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Efficiently activated carbons from corn cob for methylene blue adsorption

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Activated carbon
Corn cob
Adsortion
Microwaves and methylene blue

ABSTRACT

In this study, activated carbon was prepared from an abundant Egyptian agricultural waste material (Corn Cob) through microwaves assisted activation. The effect of using two different activating agents (potassium hydroxide and ammonium sulfate), with various ratios of impregnation (RI) (0.25, 0.75, and 1.25), on the adsorption capacities were investigated. The prepared activated carbon was characterized using Raman spectroscopy, scanning electron microscopy (SEM), and nitrogen adsorption–desorption. The efficiency of the prepared activated carbon as an adsorbent was investigated by studying the removal of methylene blue (MB) as organic pollutants from aqueous solutions. Adsorption experiments for the prepared activated carbon are described in detail. The parameters affecting the adsorption process such as contact time, initial dye concentration were discussed in detail as well. The adsorption isotherm process fits well with the Langmuir model and the maximum adsorption capacity was q\text{max} = 333 mg/g. The adsorption kinetics data fitted well with the pseudo-second-order model. Accordingly, the prepared activated carbon can be utilized for the remediation of wastewater from organic pollutants with high efficiency and superior stability.

1. Introduction

The availability of the raw materials used in the production of activated carbon leads to making it plentiful and relatively inexpensive. In the last decades, scientists have become interested in the residues or sub-products reuse to act as ecofriendly products. So, some agricultural and industrial residues have been used for the production of activated carbon. One of these agricultural wastes is corn cob [1].

The physical and chemical properties of activated carbon (AC) depend on many factors including: the raw materials used, activation process and process parameters [2,3]. AC can be processed in varying production processes. The conventional heating method normally was occurs via an electric furnace to produce heat for activated carbon preparation [4,5]. This process takes a long time. It may take from several hours to a week until to reach the required activation level. Besides, the surface heating does not promise a uniform temperature for different shape and sizes of samples. So, the thermal gradient may be obtained from the hot surface to the core of the sample particle. These thermal gradient affects on the activated carbon quality [6]. Also, there is a considerable risk of overheating of the sample portion that leads to complete combustion of the carbon [7]. Recently, microwave technique has been normally used for AC preparation. It can be used for the regeneration of activated carbon [1]. The main difference between conventional heating systems and microwave devices is the heating pattern. The activation step is desired to enhance the characteristics of AC.

Many various activating agents exist as sodium hydroxide, potassium hydroxide, sulfuric acid, phosphoric acid etc., can be used for chemical activation. The change in these activation properties controls the porosity and the volume distribution of pores in the carbon [8–10].

The treatment of wastewater containing different classes of dyes can be made by adsorption process which is one of the most effective methods. Thus, the expensive commercial activated carbon is nowadays widely employed as preferred adsorbent. Recognizing this economic drawback of commercial activated carbon [11,12]. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, sawdust, buffing dust of the leather industry, coir pith, crude oil residue, tropical grass, olive stone, almond shells, pine bark, wood waste, coconut shell, etc., as carbonaceous precursors for the removal of dyes from water and wastewater [11,13–15].

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The objective of this study is to find the possibility for production of activated carbon by using corn cob (Egyptian agriculture waste material) as a raw material with using ammonium sulfate (NH₄)₂SO₄ and potassium hydroxide (KOH) as activating agents and thermal heating by using microwaves. Activated carbon was applied as a promising material for water treatment. AC was being prepared by the facile method with superior adsorption efficiency.

2. Experimental work

2.1. Materials and methods

Corn cob is an agricultural waste that is used as the precursor in this present study. It was picked from a local market waste using hand gloves and collected into poly-ester bags. The amount of main structure in the corn cobs used in the experiment such as moisture and ash content was 8.53 and 1.2 wt%, respectively which was closely with previous report [16]. Firstly, the raw material was washed thoroughly using distilled water to eliminate any adhering dirt sticking on the surface. Secondly, it was sun-dried for 6 h, followed by dehydrated in an oven at a temperature of 100 °C overnight. The dried precursor was then cut, crushed and finally sieved to a particle size less than 2 mm. The two activating agents used in this study are potassium hydroxide ≥95% and ammonium sulfate pellets ≥99.0%. They were purchased from Sigma-Aldrich and used without any further purification.

2.2. Carbonization via microwave-assisted activation process

100 g of the precursor was loaded into a modified muffle furnace with nitrogen gas flow (150 cm³/min). It was heated up to a temperature of carbonization 700 °C for 2 h, then it was carbonized with a rate of heating about 10 °C/min for 2 h. The char produced was then mixed with two different activating agents.

The char produced was then mixed with the activating agent pellets of potassium hydroxide or ammonium sulfate with three Ratios of Impregnation (RI) as (0.25, 0.75 and 1.25) for each one, defined as:

\[
RI = \frac{W_{\text{activating agent}}}{W_{\text{char}}}
\]

(1)

where, \(W_{\text{activating agent}}\) is the weight of activating agent pellets and \(W_{\text{char}}\) is the weight of corn cob char in grams, respectively.

The impregnated samples with potassium hydroxide with (RI) (0.25, 0.75 and 1.25) defined as (K, 3 K and 5 K), also the impregnated samples with ammonium sulfate with (RI) (0.25, 0.75 and 1.25) defined as (M, 3 M and 5 M).

The mixture was blended well for 1 h to ensure that it was mixed properly. They were then placed separately in a modified microwave oven. The frequency was adjusted at a fixed value of 2.45 GHz. The power of the microwaves was 600 W for an irradiation time of 10 min. Nitrogen gas flow was used to purge air in the microwave oven before starting heating and its purge continued during the cooling stage. The activated product was then washed several times by deionized water and ethanol, dried at a temperature of 105 °C for 1 h. Finally, the dried activated samples were ground and sieved to get a particle size of 125 – 250 μm. They are stored in sealed plastic containers for further use.

The activation yield can be defined as the ratio between the dry weight of produced activated carbon to the weight of the carbonized material and was determined using the following equation:

\[
Y = \frac{W}{W_o} \times 100\%
\]

(2)

where \(W\) is the weight of the produced activated carbon and \(W_o\) is the weight of the carbonized char material.

2.3. Characterization of powdered corn cob activated carbon (PCCAC)

The prepared samples were characterized by using different techniques as dispersive Raman spectroscopy (model Sentera, Bruker, Germany) used for analyzing carbon-based materials. Scanning electron microscopy (a Hitachi S4800) is used for detecting the morphology. The surface area of the prepared materials was specified from nitrogen adsorption/desorption isotherms utilize Micrometrics ASAP 2010 equipment (outgassing conditions: 200 °C, 12 h).

2.4. Adsorption experiments

2.4.1. Dye solution preparation and determination

A stock methylene blue (MB) dye solution 1000 mg/L was prepared by solve 1 g of MB in 1 L of distilled water. Different MB concentrations have been acquired by utilizing methods of dilution. A spectrometer UV/Vis/NIR (Perkin Elmer Lambda 9) was used for absorbance measurements at \(\lambda_{\text{max}} = 664\) nm (the maximum wavelength of MB).

2.4.2. Kinetics experiments

50 ml of MB dye solution with a concentration of 100 mg/L was added in a conical flask with 0.04 g of different samples of activated carbon adsorbent (commercial sample, 1 K, 3 K, 5 K, 1 M, 3 M and 5 M), then kept in a shaker vibrating at 110 rpm at 25 °C. The dye solution was separated practically from the adsorbent by using a micropipette, centrifuge at different intervals of time like 5, 10, 20, 30, 60, 90 and 120 min until equilibrium reaches. The absorbance of solutions is measured at the max wavelength (\(\lambda_{\text{max}}\)) at 664 nm, using UV/vis spectrophotometer. The concentration of MB was determined from a predetermined calibration curve of MB.

The adsorption capacity \(q_e\) (mg/g) can be calculated at any time \(t\), using the following formula:

\[
q_e = \left( C_o - C_e \right) \frac{V}{M}
\]

(3)

where, \(C_i\) is the initial concentration and \(C_e\) is the concentration of the pollutant at any time in (mg/L), \(V\) is the volume dye solution (L), \(M\) is the weight of adsorbent (g). The adsorbed amount at equilibrium \((q_e)\) (mg/g) can be determined by the formula [17]:

\[
q_e = \left( C_o - C_i \right) \frac{V}{M}
\]

(4)

where, \(C_i\) is the initial concentration and \(C_e\) (mg/L) is the concentration at equilibrium (mg/l).

Also, the percentage of removal efficiency of MB was determined with the effects of contact time can be determined using the formula as follow [17]:

\[
\eta = \frac{(C_o - C_e)}{C_o} \times 100
\]

(5)

where, \(\eta\) % Removal efficiency, \(C_i\) is the initial concentration of MB solution and \(C_e\) is the concentration of the solution of the pollutant after adsorption at any time in (mg/L). The results obtained were applied in pseudo-first-order and pseudo-second-order kinetic models to determine the rate of adsorption.

1. The pseudo-first-order model [18,19]

\[
\log (q_e - q_t) = \log (q_e) - \frac{(K_1t.2.03)}{1}
\]

(6)

where the terms of the given equation can be defined as \(q_t\), \(q_e\), \(K_1\) and \(t\) are adsorbed amount in (mg/g) at equilibrium, the adsorbed amount in (mg/g) at time \(t\), rate constant (1/min), and time in (minutes), respectively. A relation between \(\log (q_e - q_t)\) and time \(t\) was plotted. The value of \(K_1\) and \(q_e\) can be determined from the slope and the intercept of the curve.

2. The pseudo-second-order model [20,21]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \left( \frac{1}{q_e} \right) t
\]

(7)

where \(q_t\), \(q_e\), \(K_2\) and \(t\) are the adsorbed amount in (mg/g) at equilibrium, adsorbed amount (mg/g) at time \(t\), is the pseudo-second-order rate constant (g/mg.min) and time in (minutes), respectively. A relation between \(t / q_t\) and time \(t\) was plotted. The value of \(k_2\) and \(q_e\) can be calculated from the slope and the intercept of the curve [22,23].
2.4.3. Langmuir and Freundlich models

Adsorption isotherm experiments were performed at ambient temperature by adding 0.04 g of adsorbent in 50 mL aqueous solution of initial MB with different concentrations of 100, 200, 300, 400, 500 ppm. The solution was shaken at 110 rpm and was left for 120 min until reach equilibrium. The best two samples in adsorption according to the maximum adsorption capacity are determined as (5 K, 5 M).

Langmuir equation is applied and given by a linear form of the following equation [24,25]:

$$\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{(K_e \cdot q_{\text{max}} \cdot C_e)}$$

(8)

Therefore, $q_e$ is the amount adsorbed at equilibrium in (mg/g), $C_e$ is the concentration at equilibrium in (mg/L), $b$ is constant related to the affinity of binding sites, $q_{\text{max}}$ is the maximum adsorption capacity to form a complete monolayer on the surface in (mg/g).

The following equation describes the logarithmic form of Freundlich model [25]:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f$$

(9)

Therefore, $K_f$ is related to adsorption capacity, $n$ refers to adsorption Intensity. Note that, as the value of $n$ increase, the adsorption capacity becomes higher [26]. Freundlich constants $K$ and $n$ can be determined from the plot of log $q_e$ versus log $C_e$.

2.4.4. Adsorption thermodynamic

Thermodynamic analysis of MB dye adsorption onto prepared activated carbon was detected by the adsorption performing at variable temperatures (298–328 K). The parameters of thermodynamics as the adsorption entropy change ($\Delta S^0$, J/mol.K), the adsorption Gibbs free energy change ($\Delta G^0$, kJ/mol), and the adsorption enthalpy change ($\Delta H^0$, kJ/mol) were measured referring to these equation; where $R = 8.314$ J/mol.K, $T$ is absolute temperature K and $K_d$ (L/g) is the distribution coefficient of adsorbent that equals to $q_e/C_e$:

$$\Delta G^0 = -R.T. \ln K_d$$

(10)

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

(11)

3. Result and discussion

3.1. Characterization of fresh powdered activated carbon

3.1.1. Raman spectroscopy

The Raman spectra of the prepared activated carbon impregnated with KOH (1 K, 3 K and 5 K) were revealed in Fig. 1.a. The sharp Raman band around 1581, 1582 and 1594.5 cm$^{-1}$ for the prepared activated carbon samples of 1 K, 3 K and 5 K, respectively was characteristic to the graphitic ordering and known as G-band. The G band means that there is a c-c bond stretching of all pairs of sp$^2$ atoms in both rings and chains. It is attributable to the $E_{2g}$ Raman active vibration mode [27]. In particular, the G peak is the main Raman signature for sp$^2$ carbon.

The additional band present in the Raman spectra for samples 1 K, 3 K and 5 K at 1338.5,1336 and 1332 cm$^{-1}$, respectively was referred to some bonds of carbon that have different bond energies in the graphite sample. It is known as the D band. The D band disordered carbon atoms and therefore highlights defects in the crystalline structure. The D is a result of the $A_{1g}$ Raman mode. The intensity ratio between the D band and G band ($R = I_D/I_G$) can be expressed as a measure of the extent of the disorder.

It is noticed that the ratio of ($I_D/I_G$) for (1 K, 3 K and 5 K) samples are (1.02,1.03 and 1.09), respectively. The ratio of ($I_D/I_G$) is nearly the same. It means that functionalization by KOH as an activating agent with increasing its impregnation ratio till 1.25 RI does not affect badly on the structural shape of corn cob activated carbon (CCAC). The D band of the three samples (1 K, 3 K and 5 K) have approximately the same range of wavenumber from 1332 to 1340 cm$^{-1}$. Fig. 1.b shows three different Raman spectra of activated carbon have been impregnated with ammonium sulfate (NH$_4$)$_2$SO$_4$ (1 M, 3 M and 5 M). They give a sharp intensity at (1573, 1598 and 1582 cm$^{-1}$) for the three samples of activated carbon (1 M, 3 M and 5 M), respectively. The D band was appeared at (1361,1336 and 1336 cm$^{-1}$) for samples (1 M, 3 M and 5 M), respectively. The Raman intensity ratio (R) for (1 M, 3 M and 5 M) is (0.99, 1.04 and 1.05), respectively. In sample 1 M, the D band intensity is slightly less than the G band. It means that the sample M at low RI is slightly disordered. The D band becomes more intense than the G band in (3 M and 5 M). That refers to there is a large number of disordered carbon atoms without destroying the structural shape of CCAC [28].

3.1.2. Nitrogen adsorption–desorption and BET surface area

BET surface area values of 1 K, 3 K, 5 K, 1 M, 3 M and 5 M activated carbons samples were: 376, 382, 492, 71, 92 and 113 m$^2$/g, respectively. However, the BET surface area of the commercial sample was 450 m$^2$/g. All isotherm profiles are presented in Fig. 2 (a and b) and Fig. S1. The sample (5 K) achieved the best BET surface area among the impregnated samples and was about 492 m$^2$/g. The modification in the surface area of 5 K can be described due to the development of the porosity (mesoporous and microporous structure). It was confirmed with the profiles of isotherm shown in Fig. 2. Moreover, the pores size distribution of 5 K presented majority of micropores and less amount of mesopores as presented in Fig. S2; (macropores $>$50 nm, mesopores: 2–50 nm and micropores: $<2$ nm [29]).

The adsorption isotherms profiles for all samples are a type IV isotherms, which are corresponding to mesoporous materials. The hysteresis loop also has been presented in the isotherms at around $P/P_0 = 0.4$–1 for 1 K, 3 K and 5 K and around $P/P_0 = 0.8$–1 for 1 M, 3 M and 5 M. Where, the process of adsorption–desorption have capillary
condensation due to bimodal micro-mesoporous structure as recorded for porous corncob activated carbon [30].

3.1.3. Scanning electron microscopy (SEM)

Figs. 3 and S3 show The SEM micrograph of activated carbon samples (1 K, 3 K, 5 K, 1 M, 3 M, 5 M and commercial sample). For K and M samples, the differences in the morphology of the images, reveals that the activation with KOH and (NH₄)₂SO₄ allows producing carbons with homogeneous morphology. The 5 K sample has the highest exfoliation carbon sheets with the lateral dimensions thickness around 6-8 μm. Which leads to improving the absorptivity.

3.2. MB adsorption studies on AC

3.2.1. Effect of contact time

The influence of contact time was investigated through a batch adsorption experiment. The contact time effect on the concentration and adsorption capacity and removal efficiency of MB for commercial and different prepared samples of activated carbon (1 K, 3 K and 5 K) and (1 M, 3 M and 5 M) was studied. Fig. 4.a describes the relationship between the contact time and the removal percent of MB for samples (commercial, 1 K, 3 K and 5 K). It is observed that within the first 10 min fast dye removal is obtained and the concentration of the MB decreased very rapidly in the solution with increasing the time. In the next 20 min, the percentage of adsorption increases slightly with increasing shaking time until the maximum slope reached. The adsorption becomes very slow in later stages till saturation is reached within 90 min [23,31]. The adsorption capacity of MB for commercial, 1 K, 3 K and 5 K samples was about 48.2, 91.5, 110.7 and 124.1 mg/g, respectively. The maximum removal efficiency for the samples (commercial, 1 K, 3 K and 5 K) were (38.6, 73.2, 88.5 and 99.3%) respectively. As a result, we can say that the best sample due to its adsorption capacity and its percentage of MB removal was 5 K samples.

Fig. 4.b shows the relation between the contact time and the MB removal percent for samples (commercial, 1 M, 3 M and 5 M). The adsorption increases very rapidly at the beginning (mainly through the first 10 mins) with increasing the contact time. Then the MB removal slightly increased until reach to steady state at 60 min. This means, the active sites became almost saturated and no more adsorption will take place. The adsorption capacity of MB for commercial, 1 M, 3 M and 5 M samples was about 48.2, 64.1, 90.4 and 105.1 mg/g, respectively.

3.2.2. Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models have been applied for commercial and activated carbon samples (1 K, 3 K, 5 K, 1 M, 3 M and 5 M) to study the adsorption kinetics at 25 °C. The Pseudo
first and second-order kinetic plots of MB adsorption for samples impregnated by potassium hydroxide (1 K, 3 K and 5 K) were demonstrated in Fig. 5a and b. In addition, pseudo first and second-order kinetic plot of MB adsorption for samples impregnated by ammonium sulfate (1 M, 3 M and 5 M) were shown in Fig. 5c and d. The calculated results were listed in Table 1. The given experimental data fitted with a pseudo-second-order kinetic model \((R^2 \approx 1)\). Furthermore, the calculated equilibrium adsorption capacities values of the pseudo-second-order model acceptable with the obtained experimental values \((q_e, \text{exp})\). Accordingly, the kinetic adsorption of MB on a 5 K sample can be well explained by a pseudo-second-order model where MB molecule is adsorbed onto 2 sites of the 5 K surface, at a constant of the dye concentration \([32]\). Generally, the mechanism of dye removal can be described in the migration of the dye molecule from the solution to the adsorbent particles and diffusion through the surface. The variation in the rate of adsorption is due to that the surface of the adsorbent has active sites at the beginning so the pollutant concentration gradient decreases very rapidly. Afterward, the adsorption rate becomes slow due to the vacant sites decreases. In the end, the saturation happens and no more adsorption takes place. It was suggested there is a monolayer of MB that can act as a coverage to the surface of the prepared samples \([33,34]\).

### Table 1
Kinetic parameters for adsorption of methylene blue on activated carbon samples.

<table>
<thead>
<tr>
<th>Activating agent</th>
<th>Activated carbon</th>
<th>(q_e, \text{exp} ) (mg/g)</th>
<th>(K_1 ) (1/min)^(-1)</th>
<th>(q_e, \text{cal} ) (mg/g)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>commercial</td>
<td>50</td>
<td>2.2</td>
<td>19.3</td>
<td>0.85</td>
</tr>
<tr>
<td>KOH</td>
<td>1 K</td>
<td>93</td>
<td>2.9</td>
<td>86.8</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>3 K</td>
<td>112</td>
<td>3.2</td>
<td>93.0</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>5 K</td>
<td>126</td>
<td>2.4</td>
<td>49.0</td>
<td>0.96</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>1 M</td>
<td>86</td>
<td>2.1</td>
<td>22.8</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>3 M</td>
<td>92</td>
<td>2.2</td>
<td>21.9</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>5 M</td>
<td>107</td>
<td>2.2</td>
<td>25.4</td>
<td>0.97</td>
</tr>
</tbody>
</table>

![Figure 4](image1.png)

**Fig. 4.** The relation between the percentage of removal vs time for commercial, 1 K, 3 K and 5 K samples (a) & commercial, 1 M, 3 M and 5 M samples (b).

### Table 2
Isotherm parameters for the adsorption of Methylene blue on different samples 5 K and 5 M activated carbon.

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>5 K</th>
<th>5 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir model</td>
<td>(K_1 ) (L/mg)(^{-1}) (x)10(^{-3})</td>
<td>3</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>(R_1)</td>
<td>0.01–0.002</td>
<td>0.11–0.02</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>(q_e ) (mg/g)</td>
<td>333</td>
<td>147</td>
</tr>
<tr>
<td>Freundlich model</td>
<td>(N)</td>
<td>6.20</td>
<td>9.69</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.74</td>
<td>0.30</td>
</tr>
</tbody>
</table>

3.2.3. Adsorption isotherm

The variation of the initial concentration of methylene blue from 100 to 500 mg/L was investigated at constant time, adsorbent dosage and temperature. By increasing the initial concentration of methylene blue from 100 to 500 mg/L, the amount adsorbed per unit mass of the adsorbent increases from 124 to 327 mg/g and from 105 to 145 mg/g for samples 5 K and 5 M, respectively. The relation between \(C_e/q_e\) and \(C_e\) at ambient temperature was plotted as shown in Fig. 6-a. From the slope and the intercept of the curve, the maximum adsorption capacity, \(q_{max}\), and the langmuir constant \(K_l\) can be determined respectively. The results achieved on applying the Langmuir model through the adsorption process for samples 5 K and 5 M are presented in Table 2. Where, the Langmuir model has best fitted with a highest determination coefficient \(R^2 \approx 0.99\). The important term of the Langmuir isotherm is expressed using \(R_1\) \([35]\). It is a dimensionless constant which referred to as separation factor or equilibrium parameter defined by:

\[
R_1 = \frac{1}{1 + K_L \cdot C_0} \tag{12}
\]

where \(C_0\) is the highest initial concentration. The factor proposes the kind of isotherm to be irreversible \((R_1 = 0)\), favorable \((0 < R_1 < 1)\), unfavorable \((R_1 > 1)\). As can be seen from Table 2, the value of \(R_1\) is less than 1 which suggests that adsorption is favorable.

Freundlich model was presented in Fig. 6-b. The relation between log \(q_e\) and log \(C_e\) for samples (5 K and 5 M) are plotted as shown in Fig. 6-b. They give straight lines with slope \('1/n'\). The parameters obtained from the freundlich model equation and correlation coefficients
Fig. 5. Experimental kinetic data and linear fitted curve with kinetic models (a) pseudo-first-order for commercial, 1 K, 3 K and 5 K samples. (b) pseudo-second-order for commercial, 1 K, 3 K and 5 K samples. (c) pseudo-first-order for commercial, 1 M, 3 M and 5 M samples. (d) pseudo-second-order for commercial, 1 M, 3 M and 5 M samples.

(R²) are listed in Table 2. Consequently, the correlation coefficient is higher in the Langmuir model than the Freundlich model. This assumes that a monolayer adsorption process occurs on the homogeneous surface of an adsorbent without considering the interaction between adsorbate molecules.

3.2.4. Adsorption thermodynamic

The study of the temperature influence on the adsorption process by the prepared activated carbon (5 K) . In addition, to determine the behavior of adsorption is endothermic or exothermic in nature. The obtained values of thermodynamic parameters (Gibbs free energy (∆G0), enthalpy (∆H0) and entropy (∆S0)) are listed in Table 3, the values of Gibbs free energy change (∆G0) are negative value with rising of the temperature. This referred to the adsorption of dye molecules onto prepared activated carbon is spontaneous in nature. Moreover, ∆H0 presented with the positive value (61 kJ/mol) which referred to the adsorption was a endothermic. The positive value of entropy (∆ S0= 244 J/mol.K) confirm more randomness at interface of dye and AC (5 K sample) during the adsorption process. This endothermic adsorption process was also observed in the removal of MB by activated carbon [36].

3.2.5. Desorption and recovering

The recovering ability also seems promising. To assess whether 5 K sample could be recycled for adsorption of pollutant, the sample used for the adsorption with MB were recovered simply by filtering with filter paper, washed with ethanol and milli-Q water several times, dried at 60°C and used again for five times without any obvious activity loss (Fig. 7).

Table 3

<table>
<thead>
<tr>
<th>Thermodynamic parameters calculated for the removal of MB dye by the AC (5 K sample).</th>
<th>∆G0 (kJ/mol) at different T (K)</th>
<th>∆S0 (J/mol.K)</th>
<th>∆H0 (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>308</td>
<td>318</td>
<td>328</td>
</tr>
<tr>
<td>−1.26</td>
<td>−1.32</td>
<td>−1.42</td>
<td>−2.06</td>
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<tr>
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4. Conclusion

In this study, activated carbons were successfully prepared with well-developed surface area and high adsorption capacities from agricultural waste (corn cob) using microwave-assisted chemical activation using two different activating agents (KOH and (NH₄)₂SO₄). The activation process was facile and fast. Raman, BET and SEM diagnosis have been used to characterize the prepared samples. Experimental results showed that microwave heating could shorten the processing period and remarkably, produce a high-quality activated carbon. AC prepared by microwave-assisted KOH activation attained a maximum BET surface area as 492 m²/g at Rl=5 and maximum adsorbed capacity qₘₐₙ₉₃ (333 mg/g). The kinetic results showed that the pseudo-second-order model better described the experimental data. The langmuir adsorption isotherm model provided a better correlation for the adsorption of MB onto prepared AC. Based on these results, it is concluded that the (5 K) activated carbon sample could be a favorable adsorbent for the remediation of water from toxic organic dyes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials


References
