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Removal of malachite green from aqueous solution by biofibers prior and after chemical modification

Maria A. Andreou, Ioannis Pashalidis*

Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus,
emails: andreou.a.maria@ucy.ac.cy (M.A. Andreou), pspasch@ucy.ac.cy (I. Pashalidis)

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ABSTRACT

The adsorption characteristics of biofibers have been studied regarding the removal of malachite green (MG) from aqueous solutions. The biofibers have been obtained from the cladodes of *Opuntia ficus-indica* and have been investigated prior and after chemical modification. The effect of pH, initial concentration, contact time and temperature on the removal of MG was investigated in order to determine the most effective adsorbent and understand the adsorption mechanism. According to the experimental results, the oxidized biochar fibers (ACF) present the highest adsorption capacity ($q_{max} > 40$ g kg^{-1}) for the dye followed by the non-treated (F, $q_{max} = 36$ g kg^{-1}) and the carbonized (CF, $q_{max} = 32$ g kg^{-1}) 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 and π–π interactions increase dramatically the affinity of ACF for the cationic dye. Generally, MG adsorption by biofibers is a two-step process, which could be attributed to the diffusion and adsorption of the dye within the fiber channels. Carbonization of the biofibers results in significantly higher adsorption kinetics, which could be attributed to the channel freeing due to thermal treatment. MG adsorption by F ($\Delta H° = 33.4$ kJ mol^{-1} and $\Delta S° = 194.4$ J mol^{-1}) and CF ($\Delta H° = 33.7$ kJ mol^{-1} and $\Delta S° = 205.6$ J mol^{-1}) is an endothermic, entropy-driven process, whereas in the case of ACF ($\Delta H° = -39.7$ kJ mol^{-1} and $\Delta S° = -36.2$ J mol^{-1}) the adsorption is an enthalpy-driven process.

Keywords: Malachite green; Biofibers; Adsorption; Aqueous solutions; Mechanism

1. Introduction

Malachite green (MG) is a widely used synthetic dye and its molecular formula and mass are $C_{23}N_2H_{25}Cl$ and 364.91 g mol^{-1}, respectively. MG is a cationic dye, which is soluble in water and when dissolved the dye has a green color with an absorbance maximum at 618 nm. MG is extensively used as a dye in paper and textile industry and through the associated wastewater effluents enters the environment [1]. When present in waters, even at very low concentrations (ppm) is highly visible and aesthetically undesirable. In addition, due to its interference with light may affect metabolic process of aquatic biota and maybe toxic to certain organisms. Due to its harmful effects, MG has to be removed from industrial effluents before their discharge into natural water bodies (e.g., streams, lakes, etc.) [1,2].

Among various dye removal technologies, such as photocatalytic and electrochemical methods, chemical and biochemical dye degradation, adsorption methods, chemical precipitation, ion-exchange and reverse osmosis; adsorption is a promising method for the treatment of dye-contaminated effluents [1–3]. Advantages of the adsorption technologies include low-cost regeneration of the adsorbent, reduced waste production and sludge-free processes, dye recovery and existing know-how and technologies [3].

Because of its physicochemical characteristics such as large surface area, high adsorption capacity and chemical affinity, which expands from non-polar to ionic species,

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* Corresponding author.

activated carbon is the most widely used adsorbent for the removal of dyes from aqueous solutions [4]. However, the price of commercially available activated carbon is relatively high and this has led to the study and development of easily available and cheap adsorbents based on biomass by-products [4–9]. The use of agricultural waste materials, which have little economic value and generally pose a disposal problem, is a sustainable waste management approach in the frame of circular economy. In this line, several studies have been performed regarding MG removal from aqueous solutions and water decolorization using agricultural by-products such as fruit peels, rice and wheat husks, and nut hulls [9,10].

The present study deals with the use of biofibers as adsorbent materials for the removal of MG 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. The vascular structure of the biochar fibers leads to large surface area available for adsorption and hence increased adsorption capacities, and enables fast medium transport and adsorption kinetics. In addition, due to its high chemical stability and robustness the material can be easily regenerated and reused. Furthermore, to the best of our knowledge this is the first study, which deals with the adsorption of MG by biofibers prior and after carbonization and oxidation of the material.

2. Materials and methods

All reagents used in the experiments were of analytical grade and were obtained from Sigma-Aldrich (UK). Stock solutions of MG ($C_{23}H_{25}N_2Cl$, molecular weight: 364.91 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 [6,7] and they have been treated and chemically modified (e.g., carbonized and subsequently oxidized) as described elsewhere [11,12]. Specifically, carbonization of the fibers was carried out by *sequential* thermal treatment of the fibers at 200°C for 30 min and at 600°C for 1 h. Following, the carbonized material was oxidized by concentrated, boiling nitric acid (12 M HNO_3) for 3 h under reflux and continuous stirring. The thoroughly washed and dried product was 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 at this pH the molar extinction coefficient of the dye is insignificantly affected by small pH variations (Fig. 1) and the system is generally self-buffered at pH 4. The effect of pH of the molar absorptivity of MG was studied by obtaining the absorption spectrum of MG solutions of similar dye concentration (1×10^{-5} mol L^{-1}) at different pH values in the pH range between 2 and 11. The pH-related variation in absorptivity is related to the (de)protonation of the amino moieties, which affects mesomeric interconversion between possible resonance structures and hence the optical properties of the dye molecule. It has to be noted that the effect of pH on the molar extinction coefficient of MG has been taken into account and corrected accordingly.

The adsorption experiments studies were performed by mixing 0.01 g of the biochar fibers with 10 mL of aqueous solutions of defined initial concentrations of MG 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, Europe) at 618 and 425 nm.

The effect of the initial concentration has been studied in the concentration range between 1×10^{-6} and 5×10^{-5} mol L^{-1}, whereas the effect of pH in pH range between 2 and 9 at a dye concentration of 1×10^{-5} mol L^{-1}. Kinetic and thermodynamic measurements were performed using test solutions with a dye concentration of 1×10^{-5} mol L^{-1} and regarding the later 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 in mg g^{-1}) as well the distribution constant K_d was calculated as described elsewhere [11,12]. The K_d values have been used together with the linear form of the van't Hoff Eq. (1) and the Gibbs free energy isotherm Eq. (2) to estimate the corresponding thermodynamic data [13].

$$\ln K_d = -\frac{\Delta H^\circ}{R \cdot \mathrm{T}} + \frac{\Delta S^\circ}{R} \tag{1}$$

$$\Delta G^\circ = -R \cdot \mathrm{T} \cdot \ln K_d \tag{2}$$

3. Results and discussion

3.1. Effect of pH on dye removal

Fig. 2 presents the variation of the relative adsorption of MG at different pH values in solution and shows clearly that the adsorption efficiency increases with pH and reaches a plateau for pH > 4. The adsorption efficiency of MG increases readily with pH (pH > 3) due to the gradual deprotonation of the carboxylic moieties present on the surface of the oxidized biochar [7,11]. The negatively charged surface electrostatically attracts the positively charged dye

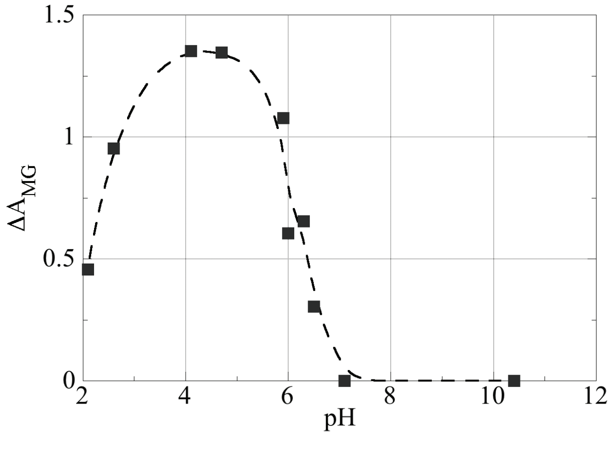

Fig. 1. Variation of the molar absorptivity of MG as a function of pH.

molecules (pK_a = 6.9) and favors the dye binding on the oxidized biochar surface.

The MG adsorption on the surface of the non-oxidized biochar fibers is based on cation–π interactions [14] and is favored with increasing pH due to the decreasing proton concentration in solution, that compete with the cationic MG molecules. Similarly, the dipole–dipole interactions between the cationic MG molecules and the polarized hydroxyl moieties on the biofiber surface are favored with increasing pH and decreasing proton concentration in solution. Moreover, in contrast to the modified fibers the non-treated biofibers present lower adsorption efficiency (~50%), which could be ascribed to the fact that the channels of the biofibers prior carbonization are only limited accessible by the MG molecules. Drying of the biofibers at 100°C does not lead to quantitative removal of water molecules from the tiny channels present in the biofiber and only after carbonization the channels are *emptied* of water and become freely accessible to adsorbates.

3.2. Effect of contact time and kinetic studies

Fig. 3 shows the relative adsorption of dye as a function of contact time at constant initial concentration (1 × 10^{-5} mol L^{-1}) and shows that for the non-treated and modified biofibers the dye is quantitatively removed after 40 min.

The adsorption process occurs in two distinct steps, the first, relatively fast step, which is completed within 5 min, and a second slower step completed within 50 min. Evaluation of the experimental data results in values for the two kinetic constants is summarized in Table 1. The first step is ascribed to the adsorption of the dye on the external surface groups, whereas the slower process is associated with diffusion and adsorption of the dye within the biochar fibers [7] and binding on the inner surface of the channels. It is clear that the second step, which is attributed to the diffusion of the dye within the channels, becomes faster after carbonization and particularly after treatment 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. Nevertheless, the values of the kinetic constants are in the range of corresponding values given in literature for the adsorption of MG from aqueous solution [9,10,15–17].

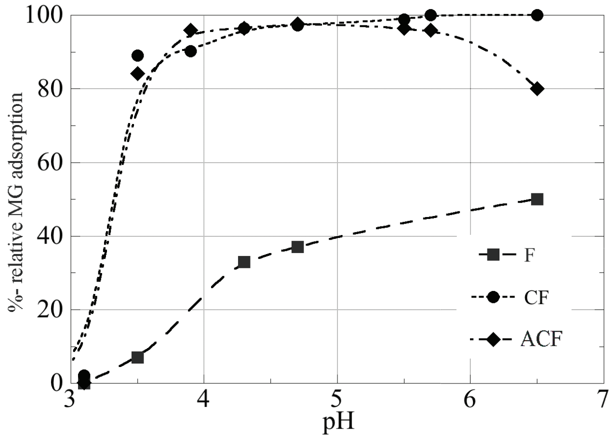

Fig. 2. Relative removal of MG from aqueous solution by biofibers prior (non-treated fibers denoted as F) and after modification (carbonized and activated biochar fibers denoted as CF and ACF, respectively) as a function of pH.

3.3. Effect of the initial concentration

Fig. 4 presents the experimental data and the corresponding fits for the adsorption isotherms, which are represented as the amount of dye adsorbed per mass adsorbent (q_e in mol kg^{-1}) as a function of the dye concentration in solution (C_e in mol L^{-1}), for the adsorption of the MG dye by the non-treated (F) and carbonized (CF) and oxidized biochar fibers (ACF).

According to Fig. 4, the data associated with ACF are well fitted by the Freundlich adsorption model and differ from the data corresponding to the non-treated (F) and carbonized (C) fibers, which are quite well fitted by the Langmuir adsorption model. The different adsorption behavior of the ACF regarding MG adsorption is attributed to the two different surface moieties MG can interact with namely, the carboxylates via electrostatic interactions and the aromatic rings via cation–π and π–π interactions [14]. Because the small number of benzene rings in the dye molecule, the latter interactions are expected to be significantly weaker than the former ones and hence of minor relevance in the present system.

The presence of two different surface active groups as schematically shown in Fig. 5 results in an inhomogeneity

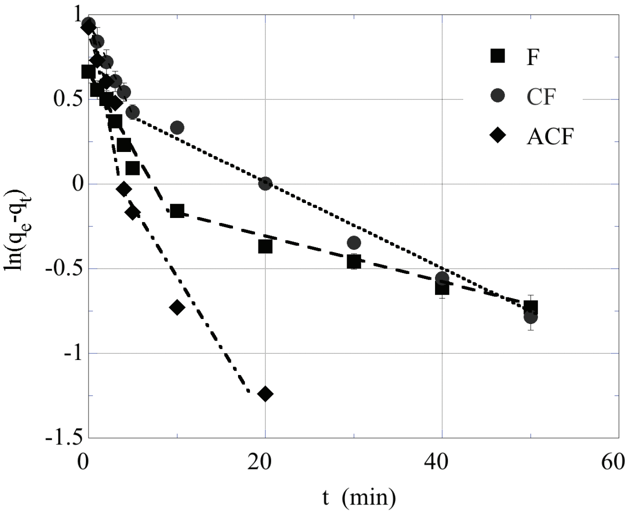

Fig. 3. Kinetics of the MG adsorption by biofibers prior (F) and after modification (CF and ACF) from aqueous solution as a function of time

Table 1
Kinetic constants determined for the adsorption of MG by biofibers prior (F) and after chemical modification (CF and ACF)

Fiber	k_1 (min^{-1})	k_2 (min^{-1})
F	0.113	0.014
CF	0.104	0.028
ACF	0.146	0.074

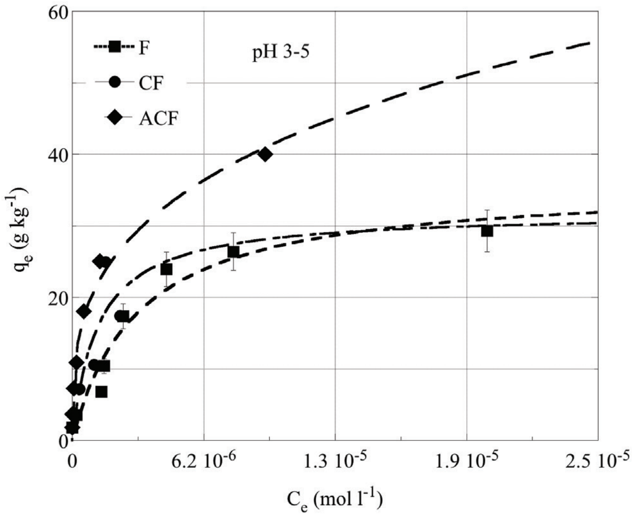

Fig. 4. Adsorption isotherms for the removal of MG from aqueous solution by biofibers prior (F) and after modification (CF and ACF) as a function of time.

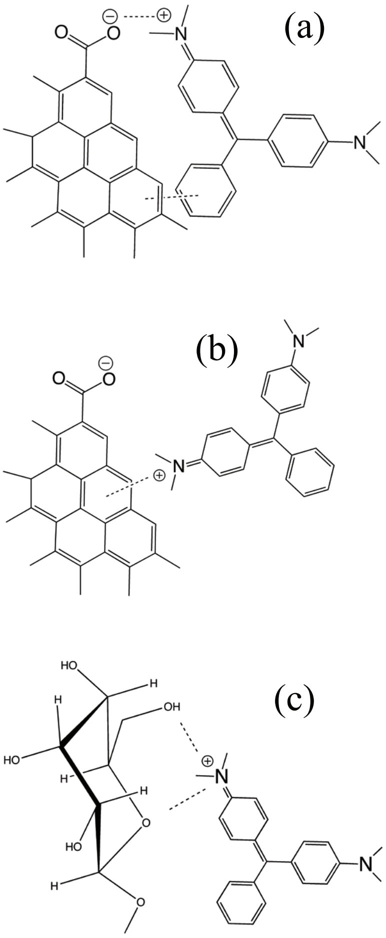

Fig. 5. Schematic illustration of the (a) electrostatic and π–π interaction of MG, (b) cation–π interaction with the (oxidized) biochar surface and (c) dipole–dipole interaction of MG with the biofiber surface.

which can be better described by the Freundlich adsorption model, which is used to describe heterogeneous adsorption systems [18]. On the other hand, the interaction of MG with the non-treated and the carbonized fibers, which is basically attributed to dipole–dipole interactions and cation–π interactions, respectively, is well described by the Langmuir isotherm model, which assumes uniform energies of adsorption and monolayer adsorption on a surface containing a finite number of identical sites [18]. The applicability of the Langmuir model indicates simple interactions between the cationic dye and the value of the adsorption capacity specifies a lignocellulosic material with increased adsorption capacity. From the data given in Fig. 4, it is clear that the ACF possess the highest adsorption capacity ($q_e > 40$ g kg^{-1}) followed by the non-treated ($q_e = 36$ g kg^{-1}) and carbonized fibers ($q_e = 32$ g kg^{-1}). These data are in the range of corresponding values given in literature for the adsorption of MG from aqueous solution by various adsorbent materials and particularly activated carbon and biochars [8–10,16,17].

3.4. *Effect of temperature*

The effect of temperature was investigated in the temperature range from 25°C to 55°C and is graphically presented in Fig. 6. The experimental data show that the adsorption of MG by the ACF is an exothermic process. On the other hand, the adsorption of MG by the non-treated (F) and carbonized (CF) fibers is an endothermic, entropy-driven process. The entropy increase associated with the adsorption of MG by ACF could be ascribed to the release of excess water molecules caused by the electrostatic interaction between the cationic MG molecule and the anionic carboxylic moieties on the biochar surface due to electrostatic compensation between the negatively charged surface and the positively charged dye molecules. Evaluation of the thermodynamic data results in the determination of the corresponding thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$, which are summarized in Table 2. The values of the thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ are similar to corresponding

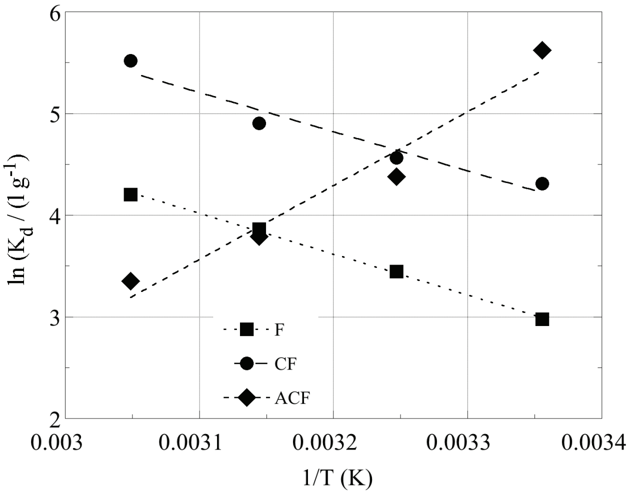

Fig. 6. The effect of temperature on the removal efficiency of MG from aqueous solution by biofibers prior (F) and after modification (CF and ACF) given as $\ln K_d$ vs. $1/T$.

values given in literature for the adsorption of MG from aqueous solution [9,10,15,16].

3.5. Effect of ionic strength

The effect of ionic strength is graphically presented in Fig. 7 and indicates that the adsorption efficiency of MG is dramatically affected in the case of the non-treated biofibers (F) followed by the carbonized fibers (CF). The strong effect of ionic strength on the adsorption efficiency of MG adsorbed by F is attributed to fact that the relative weak dipole–dipole interactions are dramatically affected by the presence of charged particles of the electrolyte and even diminished at $I < 0.2$ M. Similarly, the cation–π interactions are also significantly affected by the presence of competing electrolyte cations (e.g., Na^+) in solution. On the contrary, the adsorption efficiency of MG adsorbed by ACF is less affected (~30%) by the presence of the charged electrolyte particles, because of the relatively strong interaction between the carboxyl- and amino-moiety on the biochar surface and the MG molecule, respectively.

4. Conclusions

The results obtained from this study lead to following conclusions:

Table 2
Thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$) for the formation of surface species of MG with non-treated (F), carbonized (CF) and oxidized biochar fibres, 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
MG-F	33.4	194.4	–24.5	–26.5	–28.5	–30.3
MG-CF	33.7	205.6	–27.8	–29.4	–31.2	–36.6
MG-ACF	–39.7	–36.2	–33.3	–27.8	–28.3	–28.0

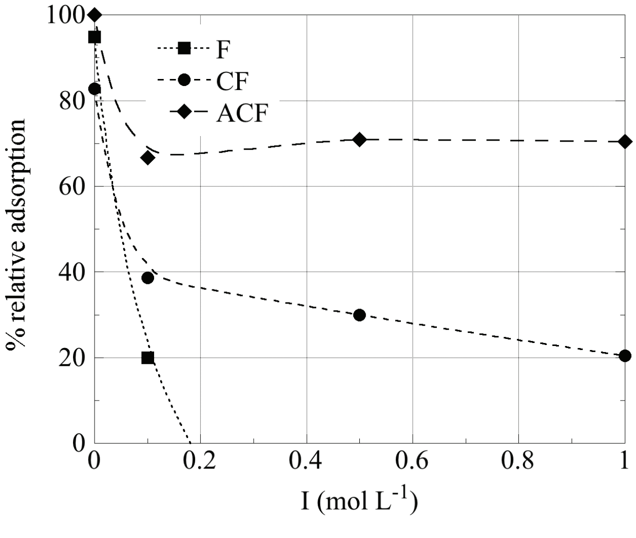

Fig. 7. Relative removal of MG from aqueous solution by biofibers prior (F) and after modification (CF and ACF) as a function of ionic strength.

- The ACF present the highest adsorption capacity (>40 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 and particularly after surface modification could be attractive candidates as adsorbent materials for the removal of MG from aqueous solutions.

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