Using Olive Stone as a Filtering Media for Industrial Wastewater

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ABSTRACT

Laboratory experiments were carried out to investigate the effect of alternate filtering media on the industrial wastewater treatment. Crushed olive stones were activated by carbonization at 773 K for two hours. The resulting activated carbon was used to remove basic blue dye (methylene blue). The influence of several factors governing the adsorption of methylene blue such as dosage, temperature, pH and contact time in addition to specific surface area of the prepared carbon have been investigated. The filter design chosen is based on three units; pH modification unit to reach industrial water between 5.5-6, a thermal unit to keep temperature at 313 K and filtering media with short residence time designed for mostly methylene blue removal. The effects of the inlet dye concentration, the flow rate, height of the column, and particles size on adsorption were studied. The results indicated that the highest dye removal of 87.8% was obtained under the following particle size of (0.5-1mm), flow rate of 4 $cm^3 min^{-1}$, fixed bed height of 4 cm, and MB concentrations of 8 mg L^{-1}. The highest bed capacity achieved of 5.56 mg g^{-1} at 20 mg L^{-1} was recorded MB, 4 mL min^{-1}, a bed height of 4 cm, and particle of 0.5-1 mm.

Keywords: Olive stone, activated carbon, wastewater, methylene blue, filter.

1. INTRODUCTION:

Dyes are important water pollutants which are generally present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries. They are synthetic aromatic compounds which are embodied with various functional groups. The worldwide high level of production and extensive use of dyes generates colored wastewaters which cause environmental pollution.

The release of dyes into wastewaters by various industries poses serious environmental problems due to various dyes' persistent and recalcitrant nature. Up to 50% of dyes may be lost directly into waterways when using reactive dyes [McMullan et al, 2001]. The coloration of the water by the dyes may have an inhibitory effect on photosynthesis affecting aquatic ecosystems. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria [Weber and Wolfe, 1987].

Several technologies of physical and chemical methods for the removal of dyes are available such as the use of Fenton's reagent, electro-chemical, adsorption, and membrane filtration. The adsorption by activated carbon is also well known and widely used. Activated carbon is often highly efficient particularly for low strength wastewater but it is relatively expensive.

Recently, the use of bio-sorbent for dye removal has been intensively investigated as an alternative, economical, and feasible method [Allen et al, 2003; Sulak et al , 2007; El Qada et al, 2006]. Examples of these bio-sorbent are bagasse pith for the adsorption of Basic Blue 69, Basic Red 22, Acid Red 114, and Acid Blue 25 [McKay et al, 1987]; banana pith for the adsorption of wastewater containing basic violet [Namasivayam and Kanchana, 1992]; palm-fruit bunch for the adsorption of Basic Yellow, Basic Red, and Basic Blue [Nassar and Magdy, 1997]; wheat straw, corncobs and barley husks for the adsorption of Cibacron Yellow C-2R, Cibacron Red C-2G, Cibacron Blue C-R, Remazol Black B, and Remazol Red RB [Robinson et al, 2002]; duckweed for the adsorption of Methylene Blue [Waranusantigul et al, 2003]; date pits for the adsorption of Methylene Blue [Banat et al, 2003] , slag (blast furnace waste), and wheal husk [Gupta et al, 2007].

The main objective of this work is using olive stone as a filtering media from industrial of activated carbon as an adsorbent (biosorption) for the removal of methylene blue from an aqueous solution.

2. MATERIALS AND METHODS:

2.1 Synthesis of activated carbon:

Local olive's stones, a by-product of food processing, were purified to remove the undesired contaminant prior to use them as adsorbents. The stones were washed, crushed and finally ground in a laboratory mill to a size of 0.5-3.0 mm followed by soxhlet extraction using ethanol solvent for 24 hours for an exhaustive extraction of oily substances from stones. After extraction, the solid matter was dried in an air oven and carbonized at 773 K for two hours.

2.2 Dye solution preparation:

Stock solutions of methylene blue (MB), (BDH, 82%), were prepared by dissolving accurately weighed dye in deionized water at a concentration of 1000 mg L^{-1} and they were diluted when necessary.

2.3 Characterization of activated carbon:

The surface area of activated carbon:

The surface area (m^2 g^{-1}), apparent particle density (ρ_p) and porosity (ε_p) of the prepared activated carbon have been calculated using the following equations;

$$S = \frac{q_{max} . 10^{-3} . N . A. 10^{-20}}{M} \qquad (1)$$

$$\rho_p = m/v \qquad (2)$$

$$\varepsilon_p = 1- \rho_p/ \rho_s \qquad (3)$$

Where:

S = the surface area (m^2 g^{-1})
q_{max} = the maximum adsorption capacity of MB (312.5 mg g^{-1})
A = the cross-section area of one molecule of MB (130 Å2)
N = Avogadro's number (6.023x1023 mol^{-1})
M = the molecular weight of MB (319.5 g mol^{-1})
m = mass of carbon (g),
v = volume of carbon (cm^3), and
ρ_s = the solid density (g cm^{-3})

2.4 Batch Sorption Study:

Batch sorption experiments were performed by using the following parameters e.g. contact time, dosage of carbon, pH, temperature and dye concentration. Batch adsorption experiments were carried out using bottle-point method [El-Geundi, 1990] in which different concentration taken in various flasks (100 ml) placed in a shaking thermostat (120 rpm). At the end of predetermined intervals, the adsorbent was collected by centrifugation and the progress of adsorption was determined spectrophotometrically using DU800 Uv/Vis. Spectrophotometer at λ_{max} = 664 nm. The solutions involved were diluted to proper concentrations, to give absorbencies in the range of

0.1-1, before making the measurements. The different parameters studied are:

Contact time:

The contact time for MB Activated carbon system was determined by adding 0.1 g of carbon in 100 ml of dye solution (400 mg L^{-1}) for different time intervals. The absorbance was measured at different time intervals. The amount of adsorption at time t, q_t (mg g^{-1}), was calculated by:

$$q_t = \frac{V\,(C_i - C_t)}{1000\ m} \qquad (4)$$

Where:

C_i = the initial dye concentration (mg L^{-1}),
C_t = the dye concentration at time t (mg L^{-1}),
V = the volume of solution (mL), and
m = the mass of carbon used (g).

Dye concentration:

0.1 g of carbon added to different concentration of dye solution with continuous stirring for four hours. After time finishing, the absorbance of dye solution was measured. The adsorption capacity of the carbon, q_e (mg g^{-1}) was determined from the concentration difference of the solution, at the beginning and at equilibrium:

$$q_e = \frac{V\,(C_i - C_e)}{1000\ m} \qquad (5)$$

Where C_e = the equilibrium dye concentrations (mg L^{-1}).

pH:

Solutions of different pH's solutions were prepared by using of 0.1 M HCl and 0.1 M NaOH 100 ml of dye solution was added using 0.1 g of carbon and then shacked for four hours, followed by measuring the absorbance.

Temperature:

Three different temperatures of (293, 303 and 313 K) were selected to study the effect of temperature on the adsorption process.

Dosage:

Different doses from activated carbon were taken to calculate the total removal (%) of MB from aqueous solution.

2.5 Filter installation:

A pilot-scale unit was set up at laboratory as shown in Figure 1. It consists of glass column (20 cm long, with an inner diameter of 1.9 cm) was packed with two bed heights (2 and 4 cm) of filter media and was loaded with effluent, which was dye methylene blue solution prepared in the laboratory. Gravel was fitted at the outlet of the column in order to support medium and prevent the loss of the adsorbent particles. Also a pH unit was involved to dose the right amount of NaOH and HCl which keep on the solution between 5.5-6 pH. In addition to thermal unit which increases the effect of activation media by keep temperature at 40^{o}C, the filtration media followed by a pH unit same to the first one for same reason.

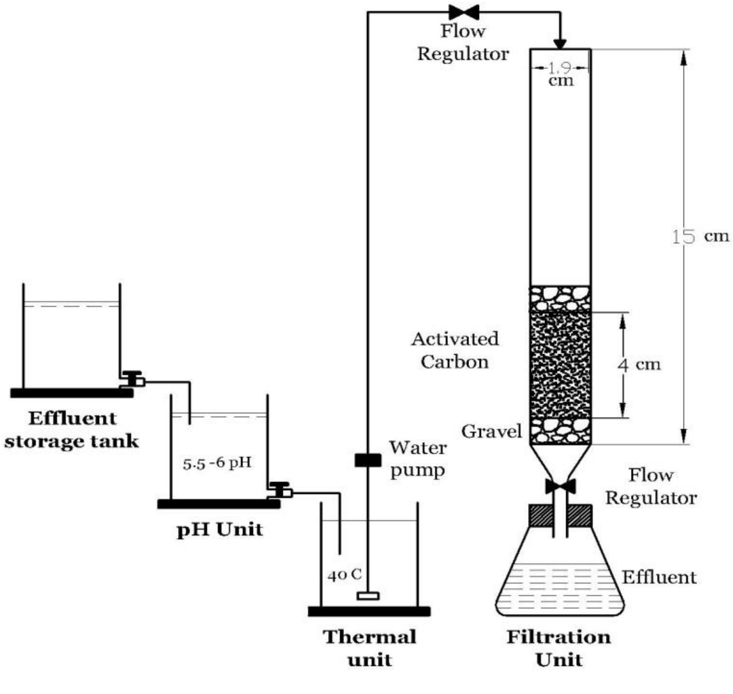


Figure (1): Filter installation

Experimental treatments:

Treatments and operational conditions are presented in table 1. Filter with an internal diameter of 1.9 cm was set up and loaded with different diameter ranges of activated carbon media (0.5-1 and 1-2 mm). Fixed-bed up-flow filter media was fed by a peristaltic pump at a constant flow rate, ranging from 5 to 30 mL min^{-1}. Each filtration run lasted 180 min.

Table (1): Experimental treatments for activated carbon filtration.

Treatments	Media size, mm	Bed height, cm	Dye concentration, mg L^{-1}	Flow rate, cm^3 min^{-1}
1	0.5 – 1	2	8	4
2	1 – 2	4	15	14
3	Mixed (0.5 – 2)	6	20	24

3. RESULTS AND DISCUSSION:

3.1 Batch adsorption study:

As shown in figure 2, the amount of dye adsorbed at various intervals of time indicates the removal of the dye initially increase with time, the adsorption process was found to be rapid initially but attain equilibrium within 45 min. However, all equilibrium experiments were allowed to run for 4 hours. Moreover, by increasing the initial concentration of MB (100, 400 and 800 mg L^{-1}) the amount of adsorbed MB also increase as shown in figure 2. The adsorption capacity of the solid phase is important for characterizing the usefulness of the adsorption process and for determining the usefulness and applicability of a mathematical model.

Figure 3 shows the effect of MB at different dosages from activated carbon on the removal percentage (R%) From the figure, it is cleared that the removal is increase the increase of the amount of activated carbon from was followed with an increase in the removal percentage and reach to 99.5% at 0.9 gm of adsorbent.

The effect of pH on adsorption process was studied at different pH values keeping other parameters constant. The result of variation on dye adsorption at pH values is shown in figure 4. It is noticed that the increase of pH from was accompanied with an increase in dye adsorption. This may be due to the number of positive charges on the adsorbent surface, which leads to the attraction of the negatively charged dye molecule and thereby, increasing the dye adsorption.

Temperature is one of the parameters with the greatest influence on the process. Three temperatures were used in this study (293, 303 and 313 K) keeping the other parameters constant. The values for q_t have been plotted against the contact time, t, for the three temperatures tested in figure 5. The sorption process can be seen to occur very rapidly at all temperatures as the maximum sorption capacity is reached practically within the first 45 min, as had been shown in the study on the influence of contact time. Also a slight influence of temperature is also seen. The higher removal due to increase temperature may be attributed to chemical reaction taking place between the functional groups of the adsorbate/adsorbent and the dye.

Figure (2): The relationship between removal ratio and time of removal under different concentration of MB.

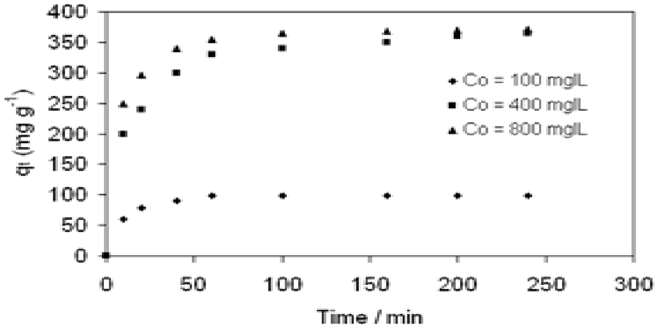


Figure (3): The relationship between removal ratio and amount of activation olive stone.

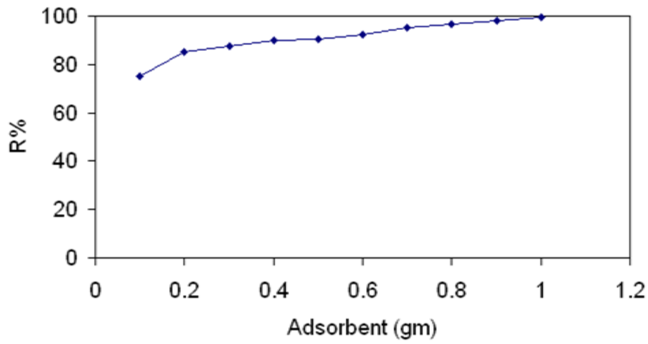


Figure (4): The relationship between removal ratio and pH.

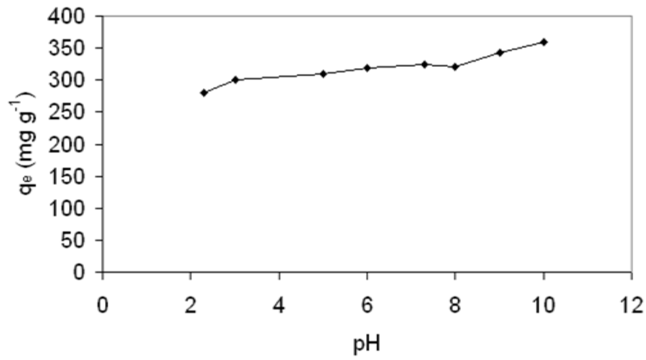
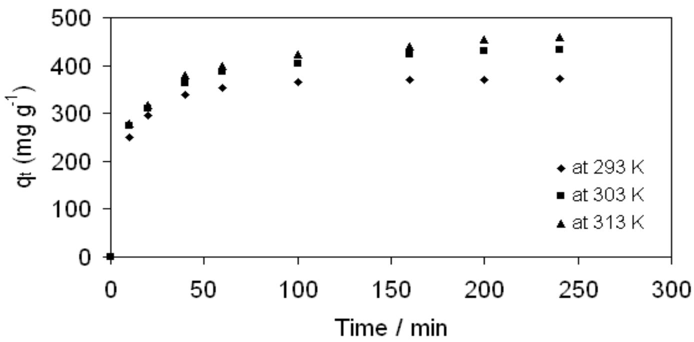


Figure (5): The relationship between removal ratio under different temperatures.



The specific surface areas of activated carbon prepared from olive stones calculated from equation (1) is 766 m^2 g^{-1}.

3.2 Fixed bed adsorption:

Effect of some parameters on adsorption process:

Dye concentration:

The effect of the three initial MB concentrations (8, 15, and 20 mg L^{-1}) on the adsorption process under different few per of uses and constant flow rate of 4 cm^3 min^{-1}, fixed bed height of 4 cm and particle size of (0.5-1mm) is shown in figure 6(a). It can be deduced that, at a lower inlet concentrations, a slower breakthrough curve and the highest treated volume will be obtained. The breakthrough point (C_t/C_o = 0.05) for the 8, 15, and 20 mgL^{-1} MB inlet concentrations occurred after 100, 90, and 80 min, respectively. The highest dye removal (85.4%) was recorded for the inlet MB concentration of 20 mg L^{-1}. The adsorption capacity of the bed also increased simultaneously with the increasing initial MB concentration. The highest bed capacity achieved was 5.56 mg g^{-1} (at 20 mg L^{-1} MB, 4 mL min^{-1}, a bed height of 4 cm, and particle of 0.5 -1mm). This is may be due that as the inlet concentration of the feed increases, the loading rate of MB on the bed and the driving force to overcome the mass transfer resistance increases [Goel et al, 2005].

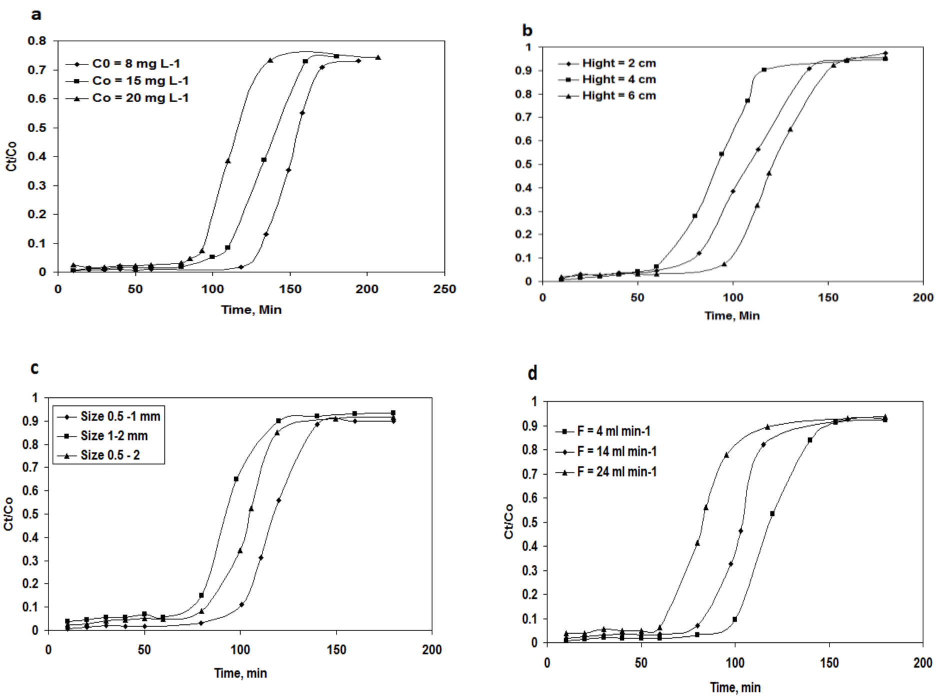
Column height:
The adsorption of MB in the packed bed column is largely dependent on the bed height, which is directly proportional to the quantity of activated carbon in the column. To produce 2, 4 and 6 cm of bed height, 1.75, 3.41, and 5.27 g of activated carbon were used, respectively. The adsorption breakthrough curves obtained by varying the bed heights at a flow rate of 4 cm^3 min^{-1}, an inlet MB concentration of 8 mgL^{-1} and particle size of (0.5-1 mm). The breakthrough curve is presented in figure 6(b). Which slows that faster breakthrough and slowest curves were observed for a bed heights of 2 cm. The bed capacity (q_e) increased from 1.8 to 5.5 mg g^{-1} when the bed height increased from 2 to 6 cm. Additionally, an increase in bed height resulted in more contact time being available for the MB to interact with the adsorbent [Han et al, 2009]. This phenomenon has allowed the MB molecules to diffuse deeper into the adsorbent. Subsequently, the percentage of dye removal increased when the bed height was increased.

Particles size:
The effect of the three particles size (0.5-1, 1-2, and 0.5-2 mm) on the adsorption process at a constant flow rate of 4 cm^3 min^{-1}, fixed bed height of 4 cm and MB concentrations of 8 mg L^{-1} is shown in Figure 6(c). The highest dye removal (87.8%) was recorded under the particle size of (0.5-1 mm). When the particles size increased from 0.5 to 2 mm, the bed capacity decreased from 5.5 to 1.4 mg g^{-1}.

Effect of flow:
The effect of flow rate on MB adsorption by activated carbon was investigated by varying the flow rate of the MB inlet solution from 4 to 24 mL min^{-1} while maintaining the initial MB concentration and bed

depth at 8 mg L^{-1}, 2 cm and particle size of (0.5-1 mm), respectively. A plot of the MB concentration versus time at various flow rates is shown in Figure 6 (d), which indicates that a faster and slowest breakthrough were achieved and higher flow rates of MB solution of the lowest flow rate of (4 mL min^{-1}) of MB solution respectively. The highest dye removal (86.4%) was recorded when the flow rate was 4 mL min^{-1}. When the inlet flow rate increased from 4 to 24 mL min^{-1}, the bed capacity decreased from 4.8 to 2.3 mg g^{-1}.

Figure (6): Breakthrough curve for activated carbon at (a) Different inlet concentration, (b) Different bed height, (c) Different flow rate (d) Different particles size.



4. CONCLUSIONS:

According to the results in this study, the activated carbon from olive's stone can be used as a new media to remove MB. Experimental data confirmed that the bed height, inlet MB concentration, particles size, and flow rate have a significant influence on MB adsorption by activated carbon. The main results of this study are:

1. Faster breakthrough curves were observed for a bed height of 2 cm, inlet concentration 20 mg L^{-1} MB, particle size of 0.5-1 mm, and flow rate of 4 mL min^{-1}, while the slowest breakthrough curve was observed at a bed height of 6 cm, inlet concentration 8 mg L^{-1} MB, particle size of 1-2 mm, and flow rate of 24 mL min^{-1}.
2. The highest dye removal (87.8%) was recorded when the particle size is (0.5-1 mm), flow rate of 4 cm^3 min^{-1}, fixed bed height of 4 cm, and MB concentrations of 8 mg L^{-1}.
3. The highest bed capacity achieved was 5.56 mg g^{-1} at 20 mg L^{-1} MB, 4 mL min^{-1}, a bed height of 4 cm, and particle of 0.5-1 mm.

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استخدام أنوية الزيتون كبيئة مرشحة لمياه الصرف الصناعي

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تهدف هذه الدراسة الى استخدام أنويه الزيتون (الكربون المنشط) كبيئة مرشحة جديدة لإزالة صبغة المثيلين من مياه الصرف الصناعي. لذلك تم اجراء تجربة عملية بتغير ارتفاع عمود المرشح (٢ – ٤ – ٦ سم) وتركيز صبغة المثيلين (٨ – ١٥ – ٢٠ ملليجرام/لتر) وحجم حبيبات بيئة الترشيح (٠.٥ – ١ مم) – (١ – ٢ مم) – (٠.٢ – ٢ مم) ومعدل التصرف (٤ – ١٤ – ٢٤ سم[٣]/دقيقة). واظهرت النتائج أن ارتفاع عمود المرشح وتركيز صبغة المثيلين وحجم حبيبات بيئة الترشيح ومعدل التصرف لهما تأثير معنوي على ادمصاص صبغة المثيلين بواسطة الكربون المنشط. وأظهرت النتائج الرئيسية لهذه الدراسة ان أسرع نسبة ادمصاص عند ارتفاع عمود المرشح ٢ سم وتركيز صبغة المثيلين ٢٠ ملليجرام/لتر وحجم حبيبات بيئة الترشيح (٠.٥ – ١ مم) ومعدل التصرف ٤ ملليلتر/دقيقة بينما كانت أبطأ نسبة ادمصاص عند ارتفاع عمود المرشح ٦ سم وتركيز صبغة المثيلين ٨ ملليجرام/لتر وحجم حبيبات بيئة الترشيح (١ – ٢ مم) ومعدل التصرف ٢٤ ملليلتر/دقيقة وكانت أكبر نسبة ازالة (٨٧.٨٪) عند ارتفاع عمود المرشح ٤ سم وتركيز صبغة المثيلين ٨ ملليجرام/لتر وحجم حبيبات بيئة الترشيح (٠.٥ – ١ مم) ومعدل التصرف ٤ ملليلتر/دقيقة وكذلك كانت أكبر كمية صبغة مزالة ٥.٥٦ ملليجرام/جرام عند ارتفاع عمود المرشح ٤ سم وتركيز صبغة المثيلين ٢٠ ملليجرام/لتر وحجم حبيبات بيئة الترشيح (٠.٥ – ١ مم) ومعدل التصرف ٤ ملليلتر/دقيقة.

الكلمات المفتاحية: نواة الزيتون، الكربون المنشط، مياه الصرف الصناعي، صبغة المثيلين، المرشح.