1 Enhanced removal performance for methylene blue by kaolin with graphene

- 2 **oxide modification**
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# 12 Abstract:

In this study, graphene oxide mo in (GO-kaolin) composites (named 2% GK, 13 5% GK, and 10% GK) were synthesized by a facile method. Characterization results 14 morfication of GO on kaolin surface. To understand the dye indicated the succe 15 sful removal performance of kaolin with GO modification, batch adsorption experiments 16 17 were carried out using methylene blue (MB) as a model dye pollutant in various experimental conditions The adsorption results showed that the increase of GO 18 19 content in modified kaolin composite could effectively enhance the removal of MB from aqueous solution in each experiment condition, which was attributed to the 20 21 increase of special surface area and active adsorption sites. Kinetic analysis of MB adsorption by GO-kaolin samples was shown a better fitting to pseudo-second-order 22

kinetic models. The adsorption isotherm data were better fitted to Langmuir isotherm models. The values of thermodynamics constants suggested that the adsorption reaction was endothermic in nature. Furthermore, adsorption process of MB on kaolin was changed after the introduction of GO. An excellent regeneration performance of 10% GK was observed via the regeneration experiment. The results show that kaolin modified with suitable GO content is a high-efficiency and reusable adsorbent in the removal of MB from wastewater.

Keywords: Kaolin, Graphene oxide modification, Methylne bue, Adsorption
process.

32 1. Introduction

With the rapidly economical development, van s of pollutants including heavy 33 metals[1,2], organic compounds[3-6], 34 nd dyes[7-10]will be inevitably or which will lead to severe environmental unconscionably released into e 35 problems. Water resource is vital for the development and survival of human, however, 36 se pollutants has become a critical issue worldwide[11]. 37 water pollution d Among these pollutants, dyes, a kind of colored chemical agents, have been attracted 38 39 great attentions due to their wide productions and applications [12]. Unfortunately, the discharge of dyes into water bodies is the major source of water pollution. Because of 40 41 their undesirable diverse colors in waters even at low concentration (less than 1 ppm) and toxicity, they have been considered as a major threat to environment. Commonly, 42 43 they will cause the abnormal coloration of surface waters, hinder the infiltration of sunlight and pose severe damage to the aquatic organisms[13,14]. To date, dyes 44

45 wastewater treatment is still a serious challenge to environmental scientists. Several 46 commonly used treatment technologies including adsorption[15-19], membrane 47 filtration[20], coagulation–flocculation[21], oxidation processes[22,23], and 48 biodegradation[24,25] have been applied for dyes removal. However, each of these 49 methods has their own benefits and limitations, which have been summarized in 50 previous reviews[26-28].

Adsorption has been considered as an efficient and attractive method in pollutants 51 removal due to its low-cost, high efficiency, and easy design 6 52 urrently, various low-cost and eco-friendly adsorbents including natural 53 c and agricultural materials have been reported for the removal or dyes from aqueous solutions. 54 Particularly, kaolin as one of the common clay miteral materials has been widely used 55 in wastewaters treatment[29-31]. Due to rechemical composition and crystalline 56 structure, the surfaces of kaolin ved to carry a constant structural negative 57 charge derived from the somerphous substitution of Si(IV) by Al(III) in silica 58 oul be used as adsorbent for the treatment of cationic dyes 59 layer[32]. Therefy wastewater [16,31-34]. However, the exist disadvantages such as severe agglomeration 60 and low adsorption capacity in solution will impede its practical applications[7,29]. 61 Methylene blue (MB), a kind of phenothiazine salt, was selected as a model cationic 62 dye in this study. In a preliminary experiment, we have verified the low adsorption 63 performance of kaolin on MB. Likewise, it has been reported that the maximum 64 65 adsorption capacity of MB by raw kaolin was only 13.99 mg/g[33]. Consequently, it is necessary to seek a simple and effective method to activate the adsorption capacity 66

67 of kaolin.

Graphene oxide (GO), one of the typical graphene materials, has an unique 68 two-dimensional (2D) atomic crystal with a single layer of  $sp^2$ -bonded carbon atoms 69 closely packed into honeycomb lattice[35,36]. It has become the research hotspot due 70 71 to the intriguing structure and physicochemical properties [37,38]. In addition, GO has abundant oxygen containing functional groups and has been reported as good 72 adsorbent for the removal of cationic dyes[39,40]. However, the separation of GO 73 from aqueous solution is difficult due to its excellent hydrophicie 74 Thus, the design of hybrid GO-based materials is important for pollutants 75 I. Previous studies have shown that GO enwrapped nanomaterial p<sup>1</sup> tocatalysts could enhance the 76 adsorption, photocatalytic activity, and stabilit [4] 42. In a word, GO modification is 77 an ideal route to improve the removal performance of other materials towards special 78 that hybridizing GO with kaolin may lead pollutants. With this in mind, it 79 to considerable performance in dyes removal. To our knowledge, however, little 80 to utilize the GO and kaolin composite for cationic dyes 81 research has been arrie removal. Thus, the application of GO as an adsorption activator on kaolin for dyes 82 83 wastewater treatment is worth exploring.

To take advantage of the recent developments in graphene and kaolin materials, a set of modified kaolin composites containing different contents of GO (GO-kaolin) using 3-aminopropyl-trimethoxysilane (APTMS) as linkage were produced in laboratory through simple electrostatic interaction. In the present study, the main objectives were to investigate the adsorption processes and behaviors of MB on the as-prepared GO-kaolin composites from aqueous solution. Herein, we deem that this
study can provide theoretical basis for further design and practical applications of
graphene modified clay composites in future work.

92 2. Materials and methods

93 2.1 Materials

GO was prepared according to the modified Hummers method[43] and was confirmed 94 before use in Supplementary Materials. APTMS, Kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>9</sub>H<sub>4</sub>), MB, and all 95 other chemicals used were purchased from Shanghai First R ent Co., China. 96 Solutions were prepared with distilled water in all experim 97 2.2 Synthesis of GO-kaolin nanocomposites 98 The synthesis of GO-kaolin was conducted by 99 electrostatic interaction using APTMS as linkage[44]. In this study, 1.0 skaolin power was first dispersed in 200 100 d ultrasonication for 2 hours. Then, adding mL distilled water by magnetic 101 4 mL APTMS into the supersion while stirring for 10 min, followed by adding 102 surpension to change the weight ratio of GO to kaolin (2%, 103 different amount. 5%, and 10%) under vigorous stirring. After stirring for another 2 hours, the 104 105 composites were separated by filtration and washed with distilled water for three times. The composites were dried at 50  $^{\circ}$  overnight to obtain the GO-kaolin samples. 106 According to the GO content, the resultant GO-kaolin samples were named as 2% GK, 107 5% GK, and 10% GK, respectively. The preparation illustration of Go-kaolin is shown 108 109 in Scheme.S1.

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## 111 2.3 Characterizations

The element compositions and surface functional groups of raw kaolin and GO-kaolin 112 113 samples were investigated by X-ray photoelectron spectroscopy (XPS), which was performed on ESCALAB 250Xi (Thermo Fisher Scientific, USA). Field Emission 114 115 Scanning Electron Microscope (FE-SEM, JSM-6700F, Japan) was used to observe the surface morphology of composites. The specific surface area was measured based on 116 Brunauer-Emmett-Teller (BET) method using nitrogen as absorbent. 117 2.4 Adsorption experiments 118 In this study, the cationic dye, MB was used as the mo 119 stant to investigate the adsorption performance of GO-kaolin samples Batch adsorption experiments 120 were carried out at room temperature (25 by adding a known amount of 121 adsorbent (80 mg) into 100 mL MB solution of 7.0) in a shaking bath with a shaking 122 speed of 180 rpm. Initial dye co ons (5-40 mg/L) were chosen to investigate 123 the concentration effect. Herein, a set initial dye concentration of 20 mg/L was used 124 potich experiments in other solution conditions. Effect of 125 for the following adse solution pH ranged from 4.0 to 11.5 on the dye removal was examined. Different 126 mass of adsorbents were employed to explore the effect of adsorbent dosage in a 127 range of 0.4–1.6 g/L. The temperatures of solutions at the desired values (15  $^{\circ}$ C, 25  $^{\circ}$ C, 128  $35 \,$ °C, and  $45 \,$ °C) were controlled for the adsorption thermodynamics analysis. To 129 study the effect of ionic strength on the dye adsorption, different concentrations of 130 131 NaCl solutions (5-50 mM) were adjusted in the mixture. The dye concentration was measured at 664 nm by using a UV-vis spectrophotometer (UV-2550) based on a 132

133 standard curve. The removal efficiency (*R*) and adsorption capacity ( $Q_e$  (mg/g)) of

134 MB were determined with the following equations, respectively:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$
$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

where  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium dye concentrations , respectively. V (L) represents the volume of dye solution, and m (g) is the mass of adsorbent added into the dye solution.

138 3. Results and discussion

139 3.1 Characterization of raw kaolin and GO-kaolin



The successful synthesis of GO was confined by haracterization analysis. As can 140 be seen from the SEM image (Fig.S1), the typical ripples are presented on GO 141 surface[45]. Moreover, Fig.S2a and Fig.S2b showed the obvious characteristic peaks 142 d G band, respectively. For example, the of oxygen-containing groups, 143 vibration bands of O-H at 3394 cm<sup>-1</sup>, the stretching vibration of the C=O group at 144 1726 cm<sup>-1</sup>, the statching vibration bands of O–C=O, C–O at 1400 cm<sup>-1</sup>, 1055 cm<sup>-1</sup>, 145 respectively, indicating the successful preparation of GO[46]. In our experiment, 146 147 GO-kaolin composites were prepared by binding GO flakes to kaolin with help of APTMS. The surface of kaolin will be positively charged after grafting with APTMS, 148 thereby combining with negatively charged GO sheets by instant electrostatic 149 interactions[44,47]. The color change of raw kaolin powder from white to brown after 150 151 GO modification verified the successful introduction of GO sheets. This phenomenon is agreement with the observation of Zhang's group[44]. The morphological 152



Fig.1. SEM images of raw kaolin (a) and GO-kaolin samples: 2% GK (b); 5% GK (c),

173 and 10% GK (d).

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Commiss		Atom percentage (%)				
Samples	C1s	N1s	O1s	Si2p	Al2p	SA (m /g)
Kaolin	8.55	0.55	58.68	17.38	14.84	9.65
2% GK	20.00	2.08	50.84	15.51	11.57	13.47
5% GK	22.18	1.86	50.26	14.52	11.18	19.06
10% GK	30.43	3.78	43.98	13.55	8.25	24.92

175 Table 1 Element composition, atom ratios, and BET-N $_2$  surface area (SA) of

176 adsorbents

177	The evidence of the introduction of GO on kaolin was further determined via the
178	chemical composition and main functional groups analysis with XPS measurements.
179	Fig.2a showed the XPS survey spectra of kaolin and CO kaolin samples. The
180	characteristic elements such as Al (80.72 eV), Si (128,7 eV), and O (540.7 eV) were
181	found in the raw kaolin[7]. The detection of a bale c and N was derived from the
182	impurities. After GO modification using APTMS as linkage, a new element N at
183	409.63 eV was emerged in GO-haoin scuples. To better understand the changes after
184	GO introduction, high-resolution scan of C1s spectra of 2% GK, 5% GK, and 10%
185	GK samples were carried out. The spectra can be deconvoluted into three different
186	peaks that correspond to carbon atoms in different functional groups. The peaks
187	centered at the binding energies of about 284.6, 285.9, and 286.7 eV were observed
188	(Fig.2b), corresponding to CC, CN, and CO[48]. The presence of CN was
189	attributed to the reaction of the introduced $-NH_2$ on the kaolin surface with the
190	-COOH and C=O on the GO surface[44,47]. Furthermore, the element contents of
191	kaolin and GO-kaolin based on XPS analysis are listed in Table 1. With the increase
192	of GO content in the modified kaolin composites, the content of carbon atom

increased from 8.55% to 30.43% and the content of oxygen atom decreased from

194 58.68% to 43.98%. The changes of elements ratio in kaolin samples indicated that the



195 successful surface modification of kaolin with GO.

- Fig.2. XPS survey spectra of kaolin and GO-kaolin emples (a), and C1s XPS spectra
  of GO-kaolin samples (b).
- 199 3.2 Adsorption studies

Effect of initial dye cond 3.2.1 200 The variations in the rem val officiency of MB at different initial concentrations 201 sor ents are shown in Fig. 3. It can be observed from the (5-40 mg/L) on 202 ır 2 figure that the adsorption trends of MB on the adsorbents showed similar decreasing 203 trends with the increase of initial MB concentration. Because the increased 204 competition for the active sites on the adsorbents at higher dye concentration solution 205 will lead to the saturation of active sites, causing the decrease of adsorption 206 efficiency[49,50]. In addition, the modification of GO on kaolin could obviously 207

- 208 enhance the removal of dye. For example, at the same initial dye concentration of 20
- 209 mg/L, the adsorption affinities of dye to four adsorbents followed the order of kaolin



220

Fig.3. Effect of initial concentration of MB on the adsorption by kaolin andGO-kaolin samples.

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223 3.2.2 Effect of adsorbent dosage

10

Initial concentration of MB (mg/L)

0

- As shown in Fig.4a, the removal efficiency of MB by four adsorbents showed similar
- 225 upward trend with the increase of adsorbent dosage. Compared with the low dosage of
- adsorbent, high adsorbent dosage possessed greater surface area and could provide

more chances to adsorb dye molecules, thus enhancing the dye removal from solution[52]. Apparently, the dye removal by 10% GK was more superior than other adsorbents. After the critical dosage (0.8 g/L) of 10% GK, the adsorption increasingly slowed down until reaching the maximum adsorption value. Herein, we selected 10% GK as a typical adsorbent to understand the variation in the removal rate of MB (20 mg/L) with time at different dosages. In addition, the increase of adsorbent dosage could increase the initial adsorption rate and decrease the equilibrium time (Fig.4b).



The removal of MB by raw kaolin and GO modified kaolin was examined at the pH range from 4.0 to 11.5 as shown in Fig.5. The increase of solution pH was beneficial to the removal of MB, as the removal efficiency of MB showed an increase trend[33]. The maximum removal values of MB by adsorbents were observed at pH 11.5. However, at low pH 4.0, the adsorbent of 10% GK can still remove large amount of MB (86.23%) from aqueous solution, whereas the removal efficiencies were lower

than 10% by other adsorbents. This may be responsible for the high content of GO inthe surface of kaolin that could provide more active sites and stronger adsorption

100 80 80 40 20 20 40 5% GK

Solution pH

246 interaction ( $\pi$ - $\pi$  interactions) even at low pH.

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Fig.5. Effect of solution pH on the removal of MB bindsorbents

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249 3.2.4 Effect of ionic strength

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The solution ionic strength is also one of most important parameters that may 250 Therefore, the effects of solution ionic influence the removal of poll 251 IB by four adsorbents were conducted. As shown in Fig. strength on the removal of 252 f N B by kaolin and GO-kaolin changed little, the adsorption 253 6, although the real of MB on kaolin and 10% GK showed opposite trends with the increase of ionic 254 strength. Generally, the screening of the surface charges caused by the presence of 255 salts solution may decrease the adsorption; however, the salts solution also can 256 enhance the adsorption of dye through reducing the degree of dissociation of the dye 257 molecules [16,31]. Thus, the decrease of removal efficiency on MB by 10% kaolin 258 indicated that the screening of the surface charges played main role in the adsorption 259 behavior. In contrast, the later effect seemed to be dominant in the adsorption by 260





Fig.6. Effect of ionic strength on the removal of MB by kaolin and GO-kaolin samples.

- 265 3.2.5 Effect of temperature
- 266 The temperature is a significant parameter for the adsorption process. Fig. 7 showed
- the effect of temperature on the removal of MB by kaolin and GO-kaolin samples.
- 268 Obviously, the removal of MB by Boole and GO-kaolin samples was more favorable
- at higher temperature. The acrea e of temperature can enhance the movability of MB
- 270 molecules, thus hereast of the interaction chance between the adsorption actives sites
- and MB molecules.



Fig.7. Effect of temperature on the adsorption of MB by kaolin and GO-kaolin samples: adsorption capacity at different temperatures (a) and thermodynamic analysis (b).

The thermodynamic parameters change in Gibb's free energy ( $\Delta G^0$ ), entropy ( $\Delta S^0$ ) and enthalpy ( $\Delta H^0$ ) for the removal of MB by kaolin and GO-kaolin samples are determined from the equations as follow [16]:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (3)$$
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (4)$$

where  $K_d$  is calculated from  $Q_e/C_e$ . *T* is absolute temperature in Kelvin (K), and *R* is the universal gas constant (8.314 kJ/(mol K)).  $\Delta H^0$  and  $\Delta S^*$  updetermined from the slope and intercept of the Van't Hoff plots of  $\ln K_d$  versus of 1/T, respectively.

Table 2 listed the values of above thermody enioparameters. It can be noticed that 282 the values of  $\Delta G^0$  decreased with the ease of temperature. However, the values of 283 GK treatments, indicating the adsorption of  $\Delta G^0$  were positive at the kaolin and 2% 284 was a non-spontaneous process. In contrast, the negative MB onto kaolin and 2% 285 except 288K) and 10% GK) suggested a spontaneous values of  $\Delta G^0$ 286 adsorption process[7]. The differences suggested that the modification of enough GO 287 288 content onto kaolin should change the adsorption process. Meanwhile, the decrease of  $\Delta G^0$  values with the increase of temperature indicated that the adsorption of MB onto 289 kaolin and GO-kaolin samples was more favorable at higher temperature. The positive 290 values of  $\Delta H^0$  were the indication of the typical endothermic nature of adsorption 291 reaction. Besides, the positive values of  $\Delta S^0$  implied that the degrees of randomness at 292 the solid-solution interface increased during the adsorption[49]. All these 293

- thermodynamics parameters above-mentioned indicated that the modification with
- GO conduced to enhance the adsorption performance of raw kaolin.

Commiss	Temperature	$\varDelta G^0$	${\it \Delta} H^{0}$	$\Delta S^{o}$
Samples	(K)	(kJ/mol)	(kJ/mol)	(J/(K mol))
	288	3.885		
Kaolin	298	3.717	0.72	16.92
	308	3.548	8.75	10.82
	318	3.380		
	288	1.935		
2% GK	298	1.512		
	308	1.089	14.12	42.31
	318	0.665	$\mathbf{}$	
	288	0.141		
5% GK	298	-0.52		
	308	840	28.76	99.37
	318	-2840		
	288	-5.764		
10% GK	208	-6.544		
	808	-7.324	16.70	78.00
	<b>1</b> 8	-8.104		

- 296 Table 2 Thermodynamic parameters for the adsorption of MB onto kaolin and
- 297 GO-kaolin samples

298 3.3 Adsorption kinetics

In our study, the effects of time on the adsorption capacity of GO-kaolin samples were investigated. As shown in Fig.8, the adsorption rate was relatively rapid at initial stage, and then became more gradual until reaching the equilibrium. Obviously, both the adsorption rate and adsorption capacity of MB by 10% GK were higher than that of 2% GK and 5% GK at the same time condition, owing to the larger SA and more active sites of 10% GK. To understand the controlling mechanism of dye adsorption by

adsorbents from aqueous solution, the experimental data were fitted with two
 commonly used kinetic models (pseudo-first-order and pseudo-second-order) [16,53].



$$\frac{t}{Q_{t}} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$
(6)

- 317 where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the pseudo-second-order rate constant. The fitted curve is
- 318 displayed in Fig.9b.



Fig.9. Pseudo-first-order kinetics model (a) and pseudo-second kinetics model (b) for 320 the adsorption of MB on GO-kaolin samples. 321 The calculated kinetic parameters of two models are give Tal le 3. It can be 322 clearly observed from the table that pseudo-second-order kinetic model for each 323 GO-kaolin sample showed a better correlation c efficient in comparison with the 324 pseudo-first-order kinetic model, indication seudo-second-order model was a 325 th better model for describing the kinetic of GO-kaolin toward MB. Generally, the 326 pseudo-second-order kinetic a is based on the assumption that chemisorption is 327 the rate-limiting step[3 as, it could be inferred that the adsorption process of 328 329 MB on GO-kaolin s was chemisorption.

330	Table 3 Kinetic	parameters for	the adsorption of	of MB onto GC	)-kaolin samples

Models	Pseudo-first-order			Pseudo-second-order		
Parameters	$Q_{e({ m cal})}$ (mg/g)	<i>k</i> <sub>1</sub> (1/min)	$R^2$	$Q_{e(\mathrm{cal})}$ (mg/g)	<i>k</i> <sub>2</sub> (g/ mg min)	$R^2$
2% GK	9.33	0.0040	0.767	9.11	0.0004	0.845
5% GK	15.85	0.0043	0.857	15.65	0.0003	0.960
10% GK	20.81	0.0046	0.986	26.52	0.0002	0.993

## 331 3.4 Adsorption equilibrium

The adsorption capacity of MB by GO-kaolin samples corresponding to the equilibrium concentration in aqueous solution is presented in Fig.10. Two most common types of isotherms, Langmuir and Freundlich isotherm models were employed to explain the interaction of adsorbate molecules and adsorbent surface. The curves of the two fitted isotherm models are shown in Fig. 10.



Fig.10. The adsorption isotherms of the by GO-kaolin samples; the data from
experiment have been fitted by Langmuir and Freundlich isotherm models.

340 3.4.1 Freundlick isok erro

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The Freundlich isotherm model is an exponential equation that applied to describe the adsorption behavior on the heterogeneous surface[32]. The well-known expression for Freundlich isotherm model is shown as following non-linear equation:

$$Q_e = K_F C_e^{1/n} \tag{7}$$

344 where  $Q_e$  (mg/g) is the equilibrium adsorption capacity of GO-kaolin towards MB,  $C_e$ 

345 (mg/L) is the concentration of MB at adsorption equilibrium.  $K_{\rm F}$  [(mg/g)(L/mg)<sup>1/n</sup>] is

the adsorption equilibrium constant of Freundlich isotherm model. n is the Freundlich

constant giving an indication of how favorable the adsorption process. When 0 < 1/n347 < 1, the adsorption is favorable; when the value of 1/n beyond 1, the adsorption is un-348 349 favorable; when 1/n = 1, indicating the adsorption is homogeneous[55]. 3.4.2 Langmuir isotherm 350 351 The Langmuir isotherm is based on the assumption that the adsorption active sites distribute homogeneously over the surface of adsorbent. These active sites have the 352 same affinity for adsorption of a single molecular layer and there is no interaction 353 between adsorbed molecules[32]. The equation of Langmuir 354 is represented as below: 355  $Q_e = \frac{Q_m K_{\rm L} C_e}{1 + K_{\rm L} C_e}$ (8) where  $Q_m$  (mg/g) is the theoretical maximum on capacity of adsorbent, and  $K_{\rm L}$ 356 (L/mg) is Langmuir isotherm constant 357 Table 4 showed the calcul s of Freundlich and Langmuir models' 358 parameters. It can be found from the correlation coefficient  $(R^2)$  of each GO-kaolin 359 otherm models were better fitted the experiment data than sample that Lan 360 uir Freundlich isotherm nodels. Furthermore, it showed that the  $Q_m$  of 10% GK (28.016) 361 mg/g) for MB was approximately 1.95 times and 3.22 times that of 5% GK (14.335 362 mg/g) and 2% GK (8.696), respectively. Compared with other reported adsorbent 363 materials (Table 5), 10% GK showed satisfactory removal performance for MB. Thus, 364 the modification on kaolin with a certain content of GO could enhance the adsorption 365

366 capacity on MB at various concentrations.

367 Table 4 The parameters of adsorption isotherms for MB onto GO-kaolin samples

Isotherms	Freundlich			ns Freundlich Langmuir			
Parameters	$K_{\rm F} \left[ ({\rm mg/g}) ({\rm L/mg})^{1/n} \right]$	1/n	$R^2$	$Q_m (mg/g)$	$K_{\rm L}({\rm L/mg})$	$R^2$	
2% GK	5.380	0.1444	0.821	8.696	1.0225	0.939	
5% GK	10.298	0.1068	0.757	14.335	1.9877	0.896	
10% GK	17.497	0.1652	0.847	28.016	1.3516	0.869	

Table 5 Maximum adsorption capacity  $(Q_m, mg/g)$  of MB by various adsorbents in

369 other reports

Adsorbents	$Q_m (mm/s)$	References
Raw kaolin	13.2	[33]
Graphene oxide	193.902	[40]
Magnetic multi-wall carbon nanotube	15.87	[17]
Zeolite	22	[52]
Coir pith carbo	5.87	[56]
10% 6	28.016	in this study

370 3.5 Desorption and rependration evaluation

The regeneration capacity of adsorbent is an important factor to evaluate the availability in the practical application[57]. In this study, desorption experiment was conducted using 10% GK as model adsorbent due to its high removal efficiency towards MB. The desorption of MB from 10% GK was performed at acidic ethanol solution. Similar to previous reports, with increasing regeneration cycles, the dye removal by 10% GK decreased, which was attributed to the increased dye molecules that attached to adsorbent surface via chemisorption[7,49]. After five cycles, the removal efficiency of MB by the regenerated 10% GK can still remain at about 75.6%,

379 which was still higher than that by raw kaolin (Fig.11). Thus, the application of

380 suitable GO-kaolin is recyclable and will reduce the overall cost for the adsorbent.



395 graphene modified clay materials for various environmental applications.

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