Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749053

51 (2013) 3284–3294
April

Taylor & Francis
Taylor & Francis Group

Biosorption of malachite green from aqueous solutions by pine sawdust: equilibrium, kinetics and the effect of process parameters

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Received 25 November 2011; Accepted 24 October 2012

ABSTRACT

The study offers the use of Scots Pine (*Pinus silvestris*) sawdust as a biosorbent for the removal of cationic dye, malachite green, from aqueous solutions. The effects of process parameters, such as contact time, sorbent concentration, initial dye concentration, pH, temperature, salinity and surfactant addition, on the biosorption process were determined. The experimental biosorption kinetics and equilibrium results were described by a range of mathematical models. The equilibrium data were best described by the Langmuir-Freundlich model, while the kinetics was best described by the pseudo-second-order model. The maximum sorption capacity of sawdust was 71.67 mg/g. An increase in pH values results in the rise of biosorption degree, mostly below pH 5. Addition of inorganic salts results in a drop in sorption capacity, but for concentrations higher than 0.5% w/w, the uptake increases along with an increase in salt concentration. The presence of an ionic surfactant (sodium dodecyl benzene sulphonate) at concentrations below critical micelle concentration enhances the sorption, while higher concentrations lead to solubilisation of dye molecules within the micelles, thus reducing the sorption efficacy. Desorption study was carried out with four different eluents.

Keywords: Biosorption; Cationic dye; Sawdust; Isotherm; Kinetics; Effect of parameters; Desorption

1. Introduction

Wastewaters from textile, paper, tannery, plastics, food, cosmetic and paint industries are main sources of constant environmental contamination. Wastewaters containing dyes may be toxic and carcinogenic, which makes them a significant threat to aqueous ecosystems. Dyes are resistant to light, temperature/oxidizers and biological degradation. Removal of dyes from the wastewaters is therefore one of the main problems faced by the industry [1].

Removal of dyes from wastewaters has become in recent years a focus of attention not only because of the toxicity of the dyes, but also due to their increased occurrence in industrial applications. Classical methods for the removal of dyes from wastewaters include mainly the physical chemical processes (adsorption, oxidation, precipitation, coagulation, etc.) All these methods are characterised by various efficacies of the process of purification of aqueous solutions, different amounts and natures of waste products, and a wide range of process costs. Literature data suggest that adsorption is the method that provides most promising results. The most popular adsorbent is activated carbon; however, this adsorption method is very

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expensive due to high price of activated carbon and the need to regenerate it. Hence, there is a need to find cheap, easily available and efficient sorbents for removal of dyes. The waste products have a great potential to be used as adsorbents. [2–4].

Malachite green, or triphenylmethane (basic green 4), is a cationic dye used for dyeing cotton, wool silk, paper and bacterial preparations. It is used by aquarium owners for the treatment of parasitic, fungal and bacterial diseases of fish and fish eggs. The dye is toxic to living organisms. Aquatic organisms metabolise malachite green into its reduced form, leucomalachite green, which is carcinogenic, mutagenic and teratogenic upon ingestion [5]. The use of this dye has been strictly forbidden in several countries, but it is still used in fish hatcheries and seafood farms.

There are many studies available in the literature regarding the adsorption of malachite green dye on various adsorbent surfaces such as chitosan coated bentonite [6], silica [7], cocoa shells [8], agro-industry wastes [9], ash [10], sawdust [11,12] and coffee husks [13].

In our study, we have used a waste material—sawmill pine sawdust—for the removal of malachite green from aqueous solutions. According to our knowledge, the use of this biosorbent in the removal of dyes has not been hitherto studied [14–16]. Dye-containing wastewaters contain a whole spectrum of other components which should be taken into consideration when conducting basic biosorption studies. There are few literature reports regarding the effect of salinity and surfactant content on the process of biosorption of dyes.

The objective of the study was to propose pine sawdust as a cheap waste biosorbent for the removal of malachite green as a representative of the cationic dyes class. The kinetics and equilibrium of the biosorption process were studied in batch systems. Several equilibrium and kinetic models were applied to describe obtained results, we verify if the model presents a good fit to the experimental data. The effects of various process conditions, such as contact time, sorbent concentration, initial dye concentration, pH, temperature, salinity and surfactant addition, on the biosorption process were also determined. Additionally desorption studies were performed.

2. Materials and methods

2.1. Biosorbent

Pine sawdust was obtained from local sawmill and used without further modifications. Particle size distribution analysis revealed mean particle sizes of $d(0.1) = 13.76\,\mu\text{m}$, $d(0.5) = 57.07\,\mu\text{m}$ and $d(0.9) = 210.1\,\mu\text{m}$. The surface area of pine sawdust was $1.65\,\text{m}^2/\text{g}$ as measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption technique.

To determine pH of biosorbent suspension, 1 g of sawdust suspension in 10 mL of distilled water was prepared. Whole was shaken and pH was measured until establishing a constant value. pH_{zpc} (point of zero charge) was determined using method available in literature [17].

Ion exchange properties of pine sawdust (H^+ and OH^- ions) were studied by potentiometric titration. Titration was performed in Erlenmeyer flask following prior deprotonation of the material by immersing 0.5 g of the sorbent in 50 mL of 0.1 M NaOH and stirring for 2 h. Titration was performed with 0.1 M HCl by gradual addition of 0.1 mL into the biosorbent mixture. After each addition, the pH was measured. The potentiometric titration curve was obtained by plotting the volume of titrant against the pH values [18].

2.2. Preparation of aqueous dye solutions

Malachite green was obtained from POCh (Poland). Dye was used without any purification. Stock dye solution was prepared by dissolving specified amount of the dye in 1 L of distilled water to achieve concentration of 1,000 mg/L. Samples for experiments were prepared by dilution of stock solution to the demanded concentrations. 0.1 M NaOH and HCl solutions were used for pH adjustments. Dye concentrations were measured spectrophotometrically at maximum wavelength 619 nm. Absorbance calibration curve was prepared for dye solutions in the concentration range of 0–10 mg/L.

2.3. Batch studies

2.3.1. Effect of contact time and initial dye concentration

Kinetic experiments were performed in order to determine the contact time required for the biosorbent to reach the equilibrium with the adsorbed dye. 200 mL batches of dye solutions at specified concentration (20, 50, and 100 mg/L) were prepared and mixed with specified amounts of the biosorbent (0.4 g). The process was carried out in flasks placed in a thermostatic stirrer (300 rpm) at fixed temperature. About 5 mL samples were taken for analysis at defined time intervals. The process was conducted until the equilibrium was reached. The concentrations of the dyes retained in the biosorbent phase (q_e, mg/g) were calculated from the following expression:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of the dye in the solution (mg/L), V is the solution volume (L) and m is the mass of the biosorbent (g).

2.3.2. Effect of adsorbent dosage

The effect of the adsorbent dosage was investigated after 60 min at 293 K for the initial dye concentration of 10–50 mg/L with various sorbent dosages (0.01–1.2 g/100 mL).

2.3.3. Effect of pH

The effect of pH (3–12) on the adsorption was investigated. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. About 100 mL of dye solution (20 and 50 mg/L) was agitated with 0.20 g of biosorbent at 293 K for 60 min.

2.3.4. Equilibrium experiments

Sorption equilibrium experiments were carried out in batch mode. 100 mL of samples of dye solutions at predetermined concentrations (10–700 mg/L) were transferred to 250 mL Erlenmeyer flasks. The sorbent (0.2 g) was added to the solutions. The experiments were carried out at pH 5.0 for 60 min.

2.3.5. Effect of temperature

Samples of biosorbent (0.4 g) were added to 200 mL of dye solutions (50 mg/L). The experiments were carried out at temperature range 20–60 °C for 60 min.

2.3.6. Effect of ionic strength

The effect of salt addition (NaCl, $MgCl_2$ obtained from POCh, Poland) on the amount of adsorbed dye was analysed over the salt concentration 0–4% (w/w). About 100 mL of a dye solution at 50 mg/L concentration, of containing a specified amount of salt, was transferred into a 250 mL Erlenmeyer flask. The adsorbent (0.20 g) was added to the solution. After 60 min of agitation, the dye concentration in the solution was determined.

2.3.7. Effect of surfactant addition

The experiments were carried out by mixing 0.20 g of adsorbent with 100 mL of dye solution (50 mg/L) in a 250 mL Erlenmeyer flask. Various initial anionic surfactant (as a representative sodium dodecyl benzene sulphonate [SDBS], obtained from Sigma-Aldrich was used) amounts were added to this solution (surfactant concentration in the range of 0–4 g/L).

2.3.8. Regeneration and reuse of biosorbent

In order to consider the practical usefulness of the biosorbent, desorption experiments were performed. After the biosorption test, 0.2 g of malachite green-loaded sorbent was stirred in 100 mL of the following solutions: distilled water, 0.1 M HCl, 0.1 M HNO_3 and 0.1 M EDTA. After 60 min of agitation, the dye concentration in the solution was determined. For the best eluent, the biosorption and desorption steps were repeated four times.

3. Results

3.1. Biosorption kinetics

Chemical kinetics is an area that studies the rates of chemical reactions, the mechanisms of these reactions and the effects of various factors on the reaction rates. Three kinetic models have been used to describe the kinetics of malachite green biosorption on pine sawdust (Table 1).

The biosorption of malachite green on pine sawdust is a two-stage process. The first stage is characterised by a high rate and involves the first 20 min of the process, while the second stage is much slower and involves concentrations approaching the equilibrium levels.

Table 1 and Fig. 1 present the results of model fitting to the experimental data. All model parameters were evaluated by non-linear regression using *OriginPro8* software. Two common error functions have been used to measure fitting of model, such as the correlation coefficient (R^2) and the sum of the squares of the errors (SSE).

$$\mathrm{SSE} = \sum_{i=1}^{p} (q_t^{\mathrm{calc}} - q_t^{\mathrm{exp}})_i^2 \quad (2)$$

The model that best describes the experimental points in three series of different initial malachite green concentrations is the pseudo-second-order model. In this model, all correlation coefficients exceeded 0.997, while the SSE error functions adopted advantageously low values. In Fig. 2, there are shown diagrams comparing experimental values of q_t and values obtained using kinetic models. The best

Table 1
Kinetic constants for malachite green biosorption on pine sawdust in various initial dye concentrations

Model		Parameters	Initial MG concentration		
			20 mg/dm^3	50 mg/ dm^3	100 mg/ dm^3
Pseudo-first-order model		$q_{e,\ \mathrm{experimental}}$ (mg g^{-1})	9.733	23.62	31.30
	$q_t = q_e(1 - e^{-k_1 t})$	$q_{e,\ \mathrm{model}}$ (mg g^{-1})	9.723	23.37	30.32
	[19]	k_1 (min^{-1})	0.801	0.315	0.329
		R^2	0.999	0.995	0.980
		SSE	0.014	0.302	13.09
Pseudo-second-order model	$q_t = q_e \frac{q_e k_2 t}{1+q_e k_2 t}$	q_e (mg g^{-1})	9.851	24.97	32.33
	[20]	k_2 (gmg^{-1} min^{-1})	0.366	0.021	0.017
		R^2	0.998	0.997	0.997
		SSE	0.148	1.177	1.911
Power function equation	$q_t = kt^v$	v	0.023	0.132	0.133
	[21]	k (mg g^{-1})	8.986	14.66	19.03
		R^2	0.995	0.974	0.986
		SSE	0.321	12.05	8.999

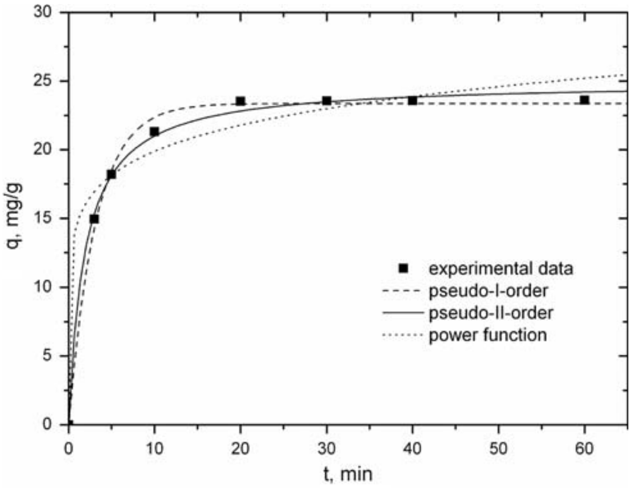

Fig. 1. Kinetics of malachite green biosorption on pine sawdust: fitting of various kinetic models ($C_0 = 50$ mg/L, $X = 2$ g/L, $T = 20$°C).

concurrence of experimental and model results was obtained with pseudo-second-order model what confirms that this model is the best for description of kinetics of malachite green biosorption on pine sawdust.

3.2. The effect of the initial dye concentration

The effect of the initial dye concentration on the biosorption kinetics was studied at three initial malachite green concentrations of 20, 50 and 100 mg/L. The biosorption process is comprised of several stages, including transport of the dye from the bulk solution to the boundary layer, diffusion transport within the boundary layer and pores and sorption of the dye onto the sorbent surface. Intense stirring facilitates fast transport from the bulk solution onto the boundary layer; therefore, this step is not the rate-limiting one. The highest limitation in mass transport is therefore associated with the transport of the dye from the boundary layer onto the surface. The increase in the initial concentration from 20 to 100 mg/L significantly increases the amount of dye bound to the sorbent surface from 9.85 to 32.3 mg/g (for the pseudo-second-order model), which is associated with an increase in the driving force of the process. However, the kinetic parameter k_2 is reduced from 0.366 to 0.017 (Table 1), probably due to limited diffusion within the boundary layer and the sorbent pores. Similar relationship was also observed for malachite green biosorption by other researchers [22].

3.3. The effect of biosorbent concentration

The effect Fig. 3 of biosorbent concentration on the process effectiveness was studied for three initial dye concentrations (10, 20 and 50 mg/L) (Fig. 3). The efficiency of the process increased with the increasing biosorbent concentration only in the range of low concentrations from 0 to 2 g/L. This was associated with the sorptive surface area increasing along with an increase in sorbent amount. A larger surface area allows a larger number of dye molecules being bound by active sites, which leads to better purification of the solution. Above 2 g/L, the sorption efficacy

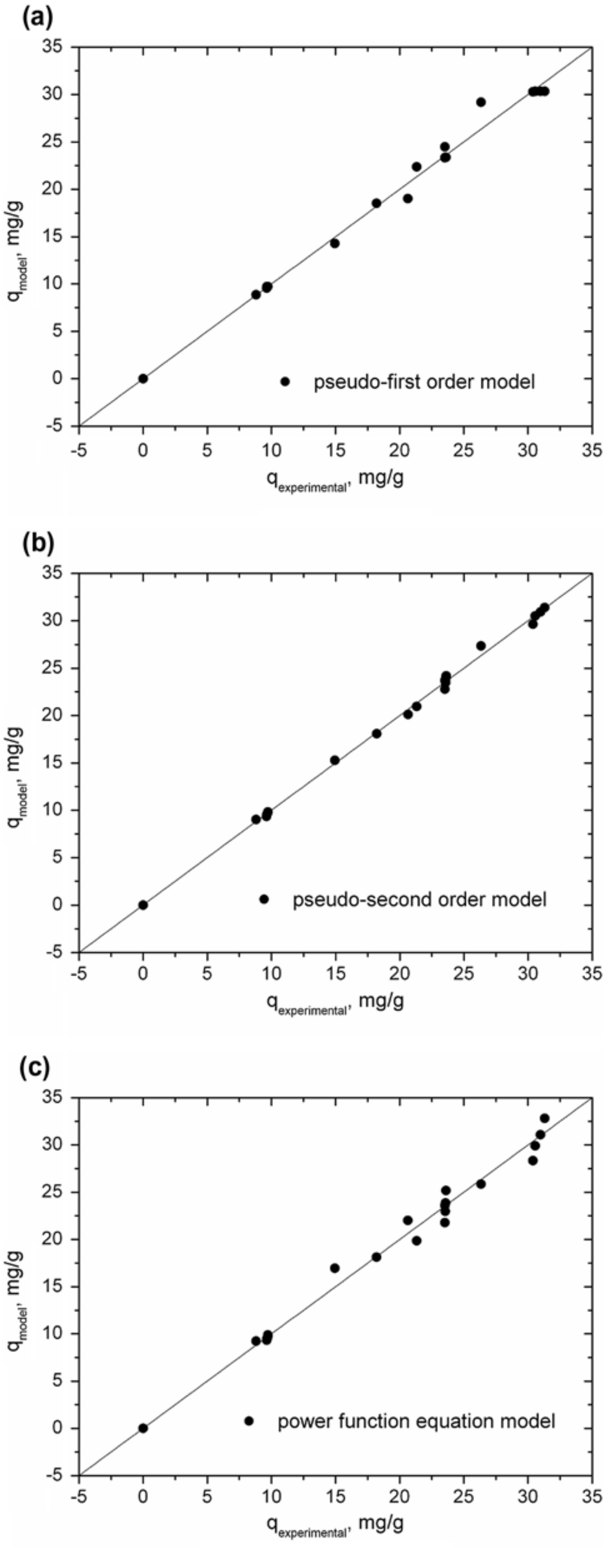

Fig. 2. Comparison of experimental values of q_t and values obtained using (a) pseudo-first-order, (b) pseudo-second-order, and (c) power function equation models.

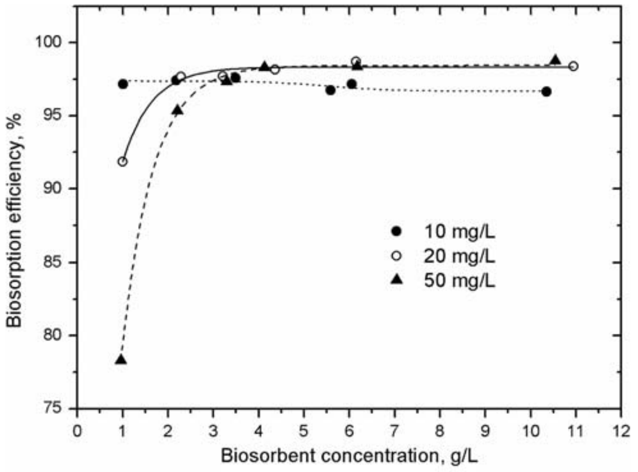

Fig. 3. Effect of biosorbent concentration on biosorption in various initial concentrations of malachite green ($C_0 = 10$–50 mg/L, $T = 20$°C).

remains constant and does not depend on adding new portions of the sorbent—the sorbent surface becomes saturated, resulting in a clear plateau on the graph. Similar relationship was also observed for cationic dye biosorption on natural biosorbents by other researchers [23,24]. Therefore, concentration of 2 g/L was selected for further experiments.

3.4. The effect of pH

pH is a very important parameter affecting biosorption, as it changes the electric charge of groups present on the sorbent surface. Plant materials are composed mostly of cellulose and lignins, and contain on their surface a range of functional groups (COOH, OH and NH_3), which may attract dye cations and bind them onto the surface.

The experimental results from the potentiometric titration were fitted to model that considered the presence of three dominant functional groups at the surface of the biosorbent [18]. Those three functional groups were determined by non-linear regression and on the basis of the first and the second derivative using Mathematica v. 3.0. Potentiometric titration graph (Fig. 4) presents three inflexion points at pH of 2.5, 6.0 and 10.5, which indicated the presence of two acidic groups and one basic group on the biosorbent surface. The pK_a values correspond to carboxylate, phosphate, amine and hydroxyl groups.

The effect of pH was studied in the range of 3–12 (Fig. 5). An increase in sorption capacity was observed along with an increase in pH values, especially below pH 5. These differences may be caused by competition

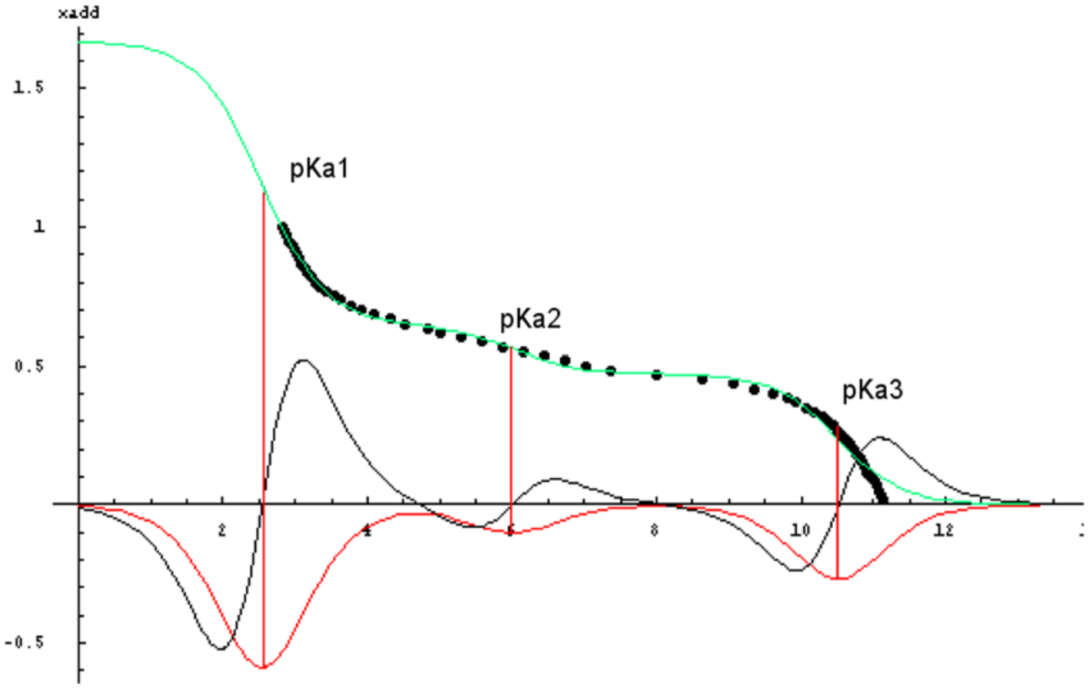

Fig. 4. Potentiometric titration curves for pine sawdust, also the first and second derivatives are shown.

between hydrogen ions and dye cations for the binding sites at the sorbent surface at low pH values. Determined sawdust suspension pH was 4.25 and its pHzpc was 4.65. In pH higher than pH_{zpc} sorbent surface has negative charge, in lower than pH_{zpc} charge is positive. It was decided to carry out experiments in pH 5.0, the functional groups on the sorbent surface are negatively charged, which facilitates the attraction of positively charged malachite green ions.

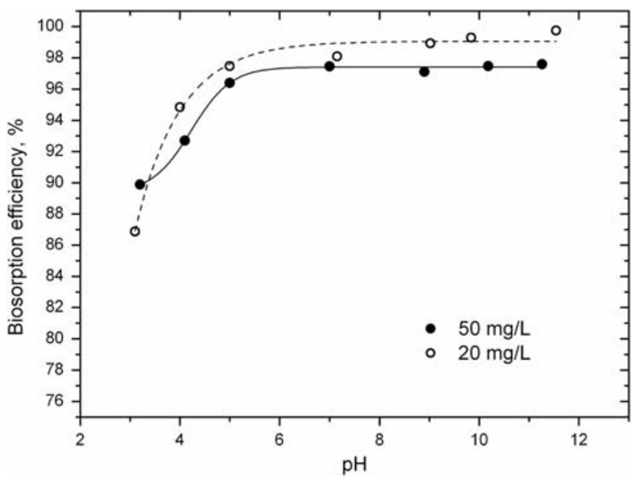

Fig. 5. Effect of pH on biosorption of malachite green on pine sawdust ($C_0 = 20$ and 50 mg/L, $X = 2$ g/L, $T = 20$°C).

3.5. *Equilibrium*

At the initial stage of the biosorption process, the rate of adsorption is very high. Over time, as molecules cover an increasingly large surface of the sorbent, the rate of adsorption decreases. The adsorption rate continues to decrease while the rate of desorption increases until equilibrium is reached. Relationships between the mass of adsorbed dye and the concentration of the dye at constant temperatures are described by isotherms. Literature contains numerous available models describing the equilibrium relationships of the biosorption process (Table 2).

The results of the experiments were described by the aforementioned isotherms, and the obtained equilibrium parameters and error functions (R^2 and SSE) are listed in Table 2.

Langmuir model is based on assumptions that adsorption occurs at specific homogeneous sites with constant energy, adsorption is monolayer and there is no interaction between molecules. Freundlich isotherm model describes the multilayer adsorption, applicable to a highly heterogeneous surface. The Langmuir isotherm was well correlated with experimental points mostly in the range of low dye concentrations. The obtained maximum sorption capacity was 71.67 mg/g and the value of b parameter was 0.111. However, a relatively low correlation coefficient (0.972) and a high SSE value (above 150) suggest suboptimal fit between

Table 2
Isotherm parameters

Models	Equations	Refs.	Parameters	Values
Langmuir	$q = q_{\max}\frac{b_L \cdot C_e}{1+b_L \cdot C_e}$	[25]	$q_{\max}$ (mg g^{-1})	71.67
			b_L (dm^3 mg^{-1})	0.111
			R^2	0.972
			SSE	150.2
Freundlich	$q = K_F \cdot C^{\frac{1}{n_F}}$	[26]	K_F (mgg^{-1})(Lmg^{-1})$^{(1/nF)}$	19.24
			n_F	4.111
			R^2	0.942
			SSE	311.9
Temkin	$q_e = \frac{RT}{b_T}\ln(k_T C_e)$	[27]	b_T (J mol^{-1})	10.05
			k_T (dm^3 mg^{-1})	4.778
			R^2	0.992
			SSE	41.45
Redlich-Peterson	$q_e = \frac{k_{RP} \cdot C_e}{1+a_{RP} \cdot C_e^{b_{RP}}}$	[28]	k_{RP} (dm^3 g^{-1})	19.47
			a_{RP} (dm^3 mg^{-1})	0.554
			b_{RP}	0.868
			R^2	0.995
			SSE	24.89
Langmuir-Freundlich (Sips)	$q = q_{\max}\frac{b_{LF} \cdot C_e^{n_{LF}}}{1+b_{LF} \cdot C_e^{n_{LF}}}$	[29]	$q_{\max}$ (mg g^{-1})	84.07
			b_{LF} (dm^3 mg^{-1})	0.187
			n_{LF}	0.617
			R^2	*0.996*
			SSE	*20.38*

the model and the obtained results. Also the Freundlich isotherm proved inadequate for describing the equilibrium ($R^2 = 0.942$ and SSE of over 311). Both models were unsatisfactory, thus the remaining three isotherms (Temkin, Redlich-Peterson and Langmuir-Freundlich) were used. Those isotherms were well correlated with experimental results (Fig. 6), as evidenced by high correlation coefficients (above 0.990). Best fit was obtained for the Langmuir-Freundlich isotherm ($R^2 = 0.996$ and SSE = 20.38); however, Redlich-Peterson model described experimental data very well too ($R^2 = 0.995$ and SSE = 24.89). Determined value of parameter b_{RP} was closer to unity (0.868) than to Zero, so the data can preferably be fitted with Langmuir model, confirms the monolayer coverage process of malachite green onto pine sawdust. The Langmuir-Freundlich and Redlich-Peterson models are often used as a compromise between Langmuir and Freundlich isotherms. Obtained results show the complex mechanism of the biosorption. The best-fitting model was Redlich-Peterson model, Langmuir model described experimental points with good effect too.

Sorption capacity values for various malachite green sorbents available in the literature were compared (Table 3). Pine sawdust proves to be competitive to other biological materials.

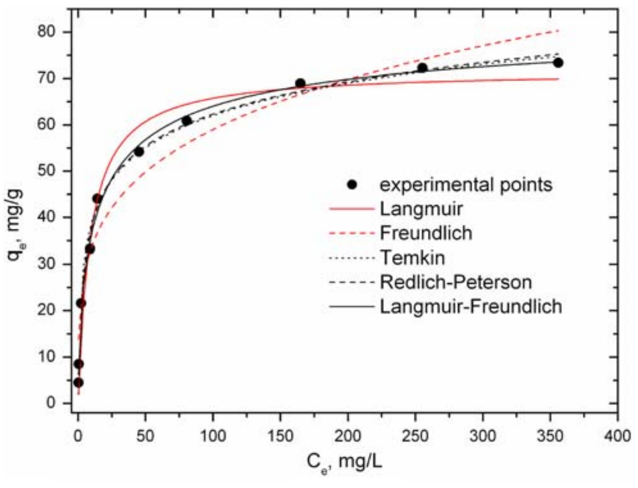

Fig. 6. Isotherm points and the corresponding curves for each fitted model.

3.6. The effect of the temperature

Table 4The effect of the temperature on the biosorption of malachite green on pine sawdust was studied within the temperature range of 20–60°C (Table 4). The amount of dye adsorbed on the sorbent

Table 3
Sorption capacities of malachite green on various biological materials

Sorbent	$q_{\max}$ (mg/g)	Refs.
Chitosan bead	93.55	[30]
Anaerobic granular sludge	85.59	[31]
Ginger waste	84.03	[32]
Pine sawdust	71.67	This study
Turbinaria conoides, brown marine algae	66.6	[33]
Rattan sawdust	62.71	[34]
Aerobic granules	56.8	[35]
Degreased coffee bean	55.3	[36]
Lemon peel	51.73	[37]
Marine alga *Caulerpa Racemosa* var. *cylindracea*	25.67	[22]
Hen feathers	10.29	[38]
Cellulose	2.422	[39]

surface remains virtually constant with increasing temperature, while the kinetic parameter determining the rate of the process is significantly increased. This phenomenon may be caused by higher frequency of interactions between the dye and the sorbent molecules, resulting from increased energy of the molecules at elevated temperatures. Similar relationships were observed by other researchers who used *Chlorella* biomass as the biosorbent [40].

The rate of the biosorption process depends on the temperature as described by Arrhenius equation:

$$k_2 = A_0 \exp\left(-\frac{E_a}{\mathrm{RT}}\right) \tag{3}$$

where k_2 is pseudo-second-order of biosorption ($\mathrm{g\,mg^{-1}\,min^{-1}}$), A_o is the constant called the frequency factor ($\mathrm{g\,mg^{-1}\,min^{-1}}$), R is the gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$) and T is the temperature of solution (K). The graphical representation of the relationship between ln k_2 and 1,000/T (data not shown) is a straight line ($R^2 = 0.960$). The line equation allows for determination of activation energy (E_a). The obtained value of activation energy is 60.64 $\mathrm{kJ\,mol^{-1}}$. The magnitude of the activation energy usually indicates the type of adsorption mechanism, being usually higher than 4–6 $\mathrm{kJ\,mol^{-1}}$ for chemical adsorption and low (below 4 $\mathrm{kJ\,mol^{-1}}$) for physical adsorption.

3.7. The effect of inorganic salts

The effect of addition of two inorganic salts, NaCl and $MgCl_2$, on the efficacy of malachite green biosorption was studied (Fig. 7). An interesting relationship was observed. For low salt concentrations (below 0.5% w/w), the increase in salt concentration rapidly reduces the biosorption efficacy from 98.3 to 81.8% and from 98.3 to 79.6% for NaCl and $MgCl_2$, respectively. This is probably due to competition between Na^+ and Mg^{2+} ions and the dye cations for the binding sites on the sorbent surface. However, the results suggest that binding of dye cations is preferred over binding of salts, considering the low dye–salt concentration ratio (dye concentration 50 mg/L, salt concentration 0–5 g/L). Higher salt concentrations improve the efficacy of the process—at 4% w/w, the

Table 4
Kinetic constants for malachite green biosorption on pine sawdust in various temperatures

Model	Parameters	Temperature					
		20℃	25℃	35℃	45℃	53℃	60℃
Pseudo-first-order model	q_e ($\mathrm{mg\,g^{-1}}$)	23.37	23.22	22.43	23.00	23.26	23.44
	k_1 ($\mathrm{min^{-1}}$)	0.315	0.468	0.844	0.843	1.106	1.349
	R^2	0.995	0.991	0.993	0.998	0.999	0.999
	SSE	0.302	3.613	0.412	0.664	0.269	0.215
Pseudo-second-order model	q_e ($\mathrm{mg\,g^{-1}}$)	24.97	24.09	22.90	23.32	23.436	23.56
	k_2 ($\mathrm{g\quad mg^{-1}\,min^{-1}}$)	0.021	0.043	0.130	0.154	0.325	0.569
	R^2	0.997	0.999	0.998	0.999	0.999	0.999
	SSE	1.177	0.539	0.129	0.043	0.049	0.105
Power function equation	v	0.132	0.069	0.036	0.023	0.012	0.001
	k ($\mathrm{mg\,g^{-1}}$)	14.66	18.04	20.04	21.21	22.33	22.81
	R^2	0.974	0.989	0.999	0.999	0.999	0.999
	SSE	12.05	5.284	0.078	0.460	0.046	0.035

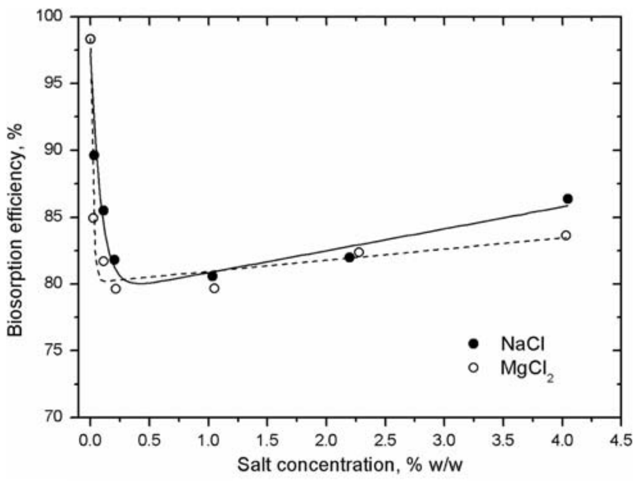

Fig. 7. Effect of inorganic salts on biosorption of malachite green on pine sawdust ($C_0 = 50$ mg/L, $X = 2$ g/L, $T = 20$°C).

process efficacy is increased by 5.3% for NaCl and by 4.7% for $MgCl_2$. Despite the reduction in sorption efficacy upon the addition of salts, the sorptive potential of the sorbent is still high and the sorbent can effectively remove dyes from aqueous solutions.

3.8. The effect of surfactant concentration

Dye-containing wastewaters often contain also other organic compounds, in particular anionic surface active agents. Concentrations of these agents in industrial wastewaters may reach as much 200–300 mg/L. At this stage of the research, the effect of the presence of an anionic surfactant (using SDBS as the example) on the malachite green biosorption process was assessed. At SDBS concentrations below 1 mM (350 mg/L), the presence of a surfactant slightly improved the sorption, as the surfactant probably affected the nature of the surface, resulting in better binding of the dye onto the biosorbent. SDBS molecules may undergo adsorption to the hydrophobic surface of the sorbent, offering new binding sites for the cationic dye. Exceeding the critical micelle concentration ([CMC], 770 mg/L for SDBS) leads to formation of micellar structures in the solution. These structures are capable of solubilising dye molecules, thus preventing them from being adsorbed onto the sorbent surface. This results in a significant drop in sorption efficacy, reaching up to 90% as shown on the graph (Fig. 8) for concentrations of above 600 mg/L. Similar results were obtained by other researchers, who studied the effect of surfactant concentration on the biosorption of methylene green on *Rhizopus arrhizus* cells [41], and of cationic dyes on beech sawdust [42].

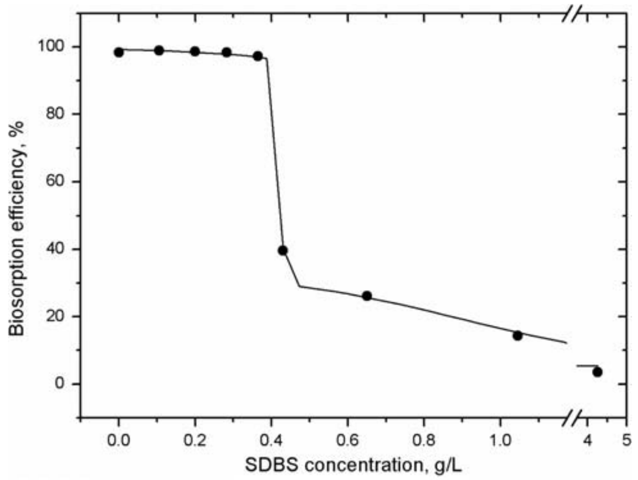

Fig. 8. Effect of anionic surfactant SDBS on biosorption of malachite green on pine sawdust ($C_0 = 50$ mg/L, $X = 2$ g/L, $T = 20$°C).

However, concentrations typical for wastewaters are not that high, and biosorption may be used for the removal of dyes from wastewaters even when surfactants are present. In case of solutions containing highly concentrated surfactants, additional membrane separation (ultrafiltration), which would allow for separation of micellar structures with solubilised dye molecules, may be proposed.

3.9. Desorption

Desorption is very important, because it enables reuse of sorbent in process. In this work, there was tested efficiency of four eluents (distilled water, 0.1 M HCl, 0.1 M HNO_3, 0.1 M EDTA). The largest recovery of malachite green was obtained for 0.1 M HCl (95.3%). The rest of the eluents were less efficient: for 0.1 M HNO_3 desorption level was 86.8%, for EDTA 61.0% and for water only 20.3%. In order to test possibility of reuse of given sorbent, four cycles of sorption and desorption with use of 0.1 M HCl as eluent were performed. There was observed insignificant decrease of sorption ability after each cycle (about 3–7%), after four cycles the biosorption capacity decreased about 23%, what is a very good result. This reduction in sorption effectiveness could be caused by damage of the biosorbent surface by a strong acid (HCl) [43].

4. Conclusions

The results of the studies suggest that pine sawdust may be successfully used as a sorbent for malachite green. Biosorption proved to be a process dependent on a number of factors such as such as contact time, sorbent concentration, initial dye concentration, pH, temperature, addition of inorganic salts or surfactants. Several models were used to describe the process equilibrium with Langmuir-Freundlich model providing the best fit to the experimental results. Maximum sorption capacity was determined from Langmuir isotherm at 71.67 mg/g. The modelling of the process kinetics showed that among the three tested equations, the pseudo-second-order model provided the best fit. The efficacy of the process increased with the increased biosorbent concentration only in the range of low concentrations from 0 to 2 g/L; above this value, the sorption efficacy was constant and did not depend on adding new portions of the sorbent. An increase in pH values results in the sorption capacity enlargement, particularly below pH 5. Presence of inorganic salts resulted in a drop in sorption capacity for concentrations below 0.5%, while at larger concentrations, the sorption capacity increased, probably due to additional interactions. Despite the reduction in sorption efficacy upon addition of salts, the sorptive potential of the sorbent was still high and the sorbent could effectively remove dyes from aqueous solutions. Addition of small concentrations of surface active agents (SDBS) resulted in improved sorption and increase in the amount of adsorbed dye, mainly due to modification of the sorbent surface by the surfactant molecules. This should be very important in case the sorbent was used for actual industrial wastewaters, which usually contain surfactants. Desorption studies revealed that this biomass can be regenerated using 0.1 M HCl and reused without significant changes in efficiency. The next stage of the research should involve the assessment of the efficacy of pine sawdust biosorption of dyes from actual industrial wastewaters.

Nomenclature

A_0 — Arrhenius constant
a_{RP} — Redlich-Peterson isotherm constant, $\mathrm{L\,mg^{-1}}$
b_L — Langmuir isotherm constant, $\mathrm{L\,mg^{-1}}$
b_{LF} — Langmuir-Freundlich isotherm constant, $\mathrm{L\,mg^{-1}}$
b_{RP} — Redlich-Peterson isotherm exponent
b_T — Temkin isotherm constant, $\mathrm{J\,mol^{-1}}$
C — bulk concentration of adsorbate, $\mathrm{mg\,L^{-1}}$
C_e — equilibrium concentration of adsorbate, $\mathrm{mg\,L^{-1}}$
C_o — initial concentration of adsorbate, $\mathrm{mg\,L^{-1}}$
E_a — activation energy, $\mathrm{kJ\,mol^{-1}}$
k — power function kinetic constant, $\mathrm{mg\,g^{-1}}$
k_1 — pseudo-first-order kinetic constant, $\mathrm{min^{-1}}$
k_2 — pseudo-second-order kinetic constant, $\mathrm{g\,mg^{-1}\,min^{-1}}$
K_a — equilibrium constant
K_F — Freundlich isotherm constant, $\mathrm{(mgg^{-1})(Lmg^{-1})^{(1/nF)}}$
k_{RP} — Redlich-Peterson isotherm constant, $\mathrm{L\,g^{-1}}$
k_T — Temkin equilibrium binding constant, $\mathrm{L\,mg^{-1}}$
m — mass of the biosorbent, g
n_F — exponent in Freundlich isotherm
n_{LF} — exponent in Langmuir-Freundlich isotherm
p — number of experimental points
q — amount of adsorbate adsorbed, $\mathrm{mg\,g^{-1}}$
q_e — amount of adsorbate adsorbed at equilibrium, $\mathrm{mg\,g^{-1}}$
q^{calc} — calculated amount of adsorbate adsorbed, $\mathrm{mg\,g^{-1}}$
q^{exp} — experimental amount of adsorbate adsorbed, $\mathrm{mg\,g^{-1}}$
q_{max} — maximum biosorption capacity, $\mathrm{mg\,g^{-1}}$
q_t — amount of sorbate sorbed at time t, $\mathrm{mg\,g^{-1}}$
R — universal gas constant, 8.314 $\mathrm{J\,mol^{-1}\,K^{-1}}$
SSE — sum of the squares error
t — time, s
T — temperature, K
V — volume, L
v — exponent in power function equation, $\mathrm{min^{-1}}$
X — biosorbent concentration, $\mathrm{g\,L^{-1}}$

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