High performance adsorption of hazardous triphenylmethane dye-crystal violet onto calcinated waste mussel shells
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ABSTRACT
Synthetic dyes are harmful to human beings, and the removal of colour from process or waste effluents is environmentally important. Crystal violet (CV) is a typical triphenylmethane dye, which is widely used in textile dyeing and paper printing industries. The present study shows that granulated and calcinated waste mussel shells (CWMS) can be used as a potential low-cost and locally available adsorbent for the removal of CV from aqueous solutions. The adsorption capacities of the CWMS for CV were investigated with respect to the effect of pH value, adsorbent dosage, contact time, initial dye concentration and temperature. Process variables were optimized, and a maximum dye adsorption of 482.0 mg/g was achieved at pH 6, 0.2 g/L adsorbent dosage, 220 min contact time and 25 °C for dye initial concentration of 100 mg/L. Adsorption kinetics and isotherms were followed by the pseudo-second order model and Freundlich isotherm models, respectively. Thermodynamic parameters demonstrated that adsorption of CV was spontaneous and endothermic in nature. The results indicated that the CWMS as a new adsorbent had the potential to serve in wastewater treatment applications, especially in the removal of CV from aqueous solutions.

Key words | adsorption, calcination, crystal violet, kinetics, mussel shells

INTRODUCTION
In recent years, as a result of the rapid increase of industrialization and urbanization, environmental problems such as water and air pollution have become a big problem in the world. One of these environmental problems is dyes present in the effluent of industrial plants. Most of the synthetic dyes used for colouring in different areas of industry such as textiles, paper and printing result in great damage to both the environment and living organisms (Sabna et al. 2018). In the dye industry, colour is described as the primary contaminant in the wastewater. Even though the concentration of a few dyes in effluent is less than 1 ppm, they are undesirable, toxic and carcinogenic pollutants (Gopi et al. 2016). Moreover, they are a hazard to aquatic life. As a cationic dye, crystal violet (CV) is one of the most used colouring agents in different industrial treatments. This dye is harmful for the living organisms exposed to it. Taking CV into the human body via respiration and the skin causes harmful diseases such as cancer and skin irritation (Mittal et al. 2010).

Mussel shells are found in different colours and shapes depending on where the mussels live. For this reason, there are many different species. When the shell characteristics of the mussel shells are examined, it is seen that there are many different layers from the inside to the outside (Bellotto & Miekeley 2007). It is known that the shell structure is rich in calcium mineral. Mussel shells are a major source of waste in some marine countries around the world. As a result of some studies on waste assessment, it has been determined that mussel shells can be effectively evaluated in different areas (Paradelo et al. 2016).
Different techniques and methods have been used to remove contaminants in wastewater including chemical, physical and biological treatments; however, these techniques have several disadvantages such as high requirements regarding equipment and energy. The adsorption technique has proven to be efficient at removing contaminants from wastewater. Many different materials and low-cost waste can be used in the adsorption process. A recent study has shown that mussel shell is efficient at adsorbing heavy metal and other pollutants (Pena-Rodriguez et al. 2013; Ramirez-Perez et al. 2013; Seco-Reigosa et al. 2013; El Haddad et al. 2014; Fernandez-Calvino et al. 2014; Garrido-Rodriguez et al. 2014; Paradelo et al. 2016).

The present study focused on the removal of CV dye molecules from aqueous solutions by adsorption on calcinated waste mussel shell (CWMS). The effects of pH, adsorbent dosage, initial dye concentration, temperature and contact time on the adsorption of the CV dye onto the CWMS were investigated. The experimental data were applied to the Langmuir and Freundlich models. Furthermore, kinetic studies of the adsorption were carried out using pseudo-first order, pseudo-second order kinetic models and the intraparticle diffusion model.

MATERIALS AND METHODS

CWMS and its characterization

The mussel shell calcination process was carried out as previously described by El Haddad et al. (2014). Mussel shells are waste obtained from the seafood processing industry in Bilecik, Turkey. CV supplied by Fluka was used as adsorbate (the structure is given in Figure 1).

Waste mussel shells were washed with tap and distilled water, respectively, and dried in an oven for about 24 h until all the water had disappeared. After a drying process, waste mussel shells were crushed into small particles. Powdered mussel shells were calcinated at 900 °C for 2 h with a heating rate of 5 °C/min. The calcinated residue was washed with distilled water and dried at 80 °C. This sample was powdered again, then washed several times with distilled water, and dried at 105 °C. A second calcination treatment was performed at 400 °C for 4 h with a heating rate of 2 °C/min.

The surface morphology of the CWMS was observed with a scanning electron microscope (SEM, Bruker, Germany). To analyse the carbon, oxygen and calcium element content of the CWMS, elementary characterization was carried out using an energy-dispersive spectroscopy (EDS, Bruker, Germany). The surface area of the CWMS was measured using a Micromeritics (ASAP 2020) BET (Brunauer, Emmett and Teller) instrument. The microstructure of the sorbent was characterized using physical adsorption/desorption of nitrogen at 77 K. Zeta potential measurements were carried out with a zeta potentiometer (Malvern Nano-ZS).

Batch experimental programme

The batch experimental adsorption studies were performed with 50 mL of dye solution with the known concentration, pH and adsorbent dosage in 100 mL Erlenmayer flasks. The flasks were agitated in a temperature controlled shaker (Termal H11960) at a constant speed of 120 rpm. Parameters affecting the adsorption process such as pH (4–11), adsorbent dosage (0.2–2.0 g/L), initial dye concentration (20–100 mg/L), contact time (up to 60 min) and temperature (25–55 °C) were studied in a batch system. Every 5 minutes, flasks were withdrawn from the shaker and the remaining dye concentrations were analysed using a UV-Visible spectrophotometer (Agilent Cary 60 UV-Vis). The UV-Vis spectrophotometer, which uses the relationship between absorbance and wavelength, was used to determine dye concentrations. Absorbance measurements of standard solution were performed at 200–800 nanometer wavelength range. An absorbance–wavelength plot was obtained from this scanning. According to the plot, the maximum absorbance for CV was determined as 590 nm.
All experiments were carried out in triplicate. The experimental data were reported by averaging these three measurements.

The amount of the dye adsorbed per unit mass of the adsorbent ($q_e$, mg/g) and the percentage removal of the dye were calculated using the following equations:

$$q_e = \frac{V(C_0 - C_e)}{m}$$ (1)

$$\text{Removal(\%)} = \frac{C_0 - C_e}{C_0} \times 100$$ (2)

where $C_e$ (mg/L) is the concentration of CV aqueous solution at the equilibrium state, $C_0$ (mg/L) is the initial concentration of CV in aqueous solution, $V$ is the volume of the dye solution (L) used in the experiments, and $m$ is the weight of the CWMS adsorbent (g).

### RESULTS AND DISCUSSION

#### Characterization

The surface characteristics affect the adsorption efficiency of the adsorbents. The surface morphology of the CWMS adsorbent was characterized using SEM. As can be seen from the enlarged view of Figure 2, the surface of the CWMS appears as spherical particles and their sizes are approximately 2 μm. Moreover, the figure shows that the shell surface is not homogeneous, with the existence of irregular forms.

Elemental analysis by EDS in point mode was conducted at the surface of the CWMS. It was determined that the CWMS contained significant amounts of calcium mineral. The mass fraction of calcium, carbon and oxygen were 41.12%, 4.84%, and 34.91%, respectively.

The value of zeta potential is a measure of the interaction between particles. The charge densities of the surfaces depend on the amount of ions present on the surface. In adsorption experiments, the adsorption mechanism is between surfaces with different charge. Zeta potential is used to determine the charge of the surfaces. In the current study, the CWMS were analysed to determine their zeta potential value. From the obtained results, it was determined that shells had a negative zeta potential value. As a result, the shell could interact with positive charged surfaces.

$N_2$ adsorption measurement indicated that the BET surface area of the CWMS was 7.6139 m²/g.

### Effect of pH

The pH of the solution affects the surface charge on the adsorbent as well as on the adsorbates in the adsorption process. The effect of pH on the adsorption of the CV dye by the CWMS was studied by varying the initial pH of the dye solution from pH 4 to pH 11. The time required for adsorption to reach equilibrium was determined for each pH value. This part of the experimental studies was carried out by 2 g/L adsorbent dosage, 60 mg/L initial dye concentration at 25 °C. To determine adsorption capacities and removal efficiencies, the adsorption process was followed for 220 min at each pH value. At all experimental pH values, the adsorption capacities of the CWMS were about 28 ± 1 mg/g and removal efficiencies were approximately 95.67 ± 1%.

CV as a basic dye has a pKa value of 0.8 (Kumari et al. 2017). The adsorption process exhibited similar behaviour due to the low pKa value of the CV dye. The dye can be ionized at all experimental pH values and exists as a cationic species (Kumari et al. 2017). Thus, all the adsorption studies were carried out at pH 6 which is the natural pH of the dye solution.

### Effect of adsorbent dosage

Adsorption dosage influences the adsorption process by affecting the adsorption capacity of the adsorbent. As seen in Figure 3, the adsorption capacity of the CWMS for the
CV dye decreases from 272.2 mg/g to 28.6 mg/g when the adsorbent dosage increases from 0.2 g/L to 2 g/L. The decrease in adsorption capacity with increasing adsorbent dosage might be due to the aggregation of the adsorption sites by the adsorbent particles. The phenomenon leads to a decrease in total surface area of the particles required for the adsorption process (Ahmad & Mirza 2018).

Effect of initial dye concentration and contact time

Adsorption time is a very important factor in all adsorption processes. A quick uptake of contaminant and reaching equilibrium in a short time signifies the efficiency of the adsorbent. Figure 4 shows the effect of contact time on the adsorption of the CV dye onto the CWMS at various initial dye concentrations (20–100 mg/L). As shown in Figure 4, for all the initial concentrations, the adsorption amounts of the CV on the CWMS increase rapidly with an increase in time and then become slower until equilibrium is reached. The adsorption capacities of the CV reach maximum at 220 min.

Adsorption kinetic models

Three kinetic models, the Lagergren pseudo-first order, pseudo-second order and intraparticle diffusion models were chosen to explain the adsorption mechanism of the CV dye on the CWMS.

The Lagergren pseudo-first order model can be expressed as (Lagergren 1898):

\[ \log\left(\frac{q_e}{q_t}\right) = \log\frac{q_e}{k_1} \frac{1}{2.303} + \frac{1}{k_1}t \]  

where \( k_1 \) (min\(^{-1}\)) is the pseudo-first order rate constant and \( t \) (min) is time. The values of \( k_1 \) and \( q_e \) were calculated from the slope and intercept of the linear plots obtained by graphical representation of \( \log\left(\frac{q_e}{q_t}\right) \) versus \( t \) (Figure 5(a)).

The pseudo-second order kinetic model can be represented in the following linear form (Ho & McKay 1999):

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \]  

where \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second order rate constant of the adsorption. The values of \( q_e \) and \( k_2 \) were calculated from the slope and intercept of the linear plots obtained by graphical representation of \( t/q_t \) versus \( t \) (Figure 5(b)).

The intraparticle diffusion model can be expressed as follows (Weber & Morris 1963):

\[ q_t = k_i t^{0.5} + c \]  

where \( k_i \) is the intraparticle diffusion rate constant (mg g\(^{-1}\) h\(^{-1/2}\)) and \( c \) is a constant (mg g\(^{-1}\)). The plot of \( q_t \) versus \( t^{0.5} \) should give the \( k_i \) and \( c \) values from the slope and intercept of the plot, respectively (Figure 5(c)).

The kinetic parameters and correlation coefficients \( R^2 \) for the pseudo-first, pseudo-second order kinetic models and intraparticle diffusion model are summarized in Tables 1 and 2. As seen in these tables, the adsorption kinetic results follow the pseudo-second order model better than the other models which is indicated by higher \( R^2 \) values. Moreover,
the experimental values $q_{e,\text{exp}}$ are very similar to the values obtained in the pseudo-second order kinetic model $q_{e,\text{cal}}$ according to Table 1. This model shows that the removal of the CV dye from a solution by the CWMS is due to physicochemical interactions between the two phases (Ho & McKay 1999).

**Adsorption isotherms**

Adsorption isotherms are used to explain how the adsorbate molecules interact with adsorbent and attain equilibrium. In order to explore the adsorption mechanism of CV dye onto the CWMS, the Langmuir and Freundlich isotherm models were used in the current study.

The Langmuir isotherm is based on the assumption that adsorption takes place at specific equal sites within the adsorbent. The monolayer adsorption model suggests that an adsorbate molecule occupies a particular site and no further adsorption takes place at that site. The Langmuir isotherm can be presented in the following linear form (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{C_0}{q_{\text{max}}} + \frac{1}{q_{\text{max}}K_L}$$

(6)

Table 1 | Parameters of the Lagergren pseudo-first order and pseudo-second order models for adsorption of the CV dye onto the CWMS

<table>
<thead>
<tr>
<th>Initial CV concentration (mg/L)</th>
<th>$q_{e,\text{exp}}$ (mg/g)</th>
<th>$q_{e,\text{cal}}$ (mg/g)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_{e,\text{cal}}$ (mg/g)</th>
<th>$k_2$ (g.mg$^{-1}$min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>94.1</td>
<td>142.9</td>
<td>0.021</td>
<td>0.9600</td>
<td>144.9</td>
<td>6.090</td>
<td>0.9902</td>
</tr>
<tr>
<td>40</td>
<td>190.6</td>
<td>212.0</td>
<td>0.025</td>
<td>0.9855</td>
<td>222.2</td>
<td>0.144</td>
<td>0.9905</td>
</tr>
<tr>
<td>60</td>
<td>287.1</td>
<td>194.5</td>
<td>0.017</td>
<td>0.9673</td>
<td>312.5</td>
<td>0.139</td>
<td>0.9913</td>
</tr>
<tr>
<td>80</td>
<td>385.7</td>
<td>180.5</td>
<td>0.028</td>
<td>0.9587</td>
<td>400.0</td>
<td>0.279</td>
<td>0.9987</td>
</tr>
<tr>
<td>100</td>
<td>482.0</td>
<td>180.9</td>
<td>0.032</td>
<td>0.9370</td>
<td>500.0</td>
<td>0.315</td>
<td>0.9992</td>
</tr>
</tbody>
</table>

Figure 5 | Pseudo-first order (a) pseudo-second order (b) and intraparticle diffusion model (c) plots for the CV dye adsorption onto the CWMS.
where \( q_e \) and \( q_{\text{max}} \) (mg/g) are the equilibrium and maximum adsorption capacity, respectively. \( K_L \) (L/mg) is the Langmuir constant and \( C_e \) (mg/L) is the equilibrium concentration. The values of \( q_{\text{max}} \) and \( K_L \) were calculated from the slope and intercept of the linear plot \( C_e/q_e \) versus \( C_e \) (Figure 6(a)).

The Freundlich model assumes that the adsorption takes place on heterogeneous surfaces and the distribution of the heat on the adsorbent surface is nonuniform. The Freundlich isotherm can be expressed by the equation (Freundlich 1906; Freundlich & Heller 1939):

\[
\ln q_e = \left( \frac{1}{n} \right) \ln C_e + \ln K_F
\]

(7)

where \( K_F \) and \( n \) are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The values of \( n \) and \( K_F \) were calculated from the slope and intercept of the linear plot \( \ln q_e \) versus \( \ln C_e \) (Figure 6(b)).

The parameters for isotherm models of the CV dye adsorption onto the CWMS are listed in Table 3. The Freundlich isotherm model showed the best fit of the isotherm data with higher correlation coefficients \( (R^2) \), indicating that dye adsorbed onto the heterogeneous surface of the CWMS was a multilayer formation.

**Effect of temperature and thermodynamic parameters**

The effect of temperature on the CV adsorption of the CWMS was investigated using thermodynamic functions. Thermodynamic parameters such as free energy change \( (\Delta G^\circ) \), enthalpy change \( (\Delta H^\circ) \) and entropy change \( (\Delta S^\circ) \) were estimated using the following formulas (Liu & Lee 2014):

\[
\Delta G^\circ = -RT \ln K_C
\]

(8)

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

(9)

\[
\ln K_C = \left( \frac{\Delta S^\circ}{R} \right) - \left( \frac{\Delta H^\circ}{RT} \right)
\]

(10)

\[
K_C = q_e/C_e
\]

(11)

The values of \( \Delta H^\circ \) and \( \Delta S^\circ \) were calculated from slope and intercept of the plot of \( \ln K_C \) against \( 1/T \). Table 4

<table>
<thead>
<tr>
<th>Initial CV concentration (mg/L)</th>
<th>( K_{\text{int,1}} ) (mg g(^{-1}) min(^{-0.5}))</th>
<th>( C_1 ) (mg/g)</th>
<th>( R_1^2 )</th>
<th>( K_{\text{int,2}} ) (mg g(^{-1}) min(^{-0.5}))</th>
<th>( C_2 ) (mg/g)</th>
<th>( R_2^2 )</th>
<th>( K_{\text{int,3}} ) (mg g(^{-1}) min(^{-0.5}))</th>
<th>( C_3 ) (mg/g)</th>
<th>( R_3^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7.9453</td>
<td>-13.264</td>
<td>0.9953</td>
<td>8.6609</td>
<td>-15.277</td>
<td>0.9861</td>
<td>3.8478</td>
<td>38.511</td>
<td>0.8992</td>
</tr>
<tr>
<td>40</td>
<td>6.2845</td>
<td>70.62</td>
<td>0.7237</td>
<td>17.782</td>
<td>-5.4144</td>
<td>0.9864</td>
<td>2.6373</td>
<td>152.49</td>
<td>0.9116</td>
</tr>
<tr>
<td>60</td>
<td>2.1947</td>
<td>180.26</td>
<td>0.9831</td>
<td>16.334</td>
<td>82.206</td>
<td>0.9435</td>
<td>5.4856</td>
<td>205.77</td>
<td>0.9572</td>
</tr>
<tr>
<td>80</td>
<td>5.08</td>
<td>269.9</td>
<td>0.9995</td>
<td>19.838</td>
<td>180.79</td>
<td>0.9634</td>
<td>0.9972</td>
<td>370.65</td>
<td>0.9175</td>
</tr>
<tr>
<td>100</td>
<td>3.8135</td>
<td>374.08</td>
<td>0.9266</td>
<td>20.102</td>
<td>278.13</td>
<td>0.9586</td>
<td>0.3022</td>
<td>477.26</td>
<td>0.8879</td>
</tr>
</tbody>
</table>

**Figure 6** | Langmuir (a) and Freundlich (b) adsorption isotherms of the CV adsorption by the CWMS with initial dye concentration in the range of 20–100 mg/L (adsorption conditions: pH 6; adsorbent dosage 0.2 g/L; temperature 25 °C; contact time 220 min).
The data presented in Table 5 compare the adsorption capacities of various adsorbents for CV dye. The comparison shows that the CWMS have a higher adsorption capacity of CV than many of the other reported adsorbents. Furthermore, the CWMS as adsorbents are quite cheap materials. Thus, it can be stated that the CWMS are attractive and economical adsorbents which can be used for treatment of wastewater containing CV dye.

**CONCLUSION**

In the present study, the adsorptions of the CV dye onto the CWMS were studied by batch tests conducted under various experimental conditions, such as pH, contact time, initial dye concentrations and temperature. The optimum conditions maintained to remove the CV dye by the CWMS were: pH 6, adsorbent dosage 0.2 g/L, and temperature at 25 °C of 100 mg/L of the CV. The maximum adsorption capacity was found to be 482.0 mg/g. The pseudo-second order kinetic model and Langmuir isotherm model were found to describe the adsorption mechanism.

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