Adsorption of methylene blue from aqueous solution onto activated carbons developed from eucalyptus bark and 
Crataegus oxyacantha core
Mohammad Ali Zazouli, Ali Azari, Samaneh Dehghan and Razieh Salmani Malekkolae

ABSTRACT

In this study, eucalyptus bark and Crataegus oxyacantha core-based activated carbon were synthesized and their morphological features characterized by scanning electron microscopy and Fourier transform infrared spectroscopy techniques. The efficiency of synthesized adsorbents in removal of methylene blue (MB) from aqueous solution was investigated in a series of batch experiments. Furthermore, the influences of various experimental factors involving the contact time, the initial dye concentration, the adsorbent dosage, and the pH of the dye solution were investigated. The point of zero charge (pHpzc) of the applied adsorbents was also determined. In addition, the experimental data were expressed by Langmuir, Freundlich and Tempkin isotherms and pseudo-first order and pseudo-second order kinetic models. Adsorption equilibrium of the two adsorbents was reached within 1 h for MB concentrations of 20 to 100 mg/L. The equilibrium data obtained at optimum conditions of MB sorption by eucalyptus bark activated carbon and Crataegus oxyacantha core activated carbon were best fitted to Tempkin and Langmuir isotherm models, respectively. Besides, it was revealed that the adsorption rate follows a pseudo-second order kinetic model. From the findings of this study, it can be postulated that these adsorbents could be of great potential as a new class of adsorbents for organic dye removal from polluted water.

Key words | activated carbon, adsorption, Crataegus oxyacantha, eucalyptus bark, methylene blue

INTRODUCTION

Dyes are very widely used in various industries such as food, rubbers, carpets, cosmetics, plastics, paper and textiles (Zazouli et al. 2013; Auta & Hameed 2014). When the coloured wastewaters from these industries discharge into natural streams, they create many significant problems, such as increasing the chemical oxygen demand and the toxicity of the effluent and also reducing light penetration, which has a detrimental effect on photosynthetic phenomena (Bulut & Aydin 2006). The release of coloured wastewaters into the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbation in aquatic life (Senthilkumaar et al. 2005). As a thiazine cationic dye, methylene blue (MB) (3,7-bis(dimethylamino)-phenothiazin-5-iiumchloride) is commonly used for colouring papers, dyeing cottons, as a temporary hair colourant and also for dyeing of silk, paper, plastics, leather and cotton mordant with tannin, etc. Moreover, it can bring about eye burns which may be responsible for permanent injury to the eyes in both humans and animals (El-Halwany 2010; Theydan & Ahmed 2012; Roosta et al. 2014a). MB has various dangerous effects on humans and animals, although it is not considered to be a highly toxic dye (Hassana et al. 2014). MB can also cause increased heart rate, shock, vomiting, cyanosis, Heinz body formation, quadriplegia, jaundice and tissue necrosis in humans at acute exposure (Theydan & Ahmed 2012; Hassana et al. 2014). The complex structure of dyes makes them more stable and more difficult to remove from water and wastewater. Consequently, it is essential to remove dyes from coloured wastewaters before discharging them into potable and
groundwater resources (Bazrafshan et al. 2013). The removal of dyes from wastewater is a major problem, because conventional wastewater treatment systems are ineffective at removing colour from industrial effluents (Bazrafshan et al. 2014). The most common methods used for dye removal typically include degradation, coagulation–flocculation, adsorption, and oxidation (Hassana et al. 2014). Of all the above-mentioned techniques, the adsorption process is a good candidate for the removal of dyes and organic compounds from wastewaters (Ghaedi et al. 2014). It has been proven that adsorption is more effective and attractive for the treatment of dye from industrial wastes, compared to the other techniques used. This process is also inexpensive and highly effective in the removal of MB from wastewaters (Qada et al. 2006; Hassana et al. 2014). The adsorption of MB using different adsorbents such as activated carbon (AC), silicate, agricultural waste products, solid wastes from industry and clay minerals have been considered so far (Hassana et al. 2014). The adsorption processes provide a possible treatment, especially if the adsorbent is cheap and readily available (Qada et al. 2008). Adsorption on AC is an extensively used technique, due to its easily availability, high efficiency, high capacity, large surface area, high degree of surface reactivity, adequate pore size distribution, relatively high mechanical strength, low sensitivity to variations, high flexibility in design and operation and excellent removal of organic materials (Ghaedi et al. 2015; Zazouli et al. 2013b; Ahmed & Theydan 2014). The commercially available ACs are still considered as costly materials for many countries owing to the use of non-renewable and relatively costly raw materials such as wood and coal. So, in recent years, this has prompted a growing research interest in the generation of ACs from renewable and cheaper precursors, mainly industrial and agricultural wastes such as coconut shell, Jatropha hull, orange peel, flamboyant pods, peanut hull, cotton stalks, olive stones, mangosteen shell, etc. (Yang & Qiu 2010; Mahapatra et al. 2012; Theydan & Ahmed 2012; Ahmed & Theydan 2014; Juniora et al. 2014). The ready availability of the agricultural by-products make them good resources as raw materials for the production of ACs (Ghaedi et al. 2015). Recently, biomass wastes have been the preferable precursors for production of AC, since these materials are cost-effective, environmentally friendly and abundant (Ahmed & Theydan 2014). Eucalyptus bark is one of these cheap materials that has so far been widely used for the removal of a large number of heavy metals such as chromium, mercury and many of the hazardous dyes and has demonstrated good performance (Boutemedjet & Hamdaoui 2009; Srivastava & Rupainwar 2009).

Hawthorn (Crataegus oxyacantha) is an ancient medicinal plant that has long been applied as a folk medicine and has been widely used in pharmaceutical preparations due, mainly, to its beneficial health effects and its low toxicity (Ghaedi et al. 2014). In this research, the effect of ACs developed from two separate plants (eucalyptus and Crataegus oxyacantha) on MB dye removal was considered.

**EXPERIMENTAL**

**Materials and instruments**

Chemicals including MB (C_{16}H_{18}ClN_{3}S, MW 319.87 g/mol) (97% purity), orthophosphoric acid, hydrochloric acid (HCl, 35–37%) and sodium hydroxide (NaOH, 93%) were obtained from Merck & Co. All the chemicals used in this study were of analytical grade. The solution pH was adjusted using a EUTECH cyberscan pH meter (model pH 5500) and stirring rate by using a SIBATA shacker (model CMS 05). The absorbance spectra for MB was recorded at 663 nm using a Hach UV–visible spectrophotometer (model DR 2800). Fourier transform infrared spectroscopy (FTIR) of the adsorbents in the range of 500–4,000 cm\(^{-1}\) was recorded using an FTIR spectrophotometer (Perkin-Elmer Spectrum GX) and the scanning electron micrograph of the adsorbents was detected using scanning electron microscopy (SEM) (KyKy-EM3200). In addition, double distilled water was used to prepare all the solutions and reagents.

**Preparation of adsorbate**

A 1,000 mg/L stock solution was prepared and 20, 40, 60, 80 and 100 mg/L solutions were prepared by the necessary dilution of stock solution. The concentrations of MB solutions were obtained from a standard calibration curve. The characteristics of MB are reported in Table 1.

**Table 1 | The characteristics of the MB used**

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>( \text{C}<em>{16}\text{H}</em>{18}\text{ClN}_{3}\text{S} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>319.86 g/mol</td>
</tr>
<tr>
<td>Chemical structure</td>
<td><img src="https://iwaponline.com/wst/article-pdf/74/9/2021/457889/wst074092021.pdf" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>
Preparation of ACs

The eucalyptus bark and *Crataegus oxyacantha* core used as raw materials were obtained from the Sari region (Mazandaran Province, Iran). The cores of *Crataegus oxyacantha* were separated and along with eucalyptus bark were rinsed several times with distilled water and then dried in an oven at 110°C for 24 h. After drying, they were cut into 5 mm pieces and then impregnated with phosphoric acid solution (35%, v/v) as an activating agent. The impregnated pieces of bark and core were put into crucibles, which were sealed with pottery mud and placed into a kiln at 750–800°C for around 1–2 h. Afterwards, the ACs were washed with distilled water four to five times until the filtrate reached neutral pH and immediately dried in an oven at 100°C for 3–4 h. ACs were screened using an 18 and 30 mesh sieve and then used as adsorbents for dye removal (Shokoohi et al. 2010; Heibati et al. 2014). Surface functional groups were detected using FTIR (Perkin-Elmer Spectrum GX Infrared Spectrometer). SEM was used in order to obtain information about the surface morphology of the eucalyptus bark activated carbon (EBAC) and *Crataegus oxyacantha* core activated carbon (COCAC).

Batch adsorption experiments

Batch adsorption experiments were conducted at a constant shaking speed of 200 rpm, using 50 mL Erlenmeyer flasks with the addition of different concentrations of MB solution (20–100 mg/L) and the adsorbent dosage (0.25–2 g/L) over a different range of pH (3–11) and contact time (5–120 min). The pH was adjusted by adding 0.1 N HCl or 0.1 N NaOH at the beginning. All tests were conducted in duplicate and an average value was used. The experiments were performed in MB solution with a certain concentration (60 mg/L) and adsorbent dosage and pH values were 2 g/L and 7, respectively. After different time intervals (5–120 min), the samples were filtered through a syringe filter with a 0.45 μm polycarbonate membrane and the residual concentrations of MB in solutions were determined using a UV–vis spectrophotometer at a maximum wavelength of 663 nm. The amount of MB adsorbed per unit mass of adsorbents (q) and the dye removal efficiency (R%) were calculated by the following equations (Fu et al. 2015):

\[
q = \frac{(C_0 - C_i)V}{M}
\]

\[
R(\%) = \left(\frac{C_0 - C_i}{C_0}\right) \times 100
\]

where q represents the amount of adsorbed dye (mg/g), \(C_0\) is the initial dye concentration (mg/L), while \(C_i\) is the residual dye concentration (mg/L). Finally, the parameter V is the volume of dye solution (L) and M is the mass of adsorbent (g).

Desorption experiments

Eight cycles of sorption and desorption were performed to examine the reusability of the ACs. For the sorption experiments, 500 mg of ACs as sorbent was added into 1 L of 10 mg/L MB solution. The solution was stirred for 1 day at 200 rpm and room temperature. The pH of the solution was set in the neutral range during the sorption process. For the desorption tests, the ACs adsorbing MB were dispersed in 100 mL NaOH 0.1 M solution. The blend was stirred for 1 h, then the sorbents were separated from NaOH solution and washed several times with deionised water and used for the next cycle of adsorption–desorption. The following formula was used to calculate the desorption percentage:

\[
\text{Desorption (\%)} = \frac{\text{desorbed MB (mg)}}{\text{adsorbed MB (mg)}}
\]

RESULTS AND DISCUSSION

SEM of adsorbents

Figures 1 and 2 show the SEM images of the ACs used in this study. Many large pores in a honeycomb shape were clearly found on the surfaces of the two ACs. This photograph shows the fibrous and porous structure of both ACs, which is derived from the inherent fiber structure of the original raw materials. SEM analyses were also performed with the purpose of confirming the adsorption of MB onto the EBAC and COCAC surfaces. Figures 1 and 2(a) and 2(b) show SEM images of the EBAC and COCAC surfaces before and after the adsorption of MB, respectively; the observed differences in the reflection of the images are derived from the presence of adsorbed MB. SEM images illustrated an irregular structure with cracks and crevices.
on the surfaces of the ACs, which confirmed their amorphous and heterogeneous structures. With a decrease in the impregnation ratio, the materials presented a more irregular surface, which could be due to the more complex network of pores. The EBAC and COCAC SEM images exhibited fiber bundles of layering and spalling. Before adsorption, the outer fiber bundles appear relatively loose, to provide a larger surface area for the adsorption of MB. After adsorption of MB onto the adsorbent surfaces, there were some changes, such as blurred edges and a relatively smooth surface, and the surface of ACs appeared to be covered with a lot of sediment, making the contour fuzzy. This may possibly be caused by an oxido-reduction reaction taking place on the ACs under the acidic conditions.

FTIR spectroscopy of adsorbents

The FTIR spectra of the original AC and the AC laden with MB in the range of 500–4,000 cm\(^{-1}\) are shown in Figure 3. The FTIR spectra of EBAC before adsorption shows broad bands and intense absorption peaks at about 3,434 cm\(^{-1}\) corresponding to \(\text{–OH}\) groups. The peaks at 2943.07–2866.90 cm\(^{-1}\) are attributed to C–H group symmetric and asymmetric vibration aliphatic acid stretching. The peaks at 2165.57–1693.14 cm\(^{-1}\) are the asymmetric stretching vibration of C=O and the peak observed at 1560.09 cm\(^{-1}\) can be assigned to a secondary amine group. Other prominent peaks are the vibrations of C–O, –CN and C–C groups in alkanes that are observed at 1200.85 cm\(^{-1}\), 828.21 cm\(^{-1}\) and 516.88 cm\(^{-1}\), respectively. Moreover, the broad peak at about 1078.36 cm\(^{-1}\) is attributed to the P–O symmetrical vibration in a polyphosphate chain (P–O–P), which were formed in the carbonized samples in the presence of phosphoric acid. Some distinct changes can be observed between the spectra of EBAC and EBAC-MB. After the adsorption of MB, there seems to be a negligible change in the intensities of infrared bands with slight changes in positions. The changes in the FTIR spectra indicated that the
The process involved is the inclusion of MB with functional groups present in the EBAC. In fact, the spectral analysis before and after MB adsorption revealed that –OH groups, C=O stretching, and secondary amine groups were all involved in MB adsorption. In simple terms, carboxyl and hydroxyl groups could induce a negative charge on the surface of the sorbent which could attract positively charged objects such as MB. Figure 4 shows the FTIR spectra of COCAC before and after adsorption in the range of 500–4,000 cm\(^{-1}\). The wavenumber in the range of 3,480–3,441.14 cm\(^{-1}\) is the N–H stretch associated with N-substituted amide. The medium absorption bands at 2,850 and 2,930 cm\(^{-1}\) are the C–H stretching. It should be noted that the absorption bands at 2,850.65 and 2,917.26 cm\(^{-1}\) in the COCAC spectra have intensified after MB adsorption. This could be associated with the C–H stretching vibration involved in MB adsorption. A band around 1,731 cm\(^{-1}\) in the COCAC and COCAC–MB spectrum is C=O stretching,
a suggestion of the presence of aldehyde coupled with the band around 2,800 cm$^{-1}$ (C–H stretching from the aldehyde). It is evident that there are some differences in the COCAC–MB. Two spectra peaks at 1731.35 and 1469.43 cm$^{-1}$ appeared, due to the stretching vibration of carboxylic and C–C, respectively. The approximate absorption bands in the COCAC adsorbent shifted to 3459.4, 1096.79 and 515 cm$^{-1}$ when it absorbed MB dye as against the approximate absorption at 3441.14, 1125.49 and 647.62 cm$^{-1}$ without the dye on it (i.e. the COCAC adsorbent without MB dye). This suggests that amides, hydroxyl and aromatic double bonds are available for bonding. The FTIR spectra of the MB in the range of 500–4000 cm$^{-1}$ is shown in Figure 5.

**N$_2$ adsorption–desorption of adsorbents**

Nitrogen adsorption and desorption analysis was used to study the specific surface area and pore structure of adsorbents (NOVA 2200, Quantachrome Corp., USA) and the results are summarized in Table 2.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Average pore diameter (nm)</th>
<th>Average pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COCAC</td>
<td>168</td>
<td>1.84</td>
<td>0.212</td>
</tr>
<tr>
<td>EBAC</td>
<td>171.23</td>
<td>1.31</td>
<td>0.231</td>
</tr>
</tbody>
</table>

The specific surface area of COCAC and EBAC were obtained as 168 and 171.23 m$^2$/g, respectively. A mean pore size of 1.84 and 1.31 nm was recorded for COCAC and EBAC, respectively. In this regard and based on the IUPAC category, the synthesized adsorbents could be classified into the mesoporous group.

**Effect of contact time on MB adsorption**

The effect of contact time as an important experimental variable on the adsorption process in the time intervals of 5 to 120 minutes on the adsorption of MB by COCAC and EBAC is illustrated in Figure 6. As can be seen from Figure 6, the removal efficiency increased with time, reaching a constant value after 60 min for two adsorbents, corresponding to the equilibrium state. Similarly, a direct relationship between the contact time and the adsorption uptake of MB have been reported by previous researchers (Pathania et al. 2013; Fu et al. 2015). According to Figure 6, the extent of removal (in terms of $q_e$) of MB by ACs increased with time, but at some point in time reached a maximum value beyond which no more MB was removed from solution. At this point, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of dye being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. The necessary contact time for MB removal with
an initial concentration of 60 mg/L to reach equilibrium state is 1 h for the two adsorbents (Mahmoudi et al. 2015).

**Effect of the initial solution pH on MB adsorption**

The surface charges of an adsorbent and dissociation of functional groups on its active sites, the degree of ionization and structural changes of dye molecules can potentially be influenced by the pH of the solution (Auta & Hameed 2014). MB adsorption by AC is very susceptible to the solution pH. To determine the effect of pH, different dye solutions with initial concentrations of 60 mg/L at pH of 3, 5, 7, 9 and 11 were prepared. Then, 2 g/L of the adsorbents were added to the coloured solution. After 60 min, the residual dye concentration was determined by the spectrophotometric method. The results of the pH effect on MB adsorption are demonstrated in Figure 7. As can be inferred from this figure, colour removal efficiency is highest for EBAC and COCAC at a pH of 11, but, above a pH of 9, no significant changes in removal efficiency were observed in the two adsorbents, so a pH of 9 is considered the optimal pH for ACs. Similar observations have also been reported from other research groups (Auta & Hameed 2014; Chen et al. 2014; Mahmoudi et al. 2015). Studies revealed that the higher the solution pH, the more the MB molecules move onto the AC surfaces (Shokoohi et al. 2010; Gokce & Aktas 2014). The basic dye gives positively charged ions when dissolved in water. Thus, in an acidic medium, the positively charged surfaces of the sorbent tend to oppose the adsorption of the cationic adsorbate. When the pH of the dye solution increases, the surfaces acquire a negative charge, thereby resulting in an increased adsorption of MB, due to an enhancement in the electrostatic attraction between positively charged dye and negatively charged adsorbent (Pathania et al. 2013; Wang et al. 2014). In order to obtain information about the surface charges of the adsorbent, the pH of zero-point charge (pH_{zpc}) was determined. The plot of the final pH versus the initial pH of the solutions is illustrated in Figure 8(a) and 8(b). The pH_{zpc} can be determined at the point where the line of the final pH crosses the line of the initial pH. According to the data, the pH_{zpc} of EBAC and COCAC are 2.6 and 3, respectively. This means that at pH values below 2.6 and 3, the EBAC and COCAC surfaces have a net positive charge, while at pH greater than 2.6 and 3, the surfaces have a net negative charge. These results are similar to the pH_{zpc} reported by other researchers (Dave et al. 2011; Chen et al. 2014; Fu et al. 2015).

As mentioned before, the pH_{zpc} of the adsorbents are 2.6 and 3. In parallel, MB is a cationic dye with pKa = 5.8; then, its molecules are dissociated in a cationic form, mainly at higher pH values. Thus, the pH increase facilitates the interaction between the negatively charged adsorbents with the MB molecules in the cationic form.

**Effect of the initial MB concentrations on its adsorption**

The results of the effect of the initial dye concentrations of 20, 40, 60, 80 and 100 mg/L, at a pH of 9, 60 min contact time and the adsorbent dosage of 2 g are shown in Figure 9. As this figure shows, with an increase in the initial concentrations of dye, the removal efficiency decreases. According to the figure, the initial dye, with a concentration of up to 60 mg/L for both absorbents, removes well and with high efficiency. Further increase in dye concentration showed a significant decrease in removal efficiency. This may be due to a reduction in immediate solute adsorption, owing to the lack of available active sites on the adsorbent surfaces.
compared to the relatively large number of active sites required for high initial concentrations of MB (Meera & Ganesan 2015). This is also due to the fact that with increasing initial dye concentrations, the driving force for mass transfer also increases. At low dye concentrations, there will be unoccupied active sites on the adsorbent surfaces. Above the optimal MB concentration, the active sites required for the adsorption of dye will be missing. This retards the overall MB adsorption by AC. Similar observations have also been reported from other research groups (Theydan & Ahmed 2012; Pathania et al. 2013; Auta & Hameed 2014).

**Effect of the adsorbent dosages on MB adsorption**

The effect of the adsorbent dosages on the adsorption isotherms was also determined. The results of the adsorbent dosage effect, including 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2 g/L at pH of 9, 60 min contact time, and dye concentration of 60 mg/L are shown in Figure 10. As this figure shows, the removal efficiency increased with increasing adsorbent dosage. Our findings are consistent with the reported results from other research groups (Pathania et al. 2013; Niu et al. 2014). The optimal dosage of adsorbents for the removal of MB by EBAC and COCAC is 1 g/L. From Figure 10, it is obvious that the MB removal efficiency increased sharply with an increase in the adsorbent concentration from 0.25 to 1 g/L. This may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents. However, no significant changes in removal efficiency were observed beyond 1 g of adsorbent dosage in two adsorbents. Due to conglomeration of the adsorbent particles, there is no increase in effective surface area of the adsorbents. So, this weight (1 g) is considered as an optimal dosage for AC loading (Cherifi et al. 2013; Li et al. 2013; Pathania et al. 2013).
Adsorption isotherm studies

In this study, experimental data were expressed by Langmuir, Freundlich and Tempkin isotherm models. The non-linear Langmuir, Tempkin and Freundlich adsorption isotherms of MB are shown in Figure 11. The $b$, $q_m$, $n$, $k_f$ values and the non-linear regression correlation coefficients ($R^2$) for the studied isotherms are given in Table 3. All isotherms displayed a sharp slope in initial concentration, indicating that the adsorbent operates at high efficiency in a low colour concentration and gets saturated with an increased colour concentration. The correlation coefficients indicate that adsorption of MB was fitted better by the Langmuir ($R^2 = 0.9$ and 0.996) and Tempkin ($R^2 = 0.983$ and 0.94) isotherms for COCAC and EBAC, respectively, as shown in Table 3. The Langmuir isotherm revealed that the adsorption process can be described by the formation of a monolayer coverage of the adsorbate on the adsorbent surface. The equation of this model is as follows (Cazetta et al. 2014):

$$\frac{q_e}{C_e} = k_1 q_m - k_1 q_e$$  (4)

where $q_m$ is the maximum adsorption capacity (mg/g), $C_e$ is the equilibrium concentration of dye at the equilibrium time (mg/L), and $k_1$ is the Langmuir constant (L/mg). This observation is in agreement with previous reports on MB adsorption onto AC prepared from the other adsorbents (Sun et al. 2013).

The Tempkin isotherm contains a factor that explicitly takes into account adsorbing species–adsorbate interactions. This isotherm assumes that: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate interactions; and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Tempkin isotherm can be expressed as (Tempkin & Pyzhev 1940):

$$q_e = q_m \ln k_T + q_m \ln C_e$$  (5)

In this model, $K_T$ is the equilibrium binding constant (L/mg), $q_m$ is the maximum adsorption capacity of MB on adsorbent (mg/g) and the other parameters are similar to the parameters in the Langmuir isotherm (Roosta et al. 2014b).

### Table 3 | The parameters of the isotherms (Langmuir, Freundlich and Tempkin)

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Sorbent</th>
<th>Constants</th>
<th>$R^2$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>COCAC</td>
<td>$q_m$ (mg/g)</td>
<td>$k_1$ (L/mg)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.51</td>
<td>0.70</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>EBAC</td>
<td>36.91</td>
<td>0.09</td>
<td>0.900</td>
</tr>
<tr>
<td>Freundlich</td>
<td>COCAC</td>
<td>$n$</td>
<td>$k_f$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td>3.59</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>EBAC</td>
<td>1.77</td>
<td>1.64</td>
<td>0.83</td>
</tr>
<tr>
<td>Tempkin</td>
<td>COCAC</td>
<td>$q_m$ (mg/g)</td>
<td>$k_T$</td>
<td>$B_T$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.59</td>
<td>0.07</td>
<td>532.70</td>
</tr>
<tr>
<td></td>
<td>EBAC</td>
<td>6.80</td>
<td>0.16</td>
<td>359.68</td>
</tr>
</tbody>
</table>

RMSE: root mean square error.
The maximum adsorption capacity \(q_m\) was determined as 32.51 and 36.91 mg/g for COCAC and EBAC, respectively. The Freundlich constant \(k_f\), demonstrating the adsorption capacity of the sorbent, was determined as 3.59 and 1.64 \((\text{mg/g})(\text{L/mg})^{1/n}\) for COCAC and EBAC. The \(n\) constant represents the measure of both the relative magnitude and diversity of energies associated with MB adsorption onto prepared adsorbents and the numerical values of \(1/n\) for both adsorbents that lie at < unity, indicating that the marginal adsorption energy decreases with increasing surface concentration and that MB are favorably adsorbed by COCAC and EBAC. To clarify the favorability for adsorption of MB, the RL factor also calculated, i.e. \(0 < R_L < 1\), revealing that the adsorption of the selected colour was favorable for both sorbents. The linear form of the Freundlich isotherm model is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface and is expressed by the following equation (Azari et al. 2015):

\[
\ln q_e = \ln K_f + n^{-1} \ln C_e
\]

(6)

where \(q_e\) is the absorbed MB per unit mass of adsorbents at equilibrium state (mg/g), \(C_e\) is the MB concentration in solution at equilibrium time (mg/L), and \(K_f\) and \(n\) are the Freundlich constants that are related to the adsorption capacity and adsorption intensity of the sorbent, respectively (Gouamid et al. 2013).

Table 4 displays the maximum adsorption capacity for MB on the EBAC and COCAC and the other adsorbents at a temperature of 298 K. It is easy to conclude that EBAC and COCAC can be employed as two excellent adsorbents and it can be stated that our findings are extremely good.

### Adsorption kinetics studies

Pseudo-first and pseudo-second order kinetics models are two of the most important kinetics for the evaluation of adsorption efficiency. In this study, these kinetic models were used in order to characterize adsorption kinetics to establish the best fitted model for the experimental data and to describe the kinetic behaviour. The related parameters of pseudo-first and pseudo-second order kinetics can be achieved from the plots of \(\ln (q_e - q_t)\) versus time and \(t/q_t\) versus time, respectively. The regression coefficient \((R^2)\) and compatibility between \(q_e\) (experiment) and \(q_e\) (calculated) can be used to choose the best kinetic models. The parameters of these models and their regression coefficients \((R^2)\) are also given in Table 5.

According to regression values, the pseudo-second order model with \(R^2 = 0.999\) in two adsorbents demonstrated good compatibility with the data, showing that the rate limiting step is chemisorption and sharing of electrons from sorbent and adsorbate involving covalent forces (Figure 12). In addition, at the pseudo-second order kinetic models \((q_e, \text{cal})\) parameter compared to other models were closer to \((q_e, \text{exp})\) (Table 5). This kinetic is given by Equation (8). In other research related to adsorption, the pseudo-second order kinetic represents a better fit of experimental data than others. This kinetic model is based on the assumption

### Table 4 | Comparison of \(q_m\) (mg/g) in different adsorbents for MB

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorbate</th>
<th>(q_m) (mg/g)</th>
<th>Isotherm</th>
<th>pH</th>
<th>Dose (g/L)</th>
<th>Conc. (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotube</td>
<td>MB</td>
<td>46.20</td>
<td>L</td>
<td>7</td>
<td>0.15</td>
<td>20</td>
<td>Yao et al. (2010)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>MB</td>
<td>10.86</td>
<td>L</td>
<td>9</td>
<td>1</td>
<td>80</td>
<td>Woolard et al. (2002)</td>
</tr>
<tr>
<td>Polyurethane foam</td>
<td>MB</td>
<td>23.03</td>
<td>T</td>
<td>7</td>
<td>0.5</td>
<td>60</td>
<td>Baldez et al. (2008)</td>
</tr>
<tr>
<td>Polyaniline nanotubes base/silica composite</td>
<td>MB</td>
<td>5.38</td>
<td>T</td>
<td>7</td>
<td>2</td>
<td>100</td>
<td>Ayad et al. (2012)</td>
</tr>
<tr>
<td>Polyaniline nanotubes</td>
<td>MB</td>
<td>4.80</td>
<td>L</td>
<td>10</td>
<td>1.2</td>
<td>50</td>
<td>Ayad &amp; El-Nasr (2010)</td>
</tr>
<tr>
<td>Wheat shells</td>
<td>MB</td>
<td>16.56–21.50</td>
<td>L</td>
<td>9</td>
<td>0.6</td>
<td>80</td>
<td>Bulut &amp; AydIn. (2006)</td>
</tr>
<tr>
<td>Jute processing waste</td>
<td>MB</td>
<td>22.47</td>
<td>L</td>
<td>9</td>
<td>1.5</td>
<td>150</td>
<td>Banerjee &amp; Dastidar (2005)</td>
</tr>
<tr>
<td>Fly ash</td>
<td>MB</td>
<td>13.42</td>
<td>L</td>
<td>8</td>
<td>0.8</td>
<td>120</td>
<td>Wang et al. (2005)</td>
</tr>
<tr>
<td>EBAC</td>
<td>MB</td>
<td>32.51</td>
<td>T</td>
<td>9</td>
<td>1</td>
<td>60</td>
<td>This study</td>
</tr>
<tr>
<td>COCAC</td>
<td>MB</td>
<td>36.91</td>
<td>L</td>
<td>9</td>
<td>1</td>
<td>60</td>
<td>This study</td>
</tr>
</tbody>
</table>
that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. Therefore, it is likely that MB adsorbed on EBAC and COCAC chemical reactions (Sun et al. 2015).

The linearized form of the pseudo-first and pseudo-second order equations are given as:

\[
\ln \left( \frac{q_e}{c_0} \right) = \ln \left( \frac{q_e}{c_t} \right) - k_1 t
\]

\[
\frac{t}{c_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( q_e \) (mg/g): adsorption capacity of the sorbent in equilibrium time, \( q_t \) (mg/g): adsorption capacity of the adsorbent at time, \( k_1 \) (min\(^{-1}\)): coefficients of reaction rate for the pseudo-first-order models, \( k_2 \) (g/mg)(min\(^{-1}\)): coefficients of reaction rate for the pseudo-second order models. The related parameters of pseudo-first and pseudo-second order kinetic can be calculated from the plots of log \( q_e - q_t \) and \( q_t/t \) versus \( t \), respectively.

In Figure 12, pseudo-first and pseudo-second order kinetics for COCAC and EBAC are shown simultaneously.

Temperature effect and the adsorption thermodynamic

To determine the influence of the temperature on MB adsorption at different initial concentrations, the temperature was varied from 293 to 323 K, while the contact time was selected as 60 min. The obtained results showed that increasing the temperature had a positive impact on the sorption process (Figure 13) and a higher temperature is preferred for removal of MB.

The distribution coefficient constant used for determining the thermodynamic values and the slope and intercept of the In \( K_l \) versus 1/\( T \) (Van't Hoff plot) are used for calculating the numerical values of the changes in the enthalpy (\( \Delta H^0 \), kJ/mol) and the amount of energy change (\( C^0 \), J/mol K), respectively, as reported (Azari et al. 2015). The MB adsorption thermodynamic parameters on COCAC and EBAC are represented in Table 6. For both COCAC and EBAC, a negative value in standard free energy (\( C^0 \), kJ/mol) reveals that the adsorption process is a spontaneous reaction. The positive value of \( C^0 \) can confirm the MB adsorption is endothermic in nature. Furthermore, the value of \( \Delta S^0 \) was found to be positive, which shows that the randomness increased in the solid/liquid interface during the MB adsorption process with increasing temperature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{e,exp} ) (mg/L)</th>
<th>( R^2 )</th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( q_{e,cal} ) (mg/g)</th>
<th>( R^2 )</th>
<th>( k_2 ) (g/mg)(min(^{-1}))</th>
<th>( q_{e,cal} ) (mg/g)</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBAC</td>
<td>34.25</td>
<td>0.691</td>
<td>0.0619</td>
<td>2.993</td>
<td>0.999</td>
<td>0.0049</td>
<td>37.03</td>
<td>1.046</td>
</tr>
<tr>
<td>COCAC</td>
<td>34.68</td>
<td>0.733</td>
<td>0.0559</td>
<td>1.660</td>
<td>0.999</td>
<td>0.0051</td>
<td>36.88</td>
<td>1.071</td>
</tr>
</tbody>
</table>

Table 5: Kinetic models for MB adsorption on EBAC and COCAC

Figure 12 | Non-linear regression of pseudo-second order and pseudo-first order kinetics for MB on to COCAC (a) and EBAC (b).
The free energy of adsorption ($\Delta G$) can be related to the Langmuir equilibrium constant by the following expression:

$$\Delta G = -RT \ln k_L$$ (9)

Enthalpy and entropy changes are also related to the Langmuir equilibrium constant by the following expression:

$$\ln k_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ (10)

$$k_L = \frac{q_e}{C_e}$$ (11)

Thus, a plot of $\ln k_L$ versus $1/T$ should be a straight line. $\Delta H$ and $\Delta S$ values could be obtained from the slope and intercept of this plot.

### Table 6 | Thermodynamic parameters for MB adsorption by COCAC and EBAC

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Conc. (mg/L)</th>
<th>Temperature (K)</th>
<th>$\text{Ln}_{k_L}$</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (kJ/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COCAC</td>
<td>20</td>
<td>293</td>
<td>7.70</td>
<td>-22.51</td>
<td>33.41</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>7.90</td>
<td>-24.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>8.22</td>
<td>-26.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>293</td>
<td>7.50</td>
<td>-18.03</td>
<td>29.37</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>7.73</td>
<td>-19.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>7.91</td>
<td>-21.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBAC</td>
<td>20</td>
<td>293</td>
<td>1.58</td>
<td>-3.86</td>
<td>18.02</td>
<td>91.2</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>1.85</td>
<td>-4.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>2.02</td>
<td>-5.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>293</td>
<td>0.51</td>
<td>-1.24</td>
<td>11.24</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>0.65</td>
<td>-1.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>0.75</td>
<td>-2.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 13](http://dx.doi.org/10.2166/wst.2016.287)

**Figure 13** | Effect of temperature on the adsorption of MB onto COCAC (red line) and EBAC (black line) (pH = 9, adsorbent dosage: 1 g/L, and contact time: 60 min (Van ‘t Hoff curve)). Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wst.2016.287.

![Figure 14](https://iwaponline.com/wst/article-pdf/74/9/2021/457889/wst074092021.pdf)

**Figure 14** | Adsorption/desorption of MB by both ACs used in this study under batch conditions.
Reusability of adsorbents

Adsorption/desorption of MB by both ACs used in the study were performed under batch conditions and represented in Figure 14. According to this figure, after eight cycles, the adsorption efficiency of ACs was reduced to 68% (Figure 14). After every cycle, NaOH was used as desorption medium to remove adsorbed MB ions from the AC surface. Therefore, we suggested that COCAC and EBAC can be repeatedly used for MB sorption without many losses in initial adsorption performance, and also, that these adsorbents can be used in other cases similar to industrial applications.

CONCLUSION

In the present study, the ability of new ACs, namely EBAC and COCAC, for the adsorption of MB from aqueous solution was tested using kinetic aspects. SEM studies showed that the ACs had porous structures with well-developed pores. The results also indicated that the adsorption capacity of the sorbents was affected by the adsorbent dosage, the contact time, the solution pH and the initial MB concentrations. Furthermore, the removal efficiency of MB increased with a decrease in initial dye concentrations. The optimum pH value was found to be 9 for ACs. The kinetics of MB adsorption onto the AC surfaces were examined using the pseudo-first and pseudo-second order kinetic models. The results revealed that the pseudo-second-order equation provided the best correlation of the sorption data. In the kinetic studies, the good applicability of the pseudo-second order kinetic model was demonstrated. Moreover, the experimental equilibrium data were fitted to Langmuir and Tempkin models. The maximum adsorption capacity \( (q_m) \) for COCAC according to the Langmuir isotherm was 28.51 mg/g and 6.8 mg/g for EBAC according to the Temkin isotherm. From the findings of this study, it can be postulated that these adsorbents could be of great potential as a new class of adsorbents for organic dye removal from polluted water.

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