Performance of new mesoporous carbon sorbent prepared from grape industrial processing wastes for malachite green and congo red removal

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ABSTRACT
Sorptive properties of a novel activated carbon (GWAC) prepared at optimized conditions from grape processing waste (GW) by ZnCl2 activation were tested using the textile dyes as cationic dye, malachite green (MG) and anionic dye, congo red (CR), from aqueous solutions. Batch experiments were conducted to study the effects of sorbent dose, initial dye concentration, agitation time and temperature at natural pH of dyes in aqueous solution on GWAC-dyes sorption systems. Equilibrium sorption isotherms and kinetics were investigated. The equilibrium experimental data were analyzed by the Langmuir and Freundlich models. Kinetic experiments revealed that the sorptions of MG and CR onto GWAC can be described with pseudo-second order model and the equilibrium isotherm data were well described by the Langmuir model. The sorption diffusion mechanisms were determined from the intra-particle diffusion model. Thermodynamic parameters showed that the process was spontaneous and endothermic. The sorption capacities of GWAC for the MG and CR removal were found to be 667 and 455 mg/g, respectively. These results clearly indicate the efficiency of GWAC as a promising sorbent for treatment of wastewater containing MG and CR.

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1. Introduction
In recent years, the developments took place in the industry have caused many problems especially in the contamination of environment. These contaminants include dyes, heavy metal, organic pollutants, etc. There has been an increasing interest among scientists to cope with these environmental problems caused by untreated or partially treated industrial effluents. It is known that many industries such as paper, textile, plastics and leather as well as cosmetic and pharmaceutical industries use dyes to color their products. Therefore, the major impact of these industries on the environment is discharging their colored effluents into natural water bodies (Cengiz et al., 2012). The textile manufacturing industry alone discharges about 1,46,000 t of dyes per year along with its wastewater that ultimately finds its way into the environment. Generally, concentrations of the wastewater containing dye range from 10 to 200 mg/L. The discharge of dye containing effluents into the natural water bodies can pose hazardous effects on the living systems because of carcinogenic, mutagenic, allergenic and toxic nature of dyes (Chowdhury et al., 2011). Therefore, it has been necessary to remove these contaminants from water bodies and the environment.

Furthermore, it is necessary to remove dyes from industrial effluents before discharging them into the environment in order to reduce all these harmful effects of dyes. In fact several physical, chemical and biological decolorization methods were developed including sorption, coagulation, flocculation,
chemical oxidation, membrane filtration, ozonation, photo-degradation and anaerobic treatment. Therefore, there is an increasing demand for efficient and low-cost technologies in order to remove dyes from natural resources such as water in the world. Sorption has been proven to be an efficient process for dye removal due to its low cost, high sorption capacity, and environmental friendliness. Porous materials, particularly activated carbon (AC), have been commonly used as sorbents for dye removal from wastewaters (Liao et al., 2012).

ACs are well known for their expanded surface areas and large total pore volumes. This is why they show large sorption capacities when they are in both gaseous and liquid phases. However, due to their high production costs, these materials seem to be more expensive than other sorbents. This has led a growing research interest in the production of activated carbons from renewable and cheaper precursors. The choice of precursor depends on mainly its availability, cost, and purity. However, the manufacturing process and intended applications of the product are also important factors. Therefore, in recent years, various kinds of activated carbon have been prepared from low-cost precursor materials, which are predominantly biomass wastes, for the cationic and anionic dyes removal. To the best of our knowledge, the present study is the first one to study the sorption of the textile dyes as cationic and anionic dyes from aqueous solutions by a novel AC (GWAC) prepared at optimized conditions from grape processing waste (GW) by ZnCl₂ activation.

The objective of this study is to examine the sorptive properties of GWAC for the textile dyes as cationic dye, mala-chite green (MG) and anionic dye, congo red (CR), removal from aqueous solutions. Optimum sorption conditions were determined according to the effects of sorbent dose, initial dye concentration, agitation time and temperature at natural pH of GWAC-MG/CR sorption systems in order to increase the reliability of the study. Sorption kinetics, isotherms and thermodynamics were also evaluated and reported. Furthermore, the GWAC, before and after sorptions of MG and CR, was compared with scanning electron microscopic (SEM), Fourier transform infrared spectroscopic (FT-IR) and X-ray photoelectron spectroscopic (XPS) analysis to brighten the corresponding sorption mechanisms.

2. Materials and methods

2.1. Materials

GWAC was prepared by ZnCl₂ (purchased from Sigma-Aldrich) activation using GW, collected from a local wine factory located in Turkey, as a precursor. Its preparation, effects of preparation parameters, some physico-chemical characterizations, production yield and cost-estimation were discussed in our previous study (Saygılı et al., 2015). It’s some physico-chemical characteristics are given in the Table 1. MG and CR were obtained from Sigma-Aldrich Company. The general characteristics of MG and CR are given in Table 2. All the chemicals used were of analytical grade.

2.2. Batch sorption experiments

2.2.1. Optimization studies of MG and CR sorption conditions

Sorption experiments were conducted in 50 mL Erlenmeyer flasks. They were shaken at 120 rpm for the time required in a water bath shaker (Daihan-WSB-30). The effects of various operating parameters such as sorbent dosage (0.01–0.05 g), initial concentration of dyes (200–400 mg/L), contact time (5–480 min) and temperature (25–55 °C) on sorption at natural pH (4.0 for MG; 6.95 for CR) level in aqueous solutions of both dyes were studied by varying the parameters under study and keeping other parameters constant. The residual concentrations of MG and CR after sorption process were analyzed by a UV–vis spectrophotometer (Perkin Elmer-Lambda 25) at maximum wavelengths.

The surface physical morphologies of GWAC before and after MG and CR sorptions were identified by using SEM technique (JEOL, JSM-6335F, USA). FT-IR spectrum of the activated sludge was recorded with a PerkinElmer spectrum 100 spectrophotometer within the scanning range of 4000–650 cm⁻¹. The XPS measurements were performed using an XPS spectrometer (XPS, Thermo Scientific K-alpha) with an Al Kα monochromatized source.

2.2.2. Kinetic studies

For kinetic studies, 10 mg of GWAC was added into 50 mL of dye solutions with initial concentrations between 200 and 400 mg/L, temperature of 25 °C and agitation speed of 120 rpm at the natural pH (4.0 for MG; 6.95 for CR) of MG/CR-GW/AC sorption systems. At predetermined time intervals (5–480 min), 10 mL samples were taken out and filtered. The amount of sorption, qₜ (mg/g), at time t (min), was calculated by using Eq. (1) given below.

\[ qₜ = \frac{(C₀ - Cₜ)V}{m} \]

where, C₀ and Cₜ (mg/L) are concentrations of dye at initial and time t, respectively. V is dye volume of the solution (L), and m is the mass of sorbent (g). In this study, two kinetic models namely, pseudo-first order (Lagergren, 1898) and pseudo-second order (Ho and McKay, 1998) models were tested to find the best-fitted model for the experimental kinetic data. Besides, to elucidate the diffusion mechanism, the kinetic results were analyzed and fitted to the intra-particle diffusion model (Weber and Morris, 1963). The linearized kinetic equations used are as follows:

Pseudo – first order : \( \ln(q_e - q_t) = \ln q_e - k₁ t \) (2)

Pseudo – second order : \( \frac{t}{q_t} = \frac{1}{k₂q_e^2} + \frac{1}{q_e} t \) (3)

Intra – particle diffusion : \( q_t = k₃d₁^{1/2} + I \) (4)

where, k₁ (1/min) and k₂ (g/mg min) are the rate constants of first-order and second-order, respectively. k₃ (mg/g min¹/²) is the intra-particle diffusion rate constant, and I (mg/g) is a constant that gives an idea about thickness of the boundary layer. A value of I close to zero indicates that diffusion is the only controlling step of the sorption process. Besides, the value of correlation coefficient, R², the applicability of the kinetic models to describe the sorption process was further validated by normalized standard deviation, Δq (%), which is defined as:

\[ Δq(%) = \sqrt{\frac{\sum_{i=1}^{N} \left( \frac{q_{exp} - q_{calc}}{q_{exp}} \right)^2}{N - 1}} \times 100 \] (5)
Table 1 – Physico-chemical characteristics of GWAC (Saygılı et al., 2015).

<table>
<thead>
<tr>
<th>Ultimate Analysis (dry basis, %)</th>
<th>Proximate analysis (dry basis, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Carbon</td>
</tr>
<tr>
<td>Ash</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Yield</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Burn off</td>
<td></td>
</tr>
<tr>
<td>Textural characteristics</td>
<td></td>
</tr>
<tr>
<td>S_{BET}(m^2/g)</td>
<td>Surface chemical characteristics</td>
</tr>
<tr>
<td>V_{mic}(cm^3/g)</td>
<td></td>
</tr>
<tr>
<td>V_{mes}(cm^3/g)</td>
<td></td>
</tr>
<tr>
<td>V_{tot}(cm^3/g)</td>
<td></td>
</tr>
<tr>
<td>V_{mic} (%)</td>
<td></td>
</tr>
<tr>
<td>V_{mes} (%)</td>
<td></td>
</tr>
<tr>
<td>V_{tot} (%)</td>
<td></td>
</tr>
<tr>
<td>P(Å)</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>pH_{pzc}</td>
<td></td>
</tr>
<tr>
<td>Acidity (meq/g)</td>
<td></td>
</tr>
<tr>
<td>Basicity (meq/g)</td>
<td></td>
</tr>
<tr>
<td>Lactonic (meq/g)</td>
<td></td>
</tr>
<tr>
<td>Carboxylic (meq/g)</td>
<td></td>
</tr>
<tr>
<td>Phenolic (meq/g)</td>
<td></td>
</tr>
<tr>
<td>(mg/g)</td>
<td></td>
</tr>
<tr>
<td>% mesopore</td>
<td></td>
</tr>
<tr>
<td>% micropore</td>
<td></td>
</tr>
</tbody>
</table>

* By difference.

(SBET: BET surface area; Vtott: total pore volume; Vmic: micropore volume; Vmes: mesopore volume; Vmics(%) : micropore contribution; Vmes(%) : mesopore contribution; DP: average pore diameter; pHpzc: point of surface zero charge)

where, N is number of the data points, \( q_{e,\text{exp}} \) and \( q_{e,\text{cal}} \) (mg/g) are the experimental and calculated sorption capacities, respectively. The higher the value of \( R^2 \) and lower the value of \( \Delta q^2 \), the more accurate is the model that predicts the experimental data.

2.2.3. Equilibrium studies

Equilibrium studies were conducted at various temperatures by using several solutions with different concentrations of both dyes under optimized sorption conditions determined before. The amount of dye sorbed onto per gram of sorbent, \( q_e \) was calculated by using Eq. (6).

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

where, \( C_e \) is dye concentration at equilibrium (mg/L). In this study, two famous isotherm models, namely the Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherm models, were applied to the experimental equilibrium data at different temperatures ranging from 25 °C to 55 °C. The linearized isotherm equations used are as follows:

Freundlich isotherm: \( \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \) (7)

Langmuir isotherm: \( \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m C_e} \) (8)

where, \( q_m \) (mg/g) is the Langmuir maximum sorption capacity of sorbate per unit mass of sorbent, \( b \) (L/mg) is Langmuir constant related to the sorption equilibrium. \( K_F \) (meq/g) (L/mg)^1/n) and \( n \) are Freundlich constants that give a measure of sorption capacity and intensity, respectively.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, \( R_L \) given by (Hall et al., 1966):

\[
R_L = \frac{1}{1 + bC_0}
\]

\( R_L \) indicates the type of isotherm to be reversible \( (R_L = 0) \), favorable \( (0 < R_L < 1) \), linear \( (R_L = 1) \) or unfavorable \( (R_L > 1) \).

Besides, sorption equilibrium studies at various temperatures could also provide valuable information about sorption thermodynamics. Thermodynamic behaviors were interpreted by the thermodynamic parameters including the change in \( \Delta G^0 \), \( \Delta H^0 \) and \( \Delta S^0 \). These parameters are calculated by the following equations (El-Sayed, 2011):

\[
\Delta G^0 = -RT \ln K
\]

Table 2 – General characteristics of MG and CR dyes.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Malachite green (MG)</th>
<th>Congo red (CR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₂₃H₁₁₂Cl₂N₂</td>
<td>C₂₂H₁₀₂N₂O₂S₂</td>
</tr>
<tr>
<td>C.I. number</td>
<td>42000</td>
<td>22120</td>
</tr>
<tr>
<td>C.I. name</td>
<td>Basic green 4</td>
<td>Direct red 28</td>
</tr>
<tr>
<td>Chemical class</td>
<td>Cationic</td>
<td>Anionic</td>
</tr>
<tr>
<td>Ionization</td>
<td>Basic</td>
<td>Acidic</td>
</tr>
<tr>
<td>Dye content (%)</td>
<td>99.7</td>
<td>≥85</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>364.90</td>
<td>696.67</td>
</tr>
<tr>
<td>( \lambda_{max} ) (nm)</td>
<td>617</td>
<td>497</td>
</tr>
</tbody>
</table>
Fig. 1 – Effect of adsorbent dose (a), contact time/initial concentration (b), ionic strength (c) and temperature (d) on the sorption of MG and CR onto GWAC.

\[
\ln K = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(11)

where, \( K \) equals to \( q_{\text{eq},b} \), the equilibrium constant of the sorption process. \( R \) and \( T \) are the universal gas constant (8.314 J/mol K) and absolute temperature, respectively.

2.3. Regeneration studies

Regeneration studies are essential to evaluate the reusability of sorbents for practical applications due to stringent ecological and economic demand for sustainability (Sun et al., 2011). In this study, desorption studies were conducted in ethanol solution for each dye. For this purpose, GWAC was first loaded with dye by mixing 20 mg of sorbent with 50 mL of 100 mg/L of dye solution for an hour at 25°C. The sorbent was removed from the solution, and the sorption capacity for each dye was determined. Then, the dye loaded sorbent was washed with ultrapure water and dried. Thereafter, the dye-loaded GWAC was mixed with ethanol solution (50%, V/V) for 1 h at 298 K. This sorption-desorption cycle was repeated for five times.

3. Results and discussion

3.1. Optimization of MG and CR sorption conditions

3.1.1. Effect of GWAC dose

Different amounts of GWAC (varying from 0.01 to 0.05 g/50 mL) were added into MG and CR solutions with an initial concentration of 100 mg/L to observe the effect of sorbent dose on dye sorption. The mixtures were shaken in 50 mL stoppered flasks at temperature 25°C, natural pH in aqueous solution of both dye and stirring speed of 120 rpm until the equilibrium time was reached. As presented in Fig. 1a, amounts of both dyes sorbed onto the GWAC were found to be decreasing with increasing sorbent dose. This may be due to either the flux or the solute concentration gradient between the solution and the sorbent surface (Liu et al., 2014) or reduction in total sorption surface area available to both dyes resulting from overlapping or aggregation of sorption sites, and an increase in diffusion path length (Porkodi and Kumar, 2007). Based on these results, optimum dose for further studies was chosen as 0.01 g/50 mL for MG and 0.02 g/50 mL for CR.
3.1.2. Effect of dyes used onto GWAC at different initial concentrations was studied as a function of contact time in order to determine the necessary sorption equilibrium time. For this reason, sorption of both dyes onto GWAC at various initial concentrations was studied as a function of contact time in order to determine the appropriate sorption equilibrium time. Furthermore, MG and CR solutions with initial concentrations of 200–400 mg/L were agitated with 0.01 g and 0.02 g of GWAC, respectively, at natural solution pH values of MG/CR-GWAC systems. As it can be seen in Fig. 1b, the effects of contact time and initial concentration on sorption of dyes by GWAC and the sorption at different dye concentrations are rapid at the initial stages, and then it proceeds slowly until reaching the equilibrium. The rapid sorption at the initial contact time may be due to the presence of several active sites and functional groups available on the sorbent at the initial stage. The slow rate of dye sorption is probably due to the slow pore diffusion of the solute ion into the bulk of the sorbent (Chen et al., 2010). As shown in Fig. 1b, the contact time needed for MG and CR solutions to reach equilibrium was 120 min and 180 min, respectively. However, longer equilibrium time was required for higher initial concentration values of MG and CR solutions and the time required for equilibrium sorption of MG was a little longer than that of CR. The higher concentration solution of dyes employed, the longer equilibrium time was needed. From the contact time studied, it was revealed that 180 min of agitation time is sufficient to reach equilibrium when 100 mg/L of dyes concentration was employed. Therefore, for further studies, equilibrium time of 180 min was selected for the sorption of both dyes. It was also observed that an increase in initial dye concentrations resulted in increased dye uptake. As it can be seen in Fig. 1b, sorption curves were single, smooth and continuous leading to saturation. It indicated the possible monolayer coverage on the surface of the sorbent by the dye molecules (Alkan et al., 2008). The sorption capacity at equilibrium increased from 135.43 to 260.22 mg/g with an increase in the initial MG concentrations from 200 to 400 mg/L. In addition, the sorption capacity of sorbed at equilibrium increased from 110.12 to 165.60 mg/g with an increase in the initial CR concentrations from 200 to 400 mg/L, respectively.

3.1.3. Effect of ionic strength

The effect of ionic strength on the sorption capacities of MG/CR onto GWAC was studied at 0–0.5 mol/L of NaCl concentrations at 298 K and natural solution pH values of both dyes. Fig. 1c shows the effect of ionic strength on both dyes sorption. As it can be seen in this figure, increasing ionic strength has significantly increased the sorption capacity of both dyes. However, this increase in CR sorption is greater

Fig. 2 – Linear pseudo-first order (a), pseudo-second order (b) and intra-particle diffusion (c) kinetic plots for the sorption of MG and CR at different initial concentrations onto GWAC.
than the increase in MG. The values of $q_e$ increased from 80.85 to 111.79 mg/g and 27.95 to 86.99 mg/g for the GWAC-MG and GWAC-CR sorption systems, respectively, as the concentration of NaCl increased from 0 to 0.5 mol/L.

The increased MG sorption is attributed to the high owing to the partial neutralization of positive charge on the GWAC surface and a consequent compression of the electrical double layer by the Cl⁻ anion. The chloride ion also enhances sorption of MG dye ions by pairing their charges, and hence reducing the repulsion between MG ions sorbed on the surface. This initiates GWAC to sorb more positive MG ions. Similar explanations were stated by some other researchers (Guo et al., 2003; Baskaran et al., 2011). The increase in sorbed amount of CR was due to the increase in the electrostatic interaction between CR and GWAC caused by the increase in positive charges of the GWAC surface with increased ionic strength. Similar explanations have been given by other researchers for CR sorption onto some sorbents (Hu et al., 2010).

3.1.4. Effect of temperature
In order to determine whether the dye sorption process was endothermic or exothermic, the effect of temperature on the sorption capacities of MG and CR onto GWAC were investigated at 25, 35, 45 and 55 °C over a range of initial dye concentrations, while other optimum operating parameters were kept constant. The results are displayed in Fig. 1d. As seen in this figure, sorption increased with an increase in the temperature for both, which indicates that these processes were endothermic. The shape of isotherms indicates high affinity between GWAC surface and dye molecules. The experimental equilibrium points rise sharply in the initial stages, low $C_e$ and $q_e$ values, thus indicating that there are plenty of readily accessible sites and there is a great affinity of GWAC for MG molecules. The sorbent is saturated when the plateau is reached. The decrease in the slope of isotherm is due to the fewer active sites available at the end of the sorption process. The sorption isotherms of CR show similar tendencies as sorption isotherms of MG do. However, the sorption capacities of MG at studied temperatures are much higher than of CR. This difference is mostly related to higher affinity of MG for the sorbent surface than CR.

3.2. Kinetic modeling

The experimental kinetic data have been plotted as sorbed amounts vs. contact time as shown in Fig. 1b. The applied linear form equations (Eqs. (2) and (3)) of pseudo-first order and pseudo-second order kinetic models were used to correlate the experimental kinetic data. The kinetic parameters related to pseudo-first order and pseudo-second order kinetic models were obtained according to the intercept and slope from the plots between $\ln(q_e - q_t)$ vs. $t$ and $1/t$ vs. $t$, respectively (Fig. 2a and b). The applicability of the kinetic model is compared by evaluating $R^2$, and $\Delta q$ (%), and the agreement between the calculated $q_e$($q_{e,cal}$) and the experimental $q_e$($q_{e,exp}$) values. The kinetic parameters, $R^2$ and $\Delta q$ (%) values of both dye sorption under various conditions were calculated and listed in Table 3. The $R^2$ values of pseudo-second order kinetic model are higher than those of pseudo-first order kinetic model, while the $\Delta q$% values of pseudo-second order kinetic are much lower than the latter. Meanwhile, the $q_{e,cal}$ values calculated by pseudo-second order kinetic model are much closer to the $q_{e,exp}$ than fitting by pseudo-first order kinetic model. Therefore, the pseudo-second
order kinetics model is more appropriate to describe the sorption behavior of both dyes onto GWAC.

3.3. Diffusion mechanism

The pseudo-first order and pseudo-second order kinetic models cannot identify the diffusion mechanism and rate controlling steps that affect sorption process. The plots given in Fig. 2c are multi-linear, and there are three various portions indicating different stages in sorption. The first sharper portion represents the external mass transfer, whereas the second portion is the gradual sorption stage, where intra-particle diffusion is rate-limiting. The third portion is the final equilibrium stage, where intra-particle diffusion starts to slow down due to the extremely low sorbate concentrations left in the solutions (Wu et al., 2005). According to the intra-particle diffusion model, a plot of \( q_t \) vs. \( t^{1/2} \) should be linear if intra-particle diffusion is involved in the sorption process, and if this line passes through the origin, the intra-particle diffusion is the rate controlling step. When the plot does not pass through the origin, this indicates some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate limiting step, but also other kinetic models may control the rate of sorption, all of which may be operating simultaneously (Kumar et al., 2010). As it can be seen in Fig. 2c, the linear plots at each initial concentration did not pass through the origin, which indicates that the intra-particle diffusion was not only a rate controlling step.

The values of \( k_{id} \) and \( I \) were obtained through fitting the experimental data at second linear portion and were summarized in Table 3. The values of \( I \) were observed to be increasing with the initial concentration of both dyes, which indicates an increase in the thickness and the effect of the boundary layer (Khaled et al., 2009). The large \( I \) values (85.98–247.94 mg/g for MG; 47.08–106.73 mg/g for CR) of all kinetic studies for both dyes confirm that the intra-particle diffusion was involved in the sorption process, but not the sole rate-limiting step. Furthermore, the \( k_{id} \) values of both dye sorptions increased with increased initial dye concentration. This is probably because the initial dye concentration gives the driving force to overcome the resistance to the sorbate transfer from the bulk solution to the sorbent particle. The higher initial dye concentration resulted in higher driving force, which further increased the diffusion rate of the molecular dye in pore (Yu and Luo, 2014).

3.4. Isotherm modeling

The equilibrium isotherms were studied at different temperatures under optimized conditions determined at natural pH values in aqueous solution for MG and CR (Fig. 1d). The experimental equilibrium data in Fig. 1d for sorptions of both dyes are fitted with Freundlich (Eq. (7)) and Langmuir isotherm models (Eq (8)), and presented in Fig. 3a and b, respectively. The calculated isotherm parameters and \( R^2 \) values are listed in Table 4. Higher \( R^2 \) values obtained from used isotherm models revealed that the equilibrium data for both dyes fitted well

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**Table 4 – Isotherm parameters for MG and CR sorption onto GWAC at different temperatures.**

<table>
<thead>
<tr>
<th>Dyes</th>
<th>T (K)</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( K_f ) (mg/g) ( (L/mg)^{1/n} )</td>
<td>( 1/n )</td>
</tr>
<tr>
<td>MG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>73.05</td>
<td>0.299</td>
<td>0.8565</td>
</tr>
<tr>
<td>308</td>
<td>81.15</td>
<td>0.296</td>
<td>0.8275</td>
</tr>
<tr>
<td>318</td>
<td>99.69</td>
<td>0.289</td>
<td>0.8727</td>
</tr>
<tr>
<td>328</td>
<td>105.38</td>
<td>0.273</td>
<td>0.8601</td>
</tr>
<tr>
<td>298</td>
<td>21.76</td>
<td>0.386</td>
<td>0.8555</td>
</tr>
<tr>
<td>308</td>
<td>39.32</td>
<td>0.319</td>
<td>0.8886</td>
</tr>
<tr>
<td>318</td>
<td>45.74</td>
<td>0.314</td>
<td>0.8940</td>
</tr>
<tr>
<td>328</td>
<td>54.88</td>
<td>0.308</td>
<td>0.8945</td>
</tr>
</tbody>
</table>
to both Freundlich and Langmuir under the studied equilibrium conditions. The magnitude of \( K_r \) indicated relatively easy uptake of MG and CR. The \( K_r \) and \( 1/n \) values obtained for MG sorption were lower in comparison to CR sorption leading to a conclusion that GWAC is a more efficient sorbent for removal of cationic dye compared to anionic dye. The maximum sorption capacity \( (q_m) \) of the MG and CR under the examined conditions was calculated by the Langmuir equation and is 667 and 455 mg/g, respectively (Table 4). As it can be seen in Table 1, GWAC has a relatively higher surface area with advanced micro and mesopores. In addition, mesopores contribution (94.61\%) to the pore structure of GWAC is much more than that of micropores (5.39\%). The high sorption capacity of GWAC for both dyes may result from these features. It can be seen from these results that the uptake of MG is higher than that of CR; this may be due to the smaller molecular size of MG \((1.26 \text{ nm})\) compared to that of CR \((2.65 \text{ nm})\) \((\text{Van der Bruggen et al., 1999})\). Furthermore, the higher sorption of these dyes having different ionic character by the GWAC is due to the fact that having a surface to be called nearly amphoteric because of having slightly negatively charged as revealed by the \( \text{pH}_{\text{ZPC}} \) \((6.20)\) (Table 1). Furthermore, this result is originated from that the GWAC has more surface acidic groups than the surface basic groups according to the data obtained from Boehm’s titration results. Moreover, \( K_r \) values determined at four temperature values for both dye sorptions that are less than unity \((R_s < 1)\), which indicate the favorability of sorption on GWAC.

3.5. SEM, FT-IR and XPS analysis

SEM micrographs of GWAC and before and after its MG and CR sorptions are shown in Fig. 4(a–c). As can be seen from Fig. 4(a), the GWAC is full of cavities compared with GW, and the pores were at different sizes and shapes \((\text{Saygılı et al., 2015})\). This image also showed bright dark color on the surface. The surface after sorption of both dyes was turned to light color (Fig. 4(b–c)). These may be due to the sorptions of MG and CR dyes onto the surface of GWAC.

The FT-IR spectra before and after sorption of GWAC are shown in Fig. 5. In the FT-IR spectra of GWAC, the peaks at the range of \(1500–1000 \text{ cm}^{-1}\), correspond to carbonyl group, carboxylate ion, ash component and chelat bonded carboxylate structures \((\text{Saygılı et al., 2015})\). The FT-IR spectra of GWAC after sorption of MG and CR dyes were analyzed to determine the vibration frequency changes in their functional groups within the range of \(4000–650 \text{ cm}^{-1}\) and are shown in Fig. 5. From the figure, after sorption of MG dye molecules it was found that, the absorption band at \(3196.24 \text{ cm}^{-1}\) corresponds to the \(\text{OH}\) stretching vibration was disappeared. The specific peaks in fingerprint region \((500–1500 \text{ cm}^{-1})\) for the mono-substituted and para-disubstituted benzene rings which is supporting to the peak at \(1582.65 \text{ cm}^{-1}\) for the \(\text{C=C}\) stretching of the benzene rings and the sharp peak at \(1359.94 \text{ cm}^{-1}\) for \(\text{C=N}\) stretching vibration corresponds to the aromatic tertiary amine group were observed \((\text{Ramezani et al., 2013})\). FT-IR spectra of GWAC after CR sorption are presented in Fig. 5. The major differences are: the absorption band at \(3196.24 \text{ cm}^{-1}\), corresponding to the stretching vibration of \(\text{O=H}\) GWAC, shifted to higher wave number \(3348.07 \text{ cm}^{-1}\). This is indicative of hydrogen bond formation between the hydroxyl groups of GWAC and the amine group of dye molecules. Furthermore, the appearance of the peaks at \(1173.36\) and \(1040.48 \text{ cm}^{-1}\) could be assigned to the \(\text{S=O}\) stretching vibration. The new absorption peaks at \(755.53\) and \(829.42 \text{ cm}^{-1}\) were observed on GWAC after CR sorption assigned to characteristic sorption of aromatic skeletal groups \((\text{Ahmad and Kumar, 2010})\). The results suggest that MG and CR dyes were successfully adsorbed onto GWAC.

XPS C1s and O1s spectra analyses of GWAC before and after sorptions are shown in Fig. 6(a–f). The C1s spectrum has been deconvoluted into three characteristic bands with binding energies corresponding to: graphite type \((\text{C—C—H}\_x: \text{284.45 eV})\); alcohol and/or ether \((\text{C—O: 286.19 eV})\), carboxylic acid and/or ester \((\text{O—C—O: 288.85 eV})\) \((\text{Figaro et al., 2006; Zhu et al., 2014; Wu et al., 2014})\). The O1s spectrum of GWAC (Fig. 6(b)) was fitted to two components: oxygen singly bonded to carbon in alcohol and/or ether \((\text{532.61 eV})\) and carboxylic acid and/or ester \((\text{530.90 eV})\) \((\text{Burg et al., 2002; Biniak et al., 2013})\). The presence of oxygen on the surface of GWAC confirmed that some surface oxygen-containing functional groups formed on the surface of GWAC,
which is in compliance with the Boehm titration results (Table 1) and FT-IR spectra (Fig. 5). After sorption a drastic increase in relative content of elemental carbon was observed for GWAC (65.34% and 64.67%), in comparison to before sorption (51.95%), indicating the good capacity to adsorb MG and CR dyes (Fig. 6(e–f)). Besides, the XPS spectra show that the sorption of MG and CR by GWAC led to a shift to higher energies for the O 1s peaks, from 530.9 eV to 531.07 and 530.96 eV respectively. Consequently, it may suggest that the interactions should take place between GWAC and MG, CR dyes.

3.6. Thermodynamic analysis

Thermodynamic parameters were calculated from Eqs. (10) and (11), respectively. By plotting the graph of ln K vs. 1/T from Eq. (11), the values ΔH° and ΔS° can be estimated from the slopes and intercepts, respectively (figure is not shown). The ΔH° values are 12.02 and 18.03 kJ/mol for MG and CR, respectively. The positive values of ΔH° for both dyes indicate the endothermic nature of the sorption processes. The ΔS° values are 55.33 and 66.24 J/mol for MG and CR, respectively. The positive values of ΔS° showed the affinity of GWAC for both dyes and the increasing randomness at the solid-solution interface during the sorption process (Albadarin et al., 2012). The ΔG° values determined for both dyes sorptions at 25, 35, 45 and 55 °C are −4.39, −5.07, −5.68 and −6.44 kJ/mol for MG and −1.46, −2.66, −3.28 and −3.98 kJ/mol for CR, respectively. The negative ΔG° values illustrated that the sorption process was feasible and spontaneous. The values of ΔG° increased with increasing temperature, which indicated that sorption of both dyes was more beneficial at higher temperatures, and this confirms the feasibility of the process and the spontaneous nature of the sorption with higher preference of MG than CR on GWAC.

3.7. Reusability of GWAC

The reusability of GWAC was investigated by conducting the sorption-desorption process for five cycles for both dyes, and the sorption capacities in each cycle is presented in Fig. 7. As
clearly seen from this figure, the sorption capacities of GWAC decrease for each new cycle after desorption with five cycles. The original sorption capacities of GWAC for MG and CR dyes are 90.49 mg/g and 66.61 mg/g, respectively. After five cycles, the sorption capacities of sorbent drop down to 50.80 mg/g and 24.96 mg/g for MG and CR dyes, respectively. The desorption results showed that GWAC could be regenerated and repeatedly used in wastewater treatment.

3.8. Comparison of sorptive characteristics of GWAC

The comparison of sorptive characteristics related to the MG and CR of GWAC and some biomass waste-based activated carbons reported in literatures are summarized in Table 5. These characteristics showed that the GW seemed to be an alternative precursor in production of the commercial activated carbon for the removal of cationic and anionic dyes from aqueous phases.

Fig. 6 – XPS C1s and O1s spectra of GWAC before (a–b) and after adsorption of MG (c–d) and CR (e–f) dyes.

Fig. 7 – Effect of regeneration cycles on the sorption capacities of MG and CR dyes onto GWAC.
4. Conclusion

This study showed that GWAC acts as a good sorbent for the removal of MG and CR dyes from aqueous phase. The sorbed amounts of both dyes were found to be dependent on sorbent dose, initial dye concentration, contact time, temperature and ionic strength. The experimental data of sorption kinetics fit the pseudo-second order model better than the pseudo-first order model. The equilibrium data were consistent with both models of Langmuir and Freundlich. The maximum sorption capacities were determined as 667 mg/g for MG and 455 mg/g for CR, respectively. Thermodynamic studies demonstrated the spontaneous and endothermic nature of sorption.

In conclusion, GWAC can be actually used as a sorbent material for the removal of cationic and anionic dyes from aqueous solution, in which its sorption capacity is higher than many commercial and other biomass waste-based activated carbons.

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