Water Decolourisation Using Olive Mill Waste As Activated Carbon

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الملخص

تعد ليبيا واحدة من أكبر الدول في إنتاج زيت الزيتون مما يؤدي إلى إنتاج كميات هائلة من مخلفات عصر الزيتون خلال عملية الاستخلاص كل عام. لذلك ، تهدف هذه الدراسة العملية إلى التحقق من إمكانية استخدام مخلفات عصر زيت الزيتون (الفاتوره) كمصدر طبيعي منخفض التكلفة لتحضير الكربون المنشط (AC). في هذه الدراسة تم تفحيم بقايا مطحنة زيت الزيتون الصلب عند 200 درجة مئوية وتنشيطها كيميائيًا باستخدام طريقتين تشمل النموذج الأول (25٪ $Zncl_2$) والنموذج الثاني (25٪ $Zncl_2$ + 25٪ H_2SO_2) . للتحقق من كفاءة الكربون المنشط المحضر ، تم إجراء إزالة لون صبغة Methylene Blue الموجودة في محلول مائي. تمت دراسة فعالية هذه العملية من خلال تأثيرات المعلمات الرئيسية مثل وقت التلامس ودرجة الحموضة وكمية الكربون المنشط المستخدم. أظهرت النتائج المتحصل عليها أن إزالة اللون باستخدام النموذج II كان أكثر كفاءة من النموذج الأول. القيم المثلى للأس الهيدروجيني ووقت التلامس وكمية AC كانت 5 و 120 دقيقة و 2.5 جم / لتر على التوالي. في هذه الظروف التشغيلية كان الحد الأقصى لإزالة الميثيلين الأزرق من الماء 75%. تشير النتائج إلى أن مخلفات عصر زيت الزيتون لديها إمكانية في تطبيقات معالجة المياه في المستقبل بسبب قدرتها العالية على الامتصاص.

ABSTRACT

Libya is one of the largest countries in the olive oil production leading to generate massive amounts of olive-waste cakes during the manufacture process every year. Therefore, this experimental study aims to investigate the potential of olive-waste cake as a low-cost natural source for preparation activated carbon (AC). The solid olive oil mill residue was carbonized at 200 ^{0}C and chemically activated using two methods including Model I (25% $Zncl_2$) and Model II (25% $Zncl_2$ + 25% H_2SO_2) . To investigate the efficiency of prepared AC, decolourization of methylene blue founded in an aqueous solution was conducted. The effectiveness of this process was studied via key parameters effects such as contact time, pH, and AC dose. The achieved results showed that the decolourization using Model II was more than of Model I. The optimum values of pH, contact time, and AC dose were 5, 120 min, and 2.5 g/L respectively. At these conditions the maximum methylene blue removal was 75%. The results indicate that olive-waste cake has a potential in future water treatment applications due to its high adsorption capacity.

Keywords: Olive mill waste, activated carbon, methylene blue

1. INTRODUCTION

Colour is the most clear indicator of water pollution. These coloured waters usually generate from textile, pulp, and paper industries. About ten thousand of different dyes and over $7x10^5$ tons are generated in the world every year (Pala et al., 2006). Dyes are adhered to the material structure via covalent bonds to give their colours (Bafana et al., 2011). The discharge of effluents containing dyes into water receiving bodies can be toxic to aquatic life (Kadirvelue et al., 2003). Furthermore, light penetration through water can be decreased via dyes , leading to the lack of oxygen in water. Coloured waters are also toxic to people and might cause several diseases such as skin irritation and eye burn (Ming et al., 2015). Among these dyes Methylene Blue is one of the most dye used in the industry. Figure 1 shows the molecular structure of methylene blue.

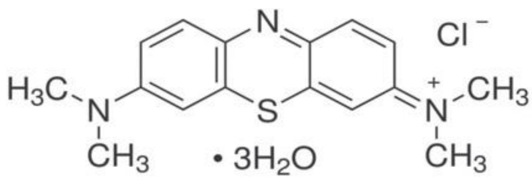

Figure 1 Molecular structure of methylene blue

The treatment of colored water is usually conducted by conventional ways such as adsorption (McKay, 1989) and biological oxidation (Paprowicz and Slodczyk, 1988).

Activated carbon adsorption can be effectively used to treat different kinds of water pollution which include dye removal (Hock et al., 2018), the removal of metallic micro pollutants, organic compounds, and pesticides (Njau at al., 2014). Activated carbon (AC) is the most promising method due to its safe use, cost-effective, and simple equipment design (Ioannidou, and Zabaniotou, 2007). However, the cost of using this technique mainly depends on the source of activated carbon used in this process. Therefore, the use of agriculture wastes have been a significant economical solution to this issue (Toscazo et al., 2005).

Various sources of natural materials have been widely used for the industrial production of activated carbon such as coal, coconut shell, and wood (Hettiarachchi et al., 2017, Musa et al., 2019). Moreover, other agriculture by-products were used including date stones (Girgis et al., 2002), rice husks (Chuah et al., 2005), peach stones (Ioannidou et al., 2007) and grain sorghum (Diao et al., 2002). Regarding olive-waste cakes as a source of activated carbon there has been a few studies that covered this topic (Sellami et al., 2008 and Baccar et al., 2009).

In fact, Libya is one of the largest countries in the olive oil production so there are massive amounts of olive-waste cakes generating during the manufacture process every year. In general, the olive oil production process generates about 20% of oil, 30% of waste solids, and 50% of wastewater (Chuah et al., 2005), According to (Baccar et al., 2009), the yearly average of olive-waste cakes production is about 200000 tons which can be varied from country to another. Beside the use of these large amounts to produce activated carbon for water treatment purposes it can also contributes to minimize the solid wastes in the environment.

The production of effective activated carbon depends on the nature of raw materials and the preparation method. This method includes physical and chemical procedures as well as key parameters (Suarez et al., 2002 and Vinke et al., 1999). Drying, grinding and carbonizing are the most important steps of the physical treatment process that control the porous size and surface area of AC. For chemical procedures different chemicals have been used as a dehydrating agents such as $Zncl_2$, ($Zncl_2$ + H_2SO_2), KOH, and H_3PO_4 (Thomas and George, 2015). The general activation procedures can be categorized as shown in Figure 2 (Sellami et al., 2008).

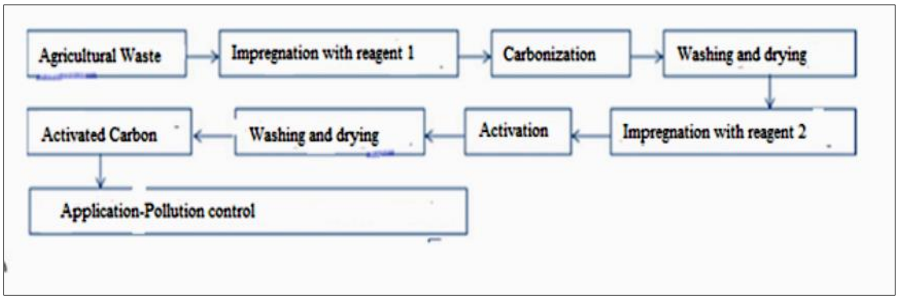

Figure 2 A general method of preparation of activated carbon from natural source.

Therefore, the present work aims to prepare activated carbon from Libyan olive-waste cakes as a natural source. Furthermore, it investigates key parameters affecting the efficiency of the production process. Finally, the use of the prepared activated carbon to remove methylene blue from water.

2. MATERIALS AND METHODS

2.1 Materials and Equipment

All chemicals used in these experiments were checked for expire dates. 30 ppm of methylene blue ($C_{16}H_{18}ClN_3S$), 25% of sulphuric acid (H_2SO_4), and 25% of zinc chloride ($ZnCl_2$) were prepared. Figure 3 shows equipment used in this work including JENWAY 6300 Spectrophotometer, magnetic stirrer CAT M17.5.

Figure 3 Spectrophotometer and magnetic stirrer

2.2 Preparation of activated carbon

Olive-waste cakes were collected from an olive oil mill located in Gharyan, Libya. This solid residue was used as a raw material for the production of activated carbon. The activation method can be defined as physical and chemical processes that enormously increase carbon surface area through removing hydrocarbons (Musa et al., 2019). The process of changing the olive-waste cake into coal is called carbonization while the chemical decomposition of by heating it without oxygen is called pyrolysis (Charcoal, 2014 and Tseng et al., 2008). First of all, 500 g of olive-waste cake was wished with distillated water and dried at 200 ^{0}C for 180 min. Then the carbonized sample was crushed till became homogeneous powder. After that the powder taken into a thermal frying pan and covered by aluminium foil. This pan was put in the furnace at 300 ^{0}C for 3hr in order to perform the pyrolysis step. The carbonization material was again crushed to get more smaller particles. For model I (25% of $ZnCl_2$) Chemical activation was performed using which mixed with the powder to make a paste. Then the mixture was taken into the furnace at 100 ^{0}C and 30 min for drying. Finally, the prepared activated carbon was washed using distillated water and filtered to get the final form of the activated carbon. Figure 4 shows the raw material of olive-waste cake and prepared carbon.

(a) (b)

Figure 4 (a) Olive-waste cake (raw material), (b) Prepared AC

All above procedures were repeated for model II (25% of $ZnCl_2$ and 25% H_2SO_4). Both models were leaven to naturally dry for three days at the room temperature.

2.3 Calibration curve of methylene blue

Stock solution of methylene blue (1000 ppm) in distilled water was prepared and stirred for 15 min for more homogeneous. Then, different concentrations (5 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm, and 35 ppm) of methylene blue were prepared by diluting the stock solution. The absorbance of these concentrations were measured at λ_{max}=664 nm using UV/vis spectrophotometer (JENWAY 6300) to get the absorbance equation for various concentrations. Figure 4 shows the relation between absorbance and concentrations.

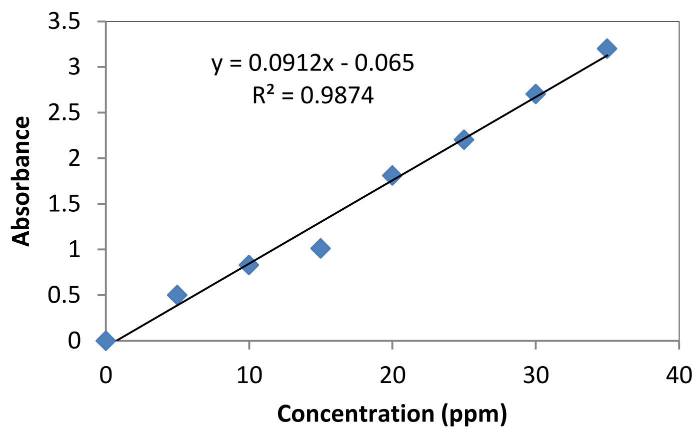

Figure 4 Calibration curve of methylene blue

2.4 Use of activated carbon (AC)

Two models of activated carbon (AC) were used to removal methylene blue from an aqueous solution at pH 7. Two grams of AC (Model I) was added to 1L of 30 ppm methylene sample and continuously stirred for 5 min before taking first sample for degradation reading. Then five samples were taken at 15 min, 45 min, 90 min, 120 min, and 150 min respectively. To study the effect of pH and the initial concentration of AC the above steps were repeated for various values. Furthermore, the same procedures were implemented for AC (Model II).

3. RESULTS AND DISCUSSION

3.1 Comparison between Model I and Model II

The efficiency of methylene blue decolourization for each condition at fixed time interval was determined. The removal percentage of the colour from wastewater was calculated using the following equation:

$$\text{Decolourization (\%)} = [(C_0 - C_e)/C_0] \times 100 \qquad (1)$$

Where, C_o and C_e are the dye concentration at initial stage and equilibrium stage respectively (ppm).

To investigate the influence of acid addition on the preparation method of AC, two models were used at the same conditions (2 g AC, pH 7, 150 min) to Decolourization of 30 ppm methylene blue. Figure 5 shows the obtained experimental results of this comparison.

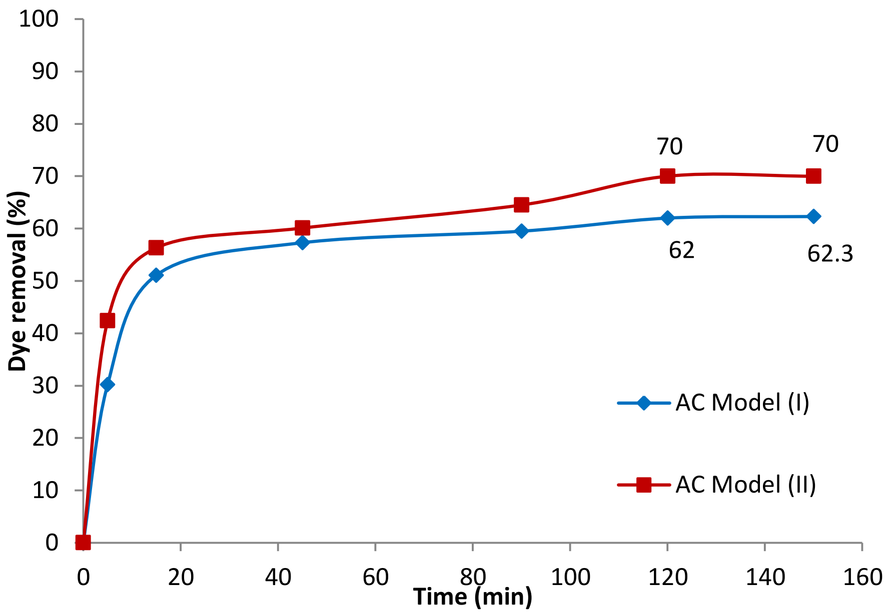

Figure 5 Comparison between AC models I & II (pH 7, 2 g/L AC, 30 ppm MB)

It can be seen that the activated carbon treated with sulfuric acid was more effective than zinc chloride alone. This result might be due to lower the total ash content of the carbon and more dry of water content. Acid washed activated carbon is desirable for treating drinking water and food grade applications (Bedia et al., 2020). Furthermore, the maximum decolourization for both models was at 120 min of contact time.

3.2 Effect of AC dose

The influence of the initial concentration of activated carbon on the dye removal was investigated. In this part the model II was used to study this effect due to its higher efficiency comparison to model I. Different initial AC doses was used at following conditions involving 30 ppm of methylene blue, free pH, and 150 min contact time. Figure 6 shows the obtained results and can be clearly seen the removal efficiency increases with increasing AC concentrations and the maximum value was at 2.5 g/L then the decolourization percentage started decreasing which might be due to unsaturated active centers.

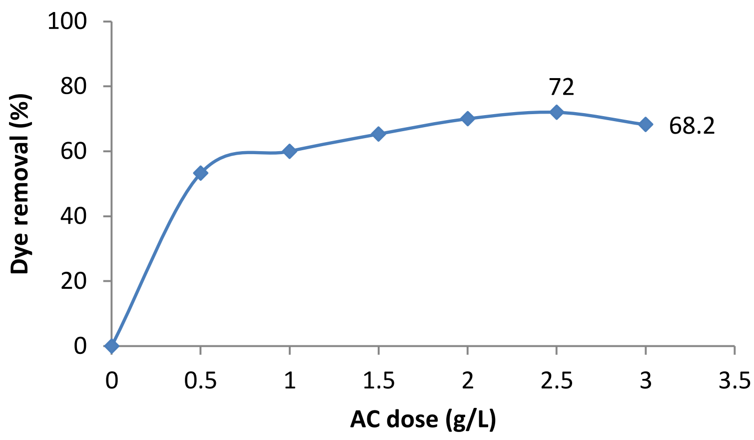

Figure 6 Effect of AC dose on methylene blue adsorption (Model II, 30 ppm MB, and 150 min)

3.2 Effect of pH

pH is a key parameter playing important role in adsorption processes. Influence of pH on the removal of methylene blue from the synthetic wastewater was investigated. The adsorption of the dye onto the surface of activated carbon is mainly affected by the surface charge in other world the value of pH. Figure 7 shows the achieved results of the pH effect on the dye adsorption onto AC (Model II) from aqueous solution.

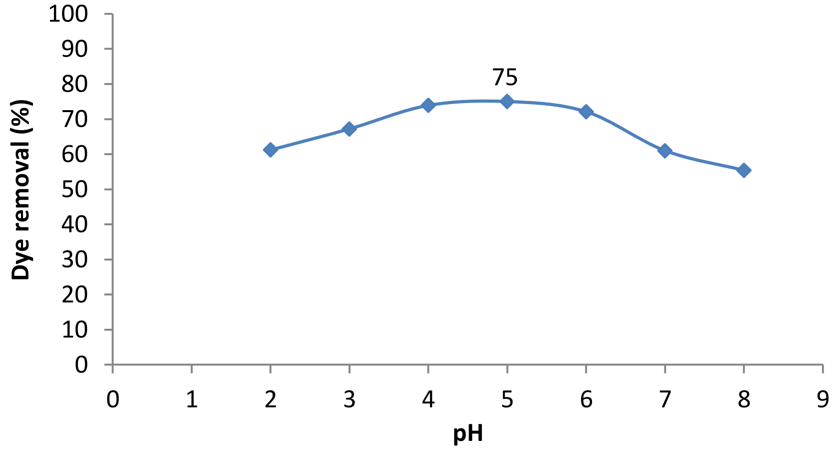

Figure 7 Influence of pH on the adsorption of 30 ppm methylene blue (2.5 g/L AC Modell II, 120 min)

It can be seen that the maximum removal efficiency was detected at pH 5, meaning the surface has a positive charge due to excess protons in the solution. It is known that the decrease of pH value leading to rise in the H^+ concentration in the aqueous solution and the activated carbon surface gains positive charge by absorbing H^+ ions. As a result when the adsorbent surface is positively charged the dye species own a strong attraction with positively charged of the carbon surface (Hettiarachchi et al., 2017). Above this optimum pH value, adsorption of the dye decreased which might be due to weakening of electrostatic force of attraction between adsorbate and adsorbent.

4. CONCLUSION

The achieved results of the present work show that the activated carbon prepared from Libyan olive-waste cake has a good potential for dye removal from aqueous solution. The chemical activation of activated carbon via zinc chloride with sulphuric acid is more effective than zinc chloride alone. The adsorption is significantly dependent on pH and the initial dose of the activate carbon. The acidic medium is found to be suitable for the dye adsorption onto prepared activated carbon. Olive-waste cake as a natural source and low cost adsorbent of activated carbon is promising to be efficient for other water treatments due to its high adsorption capacity.

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