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Removal of Crystal Violet from aqueous solution by biofibers

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ABSTRACT

The adsorption characteristics of activated biochar fibers, which have been prepared from biofibers obtained from the cladodes of *Opuntia ficus-indica*, for the removal of the basic dye Crystal Violet (CV) from aqueous solutions, have been investigated prior and after chemical modification of the fibers (e.g., carbonization and following oxidation of the fibers). The effect of the initial concentration, contact time and temperature on the removal of CV was investigated in order to elucidate the adsorption process. According to the experimental results, the oxidized biochar fibers (ACF) present the highest adsorption capacity (q_{max} >> 50 mg g^{-1}) for the dye, followed by the non-treated (F, q_{max} = 54 mg g^{-1}) and the carbonized (CF, q_{max} = 27 mg g^{-1}) fibers. The increased adsorption capacity of ACF is attributed to the carboxylate moieties present on the fibers surface, which in addition to the cation–π interactions favor the affinity of ACF for the cationic dye. Generally, the CV adsorption by the biofibers is a two-step process and carbonization of the biofibers results in significantly faster adsorption kinetics, which could be attributed to channel freeing due to thermal treatment. In the case of the oxidized biochar fibers, the channel freeing to such an extent that diffusion of the dye within those biochar fibers is only of minor relevance. In addition, in all cases, the adsorption is an endothermic, entropy-driven process.

Keywords: Crystal Violet; Biofibers; Dye removal; Aqueous solutions; Adsorption mechanism

1. Introduction

Crystal Violet (CV) is a widely used synthetic dye and its molecular formula and mass are $C_{25}N_3H_{30}Cl$ and 407.99 g mol^{-1}, respectively. CV a cationic dye is soluble in water, and when dissolved the dye has a violet color with an absorbance maximum at 590 nm. CV is extensively used as a dye in paper and textile industries, which generate large amounts of wastewater effluents containing the dye and if not treated may contaminate natural water bodies [1]. In addition to the visual pollution and the reduced photosynthesis due to the limited light penetration in the affected aquatic bodies, CV is a toxic and even carcinogenic substance. Hence, CV has to be removed from industrial effluents before their discharge into natural water bodies (e.g., streams, lakes, etc.) [2].

Compared with various dye removal technologies, adsorption is a promising method for the treatment of dye-contaminated effluents [1,3]. Adsorption technologies are generally low cost, produce low amounts of waste, are sludge-free processes and enable dye recovery. Moreover, adsorption-based technologies, which have been extensively studied, are widely applied and there is a long-term know-how available [4]. Activated carbon (AC) is an adsorbent that has been widely used for the removal of dyes from aqueous solutions. This is because AC has a large surface area, high adsorption capacity and chemical affinity for non-polar and ionic species [5]. The only restriction for using AC in the wastewater treatment is the relatively high price of the commercially available AC. However, biochar that possesses similar properties to AC can be produced from agricultural waste materials with little economic value and can be used as alternative carbon adsorbent material [5,6].

This study deals with the use of biofibers as adsorbent materials for the removal of CV from aqueous solutions. The adsorption data corresponding to three different types

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of biofibers (F, CF and ACF) are discussed and compared with one another. The fibers (F) have been obtained from the cladodes of the cactus plant *Opuntia ficus-indica,* and have modified by carbonization (CF) and subsequent oxidation (ACF) of the non-treated fibers (F).

2. Materials and methods

All reagents used in the experiments were of analytical grade and were obtained from Sigma-Aldrich (MerckKGaA, Germany). Stock solutions of CV ($C_{25}H_{30}N_3Cl$, MW: 407.99 g mol^{-1}) were prepared by dissolving the dye in distilled water. The *O. ficus-indica* fibers have been obtained from the cladodes of locally grown plants and they have been treated and chemically modified (e.g., carbonized and subsequently oxidized) as described elsewhere [7,8]. To obtain the carbonized product (CF), the dried biofibers (F) were thermally treated at 600°C and then suspended and boiled in 12 M HNO_3 for 3 h under reflux and continuous stirring to prepare the oxidized/activated product (ACF). The biochar products (CF and ACF) have been washed several times with distilled water, and the neutralized products were finally dried in the oven at 100°C. The dried products have been used for the adsorption experiments.

The adsorption studies have been conducted by batch-type experiments under ambient conditions (at 25°C) in a thermostated orbital shaker and pH 4. The experiments have been conducted at pH 4, because the system is generally self-buffered at this pH. The adsorption experimental studies were performed by mixing 0.01 g of the biochar fibers with 10 mL of aqueous solutions of defined initial concentrations of CV in 100 mL screw capped polypropylene containers. After equilibrium, the adsorbent was separated from the aqueous phase, and the residual dye concentration in solution was determined by UV-Vis spectrophotometry (UV-2401 PC/Shimadzu) at 590 nm.

The effect of the initial concentration has been studied in the concentration range between 1×10^{-6} mol L^{-1} and 5×10^{-5} mol L^{-1}, and kinetic and temperature-effect investigations were performed using test solutions with a dye concentration of 1×10^{-5} mol L^{-1}. Regarding the latter investigations, the temperature has been varied between 25°C and 55°C. The relative dye removal at equilibrium and the amount of dye adsorbed by the adsorbent (q_e/mg g^{-1}), as well as the evaluation of the thermodynamic parameters K_d, $\Delta H°$, $\Delta S°$ and $\Delta G°$ were calculated as described elsewhere [9].

3. Results and discussion

3.1. Effect of the initial concentration

Fig. 1 presents the experimental data and the corresponding fits (dashed lines) for the adsorption of the CV dye by the non-treated (F), carbonized (CF) and oxidized biochar fibers (ACF). The experimental data have been fitted to the Langmuir and Freundlich isotherm models and the associated data are summarized in Table 1. According to Fig. 1 and Table 1, the experimental data corresponding to the three different types of fibers are better fitted by the Freundlich adsorption model. This assumes a non-uniform distribution of the heat on the adsorbent surface and hence a heterogeneous adsorption, which can be attributed to the different possible interaction modes between the surface active groups and the dye molecule.

Regarding the adsorption behavior of the oxidized biochar fibers (ACF), mainly two different surface moieties (e.g., carboxylates and aromatic rings) interact strongly with CV via electrostatic interactions and cation–π interactions, respectively [10]. The presence of the two different surface active groups, which are schematically shown in Fig. 2(a), results in an inhomogeneity which can be better described by

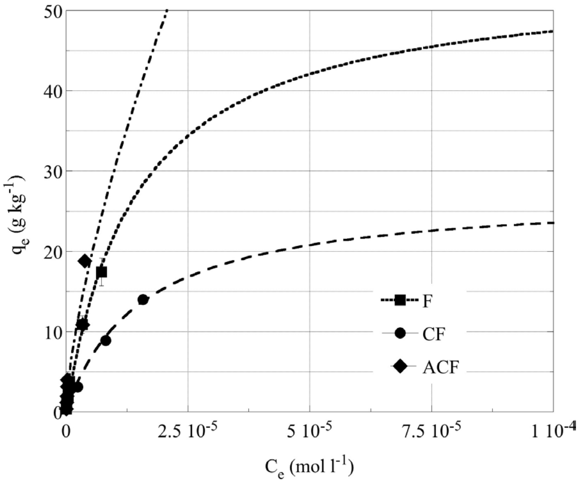

Fig. 1. Adsorption isotherms for the removal of CV from aqueous solution by biofibers prior (F) and after modification (CF and ACF).

Table 1
Isotherm parameters evaluated by fitting the experimental data to Langmuir and Freundlich adsorption isotherm models

Isotherm model/parameters	Fiber product		
	F	CF	ACF
Langmuir			
q_{max} (mg g^{-1})	54.0	27.0	670.0
K_L (L g^{-1})	69.1	64.4	6.4
R^2	0.98	0.96	0.88
Freundlich			
K_F	69.1	20.2	83.4
$1/n$	1.4	1.5	1.5
R^2	0.99	0.99	0.91

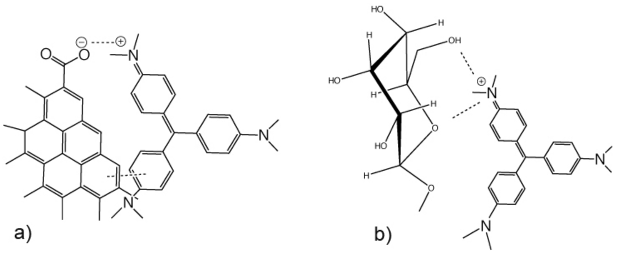

Fig. 2. Schematic illustration of the (a) electrostatic and p–p interaction of CV and (b) dipole–ion interaction of CV with the biofiber surface.

the Freundlich adsorption model. On the other hand, the interaction of CV with the non-treated (F) and the carbonized (CF) fibers, which is mainly attributed to dipole–ion interactions (Fig. 2(b)), and cation–π interactions, respectively, is also well described by the Langmuir adsorption model than the CV adsorption by ACF.

The applicability of the Langmuir model indicates the predominance of single type of interaction between the cationic dye and the value of the maximum adsorption capacity can be evaluated from the experimental data. The evaluation of the data given in Fig. 1 by means of the Langmuir model indicates that the oxidized biochar fibers possess the highest adsorption capacity (ACF, $q_{\max} >> 50$ mg g^{-1}) followed by the non-treated (F, $q_{\max} = 54$ mg g^{-1}) and carbonized fibers (CF, $q_{\max} = 27$ mg g^{-1}). The maximum adsorption capacity data for F and CF are within the range of values given in the literature for adsorption capacity data (6.1 mg g^{-1} < $q_{\max}$ < 1,273 mg g^{-1}) related to the removal of CV from aqueous solutions [11–15]. However, the maximum adsorption capacity value evaluated for ACF is rather high and this could be attributed to the fact that particularly the data corresponding to ACF are not well fitted by the Langmuir model. Nevertheless, the data clearly indicate that after activation/oxidation of the biochar fibers their adsorption capacity increases dramatically regarding CV adsorption. Of particular interest is also the fact that ACF presents significantly higher adsorption capacity for CV than for malachite green (MG), although the structure of MG is very similar to that of CV [15].

3.2. *Effect of contact time and kinetic studies*

Fig. 3 shows the adsorption kinetics of the dye as a function of contact time at constant initial concentration (1 × 10^{-5} mol L^{-1}). In contrast to the adsorption of CV by the oxidized biochar fibers (ACF), which seems to be a single-step process, the adsorption process by the non-treated (F) and carbonized (CF) fibers occurs in two distinct steps. First, relatively fast step, which is completed within 5 min, and the second slower step completed within 40 min.

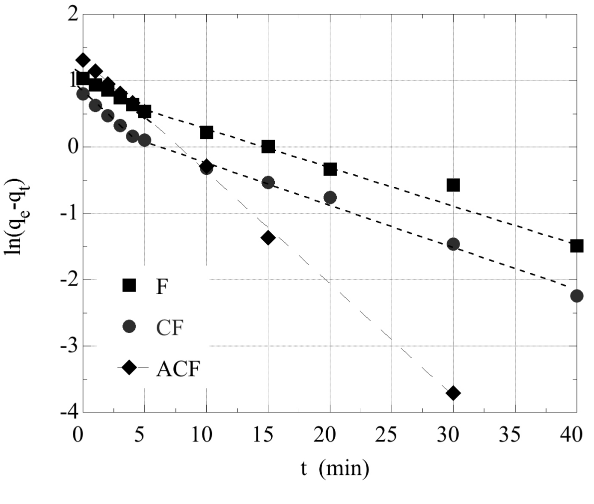

Fig. 3. Kinetics of the CV adsorption by biofibers prior (F) and after modification (CF and ACF) from aqueous solution as a function of time.

The first step is attributed to the surface complexation process, whereas the second step could be related to the diffusion of the dye molecules within the channels of the fibers. The absence of the second step in the adsorption of CV by ACF could be ascribed to the fact that carbonization and HNO$_3$ treatment of the biochar fibers results in channel freeing and fast material transport within the channels.

Evaluation of the experimental data by the first-order rate expression described by Lagergren [16] results in values for the kinetic constants, which are summarized in Table 2. It is clear that the second step, which is attributed to the diffusion of the dye within the channels, becomes faster after carbonization and disappears after treatment/oxidation of the carbonized material with HNO$_3$. This is in agreement with fact that the inner-channel surface of the non-treated biofibers is only limited accessible. Generally, the values of the kinetic constants are in the range of corresponding values given in literature for the adsorption of CV from aqueous solutions (0.031 min^{-1} < k_1 < 0.083 min^{-1} and 0.005 min^{-1} < k_2 < 0.118 min^{-1}) [15,17–19]. It is noteworthy that the kinetics between CV and MG regarding their adsorption by ACF differ significantly from one another. Despite their similarities, the adsorption of CV by ACF is a single-step process, whereas the adsorption of MG by ACF is a two-step process [15], indicating that the third aromatic amino group in the structure of CV favors the cationic character of the dye molecule and increases the affinity toward the anionic surface of the oxidized biochar fibers.

3.3. *Temperature effect*

The effect of temperature was investigated in the temperature range from 25°C to 55°C and the experimental data are graphically summarized in Fig. 4. The experimental data show that the adsorption of CV by the non-treated, carbonized (CF) and oxidized biochar fibers (ACF) is an endothermic, entropy-driven process. Evaluation of the thermodynamic data, which was performed as described elsewhere [9,10], results in the determination of the corresponding thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$, which are summarized in Table 3. These values are within the range or even higher than values given in literature for $\Delta G°$ (−25.1 kJ mol^{-1} < $\Delta G°$ < −0.5 kJ mol^{-1}), $\Delta H°$ (−68.5 kJ mol^{-1} < $\Delta H°$ < 53.6 kJ mol^{-1}) and $\Delta S°$ (−14.0 J mol^{-1} < $\Delta S°$ < 79.6 J mol^{-1}), and are related to the removal of CV from aqueous solutions [12–15,19]. Comparison of the thermodynamic parameters corresponding to the adsorption of CV and MG by ACF also shows a significant difference, which is in agreement with the results obtained from the kinetic and adsorption isotherm data. The adsorption of CV by ACF is an endothermic process, whereas the adsorption of MG by ACF is an exothermic process [15].

Table 2
Kinetic constants determined for the adsorption of CV by biofibers prior (F) and after chemical modification (CF and ACF)

Fiber	k_1 (min^{-1})	k_2 (min^{-1})
F	0.100	0.054
CF	0.144	0.065
ACF	0.157	–

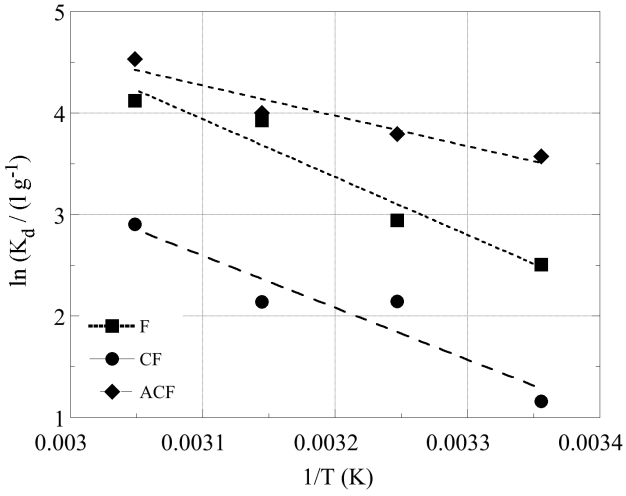

Fig. 4. The effect of temperature on the removal efficiency of CV from aqueous solution by biofibers prior (F) and after modification (CF and ACF) given as lnK_d vs. 1/T.

Table 3
Thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$) for the formation of surface species of CV with non-treated (F), carbonized (CF) and oxidized biochar fibers, obtained from varying temperature experiments

Complex	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1})	$\Delta G°$ (kJ mol^{-1})			
			298 K	308 K	318 K	328 K
CV–F	47.4	237.05	−23.3	−25.2	−28.6	−30.1
CV–CF	42.7	211.2	−20.0	−23.2	−23.9	−26.8
CV–ACF	24.8	170.0	−26.0	−27.4	−28.8	−31.2

4. Conclusions

The results obtained from this study lead to the following conclusions:

- The oxidized biochar fibers (ACF) present the highest adsorption capacity (>100 g kg^{-1}) for the dye, followed by the non-treated (F) and the carbonized (CF) fibers.
- The increased adsorption capacity of ACF is attributed to the carboxylic moieties present on the fibers surface, which in addition to the cation–π interactions increase dramatically the affinity of ACF for the cationic dye.
- Carbonization of the biofibers results in channel freeing and subsequently to significantly faster adsorption kinetics.
- Biochar fibers particularly after surface modification could be attractive candidates as adsorbent materials for the removal of CV from aqueous solutions.

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