

*Dedicated to Professor Luminița Silaghi-Dumitrescu  
on the occasion of her 65<sup>th</sup> anniversary*

## **ADSORPTION, EQUILIBRIUM AND KINETIC STUDY OF MALACHITE GREEN REMOVAL FROM AQUEOUS SOLUTIONS USING FIR (*ABIES NORDMANNIANA*) CONES BIOMASS**

**ANA-MARIA SĂCARĂ<sup>a</sup>, CERASELLA INDOLEAN<sup>a\*</sup>,  
LIANA MARIA MUREȘAN<sup>a</sup>**

**ABSTRACT.** Adsorption of Malachite Green (MG) dye on a biomass prepared from fir (*Abies nordmanniana*) cones, followed by UV–Vis detection has been studied. The biomass was characterized using scanning electron microscopy (SEM). The maximum adsorption capacity of MG onto fir cones biomass was determined to be 2.197 mg/g. The influence of pH on the removal of the MG dye was investigated and the results showed that the best adsorption capacity were obtained in the most acidic environment (pH=2). The adsorption rates were evaluated by fitting the experimental data to conventional kinetic models such as pseudo- first- and pseudo-second-order models. From the Dubinin–Radushkevich isotherm model, a 5.95 kJ/mol value for the mean free energy was calculated, indicating that MG adsorption could include an important physisorption stage.

**Keywords:** *adsorption, cones biomass, Abies nordmanniana, kinetics, dyes, malachite green*

### **INTRODUCTION**

Malachite green (MG) is a cationic dye used extensively in the textile finishing industry for dyeing cotton, silk, wool and leather products [1] as well as in aquaculture to treat parasites, fungal and bacterial infections [2].

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<sup>a</sup> Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania,

\* Corresponding author [cella@chem.ubbcluj.ro](mailto:cella@chem.ubbcluj.ro)

Due to its potential carcinogenicity, mutagenicity and teratogenicity [3] MG should be removed from wastewater and this process has become an important environmental issue.

One of the simplest and most cost-effective techniques to remove MG from aqueous effluents consists in its adsorption on different materials such as zeolites [4], clays [5], compost [6], active carbon prepared from different biomaterials such as pine sawdust [7], oak wood [8], olive stones [9] cherry stones [10] etc., but mostly on biosorbents derived from renewable resources [11-14]. By contrast with carbon-based and other inorganic adsorbents, biosorbents have some significant advantages. They exhibit excellent adsorption capacity, fast adsorption kinetics and simplicity of design together with low cost and availability [15].

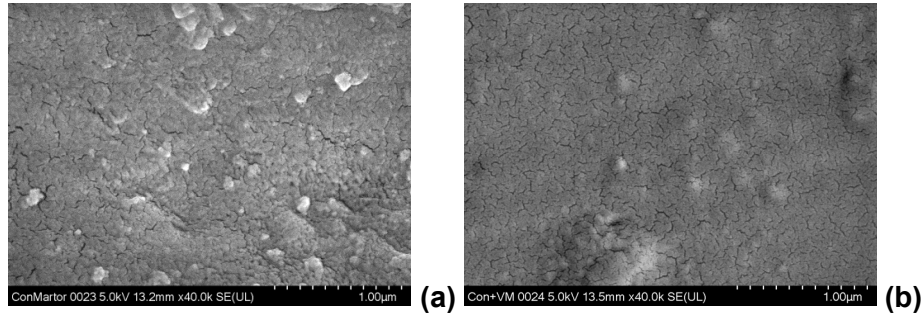
Numerous physicochemical factors affect dye adsorption, including: (i) characteristics of the adsorbent (*i.e.* surface area, pore structure, surface treatments, particle size); (ii) characteristics of the dye molecule, and (iii) operational conditions, such as pH, temperature, contact time etc. [16]. The interactions occurring between the adsorbate and adsorbent have to be also taken into consideration.

In this context, adsorption of MG dye on biomass prepared from fir tree (*Abies nordmanniana*) cones biomass, followed by UV–Vis detection has been developed for the removal of the dye from aqueous solutions. The biomass was subsequently characterized using scanning electron microscopy (SEM). The influence of pH on the removal of MG was investigated. The adsorption rates were evaluated by fitting the experimental data to conventional kinetic models such as pseudo first- and second-order models.

## RESULTS AND DISCUSSION

### SEM characterization of the biomass

Scanning electron microscopy (SEM) images of the biomass surface were taken before and after the adsorption of MG. As can be seen from figure 1a, the crevices and the pores of the adsorbent offer good conditions for dye adsorption. Figure 1b shows clearly a smoother surface, resulted after filling the crevices with dye molecules.

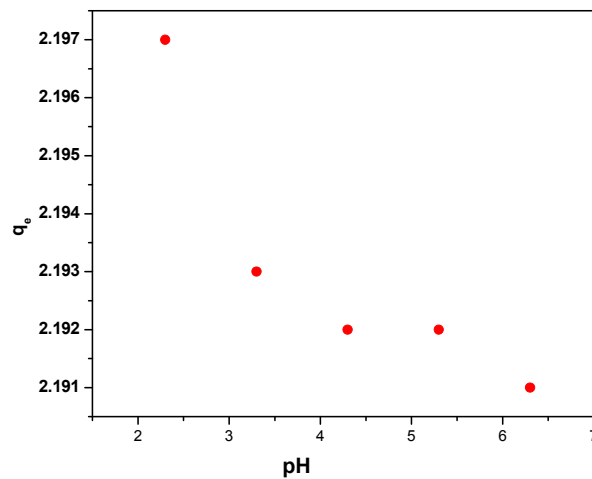


**Figure 1.** SEM images of the fir cones biomass before (a) and after (b) MG adsorption

### Effect of pH

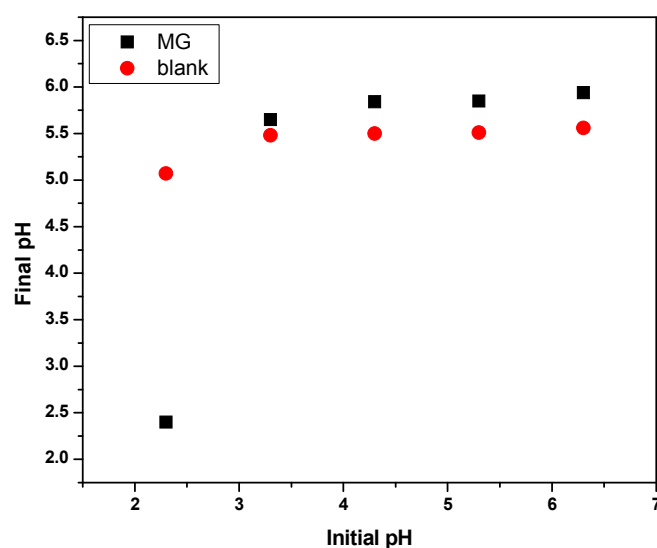
Initial pH of the solution can significantly influence the dye adsorption on the adsorbent surface. Consequently, the effect of pH was investigated in the range of 2 to 6 imposed by the solubility of MG, which is better at acidic pHs. At basic pH values, new species of the dye can form [17] which could impede on the accuracy of the experimental results.

It was observed that the best adsorption capacities were obtained in the most acidic environment, as can be seen in Figure 2. These results are different from those of some similar studies on MG [18], but are in agreement with the observations of some authors relative to other basic dyes, such as Maxilon Blue [19]. This could be attributed to the better solubility of MG, as could be observed during the experiments.



**Figure 2.** Initial pH influence on MG adsorption capacity of cones biomass, 5g, 0.2-0.4 mm,  $t=20^{\circ}\text{C}$ ,  $C_0=100\text{mg/L}$  MG, 100mL solution

Moreover, the fir cone biomass was observed to have a notable buffering effect on the solutions with pH between 3 and 6 (figure 3), by shifting the solution pH toward 6, irrespective to the initial pH value. At this pH, adsorption of MG is favored and involves interactions of the dye with the functional groups of the adsorbent [20]. At strong acidic environments, the MG acts itself as an acid according to its pKa (6.9) [21], counteracting the buffering effect of the biomass (Figure 3).



**Figure 3.** Initial pH influence over final pH for blank and MG adsorption, 5g biomass, 0.2-0.4 mm,  $t=20^{\circ}\text{C}$ ,  $C_0=100\text{mg/L}$  MG, 100mL solution.

Blank sample (shown in Figure 3) refers to the values obtained in batch experiments conducted under identical conditions (biomass:solution ratio, temperature and contact time) with distilled water instead of MG solution, in order to establish the contribution of MG on the global pH shift.

### Adsorption isotherms

In order to characterize the adsorption process, the experimental data were analyzed according to the linear forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) equilibrium isotherms (Figure 4).

Langmuir isotherm proposes that the adsorption sites on the surface are identical, the final result being a monolayer of adsorbate.

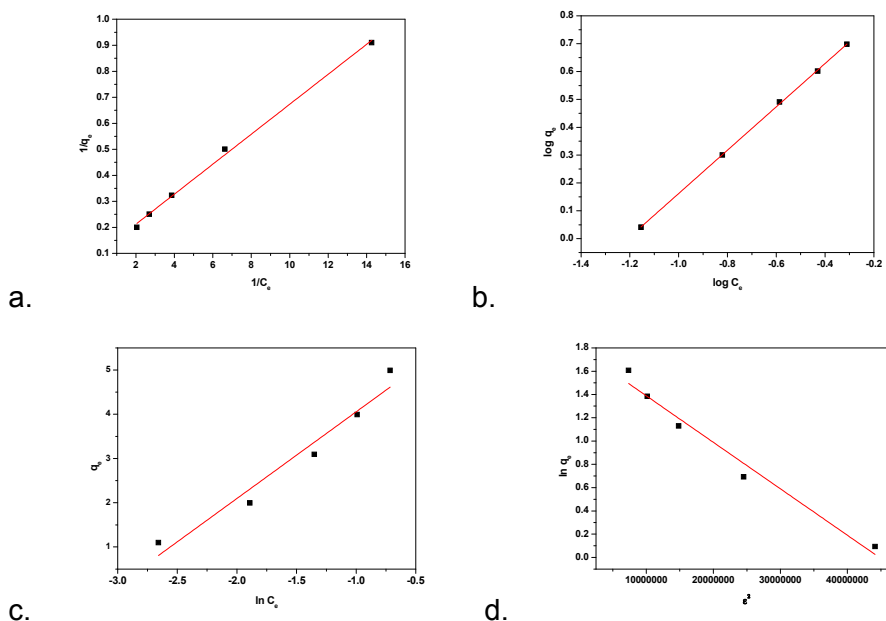
Freundlich isotherm assumes that a heterogeneous adsorption occurs, the active sites are different by nature and energy and that there is a link between adsorption capacity ( $q_e$ ) and dye concentration at equilibrium. [17]

Temkin isotherm takes into account adsorbent-adsorbate interactions, assuming that the heat of adsorption, expressed as a function of temperature, decreases linearly with coverage [22] while D-R isotherm model is applied to uncover the nature of the process, as physical or chemical sorption [23].

Characteristic parameters were calculated and are shown in Table 1. The values are comparable to results obtained in other similar studies [24, 25]

In Table 1,  $A_T$  is Temkin isotherm constant,  $\text{dm}^3/\text{mol}$ ;  $B_D$ - Dubinin-Radushkevich isotherm constant,  $\text{mol}^2/\text{J}^2$ ;  $b_T$  -Temkin isotherm constant;  $C_e$ - is the adsorbate concentration at equilibrium  $\text{mg}/\text{dm}^3$ ;  $E$  - free energy of sorption,  $\text{J}/\text{mol}$ ;  $K_L$ - Langmuir isotherm constant,  $\text{dm}^3/\text{g}$ ;  $K_F$ - Freundlich isotherm constant;  $n_F$  - Freundlich isotherm exponent;  $q_e$  is the equilibrium adsorption capacity ( $\text{mg}/\text{g}$ ) and the other symbols have the usual significance.

From the Dubinin–Radushkevich isotherm model, a 5.95 kJ/mol value for the mean free energy was calculated, indicating that MG adsorption could be a physisorption process [26, 27].



**Figure 4.** Isotherm models: Langmuir (a)., Freundlich (b)., Temkin (c). and Dubinin-Radushkevich (d), for MG adsorption on *Abies nordmanniana* cones biomass, 5g, 0.2-0.4 mm,  $t=20^\circ\text{C}$ ,  $C_0=100\text{mg}/\text{L}$  MG, 100mL solution.

After examining the similarity between the different adsorption isotherms models and the experimental results, it seems that Freundlich isotherm is most adapted for the fitting of MG adsorption, as encountered in many similar studies [28].

**Table 1.** Characteristic parameters of adsorption isotherms

| Isotherm            | Equation  | R <sup>2</sup> /N | Parameters                                 | Values                |
|---------------------|---|-------------------|--|-----------------------|
| Langmuir            | $1/q_e = 1/q_m K_L C_e + 1/q_m$   | 0.9976/5          | $q_m$ (mg/g)                               | 10.27                 |
|                     |   |                   | $K_L$ (dm <sup>3</sup> /g)                 | 1.69                  |
| Freundlich          | $\lg q_e = \lg K_f + 1/n \lg C_e$   | 0.9998/5          | $n_F$                                      | 1.29                  |
|                     |   |                   | $K_F$                                      | 2.56                  |
| Temkin              | $q_e = RT/b_T \ln(A_T C_e)$   | 0.9577/5          | $b_T$ (J/mol)                              | 1244.77               |
|                     |   |                   | $A_T$ (dm <sup>3</sup> /mol)               | 3.00                  |
| Dubinin-Raduskevich | $\ln q_e = \ln q_D - B_D R^2 T^2 [\ln(1+1/C_e)]^2$<br><br>* $\ln(1+1/C_e) = \varepsilon$ for graph 4d | 0.9755/5          | $B_D$ (mol <sup>2</sup> /kJ <sup>2</sup> ) | 1.41x10 <sup>-6</sup> |
|                     |   |                   | $E$ (kJ/mol)                               | 5.95                  |
|                     |   |                   | $q_D$ (mg/g)                               | 5.88                  |

### Kinetics of adsorption

Kinetics of adsorption is one of the most important characteristics in defining the adsorption efficiency. In order to describe the mechanism of MG removal on fir cones biomass, pseudo-first and pseudo-second order kinetics as well as film layer and intra-particle diffusion were taken into consideration.

It is common knowledge that, if the adsorption is the only phenomenon occurring on the surface, the variation of the reaction rate should be proportional to the first power of adsorbate concentration (pseudo-first-order kinetics) [26, 29]. Lagergren suggested a first-order equation for the adsorption of liquid/solid system based on solid capacity, which can be expressed in linear form as follows [26, 27]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where,  $q_e$  and  $q_t$  are the amounts of adsorbate for 1 g of adsorbent (mg/g) at equilibrium and time  $t$ , respectively,  $t$  is time (min),  $k_1$  is the rate constant of the first order adsorption (1/min).

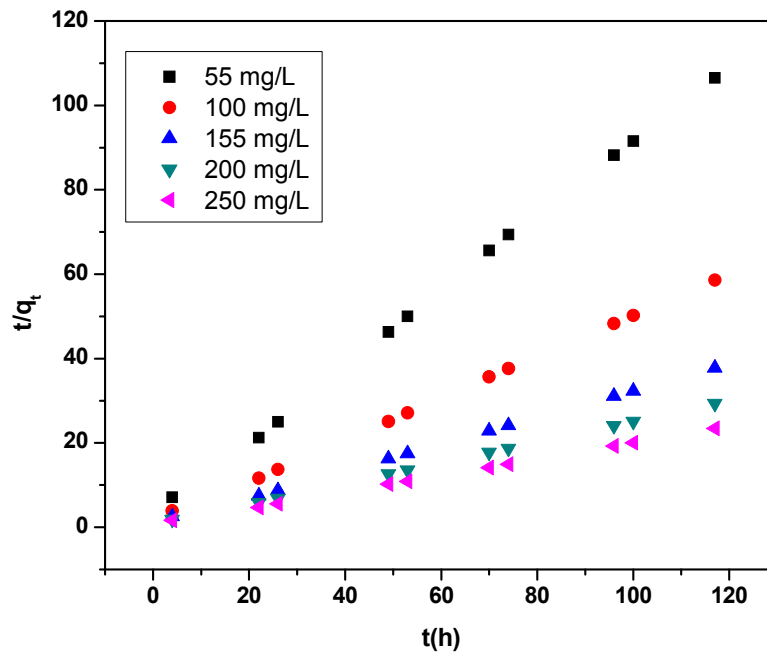
If diffusion (both on the adsorbent's surface and through its pores) has a contribution to the global mechanism, limiting the adsorption process, the dependence between the concentration and rate will not be linear.

The pseudo-second-order kinetic model is derived on the basis of the adsorption capacity of the solid phase. The linear form of the model is expressed as follows [28, 30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where,  $q_e$  and  $q_t$  are the amounts adsorbed at equilibrium and time  $t$ , respectively (mg/g),  $t$  is time (min),  $k_2$  is the rate constant of the second order adsorption (g/mg·min).

An analysis of the experimental data allowed us to conclude that the  $q_e$  value calculated based on the pseudo-second order model compared to  $q_e$  values obtained from experimental data are closer. Also taking into consideration the fact that the correlation coefficient is  $R^2 = 0.999$ , for all five initial concentrations (55, 100, 155, 200 and 250 mg MG/L), (Figure 5, Table 2), in the case of pseudo-second-order model, we concluded that this model describes the considered adsorption process.



**Figure 5.** Pseudo-second order kinetics for MG adsorption on *A. nordmanniana* cone biomass, 5g, 0.2-0.4 mm,  $t=20^\circ\text{C}$ ,  $C_0=55\text{-}250\text{mg MG/L}$ , 100mL solution.

**Table 2.** The correlation coefficient ( $R^2$ ) for pseudo-first and pseudo-second order models and different initial MG concentrations.

| Kinetic model       | Initial MG concentration [mg MG/L] | $R^2$ |
|---------------------|------------------------------------|-------|
| Pseudo-first order  | 55                                 | 0.448 |
|                     | 100                                | 0.447 |
|                     | 155                                | 0.445 |
|                     | 200                                | 0.444 |
|                     | 250                                | 0.463 |
| Pseudo-second order | 55                                 | 0.999 |
|                     | 100                                | 0.999 |
|                     | 155                                | 0.999 |
|                     | 200                                | 0.999 |
|                     | 250                                | 0.999 |

The results are in agreement with most adsorption studies concerning MG [28-31].

As already mentioned, adsorption processes are accompanied by two types of diffusion: one on the material's surface (liquid layer, or external diffusion) and the other through the pores of the adsorbent (internal diffusion). One of these two types is often rate determining for the entire process, therefore determining their implication is important.

To identify the diffusion mechanism involved in MG retention on cones biomass, the model based on the theory of Weber and Morris was considered and can be written as follows: [32].

$$q_t = k_{ip} \cdot t^{0.5} \quad (3)$$

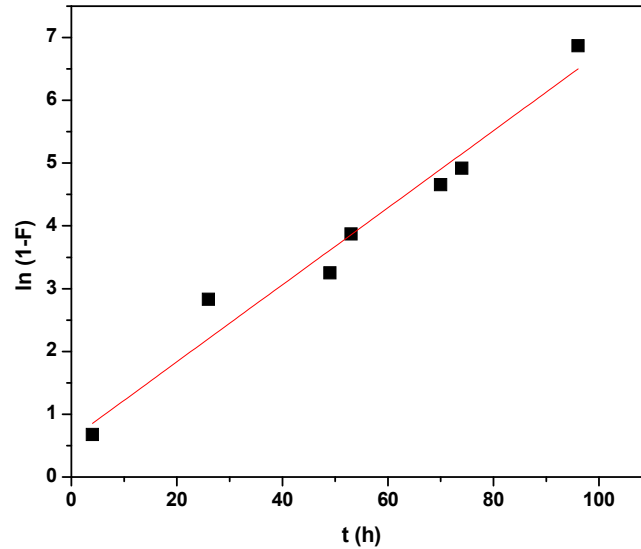
where,  $k_{ip}$  is the intra-particle diffusion rate constant ( $\text{mg/g} \cdot \text{min}^{0.5}$ ).

According to this theory, if intraparticle diffusion is the rate determining step, the adsorbate uptake,  $q_t$  should be directly proportional to  $t^{1/2}$  and the plot  $q_t$  vs.  $t^{1/2}$  passes through the origin. If the plots do not pass through the origin, it is possible that intraparticle diffusion is not the only rate controlling step.

By examining the plot it could be seen that it not linear, meaning that the intraparticle diffusion is not the rate determining step, therefore results are not shown, but the correlation coefficients ( $R^2$ ) and intercept values for intra-particle and liquid layer diffusion can be seen in Table 2.

As expected, at the beginning, the adsorption is fast, the high adsorption rate being due to the availability of the uncovered surface area of the adsorbent [19].





**Figure 6.** Liquid layer diffusion pattern of MG on fir cone biomass, 5g, 0.2-0.4 mm,  $t=20^{\circ}\text{C}$ ,  $C_0=100\text{mg/L}$  MG, 100mL solution.

Regarding the liquid layer (external) diffusion, the kinetic data have been analyzed using the model proposed by Boyd et al. [33]:

$$\ln(1-F) = -B_t - \ln\left(\frac{6}{\pi^2}\right) \quad (4)$$

where  $F$  represents the fraction of solute adsorbed at any time  $t$  (min),  $F = q_t/q_0$  and  $B_t$  is a mathematical function of  $F$ .

Analyzing the experimental plot it suggests that intra-particle diffusion has a more important contribution to the global process.

The fact that the  $R^2$  value is higher (0.9748) and the intercept is different, but closer to 0 (0.173 compared to 0.32 for liquid layer diffusion) confirms that in the given experimental conditions the intra-particle diffusion is most probably the rate determining step.

**Table 3.** The correlation coefficients ( $R^2$ ) and intercept values for intra-particle and liquid layer diffusion

| Diffusion type | $R^2$  | Intercept |
|----------------|--------|-----------|
| Intra-particle | 0.9748 | 0.173     |
| Liquid layer   | 0.9568 | 0.32      |

## CONCLUSIONS

Fir (*Abies nordmanniana*) cones biomass was successfully used as a low cost adsorbent for the removal of toxic MG dye from aqueous solutions. The maximum adsorption capacity was determined to be 2.197 mg/g.

Four isotherms were used to model the adsorption of MG on the fir cones biomass. The classification of the models obtained by simulation of the corresponding equations and correlation with the experimental data was Freundlich > Langmuir > Dubinin-Radushkevich > Temkin. Between the four isotherm models considered, Freundlich model describes better MG dye adsorption onto fir cones biomass ( $R^2 = 0.9998$ ). From the Dubinin-Radushkevich isotherm model, a 5.95 kJ/mol value for the mean free energy was calculated, indicating that MG adsorption could be a physisorption process.

Kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model, with a correlation coefficient of 0.999 for all five initial concentrations (55, 100, 155, 200 and 250 mg MG/L, respectively).

## EXPERIMENTAL SECTION

### Preparation of dye solution

Analytical grade triphenylmethane dye MG ( $\lambda = 618$  nm) in oxalate salt form was procured from Penta - Ing. Petr Švec, Czech Republic. Stock solution was obtained by dissolving 1 g of anhydrous powder in 1L of distilled water. Experimental solutions of different concentrations (55, 100, 155, 200 and 250 mg MG/L) were realised by subsequent dilutions.

### Preparation and characterisation of adsorbent

The fir (*Abies nordmanniana*) cones used in this study were collected from a natural forest biotope in Cluj-Napoca, Cluj county, Romania. The cones were washed with tap water and left to dry out naturally, then grounded with a ball mill. The resulting material was boiled for 20 min to extract the natural colorant, then washed with distilled water and dried at 65-75°C for 3 days and sieved into five particle size fractions (<0.2, 0.2-0.4, 0.4-0.6, 0.6-1, 1-1.25 mm).

SEM images of the biomass were obtained on a with a JEOL (USA) JSM 5510 LV apparatus.

### Adsorption studies

The MG adsorption on fir cones biomass was studied using the batch technique, with immobilized phases. Experiments were carried out by contacting different quantities of adsorbent, at 23°C, with 100 mL MG in aqueous solutions, with different initial concentrations (55–250 mg/L), until the equilibrium was reached.

Samples were collected and the residual concentration of MG was determined with a UV-Vis spectrophotometer Cintra 202 (GBC Scientific Equipment Ltd.) at 618 nm.

The amount of adsorbed MG dye (adsorption capacity  $q_e$ , mg/g) was calculated using Equation (5). Removal efficiency (E, %), Equation (6) was also calculated, in order to establish the effectiveness of the considered biomass in the Cd (II) removal process.

$$q_e = \frac{(C_0 - C_e)}{w} \times \frac{V}{1000} \quad (5)$$

$$E, (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (6)$$

where,  $C_0$  is the initial MG concentration (mg/L),  $C_e$  is MG concentration at equilibrium (mg/L),  $V = 100$  mL, and  $w$  is the quantity of the adsorbent (g). [27].

The influence of initial pH (2-6) on the adsorption efficiency was studied. Its initial value was altered with 0.1M NaOH or 0.1M HCl solution, respectively.

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