Original Article

Effective utilization of *Moringa* seeds waste as a new green environmental adsorbent for removal of industrial toxic dyes

**Nofal khamis Soliman** a,*, **Ahmed Fathy Moustafa** b, **Ahmed A. Aboud** c, **Khaled Saad Abdel Halim** d, e

---

**A R T I C L E   I N F O**

Article history:
Received 22 December 2018
Accepted 22 December 2018
Available online 31 January 2019

**Keywords:**
Moringa seeds waste
Solid waste management
Dye removal
Adsorption isotherm and kinetic
Wastewater treatment
Green adsorbent

**A B S T R A C T**

The *Moringa* seeds waste (MSW), which resulted from the oil extraction industry, contains many varieties of natural organic components such as flavonoid, tannins, phenolic and hydrolyzable carbohydrates. The MSW could be considered a promising and an efficient green adsorbent for wastewater treatment as it reduces the environmental impact of hazardous chemicals existing in the industrial wastewater. The present work is designated to clarify the possibility of using MSW for the removal of industrial dispersed red 60 (DR60) and Congo Red (CR) dyes from aqueous solutions. The factors affecting the adsorption process such as initial dye concentration, catalyst weight, pH value, and solution temperature were investigated. It was found that the adsorption rate for both dyes was very high at the initial stages of the process and then decreases until reaches the equilibrium. The adsorption rate of the DR60 dye was not affected by catalyst weight, pH or the solution temperature. Whereas the percentage of the CR dye removal is found to be 100% for all dyes concentrations except for the CR dye with high initial concentration (100 mg/L), which reached only 85.3%. It was observed that the adsorption % of CR dye increases by increasing the temperature from 25 to 40˚C. With more increases in the reaction temperature from 40 to 80˚C, the CR removal decreases from 88.7 to 57.7%, respectively. This behavior can be attributed to the desorption behavior of the adsorbed dye molecules at a higher temperature. Accordingly, the optimum temperature for the CR dye adsorption is found at 40˚C. A detailed study of the dye adsorption isotherms and kinetics was carried out and the results show that the dyes adsorption isotherms and kinetics are followed by Freundlich and pseudo-second-order models. Maximum amounts of dyes adsorbed were found to be 170.7 and 196.8 mg/g for both CR and DR60 dyes, respectively, at 100 mg/L concentration, 25˚C and pH 7. The overall rate of adsorption process seems to be controlled by a chemical process mechanism involving valence forces through exchange or sharing of electrons between dyes and MSW adsorbent.

© 2019 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

---

* Corresponding author.
E-mail: Nofal.khamis@nub.edu.eg (N.k. Soliman).

https://doi.org/10.1016/j.jmrt.2018.12.010

2238-7854/© 2019 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. **Introduction**

The industrial areas all over the world are now suffering a speedy increase in the production of solid wastes. Accordingly, much more efforts should be exerted and extended for the management of solid waste processes. Furthermore, the environmental pollution of solid wastes and its control is an emerging global issue that needs to be addressed for a healthy green environment. Thus the solid waste management is a growing technology, which needs to be improved, by exploring new solutions and consequently increasing economic valorization of waste materials [1].

The solid waste of agriculture ore, biosorbents, and biocomposite based on biomaterials have received much interest recently due to their environmentally friendly nature and efficiency for adsorbing dyes and heavy metals from textile and industrial wastewater [2–10]. For example, orange peel was used as an adsorbent for dyes removal at different doses from textile wastewater to establish it as a standard wastewater treatment process for the industry of composite knit [2]. The orange peel sorbent was evaluated at different adsorbent amounts, pH values and retention time. It was concluded that the orange peel can be considered a promising natural sorption where it removes about 60–70% of the dyes [2].

The wastewater containing synthetic dyes represents a global problem, especially those containing quinone and azo dye compounds. The annual production of organic dyes compounds is more than 700 thousand tons since they are widely used in cosmetics, food, pharmaceutical, textile, and leather industries. They produce huge environmental load in wastewater [11–14].

It is well known that the Congo Red (C32H22N6Na2O6S2) and dispersed red 60 (C20H13NO4) dyes are commonly used within laboratory assays, textiles, paper printing, and other commercial products [12,15]. These dyes have a harmful effect on the human body where they cause digestive tract irritation and skin sensitization. They are considered insurgent and wilful pollutants that constitute a significant load on the environment [12–14,16]. In addition, most of the known dyes show carcinogenic effect since they are made from known carcinogens such as benzidine and other aromatic compounds. Recent researches reported the toxicity and carcinogenic nature of most dyes and heavy metals [17–22]. Therefore, owing to the high toxicity and contamination of wastewater with Congo red (CR) and dispersed red 60 (DR60) dyes, the efficient degradation and/or adsorption techniques have become an important challenge and essential task for wastewater treatment. Hence, it is a matter of concern to treat wastewater and explore a new green adsorbent for the efficient treatment of CR and DR60 dyes [12–14,16].

However, *Moringa* seeds waste (MSW), which was obtained from the oil extraction industry, can be used as an ideal adsorbent for wastewater treatment using a simple, effective, and economical way. MSW eliminates approximately 90–99% of bacteria contained in water due to the presence of an active antimicrobial agent 4a Lrhamnosylxy-benzyl isothiocyanate [23]. Using MSW as an alternative green adsorbent for wastewater treatment will represent a new approach for the conservation of traditional chemical resources. It will eliminate the use of hazardous substances such as Al2(SO4)3, FeCl3, H2SO4 and organic polymers as these materials are being used in wastewater treatment's stations in order to reduce the environmental impact and load of industrial wastewater. This may be considered a new concept for the management of resources.

Based on the above background, the goal of the present work is to use the MSW as a new green adsorbent for removal of toxic CR and textile DR60 dyes. The MSW exists in nature in huge amount and can be used for wastewater treatment to replace expensive and hazardous chemicals. The MSW is a cheap and effective green adsorbent. It can be considered a new approach for the conservation of resources. Also, this concept will represent the development of environmentally improved routes that establish important industrial procedures in wastewater treatment stations particularly in the oxidation pools step for adsorption of textile dyes. The factors affecting the adsorption process of these dyes by MSW were investigated. The adsorption isotherm and kinetics of the process were demonstrated.

2. **Experimental procedures**

The extraction process of *Moringa* seeds was discussed elsewhere [24]. The obtained extracts were examined to determine the present components and the active ingredients of MSW. The total flavonoid content (TFC) was determined spectrophotometrically by the aluminum chloride method as expressed by Zhishen et al. [25]. While the total tannins content (TTC) was measured by using the Folin-Ciocalteu reagent assay [26]. The total hydrolyzable carbohydrates were determined spectrophotometrically using the phenol-sulphuric acid method [27]. The phenolic compounds of cold water extract were identified using high pressure liquid chromatography (HPLC). All chemicals and solvents used were HPLC spectral grade [28].

The Congo red dye (CR) with purity 99.1% was purchased from Pio-Chem. Company (Cairo, Egypt). The dispersed red 60 dye (DR60) with purity 96% was purchased from Alfa Chemistry Company (USA). The chemical structural formula of both dyes is shown in Fig. 1.

The solutions of the tested dyes (CR and DR60) with different concentrations were prepared by dissolving the dyes in distilled water [29].

Four series of adsorption tests as shown in Table 1 were performed on both dyes using MSW catalyst at different reaction conditions including the initial dyes concentration, pH values, temperature and MSW catalyst weight. The time of the experiment was fixed at 45 min in all tests. The changes in the concentration of the tested dyes were measured from their characteristic absorption peaks using UV–vis spectrophotometer.

The amount of dye adsorbed at equilibrium $q_e$ (mg/g) and the amount of dye adsorbed at certain time $q_t$ (mg/g) together with the dye removal percentage were calculated from literatures [30,31] according to the following equations:

$$q_e = \frac{V(C_0 - C_e)}{m}$$  

(1)
3. Results and discussion

3.1. Adsorbent characterization

The activities of MSW in the area of water treatment for removing organic toxic dyes are still limited. The MSW possesses various types of organic compounds that represent the synergetic effect as a new green adsorbent for dyes removal. The hot and cold water extraction processes were carried out to identify the active components of the new green adsorbent. The active ingredients of hot and cold water extract for Moringa Oleifera seed were discussed elsewhere [24]. The active ingredients, Phenolic (TP), flavonoids (TF), tannins compounds (TT), total hydrolyzable carbohydrates (THC) and polysaccharide were identified and quantified in both extracts using high pressure liquid chromatography (HPLC). The total phenolic contents (TP) were found to be 15.76 ± 0.20 and 15.01 ± 0.24 (mg/g) DW in cold and hot water, respectively. The TP has been found as strong antioxidants scavenger against the influence of free radicals and ROS, which is the basis of several chronic human infections [32]. In addition, the TP compounds have a reducing activity, which may be attributed to the presence of hydroxyl group which could act as electron donors.

The concentrations of flavonoids in both extracts were 3.11 ± 0.03 and 3.09 ± 0.03 (mg/g) DW. Flavonoids are important components because they have different biological activities; their regular consumption may have serious consequences for health.

The tannins compounds (TC), are considered important photochemical with a wide range of medicinal properties, as anticancer, antioxidant, anti-inflammatory and antibacterial. The concentration of TC was found to be 4.99 ± 0.06 and 5.48 ± 0.15 (mg/g) for cold and hot water, respectively. The total carbohydrate % and fractionation of sugar contents

\[
\text{where } C_0: \text{ initial dye concentrations in mg/L; } C_t: \text{ solution concentration after time } t; C_e: \text{ solution concentration at equilibrium; } m: \text{ sorbent dose in milligrams; } V: \text{ solution volume in milliliters.}
\]

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

\[
\text{Dye removal, } \% = 100 \left( \frac{C_0 - C_t}{C_0} \right)
\]

Fig. 1 – The chemical structure of the tested dyes where (a) Congo red (b) Dispersed red 60.

<table>
<thead>
<tr>
<th>Table 1 – Conditions of experimental tests.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series #</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>
of MSW were identified using HPLC, and it was determined to be 15.14%. The significant importance of carbohydrate in MSW may be attributed to the high percentage of mono sugars [24]. The present mono sugars possess some nutritional advantages and show multiple and complex biological activities such as antioxidant, anticancer, anti-inflammatory and antitumor [33].

3.2. Influence of operation parameters on the removal of dyes using MSW catalyst

Initial dye concentration

Figs. 2 and 3 illustrate the effect of initial dyes concentration and reaction time on the removal % percentage and the amounts of adsorbed dyes using MSW as a green adsorbent. From Fig. 1, it was deduced that at the first stage, the rate of adsorption was very high during the first 8 min, then it slowed down till it reached the equilibrium state. For all dye concentrations, the adsorption percentage reached 100% except for CR dye with initial dye concentration of 100 mg/L, which represents only 85.3%. The rapid adsorption rate at the initial stage may be due to the presence of a great number of unoccupied adsorption positions existing on the adsorbent surface. With time, these vacant sites become occupied by the adsorbed dyes that produce a repulsive force between the molecules of adsorbate dyes on the MSW surface and in bulk liquid phase as obtained from Fig. 2 [34].

For the two tested dyes, the MSW catalyst showed 100% removal percentage for all dyes concentrations at different times except for CR dye with an initial concentration of 100 mg/L. Such kind of behavior may be attributed to the synergistic effect of the active ingredients of MSW. Both dyes CR and DR 60 show the same behavior as the dye removal% increases with the decreasing initial dye concentration. From Fig. 3(a and b), the amounts of adsorbed dyes increase with increasing the initial dyes concentration. This phenomenon might be owing to the increase in the concentration gradient with increasing dye initial concentration. Consequently, the driving force, which has the capability to overcome the resistance of mass transfer between the liquid and solid phases, will be increased [35].
The maximum amounts of dyes adsorbed were found to be 170.7 and 196.8 (mg/g) for CR and DR60 dyes, respectively at 100 mg/L concentration, temperature of 25 °C and pH value of 7.

3.2.1. MSW weight
The mass dose used in adsorption process is a vital factor as it determines the equilibrium between the sorbent and sorbit in the reaction system and can also be used to determine the cost of treatment of MSW adsorbent per unit of CR and DR60 dyes solutions. The effect of catalyst weight on the removal % of CR and DR60 dyes is shown in Fig. 4. It can be deduced that the effect of catalyst dose is significant only on the removal % of CR dye as it increased by increasing the weight of MSW. This behavior can be attributed to the increase of the surface area of the MSW [36]. The insignificant effect of the MSW weight on the removal % of DR60 dye is clear as it reached 100% with the minimum catalyst dose (0.1 g) and keep constant with the further increase in the MSW dose. Once the maximum limit of dye removal was attained by the adsorbent, there will be no effect for the increasing of adsorbent dose [37].

3.2.2. PH value of the solution
The value of pH of the solution has also a considerable effect on the removal of dyes over MSW catalyst. The pH values represent a significant influence on the adsorption capacity due to their effect on the absorbent surface and ionization/dissociation of the sorbent molecules [38]. The effect of pH values of the aqueous solutions on the removal % of CR and DR60 dyes using MSW is shown in Fig. 5. The removal % of CR dye at pH 3, 5, 7, 9 were found to be 53, 73, 85 and 75%, respectively. The lower adsorption capacity for CR dye in an acidic environment is due to the high mobility of H+ ions and protonation of the absorbent surface. The H+ ions compete with the molecules of CR and DR60 dyes during the adsorption process [39]. Increasing the pH values will decrease the hydrogen ions concentration, which increases the uptake of dye molecules by the MSW [40]. With more and more increase in pH value, as in the case of pH value equal 9, the surface of the MSW becomes negatively charged, so the polarity of the electric double layers changes. Hence, the adsorption percentage of CR dye decreases as shown from Fig. 5 [41].

On the other hand, the removal % of industrial DR60 dye at pH 3, 5, 7, 9 were found to be 100% at constant operational parameters. The obtained results indicate that the value of pH is useless and show no effect on the removal % of industrial DR60 dye over the surface of MSW as deduced from Fig. 5.

3.2.3. Reaction temperature
The effect of experimental temperature on the adsorption process of CR and industrial DR60 dyes over MSW was investigated at different temperatures (25, 40, 60 and 80 °C) and the results are shown in Fig. 6. As the temperature increased from 25 to 40 °C, the CR removal % increased from 85.3 to 88.7%. With more increase in the reaction temperature from 40 to 80 °C, the CR removal % decreases from 88.7 to 57.7%. This behavior may be attributed to the desorption behavior of the
adsorbed dye molecules at a higher temperature. Therefore, the optimum temperature for CR dye adsorption is 40 °C which represents the economic cost of the adsorption process.

The industrial DR60 dye shows constant removal % (approximately 100%) at all adsorption temperatures (25, 40, 60 and 80 °C), hence the adsorption temperature has no effect on the removal % of DR60 dye over MSW.

3.3. Adsorption isotherm

In order to understand how the dye distributes between the adsorbent solid phase and solvent liquid phase, an adsorption isotherm is portrayed by certain constant values that give an indication for the affinity of the adsorbent and the surface properties. It can also be used to compare the adsorptive capacities of the MSW for distinctive pollutants dyes.

Equilibrium results can be analyzed using different recognized adsorption models. Many mathematical models can be used to describe experimental data for adsorption isotherms. In the present article, three adsorption isotherm models namely, Freundlich, Langmuir, and Tempkin were used to observe the adsorption isotherm for the investigated dyes.

The Langmuir isotherms model assumes that adsorption occurs at the active sites of the adsorbent with monolayer adsorption and there is no interaction between the adsorbed dye molecules. The Langmuir isotherm equation is represented by Eq. (4) [42]:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$

where \(q_e\) is the amount of dye adsorbed at equilibrium time (mg of dye/g of MSW), \(Q_m\) is the maximum quantity of dye adsorbed (mg of dye/g of MSW), \(C_e\) is the concentration of the dye in the solution at equilibrium (mg of dye/L of solution) and \(K_L\) is called Langmuir constant (L/mg).

The Freundlich model considers multilayer adsorption with unequal available heterogeneous sites. These sites are associated with extraordinary energies of adsorption as a result of the interaction between adsorbed dye molecules. The Freundlich isotherm model can be expressed in Eq. (5) [43]:

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

(5)

where \(K_f\) is the capacity of the adsorbent and \(n\) is the adsorption intensity constant.

The third model is the Tempkin isotherm model. The model assumed that the heat of adsorption decreases linearly with coverage. The adsorption processes are characterized by binding energies uniform distribution, up to certain maximum binding energy [44]. This model can be described in Eq. (6):

$$q_e = B \ln K_T + B \ln C_e$$

(6)

where \(B\) is constant and equal RT/h, it is related to the heat of adsorption and \(K_T\) is the Tempkin’s constant measured in
Table 2 – Isotherm constants for Congo red and Dispersed red 60 dyes adsorption onto 0.5 g MSW at 25 □C and pH 7.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Temkin isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Qc (mg/g)</td>
<td>Ki (L/mg)</td>
<td>Kf (L/mole)</td>
</tr>
<tr>
<td>Congo red</td>
<td>238.6</td>
<td>166.9 \times 10^{-3}</td>
<td>36.779</td>
</tr>
<tr>
<td>Dispersed red 60</td>
<td>-166.6</td>
<td>359 \times 10^{-3}</td>
<td>103.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dye</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Congo red</td>
<td>0.58</td>
<td>36.779</td>
<td>0.9651</td>
</tr>
<tr>
<td>Dispersed red 60</td>
<td>1.5066</td>
<td>103.7</td>
<td>0.9892</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dye</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B (L/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Congo red</td>
<td>43.223</td>
<td>2.613</td>
<td>0.9095</td>
</tr>
<tr>
<td>Dispersed red 60</td>
<td>126.77</td>
<td>2.69</td>
<td>0.9631</td>
</tr>
</tbody>
</table>

L/mole which corresponds to the maximum binding energy. The absolute temperature T is measured in °K. R is the universal gas constant (8.314/\text{mol.} \text{K}).

The applicability of the three models for the CR and DR60 dyes adsorption process at different initial dye concentrations were estimated. Linear plots of C0/qe against C0, log qe against log C0, and qe against ln C0 were plotted. The linearized Freundlich, Langmuir, and Temkin isotherms are shown in Figs. 7-9. Table 2 represents the estimated model parameters with the correlation coefficients (Qc, Ki, Kf, and 1/n, Kf, B, and R2) for the three models. The values of R2 (correlation coefficient) are taken into consideration as a measure of the applicability and goodness of fit of the experimental data to the isotherm models.

The data in Table 2 confirm that CR and DR60 dyes adsorption does not follow Langmuir or Temkin isotherms. The value of R2 is the greatest in case of Freundlich isotherm indicating that the adsorption process follows approximately the Freundlich models. Hence the adsorption occurs as active sites on the adsorbent with multilayer adsorption and unequal available heterogeneous sites. As a result, different energies of the adsorption reactions appeared with a significant interaction between adsorbed molecules.

The observed correlation coefficients for Freundlich isotherms were 0.9651 and 0.9892 at 25 °C for CR and DR60 dyes, respectively. The n value, which is a stoichiometric coefficient, represents the number of dye molecules adsorbed per active site on MSW surface. The estimated n values of dye molecules adsorbed per site of MSW surface are 1.72 and 0.66 for CR and industrial DR60 dyes, respectively. The obtained values indicate that the adsorption of CR and DR60 occurs by multilayer adsorption and multi-anchorage adsorption mechanisms, respectively [45].

3.4. Adsorption kinetics

The adsorption kinetics of CR and industrial DR60 dyes over MSW are analyzed by four adsorption kinetic models namely, pseudo first order, pseudo-second order, simple Elovich kinetic, and Intraparticle diffusion models in order to explore the adsorption behavior and the steps that control its rate.

Fig. 10 – Pseudo-first-order sorption kinetics of dyes onto 0.5 g MSW at 25 °C and pH 7. (a) Congo red (b) Dispersed red 60.
3.4.1. Pseudo-first-order model

Pseudo-first-order rate equations usually portray the adsorption performance of adsorbate from the tested dye aqueous solution. It can be represented by Eq. (7) [46–48].

\[
\ln (q_e - q_t) = \ln q_e - kt
\]  

where \(q_e\) is the equilibrium adsorption quantity (mg/g), \(q_t\) is the amount of dye adsorbed at time \(t\) (mg/g), and \(K\) is the rate constant (min\(^{-1}\)). Pseudo-first-order model assumes that the rate of adsorption sites covering is proportional directly to the number of free active sites. The plot between \(\ln (q_e - q_t)\) and \(t\) gives a straight line relationship, as shown in Fig. 10, indicating that the model is applicable for the adsorption process. The rate parameters \((K, q_e, \text{and } R^2)\) were calculated as shown in Table 3. Fig. 10 illustrates the pseudo-first-order sorption kinetics of CR and industrial DR60 dyes over MSW for different initial dye concentrations (12.5, 25, 50 and 100 (mg/L)) of 1000 mL of each concentration and catalyst weight 0.5 g.

3.4.2. Pseudo-second-order model

This model considers that the adsorption rate is dependent on the square of the number of free active positions on the catalyst surface. The adsorption rate in the pseudo-second-order model can be expressed in Eq. (8) [49–51].

\[
\frac{t}{q_t} = \frac{1}{k_1q_e^2} + \frac{t}{q_e}
\]  

where \(k_1\) is the second order rate constant.

A plot of \(t/q_t\) versus \(t\) should give a straight line for the appropriateness of the second order kinetic and from which \(k_1, q_e, \text{and } R^2\) are estimated as shown in Table 3. Fig. 11 (a and b) illustrates the pseudo-second-order sorption kinetics of CR and industrial DR60 dyes over MSW at different initial dye

![Fig. 10](image-url)
concentrations (12.5, 25, 50 and 100 (mg/L)) of 1000 mL of each concentration and catalyst weight 0.5 g. It can be observed that straight lines are obtained for both dyes at different concentrations. This finding confirms the validity of the pseudo-second-order model for the adsorption processes of CR and DR 60 over MSW.

3.4.3. Intraparticle diffusion kinetic models

This model represents a transfer of dissolved ions from the solutions to the surface of adsorbent materials followed by intraparticle diffusion process [52]. Eq. (9) that describes this model can be written as the following:

\[ q_t = k_2 t^2 + I \]  

where \( k_2 \) is the intraparticle rate constant and \( I \) is the intercept, which is related to the boundary layer thickness.

A linear relationship of the plot of \( q_t \) versus \( t^2 \) indicates the applicability of this kinetic model. Consequently, the \( k_2 \), \( I \) and \( R^2 \) can be calculated as shown in Table 3. Fig. 12 (a and b) represents the intraparticle diffusion sorption kinetics of CR and industrial DR60 dyes over MSW for different dye concentrations.

3.4.4. Elovich kinetic model

If the adsorbent surfaces are not energetically homogeneous, Elovich model can be considered as a special case of the second-order kinetics [53]. The Elovich model equation can be expressed by Eq. (10) [53]:

\[ q_t = \frac{1}{\beta} \ln \alpha + \frac{1}{\beta} \ln t \]

where \( \alpha \) (mg/min) is the rate of initial adsorption at contact time \( t = 0 \) min and \( \beta \) (g/mg) is the extent of surface coverage and activated the energy.

Fig. 13 represents the Elovich sorption kinetics of CR and industrial DR60 dyes over MSW for different initial dye
concentrations. From the linear plots in Fig. 13 of \(q_t\) versus \(\ln t\), \(a\) and \(b\) constants can be calculated from the slope and intercept of the graph as shown in Table 3.

In conclusion, the linear fit of all kinetic models and the values of \(R^2\) in Table 3 show that the adsorption kinetics of the investigated dyes follows the second-order kinetic model. In addition, the experimental amounts of adsorbed dye (\(q_{\text{Exp}}\)) were found to be in agreement with the calculated amounts of adsorbed dye (\(q_e\)) obtained from the linear plots of pseudo-second-order model for all dyes concentrations. These findings revealed that the adsorption of CR and industrial DR60 dyes over MSW completely agrees with the pseudo-second-order kinetic model. The previous data recommended that the principal mechanism for this adsorption is the pseudo-order mechanism and generally the rate of sorption process seemed to be administrated by a chemical process including valence forces through sharing or exchange of electrons between adsorbed dyes and MSW adsorbent. In addition to that the rate constant of the process is reduced with increasing the initial concentration of the investigated dyes [36,54,55].

**Conclusion**

MSW produced from oil extraction industry could be considered a promising new green adsorbent to remove CR and DR60 dyes from wastewater. The new adsorbent contains effective organic ingredients that represent the synergetic effect for the adsorption process.

The adsorption of DR60 dye is not affected by catalyst weight, pH values, and the operating temperature. On the other hand, the adsorption rate of CR dye increases by increasing the temperature from 25 to 40°C. With further increases in the reaction temperature, the removal % decreases. The maximum amounts of dyes adsorbed were found to be 170.7 and 196.8 mg/g for CR and DR60 dyes, respectively at 100 mg/L, temperature 25°C and pH 7. The adsorption rate of CR dye increases by increasing pH values of the solution from 3 to 7 and decreases again with higher pH values.

The dye adsorption isotherms and kinetics were investigated and it was concluded from results that the adsorption process followed Freundlich isotherms and pseudo-second-order kinetics for both dyes.

The obtained data indicate that MSW can be proposed as a green cheap effective adsorbent for the removal of CR and DR60 dyes for wastewater treatment. Also, this concept considers a new approach for the conservation of traditional chemicals used for wastewater treatment. This concept will reduce the environmental impact of hazardous chemicals used for wastewater treatment.

**Conflicts of interest**

The authors declare no conflicts of interest.

**References**


