Determination of the effectiveness of carbons obtained from the co-carbonization of duckweed and waste coffee on crystal violet removal

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Abstract
With the development of industry, the rate of industrial dyes in municipal wastewater is increasing day by day. The use of environmentally friendly, economical and highly efficient adsorbents for their removal has recently gained importance. In this study, crystal violet (CV) in wastewater was removed by carbonizing waste coffee (wC) and duckweed (DW) formed on the surface of municipal wastewater treatment plant pools. DW and wC samples were carbonized together and separately at N₂ of 100 mL/min and 800 °C in a tubular reactor for 90 minutes. Adsorption experimental studies were performed at adsorbent amount of 0.5 g, 6 pH, temperature of 30 °C, initial concentration of 50-100 mg/L and contact time of 60 min. SEM and FTIR analyzes were performed for the characterization of the adsorbents. In XRD analysis, wC and carbonized wC (cwC) were amorphous, and co-carbonized wC and DW (cDW/wC) was semi-crystalline. The most effective adsorbent for CV dye removal is DW/wC. Its adsorption capacity was 8.29 mg/L, and its CV removal was 83%.

1. Introduction
Activated carbons, which have a high surface area, can be produced from many sources such as biomass and waste plastics [1], [2]. They are used as separation/purification of gases and liquids, removal of toxic substances, catalyst/catalyst support, supercapacitor and electrode [3]-[6]. Generally, activated carbon is obtained from biomass/wastes in an inert gas (N₂, etc.) environment at a temperature of 400-1000 °C in a process time of 30-90 minutes [7]-[10]. Subsequently, the resulting carbons can increase the physical/chemical activation process surface areas and surface activity [11]. After the carbonization process of a biomass, many micro, meso and macro pores are formed in its structures [12], [13]. If physical or chemical activation is not performed before/after the carbonization process, micropores will not form significantly [14], [15]. In this study, activated carbons were produced from duckweed (DW) which is grown on the surfaces of biological treatment ponds in municipal wastewater treatment plants and disposed as a waste, and waste coffee (wC) resulting from the use of filter coffee. DW and wC were carbonized both together and separately, and their effectiveness on the removal of crystal violet (CV) in wastewater was investigated. Chemical formula of CV is C₂₅H₃₀N₃Cl, its molecular weight is 407.98 g mol⁻¹.

Duckweed (DW) is a fast-growing biomass in ponds and stagnant freshwater sources of municipal wastewater biological treatment plants [16], [17]. Due to the potential of this biomass source, there are many studies on biofuel production and activated carbon. It contains approximately 47% carbon (C), 47% oxygen (O), 6% hydrogen (H) and 1% other ingredient [18], [19]. Coffee, one of the most consumed beverages, its cone contains 55% C, 7% H, 35% O, 3% N+S [20], [21]. Activated carbon was produced from these carbon-rich wastes. The efficacy of the produced activated carbons was determined by removing crystal violet (CV), a cationic dye used in the paint industry [22].

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The cationic dyes are more harmful than anionic dyes as they easily interact with cell membrane surfaces and can be concentrated in the cytoplasm inside the cell [23], [24]. In addition, CV is widely used in applications such as medicinal solutions, animal feeds [25]. However, as a result of these applications, its discharge into the seas and lakes through municipal wastewater is considered a biological life-threatening substance, as it is a strong carcinogen and allows tumor growth [26], [27]. Therefore, the removal of CV from wastewater is very important in terms of environment and biological life.

2. Material and Method

DWs, which are genus lemne minor, were obtained from the municipal wastewater treatment plant in Malatya, Turkey. wCs were collected and used as a result of the use of Nestle brand filter coffee. DWs and wCs were ground to 0.1-0.25 mm after drying at room temperature (25 °C, 1 atm). In ultimate analysis of wC, it contains 48% C, 6% H, 0.3% N and 45.7% O. The O was calculated from difference. The samples were carbonized in N₂ (100 mL/min) medium for 90 min at 800 °C in a tubular reactor. The resulting products were used in experimental studies on subjects in an airtight glass tube. In experimental studies, crystal violet (Carlo Erba, C.I.: 42555, Cas No: 548-62-9, purity: 99%) was used as adsorbate. CV solution was prepared by dissolving 1000 mg/L in distilled water and used in adsorption experiments.

The amount of CV adsorbed (adsorption capacity, qₑ) and the removal percentage of CV (Removal %) were calculated by applying the Eqs. (1) and (2), respectively.

\[ qₑ = \frac{C₀ - Cₑ}{m} \times V \]  

\[ \text{Removal} \ (\%) = \frac{C₀ - Cₑ}{C₀} \times 100 \]  

Where, qₑ is the amount of CV adsorbed per gram of activated carbon (mg/g). Cₑ is the concentration (mg/L) of non-adsorbed CV in solution. C₀ is the initial concentration of CV (mg/L). m is the amount of activated carbon (g). V is the volume (L) of the CV solution.

3. Results and Discussion

3.1. Characterization of adsorbent

Activated carbons obtained from carbonization of wC, DW and the DW/wC were analyzed by SEM (LEO-EVO 40) for natural, pre-adsorption and post-adsorption characterization. Adsorption experiments were analyzed in Thermo Electron Corporation Evolution 500 UV device at maximum CV wavelength (λᵥmax=590 nm). Quantitative determinations of DW before and after carbonization were made with FTIR (PerkinElmer Spectrum One) device with 128 scans, 2 cm⁻¹ resolution and 4000-650 cm⁻¹ spectrum range. SEM analyzes of DW before and after carbonization are given in Figure 1. SEM analyzes of wC before and after carbonization are given in Figure 2. SEM analyzes of DW and wC after co-carbonization and after adsorption are given in Figure 3. As seen in Figure 1a, there were no porous structures in the surface morphology of DW before carbonization, while porous structures were observed after carbonization (Figure 1b). Similarly, as seen in Figure 2a, it was observed that wC did not have porous structures before carbonization, but these pores were formed after carbonization (Figure 2b). As seen in Figure 3a, porous structures were formed in the surface morphology of DW and wC after carbonization together. These pores were more than DW (Fig. 1b) and wC (Fig. 2b). Similarly, Li et al. showed that more microporous, mesoporous and macroporous structures were formed after coal and poplar bark biomass co-carbonization treatment than alone [28]. As seen in Figure 1-3, it can be said that mostly meso and macropores are formed after carbonization.
In the FTIR analysis of natural wC given in Figure 4, the main peaks occurred at 3786 cm$^{-1}$, 3659 cm$^{-1}$, 2917 cm$^{-1}$, 2853 cm$^{-1}$, 1739 cm$^{-1}$, and 1025 cm$^{-1}$. They related to O-H stretch at 3780 cm$^{-1}$ and 3652 cm$^{-1}$, and C-H stretching at 2917 cm$^{-1}$ and 2863 cm$^{-1}$, C-O-C stretching at 1025 cm$^{-1}$, and C-H deformation vibration at 1376 cm$^{-1}$, and C-OH band at 1151 cm$^{-1}$ [29], [30]. The C-O-C stretch of wC at 1025 cm$^{-1}$ indicates the presence of cellulose and semi-cellulosic structures [31], [32]. The presence of 2917 cm$^{-1}$ and 2853 cm$^{-1}$ peaks indicates asymmetric and symmetrical stretching of the C-H bonds in the aliphatic chains of wC [33]. In other words, it shows the presence of methyl and methylene groups in wC [34]. The band of wC at 1739 cm$^{-1}$ depends on the carbonyl (C=O) vibration associated with the ester group in triglycerides [35]. These bands almost all disappeared after carbonization (cwC). Briefly, no functional group was almost observed because of high carbon content of the cwC. Because the absence of bands caused by stretch and vibrations containing hydrogen (H) and oxygen (O) is an indication of high rates of carbonization, and this may result in the absence of FTIR spectrums [36]. When FTIR analysis was examined in DW and wC co-carbonization (cDW/wC), 3786 cm$^{-1}$, 3659 cm$^{-1}$, 2308 cm$^{-1}$, 1376 cm$^{-1}$ and 1000 cm$^{-1}$ peaks were dominant. The cDW/wC shows the presence of 3786
cm$^{-1}$ and 3659 cm$^{-1}$ O-H groups of the adsorbent, and peaks in the range of 1300-1000 cm$^{-1}$ indicate the presence of C-O groups, and a peak of 1376 cm$^{-1}$ indicates O-H bending vibrations [37, 38]. The peak at 2308 cm$^{-1}$ represents the presence of ketone groups (C=O stretches) [39].

In the XRD analysis of wC, the formation of a 23° broad diffraction peak and the absence of any prominent diffraction peaks indicated that its structure was amorphous (Figure 5). It was observed that the structure of wC (cwC) did not change after carbonization. However, a broad diffraction peak occurred at 2θ =10°, indicative of the presence of graphene oxides formed in disordered microcrystalline structures [40]. In co-carbonization of DW and wC (cDW/wC), broad diffraction peaks and intensity decreased at 10° and 23° diffuson. However, they appeared peaks at 28°, 31°, 40°, 44° and 50°. In the XRD phase analysis of the cDW/wC, the diffraction peaks of KCl, CaS and Ca were indexed. These inorganic substances may have caused the formation of the crystal structure. As a result, it can be said that wC and the cwC are amorphous and the cDW/wC is semi-crystalline.

[Figure 4: FTIR analysis; wC: waste coffee, cwC: carbonized waste coffee, cDW/wC: carbonized duckweed and waste coffee]

[Figure 5: XRD analysis; wC: waste coffee, cwC: carbonized waste coffee, cDW/wC: carbonized duckweed and waste coffee]
3.2. Adsorption capacity of adsorbent

The removal (%) values of crystal violet dye in wastewater of activated carbons produced from DW, wC and their mixtures are given in Table 1. Adsorption experimental studies were performed at adsorbent amount of 0.5 g, 6 pH, temperature of 30 °C, initial concentration of 50-100 mg/L and contact time of 60 min. As shown in the SEM analysis in Figure 3b of activated carbons obtained as a result of the co-carbonization of DW and wC, CV dye was observed to absorb. While 25% of CV was removed with wC activated carbons (wC50) at an initial concentration of 50 mg/L, it increased to 96% with DW activated carbons (DW50). However, when the CV concentration was increased from 50 mg/L to 100% mg/L, the CV removal decreased to 70% (DW100). It can be said that it is caused when the amount of adsorbent is not sufficient for removal with the increase of the CV concentration in the solution [41]. However, the removal of CV increased by 83% when the DW/wC adsorbent (DW/wC100) was used instead of DW activated carbons (DW100). It can be said that the DW/wC has better CV removal than DW and wC.

In Figure 6, the adsorption capacity of activated carbons obtained after carbonization of wC in 50mg/L CV solution is 2.52 mg/L (wC50). The DW was 9.62 mg/L (DW50). The adsorption capacity of DW in 100 mg/L CV solution was 7.03 mg/L (DW100). Activated carbons obtained as a result of co-carbonization of DW and wC were 8.29 mg/L (DW/wC100). It can be said that the adsorption capacity of DW is better than wC (Figure 6). This is thought to be due to the differences in the functional groups in the structures of DW and wC (Figure 4). However, in the carbonization process of CV with DW, the adsorption capacity was higher than that of DW. As a result, it was observed that all the obtained adsorbents were able to remove crystal violet (CV) dye from wastewater, and the best adsorbent was the DW/wC.

Table 1: Removal of CV

<table>
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<th>Sample name</th>
<th>initial concentration of CV (mg/L)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wC50</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>DW50</td>
<td>50</td>
<td>96</td>
</tr>
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4. Conclusion and Suggestions

This study investigated the effect of carbonized duckweed (DW), waste coffee (wC) and their blends on the removal of crystal violet (CV) in wastewater.

- In the FTIR analysis, the peaks of the functional groups of DW and wC changed after carbonization.
- According to SEM analyzes and adsorption studies, DW, wC and the DW/wC adsorbents removed CV dye.
- The highest adsorption capacity and CV removal were 8.29 mg/L and 83% in the co-carbonization of DW and wC, respectively.
- The lowest adsorption capacity and CV removal were 2.52 mg/L and 25% in carbonization of wC, respectively.
- According to XRD analysis, wC and the cCW are amorphous and the cDW/wC is semi-crystalline.

Adsorbents were found to be effective and inexpensive for CV dye removal in wastewater. For optimum conditions of DW/wC in CV removal, adsorption parameters need to be determined.

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

Research and publication ethics compiled within the study.
References


