

Scientific paper

# Adsorptive Removal of Malachite Green from Model Aqueous Solutions by Chemically Modified Waste Green Tea Biomass

Cerasella Indolean,<sup>\*1</sup> Silvia Burcă<sup>1</sup> and Andrada Măicăneanu<sup>\*2</sup><sup>1</sup> Department of Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos st., RO-400028, Cluj-Napoca, Romania<sup>2</sup> Department of Chemistry, Indiana University of Pennsylvania, Indiana, PA 15705, USA\* Corresponding author: E-mail: cella@chem.ubbcluj.ro; sanda.maicaneanu@iup.edu  
tel: +40 264 593833 ext. 5761. fax: +40 264 590818

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## Abstract

The adsorption of malachite green (MG) from aqueous solution by waste green tea (WGT) biomass was investigated. A series of experiments in batch conditions were conducted in order to assess the MG removal on WGT, following adsorbent quantity and temperature influences. Maximum removal efficiency for untreated WGT was 89% (4 g biomass, 100 mL solution of 94 mg/L, 316 K). It was found that the adsorption of MG increased by increasing temperature from 296 to 316 K. Thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ ) were calculated, and indicated that dye adsorption onto the studied biomass was endothermic and non-spontaneous. Six chemical treatments were tested (four acidic –  $H_3PO_4$ ,  $H_2SO_4$ , HCl, and tartaric acid, one oxidant –  $H_2O_2$ , and one basic – NaOH) in order to study the chemical groups responsible for MG adsorption onto WGT biomass. The alkali and acidic treatments led to an increase of adsorption efficiency up to 92% and 95% ( $H_2SO_4$ ) respectively. The FTIR spectroscopy results emphasized the modifications of the biomass surface and how these are influencing the adsorption process.

**Keywords:** Waste green tea, chemical treatment, adsorption, malachite green, SEM analysis

## 1. Introduction

Dyes are usually used in industries such as textile, paper, drug, rubber, food, cosmetic, plastic, printing, etc., activities, which have as result considerable amount of colored wastewater. Dye is the first contaminant to be recognized in wastewater, because not only damage the aesthetic nature of freshwater, which will reduce sun penetration, but also many of them possess a serious threat for human beings, aquatic life, and for environment, in general.<sup>1</sup>

The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable.<sup>2</sup> Thus, the development of clean-up technologies for the treatment of water contaminated with dyes is of major interest.<sup>3</sup> A number of technologies are available to control and reduce the water pollution with dye contaminants. Among them are coagulation<sup>4</sup>, filtration<sup>5</sup>, ion-exchange,<sup>6</sup> electrolysis,<sup>7</sup> advanced oxidation processes<sup>8</sup>, foam flotation,<sup>9</sup> etc. The removal of dyes in an economic

way remains an important problem, although a number of systems have been developed using adsorption techniques.<sup>10</sup> Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Among many techniques for water re-use, adsorption has been found to be superior in terms of ease of operation, low initial cost, flexibility and simplicity of design, and insensitivity to toxic pollutants.<sup>11</sup> Also, adsorption does not result in the formation of harmful substances due to partial degradation as some chemical or biological methods would.<sup>12</sup> Adsorption of most of the adsorbents including agricultural by-product is controlled by physical forces, with some exception of chemisorption.<sup>1</sup> The main physical forces controlling adsorption are van der Waals forces, hydrogen bonds, dipole-dipole  $\pi$ - $\pi$  interactions, etc.<sup>13</sup>

Many low-cost adsorbents, such as rice husk, wheat bran, coconut bunch waste, orange peel, banana peel, garlic peel, papaya seed, pineapple stem waste, sunflower stalks, silk cotton hull, maize cob, etc., which are able to

bind dyes molecules, have been previously researched and evaluated.<sup>14</sup>

Waste green tea could be also an economical alternative for dyes removal from wastewater. Tea plant, called *Camellia sinensis*,<sup>15</sup> is native to South-East Asia, but is cultivated today in over 30 countries in several areas of the world and belongs to the genus *Camellia*, *Theaceae* family.<sup>16</sup> Taking into consideration the quantity of tea and tea based drinks consumed annually, which gives rise to a disposal problem, utilization of such waste is extremely desirable.<sup>17–18</sup>

The cell wall of tea consist of cellulose and hemicelluloses, lignin, condensed tannins, and structural proteins. In short, tea waste have a good potential as dyes scavengers from aqueous solution since its constituents contain several functional groups.<sup>19</sup> Previous studies have centered their attention on the preparation of waste tea activated carbon<sup>17,20</sup> or on various treatments involving acetylation, isopropyl alcohol, formaldehyde, HNO<sub>3</sub>, pressure, and ultrasound.<sup>17,20–24</sup>

The aim of this study was to realize malachite green (MG) adsorption onto chemically modified waste green tea (WGT). Influence of the adsorbent quantity and temperature over the MG removal were also considered in order to investigate the WGT potential as a biosorbent. Influence of carboxyl, carbonyl, sulfonate, sulfhydryl, phosphate, and hydroxyl groups from the biomass surface over the adsorption of MG onto untreated and chemically modified WGT were detailed. Equilibrium and kinetic studies on the untreated WGT – MG system were considered in a previous paper.<sup>25</sup>

## 2. Materials and Methods

### 2.1. Adsorbent

The adsorbent, WGT, was collected from a local tea shop. The used green tea leaves were washed several times with distilled water to remove any adhering dirt and repeatedly boiled in distilled water until the filtered water was clear. Then it was oven dried at 80 °C for 48 h. Finally, the WGT sample was ground and sieved to obtain grains in the 200–400 μm range that will be further used in the adsorption experiments.

### 2.2. Characterization of the Biosorbent

#### 2.2.1. Elemental Analysis

In order to obtain information about the elemental composition of the studied materials, the C, H, N, S, and O content of untreated and chemically modified WGT, before and after MG adsorption (for all considered treatments) was determined. Elemental analysis was carried out using Thermo Finnigan Flash EA 1112 Series equipment. The biosorbent sample was added into a tin capsule and analysed at 900 °C under O<sub>2</sub> atmosphere.

#### 2.2.2. SEM Analysis

Scanning electron microscope images were obtained with a JEOL (USA) JSM 5510 LV apparatus on samples coated with a thin layer of gold under vacuum to improve electron conductivity and image quality.

### 2.3. Preparation of MG Solutions

MG, *N,N,N,N*-Tetramethyl-4,4'-diaminotriphenyl-carbenium oxalate, is a cationic (basic) dye,<sup>26</sup> which has a positive charge that is delocalized on the entire compound by resonance. It belongs to triphenylmethanes family and is amphipathic (behaves as a polar and non-polar compound). MG is commonly used for dyeing textiles and paper, as well as is an antiparasitic and antifungal agent in aquaristics.<sup>14</sup>

Malachite green was purchased from Penta (Czech Republic) and used without further purification. Stock solution (1000 mg/L) of MG were prepared using distilled water and stored in the refrigerator. Experiments were carried out using solutions obtained by dilution of the stock solution to the desired concentration. MG concentration was determined using a double beam UV-visible spectrophotometer (GBC Cintra 202) at λ = 618 nm.

### 2.4. Adsorption Experiments

Adsorption process was conducted in batch conditions, in dynamic regime (magnetic stirring at 300 rpm), through the contact of a certain amount of adsorbent (1–5 g) with a volume of 100 mL MG dye aqueous solution 94 mg/L. The adsorption process was realized until equilibrium was reached (240 min, established from preliminary experiments). Residual dye concentration in solution was determined, at established time intervals after a preliminary centrifugation (5 min at 10000 rpm) and appropriate dilution.

In order to determine the effect of temperature on the adsorption process, experiments were carried out at three different temperatures 296, 306, and 316 K. The experiments were realized using 100 mL solution of 94 mg/L and 4 g WGT.

Adsorption efficiency expressed as percentage was calculated with equation (1):<sup>27,28</sup>

$$E = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

where, C<sub>0</sub> and C<sub>e</sub> are MB initial and equilibrium concentrations, respectively (mg/L).

The amount of the adsorbed dye (MG) onto the WGT biomass was expressed as adsorption capacity (q<sub>e</sub>, mg/g) and calculated as shown in equation (2):<sup>16,27</sup>

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where, V is solution volume (L), and m is WGT quantity (g).

All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

## 2. 5. Chemical Treatments for WGT Biomass

### 2. 5. 1. $\text{H}_3\text{PO}_4$ Treatment

10 g of WGT were mixed with 50 mL 50%  $\text{H}_3\text{PO}_4$  solution at room temperature for 24 h in a 500 mL beaker with a stirring speed of 150 rpm so that the reagent was fully incorporated into the raw material.<sup>29</sup> After this treatment, the modified WGT was filtered and washed with distilled water several times until 7 pH and filtered. Later on, the adsorbent was oven-dried at 105 °C for 12h.

### 2. 5. 2. $\text{H}_2\text{SO}_4$ Treatment (Preparation of Activated Carbon from WGT)

The activated carbon was prepared by contacting WGT with  $\text{H}_2\text{SO}_4$  98% for 24 h (1:1 acid volume to WGT weight). After that, the charred material was washed several times in distilled water until the pH of the solution becomes neutral.<sup>30,31</sup> Chemical treated WGT was dried first in air, overnight, and then in an oven at 90–100 °C for 8–10 hours.

### 2. 5. 3. HCl Treatment

10 g of WGT were slowly stirred (150 rpm) in 100 mL HCl 1N for 4 hours. The treated cellulosic WGT was left overnight in contact with HCl solution and thereafter was washed with distilled water several times until neutral pH and filtered. The HCl-treated WGT biomass was dried in a hot air oven at 80°C until constant weight (24 hours).

### 2. 5. 4. Tartaric Acid Treatment

15 g of WGT were mixed with 100 mL of 2 M tartaric acid. The mixture was stirred at 200 rpm for 4 hours. The modified WGT was subsequently washed with distilled water until neutral and filtered. The treated WGT was dried at 80 °C for 24 h.

### 2. 5. 5. $\text{H}_2\text{O}_2$ Treatment

10 g of WGT were mixed with 50 mL of 25%  $\text{H}_2\text{O}_2$  and kept in contact for 3 h at room temperature, in a closed vessel and then boiled for 15 min. The sample was washed with distilled water to neutral pH, filtered and dried in an oven at 80 °C until constant weight.<sup>32</sup>

### 2. 5. 6. NaOH Treatment

10 g of WGT were mixed with 150 mL 1% NaOH solution for 6 h at room temperature.<sup>30</sup> The cellulosic sample was then washed thoroughly with distilled water

until the sample was neutralized and dried in the oven at 80 °C for 24 h.

The material obtained after each individual chemical treatment was grounded and passed through several sieves in order to obtain the desired particle size (200–400  $\mu\text{m}$ ). Finally, the resulting material was stored in airtight containers for further use.

## 2. 6. FTIR Analysis

The FTIR spectra (1.2 mg WGT samples mixed with 300 mg KBr) were obtained using JASCO 615 FTIR spectrometer, 500–4000  $\text{cm}^{-1}$ , resolution 2  $\text{cm}^{-1}$ .

## 3. Results and Discussion

### 3. 1. Elemental Analysis

Untreated and chemically treated WGT elemental analysis performed before and after MG adsorption showed that after treatment, in some cases (exception acidic treatments with  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , and tartaric acid), carbon content decreases from the initial 52.27% (untreated WGT) to values ranging from 44.83% for NaOH treatment to 45.80% for  $\text{H}_2\text{O}_2$ , Table 1. The organic content of the material decreases significantly due to the delignification process that takes place.<sup>32</sup> In the case of  $\text{H}_2\text{SO}_4$  treatment, carbon content increases to 56.83% due to the formation of a new active carbon material (biochar). Elemental analysis of WGT samples after MG adsorption showed an increase of the carbon content in all cases, confirming the fact that organic dye is adsorbed onto the surface of the studied materials.

### 3. 2. SEM Analysis

The surface morphology of untreated WGT, before (a) and after (b) adsorptive removal of MG was determined by SEM and is presented in Figure 1.

The raw WGT surface is shown to be rough and consists of many strands of fibrous-like materials (Figure 1a).

SEM image confirmed the amorphous and heterogeneous structure of WGT. Considerable changes in surface morphology after biosorption are noted as surface protuberances become less obvious and the surface becomes smoother (Figure 1b).

### 3. 3. The Effect of Adsorbent Quantity

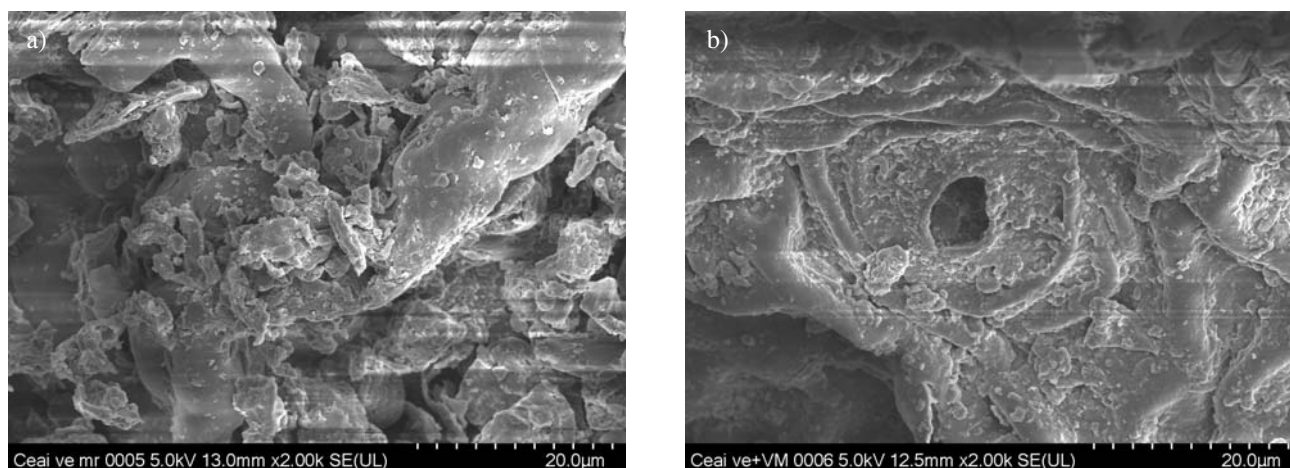
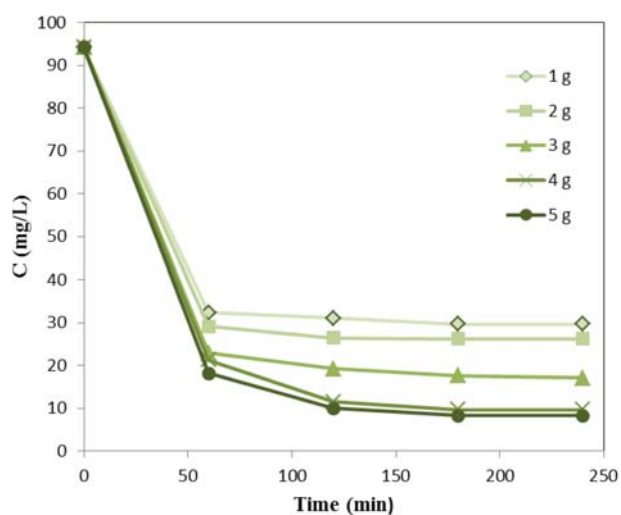
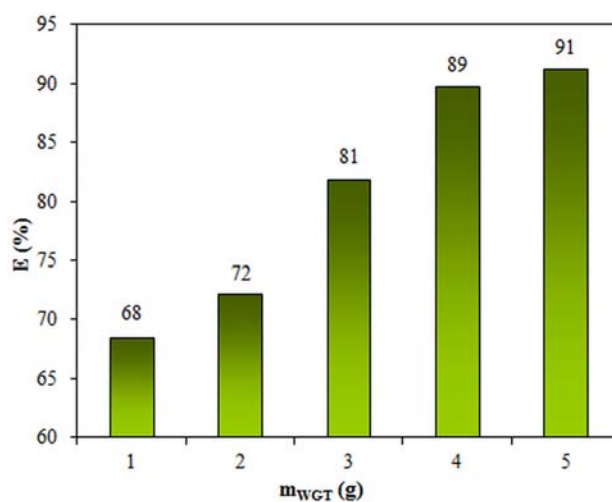
The adsorption of MG onto WGT was investigated by changing the adsorbent quantity, from 1 to 5 g, using particles of 200–400  $\mu\text{m}$  in diameter, 100 mL dye aqueous solution, 94 mg/L, magnetic stirring (300 rpm), for 240 minutes, until the equilibrium was reached, Figure 2.

As presented in Figure 3 with the increasing amount of adsorbent the adsorption efficiency increase too, due to

**Table 1.** Elemental analysis of WGT untreated and chemically modified, before and after MG adsorption (1% error)

Nr. crt.	Component	C (%)	H (%)	N (%)	O* (%)
1	WGT untreated – before adsorption	52.27	6.31	3.86	37.56
2	WGT untreated – after adsorption	53.71	5.92	3.26	37.11
3	WGT treated with H <sub>3</sub> PO <sub>4</sub> – before adsorption	54.06	3.56	1.76	40.62
4	WGT treated with H <sub>3</sub> PO <sub>4</sub> – after adsorption	58.78	4.07	2.47	34.98
5	WGT treated with H <sub>2</sub> SO <sub>4</sub> – before adsorption	56.83	5.64	3.46	34.07
6	WGT treated with H <sub>2</sub> SO <sub>4</sub> – after adsorption	60.26	5.72	3.86	30.16
7	WGT treated with HCl – before adsorption	48.19	6.59	3.67	41.55
8	WGT treated with HCl – after adsorption	49.71	6.60	4.30	39.39
9	WGT treated with tartaric acid – before adsorption	53.23	6.26	3.34	37.17
10	WGT treated with tartaric acid – after adsorption	54.07	6.49	4.13	35.31
11	WGT treated with H <sub>2</sub> O <sub>2</sub> – before adsorption	45.80	6.28	3.71	44.21
12	WGT treated with H <sub>2</sub> O <sub>2</sub> – after adsorption	46.13	6.15	3.93	43.79
13	WGT treated with NaOH – before adsorption	44.83	6.13	3.28	45.76
14	WGT treated with NaOH – after adsorption	48.25	6.34	3.09	42.32

\* Calculated by difference

**Figure 1.** Scanning electron micrographs of untreated WGT before (a) and after (b) adsorptive removal of MG.**Figure 2.** Influence of the WGT quantity (untreated) over the evolution of concentration in time (296 K, 94 mg/L, 100 mL, 200–400 μm, 300 rpm, 240 min).**Figure 3.** The effect of untreated WGT quantity over the adsorption efficiency (296 K, 94 mg/L, 100 mL, 200–400 μm, 300 rpm, 240 min).

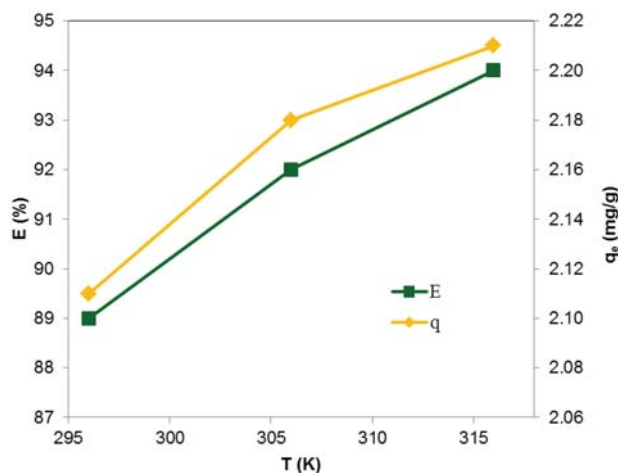
an increase of surface area and the availability of more adsorption sites, with more active functional groups.<sup>16,27</sup>

Taking into consideration that by changing the WGT quantity, from 4 to 5 g, the increase in adsorption efficiency is small ( $E_{4g} = 89\%$  and  $E_{5g} = 91\%$ ), and that higher quantities are difficult to handle in terms of sampling and separation from the aqueous solution, further experiments were carried on using 4 g of WGT.

### 3. 4. The Effect of Temperature

It well known that temperature plays an important role in the adsorption processes. A study of temperature dependence for the adsorption process gives valuable information about the enthalpy and entropy changes accompanying the adsorption processes.<sup>28</sup>

The adsorption of MG onto WGT was investigated in the 23–43 °C (296–316K) range. As it can be observed from Figure 4 an increase in temperature led to a higher quantity of dye removed, indicating that in this system adsorption takes place as an endothermic process. Similar findings were reported for other sorbent types.<sup>33–36</sup>



**Figure 4.** The effect of temperature on MG adsorption onto untreated WGT; (296 K, 94 mg/L, 100 mL, 4 g, 200–400 μm, 300 rpm, 240 min).

### 3. 5. Thermodynamic Analysis

The parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) can be estimated by the change of equilibrium constant with temperature.<sup>33</sup>

The Gibbs free energy change ( $\Delta G^\circ$ ) was calculated from equations (3) and (4), while the change of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were obtained using Van't Hoff equation (5):

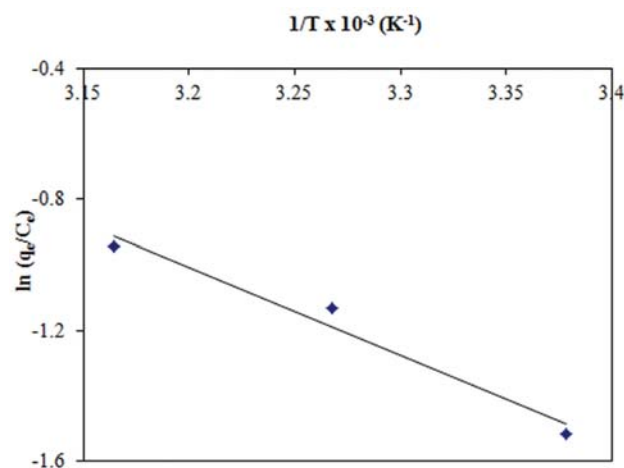
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

where, R is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/Kmol), T is absolute temperature (K), and  $K_d$  is the distribution coefficient ( $K_d = q_e/C_e$ ) (L/g).<sup>9,37</sup>

Slope and intercept values of  $\ln(q_e/C_e)$  versus  $1/T$  plot, Figure 5, were used to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$ . The values of the thermodynamic parameters are depicted in Table 2.



**Figure 5.**  $\ln(q_e/C_e)$  versus  $1/T$  plot for the estimation of thermodynamic parameters for MG adsorption onto untreated WGT.

The Gibbs free energy, which indicates the degree of spontaneity of the adsorption process,<sup>16</sup> decreased with increasing of temperature, indicating that a better adsorption is obtained at higher temperatures, and the process is more spontaneous at 316 K. The relatively small values of  $\Delta G^\circ$ , although positives, suggested that the adsorption process can be possible in a certain temperature range (between 296–316 K, in the present work).<sup>38–40</sup>

Positive value of  $\Delta H^\circ$  (22.42 kJ/kmol) shows the endothermic nature of the adsorption. This fact indicates the possibility of physical adsorption, since the heat of chemisorption generally falls into a range of 80–200 kJ/mol.<sup>41</sup> The low value of  $\Delta S^\circ$  may imply that no remarkable change in entropy occurred during the MG adsorption onto WGT. In addition, the positive value of  $\Delta S$  reflects the increased of randomness at the solid-solution interface during adsorption.<sup>42</sup>

**Table 2.** Thermodynamic parameters for MG adsorption onto untreated WGT at various temperatures; (94 mg/L, 100 mL, 4 g, 200–400 μm, 300 rpm, 240 min).

$\Delta S^\circ$ (kJ/mol K)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)		
		296 K	306 K	316 K
0.063	22.42	3.735	3.103	2.472

### 3. 6. The Effect of Chemical Treatments of WGT Biomass Onto MG Adsorption Process

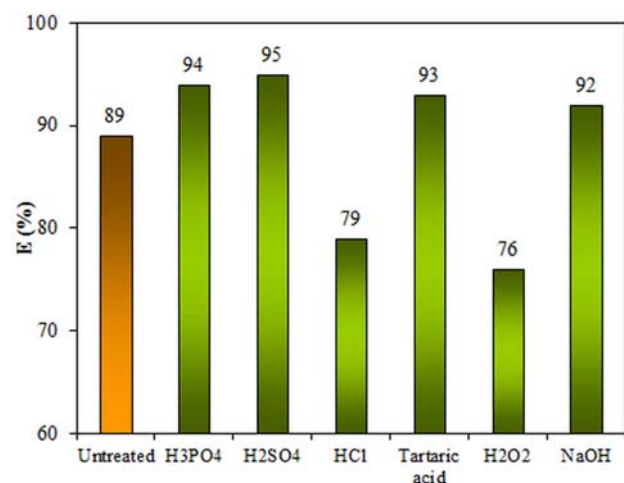
The influence of chemical treatments on adsorption efficiency of WGT is illustrated in Figure 5.

Generally, the acidic treatments change the negatively charged surface of the WGT biomass to positively charged and thus decrease the electrostatic attractions between biomass surface and the cationic molecules (of MG, for example).<sup>43</sup> Acid treatments allows the hemicellulose hydrolyze, especially xylan present in the lignocelluloses. Hemicelluloses can be degraded into xylose, mannose, acetic acid, galactose, glucose, etc. Phenolic compounds are also formed during acidic treatments from the partial breakdown of lignin.<sup>44</sup>

Tartaric acid treatment of the WGT biomass conducts to an increase of the amount of MG removed from the synthetic wastewater aqueous solutions, this chemical pretreatment converting the biomass to highly adsorbing material in terms of higher percentage of MG removed onto the modified tea surface, probably due to an increase of carboxylic groups number on the WGT surface, result that is in good agreement with others from literature.<sup>45,46</sup> The adsorption efficiency of MG increases from 89% (for untreated material) to 93% (after tartaric acid treatment).

WGT biomass treated with HCl led to a decrease of adsorption efficiency (from 89% for untreated material to 75% for HCl treatment), fact which can be attributed to the decrease in electronegativity of the biosorbent surface due to the presence of the residual  $H^+$  ions<sup>47,48</sup> Due to the fact that generally, the acid treatments lead to a decrease of adsorption, the still high values of adsorption efficiency obtained could be associated with the amount of organic matter present in the treated biomass.<sup>49</sup>

$H_3PO_4$  and  $H_2SO_4$  treatments were considered due to the fact that a different material can be obtained, acti-



**Figure 6.** Effect of chemical treatments over the adsorption efficiency of MG onto WGT; (296 K, 94 mg/L, 100 mL, 4 g, 200–400  $\mu$ m, 300 rpm, 240 min).

vated carbon (or biochar), which is commonly utilized due to its large adsorption capacity, fast adsorption kinetics, and relatively ease of regeneration.<sup>19,29</sup>

The activated carbon obtained from WGT biomass after  $H_3PO_4$  and  $H_2SO_4$  treatments provided better results for the adsorption efficiency that increases from 89 (for untreated biomass) to 94, and 95%, respectively (Figure 6), results that are in good agreement with other from the literature.<sup>16,50</sup>

In the case of alkali treatment such as NaOH, the increasing of adsorption efficiency can be explained by the fact that after treatment, hydrolysis reactions can occur, causing high dissolution of organic substances from the biomass.<sup>43</sup> The hydrolysis reactions can lead to the formation of more hydroxylic ( $HO^-$ ) and carboxylate ( $COO^-$ ) groups in the treated biomass, which enhance the cationic adsorption.<sup>51</sup> The mechanism of alkali treatment is believed to be saponification of intramolecular ester bonds crosslinking xylan hemicellulose and other component, for example, lignin.<sup>43</sup> Dilute NaOH treatment of lignocellulosic materials caused swelling, leading to a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure.<sup>30</sup>

After NaOH treatment, the WGT biomass had a better adsorption efficiency, an increase from 89 to 92% was noted. This treatment is very efficient, with a high increase in adsorption efficiency, fact that can be attributed to the changes on the biomass surface (increase in surface area, average pore volume, and pore diameter),<sup>52</sup> in addition to the already described effects of alkali treatment.<sup>30,43,47,51</sup>

As it can be seen in Figure 6, the treatment of WGT biomass with  $H_2O_2$  leads to a decrease in efficiency (76% by comparison with 89% for the untreated material), fact that confirm the hypothesis that if the concentration of oxidant agent is high (25%  $H_2O_2$ ), the modification of functional groups of the basic structure of the material takes place and the delignification of cellulosic WGT begins to occur.<sup>53</sup>

### 3. 7. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis is an important method for identifying the functional groups responsible for the retention of the dye molecules onto biomass surface. FTIR spectra were obtained for MG dye removal instead of onto untreated (Figure 7) and NaOH treated (Figure 8), before and after biosorption.

The increasing, decreasing, and shifted signals corresponding to different functional groups, were interpreted to indicate which groups participated in the adsorption process. The fact that no significant reduction in number of bands after adsorption for both untreated and treated WGT (Figures 7 and 8) was observed, could indicate that the studied process occurs mainly as physisorption).<sup>32</sup>



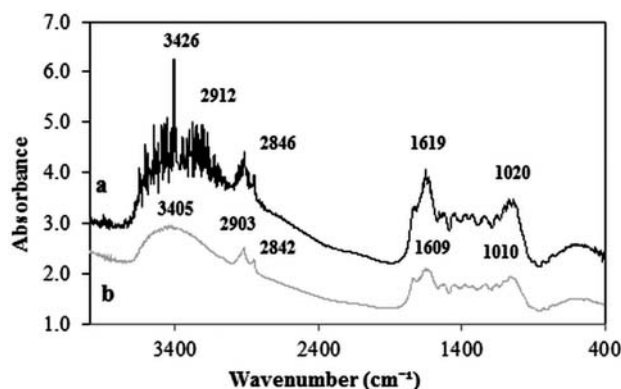


Figure 7. FTIR spectra of untreated WGT before adsorption (a) and after MG adsorption (b).

As it can see in Figure 7, the groups affected by the MG adsorption include  $\text{-OH}$ ,  $\text{N-H}$  (stretching), secondary amines,  $\text{SO}_3$  (stretching),  $\text{-C-C-}$ , and amines groups. In the spectrum of untreated WGT biomass (before adsorption), Figure 7a, a broad band from  $3600$  to  $3000\text{ cm}^{-1}$  for  $\text{-OH}$  groups of phenols/carboxyls was observed. The strong band attributed to the hydroxyl group (at  $3426\text{ cm}^{-1}$ ) might be an indication of high cellulose content. After adsorption the aspect of this band is rather flat, and the maximum is shifted to  $3405\text{ cm}^{-1}$ , suggesting the MG adsorption onto WGT surface takes place. Alkane  $\text{C-H}$  vibrations were identified at  $2919$  and  $2886\text{ cm}^{-1}$  for the untreated WGT before adsorption and shifted at  $2903$  and  $2842\text{ cm}^{-1}$  for the WGT after adsorption fact which can be explained by the change in the lignocellulosic structure.<sup>16,54</sup> A distinct band at  $1619\text{ cm}^{-1}$  was observed, Figure 7, that was shifted at  $1609\text{ cm}^{-1}$  after MG adsorption, band that was probably, the result of the stretching vibration of  $\text{C=O}$  and  $\text{C-N}$  (Amide I) peptidic bond of proteins.<sup>55</sup> Bands at  $1020\text{ cm}^{-1}$  (before adsorption) and  $1010\text{ cm}^{-1}$  (after adsorption) that could be attributed to the stretching vibration of the  $\text{C-O}$  groups, shifted after adsorption. The fingerprint region demonstrates the existence of sulfur or phosphate groups ( $800\text{--}400\text{ cm}^{-1}$ ).

All these changes identified in the FTIR spectra sup-

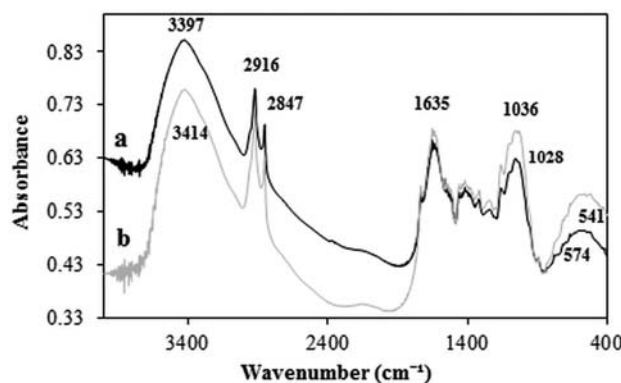


Figure 8. FTIR spectra of WGT treated with NaOH before adsorption (a) and after MG adsorption (b).

port the fact that MG dye adsorption onto WGT surface occurred.

Spectra of NaOH treated WGT before and after MG dye adsorption are depicted in Figure 8. The broad absorption peak at around  $3397\text{ cm}^{-1}$  correspond to the  $\text{O-H}$  stretching vibrations due to inter- and intra-molecular hydrogen bonding of cellulosic polymeric compounds (macromolecular associations), such as alcohols, phenols, and carboxylic acids, as in pectin, cellulose, and lignin, thus, showing the presence of hydroxyl groups on the adsorbent surface.<sup>47</sup> After MG adsorption this band was shifted at  $3414\text{ cm}^{-1}$ , fact which supports the MG adsorption. The band at  $2916\text{ cm}^{-1}$  is attributed to the  $\text{C-H}$  stretching vibration of aliphatic acids, while the band at  $1635\text{ cm}^{-1}$  is due to asymmetric stretching vibrations of  $\text{C=O}$ , from carboxyl acid groups.<sup>17,31</sup> The other prominent band at  $1028\text{ cm}^{-1}$  was shifted at  $1036\text{ cm}^{-1}$  and is due to  $\text{C-O}$  stretching vibration from cellulose. Moreover, in the case of treated WGT biomass after adsorption, a remarkable shift in positions of  $\text{-OH}$  and  $\text{C=O}$  bands was observed, which indicates that MG is binded mostly at these groups.<sup>56–59</sup> The changes in FTIR spectra confirm the binding of MG with functional groups present on the adsorbent surface. Similar observation were also reported by Pirbazari et al.<sup>25</sup> The proposed adsorption mechanism would involve the connection realized between a lone pair of the oxygen atom in  $\text{-OH}$  and  $\text{C=O}$  and the nitrogen atom  $=\text{N}^+(\text{CH}_3)_2$  in the MG molecule.

## 4. Conclusions

The efficiency of waste green tea biomass in removing malachite green dye from aqueous solution has been investigated. The removal efficiency increases with the increase of biomass quantity until no further significant change was observed ( $4\text{--}5\text{ g}$ ) and an increase in temperature, and hence the adsorption process is endothermic in nature. Six chemical treatments were tested (four acidic, one basic, and one oxidant) in order to study, first, the chemical groups responsible for the adsorption of MG onto WGT biomass, and secondly, which chemical treatment gives better results in terms of adsorption efficiency by comparison to the untreated material. For WGT biomass, the alkali (NaOH) and acidic ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , and tartaric acid) treatments led to increases of the adsorption efficiency from  $89\%$  (untreated WGT) to  $92\%$  (NaOH),  $93\%$ ,  $94\%$  and  $95\%$  for acidic treatments (tartaric acid,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{SO}_4$ , respectively).

It can be concluded that this green approach, eco-friendly, and economic cellulosic biomass, could be a promising adsorbent in environmental pollution cleanup. Also, chemical treatments applied to lignocellulosic adsorbents, improved adsorption efficiencies. Further detailed economical analysis (eg. materials and operating costs) could be used in order to design practical engineering application in the future.

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## Povzetek

Proučevana je bila adsorpcija barvila malahitno zeleno (MG) iz vodne raztopine na odpadno biomaso zelenega čaja (WGT). Izvedena je bila serija šaržnih eksperimentov z namenom ugotoviti vpliv temperature in količine biomase na adsorpcijo. Maksimalna kapaciteta odstranitve z neobdelano biomaso WGT je bila 89% (4 g biomase, 100 mL raztopine s koncentracijo 94 mg/L, 316 K), pri tem se je kapaciteta adsorpcije večala od 296 do 316 K. Izračunani termodinamski parametri ( $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ ) kažejo, da je adsorpcija endotermna in nespontana. Testiranih je bilo 6 kemijskih predobdelav biomase ( $H_3PO_4$ ,  $H_2SO_4$ , HCl, vinska kislina,  $H_2O_2$  in NaOH) z namenom ugotoviti skupine, odgovorne za adsorpcijo. Obdelava z NaOH in  $H_3PO_4$  je povečala adsorpcijsko kapaciteto na 92% in 95%. FTIR spektroskopija je pokazala modifikacijo površine biomase in s tem vpliv na adsorpcijo.