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Surface-modified scarlet firethorn: an eco-friendly and effective dye remover with excellent regeneration potential

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ABSTRACT

The surface of the scarlet firethorn biomass was modified with dimethylglyoxime. Modified biosorbent (DMGPC) was evaluated for its potential to remove methylene blue (MB) dye from contaminated solutions. Batch- and continuous-mode biosorption conditions were examined by varying initial pH (2.0–10.0), biomass dosage (0.4–4.0 g L^{-1}), time (5–60 min), initial dye concentration (10–1,000 mg L^{-1}), temperature (15–45°C), and flow rate (0.5–6.0 mL min^{-1}). Langmuir isotherm and the pseudo-second-order kinetic models were used to describe the biosorption process in addition to mechanism characterization. Good biosorption yields were recorded with small amounts of DMGPC. The maximum monolayer biosorption capacity of DMGPC was 266.92 mg g^{-1}. DMGPC exhibited almost 100% regeneration potential up to 20 cycles, and it was successfully used in the synthetic wastewater conditions. DMGPC also showed very good biosorption yield (100%) up to 2000 min in dynamic flow mode. Mechanism of the decolorization process was investigated by zeta potential measurements, IR, and SEM analysis. Results revealed that DMGPC could be a low-cost, effective, and reusable candidate for the removal of MB from aqueous solutions.

Keywords: Biosorption; Desorption; Dimethylglyoxime; Dye; Modification

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1. Introduction

Uncontrolled discharge of the colored effluents into receiving water streams can create hazardous effects on living systems in addition to visual pollution. Many dyes are carcinogenic in nature and toxic at even low concentrations. Toxic amine compounds can be produced from complex aromatic structure of dyes at degradative conditions. Physical and chemical methods such as electrocoagulation, membrane filtration, ion exchange, irradiation, coagulation, flocculation, and ozonation are suggested for the removal of different pollutants from contaminated waters. However, some technical or economical limitations encountered in the application of these methods have directed attention to search for effective alternatives [1]. Adsorption has been increasingly preferred process in this field with the advantages of high efficiency, low cost, wide adaptability, design simplicity, etc. [2]. Biosorption is a biomass-based treatment process. It utilizes adsorption potential of the different biomaterials for the removal of organic and inorganic

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pollutants [3–12]. In recent years, some efforts have been made to develop efficient biosorbents for water treatment. A number of studies have been carried out to improve the biosorption abilities of biomaterials by applying chemical modifications [13–22]. However, a limited number of studies have been reported for the utilization of surfactant-modified biomasses as efficient biosorbents in the treatment of dye-contaminated solutions so far [23–27].

In this direction, biomass obtained from scarlet firethorn (*Pyracantha coccinea*) was modified with dimethylglyoxime (DMG) and effectively used for the biosorption of methylene blue (MB) from contaminated solutions. Scarlet firethorn berries were used as a biomass source, because of their known biosorption potential toward dye molecules and good response to surface modification [25,28]. MB was selected as a model dye, because it is commonly found in the effluents from dye houses and textile industry. Although MB is not a strongly hazardous dye, it may cause serious health problems such as gastritis, abdominal and chest pain, diarrhea, nausea, profuse sweating, vomiting, severe headache, mental confusion, painful micturation, and methemoglobinemia depending on the environmental exposure [29–32]. Also hemoconcentration, hypercapnia, acidosis, hypothermia, increase in blood pressure, corneal injury, respiratory frequency and amplitude, conjunctival damage, and Heinz body formation were described as some toxic effects observed in animals exposed to this dye [31,33].

2. Materials and methods

2.1. Biosorbent modification and solutions

The mature berries of scarlet firethorn used in the present study were collected from a number of plants in autumn. Later, they were washed several times with distilled water and dried at 60˚C for 24 h. The dried biomass was grounded using a laboratory mill (IKA A11) and sieved to get size fraction of less than 212 μm. Forty grams of raw biomass sample were suspended in DMG solution (0.1%). The suspension was stirred at 200 rpm at room temperature for 24 h. DMGPC was separated from the mixture by filtration. Next, it was washed with deionized water and dried again.

The stock solution ($1.0\ \mathrm{g\,L^{-1}}$) of MB (chemical formula: $C_{16}H_{18}ClN_3S{\cdot}2H_2O$ (M.W. $355.89\ \mathrm{g\,mol^{-1}}$) maximum wavelength 663 nm) was prepared by dissolving specified amount of dye in deionized water. Other solutions used in the experiments were prepared by dilution of stock solution to the required concentrations. Fresh dilutions were used in all the experiments. About $0.1\ \mathrm{mol\,L^{-1}}$ HCl or 0.1 M NaOH solutions were used for pH adjustments.

2.2. Batch- and continuous-mode biosorption experiments

Batch biosorption studies were conducted on a multipoint magnetic stirrer and a known amount of biosorbent sample was added into 100 mL beakers containing 25 mL of dye solutions. At the end of the each experiment, the biosorbent sample was separated from the biosorption mixture by centrifugation at 4,500 rpm for 3 min. The concentration of residual dye in the supernatant was analyzed spectrophotometrically at maximum wavelength of dye. Cylindrical glass columns with 11 mm internal diameter (i.d.) and 100 cm length were used for continuous flow-mode biosorption studies. A known quantity of biosorbent was packed between two layers of glass wool filters into the columns. MB solution was pumped out with a peristaltic pump. Pump and columns were connected by tygon tubing. Eluents were collected from the bottom of the columns and analyzed for residual dye concentration. In order to investigate the regeneration potential of DMGPC in dynamic flow mode, the column was eluted with $0.01\ \mathrm{mol\,L^{-1}}$ HCl and then packed bed was washed with deionized water. So, the regenerated packed bed was reused for the next biosorption cycle. The batch- and continuous-mode biosorption performance of DMGPC was also tested in a synthetic wastewater medium including MB dye.

2.3. Biosorbent characterization

Zeta potential measurements of DMGPC were conducted by a Zetasizer Nano ZS (Malvern Instruments, UK). IR spectra of DMGPC and dye-loaded DMGPC were recorded using Bruker Tensor 27 model spectrophotometer in the wave number range of 400 and $4{,}000\ \mathrm{cm^{-1}}$. The surface microstructure of DMGPC was visualized by a scanning electron microscope (JEOL 560 LV SEM) with combined energy dispersive X-ray analyzer at 20 kV acceleration voltage and 1,000× image magnification. Prior to analyze, biomaterial was coated in a Polaron SC-7620 Sputter Coater using a gold–palladium target to improve electron conductivity and image quality.

3. Results and discussion

3.1. Effect of initial pH on the biosorption

Initial pH of the solution is an important parameter affecting the possible interactions between biosorbent and pollutant. The effect of pH on MB biosorption yields of scarlet firethorn and DMGPC was screened in the pH range of 2.0–10.0. The results in Fig. 1 indicated that the biosorption yields of both biosorbents increased with increasing pH and reached the highest level at pH 4.0. This finding may be attributed to an increase in the negative charge density on the biosorbents. As a result of deprotonation, the surface of the biosorbents becomes negatively charged and this increases the possible interactions between biosorbent surface and cationic dye. Biosorption yields were recorded as 93.80 ± 1.08 and $98.46 \pm 0.04\%$ for scarlet firethorn and DMGPC, respectively, at optimal pH value. When the initial pH of the dye solutions was adjusted to higher pH values up to 10.0, biosorption yields stayed approximately constant ($p > 0.05$). The good biosorption yields in the pH range of 4.0–10.0 for both biosorbents are also confirmed by the zeta potential measurements. The surface charges of these biosorbents lie between −20 and −30 mV in this pH range. The isoelectric point of the natural biosorbent [28] slightly shifted to ~2.2 after DMG modification. The original pH value of the dye solutions was recorded as 7.0. Therefore, MB solutions were used without pH adjustment in further biosorption trials.

3.2. Effect of biosorbent dosage on the biosorption

The decolorization performances of the scarlet firethorn and DMGPC were tested using different amounts of biosorbent and the results are presented in Fig. 2. The dye-loading yield of DMGPC increased from 81.02 ± 0.38 to $98.15 \pm 0.12\%$ when the biosorbent dosage increased from 0.4 to $1.6\ \mathrm{g\,L^{-1}}$, but at this point decolorization yield of scarlet firethorn was $93.03 \pm 0.11\%$. The initial increase in biosorption with biosorbent amount can be ascribed to stronger driving force and layer surface area [34]. Therefore, $1.6\ \mathrm{g\,L^{-1}}$ was selected as the optimum biosorbent dosage for DMGPC for cost-effective treatment of MB dye. A significantly higher decolorization yield with a small amount of DMGPC confirmed the positive effect of chemical modification on the biosorption process. The enhancement in the decolorization yield of scarlet firethorn may be attributed to the additional hydroxyl groups of DMG on the biosorbent surface after the modification process.

3.3. Effect of ionic strength on the biosorption

The presence of other competing ions in the biosorption medium can reduce the biosorption performance of a biosorbent for a target pollutant. Therefore, the effect of competing ions on the MB biosorption potential of DMGPC was studied at various ionic strengths under predetermined optimum conditions and the results are given in Fig. 3. When $NaNO_3$ concentration in the biosorption medium was increased from 0.01 to $0.2\ \mathrm{mol\,L^{-1}}$, the biosorption yield of DMGPC decreased from 88.21 ± 0.03 to $52.29 \pm 0.09\%$, from 85.49 ± 0.05 to $50.81 \pm 0.13\%$, and from 79.79 ± 0.14 to $49.86 \pm 0.03\%$ at temperatures of 15, 30, and 45˚C, respectively. The lower biosorption yield at higher ionic strength may be explained by the competition between cationic dye and sodium ions (Na^+) for the same binding sites present on the DMGPC surface. This behavior indicated that the ion exchange could be responsible for decolorization process. Another way to explain the adverse effect of ionic strength may change the activity coefficient of

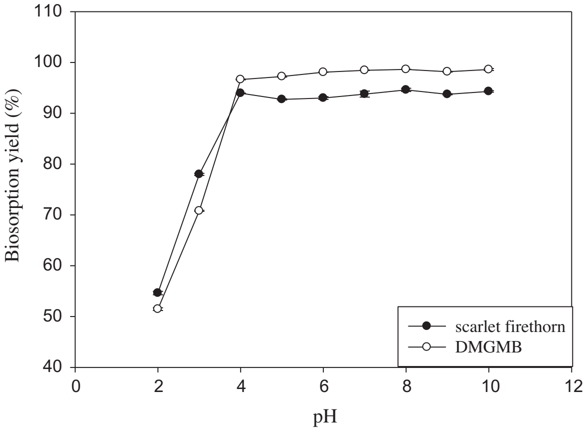

Fig. 1. Effect of pH on the MB biosorption onto scarlet firethorn and DMGPC.

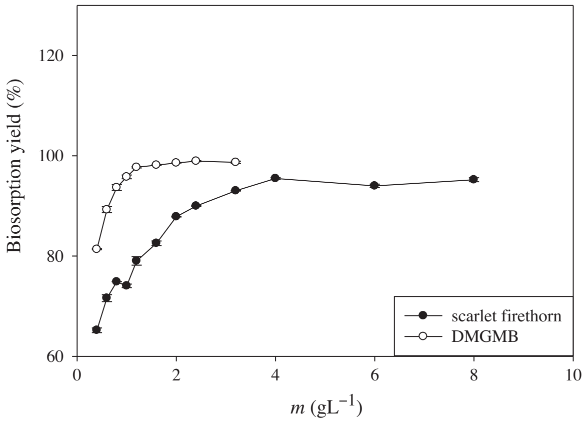

Fig. 2. Effect of biosorbent concentration on the biosorption of MB onto DMGPC.

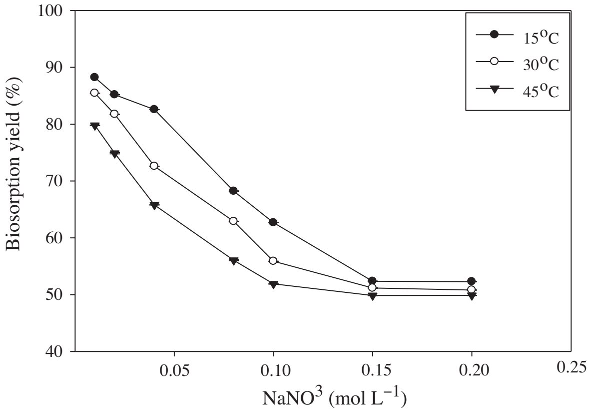

Fig. 3. Effect of salt concentration on the biosorption of MB onto DMGPC.

cationic dye molecules and thus limit their transfer to solid phase [35–37].

3.4. Kinetics of the biosorption process

The biosorption kinetics helps to understand the biosorption dynamics, to predict the most suitable models and to determine the equilibration time. This information could be used for the large-scale applications of the suggested biosorption system [38]. In order to model MB biosorption at three different temperatures (15, 30, and 45˚C), the pseudo-first-order [39] and the pseudo-second-order [40] rate equations have been used. R^2 values along with the rate constants and calculated q_e values were included in Table 1. R^2 values for pseudo-first-order model were very low and this model failed to predict q_e values accurately at all studied temperatures. The calculated q_e values from the pseudo-second-order kinetic model with R^2 values of 0.999 closely matched with the experimental values at the studied temperatures. The biosorption capacity of DMGPC decreased with increasing temperature while the biosorption rate increased proportionally with temperature. As conclusion, the biosorption process of MB onto DMGPC followed the pseudo-second-order kinetic model and exothermic in nature.

3.5. Equilibrium study

In this study, Langmuir [41], Freundlich [42], and Dubinin–Radushkevich (D–R) [43] isotherm equations were used to describe MB biosorption onto DMGPC. The Langmuir isotherm model assumes a monolayer biosorption onto a surface with a finite number of identical binding sites [44]. The essential characteristics of the Langmuir isotherm can be expressed by means of “R_L”, a dimensionless equilibrium constant defined as $R_L = \frac{1}{1+K_L C_0}$ where C_o is the highest initial dye concentration. R_L can be used to determine whether the biosorption process is favorable or unfavorable as follows [45,46]:

$0 < R_L < 1$ favorable
$R_L > 1$ unfavorable
$R_L = 1$ linear
$R_L = 0$ irreversible.

The isotherm model parameters for the biosorption of MB onto DMGPC calculated from the Langmuir ($1/q_e$ vs. $1/C_e$), Freundlich ($\ln q_e$ vs. $\ln C_e$), and D–R ($\ln q_e$ vs. ε^2) isotherm plots (figures not shown) at different temperatures are listed in Table 2. It seemed that all of the isotherm models fit well when the R^2 values are compared. Fitting degree decreased in the order of Langmuir > Freundlich > D–R in this study. The best description of MB biosorption by Langmuir isotherm means that the dye uptake occurs on a homogenous surface by monolayer biosorption. The biosorption capacity decreased with increasing temperature and the maximum monolayer capacity was found as 7.50×10^{-4} mol g^{-1} at 15˚C. This proved the exothermic nature of MB biosorption onto DMGPC. K_F values were found between 9.20×10^{-3} and 2.33×10^{-2} L mol^{-1}; n values between 0 and 10 (2.567–9.759) indicated that MB biosorption onto DMGPC was favorable at all temperatures studied [47] and tends to increase with increasing temperature. Recorded R_L values in the present study also supported the favorable biosorption of MB by

Table 1
Kinetic parameters for the biosorption of MB onto DMGPC at different temperatures

	Pseudo-first-order			Pseudo-second-order		
t (˚C)	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
15	3.44×10^{-2}	7.08	0.344	4.17×10^{-3}	120.73	0.999
30	-6.25×10^{-3}	0.52	0.773	9.48×10^{-3}	112.50	0.999
45	1.54×10^{-3}	1.93	0.197	2.09×10^{-2}	104.19	0.999

Table 2
Isotherm model constants for the biosorption of MB onto DMGPC

	Langmuir model				Freundlich model			(D–R) model			
t (°C)	$q_{\max}$ (mol g^{-1})	K_L (L mol^{-1})	R_L^2	R_L	n	K_F (L g^{-1})	R_F^2	q_m (mol g^{-1})	β (mol^2 kJ^{-2})	R_{D-R}^2	ε (kJ mol^{-1})
15	7.50×10^{-4}	1.33×10^4	0.956	4.26×10^{-2}	9.759	2.33×10^{-2}	0.993	2.86×10^{-3}	2.11×10^{-3}	0.946	10.87
30	5.12×10^{-4}	1.93×10^4	0.949	2.98×10^{-2}	2.423	1.35×10^{-2}	0.922	2.15×10^{-3}	1.94×10^{-3}	0.920	16.04
45	4.83×10^{-4}	2.02×10^4	0.970	2.85×10^{-2}	2.567	9.20×10^{-3}	0.949	1.64×10^{-3}	1.77×10^{-3}	0.970	16.80

DMGPC. The mean free energy values of biosorption are found between 10.87 and 16.80 kJ mol^{-1} at different temperatures. These findings imply that MB biosorption onto DMGPC may occur via chemical ion-exchange mechanism.

3.6. Column biosorption of MB

Column biosorption studies were carried out at different flow rates and biosorbent amounts.

The flow rate of MB solution was varied from 0.5 to 6.0 mL min^{-1} by keeping the initial dye concentration at 100 mg L^{-1}. The results are presented in Fig. 4. The biosorption yield of DMGPC strongly depends on flow rate of biosorbate and significantly decreased with an increase in flow rate. The maximum biosorption yield of DMGPC was found as 95.91 ± 0.11% at a flow rate of 0.5 mL min^{-1}. This may be attributed to the longer residence time of solute in column at lower flow rates [48]. Therefore, 0.5 mL min^{-1} was selected as optimum flow rate in this study.

DMGPC amount filled into the column was changed from 0.01 to 0.05 g in order to investigate the effect of bed height on the biosorption. The results are included in Fig. 5. The biosorption yield of DMGPC increased from 78.97 ± 0.35 to 99.59 ± 0.02% when the biosorbent amount in the column was increased from 0.01 to 0.03 g ($p < 0.05$). The higher biosorption yields at higher amounts of biosorbent can be explained by the higher bed heights. Hence, the higher bed height provides increased surface area with more binding sites and longer residence time for biosorbate in the column [49–51]. A further increase in the biosorbent amount up to 0.05 g did not cause any change in the biosorption performance of the biosorbent ($p > 0.05$). This may be due to the saturation of active sites on the biosorbent by dye molecules. Therefore, the optimum biosorbent amount was selected as 0.03 g for column biosorption studies.

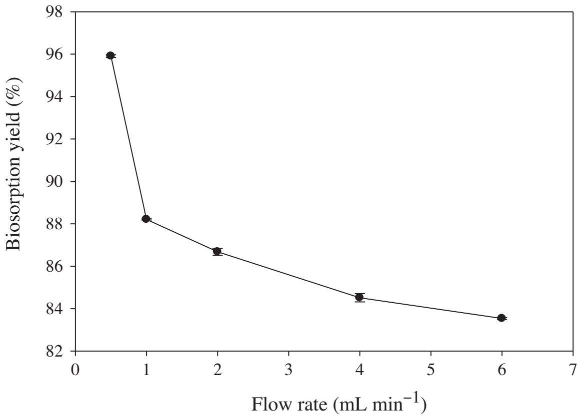

Fig. 4. Effect of flow rate on the biosorption of MB onto DMGPC in continuous system.

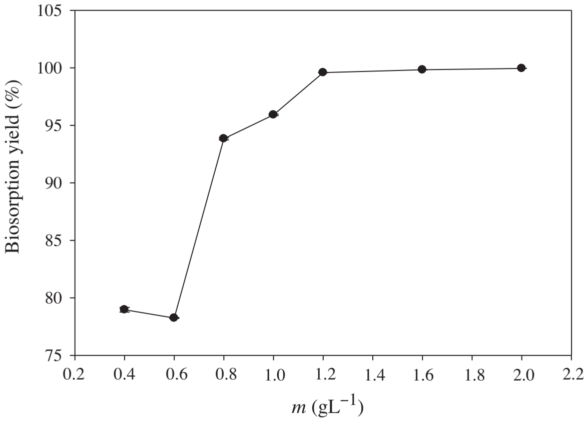

Fig. 5. Effect of biosorbent amount on the bisorption of MB onto DMGPC in continuous system.

3.7. Reusability potential of DMGPC and breakthrough study

The regeneration ability of the biosorbents is an important feature in assessing their potential for commercial applications. In order to investigate the reusability potential of DMGPC, biosorption/desorption cycles were repeated for 20 times in same packed bed column. High biosorption and desorption yields were observed for the first eight cycles. At the end of the

14th cycle, the biosorption efficiency of DMGPC decreased from 99.87 ± 0.01 to 56.56 ± 0.59% and remained almost constant up to 20th cycle. This decrease in the biosorption yield of DMGPC toward MB dye may be explained by a slight degeneration in the sorbent structure as a result of HCl treatment. However, the regeneration potential of DMGPC was almost 100% in each cycle.

In order to predict the breakthrough curve for MB biosorption onto DMGPC, 100 mg L^{-1} dye solution was fed at 0.5 mL min^{-1} into the column packed with 1.0 g of DMGPC. The breakthrough time emerged around 2000 min and packed bed column reached to exhaustion after 3,980 min. The decolorization process followed the typical *S*-shaped breakthrough curve and indicated that favourable biosorption in continuous mode treatment. Similar observation was also reported by Vijayaraghavan and co-workers for the treatment of Reactive Black 5 contaminated solutions by brown seaweed packed column [13].

3.8. Synthetic wastewater application

The batch- and continuous-mode biosorption potential of DMGPC developed in this study was tested in real wastewater conditions. For this aim, a synthetic wastewater sample was prepared by including different components and its chemical composition is given in Table 3. The biosorption yields of DMGPC were found as 53.08 ± 0.29 and 59.50 ± 0.13% in batch and column modes, respectively. According to these results, slight matrix effect was observed at synthetic wastewater conditions. This effect may be explained by the competition between dye cations and other cationic components in synthetic wastewater for binding to active sites on the biosorbent surface. In conclusion, the DMGPC could be successfully applied to industrial dye wastewater with a small decrease in its biosorption performance for MB.

Table 3
Chemical composition of synthetic wastewater sample

Compound	Amount (g)
NH_4Cl	11.46
K_2HPO_4	3.37
$(NH_4)_2SO_4$	1.50
$Ca(NO_3)_2{\cdot}4H_2O$	4.04
$MgCl_2{\cdot}6H2O$	4.18
$(NH_4)_2{\cdot}Fe(SO_4)_2$	7.02
$CuCl_2{\cdot}{}_2H_2O$	0.04
$ZnCl_2$	0.08
$MnCl_2{\cdot}2H_2O$	0.05
$NiSO_4{\cdot}6H_2O$	0.047
$CoCl_2{\cdot}6H_2O$	0.016
H_3BO_3	0.057
$Na_2MoO_4{\cdot}2H_2O$	0.001

3.9. Mechanism characterization

SEM micrograph of DMGPC indicated rough and irregular surface structure of biosorbent. This structure was considered as helpful for the biosorption of MB molecules onto different parts of biomaterial.

In order to determine the modification effect on the biosorbent, IR spectra of natural [28] and DMGPC were compared. The following differences were recorded between the peak positions of natural biosorbent and DMGPC: The peaks at 3,415 and 1,421 cm^{-1} in the IR spectrum of natural biomass shifted to 3,422 and 1,431 cm^{-1}, respectively, after the modification with DMG. The new peaks at 1,458, 1,375, and 1,161 cm^{-1} in the spectrum of DMGPC can be ascribed to $–CH_3$, $–CH_2$ bending, and –CN stretching vibrations, respectively. Also, the phosphate peak at 1,078 and C–O peak at 1,036 cm^{-1} in the spectrum of natural biomass shifted to 1,105 and 1,055 cm^{-1} in the IR spectrum of DMGPC. On the other hand, after the biosorption process, the absorption band at 1,633 cm^{-1} in the spectrum of DMGPC was observed as double band at 1,626 and 1,605 cm^{-1}. The peak at the wave number of 1,458 cm^{-1} disappeared and the intensities of the peaks at 1,161, 1,105, and 1,055 cm^{-1} decreased. The peak at 1,055 cm^{-1} also shifted to 1,034 cm^{-1}. Furthermore, a new peak at 714 cm^{-1} in the spectrum of dye-loaded DMGPC may be attributed to the aromatic –CH vibrations of dye. These findings confirmed the possible interactions between MB dye and DMGPC.

4. Conclusion

Decolorization potential of scarlet firethorn for MB dye was significantly enhanced by DMG modification. Temperature negatively affected the biosorption capacity of DMGPC and showed an exothermically controlled mechanism for MB biosorption. On the other hand, equilibrium time decreased as a result of enhanced biosorption rate with increasing temperature. MB biosorption process preferably obeyed the pseudo-second-order model, while the Langmuir isotherm best described the equilibrium data. The maximum monolayer biosorption capacity was found as 7.50×10^{-4} mol g^{-1} (266.92 mg g^{-1}). Regeneration studies over 10 consecutive cycles indicated that the suggested biosorbent maintained consistently high biosorption yield (>70%). Although a small decrease in the biosorption yield at synthetic wastewater conditions, applicability of DMGPC for MB removal from complex water media was proved. DMGPC showed an excellent dye biosorption potential for a long time (up to 2000 min) in continuous flow mode as an important advantage for industrial scale applications. Finally, MB biosorption process mainly included ion-exchange and complexation mechanisms in addition to the electrostatic interaction.

References

[1] Z. Aksu, Application of biosorption for the removal of organic pollutants: A review, Process Biochem. 40 (2005) 997–1026.

[2] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Utilization of bottom ash as a low-cost sorbent for the removal and recovery of a toxic halogen containing dye eosin yellow, Desalin. Water Treat. 52 (2013) 4508–4519.

[3] J. Mittal, V. Thakur, A. Mittal, Batch removal of hazardous azo dye Bismark Brown R using waste material hen feather, Ecol. Eng. 60 (2013) 249–253.

[4] Y. Khambhaty, K. Mody, S. Basha, Efficient removal of Brilliant Blue G (BBG) from aqueous solutions by marine *Aspergillus wentii*: Kinetics, equilibrium and process design, Ecol. Eng. 41 (2012) 74–83.

[5] H. Daraei, A. Mittal, M. Noorisepehr, F. Daraei, Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, Environ. Sci. Pollut. Res. 20 (2013) 4603–4611.

[6] M. Asgher, H.N. Bhatti, Evaluation of thermodynamics and effect of chemical treatments on sorption potential of citrus waste biomass for removal of anionic dyes from aqueous solutions, Ecol. Eng. 38 (2012) 79–85.

[7] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. 52 (2014) 227–237.

[8] A. Safa Özcan, S. Tunali, T. Akar, A. Özcan, Biosorption of lead(II) ions onto waste biomass of *Phaseolus vulgaris* L.: Estimation of the equilibrium, kinetic and thermodynamic parameters, Desalination 244 (2009) 188–198.

[9] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies, Desalin. Water Treat. (2013) 1–7, doi: 10.1080/19443994.2013.837011.

[10] Ç. Ömeroğlu Ay, A.S. Özcan, Y. Erdoğan, A. Özcan, Characterization of *Punica granatum* L. peels and quantitatively determination of its biosorption behavior towards lead(II) ions and Acid Blue 40, Colloids Surf., B 100 (2012) 197–204.

[11] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: Experimental and theoretical approaches, Desalin. Water Treat. 52 (2013) 1307–1315.

[12] A. Mittal, L. Kurup, Column operations for the removal and recovery of a hazardous dye 'Acid Red-27' from aqueous solutions, using waste materials-Bottom ash and de-oiled soya, Ecol. Environ. Conserv. Pap. 12 (2006) 181–186.

[13] K. Vijayaraghavan, Y.S. Yun, Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria* sp., Dyes Pigm. 76 (2008) 726–732.

[14] M.E. Fernandez, G.V. Nunell, P.R. Bonelli, A.L. Cukierman, Batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips, Bioresour. Technol. 106 (2012) 55–62.

[15] L.H. Chen, A. Ramadan, L.L. Lu, W.J. Shao, F. Luo, J. Chen, Biosorption of methylene blue from aqueous solution using lawny grass modified with citric acid, J. Chem. Eng. Data 56 (2011) 3392–3399.

[16] K. Vijayaraghavan, S.W. Won, J. Mao, Y.-S. Yun, Chemical modification of *Corynebacterium glutamicum* to improve methylene blue biosorption, Chem. Eng. J. 145 (2008) 1–6.

[17] K.A. Guimarães Gusmão, L.V. Alves Gurgel, T.M. Sacramento Melo, L.F. Gil, Application of succinylated sugarcane bagasse as adsorbent to remove methylene blue and gentian violet from aqueous solutions—Kinetic and equilibrium studies, Dyes Pigm. 92 (2012) 967–974.

[18] V. Ponnusami, V. Krithika, R. Madhuram, S.N. Srivastava, Biosorption of reactive dye using acid-treated rice husk: Factorial design analysis, J. Hazard. Mater. 142 (2007) 397–403.

[19] S. Chowdhury, P. Saha, Artificial neural network (ANN) modeling of adsorption of methylene blue by NaOH-modified rice husk in a fixed-bed column system, Environ. Sci. Pollut. Res. 20 (2013) 1050–1058.

[20] S. Chowdhury, S. Chakraborty, P. Saha, Response surface optimization of a dynamic dye adsorption process: A case study of crystal violet adsorption onto NaOH-modified rice husk, Environ. Sci. Pollut. Res. 20 (2013) 1698–1705.

[21] G. Bayramoğlu, G. Çelik, M.Y. Arica, Biosorption of Reactive Blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: Batch and continuous flow system studies, J. Hazard. Mater. 137 (2006) 1689–1697.

[22] G. Sharma, M. Naushad, D. Pathania, A. Mittal, G.E. El-desoky, Modification of *Hibiscus cannabinus* fiber by graft copolymerization: Application for dye removal, Desalin. Water Treat. 33 (2014) 1–8, doi: 10.1080/19443994.2014.904822.

[23] T. Akar, M. Divriklioglu, Biosorption applications of modified fungal biomass for decolorization of Reactive Red 2 contaminated solutions: Batch and dynamic flow mode studies, Bioresour. Technol. 101 (2010) 7271–7277.

[24] T. Akar, S. Celik, S.T. Akar, Biosorption performance of surface modified biomass obtained from *Pyracantha coccinea* for the decolorization of dye contaminated solutions, Chem. Eng. J. 160 (2010) 466–472.

[25] T. Akar, E. Ozkara, S. Celik, S. Turkyilmaz, S.T. Akar, Chemical modification of a plant origin biomass using cationic surfactant ABDAC and the biosorptive decolorization of RR45 containing solutions, Colloids Surf., B 101 (2013) 307–314.

[26] B.C. Oei, S. Ibrahim, S. Wang, H.M. Ang, Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution, Bioresour. Technol. 100 (2009) 4292–4295.

[27] M.X. Loukidou, K.A. Matis, A.I. Zouboulis, M. Liakopoulou-Kyriakidou, Removal of As(V) from wastewaters by chemically modified fungal biomass, Water Res. 37 (2003) 4544–4552.

[28] T. Akar, B. Anilan, A. Gorgulu, S.T. Akar, Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries, J. Hazard. Mater. 168 (2009) 1302–1309.

[29] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.

[30] R. Abdallah, S. Taha, Biosorption of methylene blue from aqueous solution by nonviable *Aspergillus fumigatus,* Chem. Eng. J. 195–196 (2012) 69–76.

[31] S.S. Auerbach, D.W. Bristol, J.C. Peckham, G.S. Travlos, C.D. Hébert, R.S. Chhabra, Toxicity and carcinogenicity studies of methylene blue trihydrate in F344N rats and B6C3F1 mice, Food Chem. Toxicol. 48 (2010) 169–177.

[32] J. Clifton 2nd, J.B. Leikin, Methylene Blue, Am. J. Ther. 10 (2003) 289–291.

[33] G. Christiansen, The toxicity of selected therapeutic agents used in cats, Vet. Med., Small Anim. Clinician: VM, SAC 75 (1980) 1133–1137.

[34] R. Jain, P. Sharma, S. Sikarwar, J. Mittal, D. Pathak, Adsorption kinetics and thermodynamics of hazardous dye Tropaeoline 000 unto Aeroxide Alu C (Nano alumina): A non-carbon adsorbent, Desalin. Water Treat. (2013) 1–8, doi: 10.1080/19443994.2013.837009.

[35] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH, Bioresour. Technol. 97 (2006) 512–521.

[36] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Influence of pH, ionic strength and temperature on lead biosorption by gelidium and agar extraction algal waste, Process Biochem. 40 (2005) 3267–3275.

[37] Z. Aksu, E. Balibek, Effect of salinity on metal-complex dye biosorption by *Rhizopus arrhizus,* J. Environ. Manage. 91 (2010) 1546–1555.

[38] S. Schiewer, A. Balaria, Biosorption of Pb^{2+} by original and protonated citrus peels: Equilibrium, kinetics, and mechanism, Chem. Eng. J. 146 (2009) 211–219.

[39] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe (About the theory of so-called adsorption of soluble substances), Kungliga Svenska Vetenskapsakademiens, Handlingar, Band 24(4) (1898) 1–39.

[40] Y.-S. HO, Review of second-order models for adsorption systems, J. Hazard. Mater. 136 (2006) 681–689.

[41] I. Langmuir, The adsorptıon of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[42] H. Freundlich, Über die absorption in lösungen (Adsorption in solutions), Z. Phys. Chem. 57 (1906) 385–470.

[43] M. Dubinin, L. Radushkevich, Equation of the characteristic curve of activated charcoal, Proc. Acad. Sci. Phys. Chem. Sec., USSR55, 331–333 (1947) 875–890.

[44] Y. Wang, Y. Mu, Q.-B. Zhao, H.-Q. Yu, Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge, Sep. Purif. Technol. 50 (2006) 1–7.

[45] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.

[46] L. Wang, J. Li, Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics, Ind. Crops Prod. 42 (2013) 153–158.

[47] E. Daneshvar, M. Kousha, M. Jokar, N. Koutahzadeh, E. Guibal, Acidic dye biosorption onto marine brown macroalgae: Isotherms, kinetic and thermodynamic studies, Chem. Eng. J. 204–206 (2012) 225–234.

[48] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column, J. Hazard. Mater. 113 (2004) 223–230.

[49] S.T. Akar, T. Akar, Z. Kaynak, B. Anilan, A. Cabuk, Ö. Tabak, T.A. Demir, T. Gedikbey, Removal of copper(II) ions from synthetic solution and real wastewater by the combined action of dried *Trametes versicolor* cells and montmorillonite, Hydrometallurgy 97 (2009) 98–104.

[50] S.T. Akar, A. Gorgulu, Z. Kaynak, B. Anilan, T. Akar, Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macrofungus *Agaricus bisporus* and *Thuja orientalis* cones, Chem. Eng. J. 148 (2009) 26–34.

[51] S.T. Akar, R. Uysal, Untreated clay with high adsorption capacity for effective removal of C.I. Acid Red 88 from aqueous solutions: Batch and dynamic flow mode studies, Chem. Eng. J. 162 (2010) 591–598.