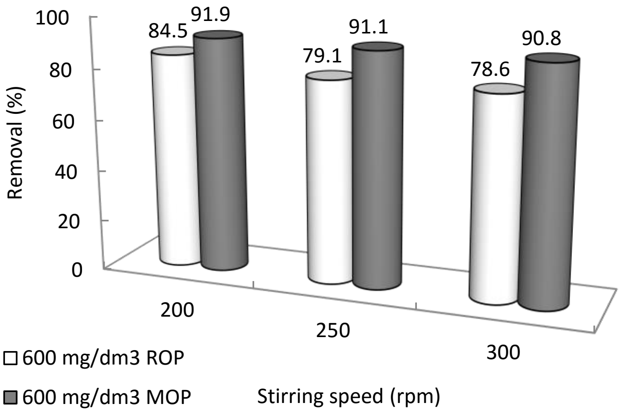

Fig. 6. Effect of stirring speed on the removal of MB by using ROP and MOP (pH = 6, MB concentration = 100 mg/dm^3)

In the experiments, a significant increase of the removal efficiency upon increasing stirring speed has not been observed. For the removal of MB, the removal efficiencies by using 600 mg/dm^3 of ROP at 200, 250, and 300 rpm were 84.5, 79.1, 78.6%, respectively. Under the same experimental conditions for MOP, they were 91.9, 91.1, 90.8%, respectively. About 15% increase in dye removal was observed for the experiments carried out with MOP at 250 rpm stirring speed when compared to ROP. Increase in stirring speed increased the contact of adsorbent with MB dye molecule by decreasing the density of diffusion layer around the adsorbent surface and resulted in an increase in the removal efficiency [20]. In the study of Garg et al. [21] performed for the removal of MB dye by using Indian Rosewood sawdust, similar results were reported for cationic dyes.

3.5. ADSORPTION ISOTHERMS

The adsorption isotherm basically reflects the interaction between solutes and adsorbents until the point where a state of equilibrium is reached. Various isotherm models, fitted to the isotherm data, have been reported in the literature [22] to optimize the effectiveness of adsorbents. In this study, fitting of experimental equilibrium data for MB removal by using ROP and MOP to Langmuir and Freundlich isotherm models was examined. In order to evaluate the ability of the models to describe the adsorption process, the correlation coefficients (R^2) were calculated. Freundlich isotherms for the removal of MB by using ROP and MOP are shown in Fig. 7, and Langmuir isotherms – in Fig. 8. The parameters and correlation coefficients of the Freundlich isotherm for MB adsorption on ROP and MOP are given in Table 2. The experimental data for MB removal by using ROP ($R^2 = 0.864$, $K_F = 10.08$ mg/g(dm^3/mg)$^{1/n}$) and MOP ($R^2 = 0.834$, $K_F = 73.08$ mg/g(dm^3/mg)$^{1/n}$) corresponded the Freundlich isotherm model. In other studies, it was found that MB adsorption by using palm kernel fiber [20] and neem leaf powder [23] better described the Freundlich isotherm model.

Table 2

Freundlich isotherm model parameters
and correlation coefficients
for the adsorption of MB on ROP and MOP

Parameter	ROP	MOP
$1/n$	0.8404	0.3635
K_F, mg/(g(dm^3/mg)$^{1/n}$)	10.08	73.08
R^2	0.8644	0.8344

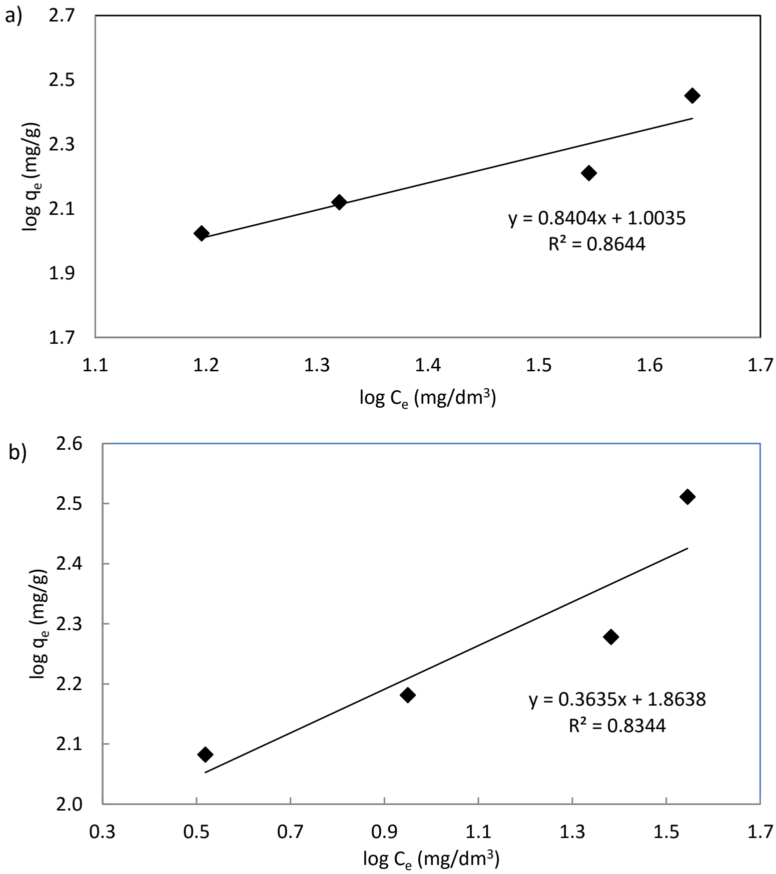

Fig. 7. Freundlich adsorption isotherms of methylene blue
on a) ROP, b) MOP (30 °C, pH = 6, 250 rpm)

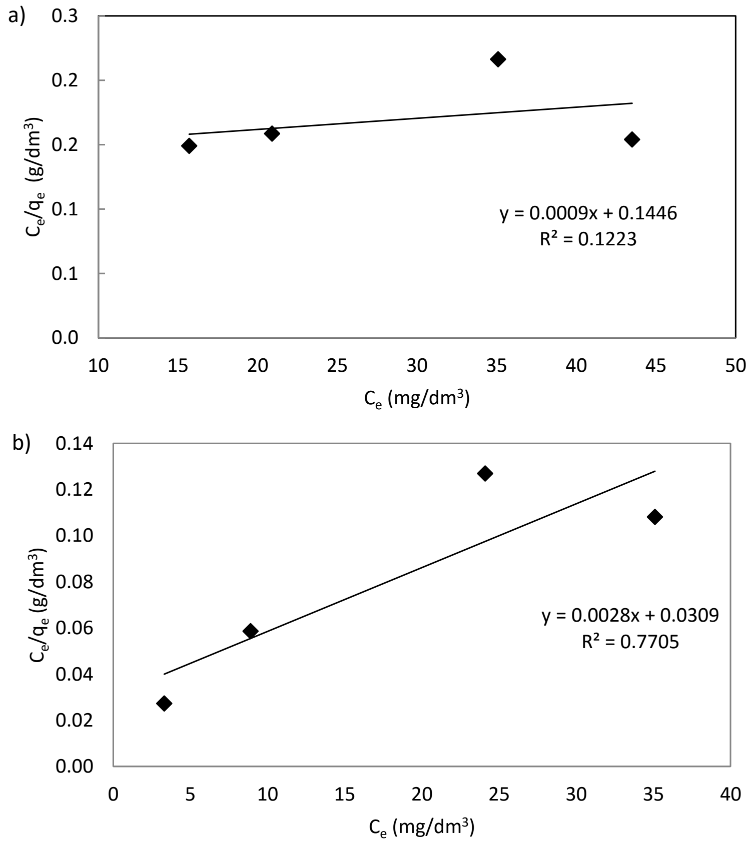

Fig. 8. Langmuir adsorption isotherms of MB on a) ROP, b) MOP
(30 °C, pH = 6, 250 rpm)

In the experiments performed using MOP, the adsorption capacity (K_F = 73.08 mg/g(dm^3/mg)$^{1/n}$) substantially increased when compared to the experiments carried out with ROP (K_F = 10.08 mg/g(dm^3/mg)$^{1/n}$). Similar results have also been reported by Oyelude and Owusu [24] for the adsorption of MB dye onto acid modified *Calotropis procera* leaf powder. Thus, it was found that modification of olive pomace with ultrasounds and acid was a significant alternative method for the modification of the adsorbent. The combination of ultrasound and the adsorption process seems to be a promising technology for the removal of macromolecules such as dyes [25].

4. CONCLUSIONS

For the removal of methylene blue from aqueous solution, the adsorption potential of olive pomace, the industrial waste of olive oil industry, was examined as its raw and modified form with ultrasonic radiation for various adsorbent dosages, contact time, solution pH, temperature, stirring speed and adsorption isotherms. The results are summarized as follows:

- Raw olive pomace can be used for the removal of MB dye and is also an effective adsorbent for the removal of cationic MB when it was used after modification. Ultrasonic and acid modification substantially increased the adsorption capacity of the olive pomace from K_F = 10.08 mg/g(dm^3/mg)$^{1/n}$ to 73.08 mg/g(dm^3/mg)$^{1/n}$.
- The adsorption of MB on ROP and MOP fits the Freundlich equilibrium isotherm.
- The adsorbent has some advantages since it is easily available, renewable, applicable in terms of region and has low cost.

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