ADSORPTIVE REMOVAL OF METHYLENE BLUE (MB) FROM WATER USING CARBON NANOPARTICLES PREPARED FROM DATE PITS

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Abstract

Recently, carbon nanostructures have played a crucial role in many vital aspects of nanoscience and nanotechnology; this can be attributed to their unique characteristics and potential applicability in a variety of fields. On the other hand, date pits have a relatively limited number of usages, which can be extended by the proposed new usage of date pits for synthesizing carbon nanoparticles. The present study provides a feasible method for synthesizing carbon nanoparticles (87.76 nm) through nitric acid reflux method using date pits as a carbon source, so as to maximize the value of the date pits. In addition, the current study evaluates the efficiency of the prepared carbon nanoparticles (CNPs) for adsorptive removal of (Methylene Blue (MB)) from waste water. In addition, parameters affecting that adsorption were also studied. The MB dye removed by the CNPs was depending on contact time, pH and concentration of dye. The optimum conditions for removal of MB dye by CNPs were: contact time of 15 hrs, at pH 7 and an adsorbent dose of 0.01 g. In this study the data fit Langmuir model and the maximum adsorption capacity was found to be 97.65 mg g⁻¹. Adsorption of MB onto CNPs followed pseudo second order kinetics. These results indicated that carbon nanoparticles may be an attractive candidate for removal of MB from wastewater.

Keywords: Date pits; carbon nanoparticles; nanotechnology; methylene blue; adsorptive removal.

Introduction

In the last few years, a growing interest was oriented toward carbon-based nanostructures because of their potential applications in many fields as a result of their unique physical and chemical properties (Nicolas et al., 2002). In this regard, several investigations were done on the potential uses of carbon nanoparticles in electronic materials (Kato & Ishibashi, 2008), medical imaging (Ya-Ping et al., 2006), drug delivery (Sunghoon et al., 2008 & Yonghui et al., 2004) and many other applications. In addition, carbon nanoparticles have an advantage of being biocompatible and chemically inert (RAY et al., 2009; Chi-Cheng et al., 2007; Koichi et al., 2002; Michael et al., 2002 & Kong et al., 2005), which makes it more benefit for medical and biological applications. On the other hand, several methods were developed to prepare carbon nanostructures such as chemical vapor deposition, arc-discharge, and plasma radiation (Xianglei et al., 2005 & Alexandrou et al., 2004); however, these methods are mostly restricted by the solid state strategies that can tolerate high levels of both energy and temperature, furthermore, their prerequisite for extreme conditions may impose many limitations in terms of large-scale and economical production since they require extreme conditions. These broad applications and limitations of preparation methods are encouraging many researchers worldwide to develop simpler and faster methods for preparing carbon nanostructures (Kang et al., 2003; Michael et al., 2007 & S.C. et al., 2009).

On the other hand, date palm is considered one of the most important fruit crops all over the world, particularly in the Middle East. The global production of dates reached 7600315 tons per year. In this context, Egypt occupies the fore among all other date-producers, with an annual production of 1465030 tons (F.A.O., 2014); among them 6-12% are pits (Barreved, 1993).

(MB) is a cationic dye that has numerous applications in chemistry, medical science and dyeing industries. Methylene blue dye is an organic dye belonging to the phenothiazine family; its long term exposure can make vomiting, nausea, anemia and hypertension (Foo, 2012 & Hameed, 2009). Methylene blue is used in manufacture of paper and other materials such as nylons and polyesters. It is mainly used for coloring blast, paper, leather, cotton, silk, and wool. Based on its wide-range applicability for coloring various industrial materials, there is a dire need for eliminating it from aqueous media (Royer et al., 2009).

There are numerous methods for removal of dyes from wastewaters such as, coagulation and flocculation, degradation, photocatalytic ozonation, photocatalytic oxidation (Sima & Hasal, 2013), Fenton process, electrochemical degradation, biological treatment. But, all these methods produced other byproducts that require continuous monitoring and identification, besides most of them are expensive (Forgacs et al., 2004).

In this paper, we report for the first time the use of date palm pits for preparing carbon nanoparticles through nitric acid reflux method and its usage for removal of the methylene blue dye, this method has the advantages of being relatively easy, inexpensive and ecofriendly.

Materials and Methods

Materials

Nitric acid and methylene blue, analytical grade of purity, were obtained from Sigma-Aldrich Company (China).

Preparation of carbon nanoparticles

Firstly, date’s pits, Sewi cultivar, were washed well using the tap water, then the pits dried at 100 °C for 24 h. Then, carbon nanoparticles were prepared from the dried pits through the nitric acid reflux method (Ray et al., 2009), in which the dried pits were pulverized well in mortar and pestle; after that, 5.0 g of the pulverized pits was mixed with 100 mL of 5M nitric acid in 250 mL flask, then refluxed at 100 °C for 12 h under stirring. The black solution was cooled and centrifuged at 500 rpm for 10 min to separate out unreacted carbons. The light brownish supernatant was then collected and centrifuged again at 4000 rpm for 10 min; the black precipitate was collected, washed from the excess nitric
acid with deionized water and dried in drier at 60 °C over night. the dried carbon nanoparticles were collected for further characterization.

Characterization of carbon nanoparticles

Carbon nanoparticles were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS).

In this regard, Infrared spectroscopy is considering one of the most important qualitative techniques that are used to characterize the surface functional groups in carbons (Moreno- Castilla et al., 2000). In our study, we used FTIR in order to investigate the functional groups on which the methylene blue will be adsorbed. Thus, FTIR was done using FTIR spectrophotometer (Jasco 4100, range 400 – 4000 cm\(^{-1}\)) on the prepared carbon nanoparticles.

Furthermore, TEM was done using the transmission electron microscope (Tecnai G20, Super twin, double tilt, FEI, Netherland) of prepared carbon nanoparticles and DLS was done using DLS Instrument (Zetasizer nano series (Nano ZS), Malvern, UK) to detect particle size distribution and zeta potential of the prepared carbon nanoparticles.

Adsorption of methylene blue onto carbon nanoparticles

Methylene blue is the targeted pollutant in this work. 1.0 g of MB powder was dissolved to produce 1000 ppm MB stock solution. 0.01g of CNPs and equal volumes of methylene blue solutions at varying concentration (50-800 mg/L) were shaken in a thermostatic shaker at the desired temperature with shaking speed of 175 rpm for 15 hours. The equilibrium concentration of methylene blue was examined spectrophotometrically. The concentration of MB was calculated using Eq (1)

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

(1)

Where \(C_0\) and \(C_e\) are the initial and equilibrium liquid phase concentration of MB (mg/L), V is the volume of solution (L), and W is the weight of adsorbent used (g).

Effect of pH was determined at different pH between 2 and 12 at constant initial MB concentration of 500 mg/L.

Effect of time determined by using 0.01 g of carbon nanoparticles with 50 mL of MB at 500 mg/L. The concentration of MB is detected as \(C_t\); adsorption capacity at a time t, \(q_t\) (mg/g) was determined using Eq (2)

\[
q_t = \frac{(C_0 - C_t)V}{W}
\]

(2)

Where \(C_t\) (mg/L) is defined as liquid-phase concentration of adsorbate at time t

Results and Discussion

Characterization of carbon nanoparticles

FTIR of carbon nanoparticles is shown in Figure (1). The black color of carbons enables them to absorb radiation in a range of 360-800 nm. FTIR spectrum is obtained as result of reaction of various types of surface functional groups with the absorbed wavelengths (Matos et al., 2011). From Figure (1), it's clear that the spectrum's peaks indicate to the presence of O-H stretching vibrations at 3754.73 and 3420.14 cm\(^{-1}\); C-H asymmetric stretching at 2920 cm\(^{-1}\); O=C=O stretching at 2375 cm\(^{-1}\); C=O stretching at 1637.27 cm\(^{-1}\); C-H bending at 1382.71 cm\(^{-1}\); C-O stretching at 1334.5 cm\(^{-1}\) and C-H bending at 776.208 cm\(^{-1}\). Among these functional groups, it was proved that O-H, C-H, C=O, and C-O are involved in adsorbing methylene blue (Liu et al., 2018). The abundance of these three functional groups in the prepared carbon nanoparticles enhances its efficiency in adsorbing methylene blue.

TEM micrograph of carbon nanoparticles is shown in Figure (2), it revealed that irregular shape of the prepared carbon nanoparticles, some of nanoparticles show a nearly spherical shape, while the other showed polygonal shapes.

Size distribution by using DLS indicated that carbon nanoparticles have particle size at 87.76 nm, as seen in Figure (3).
Also, the prepared carbon nanoparticles showed a positive zeta potential at about +30 mV, as shown in figure (4). This means that the prepared carbon nanoparticles have a moderate stability (Hanaor et al., 2012).

**Fig. 4**: Zeta potential of the prepared carbon nanoparticles as measured using Dynamic Light Scattering, showing its positive zeta potential at about +30 mV.

### Adsorption of Methylene blue

(i) Adsorption isotherm

The purpose of carrying out the batch adsorption isotherm is to describe the relation between amount adsorbed and the adsorbate concentration remains in the solution. The adsorption isotherms of MB onto carbon nanoparticles at 25°C, and pH of 7 are presented in Figure (5). The Langmuir equation is represented as (Langmuir, 1918):

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad \ldots(3)
\]

where \(q_e\) is the amount adsorbed at equilibrium time (mg/g), \(C_e\) is the equilibrium concentration of methylene blue (mg/L), \(q_m\) is the maximum adsorption capacity (mg/g), and \(b\) is known by Langmuir constant (L/mg) and it is related to the heat of adsorption. If we plot \(Ce/qe\) versus \(Ce\) for methylene blue carbon nanoparticles, we obtained straight line with a slope = 1/qm and an intercept = 1/ bqm, as shown in Figure (5B). Also, RL is known as separation factor which indicated in equation (4).

\[
R_L = \frac{1}{1+bC_0} \quad \ldots(4)
\]

Here, \(C_0\) is the highest initial solute concentration. The RL value indicated if the adsorption is unfavorable (RL >1), linear (RL=1), favorable (0< RL<1), or irreversible ((RL= 0).

### Table 1: Langmuir parameter for adsorption of MB onto investigated carbon nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNPs</td>
<td>(q_{max}) (mg/g)</td>
</tr>
<tr>
<td>CNPs</td>
<td>97.65</td>
</tr>
</tbody>
</table>

(ii) Effect of pH

The pH is an important factor that effect on removal of MB onto CNPs. Figure (6) indicated that the adsorption of MB is very high at acidic medium till pH 7, and then starts to decrease. This is attributed to MB gives positive charge ions when dissolved in water, so positive charge in acidic medium tends to oppose the adsorption of the cationic adsorbate. As pH increased the negative charge occurs in the surface, so the electrostatic attraction between positive charge of dye and negative charge of adsorbent occurs (Abd et al., 2009 & Malik, 2003). At higher pH the zwitterion of methylene blue is formed methylene blue formed (dimer) and becomes unable to enter into the pore structure of the carbon nanoparticles surface.

**Fig. 5**: Adsorption isotherms and Langmuir plots for methylene blue adsorption on carbon nanoparticle at \(C_i = 50–800\) mg/L, pH= 7, adsorbent dosage=0.01 g/L, and 25°C

**Fig. 6**: Effect of pH on adsorption of methylene blue using carbon nanoparticles
(iii) Effect of time on adsorption

The adsorptions of the methylene blue by carbon nano particles were studied at various time intervals (0.25-25 h). Figure (7) showed that the adsorption of MB was fast at the first, after that it slowed with time until the equilibrium happened. This due to large number of vacant sites which able to adsorbed MB at the first time (Hassan et al., 2014a & Hassan et al., 2014b) till a constant value at about 15 h (equilibrium time) after that active sites have been saturated, leads to a decrease in adsorption rate. To investigate the kinetics and mechanism of MB adsorption on carbon nano particles Pseudo-first (Eq. 5) and pseudo-second (Eq. 6) order equations were used to fit the kinetics process.

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2} 303t 
\]

Where \( q_e \) is the equilibrium adsorbed amount (mg/g), \( q_t \) is the amount adsorbed in time \( t \) (mg/g), \( K_1 \) is the pseudo-first-order rate constant (g/mg.min) and \( t \) is the time in minute.

Linearized form of the PSO can be expressed as

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e^2} t 
\]

Where \( K_2 \) is the pseudo second order rate constant (g/mg.min)

Figure (8) depicts the application of linear PFO and linear pseudo second order kinetics model. Upon analysis of Table 2 one can concluded that the adsorption follow pseudo-second order kinetics model based on: (i) Correlation coefficient \( R^2 \) for PSO is 0.9999 indicating the good applicability of PSO linearized form. On the other hand \( R^2 \) for PFO is very low which equal 0.42503 (ii) Calculated \( q_e \) (mg/g) from PSO model are closer to \( q_m \) (mg/g) calculated from Langmuir adsorption model while that calculated from PFO is very high.

![Fig. 7 : Kinetic adsorption curves of MB at 25 °C onto carbon nano particles](image)

![Fig. 8 : Pseudo–first order and Pseudo–second order kinetic model for removal of MB onto carbon nano particles](image)

**Table 2: Parameter of PFO and PSO kinetics model for removal of MB onto carbon nano particles**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( q_m ) (mg/g)</th>
<th>PFO Kinetic model</th>
<th>PSO Kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNPs</td>
<td>97.6</td>
<td>( q_e ) (mg/g)</td>
<td>408.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( K_1 ) (h(^{-1}))</td>
<td>5.657</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.42503</td>
</tr>
</tbody>
</table>

Conclusively, the prepared carbon nanoparticles exhibit a good adsorption capacity compared with other adsorbents that can exhibit higher or lower capacities, as shown in table [3].

**Table 3 : Adsorption capacity of the prepared carbon nanoparticles compared with some of the other adsorbents.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{max} ) (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial activated carbon</td>
<td>980.3</td>
<td>(Kannan et al., 2001)</td>
</tr>
<tr>
<td>Activated carbon from Waste cotton activated with ( \text{H}_2\text{PO}_4 )</td>
<td>344.82</td>
<td>(Ekrami et al., 2016)</td>
</tr>
<tr>
<td>Activated carbon from Watermelon rind activated with ( \text{ZnCl}_2 )</td>
<td>231.48</td>
<td>(Uner et al., 2016)</td>
</tr>
<tr>
<td>Activated carbon from Macadamia nut endocarp activated with ( \text{ZnCl}_2 )</td>
<td>194.7</td>
<td>(Junior et al., 2014)</td>
</tr>
</tbody>
</table>
**Carbon nanoparticles prepared from date palm pits**

<table>
<thead>
<tr>
<th>Material</th>
<th>Adsorption (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sewage sludge from an agri-food industry</td>
<td>87</td>
</tr>
<tr>
<td>Charcoal</td>
<td>62.7</td>
</tr>
<tr>
<td>Rice husk</td>
<td>28</td>
</tr>
<tr>
<td>Humic acid</td>
<td>15.82</td>
</tr>
<tr>
<td>Coarse grinded wheat straw</td>
<td>3.82</td>
</tr>
<tr>
<td>(Otero et al., 2003)</td>
<td></td>
</tr>
<tr>
<td>(Banat et al., 2007)</td>
<td></td>
</tr>
<tr>
<td>(Mckay et al., 1986)</td>
<td></td>
</tr>
<tr>
<td>(Inam et al., 2018)</td>
<td></td>
</tr>
<tr>
<td>(Batzias et al., 2009)</td>
<td></td>
</tr>
</tbody>
</table>

**Conclusion**

Carbon nanoparticles were prepared from date palm pits using nitric acid. The optimum condition for removal of MB was confirmed at pH7 and equilibrium time 15 h. Maximum adsorption capacities were found to be 97.6 mg/g at 25 °C. The adsorption of MB onto carbon nanoparticles follow pseudo-second order kinetic model with correlation coefficients reached to 0.9999.

**References**


