# Removal of Crystal Violet from Aqueous Solution by Activated Biocharfibers

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**ABSTRACT**

The adsorption characteristics of activated biocharfibers, which have been prepared from bio-fibers 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 initial concentration, contact time and temperature on the removal of CV was investigated in order to study the adsorption process. According to the experimental results 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. Moreover, carbonization of the bio-fibers results in significantly faster adsorption kinetics, which could be attributed to channel freeing due to thermal treatment.

**Keywords**: *crystal violet; bio-fibers; dye removal; aqueous solutions; adsorption mechanism*

## 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 is a cationic dye, which 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 industry and through the associated wastewater effluents enters the environment [1]. However, the dye is toxic and even carcinogenic and has to be removed from industrial effluents before their discharge into natural water bodies (e.g. streams, lakes etc.) [2].

Among 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, enable dye recovery and there are applied technologies and know-how available [4]. Activated carbon is the most widely used adsorbent for the removal of dyes from aqueous solutions, because of its large surface area, high adsorption capacity and chemical affinity for non-polar and ionic species [5]. The price of commercially available activated carbon is relatively high and this has led to its restricted use in wastewater treatment. However, alternatively biochar that possesses similar properties to activated carbon and is produced from agricultural waste materials with little economic value, can be used as adsorbent material [5, 6].

The present study deals with the use of bio-fibers as adsorbent materials for the removal of CV from aqueous solutions. The fibers have been obtained from the cladodes of the cactus plant *Opuntia Ficus Indica* and have been used after carbonization and oxidation of the biochar fibers.

## MATERIALS AND METHODS

All reagents used in the experiments were of analytical grade and were obtained from Aldrich Merck. Stock solutions of crystal violet ($C_{25}H_{30}N_3Cl$, MW: 407.99 g $mol^{-1}$) were prepared by dissolving the dye in distilled water. The *Opuntia Ficus Indica* fibers have been obtained from the cladodes of locally grown plants and the have been treated and chemically modified (e.g. carbonized and subsequently oxidized) as described elsewhere [7, 8].

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 this pH,because the system is generally self-buffered at pH 4. The adsorption experiments studies were performed by mixing 0.01 g of the biocharfibers with 10 mL of aqueous solutions of defined initial concentrations of CV in 100 mL screw capped PP 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 $1x10^{-6}$ mol $l^{-1}$ and $5x10^{-5}$ mol $l^{-1}$ and kinetic and thermodynamic measurements were performed using test solutions with a dye concentration of $1x10^{-5}$ mol $l^{-1}$. Regarding the thermodynamic measurements the temperature range 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 $K_d$, $\Delta H^o$, $\Delta S^o$ and $\Delta G^o$ were calculated as described elsewhere [9, 10].

## RESULTS AND DISCUSSION

*Effect of the initial concentration*

Figure 1 presents the experimental data and the corresponding fits for the adsorption isothermsfor the adsorption of the CV dye by the non-treated (F), carbonized (CF) and oxidized biochar fibers (ACF).

According to Figure 1 the data associated with oxidized biochar fibers (ACF) are well fitted by the Freundlich adsorption model. On the other hand, the data corresponding to the non-treated (F) and carbonized (C) fibers are quite well fitted by the Langmuir adsorption model. The different adsorption behavior of the oxidized biochar fibers regarding MG adsorption is attributed to the two different surface moieties (e.g. carboxylates and aromatic rings) that strongly interact with CV via electrostatic interactions and cation-π interactions, respectively [10].

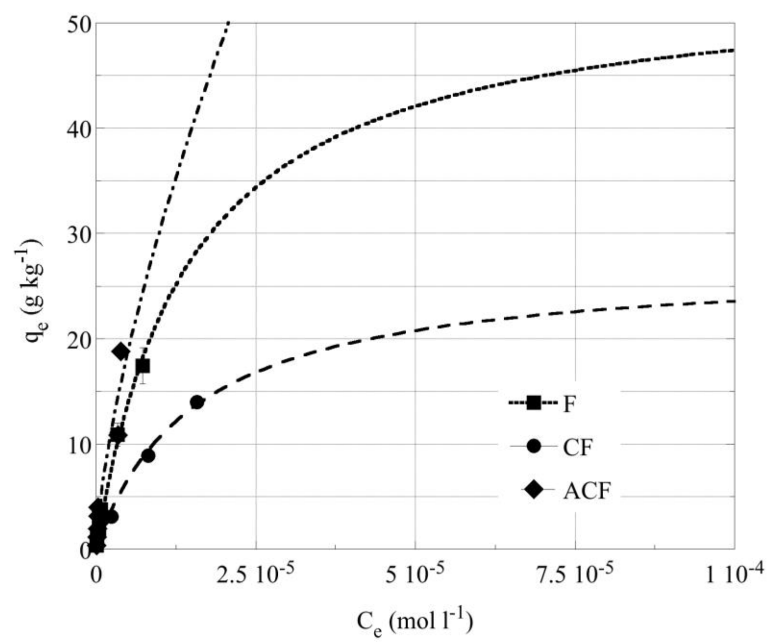
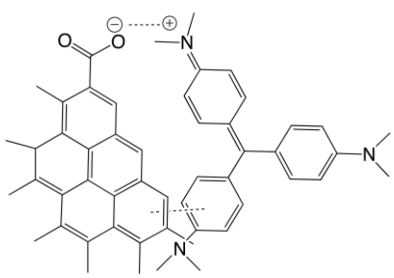



**Fig. 1** Adsorption isotherms for the removal of CV from aqueous solution by bio-fibers prior (F) and after modification (CF and ACF) as a function of time.

The presence of two different surface active groups as schematically shown in Figure 2aresults in an inhomogeneity which can be better described by 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 dipol-ion interactions (Figure 2b), and cation-π interactions, respectively, is well described by the Langmuir adsorption model. The applicability of the Langmuir model indicates the predominance of singletype of interaction between the cationic dye and the value of the maximum adsorption capacity can be evaluated from the experimental data.From the data given in Figure 1 is clear that the oxidized biochar fibers possess the highest adsorption capacity ($q_e$>100g $kg^{-1}$) followed by the not-treated ($q_e$= 54g $kg^{-1}$) and carbonized fibers ($q_e$= 27g $kg^{-1}$). The maximum adsorption data are within the range of values given in the literature for corresponding data regarding the removal of CV from aqueous solutions [11].

a)




b)

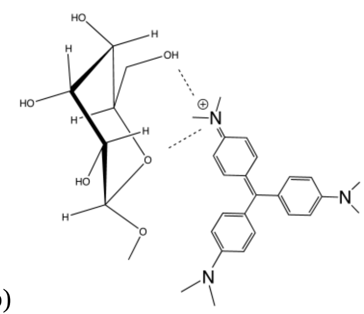



**Fig. 2** Schematic illustration of the (a) electrostatic and p-p interaction of CV and (b) dipol-ion interaction of CV with the bio-fiber surface.

*Effect of contact time and kinetic studies*

Figure 3 shows the adsorption kinetics of the dye as a function of contact time at constant initial concentration ($1x10^{-5}$ 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. A first, relatively fast step, which is completed within five minutes, and a second slower step completed within 40 minutes. Evaluation of the experimental data results in values for the kinetic constants, which are summarized in Table 1. The values of the kinetic constants are similar to or even higher than corresponding values given in literature [11].

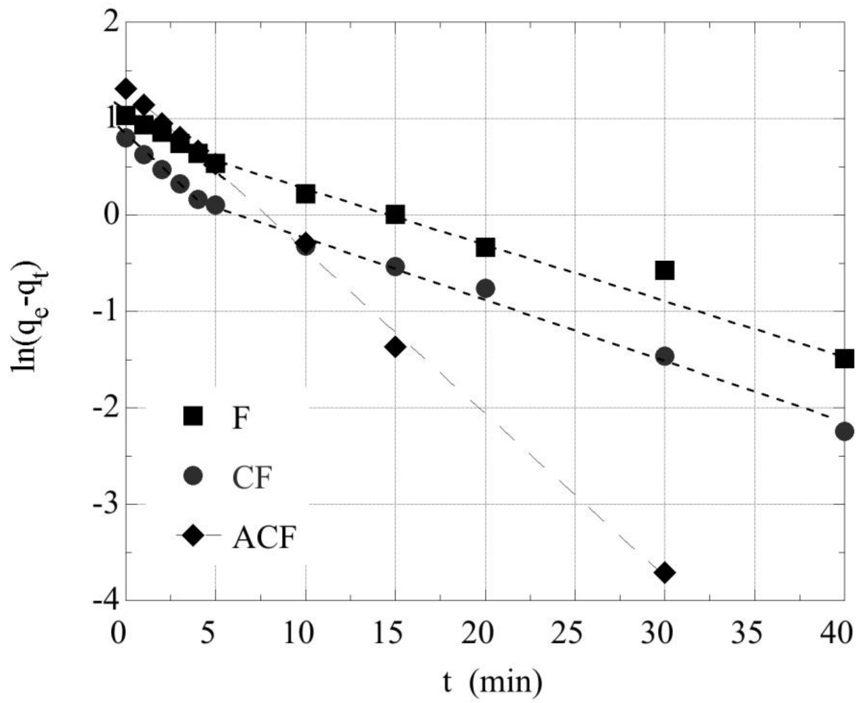



**Fig. 3** Kinetics of the CV adsorption by bio-fibers prior (F) and after modification (CF and ACF) from aqueous solution as a function of time.

**Table 1**: Kinetic constants determined for the adsorption of CV by bio-fibers 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 | - |

*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 Figure 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 thermo-dynamic data as described elsewhere [9, 10] results in the determination of the corresponding thermodynamic parameters $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$, which are summarized in Table 2. The values of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ are similar values given in the literature for corresponding data regarding the removal of CV from aqueous solutions [11].

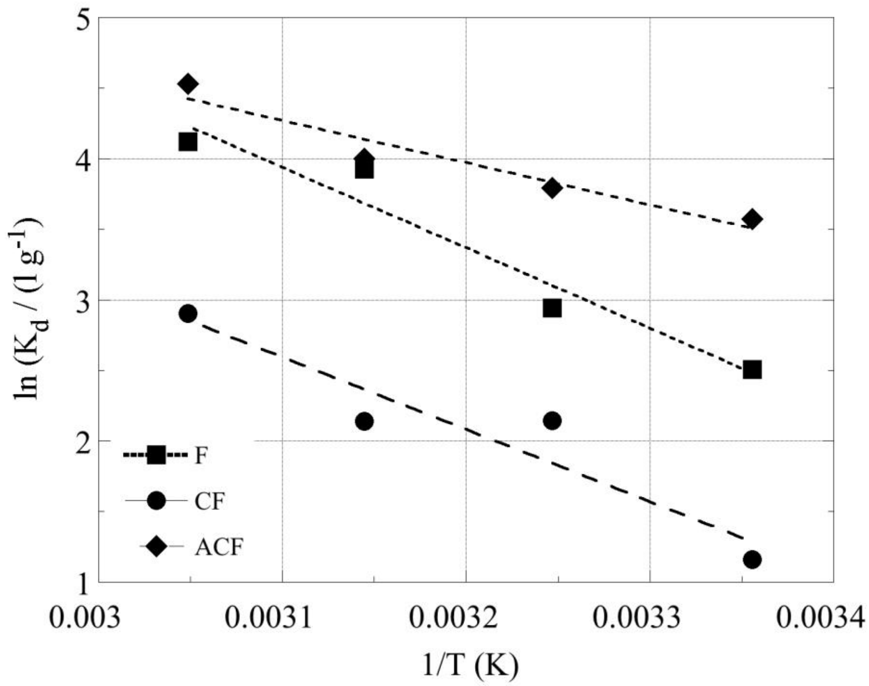



**Fig. 4** The effect of temperature on the removal efficiency of CV from aqueous solution by bio-fibers prior (F) and after modification (CF and ACF) given as $\ln K_d$ vs 1/T.

**Table 2**: Thermodynamic parameters ($\ln K_d$, $\Delta H^o$, $\Delta S^o$ and $\Delta G^o$) for the formation of surface species of CV with non-treated (F), carbonized (CF) and oxidized biocharfibres, obtained from varying temperature experiments.

| Complex | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/mol) | $\Delta G^o$ (kJ/mol) 298K | $\Delta G^o$ (kJ/mol) 308K | $\Delta G^o$ (kJ/mol) 318K | $\Delta G^o$ (kJ/mol) 328K |
|---|---|---|---|---|---|---|
| **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 |

## CONCLUSIONS

The results obtained from this study lead to 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 bio-fibers results in channel freeing and subsequently to significantly faster adsorption kinetics.
- Biochar fibers and particularly after surface modification could be attractive candidates as adsorbent materials for the removal of CV from aqueous solutions.

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