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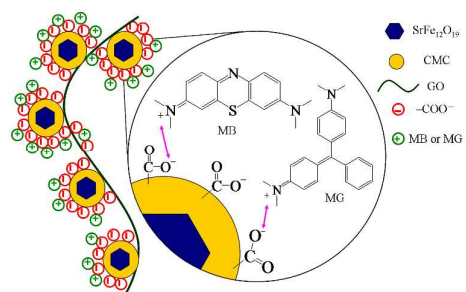
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Magnetic adsorbents with more adsorption sites can realize an efficient adsorption of cationic dyes.

23 Abstract

24 In this paper, carboxymethyl functionalized chitosan was used for synthesis of
25 magnetic polysaccharide/graphene oxide composite (SCGO). Compared with
26 magnetic chitosan/graphene oxide composite reported before, adsorption capacity in
27 this research had improved significantly. The calculated maximum adsorption
28 capacity for methylene blue (MB) and malachite green (MG) were 358.4 mg/g and
29 289.1 mg/g, respectively. The morphology, chemical properties and physical structure
30 of the SCGO were characterized by scanning electron microscopy (SEM), Fourier
31 transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD). The
32 influence factors which included pH, adsorbent dose, ionic strength and contact time
33 on the adsorption properties of MB and MG onto SCGO were investigated. The
34 adsorption kinetics of MB and MG on SCGO were well-described by pseudo-second
35 order kinetic models. The experimental data of isotherm followed the Temkin
36 isotherm model and the Langmuir model, respectively. Thermodynamic analysis was
37 also performed to calculate the changes in free energy (ΔG), enthalpy (ΔH), and
38 entropy (ΔS). The results obtained from this research suggested that SCGO was a
39 potential adsorbent for effective removal of methylene blue and malachite green.

40 **Keywords:** Carboxymethyl chitosan, Graphene oxide, Cationic dye, Magnetic
41 adsorbent

42 1. Introduction

43 In recent years, environmental problems have become a global concern because
44 of their impacts on human health. Nearly a quarter of the diseases that humans are

45 facing today are due to long-term exposure to environmental pollution which includes
46 air, soil, and water pollution ¹. The increasing attention to public health and
47 environmental quality has aroused special interest in developing and implementing
48 various methods of removing potentially toxic organic and inorganic pollutants from
49 water ². Dyeing effluent is one of the largest contributors to water contamination
50 which has a destructive impact on environment security and human health ³.
51 Particularly, the cationic dye, such as methylene blue (MB) and malachite green
52 (MG), can produce a series of grievous environmental problems.

53 MB is a kind of cationic pollutant which is quite difficult to be degraded in
54 natural environment. It has wide applications in many fields ⁴. It can induce eye burns
55 in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia,
56 dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract,
57 nausea, vomiting, and diarrhea ⁵. MG is a synthetic tri-phenyl methane dye. It has
58 been widely used for dyeing as well as a fungicide and ectoparasiticide in aquaculture
59 and fisheries ⁶. MG has aroused much concern. Not only does the dye affect the
60 chrominance of stream, but also it is carcinogenic and mutagenic ^{7,8}.

61 Therefore, there is considerable need to treat these dye effluents prior to their
62 discharge into receiving waters. To prevent dyes contamination, various methods have
63 been developed to remove dyes from aqueous environment, such as advance oxidation
64 ⁹, photocatalysis ¹⁰, adsorption ¹¹, membrane filtration ¹², and coagulation ¹³. Among
65 these methods, the adsorption technique is especially attractive because of its high
66 efficiency, simplicity of design, and ease of operation ¹⁴.

67 In the past researches, activated carbon had caused wide public concern, but its
68 high cost poses an economical problem. In recent years, many researches have
69 focused on the use of various cheaper adsorbents instead of activated carbon. The new
70 trends are focused on carbon- and polysaccharide-based materials ¹⁵.

71 Graphene, a novel one-atom-thick two-dimensional graphitic carbon system, is a
72 star in materials science and condensed-matter physics ¹⁶. In recent years, researchers
73 have developed a series of methods to prepare graphene, such as sonication induced
74 exfoliation ¹⁷, laser induced exfoliation ^{18, 19}, unzipping of carbon nanotubes either by
75 laser ²⁰ or by chemical treatment ²¹, and laser reduction of graphene oxide ^{22, 23}.
76 Graphene oxide (GO) has a layered structure similar to graphene, but the plane of
77 carbon atoms in GO is decorated by oxygen-containing groups. GO has multiple
78 oxygen-containing functional groups (carboxyl, hydroxyl and epoxy) that attached to
79 its layers covalently, resulting in a negatively charged surface. It was studied as a
80 potential adsorbent, and its ability to remove cationic dyes has been demonstrated ²⁴.
81 ²⁵.

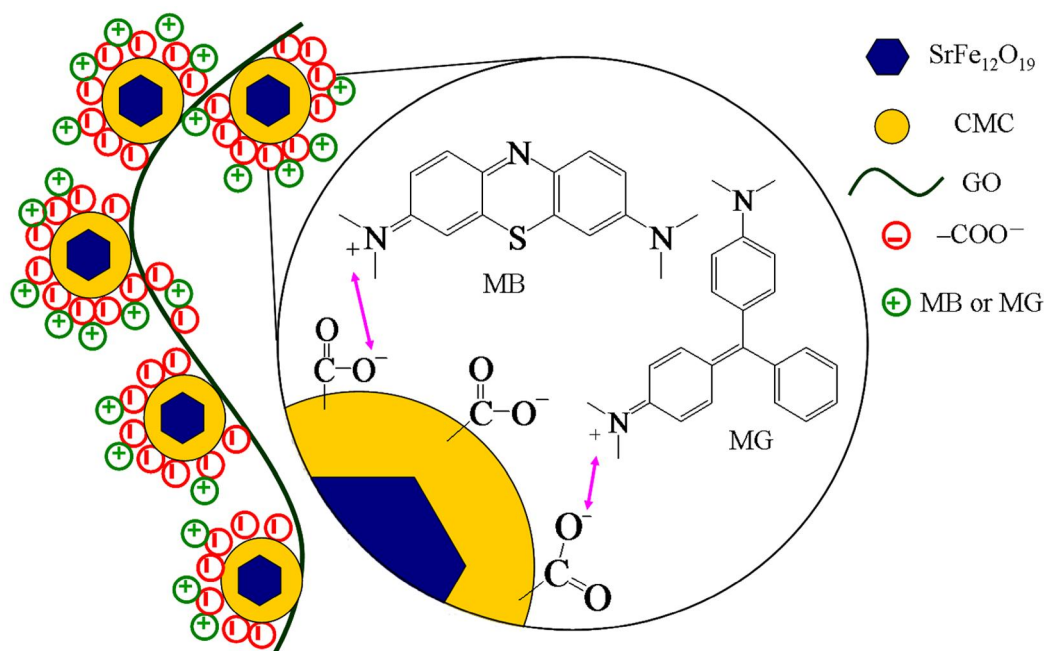
82 Chitosan is a multifunctional polymer that has hydroxyl groups and highly
83 reactive amino groups. It is used in food, cosmetics, biomedical and pharmaceutical
84 applications, etc ²⁶. Numerous investigations on the chemical activation of chitosan
85 have been carried out to increase its adsorption capacity for dyes ²⁷. However, the
86 hydrophilic property of chitosan should be improved for practical operation. In order
87 to improve the hydrophilic property and further enhance the adsorption capacity for
88 dye, chemical modification is required. Carboxymethyl chitosan (CMC) is an

89 amphiprotic chitosan derivative, which contains hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$)
90 and amine ($-\text{NH}_2$) groups in the molecule, and makes it possible to improve the
91 hydrophilic property of CMC and provide enough adsorption groups for increasing
92 adsorption capacity toward dyes²⁸.

93 The conventional absorbents have a major drawback that absorbents are difficult
94 to separate from the liquid. Magnetic separation technique has been shown to be a
95 promising method for solid-liquid phase separation. It was convenient to separate the
96 magnetic absorbents from aqueous solution in an external magnetic field^{29, 30}.
97 Strontium ferrite is a typical hard magnetic material with the hexagonal
98 magnetoplumbite type. It is not easy to be demagnetized after magnetized and has
99 been widely used in the industrial field.

100 Magnetic chitosan and magnetic graphene oxide have been widely used in drug
101 delivery^{31,32}, cell separation³³, enzyme immobilization³⁴, catalysis^{35,36}, and removal
102 of pollutants^{37,38}. Magnetic chitosan grafted with graphene oxide have been reported
103 remove dyes^{15,39,40}. However the adsorption capacity of these adsorbents was much
104 lower than expectation. The reason might be that the cross-linking agent occupied
105 effective adsorption sites. In the past researches, excessive glutaraldehyde was used as
106 the cross-linking agent to link amino groups that were the active sites of adsorption
107 and, hence, the adsorption capacity was greatly reduced. In this work, chitosan was
108 replaced with CMC, about eighty percent of amino groups in which were superseded
109 by carboxymethyl. The use of CMC not only offered linking groups ($-\text{NH}_2$), but also
110 reserved sufficient active sites ($-\text{COOH}$). The deprotonated carboxyl groups could

111 catch the cationic dyes by electrostatic interactions (Schematic 1). Adsorption
 112 performance of adsorbents was improved obviously. As-prepared strontium
 113 ferrite-CMC-GO compound (SCGO) was used to remove MB and MG and displayed
 114 excellent separation property and adsorption capacity. Furthermore, the kinetic and
 115 isotherm studies on MB and MG adsorption by SCGO were also investigated in this
 116 study.



118 Schematic 1 Proposed mechanism of MB and MG Adsorption onto SCGO.

119 2. Material and methods

120 2.1 Materials

121 Nano strontium ferrite owning an average size of about 80 nm was purchased
 122 from Nanjing Emperor Nano Material Co., Ltd. and carboxymethyl chitosan was
 123 obtained from Nantong Lvshen Biological Engineering Co., Ltd., whose substitution
 124 degree was not lower than eighty percent. Other chemicals, obtained from Sinopharm
 125 Chemical Reagent Beijing Co. Ltd., China, are of analytical reagent grade. Ultrapure

126 water (EASY-pure LF, Barnstead International, Dubuque, IA, USA) was used
127 throughout the experiment.

128 *2.2 Preparation of adsorbent*

129 *2.2.1 Preparation of GO*

130 The GO were synthesized on the basis of the improved method reported by
131 Daniela C. Marcano et al ⁴¹. For the improved method, a 9:1 mixture of concentrated
132 H₂SO₄/H₃PO₄ (72:8 mL) was added to a mixture of graphite powder (0.6 g) and
133 KMnO₄ (3.6 g). The reaction system was heated to 50 °C and stirred for 12 h. Then
134 the reaction was cooled to room temperature and poured onto ice (about 80 mL) with
135 30% H₂O₂ (1 mL). The product was centrifuged, and the supernatant was decanted
136 away. Next the remaining solid material was washed three times with HCl (0.2 mol/L)
137 and ethanol, respectively. Afterwards it was washed with ether. Finally the obtained
138 solid was dried in vacuum at 35 °C.

139 *2.2.2 Preparation of SCGO*

140 The preparation process of SCGO was as follows: 0.3 g of pure carboxymethyl
141 chitosan was dissolved in 30 mL ultrapure water, and the mixture was sonicated at
142 room temperature for 3 h. Then, 0.1 g of magnetic nanosized strontium ferrite was
143 added to the colloidal solution and the reaction system was continually stirred using
144 electric blender for 1.5 h. Subsequently, 3 mL liquid paraffin was dispersed slowly in
145 the mixture under stirring. After 0.5 h of emulsification, 3 mL of glutaraldehyde was
146 added dropwise as cross-linker. Next, 0.2 g of GO was added to the reaction flask, and
147 the mixed system was stirred continuously for 1.5 h in an oil bath at 50 °C. After that

148 the mixture was adjusted to pH 9-10 using sodium hydroxide solution, and kept in an
149 oil bath for another 1 h at 80 °C. The product was washed with petroleum ether,
150 ethanol and ultrapure water in turn. Then, the precipitate was dried in vacuum. The
151 final product (SCGO) was ground to a fine powder.

152 *2.3 Characterization methods*

153 The morphology observation of SCGO was carried out by using a QUANTA
154 FEG 250 scanning electron microscopy (FEI, United States). FTIR spectra of the
155 samples were obtained from a Perkin-Elmer Spectrum One FTIR spectrometer
156 (Perkin-Elmer, United States). The spectra were recorded from 4000 to 400 cm^{-1} .
157 X-ray powder diffraction (XRD) patterns were recorded on a D8 FOCUS X-ray
158 diffraction spectrometer (Bruker, Germany) with Cu $K\alpha$ radiation for crystalline phase
159 identification. The sample was scanned from 5° to 80°.

160 *2.4 Batch adsorption experiments*

161 The batch adsorption experiments were carried out to determine the adsorption
162 capacity for two dyes on SCGO. In a typical batch adsorption experiment procedure,
163 different quantities of adsorbent (3-13 mg) were agitated with 25 mL of a solution
164 containing 140 mg/L MB or 70 mg/L MG in 100 mL air-tight conical flask for 3 h.
165 The effect of pH on the adsorption of SCGO composites for MB and MG was
166 evaluated in the pH range of 1-10 for MB and 2-8 for MG respectively. The initial pH
167 values of solutions were adjusted using NaOH and HCl. The salt concentration was
168 adjusted for 0 to 0.10 mol/L using NaCl to investigate the effect of ionic strength.
169 Adsorption kinetics was carried out at 308 K and predetermined pH for different time.

170 The batch experiments for adsorption studies were also carried out at different
171 temperatures (298K, 308K and 318K) with different initial concentration of MB
172 (20-200 mg/L) or MG (10-150 mg/L). The solid phase was separated from the
173 solution using a magnet. The equilibrium concentrations of dyes were determined at
174 the best coloration pH of dyes using a UV-vis spectrophotometer.

175 The removal efficiency and the adsorption amount q_t (mg/g) were calculated
176 based on the difference of the MB or MG concentration in the aqueous solution before
177 and after adsorption according to the formula:

$$178 \text{ Removal efficiency (\%)} = (c_0 - c_t) / c_0 \times 100\% \quad (1)$$

$$179 q_t = (c_0 - c_t) \times V / m \quad (2)$$

180 Where c_t (mg/L) is the concentration of adsorbate at time t (min), V (L) is the volume
181 of adsorbate solution, m (g) is the mass of adsorbents, q_t (mg/g) is the adsorbed
182 amount at time t (min).

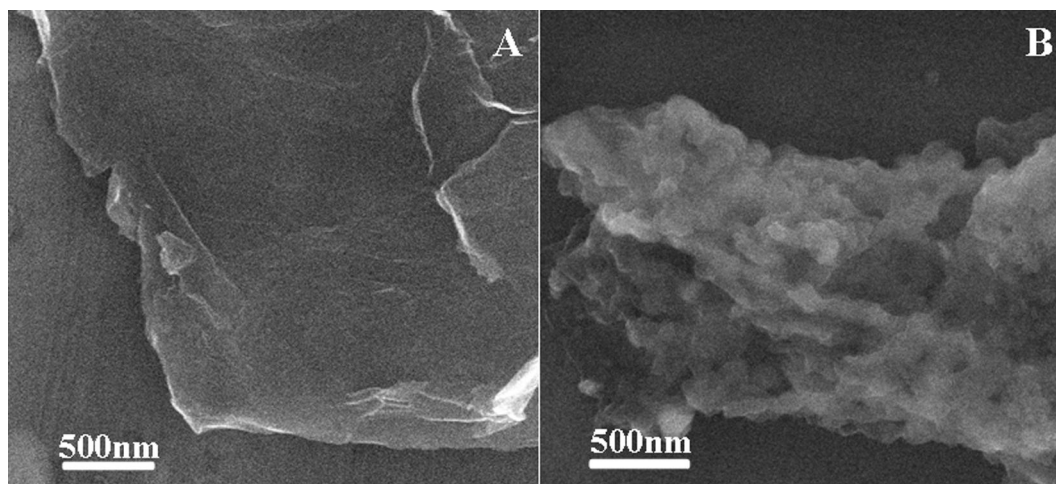
183 **3. Results and discussion**

184 A novel magnetic polysaccharide/graphene oxide composite (SCGO) had been
185 prepared, and was characterized by SEM, FTIR and XRD. The adsorption of MB and
186 MG onto SCGO was investigated to confirm the optimal adsorption conditions and
187 possible adsorption mechanism by batch adsorption experiments.

188 *3.1 Characterization of adsorbent*

189 The morphology of SCGO was investigated by scanning electron microscopy
190 (SEM). Fig. 1A shows a typical SEM image of GO, which presents a sheetlike
191 structure with large thickness, smooth surface, and wrinkled edge. After the

192 combination with nano strontium ferrite coated CMC to form the SCGO composite
193 (Fig. 1B), the SCGO exhibited a much rougher surface, revealing that nano strontium
194 ferrite coated CMC has been assembled on the surface of GO layers.



195
196 Fig. 1 SEM images of GO (A) and SCGO (B).

197 The FTIR spectra of SCGO, which was shown in Fig. 2A, revealed the presence
198 of the oxygen-containing functional groups. The broad absorption band at 3444 cm^{-1}
199 was attributed to O–H stretching vibration. The peak at 2923 cm^{-1} corresponded to
200 saturated C–H of carboxymethyl chitosan. The characteristic absorbance band at 1616 cm^{-1}
201 and the peak at 1398 cm^{-1} were due to the presence of –COOH. The peak at
202 1121 cm^{-1} was attributed to C–O–C stretching vibration and the peak at 601 cm^{-1}
203 corresponded to strontium ferrite.

204 XRD pattern of SCGO was shown in Fig. 2B. The positions and relative
205 intensities of all diffraction peaks matched well with those from the Jade PDF card
206 (shown in the top half of Fig. 2B) for strontium ferrite, indicating the existence of
207 strontium ferrite.

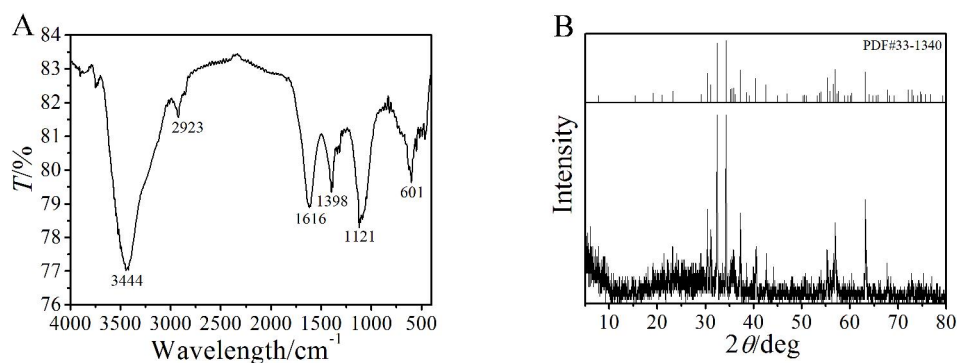


Fig. 2 FTIR spectra (A) and XRD pattern (B) of SCGO.

3.2 Effect of initial pH value on adsorption

The effect of pH is an important parameter of the general so-called adsorption process, which affects the adsorption of a pollutant. The effect of pH on the adsorption capacity of dyes was investigated in this study. Batch equilibrium adsorption experiments of MB and MG onto SCGO were carried out with a fixed 25 mL, 140 mg/L MB solution or 70 mg/L MG solution for long enough at room temperature. The pH was controlled with HCl and NaOH. As shown in Fig. 3, it could be clearly observed that there was a significant change on the adsorption capacities of MB and MG with pH increasing. The removal efficiencies of the two kinds of dyes were low at $\text{pH} < 4$, while $\text{pH} > 4$, the removal of MB and MG increased and the largest removal were over 90%.

The pH of dye solutions plays an important role in the adsorption process and particularly in adsorption capacity in the following three points: Firstly, the type and magnitude of charge on the dye species predominating in solution will determine whether the removal will take place or not. Secondly, the magnitude of the charge of the dye will determine the molar ratio adsorbent/dye suitable for maximum removal of dye. Thirdly, the nature of the dye predominant in the solution determines the state

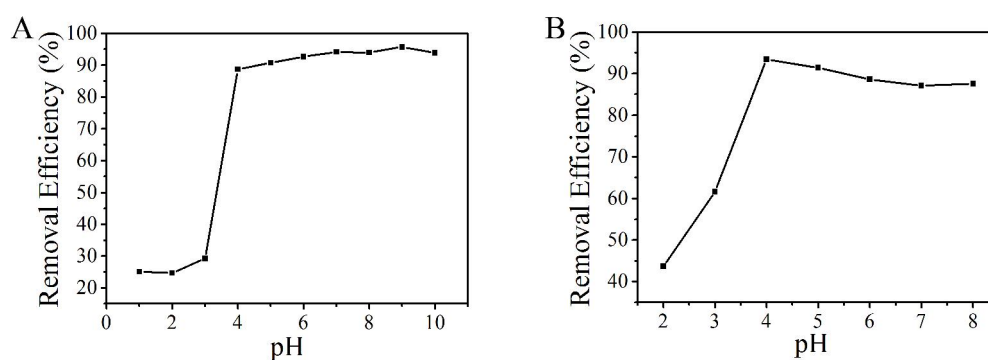
227 of the collector/dye. Therefore, it determines the mechanism of the adsorbent
 228 separation⁴².

229 The mechanisms of the adsorption process of cationic dyes on the SCGO were
 230 due to the ionic interactions of the dyes with the carboxyl groups of the SCGO. In
 231 aqueous solution, the cationic dyes were first dissolved and converted to cationic dye
 232 ions.

233 The carboxyl groups of SCGO were deprotonated under relatively alkaline
 234 conditions ($\text{pH} > 4$) according to the following reaction:



237 The adsorption process then proceeded due to the electrostatic attraction between
 238 these two oppositely charged ions.

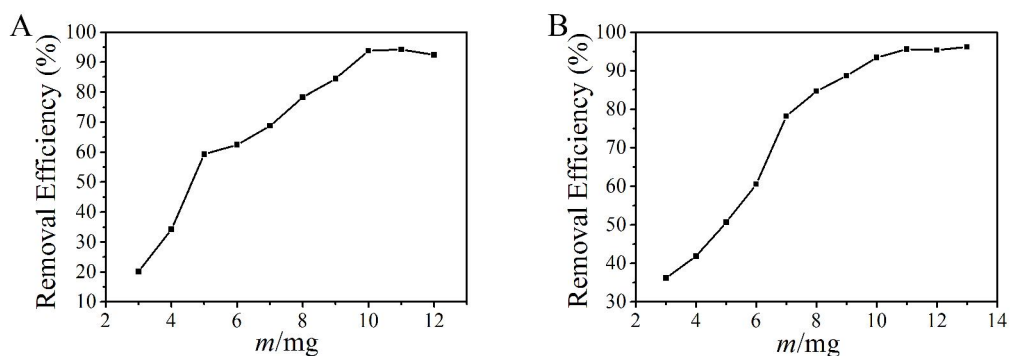


240

241 Fig. 3 Effect of pH on adsorption of MB (A) and MG (B) onto SCGO.

242 3.3 Effect of adsorbent dose

243 The effect of the adsorbent dose was investigated by addition of various amounts
 244 of SCGO in 25 mL aqueous solution (140 mg/L and 70 mg/L for MB and MG,
 245 respectively) at room temperature for 3 h.



246

247 Fig. 4 Effect of adsorbent dose on the adsorption of MB (A) and MG (B) onto SCGO.

248 As shown in Fig. 4, it was observed that the adsorption efficiency of the two dyes

249 increased with increasing initial amount of adsorbent and reached to a plateau at 10

250 mg for MB and 11 mg for MG, respectively.

251 *3.4 Effect of ionic strength*

252 The effect of ionic strength on the adsorption of MB and MG onto SCGO was

253 studied under different NaCl concentration (Fig. 5). It could be seen that the removal

254 efficiency decreased with increasing NaCl concentration. The adsorption percentages

255 of dyes on SCGO decreased by more than 20% as the concentration of NaCl in

256 solution increased from 0 to 0.10 mol/L. The ionic strength played a key role in

257 controlling electrostatic interactions. Hence, these interactions, attractive or repulsive,

258 were decreased with increasing NaCl concentration. High ionic strength would cause

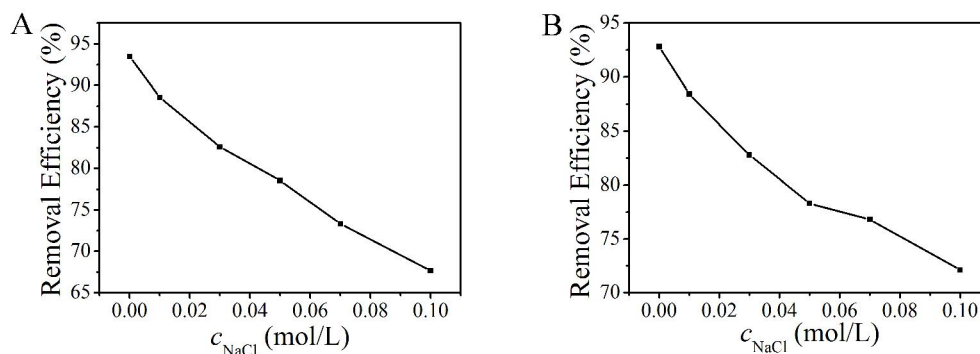
259 a screening effect⁴³. The increase in ionic strength would inhibit the electrostatic

260 interactions between the cationic dyes and the deprotonated carboxyl groups of

261 SCGO⁴⁴. Moreover, high ionic strength also could decrease the electrostatic repulsion

262 between SCGO, which results in aggregation and lower adsorption ability of SCGO

263 ⁴⁵.



264

265 Fig. 5 Effect of ionic strength on the adsorption of MB (A) and MG (B) onto SCGO.

266 *3.5 Adsorption kinetics*

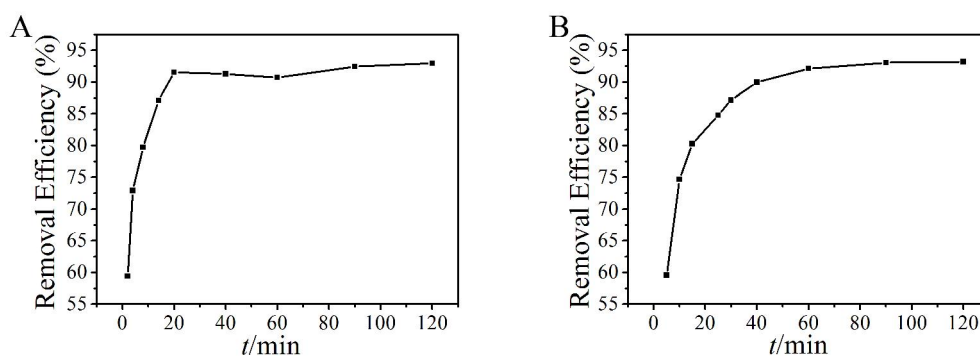
267 Kinetics of the adsorption process is vital in wastewater treatment, as it provides

268 essential information on the solute uptake rate and the reaction pathways. The effect

269 of contact time on dyes adsorption by SCGO was illustrated in Fig. 6. It showed that

270 the removal efficiency of the two dyes reached equilibrium at 20 min for MB and 60

271 min for MG.



272

273 Fig. 6 Effects of contact time on adsorption of MB (A) and MG (B) onto SCGO.

274 The adsorption kinetics data of heavy metal ions were analyzed by testing

275 pseudo-first order kinetic model and pseudo-second order kinetic model⁴⁶, which can

276 be expressed as follows:

277 Pseudo-first-order kinetics:

278
$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

279 Pseudo-second-order kinetics:

$$280 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

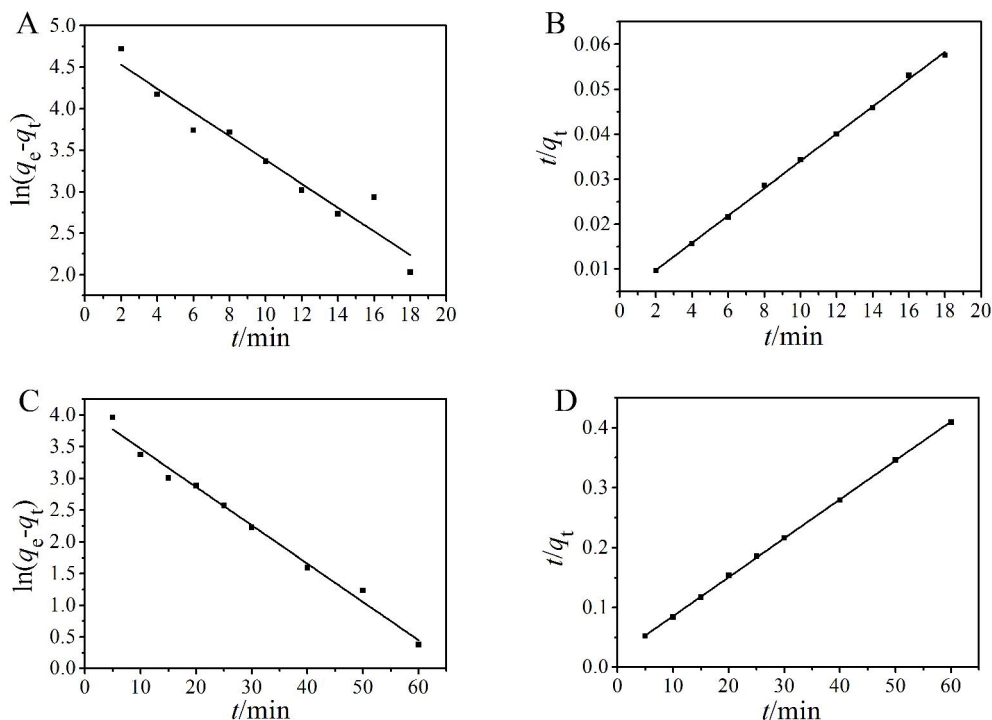
281 Where q_t (mg/g) and q_e (mg/g) are the adsorption capacities at time t (min) and
 282 equilibrium, respectively, k_1 (min^{-1}) and k_2 (g/(mg min)) are the pseudo-first-order
 283 and pseudo-second-order rate constant.

284 The fitted curves are shown in Fig. 7, and the parameters were calculated and
 285 listed in Table 1. From the fitting result, it was found that the measured kinetic data of
 286 MB and MG adsorbed by SCGO fitted pseudo-second order kinetic model with a
 287 correlation coefficient of 0.9989 and 0.9998, respectively. Moreover, the experimental
 288 equilibrium adsorption capacity of MB and MG (320.3 mg/g and 148.0 mg/g) fit well
 289 with the calculated value (330.0 mg/g and 154.1 mg/g) of pseudo-second-order kinetic
 290 model.

291 Table 1 Constants and correlation coefficients for the kinetic models.

Model	Parameter	MB	MG
Pseudo-first-order kinetic model	q_e (mg/g)	123.4	58.65
	k_1 (min^{-1})	0.1434	0.06036
	R^2	0.9312	0.9871
Pseudo-second-order kinetic model	q_e (mg/g)	330.0	154.1
	k_2 (g/(mg min))	0.002475	0.002003
	R^2	0.9989	0.9998

292



293

294 Fig. 7 Pseudo-first-order kinetics (A), pseudo-second-order kinetics (B) fit of MB and
 295 pseudo-first-order kinetics (C), pseudo-second-order kinetics (D) fit of MG adsorption
 296 on SCGO.

297 3.6 Adsorption isotherm

298 The adsorption isotherms of SCGO for MB and MG were investigated under the
 299 optimized conditions obtained before over a wide range of initial concentration of MB
 300 (20-200 mg/L) and MG (10-150 mg/L) at 308K. Four isotherm equations were
 301 selected for the study of modeling these adsorption isotherm data: Henry⁴⁷, Langmuir
 302 ⁴⁸, Freundlich⁴⁸, and Temkin⁴⁹ equations, expressed as follows:

303 Henry model:

$$304 \quad q_e = kc_e \quad (5)$$

305 Langmuir model:

$$306 \quad q_e = \frac{bq_m c_e}{1 + bc_e}, \quad \frac{1}{q_e} = \frac{1}{bq_m} \cdot \frac{1}{c} + \frac{1}{q_m} \quad (6)$$

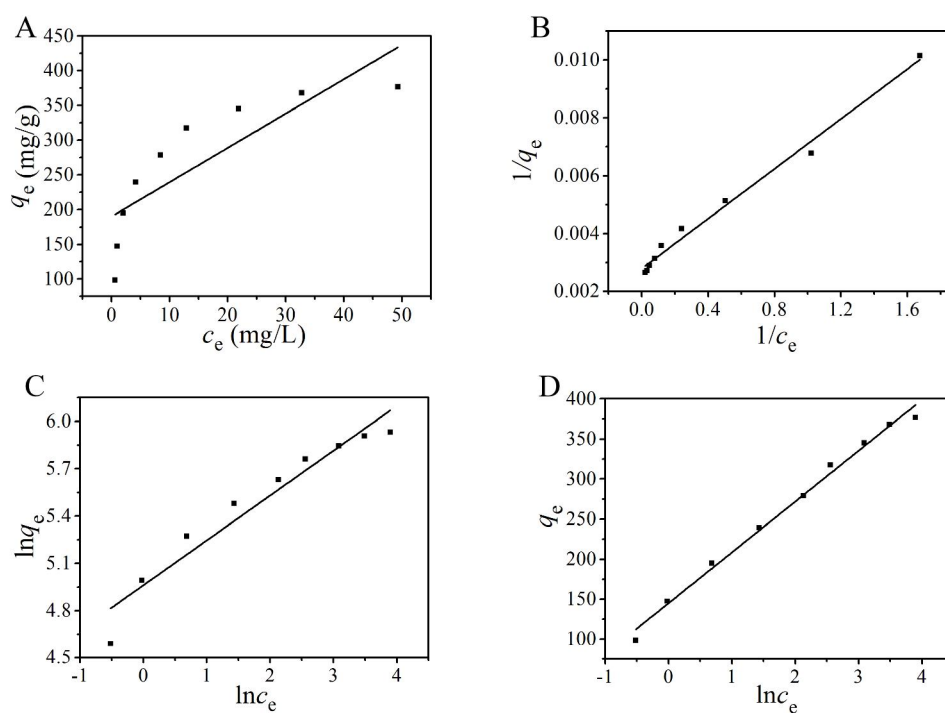
307 Freundlich model:

$$308 \quad q_e = K_F c_e^{1/n}, \ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (7)$$

309 Temkin model:

$$310 \quad q_e = \frac{RT}{b_T} \ln c_e + \frac{RT}{b_T} \ln A_T \quad (8)$$

311 The fitting results getting from the isotherms are shown in Fig. 8 and Fig. 9, and the
 312 values of correlation coefficients and other parameters obtained from the adsorbent
 313 are given in Table 2.

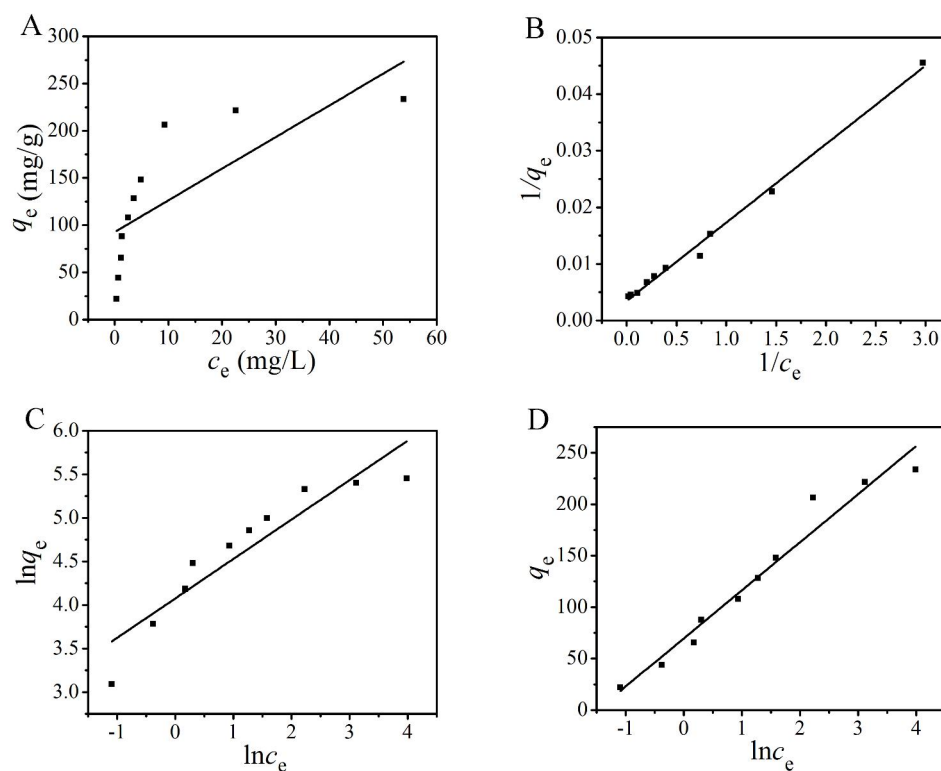


314

315 Fig. 8 Henry (A), Langmuir (B), Freundlich (C), and Temkin (D) adsorption isotherm

316

fit of MB adsorption onto SCGO.



317

318 Fig. 9 Henry (A), Langmuir (B), Freundlich (C), and Temkin (D) adsorption isotherm

319

fit of MG adsorption onto SCGO.

320

321

322

323

As shown in Table 2, it is found that the Langmuir model was suitable for describing the adsorption of MB and MG on SCGO ($R^2 > 0.98$), which implied that the adsorption of molecule is a monolayer adsorption and the adsorption of adsorbent surface is uniform.

324

325

326

327

328

While it should be noted that Temkin model was more suitable than Langmuir model for the adsorption of MB on SCGO. This result might ascribe that the concentration of MB was so high that interaction among adsorbed molecules could not be ignored absolutely. The adsorption process diverged from Langmuir model to Temkin model.

329

330

The data of maximum adsorption capacity for the adsorption of MB or MG onto various magnetic adsorbents were shown in Table 3. It could be obtained that SCGO

331 possessed higher adsorption capacity than that of many magnetic adsorbents reported
 332 before.

333 Table 2 Constants and correlation coefficients of adsorption isotherms
 334 for the adsorption.

Model	Parameter	MB	MG
Henry equation	k	4.941	3.351
	R^2	0.6538	0.580
	q_m (mg/g)	358.4	289.1
Langmuir equation	b (L/mg)	0.6473	0.2496
	R^2	0.9879	0.9939
	K_F	142.9	58.84
Freundlich equation	n	3.518	2.209
	R^2	0.9267	0.8522
	b_T	40.35	54.81
Temkin equation	A_T	9.843	4.448
	R^2	0.9908	0.9582

335

336

337

338

339

340

341 Table 3 Maximum adsorption capacity for the adsorption of MB or MG
 342 onto various magnetic adsorbents.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
GNS/Fe ₃ O ₄	MB	43.82	16
MCGO	MB	180.83	39
GO-Fe ₃ O ₄	MB	167.2	50
OC-BzM	MB	223.58	51
Fe ₃ O ₄ @HHSS	MB	71.45	52
GO-CA-Fe ₃ O ₄	MB	112	53
SCGO	MB	358.4	This work
OC-BzM	MG	144.79	51
AC/CFO	MG	89.29	54
MRGO	MG	22	55
Alg-Fe ₃ O ₄	MG	47.84	56
Fe ₃ O ₄ /MWCNT	MG	55.25	57
SCGO	MG	289.1	This work

343 3.7 Adsorption thermodynamics

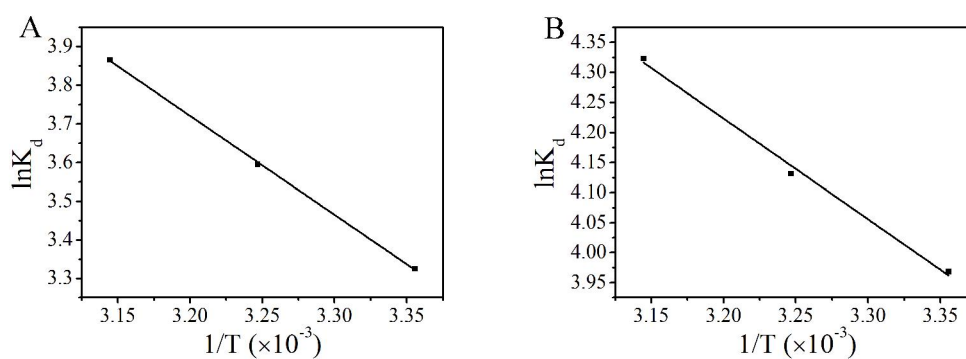
344 The investigation of temperature effect on dye molecules adsorption onto
 345 collector was carried out at temperatures ranging from 298 to 318 K. The change in
 346 ΔG was calculated with Eq. (9). ΔH and ΔS were calculated from the slope and
 347 intercept of the plot of $\ln K_d$ versus $1/T$ using Eq. (10).

$$348 \quad \Delta G = -RT \ln K_d \quad (9)$$

$$349 \quad \ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

350 Where ΔG (kJ/mol) is the Gibbs free energy change of sorption, ΔH (kJ/mol) is
 351 the enthalpy change, ΔS (J/mol K) is the entropy change, T (K) is the temperature in
 352 Kelvin, R (8.314 J/mol K) is universal gas constant and K_d (L/g) is the thermodynamic
 353 equilibrium constant that were computed by plotting $\ln(q_e/c_e)$ versus q_e and
 354 extrapolating q_e to zero⁵⁸.

355 The linear plot of $\ln K_d$ versus $1/T$ and thermodynamic parameters were listed in
 356 Fig. 10 and Table 4. The negative value of ΔG and positive value of ΔH indicated that
 357 the adsorption of MB and MG onto SCGO is a spontaneous and endothermic process.
 358 It revealed that the endothermic adsorption of MB and MG onto SCGO was enhanced
 359 by an increase in temperature. The positive value of ΔS stated clearly that the
 360 randomness increased at the solid–solution interface during the MB and MG
 361 adsorption. During adsorption, the coordinated water molecules, which were
 362 displaced by the dye molecules, gained more translational entropy than the lost by dye
 363 molecules, resulting in increased randomness in the dye–adsorbent interaction⁵⁹.



364
 365 Fig. 10 Adsorption thermodynamics of MB (A) and MG (B) onto SCGO

366

367 Table 4 Thermodynamic parameters of the adsorption of MB and MG by SCGO.

Dye	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
MB	298	- 8.24	21.30	99.09
	308	- 9.21		
	318	- 10.38		
MG	298	- 9.62	13.95	79.74
	308	- 10.35		
	318	- 11.18		

368 **4. Conclusions**

369 This study improved magnetic chitosan grafted with graphene oxide.
370 Carboxymethyl chitosan replaced general chitosan to provide more active adsorption
371 sites. The adsorption capacity of the novel adsorbent increased obviously than the
372 previous researches. Batch adsorption experiments were carried out under various
373 conditions, such as adsorbent dose, pH, ionic strength and contact time. The
374 adsorption kinetics, adsorption isotherms and adsorption thermodynamics of magnetic
375 polysaccharide/graphene oxide composite for methylene blue and malachite green
376 were investigated. The results showed that the adsorption kinetics could be modeled
377 by the pseudo second-order rate equation, and the process could reach equilibrium
378 soon. The adsorption of methylene blue and malachite green on magnetic
379 polysaccharide/graphene oxide composite conformed to Temkin model and Langmuir
380 model respectively. Both isotherm and kinetic results revealed a chemical process for
381 removal of methylene blue and malachite green. The adsorption was a spontaneous

382 and endothermic process. The results suggested that the magnetic
383 polysaccharide/graphene oxide composite could be considered as a good alternative
384 for extracting the dye from aqueous media.

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