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4 One-step synthesis of nitrogen-grafted copper-gallic acid for enhanced methylene blue removal

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4Artik Elisa Angkawijaya^{3*}, **Chintya** Gunarto², **Alchris Woo** Go³, **Maria** Yuliana¹,
Phuong Lan Tran-Nguyen⁴, **Chang-Wei** Hsieh⁵ & **Yi-Hsu**

Ju^{3,2,6} Nitrogen-grafting through the addition of glycine (Gly) was performed on a metal-phenolic network (MPN) of copper (Cu²⁺) and gallic acid (GA) to increase its adsorption capacity. Herein, we reported a one-step synthesis method of MPN, which was developed according to the metal–ligand complexation principle. The nitrogen grafted CuGA (Ng-CuGA) MPN was obtained by reacting Cu²⁺, GA, and Gly in an aqueous solution at a molar ratio of 1:1:1 and a pH of 8. Several physicochemical measurements, such as Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), N₂ sorption, X-ray diffraction (XRD), and thermal gravimetry analysis (TGA), were done on Ng-CuGA to elucidate its characteristics. The analysis revealed that the Ng-CuGA has non-uniform spherical shaped morphology with

23a pore volume of 0.56 cc/g, a pore size of

23.25 nm, and thermal stability up to 205 °C. The applicational potential of the Ng-CuGA was determined based on its adsorption capacity against methylene blue (MB). The Ng-CuGA was able to adsorb 190.81 mg MB per g adsorbent

, which is 1.53 times higher than the non-grafted CuGA. Detailed assessment of Ng-CuGA adsorption properties revealed their pH- and temperature-dependent nature. The adsorption capacity and affinity were found to decrease at a higher temperature, demonstrating the exothermic adsorption behavior. A recent trend in metal–ligand coordination research expands to the use of plant polyphenols as metal ions linkers in producing metal-phenolic networks (MPNs)¹. In principle, MPNs are formed via coordination between metal ions and phenolic acids. This kind of coordination can be observed in biological functions; for example, the formation of the Mg²⁺/porphyrin MPN during plant photosynthesis². In application, MPNs are commonly adopted as conformal coats of various substrates to promote their functionality, pH responsiveness, biocompatibility, and bioavailability^{3–6}. MPNs also have gained considerable attention due to their tunable lipo/hydrophilic properties⁷. For instance, MPN prepared from a combination of Fe³⁺-tannic acid (FTA) is reported to enhance the hydrophobicity of Zeolitic Imidazolate Framework-8 (ZIF-8). Impregnation of FTA/ZIF-8 onto the fibrous substrate (i.e., kapok fiber core) creates a superhydrophobic sorbent that can be used to treat oily water⁸. Due to their properties, the usage of MPNs has been extended into various applications such as water treatment, pharmaceutical, imaging, sensor, biofouling agent, separation application, etc^{9–13}. The use of MPN as an adsorbent has become one of its widely explored emerging applications. A study by Rahim et al. (2020) reported the preparation of an adsorbent from the combination of TA/Zn(IV) MPN for capturing heavy metal contaminants in wastewater¹⁴. Wang et al. (2019) assembled Ni-, Mg-, and Co-gallate with a tunable aperture for the adsorption and separation of acetylene from ethylene¹⁵. Within the range of available phenolic linkers, TA, gallic acid (GA), 1Department of Chemical Engineering, Widya Mandala Catholic University Surabaya, Kalijudan 37, Surabaya 60114, Indonesia. 2Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd., Taipei 10607, Taiwan. 3Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd., Taipei 10607, Taiwan. 4Department of Mechanical Engineering, Can Tho University, 3-2 Street, Can Tho City, Vietnam. 5Department of Food Science and Biotechnology, National Chung Hsing University, No. 145 Xingda Road, South District, Taichung City 40227, Taiwan. 6Taiwan Building Technology Center, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd., Taipei City 10607, Taiwan. *email: artikelisa@mail.ntust.edu.tw

Scheme 1. Illustration of the Ng-CuGA assembly process. (a) Molecular structure of the individual ligands. (b) Molecular structure of the possible coordination between gallic acid (GA), glycine (Gly), and copper (II) ion (Cu²⁺). and polydopamine (PDA) are the widely used linker for MPN synthesis^{16–19}. However, as TA and PDA overdose is postulated to cause adverse effects on human health and the environment^{20,21}; therefore, GA was chosen in this work. Besides this toxicity issue, recently, our group reported the potential usage of CuGA as an adsorbent for dye removal²²; thus, functionalization of this particular MPN is expected to improve their adsorptivity. note the adsorption capacity of adsorbents^{23–26}. Due to this advantage, various Ng methods have been extensively Nitrogen-grafting (Ng) is one of the surface functionalization techniques and had been acknowledged to pro-developed via plasma, pyrolysis, radiation, hydrothermal, or basic hydrolysis reaction^{27–31}. This study utilizes the possible binding interaction of copper (Cu²⁺), GA, and amino acids through the metal–ligand complexation principle as the foundation for the Ng-CuGA synthesis^{32–34}. To the best of our knowledge, there is no Ng-MPNs have been synthesized in similar methods nor applied for a similar purpose. Herein, we reported the modification of CuGA by the addition of glycine (Gly) as the modifying agent to provide a nitrogen functional group on the prepared MPN (Scheme 1). The synthesized Ng-CuGA were examined using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), thermal gravimetry analysis (TGA), and N₂ sorption analysis to elucidate its physicochemical properties. The adsorption performance of Ng-CuGA for methylene blue (MB) removal in an aqueous system was investigated.

31Materials and methods **Materials. The chemicals used were of analytical grade and were immediately used without further**

purification. GA (

16C7H6O5, 0.98 purity) was obtained from the **Tokyo Chemical Industry** (Tokyo, **Japan**

). Gly (C2H5NO2, 0.99 purity) was obtained from Sigma (Steinheim, Germany).

16Copper chloride dihydrate (CuCl2·2H2O, 0.99 purity) was purchased from **Kanto Chemical Co., Inc. (Japan**

).

14Sodium hydroxide (NaOH, 0.96 purity) was obtained **from Yakuri Pure Chemical (Japan). Sodium chloride (NaCl, 0.995 purity**

) and sodium carbonate (Na2CO3, 0.998 purity) were obtained from Showa Chemical and Nacalai Tesque (Japan), respectively. MB (C16H18N3SCI·3H2O, 0.95 purity) was acquired from Sigma Aldrich (St. Louis, MO). Ethanol (C2H6O, 0.95 purity) was purchased from Echo Chemical (Taiwan). The solutions used for the experiments were prepared in

33ultra-pure water with a resistance of **18.3 MΩ cm⁻¹**, which was produced from purification by **a NANO Ultrapure water system**

. Synthesis of the Ng-CuGA MPN. 10 mL of aqueous CuCl2·2H2O (5 mmol) solution was slowly added to the 10 mL aqueous mixture of GA (5 mmol) and Gly (5 mmol). To the mixture, 0.1 M NaOH was added until it reaches pH 8. The reaction was done for 4 h, under constant stirring. The synthesized Ng-CuGA was then collected

9by centrifugation, washed several times with ethanol to remove

any unreacted reactants, and subjected to drying at 50 °C under vacuum. Characterization of the complexes. The FTIR spectra were recorded

27using a **Bio-Rad FTS 3500**

FT-IR spectrophotometer in KBr pellets and

26a wavenumber range of **4000 to 400 cm⁻¹**

. The surface topography imaging was done

using a JEOL JSM-6500F Scanning Electron Microscope

. XRD patterns

were recorded using an X-ray Diffractometer Bruker D2 Phaser with Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$)

) at 30 kV and 10 mA. The isotherms of N₂ adsorption–desorption were measured

at 77 K using a BELSORP-max analyzer; samples were degassed for 12 h at 423 K

before analysis. The specific surface area was calculated from the adsorption branch using the Brunauer–Emmett–Teller (BET) model. TGA analysis was carried out using a Perkin Elmer Diamond TG/DTA in the temperature range of 30–600 °C and a heating rate of 10 °C/min under N₂ gas flow. Elemental analysis of the complex was carried out using a Thermo Flash 2000 CHNS/O Analyzers, while the copper metal content was analyzed using a JY2000-2

Inductively Coupled Plasma Atomic Emission Spectroscopy. The absence of

chloride in the Ng-CuGA was confirmed using a Dionex ICS-1000 with NaCl as a standard. pH_{pzc} determination was performed using a procedure described by Angkawijaya et al.³⁵, briefly: a series of 0.1 M NaCl solutions with adjusted pH (2 to 10) were prepared in capped vials at a volume of 5 mL. The 15 mg of sample was added to each vial and allowed to contact for 48 h in a shaking incubator operated at 200 rpm and constant temperature of 30 °C. The measures of final pH were made by using a pH meter (Denver Instrument UB-10). The pH_{final} was plotted against the pH_{initial}, the intersection of the experimental curve with the pH_{initial} = pH_{final} linear plot was identified as pH_{pzc}. Adsorption study. Effect of pH. The investigation on the effect of pH on MB adsorption was carried out in a series of micro-test tubes containing 2 mL of pH-adjusted MB solution at the initial concentration of 500 mg/L. 20 mg adsorbents were added to these working solutions and were incubated at 30 °C with constant shaking at 200 rpm. After 24 h, the adsorbents

were separated from the solutions by centrifugation at 15,000 rpm for 10 min. The concentration of remaining MB in the solution was determined using Spectrophotometer UV-Vis

(Shimadzu UV-2600) at $\lambda_{\text{max}} = 664 \text{ nm}$. The adsorption capacity, which

is the amount of MB adsorbed per g of adsorbent

Q_e (mg/g), was calculated using Eq. (1). $Q_e = \frac{C_0 - C_e}{m} \times V$ (1) where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of MB, respectively. V (L) is the total volume of the investigated system, and m (g) is the mass of

adsorbent. Effect of adsorbent dosing and salinity. The Ng-CuGA adsorbent at different dosage ranging from 0.2 to 1.1 mg/L were introduced into the working solutions of MB at initial concentration of 70 ppm. After

1024 h incubation at 30 °C, the residual concentration of

MB

was measured by UV-Vis spectrophotometer. The amount of MB that can be removed at the

different adsorbent dosing

was calculated according to Eq. (2). % Removal = $\frac{C_0 - C_f}{C_0} \times 100$ (2) where C_f

is the residual concentration of MB in the bulk solution (mg/L). The effect of

salinity was investigated by preparing MB solution in the presence of different salts. The salt-containing solutions were prepared by dissolving 2000 mg of MB in 1 L of water containing either 20 mg Na₂CO₃, 300 mg NaCl, or a combination of both salt (20 mg Na₂CO₃ and 300 mg NaCl). Subsequently, to the 20 mL of these solutions, 20 mg of the adsorbent was added. The sorption efficiency was then calculated by comparing the adsorption capacity of Ng-CuGA for MB removal in the salt-containing system (Q_{salt}) to the control (no-salt system, $Q_{control}$), according to Eq. (3). sorption efficiency = $\frac{Q_{salt}}{Q_{control}} \times 100$ (3)

Adsorption

isotherm study. A series of 2 mL MB solutions was prepared in various concentrations

without any pH adjustment. Subsequently, 20 mg of

adsorbent was added to these solutions and shaken vigorously. The adsorption

was conducted at three different temperatures (30, 40, and 50 °C). After 24 h, the concentration of residual MB at the end of the adsorption was measured using a UV-Vis spectrophotometer (Shimadzu UV 2600)22.

The adsorption data were plotted as Q_e versus C_e and

13 were fitted using two-parameter isotherm models (Langmuir, Freundlich, and Temkin) and three-parameter models (Sips and Redlich–Peterson). The Langmuir model, which

accounts for monolayer surface coverage over a homogenous adsorbent surface, is mathematically expressed as Eq. (4): $Q_e = Q_L \cdot \frac{K_L C_e}{1 + K_L C_e}$ (4) where Q_e

12 is the quantity of MB adsorbed at equilibrium (mg/g), C_e is the concentration of residual MB at equilibrium (mg/L), K_L is the Langmuir

11 affinity constant (L/mg), and Q_L is the maximum adsorption capacity (mg/g)³⁶. The

Freundlich model which able

20 to describe the multilayer adsorption with the interaction between adsorbed molecules

mathematically expressed as Eq. (5): $Q_e = K_F \cdot C_e^{1/n}$ (5)

11 where K_F is the Freundlich adsorption capacity in units of (mg/g)(mg/L

)ⁿ and $1/n$ is a dimensionless parameter characterizing the heterogeneity³⁷. The Temkin model presumes a linear rather than a logarithmic decrease of adsorption heat as an increase of surface coverage by ignoring the lowest and highest extreme of the concentration. The equation given in Eq. (6) characterizes the uniform binding energy distribution. $Q_e = B \cdot \ln(AT \cdot C_e)$ (6) $B = R \cdot T \cdot b$ (7)

10 where R is the universal gas constant (8.314 J/mol K), T is the temperature (K), b is the Temkin isotherm constant, and AT is equilibrium binding constant (L/mg

)^{38,39}. The Sips and Redlich–Peterson models are often employed as confirmatory of Langmuir and Freundlich models. Sips model is the modified form of the Freundlich equation that obeys the continuous increase of capacity as an increase of concentration but has a finite limit at the sufficient high concentration⁴⁰. The Redlich–Peterson is a versatile model applied to both homogenous and heterogeneous systems^{39,40}. The equations are mathematically given as Eqs. (8) and (9) for Sips and Redlich–Peterson, respectively. $Q_e = Q_S \cdot a_s \cdot C_e^{s_p} / (1 + a_s \cdot C_e)$ (8) $Q_e = \frac{1}{1 + K_R a_{RP} \cdot C_e} + \frac{K_R a_{RP} \cdot C_e}{1 + K_R a_{RP} \cdot C_e}$ (9) In the Sips model, Q_S

15 is the Sips maximum adsorption capacity (mg/g), as is the Sips equilibrium constant related to the adsorption affinity (L/mg), and n is the

Sips model

32 exponent that expresses the heterogeneity of the adsorbent

. Sips

27 model reduces to Langmuir model as the $n = 1$, and reduces to Freundlich when

either C_e or n is close to 0. In the Redlich–Peterson model, K_{RP} (L/g) and a_{RP} (L/mg) are the Redlich–Peterson constants for equilibrium adsorption. The Redlich–Peterson model is a combination of the Langmuir and Freundlich models. The adsorption thermodynamic parameters of the adsorption system such as Gibbs' free energy (ΔG , kJ), enthalpy (ΔH , kJ), and entropy (ΔS , J/K) were determined by the following van't Hoff equation

22 free energy (ΔG , kJ), enthalpy (ΔH , kJ), and entropy (ΔS , J/K) were determined by the following van't Hoff equation

: $\Delta G = \Delta H - T \cdot \Delta S$ (10) $\Delta G = -RT \ln KC$ (11) $\ln KC = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$ (12) where ΔG can be calculated by using Eq. (11) and KC (dimensionless) value could be obtained

17 by multiplying K_L (L/mg) by the molecular weight of the adsorbate (g/mol) by

1000 (conversion from gram to mg) and then by

1755.5 (the number of moles of pure water per liter)⁴². The

value of

4 ΔH and ΔS are obtained as the slope and intercept of $\ln KC$ versus $1/T$

plot Eq. (12)⁴³. Adsorption kinetics study. A series of 2 mL MB solutions was prepared at a specific initial concentration of 500 ppm and 2000 ppm. To these working solutions, 20 mg of the adsorbent was added. At certain incubation time (t , hour), the residual concentration of the MB (C_t , mg/L) was measured, and the

11 amount of MB adsorbed at specific t (Q_t , mg/g) was calculated. The

30 Pseudo first order Eq. (13) and Pseudo second order Eq. (14) equation were used to fit the

Q_t versus t plot and predict the adsorption rate of MB removal. $Q_t = Q_1 \cdot (1 - e^{-k_1 t})$ (13) $Q_t = \frac{Q_2 \cdot k_2 t}{1 + k_2 t}$ (14) (where Q_1 and Q_2 are the adsorption capacity as predicted by the model (mg/g); k_1 (1/h) and k_2 (g/mg h) are the adsorption rate for each model. Reusability study. Twenty mg of the freshly synthesized Ng-CuGA was introduced into 2 mL of 2000 ppm MB solution. The adsorption was allowed to proceed for 24 h at 30 °C. The MB containing Ng-CuGA was then subjected for the reusability study by first regenerating the adsorbent. The regeneration was done by immersing the post-adsorption adsorbent in 0.5 mL ethanol. Then, the adsorbent was dried in a 50 °C oven overnight before used for another adsorption cycle. Results and discussion Characterization of the Ng-CuGA. Ng-CuGA complexes were obtained by reacting equimolar amounts of GA, Gly, and Cu^{2+} in an aqueous solution, at pH 8 and room temperature. The elemental analysis and ICP results revealed that the brown-colored Ng-CuGA has the compositions (%) of C, 30.044; H, 1.923; N, 1.104; O, 35.302; and Cu, 31.628. Several physicochemical measurements were also conducted to elucidate the characteristics of the Ng-CuGA. The functional group bands of Ng-CuGA were recorded using the FTIR spectrophotometer,

6 and the result is depicted in Fig. 1. The FTIR spectra of

the parent ligands (i.e., GA and Gly) were also given for comparison. Figure 1. FTIR spectra of Ng-CuGA MPN and the parent ligands. IR spectra (cm^{-1}) Gly 1033 GA 1027 Ng-CuGA 1097 Assignment $\nu(C-O)$ or $\nu(C-N)$ 1333 1319 1385 $\nu(OH)$ —bending 1413 1426 1424 $\nu(C-O)$ or $\nu(C-N)$ – 1541 1540 $\nu(C=C)$ 3169 – 3161 $\nu(NH)$ – 3282 3329 $\nu(OH)$ —carboxyl – 3496 3421 $\nu(OH)$ —hydroxyl Table 1. Selected FTIR spectrums of the parent ligands (GA, Gly) and Ng-CuGA. As presented in Table 1, the characteristic peaks of parent ligands (Gly and GA) can be observed in the Ng-CuGA FTIR spectra. The incorporation of Gly to the CuGA was confirmed by the occurrence of characteristic peaks of Gly (N–H group vibration) at wavenumber 3161 cm^{-1} in Ng-CuGA spectra⁴⁴. The shifting of the OH groups was observed between wavenumber 3282–3496 cm^{-1} . These indicate the involvement of the NH groups of Gly and OH groups of GA during Ng-CuGA formation⁴⁵. Based on the SEM image (Fig. 2a), it can be observed that the Ng-CuGA is globular-shaped and has a non-uniform size ranging between 15 and 1500 nm in diameter. TGA was employed to determine the thermal stability of Ng-CuGA. As shown in Fig. 2b,

15 three stages of thermal decomposition were observed. The first stage

thermal decomposition occurred between 30 and 151 °C, which corresponded to the loss of water (5.72 wt.%) and was followed by the decomposition of Gly (21.93 wt.%)

6 at a temperature range of 205–321 °C. The last stage of

decomposition is due to the loss of the GA molecule, which leaving CuO as the final residue (41.77 wt.%). The

8 crystalline structure and the phase characterization of Ng-CuGA were obtained using powder XRD (Fig. 2c). The

PXRD spectra of Ng-CuGA showed a close resemblance to the diffraction spectra of unmodified CuGA²², specifically at $2\theta = 10.1, 13.2, 20.1, 28.0, 31.1, \text{ and } 42.8^\circ$. N₂ adsorption/desorption analysis was performed to determine the surface area and pore properties of the Ng-CuGA. As shown in Fig. 2d, a typical type IV isotherm curve with a hysteresis loop was observed. Based on the BET calculation, the Ng-CuGA has a surface area of 2.00 m²/g, with

8 pore volume and average pore diameter of 0.6 cc/g and 23.3 nm, respectively

. Compared to Figure 2. (a) FE-SEM of Ng-CuGA with bulky shape, inset figure show spherical-like particles at 5000 × magnification. (b) TGA, (c) powder X-ray diffraction, and (d) nitrogen adsorption–desorption isotherm of Ng-CuGA. (a) 120 100 Q_e (mg/g) 80 60 40 20 0 (b) 12 10 pH final 8 6 4 2 0 0 2 4 6 8 10 12 0 2 4 6 8 10 12 pH pH initial Figure 3. (a) Effect of initial pH on the adsorption of MB and (b) pH_{pzc} determination plot of Ng-CuGA. the non-grafted CuGA (

18 surface area of 198 m²/g, pore volume of 0.4 cc/g, and average pore diameter of 8.6 nm)²², the

Ng-CuGA possess a larger pore size. This phenomenon might be occurred due to the incorporation of small-grafting molecules (i.e., Gly), which may strain the internal pores of CuGA, and eventually caused a significant reduction in the surface area of Ng-CuGA^{24,46}. Although incorporating Gly is shown to trigger pore blockage, it is postulated that the nitrogen groups from the grafted molecules may act as the additional adsorption sites²⁴, which

5 can promote the adsorption capacity of

CuGA. Adsorption study. Effect of pH. The pH of the solution is acknowledged as one of the important factors that affect the adsorption performance of the adsorbent⁴⁷. As presented in Fig. 3a, optimum adsorption capacity (Q_e 100.44 mg/g) of Ng-CuGA can be achieved at pH 6. This adsorption capacity is gradually decreased as the pH of the solution transition to either lower or higher pH. The decline of adsorption capacity at pH > 6 might be attributed to the presence of numerous OH⁻ oxyanions in the solution⁴⁸. These negatively charged oxyanions may interact with the MB molecules, thus inhibit the electrostatic attraction between the Ng-CuGA and MB. On the other hand, at pH lower than 6, the electrostatic repulsion between the Ng-CuGA and MB might occur since both molecules are positively charged. Figure 4. Possible interactions that induce adsorption of MB by Ng-CuGA. The highest MB adsorption by Ng-CuGA occurred at pH 6 due to the contrasting charges of the adsorbent and adsorbate in this environment, which consequently induce their electrostatic interaction (Fig. 4a,b)⁴⁹. The negative surface charge of Ng-CuGA was confirmed through the pH_{pzc} value; wherein, it was found that the pH_{pzc} of Ng-CuGA is 4.73 (Fig. 3b). When the pH of a solution is higher than pH_{pzc} (i.e., pH of 6), the surface charge of Ng-CuGA tends to be negative due to the release of proton (H⁺) ions from the functional groups—COOH, —OH, and —NH₂. While most Ng-CuGA particles have a negative surface charge at pH of 6, some of their functional groups may remain protonated. These protonated Ng-CuGA postulated to contribute to MB adsorption through several possible interactions such as electrostatic H-bonding, dipole–dipole H-bonding, and n – π bonding (Fig. 4c–e)^{50,51}. Adsorption isotherm. Adsorption isotherm study was carried out to predict the interaction mechanisms of MB and Ng-CuGA at a constant temperature. The experiment was conducted at an initial solution pH of 6 since the adsorption proceeds optimally at this pH (see Fig. 3) and to eliminate the possibility of unexpected ion interaction or adsorption sites competition. The prediction of the

interaction mechanisms can be made by investigating the isotherm curve shape and modeling the isotherm data³⁹. Figure 5 shows the isotherm curves shape of MB adsorption by Ng-CuGA at different temperatures. The adsorption data points line up to form a curve with a vertical orientation at low C_e , which can be classified as an H-type isotherm, according to the classification by Giles⁵². This type of isotherm is commonly observed when the adsorption process happened due to the electro- static forces between the adsorbent and adsorbate. Based on the subclass classification of the isotherm curve, the adsorption of MB by Ng-CuGA is classified as subclass 2. Subclass 2 commonly represents the high-affinity

3interaction between the solute adsorbate molecules with the

solvent, but a low-affinity

3interaction between the adsorbed-adsorbate molecules and adsorbate molecules in bulk solution

. This behavior is also indicated by the formation of a long plateau that signifies the adsorbent saturation⁵³. The adsorption capacity based on experimental value (Q_{exp}) is given in Table 2; it can be noted that the Q_{exp} is decreased as the adsorption temperature increases. This decrease is postulated due to the rise of MB solubility at higher temperatures which consequently hinder its affinity to the adsorbent⁵⁴. The adsorption data

3modeling was done using several adsorption isotherm models (i.e., Langmuir, Freundlich, Temkin, Sips, and Redlich–Peterson

); the corresponding fitting model can be seen as the solid lines in Fig. 5. The two-parameters Langmuir and Freundlich model commonly employed to specify the adsorption behavior of the system, while the use of Temkin model is necessary to predict the heat transfer direction of the adsorption system. The value of parameters resulted from the experimental data fitting was

23listed in Table 2. The Langmuir model fit the MB adsorption

by Ng-CuGA

5better than the Freundlich model; this was indicated from the higher linear correlation

coefficients (R^2) of the

5Langmuir model. The fitting result is consistent with the previous classification by Giles⁵², where most adsorption systems with an

H type and subclass 2 curves

are well convergence with the Langmuir model. The fitting using the

Temkin model also shown a satisfactory R2 value of 0.934 to 0.942; thus, the parameter can be confidently used to characterize the adsorption system. The derived Temkin constant related to the heat of adsorption (B) is consistent (a) 250 200 (mg/g) 150 100 30°C 50 40°C 0 50°C (b) 250 200 (mg/g) 150 100 50 0 30°C 40°C 50°C (c) 250 0 200 400 600 (mg/L) 800 1000 (d) 250 0 200 400 600 (mg/L) 800 1000 (mg/g) 200 150 100 50 0 0 200 400 600 (mg/L) 800 1000 0 30°C 40°C 50°C (mg/g) 200 150 100 50 0 200 400 600 (mg/L) 30°C 40°C 50°C 800 1000 (e) 250 200 (mg/g) 150 100 50 0 30°C 40°C 50°C 0 200 400 600 800 1000 (mg/L) Figure 5. Adsorption isotherm of MB onto Ng-CuGA. The solid lines represent the fits of Langmuir (a), Freundlich (b), Temkin (c), Sips (d), and Redlich–Peterson (e) isotherm models; symbols represent experimental data. with this finding, in which the values lie between 0.0048 and 0.0065 kcal mol⁻¹ that implies the occurrence of physical sorption (physisorption). decreased as temperature increased, indicating an exothermic behavior⁵⁵; this behavior was also consistent with The adsorption of MB by Ng-CuGA is dependent on temperature. It was found that the adsorption capacity the physisorption dominant of the system. Furthermore, the decrease of the adsorption affinity at higher temperatures was well-represented by the parameters of the Langmuir model. Specifically, the monolayer adsorption capacity, Q_L, was found to decrease at high adsorption temperature. Subsequently, the K_L value, which shows the adsorption affinity, was also reduced by increasing temperature. At higher temperature, the solute molecules tend to have high kinetic energy, which increases the randomness of the molecules. Consequently, the solute and adsorbent surface interactions are delayed due to the high mobility of the solute molecules⁵⁶. The

three-parameter isotherm models (i.e., Sips and Redlich–Peterson), which incorporate the

Langmuir and Freundlich models, were often utilized to validate the two-parameter models. The

fitting results suggest that both Sips and Redlich–Peterson could well-describe the experimental data based upon the R² values. Nonetheless,

it can be seen in Fig. 5e that the fitting lines

of Redlich–Peterson tend to overestimate the experimental data before the plateau region and underestimate after the plateau. Therefore, it can be affirmed that the Sips model would best describe the adsorption isotherm. Another point to be noticed is that the Q_{exp} values for all investigated temperatures have closest resemblance with the Q_S

from the Sips model. Meanwhile, the Q_L of the Langmuir model

and Q_{RP} (K_{RP}/a_{RP}) of the Redlich–Peterson model yield a considerably lower value than the Q_{exp}. Thus, it can be stated that the Sips model can satisfactorily describe the adsorption isotherm. The heterogeneity of the adsorption system can be predicted from the sp and as parameters of the Sips model. The sp values are closer to Q_{exp} (mg g⁻¹) 30 °C 196.480 40 °C 180.458 50 °C 160.238 Langmuir Q_L (mg g⁻¹) 190.805 ± 4.214 164.854 ± 6.523 147.323 ± 4.688

6KL (L mg⁻¹) 0.178 ± 0.019 0.123 ± 0.029 0.137 ± 0.028 R2 0.978 0.927 0

.940 Freundlich KF (L g⁻¹) 59.884 ± 8.129 48.270 ± 6.909 44.111 ± 5.882 nF 4.992 ± 0.646 4.839 ± 0.603 5.102 ± 0.595 R2 0.862 0.885 0.903 Temkin B (J mol⁻¹) 27.195 ± 1.92 23.329 ± 1.633 20.048 ± 1.315 AT (L mg⁻¹) 4.047 ± 0.35 3.374 ± 0.374 3.666 ± 0.379 R2 0.934 0.936 0.942 Sips QS (mg g⁻¹) 188.172 ± 4.763 179.985 ± 13.150 160.498 ± 10.104 as (L g⁻¹) 6.307 ± 1.127 5.479 ± 1.394 5.317 ± 1.144 sp 1.105 ± 0.119 0.692 ± 0.136 0.679 ± 0.125 R2 0.979 0.940 0.954 Redlich–Peterson KRP (L g⁻¹) 36.099 ± 5.234 33.966 ± 11.390 29.060 ± 7.525 aRP (L mg⁻¹) 0.208 ± 0.056 0.342 ± 0.171 0.311 ± 0.125 β 0.983 ± 0.025 0.913 ± 0.034 0.924 ± 0.030 R2 0.978 0.946 0.958 Table 2. Experimental maximum capacity and calculated isotherm

19parameters for the adsorption of MB onto Ng-CuGA. Parameter ΔG (kJ mol⁻¹

) Temperature (K) 303 313 323 – 37.70 – 37.98 – 39.49

19ΔH (kJ mol⁻¹) – 10.45 ΔS (J mol⁻¹ K⁻¹

) 89.30 Table 3. Thermodynamics parameters of MB adsorption onto Ng-CuGA. 1, indicating that the adsorbent tends to possess homogeneous adsorption sites. Furthermore, the as values were far from zero, indicating that the Sips model would reduce to Langmuir rather than Freundlich⁵⁷.

5It is worth mentioning that the adsorption capacity of

Ng-CuGA toward MB is high at the neutral pH and room temperature (i.e., 30 °C), denoting the prospect of this adsorbent material for low-cost and practical adsorption application. Adsorption thermodynamics. The thermodynamic parameters of the adsorption of MB by Ng-CuGA are given in Table 3.

24A negative ΔG and a positive ΔS

indicate that the adsorption process proceeds spontaneously. The positive value of ΔS can

24be related to the release of water molecules on the surface of the adsorbent

as the adsorb- ate molecules are attached⁵⁸. A negative ΔH suggests the exothermic behavior of the adsorption system, which is in accordance with the prediction by the Temkin model. Adsorption kinetics. Adsorption kinetics can demonstrate the adsorption rate, which is a crucial factor to describe the efficiency of the process. Pseudo first order and Pseudo second order were used to model the adsorption kinetic data and determine MB adsorption rate into Ng-CuGA. The fitting of the models was shown by the solid line passing through the adsorption data points in Fig. 6,

9and the fitting parameters were presented in Table 4. The Pseudo second order

model was well-converged with the data, which is indicated by higher R² (i.e., 0.988 and 0.958) than the Pseudo first order (i.e., 0.972 and 0.941). The initial MB concentration (C₀) was shown to affect the adsorption rate and the number of adsorbed MB molecules (Q_t). As shown in Fig. 6, the MB adsorption increases dramatically within 4 h adsorption for the system with C₀ = 2000 ppm. Meanwhile, the adsorption proceeded faster at a lower C₀ of 500 ppm; wherein, the equilibrium was reached only after 2 h. This is in accordance with the estimated adsorption rate value by Pseudo second order (k₂), where k₂ was found to decrease at higher C₀. At a higher C₀ of 2000 ppm, the high number of (a) 250 200 (mg/g) 150 C₀ = 500ppm 100 C₀ = 2000 ppm 50 0 0 2 4 6 8 10 t (h) (b) 250 200 (mg/g) 150 C₀ = 500ppm 100 C₀ = 2000 ppm 50 0 0 2 4 6 8 10 t (h) Figure 6. Adsorption kinetics of MB onto Ng-CuGA. The solid lines represent data fitting

14 to the Pseudo first order (a) and Pseudo second order (b); symbols represent experimental data

. Model Q_{exp} (

28 mg g⁻¹) Initial concentration of MB (mg/L

) 500 70.745 ± 0.077 2000 196.399 ± 0.114 Pseudo first order Q₁ (mg g⁻¹) 67.732 ± 1.043 189.367 ± 8.069 k₁ (h⁻¹) 29.837 ± 4.217 0.894 ± 0.124

6 R² 0.972 0.941 Pseudo second order Q₂ (mg g⁻¹

) 69.189 ± 0.750 216.436 ± 10.386 k₂ (g mg⁻¹ h⁻¹) 0.627 ± 0.091 0.005 ± 0.001 R² 0.988 0.958 Table 4. Experimental maximum capacity and calculated isotherm parameters for the adsorption of MB onto Ng-CuGA. adsorbate molecules rapidly fill the vacant adsorption sites during the beginning; and therefore, the affinity of the adsorbent with the remaining adsorbate molecules in the bulk solutions become weaker, and the adsorption rate was slowing down⁵⁹. The adsorption capacity was also dependent on the C₀, and it was found that the adsorption capacity (Q_{exp}) increases at higher C₀; which is in good accordance with the adsorption capacity predicted by Pseudo second order (Q₂). At higher C₀, the abundance of adsorbate molecules provides a driving force to suppress the adsorbate-adsorbent mass transfer resistance. Thus, more adsorbate molecules can be adsorbed^{60–62}. Effect of adsorbent dose and salinity. The adsorbent dose is an essential factor in designing an economic adsorption process. The effect of adsorbent dose was studied at an initial MB concentration (C₀) of 70 ppm, mimicking dye concentration in textile industry wastewater⁶³. At a low adsorbent dosing, saturation in the adsorption sites of adsorbent may occur before the adsorption equilibrium is achieved. In contrast, an excessive adsorbent dosing may generate unnecessary vacant adsorption sites since the adsorbate had been completely removed before reaching its maximum adsorption capacity⁶⁴. Figure 7a shows the variation of MB %removal at different adsorbent doses. The highest %removal of 99.9 was obtained at an adsorbent dose of 0.5 mg/L and the usage of adsorbent at higher dosing (> 0.5 mg/L) may leads to inefficient adsorbent usage⁶⁵. Some salts such as NaCl and Na₂CO₃ were commonly found in textile wastewater

3 at a concentration of 300 ppm and 20 ppm

, respectively⁶³. Thus, it is necessary to elucidate their effect on the %removal of MB by Ng-CuGA. Figure 7b shows that the reduction of adsorption efficiency

3in the presence of salt ions. The reduction can be related to the attachment of salt cations

on the surface of the adsorbent, which consequently decreases the MB attraction to the surface of Ng-CuGA. It was also worth mentioning that the adsorption efficiency further deteriorated at the higher salt concentration. At a given Na₂CO₃ concentration of 20 ppm, the repulsion effect causes a 7% decrease of the %removal. Meanwhile, 18% and 27% decrease on the %removal was occurred at higher salt concentration, i.e., NaCl = 300 ppm and mixture of NaCl/Na₂CO₃ = 300/20ppm. For comparison purposes, the reported adsorption capacity of MB on different metal-linker coordination adsorbents is listed in Table 4. Compared with the CuGA MOF22, the adsorption capacity of MB by Ng-CuGA was 53.09% higher, indicating the synergistic effect of the N-functional groups from Gly addition. Furthermore, the higher adsorption capacity of Ng-CuGA compared to CuGA can be attributed to the immense

8pore volume and pore diameter, i.e., 0.56 cc/g and 23.25 nm

for Ng-CuGA and 0.43 cc/g, and 8.6 nm for CuGA. The bigger pores (a) (b) 100 % Removal % Adsorption efficiency 120 100 100% 93% 82% 80 73% 80 60 40 60 20 0 0 0.0 0.2 0.4 0.6 0.8 1.0 1.2 Adsorbent dosage (mg/L) Figure 7. (a) Effect of adsorbent dosage on %removal of MB, at C₀ = 70 ppm. (b) Effect of salinity on the adsorption of MB onto Ng-CuGA

3at a different salt concentration (Na₂CO₃ = 20 ppm, NaCl = 300 ppm, and

their combination). Name Ng-CuGA Metal ion Cu Linker GA Additive Q_e (mg/g) Temp (°C) pH Ref Gly 190.81 30 6 This work CuGA MOF Cu GA – 124.64 30 6 22 MOF-Fe Fe H₂BDC – 149.25 NA 9 66 Cu-BTC Cu BTC – 47.77 25 7 67 UiO-66 Zr H₂BDC – 90.48 25 9 68 Reduced graphene oxide – – – 61.5 30 – 49 – – Gly 98.9 30 – Table 5. MB adsorption capacity on various metal-linker coordination adsorbents. % Adsorption efficiency 100 80 60 40 20 0 100% 98% 80% 73% 66% 1 2 3 4 5 Cycles Figure 8. The adsorption efficiency of Ng-CuGA for the MB removal after five adsorption–desorption cycles. of Ng-CuGA may facilitate the insertion of the MB molecules into its matrix, thus increasing the amount of MB molecules that can be trapped. A similar occurrence was found on the amine-

18functionalization of MOF-Fe, in which the amine

-MOF-Fe was shown to possess a higher adsorption capacity and a bigger mean pore diameter (18.63 nm) than the unfunctionalized one (3.26 nm)⁶⁶. The presence of the electron lone pairs of the –NH₂ groups on the Ng-CuGA may account for the better attraction of positive-charged MB⁶⁶, thus improving its adsorptivity. It is also worth mentioning that the Ng-CuGA has a higher MB adsorption capacity than other materials listed in Table 5, demonstrating the potential usage of Ng-CuGA as a highly adsorptive adsorbent for MB removal. Reusability. The ability of Ng-CuGA adsorbent to undergo several repeating adsorption cycles was investigated by performing a 5-cycles reusability study. Figure 8 shows that Ng-CuGA can maintain high adsorption efficiency of 98% up to the second cycle. The adsorption capacity was then declined significantly at the third to fifth cycle which might be due to the occurrence MB remained in the adsorption sites of Ng-CuGA. Conclusion Nitrogen-grafted CuGA (Ng-CuGA) was successfully synthesized by adapting the metal–ligand complexation principle. The synthesis was done by mixing an equimolar amount of Cu, GA, and Gly at pH 8 under ambient temperature. The grafting

3 was confirmed by the occurrence of Gly characteristic peak in the FTIR spectra of

Ng-CuGA. The nitrogen functional group of Gly shown to synergistically promote the adsorption capacity of Ng-CuGA by 1.53-fold higher compared to its non-grafted analogous CuGA. The adsorptivity of Ng-CuGA shown to be closely related to the pH, temperature, and the salinity of the system. Ng-CuGA was able to maintain 80% of adsorption efficiency up to the third adsorption cycle. Received: 10 April 2021; Accepted: 26 May 2021

References

1. Kirchon, A., Feng, L., Drake, H. F., Joseph, E. A. & Zhou, H.-C. From fundamentals to applications: a toolbox for robust and multifunctional MOF materials. *Chem. Soc. Rev.* 47, 8611–8638 (2018).
2. Ko, M.-P. & Huang, C.-J. A versatile approach to antimicrobial coatings via metal-phenolic networks. *Colloids Surf. B. Biointerfaces* 187, 110771 (2020).
3. Ejima, H. et al. One-step assembly of coordination complexes for versatile film and particle engineering. *Science* 341, 154–157 (2013).
4. Zeng, T., Zhang, X., Guo, Y., Niu, H. & Cai, Y. Enhanced catalytic application of Au@polyphenol-metal nanocomposites synthesized by a facile and green method. *J. Mater. Chem. A* 2, 14807–14811 (2014).
5. Ju, Y. et al. Engineered metal-phenolic capsules show tunable targeted delivery to cancer cells. *Biomacromol* 17, 2268–2276 (2016).
6. Shen, G. et al. Interfacial cohesion and assembly of bioadhesive molecules for design of long-term stable hydrophobic nanodrugs toward effective anticancer therapy. *ACS Nano* 10, 5720–5729 (2016).
7. Hu, Z., Berry, R. M., Pelton, R. & Cranston, E. D. One-pot water-based hydrophobic surface modification of cellulose nanocrystals using plant polyphenols. *ACS Sustain. Chem. Eng.* 5, 5018–5026 (2017).
8. Li, W. et al. Superhydrophobic metal-organic framework nanocoating induced by metal-phenolic networks for oily water treatment. *ACS Sustain. Chem. Eng.* 8, 1831–1839 (2020).
9. Luo, W. et al. Engineering robust metal-phenolic network membranes for uranium extraction from seawater. *Energy Environ. Sci.* 12, 607–614 (2019).
10. Dai, Q. et al. Advancing metal-phenolic networks for visual information storage. *ACS App. Mater. Interfaces* 11, 29305–29311 (2019).
11. Pan, S. et al. Modular assembly of host-guest metal-phenolic networks using macrocyclic building blocks. *Angew. Chem. Int. Ed.* 59, 275–280 (2020).
12. Zhong, Q.-Z. et al. Spray assembly of metal-phenolic networks: formation, growth, and applications. *ACS App. Mater. Interfaces* 10, 33721–33729 (2018).
13. Yun, G. et al. Synthesis of metal nanoparticles in metal-phenolic networks: catalytic and antimicrobial applications of coated textiles. *Adv. Healthc. Mater.* 7, 1700934 (2018).
14. Rahim, M. A. et al. Self-assembly of a metal-phenolic sorbent for broad-spectrum metal sequestration. *ACS App. Mater. Interfaces* 12, 3746–3754 (2020).
15. Wang, J. et al. Adsorptive separation of acetylene from ethylene in isostructural gallate-based metal-organic frameworks. *Chem. Eur. J* 25, 15516–15524 (2019).
16. Wang, Z., Zou, Y., Li, Y. & Cheng, Y. Metal-containing polydopamine nanomaterials: catalysis, energy, and theranostics. *Small* 16, 1907042 (2020).
17. Ejima, H., Richardson, J. J. & Caruso, F. Metal-phenolic networks as a versatile platform to engineer nanomaterials and biointerfaces. *Nano Today* 12, 136–148 (2017).
18. Guo, J. et al. Influence of ionic strength on the deposition of metal-phenolic networks. *Langmuir* 33, 10616–10622 (2017).
19. Cherepanov, P. V. et al. Electrochemical behavior and redox-dependent disassembly of gallic acid/ferrii metal-phenolic networks. *ACS App. Mater. Interfaces* 10, 5828–5834 (2018).
20. Boyd, E. M., Bereczky, K. & Godi, I. The acute toxicity of tannic acid administered intragastrically. *Can. Med. Assoc. J.* 92, 1292–1297 (1965).
21. Vaillancourt, D. E., Schonfeld, D., Kwak, Y., Bohnen, N. I. & Seidler, R. Dopamine overdose hypothesis: evidence and clinical implications. *Mov. Disord.* 28, 1920–1929 (2013).
22. Azhar, B. et al. Aqueous synthesis of highly adsorptive copper-gallic acid metal-organic framework. *Sci. Rep.* 10, 19212 (2020).
23. Bibi, R. et al. Effect of amino functionality on the uptake of cationic dye by titanium-based metal organic frameworks. *J. Chem. Eng. Data* 62, 1615–1622 (2017).
24. Guo, Z., Zhang, J., Liu, H. & Kang, Y. Development of a nitrogen-functionalized carbon adsorbent derived from biomass waste by diammonium hydrogen phosphate activation for Cr(VI) removal. *Powder Technol.* 318, 459–464 (2017).
25. Kundu, S., Chowdhury, I. H. & Naskar, M. K. Nitrogen-doped nanoporous carbon nanospheroids for selective dye adsorption and Pb(II) ion removal from waste water. *ACS Omega* 3, 9888–9898 (2018).
26. Geng, J. et al. 3D nitrogen-doped graphene gels as robust and sustainable adsorbents for dyes. *New J. Chem.* 41, 15447–15457 (2017).
27. Ouyang, B. et al. Plasma surface functionalization induces nanostructuring and nitrogen-doping in carbon cloth with enhanced energy

storage performance. *J. Mater. Chem. A* 4, 17801–17808 (2016). 28. Straten, J. W. et al. Nitrogen-functionalized hydrothermal carbon materials by using urotropine as the nitrogen precursor. *Chem. Eur. J* 24, 12298–12317 (2018). 29. Sanjeeva Rao, K., Senthilnathan, J., Ting, J.-M. & Yoshimura, M. Continuous production of nitrogen-functionalized graphene nanosheets for catalysis applications. *Nanoscale* 6, 12758–12768 (2014). 30. Ma, W. et al. One-step synthesis of novel Fe₃C@nitrogen-doped carbon nanotubes/graphene nanosheets for catalytic degradation of Bisphenol A in the presence of peroxymonosulfate. *Chem. Eng. J.* 356, 1022–1031 (2019). 31. Işikel Şanlı, L. & Alkan Gürsel, S. Synthesis and characterization of novel graft copolymers by radiation-induced grafting. *J. Appl. Polym. Sci.* 120, 2313–2323 (2011). 32. Angkawijaya, A. E., Fazary, A. E., Ismadji, S. & Ju, Y.-H. Cu(II), Co(II), and Ni(II)–antioxidative phenolate-glycine peptide systems: an insight into its equilibrium solution study. *J. Chem. Eng. Data* 57, 3443–3451 (2012). 33. Fazary, A. E. et al. Complex formation between ferric(III), chromium(III), and cupric(II) metal ions and (O, N) and (O, O) donor ligands with biological relevance in aqueous solution. *J. Solution Chem.* 40, 1965–1986 (2011). 34. Tardy, B. L. et al. Protein adsorption and coordination-based end-tethering of functional polymers on metal-phenolic network films. *Biomacromol* 20, 1421–1428 (2019). 35. Angkawijaya, A. E. et al. Studies on the performance of bentonite and its composite as phosphate adsorbent and phosphate supplementation for plant. *J. Hazard. Mater.* 399, 123130 (2020). 36. Langmuir, I. The constitution and fundamental properties of solids and liquids: part i: solids. *J. Am. Chem. Soc.* 38, 2221–2295 (1916). 37. Freundlich, H. Of the adsorption of gases: Section II: Kinetics and energetics of gas adsorption: introductory paper to section II. *Trans. Faraday Soc.* 28, 195–201 (1932). 38. Amin, M. T., Alazba, A. A. & Shafiq, M. Adsorptive removal of reactive black 5 from wastewater using bentonite clay: isotherms, kinetics and thermodynamics. *Sustainability* 7, 15302–15318 (2015). 39. Al-Ghouti, M. A. & Da'ana, D. A. Guidelines for the use and interpretation of adsorption isotherm models: a review. *J. Hazard. Mater.* 393, 122383 (2020). 40. Saruchi, K. V. Adsorption kinetics and isotherms for the removal of rhodamine B dye and Pb²⁺ ions from aqueous solutions by a hybrid ion-exchanger. *Arab. J. Chem.* 12, 316–329 (2019). 41. Belhachemi, M. & Addoun, F. Comparative adsorption isotherms and modeling of methylene blue onto activated carbons. *Appl. Water Sci.* 1, 111–117 (2011). 42. Zhou, X. & Zhou, X. The unit problem in the thermodynamic calculation of adsorption using the Langmuir equation. *Chem. Eng. Commun.* 201, 1459–1467 (2014). 43. Sahmoune, M. N. Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents. *Environ. Chem. Lett.* 17, 697–704 (2019). 44. Fischer, G., Cao, X., Cox, N. & Francis, M. The FT-IR spectra of glycine and glycyglycine zwitterions isolated in alkali halide matrices. *Chem. Phys.* 313, 39–49 (2005). 45. Hirun, N., Dokmaisrijan, S. & Tantishaiyakul, V. Experimental FTIR and theoretical studies of gallic acid–acetonitrile clusters, *Spectrochim. Acta Pt. A: Mol. Biomol. Spectrosc.* 86, 93–100 (2012). 46. Virtanen, T. et al. Analysis of membrane fouling by Brunauer-Emmet-Teller nitrogen adsorption/desorption technique. *Sci. Rep.* 10, 3427 (2020). 47. Iftekhhar, S., Ramasamy, D. L., Srivastava, V., Asif, M. B. & Sillanpää, M. Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: a critical review. *Chemosphere* 204, 413–430 (2018). 48. Moosa, A. A., Ridha, A. M. & Kadhim, N. A. Use of biocomposite adsorbents for the removal of methylene blue dye from aqueous solution. *Am. J. Mater. Sci.* 6, 135–146 (2016). 49. Wang, C. et al. Glycine-functionalized reduced graphene oxide for methylene blue removal. *Appl. Organomet. Chem.* 33, e5077 (2019). 50. Swan, N. B. & Zaini, M. A. A. Adsorption of malachite green and congo red dyes from water: recent progress and future outlook. *Ecol. Chem. Eng. S* 26, 119–132 (2019). 51. Salazar-Rabago, J. J., Leyva-Ramos, R., Rivera-Utrilla, J., Ocampo-Perez, R. & Cerino-Cordova, F. J. Biosorption mechanism of Methylene Blue from aqueous solution onto White Pine (*Pinus durangensis*) sawdust: Effect of operating conditions. *Sustain. Environ. Res.* 27, 32–40 (2017). 52. Giles, C. H., Macewan, T. H., Nakhwa, S. N., Smith, D., 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, *J. Chem. Soc.*, 3973–3993 (1960). 53. Piccin, J. S., Cadaval, T. R. S. A., De Pinto, L. A. A. & Dotto, G. L. Adsorption isotherms in liquid phase: experimental, modeling, and interpretations. In *Adsorption Processes for Water Treatment and Purification* (eds Bonilla-Petriciolet, A. et al.) 19–51 (Springer International Publishing, Cham, 2017). 54. Bartell, F. E., Thomas, T. L. & Fu, Y. Thermodynamics of adsorption from solutions: iv: temperature dependence of adsorption. *J. Phys. Chem.* 55, 1456–1462 (1951). 55. Santoso, S. P. et al. Eco-friendly cellulose–bentonite

porous composite hydrogels for adsorptive removal of azo dye and soilless culture. *Cellulose* 26, 3339–3358 (2019). 56. Banerjee, S., Gautam, R. K., Jaiswal, A., Chandra Chattopadhyaya, M. & Chandra Sharma, Y. Rapid scavenging of methylene blue dye from a liquid phase by adsorption on alumina nanoparticles. *RSC Adv.* 5, 14425–14440 (2015). 57. Nethaji, S., Sivasamy, A. & Mandal, A. B. Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from *Juglans regia* shell biomass. *Int. J. Environ. Sci. Technol.* 10, 231–242 (2013). 58. Li, Y. H. et al. Adsorption thermodynamic, kinetic and desorption studies of Pb²⁺ on carbon nanotubes. *Water Res.* 39, 605–609 (2005). 59. Bharathi, K. S. & Ramesh, S. T. Removal of dyes using agricultural waste as low-cost adsorbents: a review. *Appl. Water Sci.* 3, 773–790 (2013). 60. Santoso, S. P. et al. Preparation of nanocrystalline cellulose-montmorillonite composite via thermal radiation for liquid-phase adsorption. *J. Mol. Liq.* 233, 29–37 (2017). 61. Kumar, P. S., Vincent, C., Kirthika, K. & Kumar, K. S. Kinetics and equilibrium studies of Pb²⁺ in removal from aqueous solutions by use of nano-silversol-coated activated carbon. *Braz. J. Chem. Eng.* 27, 339–346 (2010). 62. Xu, Z., Cai, J.-G. & Pan, B.-C. Mathematically modeling fixed-bed adsorption in aqueous systems. *J. Zhejiang Univ. Sci. A* 14, 155–176 (2013). 63. Avlonitis, S. A., Poullos, I., Sotiriou, D., Pappas, M. & Moutesidis, K. Simulated cotton dye effluents treatment and reuse by nano-filtration. *Desalination* 221, 259–267 (2008). 64. Kuang, Y., Zhang, X. & Zhou, S. Adsorption of methylene blue in water onto activated carbon by surfactant modification. *Water* 12, 587 (2020). 65. Gorzin, F. & Bahri Rasht Abadi, M. M. Adsorption of Cr(VI) from aqueous solution by adsorbent prepared from paper mill sludge: Kinetics and thermodynamics studies. *Adsorp. Sci. Technol.* 36, 149–169 (2017). 66. Paiman, S. H. et al. Functionalization effect of Fe-type MOF for methylene blue adsorption. *J. Saudi Chem. Soc.* 24, 896–905 (2020). 67. Lin, S. et al. Adsorption behavior of metal–organic frameworks for methylene blue from aqueous solution. *Microporous Mesoporous Mater.* 193, 27–34 (2014). 68. Mohammadi, A. A. et al. Metal-organic framework Uio-66 for adsorption of methylene blue dye from aqueous solutions. *Int. J. Environ. Sci. Technol.* 14, 1959–1968 (2017). Acknowledgements This research was supported by the National Science Council of Taiwan (MOST 109-2221-E-011-058-) and the National Taiwan University of Science and Technology (101H451403). Author contributions S.P.S.—writing, formal analysis, data curation. V.B.—writing, data curation, visualization. A.E.A.—conceptualization, funding acquisition, methodology, supervision. C.G.—writing, data curation. A.W.G., Y.-H.J., C.-W.H.— writing, supervision, resources. P.L.T.-N., M.Y.—writing, visualization. All authors reviewed the

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