Application of cellulose, lignin and camphor stem as new biosorbents for removal of brilliant green and crystal violet dyes from wastewater

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ABSTRACT

The aim of the present work was to prepare low cost and environmental friendliness biosorbents and use them for the removal of hazardous compounds from wastewater. Cellulose and lignin biosorbents were prepared from camphor stem using H$_2$SO$_4$ (1:1) and 3 M NaOH solutions. Also, many biosorbents were prepared by heating the camphor sticks at 105, 150, 200 and 250 °C which were characterized by the SEM, XDR, FTIR, UV/Vis, pH$_{ZPC}$ and surface site analysis techniques. The camphor biosorbents were applied for removal of brilliant green (Br.G) and crystal violet (Cr.V) dyes from wastewater. The camphor biosorbents were found highly efficient for removal of Br.G and Cr.V dyes (95–100%) at pH 5–7 within a period of 2–5 min. The process was described by the pseudo-second-order kinetic model with the corresponding $R^2$ value (0.999). The negative values $\Delta G$ (−8.1 and −2.4 kJ/mol) found for the removal of Br.G and Cr.V using camphor biosorbents shows the feasibility and the spontaneity of the removal process. The detection limit (LOD) and removal percentage (E%) of the tested dyes from different wastewater locations were found in the ranges 0.1–2.9 µg/L and 92–100% respectively with the relative standard deviation (RSD%) 0.05–1.16% for five replicating procedures ($n=5$).

1. Introduction

Many procedures such as adsorption, photocatalytic degradation, coagulation, oxidation or ozonation, and membrane separation processes, have been used for the removal hazardous organic compounds from wastewater (Gupta, Jain, Nayak, Agarwal, & Shrivastava, 2011; Mittal, Mittal, Malviya, & Gupta, 2010; Saleh & Gupta, 2012; Saravanan, Gupta, Narayan, & Stephen, 2014). The methods above are commonly used due to their simplicity and their proven efficiency for the treatment of wastewater (Ghaedi et al., 2015; Gupta, Atar, Yola, Üstündag, & Uzun, 2014; Saravanan et al., 2016). Adsorption technique is one of the most efficient procedures used for the removing of basic dyes from wastewater (Asfaram, Ghaedi, Agarwal, Tyagi, & Gupta, 2015; Dayi, Kyzy, Abduloglu, Cikirikci, & Akdogan, 2018; Deng, Zeng, Shi, Zhang, & Luo, 2018). A variety of agricultural biomass such as Pyracantha coccinea (Edilson, Djalma, Ana, & Carlos, 2018), orange peel (Ghuge & Saroha, 2018a), olive pomace (Ghuge & Saroha, 2018b), cypress cone chips (Azin & Moghimi, 2018), beech (Nguyen, Fu, & Juang, 2016), peat (Deniz & Kepecki, 2016), tomato plant root (Dod, Banerjee, & Saini, 2015), Miswak (Albadarin, Solomon, Mohamad, & Gavin, 2018) and deoiled soya (Deniz, 2013) have been used as adsorbents in removal of basic dyes from wastewater effluents. Chemical adsorption can occur via coordinating to the polar functional groups of biosorbents such as alcohols, aldehyde, ketone, phenolics and, ethers. Cellulose and lignin are the most abundant biological materials on the earth and comprises 80–90% of the dry mass of woody plants. This macromolecule plays a vital role in providing mechanical support to binding plant fibres together. The leaching of cellulose, lignin or other components from the wood matrix requires the treatment of biosorbents in acidic and basic medium. The cost, local availability and abundance of are primer factors to be considered in the synthesis the biosorbents. In the present study, the camphor sticks were used to prepare a number of stable biosorbents.

Brilliant green (Br.G) and crystal violet (Cr.V) dyes are widely used in biological staining, dermatological agent and to prevent the formation of parasites and fungus (Kumari, Krishnamoorthy, Arumugam, Radhakrishnan, & Vasudevan, 2017; Moawed, 2013; Moawed, Kiwaan, & Elshazly, 2017; Moawed, El-Hagrasy, & Farhat, 2017). Br.G and Cr.V dyes are highly soluble in water, therefore, the effluents of...
this dye have a negative impact on the environment, especially in drinking water and agriculture (Moawed & Abulkibash, 2016; Moawed & El-Shahat, 2016). The effluents cause irritation of the gastrointestinal tract; symptoms include nausea, vomiting and, diarrhoea and therefore, the removal of this dye from the effluent before its discharge into the environment were seen of significance (Kumar & Sunil, 2017; Mohamed, Abukhadra, & Hamdedin, 2018). Several but expensive methods were employed to overcome this problem, e.g. photodegradation (Akter et al., 2016; Navish & Garg, 2017), coagulation (De Castro Silva, Da Silva, Lima, Osajima, & da Silva, 2018; Rehman et al., 2018) and ozonation (Qi, Kang, Guo, & Sun, 2019; Taneja et al., 2018). Studies are needed to develop new, eco-friendly and environmentally preferable methods.

Camphor tree is a green tree distributed in the world. Its wood, bark and leaves can be used to extract camphor oil, which exhibit antifungal activity (Jain & Gogate, 2018; Thai, Fu, & Juang, 2016). Camphor trees are planted nearby the main roads, parks and schools of many cities.

The aim of this study is to increase the polarity of the biosorptive matrix of camphor sticks by applying heat treatment and thereby, to prevent the loss of its active components through leaching.

Also, we prepared the cellulose and lignin of camphor as new biosorbents by treating NaOH and H2SO4 solutions. The camphor biosorbents has been of interest as a collector material because of their efficiency, low cost, easy handling and storage. The highly acidic and basic characters of camphor biosorbents make them suitable for detection and removing basic dyes like brilliant green and crystal violet from wastewater. The sorption of basic dyes onto TPF has been studied to optimize the conditions for the removal of dyes from wastewater. The sorption capacities of camphor biosorbents were investigated referring to the parameters pH, contact time, initial dye concentration and temperature. The data were elaborated based on the established equilibrium, kinetic and thermodynamic models.

2. Experimental

2.1. Apparatus

All spectrophotometric measurements were performed on a JASCO (V-630UV-VIS spectrophotometer, Japan). The pH measurements were carried out using a Jenway 3510 pH-meter (Beacon Road, Stone, Staffordshire, ST15 OSA, UK). Scanning electron microscope analysis was performed using the JEOL model JSM-6510LV apparatus (USA). IR spectra were recorded using KBr disc on a JASCO FTIR-410 spectrometer in the 4000–400 cm−1 region.

2.2. Reagents and materials

Camph-1, Camph-2, Camph-3 and Camph-4 biosorbents were prepared by following the steps: the camphor tree sticks were cut into small pieces and then washed with 0.05 M NaOH, HCl and distilled water for 24 h to remove dust and other impurities. The washed sticks were dried in an oven at 105, 150, 200 and 250°C for 24 h and then blended with a food-processing blender. The Camph-1, Camph-2, Camph-3 and Camph-4 biosorbent powders were sieved to the particle size of (90–250) μm.

Cellulose of camphor (Camph-5): 100 g of Camph-1 were treated with 250 mL of 3 M NaOH for 24 h and then filtered and washed with distilled water and methanol which was followed by drying at 105°C and blending in a food-processing blender. The particles size of Camph-5 between 90 and 250 μm were used for removing process.

Lignin of camphor (Camph-6): 100 g of Camph-1 were treated with 250 mL of H2SO4 (1:1) for 24 h and then solid sample was filtered and washed with distilled water and methanol which was followed by drying at 105°C and blending in a food-processing blender. The particles size between 90 and 250 μm were used for removal process of Camph-6.

Stock solutions of brilliant green (C27H34N2O4S, 482.6 g/mol) and crystal violet (C25N3H30Cl, 407.9 g/mol) dyes were prepared by dissolving 0.1 g of each pure dye in 100 mL of distilled water.

2.3. Recommended procedures

Removal processes were carried out by mixing 0.1 g of camphor biosorbents (Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6) with 25 mL of Br.G or Cr.V dye solutions of the desired concentration. Br.G or Cr.V dye concentrations were estimated spectrophotometrically by monitoring the absorbance at 590 nm. The removal percentage and capacity of camphor biosorbents (Q, mmol/g) were calculated using the relationship:

\[
\%E = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

\[
Q = \frac{C_0 EV}{W}
\]

where \(C_0\) and \(C\) are the initial and final dye concentrations respectively and \(V\) (mL) is the volume of the solution and \(W\) (g) is the weight of biosorbents.

3. Results and discussion

3.1. Characteristics of camphor biosorbents

The camphor sticks were obtained from a plantation in Kafr Soliman, Damietta, Egypt. The pH and electrical conductivity of the camphor suspension...
sample (1% W/V) were measured as 5.8 and 0.73 mS/cm, respectively. The chemical analyses of the camphor sample showed that the camphor material contains 43.8% of cellulose and hemicellulose, 53.4% of lignin and 2.8% of fibre. The surface morphology of camphor powder was investigated by scanning electron microscope (SEM) at the magnification from 2500× to 20,000×. The microstructure of camphor images (Figure 1) showed that the surface has a structure composed of small pores and cells are nearly spherical and irregular in size and distribution.

The characteristics of camphor indicate that the soluble compounds of the camphor material have acidic and polar nature. The SEM images of camphor suggested that the pores and cells are easily accessed and lead to large surface area favouring the binding of dyes on the active sites.

The infrared spectra of camphor biosorbents were recorded using KBr pellets at 4000–400 cm⁻¹. The characteristic vibrational peaks of Camph-1 are observed at 3594–2931 cm⁻¹ (–OH), 2883 cm⁻¹ (C–H), 1773 cm⁻¹ (C = O), 1589 cm⁻¹ (C = C), 1369 cm⁻¹ (C–H) and 1230 cm⁻¹ (C–O–C). The O–H and C–H bands (3594–2931, 2883 cm⁻¹) of Camph-1 shifted to 3432–2385, 3650–1864, 3642–2975 and 3417–2447 cm⁻¹ for Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6, respectively. The position of the C = O peak was shifted from 1773 cm⁻¹ to 1743, 1737, 1693, 1687 and 1704 cm⁻¹, respectively and also the C = C band shifted from 1589 cm⁻¹ to 1571, 1652, 1600, 1587 and 1585 cm⁻¹, respectively, for the camphor samples above (Figure 2).

The electronic spectra of camphor biosorbents were recorded using the Nujol mulls method. The Camph-1 has absorption bands at 351–359 and 361–368 nm. These bands shifted to the following positions for the other camphor samples: Camph-2: 236–249, 369 and 336–347 nm, Camph-3: 340–369 nm, Camph-4: 342–369 and 369–378 nm, Camph-5: 350–354 and 369 nm and Camph-6: 349, 369, 381 and 387 nm. These bands are assigned to π–π* and n–π* transitions (Figure 3).

The pH ZPC of Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 is the pH value when the surface charges of the samples are equal to zero and the initial pH of tested solutions equals to the final pH. The differences between initial and final pH values (ΔpH) were plotted against the initial pH (Figure 4(A)). The estimated pHZPC values of Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 were 4.3, 5.6, 6.2, 5.4, 2.8 and 8.6, respectively. The different values of pHZPC for
Camphor biosorbents are attributed to the different functional groups they contain. This result appears to be in good agreement with the UV and IR spectral data. At pH < pHZPC, the surfaces of the camphor biosorbents are positively charged, and at pH greater than pHZPC, they become negatively charged.

The pH of dye solutions is a very important factor affecting the dye removal percentages and adsorption capacities of camphor biosorbents. The relation between the initial pH of the dye solutions and the removal percentages of Br.G and Cr.V was examined using the batch technique (0.1 M HCl/NaOH) and the results obtained are shown in Figures 4(B,C), respectively.

The maximum removal percentages of Br.G and Cr.V using Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and, Camph-6 were achieved in the pH ranges 5–9, 5–9, 7, 5–7, 3–11 and 3–13, respectively. The results show that the optimum pH values for the sorption of Br.G and Cr.V by camphor biosorbents falls in the region 5–9, which gives rise to the removal percentage of 85–100%.

The iodine adsorption capacity (Q) was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration. The sorption capacity of biosorbent for iodine was estimated to be 1.7, 1.8, 1.8, 1.7 and 1.6 mmol/g for Camph-1, Camph-2, Camph-3 and, Camph-4, Camph-5 and Camph-6, respectively. The camphor biosorbents were also characterized by estimation of methylene blue value (cation exchange capacity). The estimated values of methylene blue were 0.25, 0.24, 0.24, 0.24 and 0.26 mmol/g for Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6, respectively, which indicate that the surface of biosorbents contain mesopores and mesopores and also exhibit better adsorption and ion exchange capacities comparing to other biosorbents. Altering the total number of micropores and mesopores via acid activation directly influences the surface area, porosity and reactivity of the adsorbents (Caglar, Afsin, Koksal, Tabak, & Eren, 2013).

Effect of temperature on the matrix, terminal functional groups and surface structure of camphor biosorbent was examined at 150, 200 and 250°C. First, the percentages of weight losses of camphor after heating to the temperatures above were found as 4.2, 8.3 and 54.4%, respectively. The number of lactonic groups present on the surface of camphor decreased on heating from 0.1 mmol/g to 0.08, 0.05 and 0.05 mmol/g, respectively (Table 1). The number of carboxylic groups also decreased from 0.15 mmol/g to 0.08, 0.08 and 0.05 mmol/g whereas the number of phenolic groups increased from 0.10 mmol/g to 0.18, 0.18 and 0.20 mmol/g in parallel with the temperature. The amount of total acidic sites of Camph-1, Camph-2, Camph-3, Camph-4 were found as 0.35,

![Figure 4](https://example.com/figure4.png)

**Figure 4.** The pHZPC of Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 (A) Effect of pH on the removing of Br.G (B) and Cr.V (C) dyes.

**Table 1.** Physical and chemical properties of camphor biosorbents.

| Property                  | Camph-1 | Camph-2 | Camph-3 | Camph-4 | Camph-5 | Camph-6 |
|---------------------------|---------|---------|---------|---------|---------|---------|
| IR spectra                |         |         |         |         |         |         |
| \text{\text{\text{\text{\text{\text{\text{\text{\text{\text{$\nu_{\text{OH, CH}}$ (cm$^{-1}$)}}}}}}}}} | 3594–2931 | 3432–2385 | 3650–1864 | 3642–1833 | 3704–2975 | 3417–2447 |
| \text{\text{\text{\text{\text{\text{\text{\text{\text{\text{$\nu_{\text{CO}}$ (cm$^{-1}$)}}}}}}}}} | 1773 | 1743 | 1737 | 1693 | 1687 | 1704 |
| \text{\text{\text{\text{\text{\text{\text{\text{\text{\text{$\nu_{\text{C}–\text{C}}$ (cm$^{-1}$)}}}}}}}}} | 1589 | 1571 | 1652 | 1600 | 1587 | 1585 |
| UV–vis spectra (nm)        | 351–359, 361–368 | 236–249, 336–347 | 340–369 | 342–369, 369–378 | 350–354, 369 | 349, 369, 381, 387 |
| pHZPC                     | 4.3 | 5.6 | 6.2 | 5.4 | 2.8 | 8.6 |
| Iodine value (mmol/g)     | 1.7 | 1.8 | 1.8 | 1.7 | 1.7 | 1.6 |
| Methylene blue index (mmol/g) | 0.25 | 0.24 | 0.24 | 0.24 | 0.24 | 0.26 |
| Conductivity $\times 10^{-5}$ (C$^{-1}$ cm$^{-1}$) | 18.5 | 12.9 | 3.8 | 1.8 | 5.1 | 3.6 |
| Acidic sites (mmol/g)     | 0.35 | 0.34 | 0.31 | 0.30 | 0.85 | 0.28 |
| Basic sites (mmol/g)      | 0.65 | 0.70 | 0.75 | 1.00 | 1.00 | 0.20 |

ARAB JOURNAL OF BASIC AND APPLIED SCIENCES 417
0.34, 0.31 and 0.30 mmol/g and the corresponding amount of surface basic sites were determined as 0.65, 0.70, 0.75 and 1.00 mmol/g, respectively.

The electrical conductivities \( (\sigma) \) of Camph-1, Camph-2, Camph-3 and Camph-4 were measured as 18.5 \( \times 10^{-5} \), 12.9 \( \times 10^{-5} \), 3.8 \( \times 10^{-5} \) and 1.8 \( \times 10^{-5} \) \( \Omega^{-1} \) m\(^{-1} \), respectively (Table 1). These results indicate that the conductivity was decreases on heating the camphor biosorbent, which is in line with the decrease in the number of acidic sites. The \( \sigma \) values of cellulose (Camph-5) and lignin (Camph-6) were measured as 5.1 \( \times 10^{-5} \) and 3.6 \( \times 10^{-5} \) \( \Omega^{-1} \) m\(^{-1} \), respectively, which suggest the proportion relationship between the conductivity and the acidity of acidic sites.

The amounts of carboxylic and phenolic sites of camphor cellulose were found as 0.05 and 0.13 mmol/g respectively, while the amounts of the same sites in the lignin of camphor were found as 0.50 and 0.20 mmol/g, respectively. The total number of acidic sites of lignin (0.85 mmol/g) are higher than those of cellulose (0.28 mmol/g) whereas the number of basic sites of cellulose (0.85 mmol/g) are higher than those found in lignin (0.20 mmol/g).

### 3.2. Optimum conditions for the removal of Br.G and Cr.V dyes

The effect of the solution temperature (25–90 °C) on the removal of Br.G and Cr.V by camphor biosorbents was investigated (Figure 6(A,B)). The amounts of Br.G and Cr.V removed slightly changed by increasing the temperature indicating that the removal process of Br.G and Cr.V from wastewater does not depend on the temperature.

The thermodynamic parameters of the removal process of Br.G and Cr.V via camphor biosorbents were determined using the equations: \( \ln K = \Delta H/RT + \Delta S/R \) and \( \Delta G = \Delta H - T\Delta S \). The value of \( \Delta H \) for the removal of Br.G by Camph-1 was calculated as \(-3.2 \) kJ/mol (exothermic) while the average value of \( \Delta H \) for other camphor biosorbents was determined as 12.7 kJ/mol (endothermic). The average values of \( \Delta S \) and \( \Delta G \) were 0.06 and \(-8.6 \) kJ/mol for the removal of Br.G (Table 2). While the average values of \( \Delta H \), \( \Delta S \) and \( \Delta G \) were calculated as \(-6.3 \), 0.02 and \(-6.5 \) kJ/mol for removal of Cr.V. The negative values of \( \Delta G \) obtained for the removal of Br.G by camphor
biosorbents are attributed to the spontaneous nature of the sorption process.

The effect of shaking time (1–60 min) on the removal percentages of Br.G and Cr.V dyes by camphor biosorbents was followed by applying batch technique (Figure 7(A,B)). The maximum removal percentages of Br.G and Cr.V by Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 were found to be 3–5. It was noticed that the initial removal rate of dyes is very rapid, e.g. 75% of Br.G was removed from the solutions in 30 sec.

The kinetic parameters for the removal of Br.G and Cr.V dyes by Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 were determined by applying pseudo first-order \[ \log Q_e/Q_t = \log k_1t \] and pseudo second-order models \[ Q_t = \frac{k_2Q_e^2}{1 + k_2Q_e} \]. The average values of \( R^2 \) obtained for pseudo second-order sorption model (0.999) is higher than that obtained for pseudo first-order kinetic (0.273), which prove that the pseudo second order sorption is the predominant process (Table 3).

The average value of the initial rates constant (\( h = k_2Q_e^2 \)) of Br.G and Cr.V dyes was found as 0.083 g/mmol min. The activation energy (\( \Delta E = -RT \ln k_e \)) for the sorption of Br.G by Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 falls in the range of 12.8–19.4 kJ/mol. The \( \Delta E \) value changing in the range of 16–25 kJ/mol indicates that the removal process of Br.G and Cr.V by Camph-1, Camph-2, Camph-3, Camph-4, Camph-5 and Camph-6 is controlled by both ion-exchange and chemical adsorption mechanisms.

Figure 7. Effect of time on the removing of (A) Br.G and (B) Cr.V dyes.

Figure 8. Effect of dye concentration on the removing of (A) Br.G and (B) Cr.V dyes.

From the plots of Bangham model \[ \log \left( \frac{C_e}{C_t} \right) = \log \left( \frac{k_1}{k_2} \right) + \alpha \log t \], the average value of the correlation coefficient for the removal of Br.G by camphor biosorbents was calculated as 0.462. The Morris–Weber (\( Q_t = k_1t \)) model was applied to explain the diffusion mechanism of Br.G onto camphor biosorbents. The concentration of the dye adsorbed (\( Q \)) was plotted against the square root of time (\( t^{1/2} \)). The average values of \( R^2 \) are found as 0.416 for Br.G dye adsorbed onto camphor biosorbents. By applying Reichenberg diffusion model \[ Bt = -0.4977 - \ln(1 - F) \] and \[ F = \left( \frac{6}{R^2} \right)^{\frac{1}{2}} \], the relation between \( Bt \) against \( t \) for the sorption of Br.G was investigated and the \( R^2 \) value was found as 0.441.

The plot of initial Br.G and Cr.V dye concentrations against the amount of removal Br.G and Cr.V dyes per gram of camphor biosorbents yields perfect linear curves with nearly zero intercepts were 3.0 × 10^{-3} and good correlation coefficient (\( R^2 \)) 0.978 (Figure 8(A,B)). The sorption capacities of camphor biosorbents for Br.G and Cr.V dyes were estimated to be 0.26, 0.32, 0.28, 0.27, 0.41 and 0.34 mmol/g (125–198 mg/g). Comparisons for the capacities of camphor biosorbents with that of other sorbents show that they have the better capacity (Tables 1 and 4).

The equilibrium data for removing process of Br.G and Cr.V dyes were analysed using Freundlich (\( \log Q_e = \log K_f + \frac{1}{n} \log C_e \)) and Langmuir (\( \frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{C_e}{Q_m} \)) models. The plot of \( Q_t/C_e \) vs. \( C_e \) for the data according to the Langmuir model gives a good linear
3.3. Accuracy and method repeatability

The accuracy and precision for using camphor biosorbents for detection and removal of Br.G and Cr.V dyes from industrial wastewater samples are the most important criteria for judging the performance of environmental science. The limits of detection (LOD) and limits of quantitation (LOQ) for the removal of Br.G dye from industrial wastewater and washing machines wastewater samples using camphor biosorbents were estimated (Table 2). The values of LOD and LOQ were 0.1–2.9 and 0.5–9.6 μg/L (n = 5) which indicate the higher sensitivity detection of Br.G dye using camphor biosorbents. The removal percentages of Br.G dye were found to be 92.2–99.9%. The relative standard deviation (RSD) for five replicating procedures (n = 5) was 0.05–1.16%. The lower values of RSD% (< 10%), reflect the accuracy and precision of the proposed method.

3.4. Application

The removal process of Cr.V dye from wastewater samples using Camph-5 and Camph-6 was examined. 25 mL of washing machine wastewater samples were mixed with different amounts of Cr.V dye (100–500 μg) and then the solutions were shaken for 30 min in the presence of 0.1 g of camphor biosorbents (Table 3). The removal percentages of Cr.V dyes from the industrial wastewater samples were found to be 80.6–87.9% and 90.6–93.4%.
Table 6. Removal percentage and relative standard deviation for removal of Br.G dye from wastewater.

| Location | Camph-1 | Camph-2 | Camph-3 | Camph-4 | Camph-5 | Camph-6 |
|----------|---------|---------|---------|---------|---------|---------|
| RSD%     | 5.09    | 1.72    | 1.01    | 1.61    | 4.11    | 1.94    |
| Removal% | 82.7    | 93.6    | 99.8    | 90.8    | 87.5    | 90.3    |

Table 7. Removal of different amounts crystal violet dye from wastewater using cellulose and lignin biosorbents.

| Amount added (μg) | Cellulose biosorbent | Lignin biosorbent |
|-------------------|----------------------|-------------------|
|                   | Removal% | RSD% | Removal% | RSD% |
| 100               | 87.9     | 3.39 | 93.4     | 1.32 |
| 200               | 85.9     | 93.0 | 91.9     |     |
| 300               | 85.2     | 91.1 | 91.1     |     |
| 400               | 82.7     | 91.1 | 91.1     |     |
| 500               | 80.6     | 90.6 | 90.6     |     |

Table 8. Removal percentages of crystal violet dye from different location of wastewater samples using camphor biosorbents.

| Location | Camph-1 | Camph-2 | Camph-3 | Camph-4 | Camph-5 | Camph-6 |
|----------|---------|---------|---------|---------|---------|---------|
| RSD%     | 5.09    | 1.72    | 1.01    | 1.61    | 4.11    | 1.94    |
| Removal% | 82.7    | 93.6    | 99.8    | 90.8    | 87.5    | 90.3    |

respectively. The relative standard deviation (RSD) for five replicating procedures ($n = 5$) was calculated as 3.39% and 1.32%.

Camphor biosorbents were applied for removing of Cr.V dye from wastewater samples of different locations. Over thirty wastewater samples from five different localities in Damietta industrial city for the period of seven weeks were collected. 25 mL aliquot of the sample, adjusted to pH 7, was mixed with 100 μg of Cr.V dye. The average removal percentages of Cr.V from the samples were determined in the range of 82.7%–99.8% (Table 4). The average value of RSD% was found to be changing in the range 1.01–5.09% ($n = 5$), which is taken into account as a relevant value (less than 10%) for wastewater samples.

The effect of sample volume (10–100 mL) on the detection and removal of Br.G and Cr.V dyes by 0.1 g of camphor biosorbents (batch factor, $V/\text{m} = 100–1000$) was studied. The removal percentages slightly decreased from 100% to 76% by increasing of the batch factor ($V/\text{m}$) from 100 to 1000. The average removal percentages were found as 86–100% with RSD 0–3.7% ($n = 5$) (Tables 6–8).

4. Conclusion

The aim of the present work was to investigate the potential of camphor stem as a biosorbent for the removal of brilliant green and crystal violet dyes from wastewater. The equilibrium, kinetic and thermodynamic models fitting the removal of Br.G and Cr.V dyes from wastewater using camphor biosorbents were tested. In the kinetic study, the pseudo-second-order kinetic model was found to be well suited for the entire adsorption process of the tested dyes onto camphor biosorbents. The thermodynamic parameters proved that, the removal of Br.G and Cr.V dyes took place as a spontaneous process. The equilibrium process of the dyes is well described by the Langmuir model.

Disclosure statement

No potential conflict of interest was reported by the authors.

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