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Removal of malachite green from aqueous solutions using molecularly imprinted polymer

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ABSTRACT

Efficiency of malachite green molecularly imprinted polymer (MGIP) as a selective adsorbent in removal of malachite green (MG) from aqueous solutions was evaluated by using the batch adsorption experiments. Adsorption kinetics and effects of various parameters such as solution pH, adsorbent dose and initial MG concentration were investigated. Under optimized conditions (adsorbent dose 20 mg, solution pH 7, contact time 5 min), equilibrium experimental data at 293, 303, and 313 K were represented by Freundlich and Langmuir isotherms and the thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were also calculated. Results briefly show that adsorption of MG by MGIP obeys pseudo-second order lagergren kinetic model and Langmuir-1 isotherm. The capacity of proposed sorbent was determined as 303.03, 285.71 and 416.66 mg g^{-1} at 293, 303 and 313 K, respectively.

Keywords: Malachite green; Molecularly imprinted polymer; Adsorption; Kinetics; Equilibrium

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1. Introduction

Malachite green (MG), 4-[(4-dimethylaminophenyl)-phenyl-methyl]-*N*,*N*-dimethyl-aniline, also called aniline green, basic green 4, diamond green B, or victoria green B, is a synthetic dye used in silk, wool, jute, leather, cotton and paper industries [1]. Also it has traditionally been used to treat fungal infections on fish eggs in aquaculture [2]. But according to the recent studies, MG can cause several health problems due to its severe toxic properties [3]. It can be released to the environment by effluents of the related industries, so there is a vital need to design wastewater treatment plants to remove it. MG is hardly biodegraded in the environment [4], and its removal procedures such as adsorption methods were widely investigated. Activated carbon and other carbon-based adsorbents are the most reported ones [5–9], but various adsorbents such as iron humate, oxihumolite, bagasse fly ash, bentonite clay, anaerobic granular sludge, agricultural by-products, chitosan bead, dead pine needles, aerobic granules, rattan sawdust, oil palm trunk fibre, bottom ash, de-oiled soya and cyclodextrin-based compounds were reported too [10–23].

Molecular imprinting technique introduced in 1972 by Wulff and Sarhan [24] is an efficient method for synthesis of receptor molecules with high molecular recognition ability. In last decades, molecularly imprinted polymers (MIPs) have been widely used as recognition elements in chemical sensors [25–27] and

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selective sorbents in solid phase extraction [28], solid phase microextraction [29] and removal of target molecules from different matrices [30,31].

In the present study, malachite green imprinted polymer (MGIP) previously reported by Yan et al. [32] was synthesized and used for removal of MG from aqueous solutions. Equilibrium experimental data at 293, 303, and 313 K were represented by Freundlich and Langmuir isotherms and kinetic characteristics of the adsorption process were analyzed using two kinetic models and compared with those of other sorbents from literature. Thermodynamic parameters (ΔG°, ΔH°, and ΔS°) were also calculated.

2. Experimental

2.1. Chemicals and reagent

Malachite green chloride (MG), methacrylic acid (MAA), ethylenglycoldimethacrylate (EGDMA), azobisisobutyronitrile (AIBN), acetone and acetic acid were all from E. Merck (Darmstadt, Germany). Methanol, acetonitrile and water were HPLC grade and purchased from Scharlau (Barcelona, Spain). Filter papers (3–5 μm pore size) were supplied by ALBET (Barcelona, Spain). Nitrogen gas (99.999% purity) was from Air Products (UK).

2.2. Apparatus

A Perkin-Elmer model Lambda 25 UV–Vis spectrophotometer (Pekin-Elmer, USA) equipped with 10 mm matched plastic cells was used for adsorption studies. For equilibrium studies, a TS 606/2-i, WTW thermostated cabinet (WTW, Germany) equipped with an Oxi Top IS 12, inductive stirring system was used. A Hettich centrifuge model MIKRO 22R (Hettich, Germany) and a Metrohm 744 pH meter (Metrohm, Switzerland) equipped with a glass electrode were used for separation of polymer particles from solutions and pH adjustments, respectively.

2.3. Synthesis of MGIP

In this study, MGIP was synthesized according to the method reported by Yan et al. [32], which was described briefly here. 0.5 mmol MG as template, 2 mmol MAA as functional monomer, 10 mmol EGDMA as cross linker and 10 mg AIBN as initiator were dissolved in 30 mL acetonitrile as porogen and mixed well, then the solution was purged with nitrogen gas for about 5 min to remove oxygen which inhibited polymerization and then sealed under nitrogen gas. Polymerization was carried out in a water bath at 60°C for 12 h. The obtained polymer was collected and washed with acetone and then with a mixture of methanol and acetic acid mixture (9:1) until no MG was detected. Then the polymer dried at 40°C under vacuum. For the preparation of non-imprinted polymer, the procedures mentioned above were all performed in the absence of template molecules. Synthesis process and chemical structures of MG and MGIP are presented in Fig. 1.

2.4. Kinetic and equilibrium studies

For kinetic studies, 200 mg of MGIP was added into 100 mL of MG (50 mg L^{-1}) then the mixture was agitated at 300 rpm at 293, 303, and 313 K. At predetermined time intervals (0–75 min), the residual MG concentration was determined spectrophotometrically at 617 nm and the adsorbed amount of dye at time t, q_t (mg g^{-1}), was calculated.

Batch equilibrium studies were carried out by adding 20 mg of MGIP into 250 mL Erlenmeyer flasks containing 100 mL different concentrations (15–250 mg L^{-1}) of dye solutions at pH 7. The flasks were agitated in a thermostated cabinet at 293, 303, and 313 K for 5 min. Then the mixtures were centrifuged, adsorbent particles were separated and residual MG concentrations were determined and amount of adsorbed MG per gram of polymer (q_e) was calculated.

Results of equilibrium studies were analyzed using Langmuir and Freundlich isotherms to find best fitted model which can describe the adsorption process. Langmuir isotherm is based on three assumptions: (a) adsorbed molecules can create only monolayer coverage; (b) all surface binding sites are equivalent and can occupied by one adsorbed template and (c) the ability of a template to bind at a given site does not depend on the occupation of neighboring sites [33].

The original form of Langmuir isotherm can be expressed as:

$$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{a} C_\mathrm{e}}{1 + K_\mathrm{a} C_\mathrm{e}}, \tag{1}$$

where q_m is adsorbent capacity (mg g^{-1}) and K_a (mg^{-1}) is Langmuir isotherm constant. Corresponding linear forms of Langmuir isotherm, Langmuir-1, Langmuir-2, Langmuir-3, and Langmuir-4 are given as Eqs (2)–(5), respectively.

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{q_\mathrm{m}} C_\mathrm{e} + \frac{1}{K_\mathrm{a} q_\mathrm{m}}, \tag{2}$$

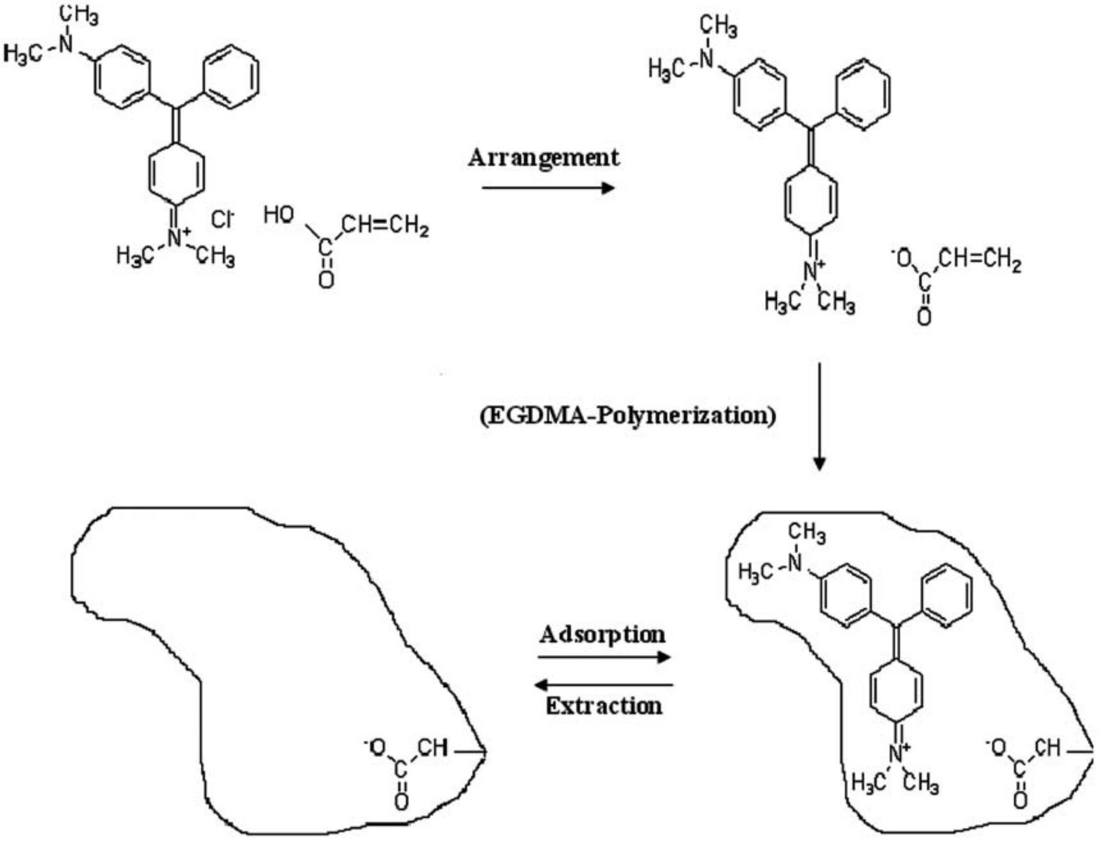

Fig. 1. Synthesis process of MGIP and chemical structure of MGIP and MG.

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}, \tag{3}$$

$$q_e = q_m - \left(\frac{1}{K_a}\right)\frac{q_e}{C_e}, \tag{4}$$

$$\frac{q_e}{C_e} = K_a q_m - K_a q_e, \tag{5}$$

Freundlich isotherm is the most common model to describe nonideal sorption on heterogeneous surfaces as well as multilayer sorption [34]. Original form of Freundlich isotherm and its corresponding linear form can be expressed as:

$$q_e = K_F C_e^{1/n}, \tag{6}$$

$$\ln(q_e) = \ln(K_F) + {}^{1}/_{n}\ln(C_e), \tag{7}$$

where K_F ((mg g^{-1}) (1/mg)$^{1/n}$) is the Freundlich constant.

3. Results and discussion

3.1. Adsorption kinetic studies

Contact time of adsorbent with sample solution is an important parameter in adsorption studies [9]. The obtained results from the experiments at 293, 303, and 313 K are shown in Fig. 2. Results indicate that the adsorption was very fast and more than 96% of dye was removed within 0.5 min, so 5 min was selected for complete removal of dye. For further studies, kinetics of MG adsorption were modeled using the pseudo-first order and the pseudo-second order Lagergren equations [35,36]. The pseudo-first order equations, which can be expressed as the following equation:

$$\frac{dq}{dt} = k_1(q_e - q_t), \tag{8}$$

where k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption. The integrated form of this equation is given as:

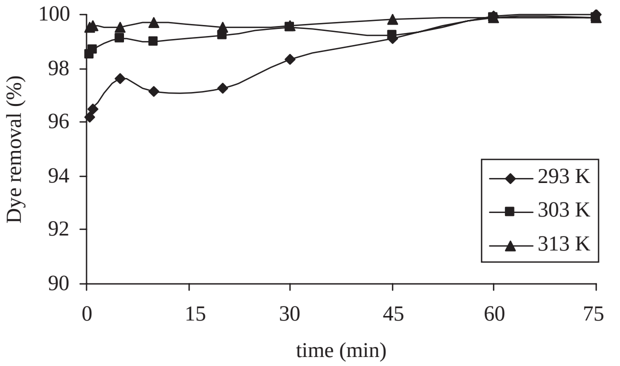

Fig. 2. Effect of contact time on dye removal from aqueous solutions at different temperatures (adsorbent dosage = 200 mg, concentration and volume of dye solution = 50 mg L^{-1} and 100 mL, respectively, pH = 7, temperature = 293, 303, and 313 K).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t. \tag{9}$$

The value of rate constant (k_1) was obtained by plotting $\log(q_e - q_t)$ vs. t.

The pseudo-second order equation is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2, \tag{10}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant for the pseudo-second order adsorption. The integrated linear form of Eq.(10) can be represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t. \tag{11}$$

The value of pseudo-second order rate constant (k_2) was obtained by plotting $\frac{t}{q_t}$ vs. t.

Related rate constants and correlation coefficients at 293 K were calculated and summarized in Table 1. Based on the regression coefficients, the adsorption process obeys the pseudo-second-order kinetic model (Fig. 3).

3.2. Effect of pH

In order to study effect of pH on adsorption process, 20 mg of MGIP was added into 100 mL solutions containing 50 mg L^{-1} of MG at 293 K with pH values adjusted at the range of 2–12. After 5 min, adsorbent was filtered and amount of residual MG was determined. According to the results (Fig. 4), percentage of removed dye increases with pH increasing. Fig. 1 shows that specific sites of MGIP for interaction with MG molecules have negative charges, so at lower pH, functional sites were protonated which causes decrease in adsorption of MG cations (pKa = 10.3) due to electrostatic repulsion. Fig. 4 shows that at pH values between 4 and 7 amounts of removed MG increase slowly. We can explain this according to the nature of molecularly imprinted polymers, in which existence of active sites in internal cavities of MGIP protects them from H^+ and it causes a slow change in amount of adsorbed MG. From pH 7, variation in removed dye percentage reaches to the plateau. So we selected pH 7 as optimum pH for MG adsorption by MGIP.

Table 1
Results of kinetic studies by pseudo-first-order and pseudo-second-order models for removal of 50 mg L^{-1} MG using MGIP at 293 K

Kinetic model	Equation	MGIP
Pseudo-first-order	$Y = -0.0325\,X - 0.0778$	$k_1 = 0.0748$, $r^2 = 0.9280$
Pseudo-second-order	$Y = 0.0167\,X + 0.0032$	$k_2 = 0.0871$, $r^2 = 0.9999$

3.3. Effect of adsorbent amount

It is obvious that amount of removed compound directly depends on the amount of adsorbent and removal of target compound increases with an increase in adsorbent amount [9]. For this purpose, the effect of 5, 10, 15, 20, 50, 100, 150, and 200 mg of MGIP was evaluated on removal of MG from a 50 mg L^{-1} dye solution at 293 K (Fig. 5). The obtained results showed that 20 mg of adsorbent removes MG up to 97.84 ± 0.43% ($n = 4$), and no significant efficiency in the removal percentage values observes with increasing the amount of MGIP. So we select 20 mg as optimum adsorbent amount for further experiments.

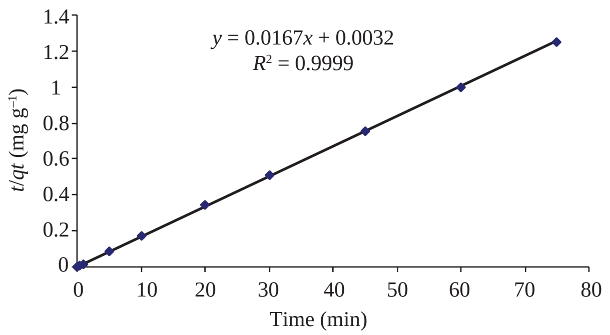

Fig. 3. Pseudo-second order Lagergren curve for MG adsorption (adsorbent dosage = 50 mg, concentration and volume of dye solution = 50 mg L^{-1} and 100 mL, respectively, pH = 7, temperature = 293 K).

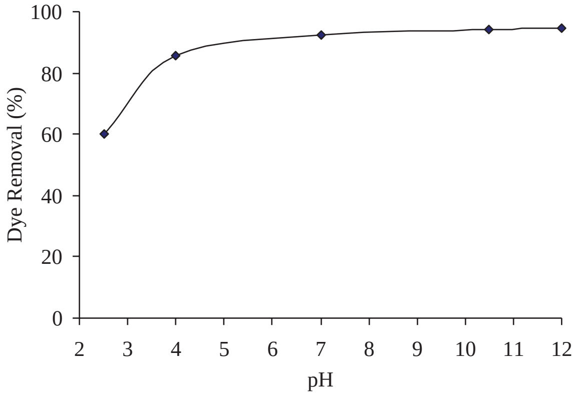

Fig. 4. Effect of solution pH on amount of removed MG (dye concentration = 50 mg L^{-1}).

3.4. *Effect of initial MG concentration*

The adsorption on MGIP was studied by changing the initial dye concentration and keeping all other parameters constant (MGIP dosage 20 mg, temperature (303 K) and pH = 7). It is well known that increase in initial MG concentration causes an increase in unit adsorption (q_e) of MG due to further contact between adsorbent particles and MG molecules, but percentage of removed MG decreases. This explanation was confirmed by results shown in Fig. 6.

3.5. *Adsorption equilibrium studies*

In order to determine the adsorptive characteristics of synthesized MGIP toward MG molecules and evaluation of the applicability of sorption process, equilibrium experimental data at 293, 303, and 313 K were collected for both MGIP and NIP. Various isotherms such as Langmuir and Freundlich were applied to analyze the experimental data. Isotherm parameters obtained from linear Langmuir and Freundlich isotherms for MGIP and NIP adsorbents, summarized in Table 2. In order to determine best fitted isotherm, linear least-square method was applied. Differences between r^2 values in different forms of linear Langmuir isotherm depend on different error distribution structure. Comparison between r^2 values shows that error distributions in Langmuir 3 and 4 are same and due to results of linear least-square method, the best fitted model is Langmuir-1 (Table 3) and other linear forms of Langmuir isotherm and also linear form of Freundlich isotherm at all temperatures cannot represent the experimental adsorption data.

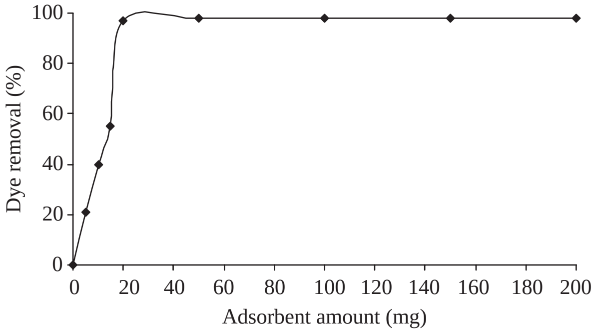

Fig. 5. Effect of adsorbent amount on dye removal from aqueous solutions (dye concentration = 50 mg L^{-1}, solution pH = 7, contact time = 0.5 min, temperature = 303 K).

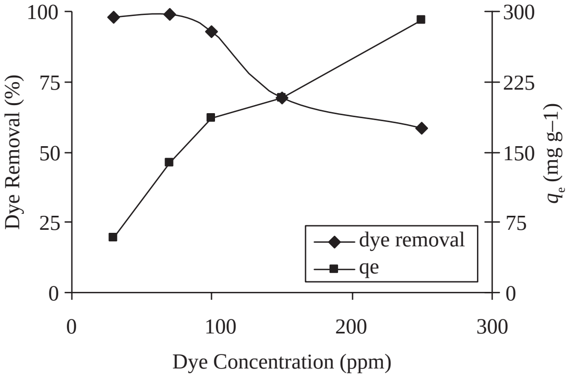

Fig. 6. Effect of initial dye concentration on the adsorption of MG by MGIP (adsorbent dosage = 50 mg, contact time = 0.5 min, solution pH = 7, temperature = 303 K, n = 4).

According to the Langmuir-1, adsorption capacities of MGIP were 303.03, 285.71, and 416.66 mg g^{-1} at 293, 303, and 313 K, respectively. A comparison between adsorption ability of MGIP and NIP can be observed in Fig. 7, which indicates high adsorption capacity of MGIPs toward MG.

3.6 *Thermodynamic study*

Thermodynamic parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the following equations:

$$\Delta G^\circ = -RT \ln K_a, \tag{12}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \tag{13}$$

where R is the gas constant, T is the absolute temperature and K_a is Langmuir constant (mol^{-1}). ΔH° and ΔS° values were determined from the slope and intercept of the plots of ΔG° vs. T. Results were collected in Table 4, which indicate adsorption process using MGIP is a spontaneous (ΔG°) and endothermic ($\Delta H^\circ > 0$) process. Also ΔS° values are positive, reflecting the affinity of the adsorbent toward MG.

Table 2
Isotherm parameters obtained by using linear method (q_m : mg g^{-1}; K_a : mg^{-1}; K_F : ((mg g^{-1})(g^{-1})$^{1/n}$)

		293 K		303 K		313 K	
		MGIP	NIP	MGIP	NIP	MGIP	NIP
Langmuir-1	q_m	303.03	38.02	285.71	34.96	416.66	51.54
	K_a	0.327	0.332	0.302	0.384	0.615	0.101
	r^2	0.968	0.994	0.973	0.984	0.941	0.999
Langmuir-2	q_m	138.28	36.76	131.57	33.89	142.86	51.28
	K_a	8.0	0.357	6.9	0.327	14.0	0.103
	r^2	0.549	0.969	0.551	0.975	0.316	0.998
Langmuir-3	q_m	177.35	35.09	165.67	36.55	203.87	51.40
	K_a	7.03	0.705	6.37	0.278	14.81	0.102
	r^2	0.428	0.474	0.398	0.674	0.234	0.995
Langmuir-4	q_m	238.83	39.45	223.23	40.02	368.87	51.50
	K_a	3.01	0.335	2.53	0.188	3.48	0.102
	r^2	0.428	0.475	0.398	0.674	0.234	0.995
Freundlich	$1/n$	0.236	0.140	0.259	0.206	0.291	0.378
	K_F	94.92	20.82	89.18	15.81	138.46	10.43
	r^2	0.839	0.692	0.881	0.756	0.783	0.975

3.7. Comparison between synthetic and natural adsorbents of MG

In order to evaluate efficiency of MGIP as a synthetic molecular recognition material in removal of MG from aqueous solutions, its adsorption capacity compared with that of some natural adsorbents reported in the literature (Table 5). Results show that MGIP has an acceptable capacity with higher adsorption rate in comparison with natural adsorbents. Also it can be washed easily and used for several times. High selectivity of synthesized polymer toward MG is another important advantage of the proposed adsorbent [32].

Table 3
Langmuir-1 isotherm for adsorption of MG onto MGIP and NIP

Temperature (K)	MGIP	NIP
293	$Y = 0.0033X + 0.0101$	$Y = 0.0263X + 0.0791$
303	$Y = 0.0035X + 0.0116$	$Y = 0.0286X + 0.0745$
313	$Y = 0.0024X + 0.0039$	$Y = 0.0194X + 0.1915$

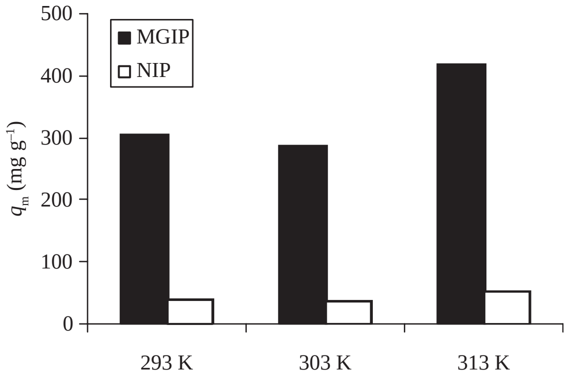

Fig. 7. Comparison between adsorption capacity of MGIPs and NIPs toward MG molecules.

4. Conclusions

In this study, adsorption of MG on MGIP optimized. 20 mg of adsorbent contact with 100 mL MG solution containing 50 mg L^{-1} of dye adjusted at pH 7 for 5 min, provides a removal yield more than 95%. Kinetic characteristics of adsorption were studied and pseudo-second-order model describes its kinetic behavior. Also Langmuir-1 isotherm is the best fitted model for adsorption experimental data. Thermodynamic

Table 4
Thermodynamic parameters of MG adsorption onto MGIP and NIP at different temperatures

Temperature (K)	ΔG° (kJ mol^{-1})		ΔH° (kJ mol^{-1})		ΔS° (kJ mol^{-1} K^{-1})	
	MGIP	NIP	MGIP	NIP	MGIP	NIP
293	−28.47	−28.5	24.46	11.05	0.18	0.13
303	−29.25	−29.85	24.46	11.05	0.18	0.13
313	−32.06	−27.37	24.46	11.05	0.18	0.13

Table 5
Comparison of MGIP and other adsorbents reported in the literature

Adsorbent	q_m(mg g^{-1})	Ref.
Activated carbon	565	6
Arundo donax root based carbon	8.69	9
Iron humate	19.20	10
Oxihomolite	0.10	11
Bagasse fly ash	170.30	12
Bentonite clay	7.72	13
Granular sludge	133.95	14
Agricultural by-products	16–75	15
Chitosan bead	93	16
Dead pine needle	33.56	17
Aerobic granules	66.66	18
Rattan sawdust	62.70	19
Oil palm trunk fibre	149.35	20
Bottom ash	4.30–6.20	21
De-oiled soya	8.64–12.88	22
Cyclodextrin based adsorbent	91.90	23
MGIP	303.03	This study

parameters (ΔG°, ΔH°, and ΔS°) indicates that adsorption of MG onto MGIP is a spontaneous and endothermic process.

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