Adsorption efficiency evaluation for malachite green onto Apricot Kernel Shells: Kinetic, Isotherms and Thermodynamic

Accepted 2nd November, 2020

ABSTRACT

Adsorption is one of the efficient techniques for the remediation of waste water. The dye adsorption experimental data was analysed using various kinetic parameters such as isotherms, kinetics and thermodynamics models. Maximum adsorption capacities of malachite green was 270.889 mg/g at the pH 10, adsorbent dose 0.1 g, contact time 24 hours, 25°C and 100 mg/L initial concentration of the dye. The malachite green adsorption onto apricot kernel shells followed Langmuir isotherm model (Qmax=270.889). Pseudo second order the best explained the dye adsorption kinetics. Scanning electron microscopy (SEM) was used to follow the changes in the apricot kernel shells before and after adsorption.

Key words: Adsorption, isotherms, kinetics, thermodynamics.

INTRODUCTION

Dyes are widely used in many sectors such as paper, textile, cosmetic, leather and food. Every year there are large volume of dye contaminant effluents discharged in aqueous environment. In aqueous environment dyes can cause cancer, mutation, skin irritation and allergic dermatitis. It is necessary to treatment from the wastewater. There are many methods for the dye removal such as chemical oxidation, filtration, adsorption, aerobic/anaerobic degradation, coagulation and flocculation. Adsorption process can effectively remove dyes from wastewater. Activated carbon is the most effective and widely used adsorbent for the removal of textile effluents. However, it is high cost (Karagozoglu, 2007). A great number of researchers have studied for efficient and cheaper alternative substitutes to remove dyes from waste water such as agricultural waste (Kadirvelu, 2000; Demirbas, 2004), natural adsorbents (Sun, 2003; Chakraborty, 2005) and fly ash (Wang 2005; Wang 2006). The leading country for the production of apricot is Turkey. Malatya in Turkey has rich genetic resources for apricot. Also, it produces high quality dried apricot cultivars. On the other hand, Iran, Iraq, USA, India, Morocco, Spain, Italy, France and Pakistan produce apricot (Fadhil, 2017). The objective of this study was to evaluate the use of apricot kernel shells as an adsorbent for the removal of malachite green from aqueous solution by a batch method. Effects of various parameters such as initial dye concentration, pH and adsorbent dose were investigated. Both Langmuir and Freundlich methods were applied to the experimental data and SEM was used for changes in characteristics.

MATERIALS AND METHODS

Materials

Apricot kernel shells that are obtained from Yeşilyurt Malatya in Turkey were used for removal of malachite green from aqueous solutions. Shells were washed in pure water and dried under sunlight. Then, cut into small pieces. Figure 1 shows apricot kernel shells after shred. Malachite green was obtained from Carlo Erba Reagent. This dye used without any purification. Stock solution of malachite green was prepared in distilled water in room temperature pH values were adjusted by addition of 0.1 M HCl or NaOH. Properties of Malachite green are shown in Table 1.
Table 1: Properties of Malachite green.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>364.90</td>
</tr>
<tr>
<td>Color</td>
<td>Green</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>619</td>
</tr>
<tr>
<td>Dye purity</td>
<td>&lt;90%</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>( \text{C}<em>{23}\text{H}</em>{25}\text{ClN}_{2} )</td>
</tr>
</tbody>
</table>

Methods

The effect of pH, initial dye concentration, time and adsorbent dose were investigated by batch adsorption method. In each experiment 0.1 g of apricot kernel shells was put in a 250 mL flask and shaken in a shaker (VWR) at constant agitation speed 250 rpm. After shaken, liquid was separated from the shells by centrifugation. The remaining concentration of malachite green in solution was measured spectrophotometrically on a Shimadzu UV 1208 UV-visspectrophotometer. The pH of the dye solution was measured in digital pH meters (WTW 82362 Weilheim). The removal efficiency of malachite green dye was calculated as follows, Equation 1:

\[
\text{Dye Removal} (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)
\]

\( C_0 \): The initial dye concentration (mg/L)

\( C_t \): The dye concentration after sorption time t (mg/L) (10).

RESULTS AND DISCUSSION

Effect of pH

The pH controls the chemistry of the solution in the adsorption of the dye to the adsorbent. The pH effect was studied in the range of 2.6-10 for malachite green at adsorbent dose 0.1 g/30 mL of dye solution (100 mg/l) for 24 hours contact time and 250 rpm at 25°C. Figure 2 shows the effect. The maximum adsorption was achieved at pH value of 10 for malachite green. Similar results were gotten by Alkaim and Alqalaguly (2013). They prepared activated carbon from apricot stone and removal of basic yellow 28 from aqueous solution at pH 10. By increased the pH, the adsorption efficiency was increased.
The effect of initial dye concentration (100-1700 mg/L) for the removal of malachite green was carried out pH 10 at 24 hours. The initial concentration from 100-900 mg/L the amount of dye adsorbed increased. Similar results were reported for the dye adsorption such as astrazon yellow 7GL onto apricot stone activated carbon (Demirbaş E., 2008). The effect of dye concentration is shown in Figure 3.

Effect of adsorbent dose

Adsorption dose effect adsorption considerably and this can be seen in the study using a dose of 0.05-0.2 g range. The shells as an adsorbent showed the maximum adsorption capacity at 0.05 g. The adsorption dose was increased, the adsorption efficiency was decreased which might be due to the fact that the area of surface and binding sites were unavailable at higher dose. The aggregation of
adsorbent reduced the area of surface at a higher adsorbent
dose (Ishtiaq et al., 2020; Noreen et al., 2020; Tahir et al.,
2016). Figure 4 shows the effect of adsorbent dose.

**Effect of contact time**

The adsorption capacity for malachite green was recorded
to be 270.889 mg/g (Figure 5). The optimum contact time
is in the range of 10-150 min. The removal efficiency was
increased up to 10 min. The adsorption did not change
considerably. Initial adsorption increased owing to
availability of active sites, until equilibrium is attained
(Noreen et al., 2020; Tahir et al., 2016; Shoukat et al., 2017).
After that the adsorption did not increase owing to non-
availability of active sites for further adsorption of dye ions
and occupation of active sites on adsorbent surface (Tahir
et al., 2016).


**Figure 6: Langmuir Isothem.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>$K_L$ (L/g)</th>
<th>$a_L$ (L/mg)</th>
<th>$Q_{max}$ (mg/g)</th>
<th>$R^2$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apricot kernel shells</td>
<td>Malachite green</td>
<td>93.457</td>
<td>0.345</td>
<td>270.889</td>
<td>0.9999</td>
<td>This study</td>
</tr>
</tbody>
</table>

**Adsorption Isotherms**

Langmuir isotherm (Figure 6) is used to described monolayer adsorption processes, identical nature and homogeneous surface. For liquid phase adsorption, Langmuir model is commonly use in literature (Erdoğan, 2005). Both Langmuir and Freundlich isotherm models are selected for this study. Table 2 shows Langmuir constants. Langmuir isotherm equations are given as following equations:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e
\]

\[
q_e = \frac{Q_{max} a_L C_e}{1 + a_L C_e}
\]

Ce : The equilibrium concentration of adsorbate in solution after adsorption (mg/L)

$K_L$ (L/g); $a_L$ (L/mg) : Langmuir constants.

The Freundlich isotherm which is seen in Figure 7 does not assume monolayer capacity and describes equilibrium on heterogenous surfaces. Table 3 shows the Freundlich constant. Table 4 shows the comparison of apricot kernel shells performances from previous studies. Freundlich isotherm equation is given as following equations:

\[
q_e = K_F C_e^{\frac{1}{n}}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

$K_F$ (L/g) : The adsorption capacity

$1/n$ : Intensity of adsorption

**Adsorption Kinetics**

Three kinetic models which are pseudo first order, pseudo second order and intra particle diffusion, have been applied for the experimental data to analyze the adsorption kinetics of malachite green dyes. The kinetic parameter for pseudo second order model and correlation coefficient ($R^2$) was calculated and listed in Table 5. These results imply that the adsorption system studied follows pseudo second order kinetic model ($R^2$=1). The pseudo second order isorthem is seen in Figure 8. We studied three adsorption models however we presented pseudo second order model as follows:

\[
\frac{q_e}{q_{t}} = \frac{1}{K_{2,cal} q_{eq}^2} + \frac{1}{q_{eq}} t
\]

\[
\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt
\]
Table 3: Freundlich constant

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>( n_F )</th>
<th>( K_F )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apricot kernel shells</td>
<td>Malachite green</td>
<td>9.615</td>
<td>146.386</td>
<td>0.6446</td>
</tr>
</tbody>
</table>

Table 4: Comparison of apricot kernel shells performances from previous studies.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>Maximum adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apricot stone activated carbon</td>
<td>Congo red</td>
<td>23.42</td>
<td>Abbas and Trari, 2015</td>
</tr>
<tr>
<td>Apricot stone activated carbon</td>
<td>Tartrazine</td>
<td>76</td>
<td>Albroomi et al, 2017</td>
</tr>
<tr>
<td>Apricot stone activated carbon</td>
<td>Malachite green</td>
<td>83.33</td>
<td>Abbas and Aksil, 2017</td>
</tr>
<tr>
<td>Apricot stone</td>
<td>Disperse yellow 211</td>
<td>156.25</td>
<td>Erdoğan, 2017</td>
</tr>
<tr>
<td>Apricot stone activated carbon</td>
<td>Methylgreen</td>
<td>88.11</td>
<td>Abbas et al, 2018</td>
</tr>
<tr>
<td>Apricot stone activated carbon</td>
<td>Malachite green</td>
<td>116.27</td>
<td>Başar, 2006</td>
</tr>
<tr>
<td>Apricot stone activated carbon</td>
<td>Methylene blue</td>
<td>36.68</td>
<td>Djilani et al, 2015</td>
</tr>
<tr>
<td>Apricot shells</td>
<td>Methylene blue</td>
<td>24.31</td>
<td>Sotaric et al, 2015</td>
</tr>
<tr>
<td>Apricot kernel shells</td>
<td>Malachite green</td>
<td>270.889</td>
<td>This study</td>
</tr>
</tbody>
</table>

Table 5: Pseudo second order kinetic coefficient.

<table>
<thead>
<tr>
<th>Initial dye concentration (mg/L)</th>
<th>( q_e )</th>
<th>( k_{2,ad} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>29.761</td>
<td>0.250</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>59.880</td>
<td>0.099</td>
<td>1</td>
</tr>
<tr>
<td>300</td>
<td>90.090</td>
<td>0.082</td>
<td>1</td>
</tr>
<tr>
<td>400</td>
<td>120.481</td>
<td>0.062</td>
<td>1</td>
</tr>
</tbody>
</table>
qe: The amount of substance adsorbed per gram of adsorbent at equilibrium (mg/g)

qt: The amount of substance adsorbed by the gram of the adsorbent at any given moment (mg/g)

$k_{1,ad}$: Lagergren adsorption rate constant (dk⁻¹)

$k_{2,ad}$: Pseudo-second order adsorption rate constant (g/mg.dk)

k: Second order adsorption rate constant (g/mg.dk)

$q_{eq}$: Calculated amount of adsorbed substance (mg/g)

$k_1$, $k_2$ and k values are calculated by plotting log (qe/qt), t / qt and 1 / (qe/qt) values against the t value (20).

CONCLUSION

In this study, evaluation of apricot kernel shells as an adsorbent used for adsorption of malachite green from aqueous solution was carried out. First of all, apricot kernel shells were characterized with using SEM. Effect of pH, initial dye concentration and time were evaluated. Langmuir and Freundlich isotherm models were studied. The adsorption data fitted well the Langmuir isotherm for apricot kernel shells. Maximum adsorption capacity was 270.889 mg/g. Apricot kernel shells in this study have got highest adsorption capacity. The kinetics adsorption of malachite green onto apricot kernel shells in Malatya region was studied by using three kinetics models. The adsorption of malachite green from aqueous solution onto apricot shells follows pseudo second order kinetic model which provides the best correlation of the data. The results of this study showed that apricot kernel shells in Malatya region are potentially useful, low-cost and effective adsorbent for removal of malachite green from aqueous solution.

REFERENCES


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