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# Malachite green removal from aqueous solution using the system rapeseed press cake and fungus *Myrothecium roridum*

Anna Jasińska*, Przemysław Bernat, Katarzyna Paraszkiewicz

*Department of Industrial Microbiology and Biotechnology, Faculty of Biology and Environmental Protection,*
*University of Lodz, Banacha 12/16, 90-237 Łódź, Poland*
*Tel. +48 (42) 6354146; email: ajas@biol.uni.lodz.pl*

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## ABSTRACT

The waste of rapeseed press cake (WRPC), obtained after the preparation of microbial culture medium, was investigated in a batch system as an adsorbent of malachite green (MG). The effects of the contact time, the temperature, the initial dye concentration and the adsorbent dosage were examined using MG aqueous solutions of pH 6.5. The highest sorption of MG was observed after 180 min in solution containing 50 mg/L of MG and 2.5 mg/L of WRPC. Equilibrium isotherm data was described by the Langmuir, Freundlich and Dubinin-Radushkevich models. The Langmuir expression was found to provide the best correlation. Kinetic models and thermodynamic parameters (Gibbs free energy, enthalpy, and entropy) were also investigated. Experimental data revealed that MG sorption followed the pseudo-second-order rate kinetics. MG desorption efficiency (94.5%) from WRPC with the use of 0.1 M NaOH solution was determined. Biological degradation of the dye-loaded sorbent in a submerged culture of the filamentous fungus *Myrothecium roridum* IM 6482 was also demonstrated.

*Keywords:* Malachite green sorption; Rapeseed press cake; Isotherm; Kinetics; Desorption; *Myrothecium roridum*

## 1. Introduction

Malachite green (MG), an *N*-methylated diaminotriphenylmethane dye is utilized for coloring a variety of materials (e.g. cotton, wood, silk, leather, paper and jute) as well as in manufacture of paints or printing inks [1]. Due to its antifungal, antibacterial and antiparasitical activity, MG is commonly applied in aquaculture, commercial fish hatchery and animal husbandry [2]. The available toxicological information reveals that MG is toxic to mammalian cells and possibly causes carcinogenic, mutagenic and teratogenic effects in humans [3]. Moreover, MG is easily reduced in organisms to persistable leucomalachite green, which also acts as a tumor promoter [4].

In response to concerns regarding the health risks associated with the use of MG, adsorption is, by far, the most versatile and widely used technique for the removal of dyes from aqueous solutions [5]. Currently, the most commonly used adsorption agent in industry is activated carbon [6]. However, there is a continuous search for alternate low-cost sorbent materials to replace high cost activated carbon used for water and wastewater treatment. Among sorbents,

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*Corresponding author.

those originating from agricultural by-products, such as crop wastes, are particularly interesting because of their low-cost and ubiquity [7–9].

In many European countries, rapeseed (*Brassica napus* L.) and sunflower (*Helianthus annuus* L.) are the most frequently grown oleaginous plants [10]. Especially, rapeseed is a source of food grade oil as well as provides compounds utilized in biodiesel manufacturing. Therefore, in Poland and many other EU countries rapeseed press cake (RPC) is a by-product abundantly remaining after oil extraction. Having a high energy content RPC may be incinerated to derive thermal energy. It may also be used as a protein supplement in animal feeding [11]. In our laboratory RPC is a source of nutrient compounds in some growth media used for filamentous fungi culturing.

Agricultural residues including e.g. press cakes are often examined as a sorption material. Nevertheless, very little information is available on RPC sorption capabilities. RPC has been successfully utilized for the sorption of heavy metals ions [12] and the removal of atrazine from water solutions [13]. To our best knowledge, there are no reports concerning exploitation of waste obtained from RPC as a sorption material.

The aim of the present investigation was to study the removal of MG from aqueous solutions by the waste of rapeseed press cake (WRPC) achieved after a water extraction of RPC particles. The obtained extract was used as a growth medium for various filamentous fungi culturing. The effects of different experimental conditions such as the contact time, the initial concentration of dye cation, the biosorbent mass and the temperature on the removal kinetics were studied. Langmuir and Freundlich equations were used to fit the equilibrium isotherms. The kinetics of adsorption was determined using pseudo first-order, pseudo-second-order reaction and intraparticle diffusion. MG desorption from the WRPC, reuse of sorbent for dye removal and finally fungal degradation of reused the WRPC were also studied.

## 2. Materials and methods

### 2.1. Adsorbent

The batch sorption studies were conducted using RPC obtained from Bio-Tech Ltd (Gorczyn, Poland). Crude RPC was characterized by moisture content 8.02%, oil content 8.50%, fibre content 9.00–10.00% and protein content 35.00%. An aqueous suspension of RPC was sterilized in an autoclave (117˚C, 20 min) and then filtered. The supernatant was resterilized (117˚C, 10 min) and used as growth medium of various filamentous fungi (e.g. *Myrothecium roridum* and *Paecilomyces marquandii*) in another experiments performed in our laboratory. The WRPC was employed as an MG sorbent. Prior to use, the WRPC was crushed and sieved to obtain particles smaller than 650 μm. The sorbent was rinsed with deionised water to remove the fines and dried at oven temperature 70˚C.

### 2.2. Malachite green

MG, an *N*-methylated diaminotriphenylmethane dye of a technical grade was kindly supplied by the Boruta-Zachem Color Co. (Zgierz, Poland). The MG solutions were prepared by dissolving the colorant in deionised water at desired concentrations before each experiment.

### 2.3. Sorption experiments

Experiments were conducted in 100 mL Erlenmeyer flasks containing 25 mL of the MG solution at pH of 6.5 at an orbital shaking of 120 rpm. Samples were withdrawn at the pre-determined time intervals (from 5 to 360 min) and the adsorbent was separated from the solution by centrifugation at 3,000 *g* for 30 min. The absorbance of the supernatant solution was analyzed with spectrophotometer SPECORD 200 (Analytik Jena) at the wavelength of 615 nm to determine the MG concentration. In the present study, we examined the effect of the initial concentration of the dye, the biosorbent dose, the contact time and the temperature on biosorption. The experiments were done using various amounts of the adsorbent (2.5, 5 and 10 g/L), the initial dye concentration (10, 25 and 50 mg/L) and the temperature of incubation (301.15, 311.15 and 321.15 K) at different time intervals. Each experiment was conducted in triplicates and mean values were used for the data analysis. Standard deviation and analytical errors were calculated and maximum errors were found to be within ±8% of the measured values.

### 2.4. Desorption studies

A dye-loaded adsorbent was obtained from a batch process in which 25 mL of MG solution (50 mg/L) was treated with 250 mg of the WRPC for 24 h at 28˚C on a rotary shaker (120 rpm). Then the MG-loaded adsorbent was gently washed several times with distilled water to remove the unadsorbed dye. The desorption process was carried out for 3 h under agitation (120 rpm) with 25 mL of one of the following eluents: NaOH (0.1 M); NaOH (1 M); ethanol (70%) and acetone (70%). The desorption ratio was calculated based on spectra analysis, with respect to MG calibration curves prepared in appropriate NaOH, ethanol or acetone solutions by using the following equation:

$$\text{Des}\ (\%) = \text{Q}/\text{d}\times 100\% \tag{1}$$

Q—amount of MG desorbed to the eluent [mg];

D—amount of MG adsorbed on the WRPC [mg].

After MG desorption the WRPC was thoroughly washed with distilled water, dried for 24 h and reused for an adsorption study in conditions described earlier. The samples were then analysed in a spectrophotometer as mentioned above.

### 2.5. Fungal degradation of MG-loaded WRPC

MG-loaded WRPC obtained as described in point 2.4. was dried at 60°C and sterilized by autoclaving. Liquid Czapek-Dox medium (18 mL) containing 1 g of dye-loaded WRPC was inoculated with 2 mL of *Myrothecium roridum* IM 6,482 homogenous second-step preculture prepared according to Jasińska et al. [14]. The culture was incubated in 100 mL Erlenmayer flask on a rotary shaker (150 rpm) at 28°C. After 72 h the morphology of fungal cells and the RPC appearance were inspected by use of an Axiovert 200 M microscope with a confocal scanning module LSM 5 PA (Zeiss, Germany) and Nomarski differential interference. To quantitative estimation of MG content, samples of fungal cultures were homogenized, extracted and analyzed with the HPLC-MS/MS method described by Jasińska et al. [14].

### 2.6. Data analysis

The amount of MG uptake by the WRPC in the equilibrium, $q_e$ (mg/g) was estimated as follows:

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

where $V$ is the volume of solution (L) and $m$ is the mass of the sorbent (g) used in this study. $C_0$ (mg/L) and $C_e$ (mg/L) are the initial and the equilibrium concentrations of MG, respectively.

### 2.7. Thermodynamic studies

The influence of the temperature on the sorption of MG by the WRPC was studied with a constant initial concentration of 50 mg/L, a sorbent mass of 10 g/L. Using the experimental data, some thermodynamic parameters, including a change in the Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) were determined using the following equations.

$$\Delta G^\circ = -RT \ln K_d \tag{3}$$

$$K_d = \frac{q_e}{C_e} \tag{4}$$

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

where $q_e$ was the amount of MG (mg) sorbed by the WRPC per 1 L of the solution at the equilibrium, $C_e$ is the equilibrium concentration (mg/L) of MG in solution, $K_d$ is the distribution coefficient for the sorption and $R$ the gas constant (8.314 J/mol/K), $T$ is the solution temperature (K).

### 2.8. Equilibrium isotherms and kinetic models

The correlation between the level of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich, and Dubinin-Radushkevich

Table 1
Empirical models used for data analyses

| | Non-linear form | Linear form | Eq. no. |
|---|---|---|---|
| *Equilibrium isotherm models* | | | |
| Langmuir | $q_e = \frac{Q_m K_a C_e}{1 + K_a C_e}$ | $\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} C_e$ | 6 |
| Freundlich | $q_e = K_F C_e^{1/n}$ | $\log q_e = \log K_F + \frac{1}{n} \log C_e$ | 7 |
| The Dubinin-Radushkevich (DR) isotherm | $q_e = X_m \exp(-K\varepsilon^2)$ | $\ln q_e = \ln X_m - K\varepsilon^2$ | 8 |
| *Reaction-based kinetic models* | | | |
| Lagergren pseudo-first-order | $\frac{dq_t}{dt} = k_1(q_e - q_t)$ | $\ln(q_e - q_t) = \ln q_e - k_1 t$ | 9 |
| Pseudo-second-order | $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ | 10 |

(DR) isotherm equations [15–17] (Table 1) Eqs. (6)–(8). The MG sorption kinetics was analyzed with both reaction-based and diffusion-based models as summarized in Table 1. The models used included the Lagergren pseudo-first order [18] and the Ho's pseudo-second order [19] for diffusion-based kinetics Eqs. (9) and (10).

## 3. Results and discussion

### 3.1. *Effect of the contact time and the initial MG concentration*

The relations between the removal of MG and the reaction time were studied to check the rate of dye removal. Fig. 1 illustrates the sorption of MG for different initial dye concentrations for a sorbent dose of 2.5 g/L as a function of the contact time. It is evident that the amount of MG adsorbed on the WRPC at a lower initial MG concentration was smaller than the amount of the dye when higher initial concentrations were used. A similar phenomenon was observed by Bulut et al. for MG adsorption onto betonite [20]. Probably the adsorption of MG onto WRPC was due to the increased driving force of the concentration gradients. Chowdhury et al. described quite similar tendency for sorption of MG from aqueous solution onto chemically modified rice husk [21]. It can also be seen from Fig. 1 that the MG initial concentration had an influence on the contact time necessary to reach the equilibrium. For a concentration of 10 mg/L, the equilibrium was reached after 60 min, while for 50 mg/L it occurred after 180 min.

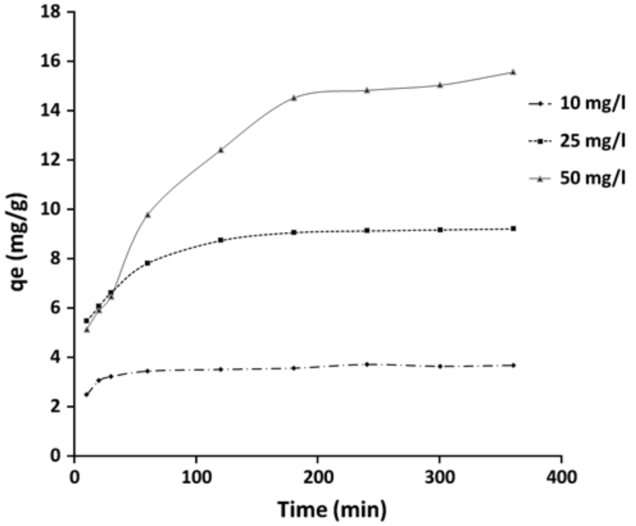

Fig. 1. Effect of the initial concentration of the dye on the sorption of MG by the waste of rapeseed press cake.

### 3.2. *Effect of the adsorbent mass on MG adsorption*

Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The influence of the WRPC dose investigated in the range of 2.5 to 10 g/L was selected experimentally. The adsorption of MG on the WRPC was studied by changing the quantity of the adsorbent (2.5, 5, 10 g/L) in the test solution where the initial MG concentration (50 mg/L), the temperature (28°C) and the pH (6.5) were constant for 360 min (Fig. 2). The amount of dye sorbed per unit mass of the sorbent decreased with an increase in the sorbent dose. From Fig. 2, it can also be seen that the sorbent dosage had an influence on the contact time necessary to reach the equilibrium. For the smallest WRPC dosage (2.5 g/L) the equilibrium was reached after about 180 min, while for the highest sorbent dosage (10 g/L) it occurred after 60 min. Thus, the necessary time to reach the equilibrium decreased along with an increase in the sorbent dosage. The higher the sorbent dosage, the lower the time necessary to reach the equilibrium was. This is due to the availability of sorption sites for a higher sorbent dosage [2].

### 3.3. *Effect of the temperature*

The temperature has great effect on the sorption process. From the slope and the intercept of the plot of ln $K_d$ vs. $1/T$, as presented in Fig. 3, enthalpy change ($\Delta H^\circ$) and $\Delta S^\circ$ values were calculated. The parameters obtained using the above equations are presented in Table 2.

The negative value of Gibbs free energy shows the spontaneous nature of MG sorption on WRPC. The

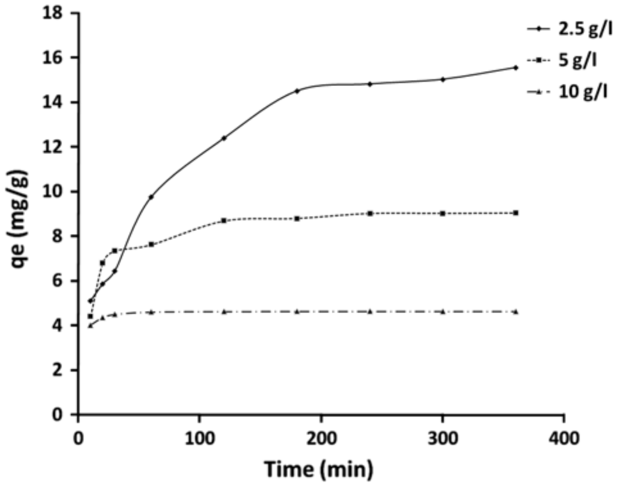

Fig. 2. Effect of the waste of rapeseed press cake dose on the MG sorption.

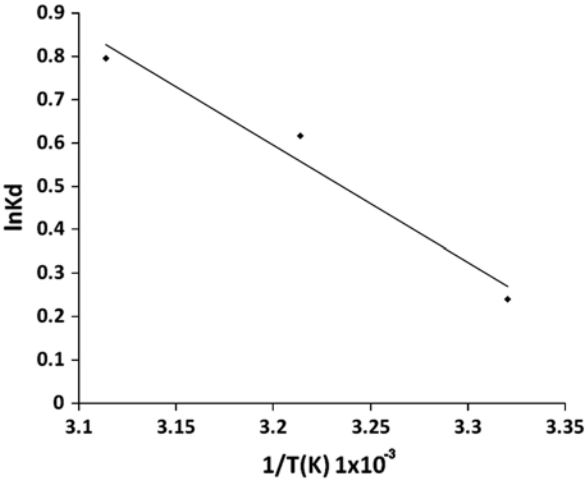

Fig. 3. Plot of ln $K_d$ vs. $1/T$.

Table 2
Thermodynamic parameters for the sorption of MG onto the waste of rapeseed press cake

| $\Delta H^\circ$ (kJ/mol$^{-1}$) | $\Delta S^\circ$ (J/mol$^{-1}$) | $\Delta G^\circ$ (kJ/mol$^{-1}$) | | |
|---|---|---|---|---|
| | | 301.15 K | 311.15 K | 321.15 K |
| 21.317 | 73.07 | −0.601 | −1.545 | −1.993 |

positive value of $\Delta H^\circ$ indicates the endothermic nature of sorption. Similar results for endothermic adsorption of MG were also observed on bentonite, activated carbon prepared from de-oiled soya, activated carbon prepared from Tunçbilek lignite, hen feathers and *Borassus aethiopum* flower biomass [4]. In addition, the positive value suggests that sorption is favored by the rise in the solution temperature. The positive value of $\Delta S^\circ$ demonstrates some structural changes at the solid–liquid interface and shows increased disorder at the solid–solution interface during the adsorption of the dye [20]. The absolute magnitude of $\Delta G^\circ$ may give an idea about the type of adsorption. Chemisorption has an energy range of 80–400 kJ per unit mole, physical sorption has a range of 0 to −20 kJ per unit mole [22]. Since $\Delta G^\circ$ values obtained in this study are in the range 0 to −20 kJ/mol, MG sorption onto the WRPC can be considered as a physisorption process. Similar results for endothermic adsorption of MG were also observed on bentonite, activated carbon prepared from de-oiled soya and a chitosan bead [20,23,24].

### 3.4. Isotherm data analysis

Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of the adsorbate and its degree of accumulation onto the adsorbent surface at a constant temperature. The most widely accepted surface adsorption models for single-solute systems are the Langmuir, Freundlich and DR models. The adequacy of the isotherms was compared using the linear forms of the equations as presented in Table 1 (Eqs. (6)–(8)).

#### 3.4.1. The Langmuir isotherm

The theoretical Langmuir isotherm Eq. (6) is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites [25]. The results obtained from the Langmuir model for the removal of MG onto the WRPC are shown in Table 3. The applicability of the linear form of the Langmuir model to the WRPC was proved by high correlation coefficients $R^2 > 0.99$. This suggests that the Langmuir isotherm provides a good model of the sorption system and indicates that the adsorption of MG takes place as monolayer adsorption on a surface that is homogenous in adsorption affinity. The Langmuir equation also showed high conformity to other MG adsorbents, such as betonite [20], natural sorbent, *Luffa cylindrica* [22] or chitosan bead [23].

Table 3
Comparison of the coefficients isotherm parameters for MG adsorption onto the waste of rapeseed press cake

| | | | | |
|---|---|---|---|---|
| Langmuir isotherm | $Q_m$ (mg/g) | $K_a$ (L/mg) | $R^2$ | |
| | 17.857 | 0.412 | 0.997 | |
| Freundlich isotherm | $K_F$ (mg/g) | $1/n$ | $R^2$ | |
| | 4.989 | 0.461 | 0.910 | |
| The Dubinin-Radushkevich isotherm | $Q_m$ (mg/g) | $K$ ($\times 10^{-5}$ mol$^2$/kJ$^2$) | $E$ (kJ/mol) | $R^2$ |
| | 2.593 | 0.03 | 1.29 | 0.967 |

Table 4
Comparison of the first- and second-order adsorption rate constants as well as calculated and experimental $q_e$ values for different initial MG concentration

| Parameter model | | First-order kinetic | | | Second-order kinetic model | | |
|---|---|---|---|---|---|---|---|
| MG (mg/L) | $q_e$ (experimental) (mg/g) | $k_1$ (1/min) | $q_e$ (calculated) (mg/g) | $R^2$ | $k_2$ (g/mg min) | $q_e$ (calculated) (mg/g) | $R^2$ |
| 10 | 3.71 | 0.010 | 0.80 | 0.99 | 0.068 | 3.65 | 1 |
| 25 | 9.12 | 0.021 | 4.98 | 0.81 | 0.009 | 9.61 | 0.99 |
| 50 | 14.83 | 0.024 | 14.33 | 0.90 | 0.001 | 18.18 | 0.97 |

### 3.4.2. The Freundlich isotherm

The Freundlich model is known to characterize the adsorption on heterogeneous surfaces. The isotherm can be derived assuming a logarithmic decrease in the enthalpy of adsorption accompanied by the increase in the fraction of occupied sites [25] and its logarithmic form is given by Eq. (7).

The value of the correlation coefficient is much lower than the Langmuir isotherm (Table 3). This suggests that the Freundlich isotherm fails to represent the experimental adsorption data.

### 3.4.3. The DR isotherm

The DR model is used to describe gas adsorption onto non-energetically uniform surfaces of microporous solids. It should be noted that this model has also been successfully applied to many biosorption processes [24]. The DR model has commonly been applied in Eq. (8). The Polanyi potential can be obtained as follows:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

where $C_e$ is the equilibrium concentration of the dye (mol/L), $T$ is the absolute temperature (K) and $R$ is the universal gas constant, 8.314 J/(mol K).

The mean free energy of adsorption ($E$), defined as the free energy change when one mole of ion is transferred from infinity in the solution to the surface of the solid, was calculated from the $K$ value using the following relation:

$$E = \frac{1}{\sqrt{2K}} \tag{7}$$

The magnitude of $E$ is useful in estimating the mechanism of the adsorption reaction. In the case of $E < 8$ kJ/mol, physical forces may affect the adsorption. If $E$ is in the range of 8–16 kJ/mol, the adsorption is governed by the ion exchange mechanism, while for the values of $E > 16$ kJ/mol, the adsorption may be dominated by particle diffusion [20]. The value of $E$ calculated using Eq. (12) is 1.29 kJ/mol, which indicates that the physical-sorption process plays a significant role in the adsorption of MG onto the WRPC.

### 3.5. Kinetic models applied to the adsorption of MG onto WRPC

The kinetics of MG adsorption onto the WRPC is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful in the prediction of the adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of MG adsorption onto the WRPC was analyzed using the Lagergren-first-order model and the Ho's pseudo-second-order model [26] as summarized in Table 1.

The calculated $q_e$ values obtained from the Lagergren pseudo-first-order model did not reach expected levels (except 50 mg/L) and their correlation coefficients were lower than for the second-order kinetics model (Table 4). The theoretical $q_e$ values for the described system were very close to the experimental $q_e$ values in the case of the pseudo second-order equation and MG concentrations of 10 mg/L and 25 mg/L (Table 4). It is clear from the accuracy of the model that the adsorption kinetic of the MG is better described by a pseudo second-order chemical reaction. The adsorption system obeys the pseudo-second-order kinetic model also for other adsorbents such as chitosan beads or *Luffa cylindrica* [22,23].

### 3.6. Comparison with other adsorbents

MG adsorption on activated carbon has been reported in the literature [27]. Also a number of low-cost adsorbents have been studied [28,29]. Data on the

Table 5
Comparison of adsorption capacities of various MG adsorbents

| Adsorbent | $Q_m$ (mg/g) | Temperature (℃) | Reference |
|---|---|---|---|
| Rattan sawdust | 62.71 | 30 | [33] |
| Hen feathers | 10.31 | 30 | [34] |
| Activated carbon from *Borassus aethiopum* | 14.91 | 27 | [4] |
| *Luffa cylindrica* | 23.8 | 25 | [21] |
| *Ricinus communis* | 27.78 | 27 | [24] |
| Pineapple leaf powder | 54.64 | 25 | [28] |
| Conch shell powder | 92.25 | 30 | [29] |
| Rapeseed cake | 17.85 | 28 | This paper |

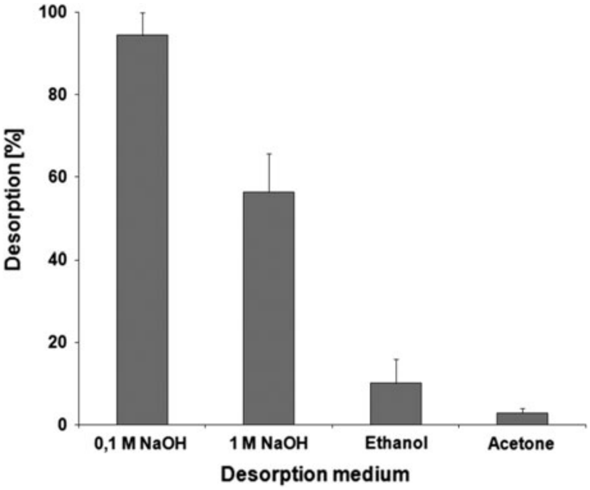

Fig. 4. Desorption of MG from the waste of rapeseed press cake after 3 h of incubation of the adsorbent in various desorption media.

MG sorption capacity (values of Qm derived from the Langmuir equation), some of these adsorbents and experimental values from the present study, are summarized in Table 5. The results obtained in this study indicate that the WRPC could be successfully used as an MG adsorbent.

### 3.7. Desorption and repeated use of the WRPC

In order to make the adsorption process more economical, it is important to desorb the spent adsorbent. Desorption allows reusing the spent adsorbent for the next cycle of adsorption and recovering the adsorbed dye. It makes the adsorption process more eco-friendly and helps to determine the mechanism of adsorption. In this paper, the desorption studies were carried out by a batch process using 0.1 M or 1 M NaOH, 70% ethanol and 70% acetone as eluents. The results shown in Fig. 4 revealed that the ethanol and acetone solutions exhibited poor desorption efficiencies, not exceeding 10%. In contrast, NaOH solutions had a very good desorption capability and the maximum MG desorption (94.5%) was achieved with the use of 0.1 M NaOH. Vijayaraghavan et al. [30] found that 0.1 M NaOH was the most efficient medium for reactive black five desorption from fermentation waste biomass of *Corynebacterium glutamicum*. Our results indicate that the electrostatic attraction of the positively charged MG with a negatively charged biosorbent was involved in the process. This result is consistent with the desorption data reported by Pavan et al. [31], who confirmed that the triphenylmethane dye–methylene blue adsorption onto yellow passion fruit occured via electrostatic attraction.

Spent the WRPC after MG desorption by 0.1 M NaOH was used for repeated decolorization of dye solution. The adsorbent exhibited good stability and

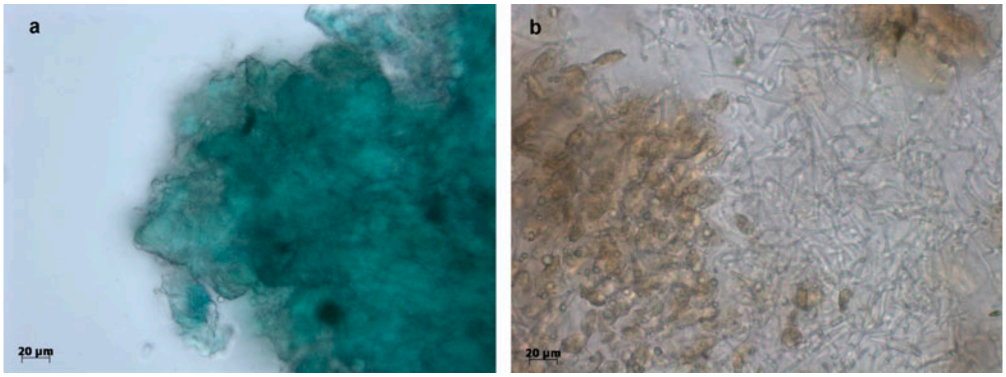

Fig. 5. The dye-loaded waste of rapeseed press cake (a) before and (b) after *M. roridum* IM 6,482 digestion in submerged culture.

95% of MG uptake capacity in the next cycle of adsorption was achieved (data not shown).

### *3.8. Fungal degradation of MG-loaded WRPC*

Biosorption of dyes does not solve the pollution problem because the toxic compounds are not destroyed but only bound to the adsorbent particles. Thus MG-loaded WRPC was added to a liquid culture of *M. roridum* IM 6,482 in order to asses it susceptibility to biological degradation. Microscopic investigation revealed that the dye-loaded WRPC was easily digested by *M. roridum* IM 6,482. After 72 h of cultivation sorbent particles were heavily colonized by mycelium and MG was totally eliminated (Fig. 5). Additionally, HPLC-MS/MS analysis revealed disappereance of more than 90% of MG. Similarly, Pappinutti et al. [32] reported that *Fomes sclerodermeus* could decolorize MG-adsorbed wheat bran during solid state fermentation. The observed dye removal might have been the effect of extracellular enzymes activity (e.g. *laccase* or *MG reductase*). According to Jasińska et al. [14] MG decolorization by the submerged culture of *M. roridum* IM 6,482 was accompanied by the stimulation of *laccase* production. However, due to the toxic effect of MG on the fungal growth, the decolorization process was carried out in the medium amended only with 10 mg/L of MG. The results described in this report revealed that MG adsorption on the WRPC allows removing a higher amount of MG (50 mg/L). This method seems to be suitable for toxic dye removal from large volumes of textile effluents. Moreover, after dye adsorption on WRPC the decolorized effluent can be accepted by the municipal wastewater network for treatment and simultaneously the waste adsorbent can be utilized by fungi.

## 4. Conclusion

The results of this investigation show that the WRPC has a suitable adsorption capacity for the removal of MG from aqueous solutions. The equilibrium adsorption is achieved in 60–180 min. Adsorption behavior is described by a monolayer Langmuir-type isotherm. The data indicate that the adsorption kinetics follows the pseudo-second-order rate. The negative values of free energy changes ($\Delta G^o$) and enthalpy changes ($\Delta H^o$) indicate that the MG adsorption on WRPC is a physisorption spontaneous endothermic process. MG is succesfully desorbed from dye-loaded WRPC with use of a 0.1 M NaOH solution and this process allows the reuse of the sorbent. Finally, MG-loaded WRPC is also found to be easily digested in submerged culture of filamentous fungus *Myrothecium roridum* IM 6,482. The present study concludes that WRPC could be employed as a low-cost adsorbent for toxic dye removal from large volumes of textile effluents. Moreover, due to the high biodegradability and the low cost it could be being an alternative to commercial activated carbon.

### List of symbols

$C_0$ — initial malachite green concentration, mg/L
$C_e$ — equilibrium malachite green concentration, mg/L
$E$ — characteristic free energy of adsorption, kJ/mol
$\Delta G^o$ — Gibb's free energy change, kJ/mol
$\Delta H^o$ — enthalpy change, kJ/mol
$K$ — Dubinin-Radushkevich constant related to sorption energy, mol$^2$/kJ$^2$
$k_1$ — constant of pseudo-first order adsorption, l/min
$k_2$ — pseudo-second order rate constant, g/mg min
$K$ — constant related to sorption energy, mmol$^2$/J$^2$
$K_a$ — equilibrium constant in Langmuir model, l/mg
$K_d$ — thermodynamic distribution coefficient for the sorption
$K_F$ — Freundlich constant, mg/g
$n$ — Freundlich constant
$q_e$ — sorption capacity at equilibrium, mg/g
$Q_m$ — Langmuir constant related to monolayer capacity, mg/g
$q_t$ — sorption capacity of malachite green at time $t$, mg/g
$R$ — gas constant (8.314 J/mol/K)
$R^2$ — correlation coefficient
RPC — rapeseed press cake
$\Delta S^o$ — entropy change, J/mol/K
$T$ — temperature of solution, K
WRPC — waste of rapeseed press cake
$X_m$ — Dubinin-Radushkevich monolayer capacity, mg/g
$\varepsilon$ — Polanyi potential

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