1 Efficient removal of methylene blue from aqueous solutions using

2 magnetic graphene oxide modified zeolite

- 3 Tiantian Huang^{a,1}, Ming Yan ^{a,1}, Kai He^{a,1}, Zhenzhen Huang^{a,1}, Guangming Zeng^{a,*},
- 4 Anwei Chen^{b,*}, Min Peng^a, Hui Li^a, Lei Yuan^a, Guiqiu Chen^a.
- 5 a. College of Environmental Science and Engineering, Hunan University and Key
- 6 Laboratory of Environmental Biology and Pollution Control (Hunan University),

7 Ministry of Education, Changsha 410082, PR China

- 8 b. College of Resources and Environment, Hunan Agricultura University, Changsha
- 9 *410128,PR China*
- ¹ These authors contribute equally to this article.

, cce

- 11 For corresponding authors at: E-mail addresser. zgming@hnu.edu.cn (G. Zeng),
- 12 A.Chen@hunau.edu.cn (A. Chen). Tel.: +86 31 88822829; fax: +86 731 88823701.
- 13

14 Abstract

In this study, magnetic graphene oxide modified zeolite (Cu-Z-GO-M) composites 15 with two different ratios of GO to zeolite (named Cu-Z-GO-M 1:2 and Cu-Z-GO-M 16 1:1) were synthesized by solid-state dispersion (SSD) method. The properties of 17 zeolite-based composites were characterized by SEM, XRD, FTIR, XPS, and 18 magnetization curves. In order to understand the pollutant removal performance of the 19 as-prepared composites, methylene blue (MB) was used as the target pollutant in 20 adsorption experiments. The removal efficiency of MB onto C 21 Z-GO-M composite was enhanced obviously with pH > 9. The adsorption capacities of MBonto Cu-Z-GO-22 M 1:1 were 82.147, 89.315, 97.346 mg/g at 298, 208, and 38 K, respectively. The 23 removal ability of MB increased with the increase f GO content in modified 24 U described using a pseudo-secondcomposites. The adsorption behavior cal 25 be w 26 order kinetic and Freundlich isothern model. The thermodynamic analysis indicated I was aspontaneous and endothermic reaction. The 27 the MB adsorption by Cu-Z ed Cu-Z-GO-M composite could be a promising 28 results showed that e pr sorption capacity and reusability for MB removal from 29 adsorbent with wastewater. 30

31 Key words: Zeolite, Graphene Oxide, MnFe₂O₄, Methylene blue, Adsorption

32 **1. Introduction**

Dyes effluent discharged from textile, paper-making, printing, food additives, leather, cosmetic and other industries have caused serious environmental pollution [1, 2]. Nowadays, dye pollution has attracted great attention over the world, due to its toxicity to human being as well as the fauna and flora even at a low concentration [3].

The toxic effects of dyes effluent on human being will cause allergy, cutitis, skin 37 stimulus, and even cancer [4, 5]. Therefore, the waste water containing dyes must be 38 39 treated before discharging into the natural water bodies. Various approaches including precipitation [6], ion exchange [7], photocatalytic degradation [8, 9], biological 40 oxidation [10, 11], adsorption [12, 13], membrane filtration [14] and electrochemical 41 function have been applied to remove dyes from wastewater. Among these methods, 42 adsorption has been regarded as a most commonly used method for water purification, 43 because of its low cost, easy operation and flexibility [15]. 44 Zeolite, a common mineral absorbent with adequat 45 its, low cost, and organophilic cations [16], has been widely used for ve adsorption from wastewater. 46 For example, the natural zeolite has been remany investigations for dye 47 48 removal [17-19]. However, the lower adsor tion capacity of natural zeolite limits its der to improve its adsorption performance, widely application as an absorb 49 various modified zeolite composites have been fabricated. Jin et al. [18] reported that 50 SVBS-modified zeolite was twice larger than that of original 51 the adsorption can zeolite towards anionic orange II. Erol Alver et al. [20] also reported that the adsorption 52 capacities of anionic dyes (reactive red 239 and reactive blue 250) onto zeolite with 53 hexamethylenediamine modification were up to 28.57 and 17.63 mg/g at 293 K, 54 respectively. Although, these reports showed that modified zeolites had higher 55 adsorption capacity as compared to that of the unmodified zeolite, those modification 56 57 approaches still could not obtain a satisfactory adsorption performance. Therefore, seeking an appropriate modification method to functionalize zeolite and improve its 58

59 performance is still required.

80

Graphene oxide (GO), a typical product of graphene, has a particular structure of 60 a two-dimensional (2D) honeycomb lattice with a single layer of sp² carbon atoms [21-61 23]. To date, GO has been applied as an efficient adsorbent for pollutant removal owing 62 to its unique structure and physicochemical properties, such as a large surface area, 63 abundant oxygen-containing functional groups [24, 25] and excellent physicochemical 64 abilities [26, 27]. However, it is difficult to separate GO from aqueous solution due to 65 its excellent hydrophilicity. Therefore, the design of solid hybrid based materials 66 is a good method to improve its application in pollutants 67 I. Importantly, the pollutant removal performance of raw material could be enhanced after its 68 modification [28, 29]. To our knowledge, earch on the application of GO 69 tie modified zeolite composite for cationic dycremoval is limited. Thus, it is worth to 70 d zeolite composite. In order to make the explore the dye removal by G 71 synthesis of hybrid successfully, $\int u^{2+}$ ions were used as a coordination cation to bond 72 Nevertheless, composites modified by GO are difficult to 73 zeolite to GO she collect after reaction Magnetic separation technology has been widely applied for the 74 solid-liquid separation. Herein, MnFe₂O₄ with short synthesis time, high crystallinity 75 and low cost was introduced onto Cu-Zeolite/GO composites to make it possible to 76 77 reuse the materials [31], which can be conveniently separated by an external magnet. In this study, magnetic Cu-Zeolite/GO composites were fabricated using a facile 78 79 method. In order to investigate their pollutant removal performance, methylene blue

4

(MB), a typical cationic dye was selected as a model pollutant for adsorption

81	experiments. A series of experiments were carried out to determine the influence of
82	various factors such as pH, time, and temperature on dyes adsorption by magnetic Cu-
83	Zeolite/GO composite.
84	2. Experimental
85	2.1 Materials

- 86 GO was prepared according to the modified Hummer method [32, 33]. Artificial zeolite (Na₂O Al₂O₃ xSiO₂ yH₂O) was obtained from Sinoph 87 and chemical Reagent Co., Ltd., Ethanol, CuSO₄ 5H₂O, FeCl₃ 6H₂O, MnSO and all other 88 chemicals used were analytical reagent grade and purchased from Sinopharm chemical 89 90 Reagent Co., Ltd without further purification ior ized water was used in all experiments. 91 2.2 Synthesis of composites 92
- 93 2.2.1 Synthesis of MnFe₂O₄ comparticles

Magnetic nanovarticles were synthesized by the coprecipitation method [34-37]. Briefly, 2.703 g of FeCl₃ 6H₂O and 0.845g of MnSO₄ H₂O were dissolved in 100 mL of deionized water under stirring to get a molar ratio of Mn:Fe in the solution at 1:2. Then, solution pH was slowly adjusted to 10 using 8M NaOH until the solution turned orange into black brown, followed by continuous stirring for another 30 min. After the homogeneous dispersion was placed at 90 °C in water bath for 2 h, the black precipitates were magnetically separated by a magnet and washed with deionized water for several times to remove the unreacted part. Finally, the precipitates (MnFe₂O₄) were dried at 60 $^{\circ}$ C overnight.

103 2.2.2 Synthesis of Cu-Z-GO-M composites

104	To prepare the Cu-Zeolite, 1 g of zeolite was added into 100 mL of CuSO ₄ 5H ₂ O
105	solution (0.02 M), followed by magnetic stirring for 24 h [36]. Whereafter, the
106	suspension was washed with 0.01 M sulfuric acid and deionized water to remove
107	residues. Ultimately, Cu-Zeolite was dried in air and ground into powder for further use.
108	The preparation of Cu-Z-GO-M was conducted by SD method [38]. Different
109	amounts of GO were added into ethanol followed by ultrasonication treatment for 3 h.
110	Then, 0.125 g of as-prepared Cu-Zeolite and 0.8 g or magnetic particles MnFe ₂ O ₄ were
111	added into the homogeneous distributed supersion to get the mixture of two different
112	mass ratios of GO to Cu-zeolite (w/w, 1:1 and 1:2). Subsequently, the above-mentioned
113	mixtures were stirred by the audio contil the solvent of the solution was all evaporated.
114	Finally, the achieved blackist precipitate was dried at 60 $^{\circ}$ C.

115 2.3 Characterization

The surface morphology of zeolite-based samples was investigated by Field Emission Scanning Electron Microscope (FE-SEM, JSM-6700F, Japan). The X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental compositions and the surface functional groups of the zeolite samples, which was performed on ESCALAB 250Xi (Thermo Fisher Scientific, USA). The surface chemical properties of the samples were characterized by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, NICOLET 5700 FT-IR Spectrometer, USA), which
was recorded between 400 and 4000 cm⁻¹. The structure and crystallinity of samples
were recorded on an X-ray diffractometer (XRD) (D/max-2500, Rigaku, Japan) in a 20
range of 4-70 °. The specific surface area (SSA) was recorded on Brunauer-EmmettTeller (BET) method and the nitrogen was used as absorbent. Magnetic properties of
the samples were characterized on a vibrating sample magnetometer (VSM, Mpms
(squid) XL-7, Quantum, USA) at 25 °C.

129 2.4 Adsorption tests



In this work, MB, one of the most common ationic dyes, was used as a target 130 pollutant to study the adsorption performance Z_{-} O-M composites. A series of 131 adsorption experiments were carried out appending a certain amount of absorbent 132 (10 mg) into 30 mL MB solution in a shaker (160 r/min) at room temperature (25 $^{\circ}$ C). 133 The influence of initial MI tion on the adsorption was carried out with MB 134 concentration ranging from 10 to 70 mg/L. Herein, initial dye concentration at 40 mg/L 135 stigate adsorption in other influenced conditions. The effect of 136 was applied to inv solution pH on the MB removal was carried out from pH 4.0 to 10.0. The adsorption 137 thermodynamic was investigated at different temperatures (25, 35, and 45 $^{\circ}$ C). 138 Different concentrations of NaCl solutions (0.01, 0.05, 0.1, 0.2, and 0.5 M) were 139 140 employed to examine the effect of ionic strength on the dye removal. After adsorption, Cu-Z-GO-M composites were separated using an external magnet. The initial and 141 residual concentrations of MB were measured by a UV spectrophotometer (Pgeneral 142

143 T6, Beijing, China) at 664 nm. The removal efficiency R (%) and the amount of MB 144 adsorbed q_e (mg/g) at equilibrium per unit mass of samples were calculated with the 145 following equations:

146
$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$
 (1)

 $Q_e = \frac{(C_0 - C_e)}{m} \times V \tag{2}$

where C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium concentrations of MB, respectively. V (L) stands for the volume of MB solution, and m (g) represents the mass of samples added into the MB solution.

- 151 **3. Results and discussion.**
- 152 3.1 Characterizations of samples

The morphology of raw zeolite, GO and Cu-Z-GO-M samples was observed by 153 SEM micrograph (Fig. 1). As shown a Fig 1a, the crystal surface of zeolite is obvious. 154 such as the smooth surface, the wrinkled ripples The typical properties of G 155 Timà and a thinner layer are also observed (Fig. 1b) [39]. Additionally, Cu-Zeolite is more 156 densely distributed in GO sheets in Fig. 1c comparing with that in Fig. 1d. The rough 157 morphology of Cu-Z-GO-M sample (1:1) could provide more adsorption sites owing to 158 a larger surface area. 159

The XRD patterns of GO, raw zeolite, MnFe₂O₄ and Cu-Z-GO-M composites are displayed in Fig. 2a. The characteristic peak at $2\theta = 10.8^{\circ}$ is corresponding to GO, manifesting abundant existence of oxygen function groups on the GO layers [40]. MnFe₂O₄ and Cu-Z-GO-M composites exhibited similar XRD patterns in Fig. 2a. The standard peaks of MnFe₂O₄ at the $2\theta = 30.04^{\circ}$, 35.50° , 42.98° , 53.32° , 56.74° and 62.56° are all presented on these three XRD patterns, as mentioned above [41]. The weak peaks at $2\theta = 7.19^{\circ}$, 10.19° , 12.54° , 21.39° , 27.64° , 30.19° and 35.59° are related to zeolite [38], which are presented in the XRD patterns of Cu-Z-GO-M samples. There are no significant peaks of GO sheets in Cu-Z-GO-M composites, which might attribute to the strong signals of MnFe₂O₄ flow the relatively weak carbon peaks. These results indicated the preparation of the Cu-Z-GO-M composites was successful.

As shown in Fig. 2b, the magnetization hysteresis curves of C GO-M samples 171 at room temperature display a typical shape like a letter ' 172 ero retentivity and coercivity in Fig.2b demonstrate the super magnetiz on of the Cu-Z-GO-M [42]. The 173 saturations magnetization of Cu-Z-GO-M (1:1 ar u-Z-GO-M (1:2) are 0.02829 and 174 0.01478 emu/mg, respectively, which indicates the ferromagnetic properties and the 175 ternal magnet. Furthermore, the separation success of solid-liquid separation 176 behavior is displayed in the instead of Fig. 2b, which indicates that the Cu-Z-GO-M 177 from the reaction system by a magnet. Hence, the 178 samples could sep magnetization property of Cu-Z-GO-M samples made it easier to collect from the 179 reaction solution to save the cost. 180

As shown in Fig. 3a, the FTIR spectra of samples are tested in the range of 4000-400 cm⁻¹. The FTIR spectra show characteristic peaks (449, 602, 704, and 1027 cm⁻¹) in the curve of Cu-Z-GO-M composites which relate to TO₄ (T = Si and Al) of zeolite. Several typical peaks of GO, such as C-O-C (1053 cm⁻¹), C=O (1730 cm⁻¹), and O-H (3408 cm⁻¹) are also observed in the spectra of Cu-Z-GO-M samples, indicating that the 186 Cu-Z-GO-M samples were successfully synthesized by GO. Additionally, the
187 characteristic peak of Fe-O at 580 cm⁻¹ comes from the magnetic material of MnFe₂O₄.
188 Therefore, the analysis mentioned above proved the Cu-Z-GO-M samples were
189 synthesized successfully by SSD method.
190 The XPS spectra of zeolite and Cu-Z-GO-M (1:1 and 1:2) samples are represented

in Fig 3b. The XPS survey spectrum of raw zeolite shows five elements peaks, 191 containing Al, Si, C, O, and Na, locating at 80.72, 108.7, 284.6, 533.0 and 1072.2 eV, 192 respectively. The full scan spectra of Cu-Z-GO-M samples show peaks at binding 193 energies of 642 and 711.4eV which correspond to Mn 2p and 194 species respectively. To further determine the chemical composition and gain functional groups, the C1s 195 XPS spectra of 1:2 Cu-Z-GO-M (Fig. 3c) and 1:2 u-Z-GO-M (Fig. 3d) were carried 196 out. Three peaks center at the binding energy of about 284.6, 286.2, and 286.9 eV are 197 -C/C-C, C-O, and C-O-C, respectively [43]. observed from Fig. 3d, correspondence 198 Additionally, the element analysis of zeolite and Cu-Z-GO-M samples based on 199 able 1. With the introduction of GO and MnFe₂O₄, the content XPS spectra is list 200 d in' of carbon atom raised from 13.97% to 34.80% and 36.78%, the content of Na reduced 201 from 11.54% to 0.29% and 0.11%, and the content of Si and Al were both decreased. 202 The variations of element ratio in these three samples manifested that the successful 203 modification of its surface properties. Furthermore, the surface area of zeolite samples 204 increased (from 25.566 to 46.696 m^2/g) with the increasing content of GO adding to 205 zeolite samples. The higher surface area might provide more adsorption sites which are 206 beneficial for the removal of MB. The analysis results of XPS indicate that the Cu-Z-207

GO-M samples are successfully prepared by the method in this study. These results werecompliant with the XRD and FTIR characteristics.

210 3.2 Adsorption tests

211 3.2.1 Effect of pH

The variations in the removal efficiency of MB at different solution pH are shown 212 in Fig. 4. The solution pH could not only influence the degree of deprotonation and the 213 formation of surface functional groups of the absorbent, but, alo ct the species of 214 the MB [44]. As shown in Fig. 4, with the increase of pH, the removal 215 efficiency of MB onto Cu-Z-GO-M (1:1) was higher than two other composites. The 216 removal efficiency of MB by Cu-Z-GO-M (11) orbent was still at the maximum 217 (64.09%) as the pH value was 4.0, whereas the removal efficiencies of Cu-Z-GO-M 218 , respectively, which might due to that the (1:2) and zeolite were 38.27% 219 addition of the large amount of **GO** to zeolite could offer more adsorption sites and 220 dsorption (π - π interactions) [28]. When pH < 8.0, the removal powerful interact 221 of efficiencies toward NB of three composites showed no remarkable change. However, 222 the removal efficiency of MB onto Cu-Z-GO-M composites were significantly 223 enhanced at pH > 8.0 as compared with that of zeolite because the high concentration 224 of H₃O⁺ under acid condition led to great competitive with MB for adsorption sites, 225 further attributing to the relatively low MB removal. 226

227 3.2.2 Effect of contact time and adsorption kinetics

228 The effect of contact time on the removal efficiency of MB was investigated with the contact time from 0 to 24 h. It is obvious that the removal rate of MB by Cu-Z-GO-229 M samples is very rapid and the adsorption reaches equilibrium within 10 h (Fig. 5a). 230 Furthermore, the absorption capacities are 27.486, 59.148, and 99.162 mg/g for zeolite, 231 Cu-Z-GO-M (1:2), and Cu-Z-GO-M (1:1), respectively (Fig. 5b). Significantly, the 232 adsorption quantity of decorated zeolite was much larger than that of undecorated 233 zeolite. The absorption capacity of Cu-Z-GO-M (1:1) for M 234 s ap roximately 1.7 times larger than that of Cu-Z-GO-M (1:2), which was attributed to a larger amount of 235 oxygen-containing functional groups on the surface of the Cu-Z-GO-M (1:1). 236 chaism of zeolite composites, the 237 In order to figure out the adsorption experimental data was fitted with ty equently-used kinetic models (pseudo-first-238 order and pseudo-second order) The detailed equations of the kinetic models 239 240 above-mentioned are de follows: 241 Pseudo-first-orde $q_t = q_{e,l} (1 - e^{-k_l t})$ 242 (3)

243 Pseudo-second-order kinetic model

244
$$q_t = \frac{q_{e,2}^2 k_2 t}{I + k_2 q_{e,2} t}$$
(4)

where $q_t (\text{mg/g})$ is the amount of absorbed MB onto the absorbent at different time (min), $q_{e,1}$ and $q_{e,2}$ are the mass of the adsorption quantity of MB onto absorbents by non-linear pseudo-first-order and non-linear pseudo-second-order models, respectively, and k_1 248 (\min^{-1}) and k_2 (g/mg min) are the rate constants of the pseudo-first-order and the pseudo-249 second-order models, respectively.

250 After being fitted by the two kinetic models displayed in Fig. 5b, the calculated parameters for the MB onto zeolite composites are listed in Table 2. It is clearly seen 251 from Table 2 that the adsorption of MB onto the three absorbents is better described by 252 the pseudo-second order model according to the value of correlation coefficient (R^2) . 253 From this result, it follows that the adsorption process of MB onto the absorbents 254 proceeded by chemisorption mechanism [47]. 255 3.2.3 Effect of temperature and adsorption isotherm 256 MB onto Cu-Z-GO-M (1:1) A series of experiments with initial concer 257 were executed to figure out the adsorption behavior between solid and liquid phase as 258 259 the adsorption reached saturation [48]Fig 6 displays that a higher temperature is more beneficial to the adsorptio onto Cu-Z-GO-M (1:1). In this study, the two 260 common adsorption is chern models, the Langmuir and Freundlich models, were used 261 to investigate the interaction of molecules and surface of adsorbent by the data at 262 adsorption equilibrium. The slow adsorption rate might be due to the reduction of the 263 active sites on the surface of Cu-Z-GO-M (1:1) [49]. 264 Langmuir adsorption isotherm model 265

The Langmuir isotherm is on the basis of the assumption that adsorption sites on the surface of the adsorbent are restricted and distributed homogeneously. The adsorbate is absorbed without mutual interaction and has the same attraction for adsorption. It is represented by the equation as below:

270
$$q_e = \frac{q_{max} K_{\rm L} C_e}{I + K_{\rm L} C_e}$$
(5)

 $q_e = K_{\rm F} C_e^{l/n}$

where $q_e \text{ (mg/g)}$ and $C_e \text{ (mg/L)}$ represent quantity and the concentration of adsorption respectively, and $q_{max} \text{ (mg/g)}$ is the theoretic adsorption quantity at equilibrium. K_L (L/mg) is Langmuir isotherm constant which reflects the power of adsorption experiments.

Freundlich adsorption isotherm model
The Freundlich isotherm model is used to give a description of the adsorption
behavior that occurs on the heterogeneous surface [55]. The well-known expression for
Freundlich isotherm model is presented in the following form:

(6)

where $q_e \text{ (mg/g)}$ and $C_e \text{ (ng/L)}$ are on the behalf of the adsorption quantity and concentration of MB twards Cu-Z-GO-M (1:1) at the equilibrium, respectively. K_F [(mg/g)(L/mg)^{1/n}] is Freundlich isotherm constant. The value of n in the equation is another constant in Freundlich isotherm model to indicate how favorable the adsorption process. If 0 < 1/n < 1, the adsorption process is in favor of the reaction condition; if 1/n > 1, it is un-favorable; if 1/n = 1,manifesting the process is homogeneous [51].

Adsorption parameters are presented in Table 3. It is significant that the correlation coefficient (R^2) of Freundlich isotherm model is much higher than that of Langmuir isotherm model, which indicates that the Freundlich model describes the adsorption

process better. Furthermore, the adsorption of MB adsorption is heterogeneous and 289 multilayer [52]. Otherwise, Table 2 displays that the q_{max} of MB onto Cu-Z-GO-M (1:1) 290 291 in the Langmuir model is enhanced with increasing temperature, which might be due to the fact that the interaction between MB and the active sites were reinforced in the 292 enhancement of temperature. Compared with other reported absorbents displayed in 293 Table 4, Cu-Z-GO-M (1:1) exhibits approving adsorption performance towards MB. 294 Therefore, the zeolite modified by a certain content of GO could enhance the adsorption 295 capacity of MB. 296 To further evaluate the influence of adsorption factor 297 adsorption process by Cu-Z-GO-M (1:1), the effect of temperature on act rption process was investigated. 298 308, and 318 K) were set to As shown in Fig. 6, three different temperatures 299 expand the adsorption experiments of MB outo Cu-Z-GO-M (1:1). Significantly, the 300 hoval ability of MB by Cu-Z-GO-M (1:1), higher temperature could impro 301 which might be explained by the inhanced interaction between the active sites and MB 302 eraure. Commonly, the thermodynamic parameters, such as molecules at high 303 ten Gibbs free energy (ΔG^0) , entropy (ΔS^0) , and enthalpy (ΔH) , were calculated from the 304 following equations [55]: 305

$$\ln K_{\rm d} = \frac{\Delta S^{\theta}}{\rm R} - \frac{\Delta H^{\theta}}{\rm RT}$$
(7)

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{8}$$

where K_d is produced by q_e/C_e . T (K) is the absolute temperature in Kelvin, ΔS [KJ (K⁻ 1 mol⁻¹)] is the entropy change, ΔH (KJ/mol) is the enthalpy constant, and *R* is the universal gas constant [8.314 KJ/(mol K)]. The values of ΔS and ΔH are determined from the slope and intercept of the Van't Hoff plots of $\ln K_d$ versus of 1/T in Fig. 6.

Table 5 presents the detailed values of the thermodynamic parameters. The values of ΔG decrease from -2.789 to -3.509 with the temperature increasing from 298 to 318 K, manifesting that the adsorption of MB onto absorbent in this study is spontaneous [56]. Additionally, the value of ΔH is positive, indicating the reaction is endothermic [57]. Furthermore, the positive value of ΔS elucidates the randomness on the surface of solid/solution, showing an increasing trend during the attachment process [58].

318 3.2.4 Effect of the ionic strength

319 The ionic strength of solution is another Associated with the removal efficiency of MB [59]. In our work, the effect of ionic strength was conducted with 320 321 NaCl concentrations of 0, 0.01, 0.0 0.1 0.2, and 0.5 M in the adsorption systems g of absorbent. Fig. 7 displays that the removal containing 40 mg/L of MB 322 ind efficiency of MB by Cu-T-GO-M absorbent changes little with the increasing 323 cl. Whereas, the presence of NaCl has a significant effect on MB 324 concentration of Na removal by raw zeolite. This phenomenon may be caused by two reasons: on one hand, 325 the existence of NaCl might screen the surface charges which could suppress the 326 adsorption reaction owing to competitive adsorption, on the other hand it can also 327 enhance the adsorption behavior between MB and three different absorbents by 328 dissociating MB to MB⁺ [60, 61]. The results indicated that the surface charges also 329 played a primary role in the absorption process especially when the absorbent was raw 330

331 zeolite.

332 3.3 Desorption and reusability evaluation

Reusability is another vital factor to assess the application performance of the 333 adsorbent [62]. In this study, Cu-Z-GO-M (1:1), was regarded as the model absorbent 334 due to its highest removal efficiency of dye. Additionally, 0.1 mol/L HCl was chosen 335 336 as the strippant in this work to realize the release of the MB from the saturated absorbent [63]. Five cycles were applied to verify the stability and reusable of the material. The 337 related results are displayed in Fig. 8. As the regeneration ed, the removal 338 efficiency of MB onto Cu-Z-GO-M decreased (from 89.59% to 76.86%), possibly due 339 340 to the decline in surface area, the blockage of a d the decrease of active sites available [64]. Although the adsorption recreased, the reduction trend of removal 341 342 efficiency was not large, which i nat the reusability of absorbent (Cu-Z-GOed M) was relatively excellen 343

4. Conclusions

Based on the previously published works [18-20, 28-30], this work demonstrated that the magnetic GO modified zeolite samples could be synthesized to facilitate surface characterizations and adsorption capacity towards MB. The introduction of GO to zeolite could enhance the removal ability of MB comparing with zeolite undecorated, which was attributed to the incremental surface area and active sites. The adsorption is better described by pseudo-second-order kinetic and Freundlich isotherm model. A higher temperature and pH are more favorable to MB adsorption. Thermodynamic parameters depicted that the reaction was a spontaneous and endothermic process. After five reused cycles, the removal efficiency of MB onto Cu-Z-GO-M (1:1) was still at a high level (76.86%). This work provided a facial method combined GO and zeolite together to improve the application as well as the adsorption ability of zeolite as the absorbent. Besides, the new findings could not only help us understand how the factors influence the adsorption behavior of MB onto Cu-Z-GO-M, but also prove potential application of Cu-Z-GO-M to solve the dye pollution in the environment.

359

360 Acknowledgements



This study was financially supported by the National Natural Science Foundation of China (51579099, 51521006 and 5187(10), mnovative Research Team in University (IRT-13R17), and the Hunan Provincial Innovation Foundation for Postgraduate (CX2016B134).

368 [1] Y. Xiong, P.J. Strunk, H. Xia, X. Zhu, H.T. Karlsson, Treatment of dye wastewater

- 369 containing acid orange II using a cell with three-phase three-dimensional electrode,
- 370 Water research 35(17) (2001) 4226-4230.
- 371 [2] Y. Wang, Y. Zhu, Y. Hu, G. Zeng, Y. Zhang, C. Zhang, C. Feng, How to Construct
- 372 DNA Hydrogels for Environmental Applications: Advanced Water Treatment and
- 373 Environmental Analysis, Small 14(17) (2018) 1703305.

- [3] L. Zhang, J. Zhang, G. Zeng, H. Dong, Y. Chen, C. Huang, Y. Zhu, R. Xu, Y. Cheng,
- 375 K. Hou, Multivariate relationships between microbial communities and environmental
- variables during co-composting of sewage sludge and agricultural waste in the presence
- of PVP-AgNPs, Bioresource technology 261 (2018) 10-18.
- 378 [4] R. Pandimurugan, S. Thambidurai, Synthesis of seaweed-ZnO-PANI hybrid
- composite for adsorption of methylene blue dye, Journal of environmental chemical
- engineering 4(1) (2016) 1332-1347.
- 381 [5] H. Wang, H. Gao, M. Chen, X. Xu, X. Wang, C. Pan, J. Gao, Microwave-assisted
- 382 synthesis of reduced graphene oxide/titania nanocomposues as an adsorbent for
- methylene blue adsorption, Applied Surface Science (2016) 840-848.
- [6] M.-X. Zhu, L. Lee, H.-H. Wang, Z. Vanz, Removal of an anionic dye by
 adsorption/precipitation processes using analysine white mud, Journal of Hazardous
 Materials 149(3) (2007) 735-741
- 387 [7] H. Yi, D. Huang, G. Zeig, C. Lai, L. Qin, M. Cheng, S. Ye, B. Song, X. Ren, X.
- 388 Guo, Selective plynared sarbon nanomaterials for advanced photocatalytic application
- in environmental polutant treatment and hydrogen production, Applied Catalysis B:
- 390 Environmental (2018).
- [8] D. Xu, B. Cheng, S. Cao, J. Yu, Enhanced photocatalytic activity and stability of Z-
- 392 scheme Ag₂CrO₄-GO composite photocatalysts for organic pollutant degradation,
- Applied Catalysis B: Environmental 164 (2015) 380-388.
- [9] Y. Yang, C. Zhang, C. Lai, G. Zeng, D. Huang, M. Cheng, J. Wang, F. Chen, C.
- Zhou, W. Xiong, BiOX (X= Cl, Br, I) photocatalytic nanomaterials: Applications for

fuels and environmental management, Advances in colloid and interface science(2018).

398 [10] D.R. Manenti, A.N. Módenes, P.A. Soares, F.R. Espinoza-Quiñones, R.A.

Boaventura, R. Bergamasco, V.J. Vilar, Assessment of a multistage system based onelectrocoagulation, solar photo-Fenton and biological oxidation processes for real

401 textile wastewater treatment, Chemical Engineering Journal 252 (2014) 120-130.

402 [11] X. Ren, G. Zeng, L. Tang, J. Wang, J. Wan, H. Feng, B. Song, C. Huang, X. Tang,

- 403 Effect of exogenous carbonaceous materials on the bioavailability of exganic pollutants
- and their ecological risks, Soil Biology and Biochemistry 19 (2018) 70-81.
- 405 [12] S. Fan, J. Tang, Y. Wang, H. Li, H. Zhang, Lang, Z. Wang, X. Li, Biochar
- 406 prepared from co-pyrolysis of municipal sewage sludge and tea waste for the adsorption
- 407 of methylene blue from aqueous solutions, kinetics, isotherm, thermodynamic and
- 408 mechanism, Journal of Molecula Dipute 220 (2016) 432-441.
- 409 [13] K. He, Z. Zeng, A. Clen, G Zeng, R. Xiao, P. Xu, Z. Huang, J. Shi, L. Hu, G.
- 410 Chen, Advancement of Ag-Graphene Based Nanocomposites: An Overview of
- 411 Synthesis and Its Applications, Small 14(32) (2018) 1800871.
- 412 [14] Q. Li, Y. Li, X. Ma, Q. Du, K. Sui, D. Wang, C. Wang, H. Li, Y. Xia, Filtration and
- adsorption properties of porous calcium alginate membrane for methylene blue removal
- 414 from water, Chemical Engineering Journal 316 (2017) 623-630.
- 415 [15] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review,
- 416 Bioresource technology 97(9) (2006) 1061-1085.
- 417 [16] Z. Huang, G. Chen, G. Zeng, A. Chen, Y. Zuo, Z. Guo, Q. Tan, Z. Song, Q. Niu,

- Polyvinyl alcohol-immobilized Phanerochaete chrysosporium and its application in the
 bioremediation of composite-polluted wastewater, Journal of hazardous materials 289
 (2015) 174-183.
- 421 [17] S. Wang, Z. Zhu, Characterisation and environmental application of an Australian
- 422 natural zeolite for basic dye removal from aqueous solution, Journal of hazardous
- 423 materials 136(3) (2006) 946-952.
- 424 [18] X. Jin, M.-q. Jiang, X.-q. Shan, Z.-g. Pei, Z. Chen, Adsorption of methylene blue
- 425 and orange II onto unmodified and surfactant-modified zeolite, Journal of Colloid and
- 426 Interface Science 328(2) (2008) 243-247.
- 427 [19] R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao, M. Dug, Study of equilibrium, kinetic
- 428 and thermodynamic parameters about methylene due adsorption onto natural zeolite,
- 429 Chemical Engineering Journal 145(3) (2009) 496-504.
- 430 [20] E. Alver, A.Ü. Metin, Anionic the real oval from aqueous solutions using modified
- 431 zeolite: Adsorption kinetics and sotherm studies, Chemical Engineering Journal 200
 432 (2012) 59-67.
- 433 [21] K. Haubner, J. Nurawski, P. Olk, L.M. Eng, C. Ziegler, B. Adolphi, E. Jaehne, The
- route to functional graphene oxide, ChemPhysChem 11(10) (2010) 2131-2139.
- 435 [22] Z. Huang, Z. Zeng, A. Chen, G. Zeng, R. Xiao, P. Xu, K. He, Z. Song, L. Hu, M.
- 436 Peng, Differential behaviors of silver nanoparticles and silver ions towards cysteine:
- Bioremediation and toxicity to *Phanerochaete chrysosporium*, Chemosphere 203 (2018)
- **438** 199-208.
- 439 [23] K. He, G. Chen, G. Zeng, A. Chen, Z. Huang, J. Shi, T. Huang, M. Peng, L. Hu,

- 440 Three-dimensional graphene supported catalysts for organic dyes degradation, Applied
- 441 Catalysis B: Environmental (2018).
- 442 [24] C.J. Madadrang, H.Y. Kim, G. Gao, N. Wang, J. Zhu, H. Feng, M. Gorring, M.L.
- 443 Kasner, S. Hou, Adsorption behavior of EDTA-graphene oxide for Pb (II) removal,
- 444 ACS applied materials & interfaces 4(3) (2012) 1186-1193.
- 445 [25] Z. Huang, P. Xu, G. Chen, G. Zeng, A. Chen, Z. Song, K. He, L. Yuan, H. Li, L.
- 446 Hu, Silver ion-enhanced particle-specific cytotoxicity of silver nanoparticles and effect
- 447 on the production of extracellular secretions of *Phanerochaeten chrysosporium*,
- 448 Chemosphere 196 (2018) 575-584.
- 449 [26] Z. Huang, K. He, Z. Song, G. Zeng, A. Chen, Yuan, H. Li, L. Hu, Z. Guo, G.
- 450 Chen, Antioxidative response of *Phanerochiete chrysosporium* against silver
- nanoparticle-induced toxicity and its potential mechanism, Chemosphere 211 (2018)
- 452 573-583.
- 453 [27] Z. Huang, G. Chen, G Zeng Z. Guo, K. He, L. Hu, J. Wu, L. Zhang, Y. Zhu, Z.
- 454 Song, Toxicity mechanicus and synergies of silver nanoparticles in 2, 4-dichlorophenol
- degradation by *Phalerochaete chrysosporium*, Journal of hazardous materials 321
- 456 (2017) 37-46.
- 457 [28] K. He, G. Chen, G. Zeng, A. Chen, Z. Huang, J. Shi, M. Peng, T. Huang, L. Hu,
- 458 Enhanced removal performance for methylene blue by kaolin with graphene oxide
- 459 modification, Journal of the Taiwan Institute of Chemical Engineers (2018).
- 460 [29] Y. Yu, B.N. Murthy, J.G. Shapter, K.T. Constantopoulos, N.H. Voelcker, A.V. Ellis,
- 461 Benzene carboxylic acid derivatized graphene oxide nanosheets on natural zeolites as

- 462 effective adsorbents for cationic dye removal, Journal of hazardous materials 260 (2013)
 463 330-338.
- [30] M. Khatamian, N. Khodakarampoor, M. Saket-Oskoui, Efficient removal of
 arsenic using graphene-zeolite based composites, Journal of colloid and interface
 science 498 (2017) 433-441.
- 467 [31] P.T.L. Huong, V.N. Phan, T.Q. Huy, M.H. Nam, V.D. Lam, A.-T. Le, Application
- 468 of graphene oxide-MnFe₂O₄ magnetic nanohybrids as magnetically separable adsorbent
- 469 for highly efficient removal of arsenic from water, Journal of Electronic Materials 45(5)
- 470 (2016) 2372-2380.
- 471 [32] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. M.H. Zhao, C. Lai, Z. Wei, C.
- Huang, G.X. Xie, Use of iron oxide nanomatorials in wastewater treatment: a review,
 Science of the Total Environment 424 (2012) 1-10.
- 474 [33] Y.-g. Liu, X.-j. Hu, H. Wan, 7 Chen, S.-m. Liu, Y.-m. Guo, Y. He, X. Hu, J.
- 475 Li, S.-h. Liu, Photoreduction of Cr (VI) from acidic aqueous solution using TiO₂-
- impregnated gluttrelder decrosslinked alginate beads and the effects of Fe (III) ions,
- 477 Chemical engineering journal 226 (2013) 131-138.
- 478 [34] X. Tang, G. Zeng, C. Fan, M. Zhou, L. Tang, J. Zhu, J. Wan, D. Huang, M. Chen,
- 479 P. Xu, Chromosomal expression of CadR on Pseudomonas aeruginosa for the removal
- 480 of Cd (II) from aqueous solutions, Science of The Total Environment 636 (2018) 1355-
- 481 1361.
- 482 [35] J.-L. Gong, B. Wang, G.-M. Zeng, C.-P. Yang, C.-G. Niu, Q.-Y. Niu, W.-J. Zhou,
- 483 Y. Liang, Removal of cationic dyes from aqueous solution using magnetic multi-wall

- 484 carbon nanotube nanocomposite as adsorbent, Journal of hazardous materials 164(2-3)
 485 (2009) 1517-1522.
- 486 [36] Y. Yang, Z. Zeng, C. Zhang, D. Huang, G. Zeng, R. Xiao, C. Lai, C. Zhou, H. Guo,
- 487 W. Xue, Construction of iodine vacancy-rich BiOI/Ag@ AgI Z-scheme heterojunction
- 488 photocatalysts for visible-light-driven tetracycline degradation: Transformation
- pathways and mechanism insight, Chemical Engineering Journal 349 (2018) 808-821.
- 490 [37] S. Kumar, R.R. Nair, P.B. Pillai, S.N. Gupta, M. Iyengar, A. Sood, Graphene
- 491 oxide–MnFe2O4 magnetic nanohybrids for efficient removal or leadend arsenic from
- 492 water, ACS applied materials & interfaces 6(20) (2014) 17430, V436
- 493 [38] M. Khatamian, N. Khodakarampoor, M.S. Oskini, N. Kazemian, Synthesis and
- 494 characterization of RGO/zeolite composite for the removal of arsenic from
- 495 contaminated water, RSC Advances 5(45) (215) 35352-35360.
- 496 [39] M. Liu, C. Chen, J. Hu, X. Wu X. Wang, Synthesis of magnetite/graphene oxide
- 497 composite and application for conalt (II) removal, The Journal of Physical Chemistry
 498 C 115(51) (2011) 35234 25240.
- 499 [40] A. Ye, W. Fan, Q. Zhang, W. Deng, Y. Wang, CdS-graphene and CdS-CNT
- nanocomposites as visible-light photocatalysts for hydrogen evolution and organic dye
- degradation, Catalysis Science & Technology 2(5) (2012) 969-978.
- 502 [41] H. Liu, S. Ji, Y. Zheng, M. Li, H. Yang, Modified solvothermal synthesis of
- 503 magnetic microspheres with multifunctional surfactant cetyltrimethyl ammonium
- bromide and directly coated mesoporous shell, Powder technology 246 (2013) 520-529.
- 505 [42] C. Cao, L. Xiao, C. Chen, X. Shi, Q. Cao, L. Gao, In situ preparation of magnetic

- 506 Fe₃O₄/chitosan nanoparticles via a novel reduction-precipitation method and their
- application in adsorption of reactive azo dye, Powder Technology 260 (2014) 90-97.
- 508 [43] V. Chandra, J. Park, Y. Chun, J.W. Lee, I.-C. Hwang, K.S. Kim, Water-dispersible
- 509 magnetite-reduced graphene oxide composites for arsenic removal, ACS nano 4(7)
- 510 (2010) 3979-3986.
- 511 [44] S. Luo, X. Xu, G. Zhou, C. Liu, Y. Tang, Y. Liu, Amino siloxane oligomer-linked
- 512 graphene oxide as an efficient adsorbent for removal of Pb (II) from wastewater, Journal
- 513 of hazardous materials 274 (2014) 145-155.
- 514 [45] A. Tehrani-Bagha, H. Nikkar, N. Mahmoodi, M. Markar, F. Menger, The sorption
- 515 of cationic dyes onto kaolin: Kinetic, isothere and thermodynamic studies,
- 516 Desalination 266(1-3) (2011) 274-280.
- 517 [46] Z. Yin, Y. Liu, S. Liu, L. Jiang, X. Tan, G. Zeng, M. Li, S. Liu, S. Tian, Y. Fang,
- 518 Activated magnetic biochar some synthesis: Enhanced adsorption and
- coadsorption for 17β-estratiol and copper, Science of The Total Environment 639
 (2018) 1530-1544
- [47] L. Jiang, Y. Liu, G. Zeng, S. Liu, X. Hu, L. Zhou, X. Tan, N. Liu, M. Li, J. Wen,
 Adsorption of estrogen contaminants (17β-estradiol and 17α-ethynylestradiol) by
 graphene nanosheets from water: Effects of graphene characteristics and solution
 chemistry, Chemical Engineering Journal 339 (2018) 296-302.
- 525 [48] W. Zeng, Y.-g. Liu, X.-j. Hu, S.-b. Liu, G.-m. Zeng, B.-h. Zheng, L.-h. Jiang, F.-y.
- 526 Guo, Y. Ding, Y. Xu, Decontamination of methylene blue from aqueous solution by
- 527 magnetic chitosan lignosulfonate grafted with graphene oxide: effects of environmental

- 528 conditions and surfactant, RSC Advances 6(23) (2016) 19298-19307.
- 529 [49] G. Ramesha, A.V. Kumara, H. Muralidhara, S. Sampath, Graphene and graphene
- 530 oxide as effective adsorbents toward anionic and cationic dyes, Journal of colloid and
- 531 interface science 361(1) (2011) 270-277.
- 532 [50] B.K. Nandi, A. Goswami, M.K. Purkait, Adsorption characteristics of brilliant
- green dye on kaolin, Journal of hazardous materials 161(1) (2009) 387-395.
- 534 [51] M. Rauf, S. Bukallah, F. Hamour, A. Nasir, Adsorption of dyes from aqueous
- solutions onto sand and their kinetic behavior, Chemical Engineering Journal 137(2)
- 536 (2008) 238-243.
- 537 [52] W. Xiong, Z. Zeng, X. Li, G. Zeng, R. Xiao, Z. Yag, Y. Zhou, C. Zhang, M. Cheng,
- 538 L. Hu, Multi-walled carbon nanotube/amino-functionalized MIL-53 (Fe) composites:
- 539 Remarkable adsorptive removal of antibiotics from aqueous solutions, Chemosphere
- 540 210 (2018) 1061-1069.
- [53] D. Ghosh, K.G. Bhatacharyya, Adsorption of methylene blue on kaolinite,
 Applied Clay Scheree 2 (6) 2002) 295-300.
- 543 [54] E. Haque, J.W. Jun, S.H. Jhung, Adsorptive removal of methyl orange and
- 544 methylene blue from aqueous solution with a metal-organic framework material, iron
- terephthalate (MOF-235), Journal of Hazardous Materials 185(1) (2011) 507-511.
- 546 [55] L. Fan, C. Luo, X. Li, F. Lu, H. Qiu, M. Sun, Fabrication of novel magnetic
- 547 chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue,
- 548 Journal of hazardous materials 215 (2012) 272-279.
- 549 [56] C. Zhou, C. Lai, C. Zhang, G. Zeng, D. Huang, M. Cheng, L. Hu, W. Xiong, M.

- Chen, J. Wang, Semiconductor/boron nitride composites: synthesis, properties, and
 photocatalysis applications, Applied Catalysis B: Environmental (2018).
- 552 [57] L. Qin, G. Zeng, C. Lai, D. Huang, P. Xu, C. Zhang, M. Cheng, X. Liu, S. Liu, B.
- Li, "Gold rush" in modern science: fabrication strategies and typical advanced applications of gold nanoparticles in sensing, Coordination Chemistry Reviews 359 (2018) 1-31.
- 556 [58] S. Ye, G. Zeng, H. Wu, C. Zhang, J. Liang, J. Dai, Z. Liu, W. Xiong, J. Wan, P. Xu,
- 557 Co-occurrence and interactions of pollutants, and their impacts in seit remediation—A
- review, Critical Reviews in Environmental Science and Jerbology 47(16) (2017)
- 559 1528-1553.
- 560 [59] B. Meroufel, O. Benali, M. Benyahia, T. Pennoussa, M. Zenasni, Adsorptive
- removal of anionic dye from aqueous solutions by Algerian kaolin: Characteristics,
- isotherm, kinetic and thermodynamic spenes, J. Mater. Environ. Sci 4(3) (2013) 482491.
- [60] B. Nandi, A. Goswand, M. Purkait, Removal of cationic dyes from aqueous
 solutions by kaolin: kinetic and equilibrium studies, Applied Clay Science 42(3-4)
 (2009) 583-590.
- 567 [61] X. Ren, G. Zeng, L. Tang, J. Wang, J. Wan, Y. Liu, J. Yu, H. Yi, S. Ye, R. Deng,
- 568 Sorption, transport and biodegradation-an insight into bioavailability of persistent
- organic pollutants in soil, Science of the Total Environment 610 (2018) 1154-1163.
- 570 [62] M. Peng, G. Chen, G. Zeng, A. Chen, K. He, Z. Huang, L. Hu, J. Shi, H. Li, L.
- 571 Yuan, Superhydrophobic kaolinite modified graphene oxide-melamine sponge with

- excellent properties for oil-water separation, Applied Clay Science 163 (2018) 63-71.
- 573 [63] S. Ye, G. Zeng, H. Wu, C. Zhang, J. Dai, J. Liang, J. Yu, X. Ren, H. Yi, M. Cheng,
- 574 Biological technologies for the remediation of co-contaminated soil, Critical reviews in
- 575 biotechnology 37(8) (2017) 1062-1076.
- 576 [64] M. Auta, B. Hameed, Chitosan–clay composite as highly effective and low-cost
- adsorbent for batch and fixed-bed adsorption of methylene blue, Chemical Engineering
- 578 Journal 237 (2014) 352-361.

h contraction of the second se

580 **Figure captions**

- 581 **Fig. 1.** SEM images of raw zeolite (a), GO (b), Cu-Z-GO-M (1:2) (c) and Cu-Z-GO-M (1:1) (d)
- 582 Fig. 2. XRD patterns (a) of GO, Zeolite, MnFe₂O₄, Cu-Z-GO-M (1:2) and Cu-Z-GO-
- 583 M (1:1); Magnetization curves (b) of Cu-Z-GO-M (1:2) and Cu-Z-GO-M (1:1) at room
- 584 temperature.
- 585 Fig. 3. FTIR spectra (a) of zeolite, GO, MnFe₂O₄, and Cu-Z-GO-M samples (1:2 and
- 1:1); XPS full scans (b) of zeolite and GO-Z-GO-M samples; C1s XPS spectra of (c)
- 587 Cu-Z-GO-M (1:2) and (d) Cu-Z-GO-M (1:1).
- **Fig. 4.** Effect of solution pH on the removal efficiency of MS onto absorbents.
- 589 Fig. 5. Effect of contact time (a) on the removal sciency of MB onto absorbents,
- 590 pseudo-first-order (solid) and pseudo-second-order (dot) non-linear plots (b) of
- adsorption kinetics for MB onto adsorbents.
- 592 Fig. 6. Effect of the temperature of the adsorption of MB onto Cu-Z-GO-M (1:1):
- Langmuir model (solid) and Freundlich model (dot) non-linear plots of the adsorption
- isotherm for Mi onto CuZ-GO-M (1:1) at different temperatures (a), and the thermodynamic analysis (b).
- 596 Fig. 7. Effect of ionic strength on the removal efficiency of MB adsorption onto
- 597 absorbents.
- **Fig. 8.** Removal efficiency of MB onto Cu-Z-GO-M (1:1) in five cycles.
- 599







- 1:1); XPS full scans (b) of zeolite and G Z-GO-M samples; C1s XPS spectra of (c) 609
- Cu-Z-GO-M (1:2) and (d) C) 610



Fig. 4. Effect of solution pH on the removal efficiency of MB optimalsorbents.





Fig. 5. Effect of contact time (a) on the removal efficiency of MB onto absorbents,

617 pseudo-first-order (solid) and pseudo-second-order (dot) nordinear plots (b) of

, ve

xcet

adsorption kinetics for MB onto adsorbents.



Fig. 6. Effect of the temperature on the adsorption of MB onto Cu-Z-GO-M (1:1):

621 Langmuir model (solid) and Freundlich model (dot) non-linear plats of the adsorption

622 isotherm for MB onto Cu-Z-GO-M (1:1) at different tenteratures (a), and the

rcet

Q'E

623 thermodynamic analysis (b).





Fig. 7. Effect of ionic strength on the removal efficiency of B adsorption onto

627 absorbents.











632 **Table captions**

- **Table 1** Element composition, atom ratios, and BET-N₂ surface area (SA) of adsorbents
- **Table 2** Parameters of kinetic models for the adsorption of MB onto absorbents.
- **Table 3** Constants and correlation coefficients of Langmuir and Freundlich models for
- 636 MB adsorption onto Cu-Z-GO-M (1:1) at different temperatures.
- **Table 4** Maximum adsorption capacity $(Q_m, mg/g)$ of MB by various absorbents in
- 638 other reports.
- **Table 5** Thermodynamic analysis data for the adsorption of ML onto Cu-Z-GO-M (1:1).

640



Samples	Atom percentage				SA	
	C1s	O1s	Si2p	Al2p	Na1s	(m ² /g)
zeolite	13.97	52	13.93	8.55	11.54	25.566
1:2 Cu-Z-GO-M	34.80	51.49	6.46	6.96	0.29	43.068
1:1 Cu-Z-GO-M	36.78	52.02	5.42	5.67	0.11	46.696

Table 1 Element composition, atom ratios, and BET-N₂ surface area (SA) of adsorbents.

2,05 x cook

Models	Pseudo-first-order			Pseudo-second-order		
	$q_{ m e,1}$	$k_1 \times 10$	R^2	$q_{ m e,2}$	$K_2 \times 10^3$	R^2
Parameters	(mg/g)	(min ⁻¹)		(mg/g)	(g/mg·min)	
Cu-Z-GO-M (1:1)	86.635	0.337	0.895	93.781	0.472	0.963
Cu-Z-GO-M (1:2)	49.419	0.389	0.831	53.200	0.993	0.916
Zeolite	22.701	1.288	0.805	23.931	8.725	0.907

Table 2 Parameters of kinetic models for the adsorption of MB onto absorbents.

T (K)		298 K	308 K	318 K			
Langmuir	$q_{ m m}$ (mg/g)	94.481	95.369	115.322			
	$K_{\rm L}$ (L/mg)	0.513	2.371	1.223			
	\mathbb{R}^2	0.730	0.579	0.834			
Freundlich	$K_{\rm F}$ (L/mg)	54.236	61.704	68.177			
	1/n	0.157	013	0.162			
	R^2	0.998	0.980	0.992			
Accest							

Table 3 Constants and correlation coefficients of Langmuir and Freundlich models for
MB adsorption onto Cu-Z-GO-M (1:1) at different temperatures.

Table 4 Maximum adsorption capacity (Q_m , mg/g) of MB by various absorbents in 650 other reports.

	Absorbents	$Q_{\rm m}~({\rm mg/g})$	References
	Raw zeolite	6.1	[18]
	Raw kaolin	13.99	[53]
	Graphene oxide	193.902	[28]
	Magnetic multi-wall carbon nanotube	15.87	[35]
	MOF-235	187	
	1:1 Cu-Z-GO-M	94.481	In this study
651	Accer		

T (K)	lnk^0	$\Delta G^0 (KJ/mol)$	ΔS^0 (J/K mol)	ΔH^0 (KJ/mol)	\mathbb{R}^2
298 K	1.126	-2.789	5.765	-1.379	0.970
308 K	1.307	-3.237			
318 K	1.416	-3.509			

Table 5 Thermodynamic analysis data for the adsorption of MB onto Cu-Z-GO-M (1:1).

