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7Aqueous synthesis of highly adsorptive copper–gallic acid metal–organic framework

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A greener route to synthesize mesoporous

11copper–gallic acid metal–organic framework (CuGA MOF) than the

conventional method using harmful DMF solvent was proposed in this study. Various synthesis attempts were conducted by modifying the synthesis conditions to produce CuGA MOF with comparable physical properties to a reference material (DMF-synthesized CuGA NMOF). The independent variables investigated include the molar ratio of NaOH to GA (1.1 to 4.4) and the synthesis temperature (30, 60, 90 °C). It was found that proper NaOH addition was crucial for suppressing the generation of copper oxide while maximizing the formation of CuGA MOF. On the other hand, the reaction temperature mainly affected the stability and adsorption potential of CuGA MOF. Reacting Cu, GA, and NaOH

3**at a molar ratio of** 1:**1**:2.2 **and a temperature of**

90 °C, produced mesoporous MOF (CuGA 90–2.2) with a surface area of 198.22 m2/g, a pore diameter of 8.6 nm, and a thermal stability of 219 °C. This MOF

17**exhibited an excellent adsorption capacity for the removal of methylene blue**

(

17**124.64 mg/g) and** congo red (**344.54 mg/g). The**

potential usage of CuGA 90–2.2 as a reusable adsorbent was demonstrated by its high

4**adsorption efficiency** (> 90%) **after** 5 **adsorption– desorption cycles. The** ever-growing population **and**

developing industries cause major impact on the environment. Water emerges as one of the highly affected resources due to the increasing usage of synthetic dyes in various sectors, including food processing, pharmaceutical, cosmetic, plastic and textile industries1. Annually, over 7·105 tons of synthetic dyes have been generated and approximately 10–15% of it was leached out during coloring process and may end up in the water bodies. Anionic dyes (i.e., congo red, CR) and cationic dyes (i.e., methylene blue, MB) are the most frequent synthetic dyes found in dye-contaminated water2,3. Earlier studies have reported the adverse effect of these dyes for environment and human health, where extended contact may trigger kidney disease, cancer and allergies4,5. Due to the severity of dye contamination, several removal methods, such as electrolysis, membrane filtration, photo-assisted degradation, and adsorption, have been developed6–8. Among these methods, adsorp- tion is a favorable approach due to its low energy consumption and processing cost, safer by-product, and simple regeneration techniques9,10. Therefore, it triggers researches on the development of various adsorbent material with efficient dye removal ability. In the past decades, metal–organic frameworks (MOFs) have emerged as one of the extensively studied adsorbents. MOFs offer better adsorptive performance than the commonly used adsorbent such as bentonite, activated carbon, and zeolite11–14. This superiority is attributed

22**to their high surface area, large pore volume, and**

numerous adsorption sites15. Copper-gallic acid MOF (CuGA MOF) is a bio-MOF since it composes biologically active phytochemical (i.e., GA) and essential metal element (i.e., Cu)16,17. To date, the applicability of CuGA MOF is inferior to other extensively studied

22**MOFs such as MIL-100, MIL-101**

, UiO-66, ZIF-818. While the application of CuGA MOFs as drug carrier with superior antitumor activity has been reported previously19, their adsorptive behavior remains elusive. The preparation of CuGA MOF was

first introduced by Sharma et al. who reacted Cu(II) 1Department

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Rd., Taipei 106, Taiwan. 2Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, #43, Sec. 4, Keelung Rd., Taipei 106, Taiwan. 3Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60133, Indonesia. 4Department of Mechanical Engineering, Can Tho University, Campus II, 3/2 street, Can Tho city 900100, Vietnam. 5Taiwan Building Technology Center, National Taiwan University of Science and Technology, #43, Sec. 4, Keelung Rd., Taipei 106, Taiwan. *email: artikelisa@mail.ntust.edu.tw Figure 1. (a) Yield and (b) PXRD of CuGA synthesized at 60 °C with different molar ratio of NaOH to GA. The reference XRD pattern was adopted from reported data by Sharma et al.19. and GA with a mixture of solvents containing Aerosol OT, n-butanol, and N,N-dimethylformamide (DMF)19. However, the use of DMF is not desirable due to its harmful potential to the environment20. Hence, it is necessary to develop a greener route for synthesizing CuGA. In this work, the aqueous synthetic method involving the use of NaOH is explored. NaOH was used to create alkaline condition to trigger the dissociation of organic ligands making it accessible for interaction with the metal core16,21,22. The optimum molar ratio of NaOH to GA which is a prerequisite for the formation of CuGA MOF was determined. This optimum ratio restricts the formation of undesirable product, such as metal hydroxide and oxide species, which were commonly found in NaOH-rich condition22,23. Concurrently, the developed syn- thesis method eliminates the use of organic solvent and reduces the reaction time to 2 h. In addition, the effect of synthesis temperature on the adsorption ability of the CuGA MOFs was highlighted and the reusability of CuGA MOF for the removal of CR and MB was assessed in this study. Results and discussion In the following sections, the synthesized CuGA MOF samples were designated as CuGA T-X; with T refers to the synthesis temperature, and X refers to the molar ratio of NaOH to GA. Effect of NaOH to GA molar ratio on the characteristics of CuGA. To obtain the optimum condi- tions for CuGA MOFs synthesis, reactions were carried out at different reaction temperatures and molar ratios of the reactants. The first set of reactions were done by varying X with temperature fixed at 60 °C. The purpose was to determine the proper amount of NaOH required to produce CuGA MOF with comparable characteristics to that of the reference material, CuGA NMOF19. Product yield and XRD pattern were employed as the basis for this screening. As shown in Fig. 1a, the highest yield (34.66%) was obtained at X = 2.2. A comparison of the PXRD patterns between CuGA 60-X and reference CuGA NMOF is given in Fig. 1b. The closest resemblance to the CuGA NMOF PXRD pattern was observed in the CuGA 60–2.2, specifically with the occurrence of peaks at 2θ = 10.1, 13.2, 20.1, 28.0, 31.1, and 42.8°. The PXRD pattern of CuGA NMOF was also quite prominent for CuGA 60–3.3, albeit the inclusion of Cu_2O characteristic peaks at 2θ = 36.56° and 42.39°. Figure 2. (a) PXRD of CuGA synthesized at different synthesis temperatures The reference XRD was based on the reported CuGA NMOF19. (b) Adsorption ability of CuGA T-2.2 for removal of 1000 ppm CR dye. The formation of Cu_2O can be attributed to the oxidation activity that occurs due to the presence of excessive NaOH24. These results suggest that X = 2.2 is the most suitable NaOH to GA molar ratio for the synthesis of CuGA MOF, and therefore, this NaOH concentration was chosen for further studies. The amount of NaOH involved in the synthesis also significantly affected the crystallinity of the CuGA. Based on the PXRD pattern analysis, it was observed that CuGA 60–1.1 exhibited lower crystallinity (23.9%) than that of CuGA 60–2.2 (40.1%) and CuGA 60–3.3 (35.4%). These results illustrate the importance of NaOH in the formation of CuGA. NaOH has a modulatory role in promoting the coordination between Cu and GA. As a base, NaOH triggers the deprotona- tion of carboxylic acid and hydroxyl group of GA, thus produces electron-rich GA. This negatively-charged GA then provides better attraction towards the surrounding metal ions and facilitates interaction of Cu and GA19. At a lower NaOH concentration (X = 1.1), there was only a limited amount of OH− ions available for GA depro- tonation. Therefore, the affinity of GA molecules toward the metal ions was low. On the other hand, at a higher NaOH concentration (X = 3.3 and 4.4), excessive OH− ions may inhibit the Cu to GA coordination

bonds and triggers the formation of metal hydroxide compound instead[22]. Effect of temperature on the synthesis of CuGA. To evaluate the effect of temperature on the charac- teristic of CuGA, X was set at 2.2 while synthesis temperatures of 30, 60, and 90 °C were used to produce CuGA 30–2.2, CuGA 60–2.2, and CuGA 90–2.2, respectively. As presented in Fig. 2a, the PXRD patterns for CuGA 30–2.2 and CuGA 90–2.2 samples are comparable to CuGA 60–2.2 (Fig. 1b) and the reference CuGA NMOF. While temperature may not significantly affect the crystal patterns of the CuGA MOFs, it did significantly affect their adsorption ability (Fig. 2b). After 24 h of incubation, CuGA MOF 90–2.2 showed significant removal of CR, as justified by the transparent supernatant. Meanwhile, brownish-green-colored supernatants were formed in the systems containing CuGA 30–2.2 and CuGA 60–2.2. This aberrant discoloration can be attributed to the presence of radical species that were generated from the MOF degradation which sequentially triggered chro- mogenic reaction of CR[25]. This result suggests that higher synthesis temperature is preferred to form more stable coordination between Cu and GA. Figure 3. (a) FTIR chromatogram, (b) TGA thermogram, (c) N_2 sorption isotherm, and (d) SEM image of CuGA 90–2.2. Characterization of CuGA MOF. As described above, CuGA 90–2.2 showed similar PXRD pattern to that of the reference material and exhibited excellent adsorption potential. Thus, this MOF was further characterized. The comparison between the FTIR spectra of GA and CuGA 90–2.2 is shown in Fig. 3a. It was observed that the bands correspond to the vibration of the hydroxyl (–OH) groups at 3494, 3338, 3263 cm−1 and the vibra- tion of the carbonyl (C=O) group at 1699 cm−1 disappear in the CuGA 90–2.2 chromatogram, confirming the participation of the –OH and the C=O groups in the formation of CuGA. In addition, several band shifts can be observed in the CuGA 90–2.2 chromatogram. A shift in the C−O stretching vibration band from 1421 cm−1 in GA to 1416 cm−1 in CuGA 90–2.2 was observed. Peak shifts at 1305, 1253, and 1022 cm−1 in GA spectra to 1309, 1205, and 1050 cm−1, respectively in CuGA 90–2.2 spectra all are related to C–O (at phenol) vibration. The shift in the spectral bands suggests a change in the bond length for these groups[26], which can be attributed to the coordination between GA and Cu. The TGA result (Fig. 3b) shows that CuGA 90–2.2 was thermally stable up to 219 °C. At higher temperature (220–257 °C), significant weight loss at approximately 43.7% was observed which indicates thermal degrada- tion of the ligand building blocks. A constant weight was observed as the temperature was increased further (> 257 °C). This suggests that no additional breakdown occurred in the sample, and approximately 48.8% weight of Cu-residue remain in metal oxide form. This TGA result is congruent with results on the elemental analysis of the CuGA 90–2.2; calculated formula $Cu_2C_8H_6O_8$ (fw.296): 26.90% C, 1.80% H, and 35.30% O. N_2 adsorption/desorption isotherm of CuGA 90–2.2 is shown in Fig. 3c. A hysteresis loop was observed at P/P0 = 0.5, and the curve is a type IV isotherm curve which indicates that CuGA 90–2.2 has a mesoporous structure with an H3 hysteresis loop caused by a delay of the desorption process[27–29]. The calculated

[18]**BET surface area, total pore volume, and average pore diameter of**

CuGA 90–2.2 are 198.22

[18]**m2/g, 0**.4262 cc/**g, and** 8.6 **nm, respectively**

which are comparable to the CuGA NMOF reported by Sharma et al. (172 m2/g,

[11]**0.73 cc/g, and 2.2 nm, respectively**)[19]. **These** results suggest that **the**

newly developed synthetic method at relatively low tem- perature (90 °C) and in the absence of solvents can be used to produce CuGA MOF with similar characteristics as the DMF-synthesized CuGA NMOF. The SEM image of CuGA (Fig. 3d) shows the irregular granular shaped particles with rough surface morphology. Meanwhile, no specific geometry shape can be observed. Effect of pH on the adsorption of dye by CuGA

90–2.2. One of the critical variables that affect the adsorption process is the initial pH of solution since it affects the surface charge of adsorbent and adsorbate[30]. Figure 4a

> [2]shows the effect of initial pH value on the adsorption efficiency of

CuGA 90–2.2

> [5]for MB and CR removal. The percent removal of MB and CR peaked at

pH 6 and 7, respectively. This pH-

> [2]dependent adsorption behavior of MB and CR onto the

adsorbent can be explained from the pHPZC and zeta potential of CuGA 90–2.2, as shown in Fig. 4b. The pHPZC of the CuGA 90–2.2 is about 4.41; thus, at pH 6 and 7, the surface charge of this MOF is negative. Figure 4. (a) Effect of pH on the efficiency of CuGA 90–2.2 for MB (blue bar) and CR (red bar) removal. (b) Zeta potential and (c) pHPZC measurement of CuGA 90–2.2 at different pH. The negative surface charge is also confirmed from the zeta potential value (Fig. 4c). At pH 6, CuGA 90–2.2 has a surface charge that is opposite from the cationic MB, suggesting that their interactions was driven by elec- trostatic forces[31]. Meanwhile, binding mechanisms such as π–π stacking[32], might be the contributing force for the interaction of CuGA 90–2.2 and CR since both are

> [3]negatively charged at pH 7. Adsorption isotherm. The adsorption isotherm gives the

relationship between adsorbate and adsorbent

> [2]in equilibrium condition. The adsorption isotherm curves of MB and CR at 303, 313, and 323 K on the

CuGA 90–2.2 are presented in Fig. 5. Based on the shape of the initial slope, the curves belong to class H-curve with subclass 2; which indicate that the adsorbate molecules have high affinity toward the adsorbent[33]. Furthermore, a long plateau was observed in the curve, which shows that the adsorption of adsorbate reached saturation[34]. 2-Parameter models (i.e.,

> [3]Langmuir, Freundlich) and 3-parameter Sips model were used to fit the adsorption

data. The calculated parameters,

> [2]along with R2 values, are presented in Table 1

. The R2 values are close to 1 for Langmuir and Sips models, indicating good fittings. Furthermore, the calculated qmax of Langmuir and Sips (qmax,L and qmax,S) models also show good agreement with the highest adsorption capacity obtained from experimental data (qexp). The dimensionless n parameter of the Sips model can show the heterogeneity tendency of the adsorbent. The value of n parameter in Sips, which is close to 1 implies a homogeneous adsorption process. Although a lower R2 was obtained for the Freundlich model, the value of n in the Freundlich model can show the favorability of the adsorption. The n parameter of the Freundlich model falls between 2–10 for all systems, indicating that the adsorption is favorable[34]. CuGA 90–2.2 can adsorb a higher amount of CR than MB as indicated by the qmax and qexp values. While the adsorbent-adsorbate electrostatic attractions cannot explain this phenomenon, the interaction can be related to the presence of Cu-nodes in CuGA 90–2.2. In hard-soft acid–base theory, Cu is classified as borderline-soft acid that has better interaction with borderline base[35,36]. Based on its molecular feature, CR possesses sulfonate groups, a borderline base, thus provide better interaction to the Cu-nodes of CuGA 90–2.2. In addition, the presence of benzene rings in CR and MB structures may contribute to dye adsorption onto CuGA due to the occurrence of π–π interaction (Fig. 6). The greater number of benzene rings in the CR structure facilitates π–π interactions with the CuGA 90–2.2[32]. The FTIR,

CuGA 90–2.2. The FTIR chro- matogram of the dye-loaded CuGA 90–2.2 (referred to as MB@CuGA and CR@CuGA) shows the alteration on the spectral shape compared to the spectra of CuGA 90–2.2 before adsorption. Several new absorption bands appear in the spectra of MB@CuGA and CR@CuGA (Fig. 7a), which confirms the adsorbate and adsorbent Figure 5. Adsorption isotherm curves of (a) MB and (b) CR on CuGA 90–2.2 at different temperatures. Dye T (K) 303 Qe (mg/g) 115.60 Langmuir qmax,L (mg/g) 110.09 KL (L/g) 0.175 R2 0.946 Freundlich KF 39.71 n 6.072 R2 0.906 Sips KS (L/ qmax,S (mg/g) mg) 124.64 0.299 n 0.551 R2 0.989 MB 313 133.85 133.78 0.072 0.986 38.49 5.168 0.885 141.25 0.127 0.752 0.995 323 151.55 152.94 0.072 0.979 44.54 5.196 0.883 161.39 0.131 0.748 0.987 303 343.71 344.54 0.343 0.946 158.06 7.871 0.772 344.54 0.3430 1.000 0.946 CR 313 357.30 362.92 0.266 0.928 162.21 7.474 0.739 362.92 0.266 1.000 0.928 323 375.58 379.19 0.257 0.939 163.55 6.835 0.758 379.19 0.257 1.000 0.939

Sips models. interactions. In MB@CuGA chromatogram, new peaks appear at 1170, 1360, and 1363–1591 cm−1 correspond- ing to the C=C, aromatic ring, and C–H asymmetric vibration peaks of MB, respectively[37]. On the other hand, the adsorption of CR onto the CuGA surface is indicated by the appearance of CR characteristic peaks at 829, 1051, 1409, and 1575 cm−1, which are attributed to the vibration of aromatic rings, S=O stretching vibration, Figure 6. Illustration of possible mechanism of (a) CR and (b) MB adsorption onto CuGA 90–2.2. and –N=N– stretching vibration of CR, respectively[38]. SEM images of the MB@CuGA and CR@CuGA was also observed. However, no apparent alteration was observed from the SEM images of the dye-loaded CuGA (Fig. 7c,d). It worths noting that the synthesized CuGA 90–2.2 has higher adsorption capacity toward MB and CR than the other MOF-adsorbents reported in literatures, as shown in Table 2. The maximum adsorption capacity of CuGA 90–2.2 is 1.4 to 5.7 times higher for MB, and 1.4 to 5.3 times higher for CR than the other reported MOFs. This shows that the synthesized CuGA 90–2.2 can be a promising adsorbent for either anionic or cationic dye adsorption. Furthermore, the aqueous synthesis of CuGA 90–2.2 can be considered as an eco-friendly process. Adsorption thermodynamics. The thermodynamic parameters, including the changes in enthalpy (ΔH), free energy (ΔG), and entropy (ΔS), in the adsorption of MB and CR onto CuGA 90–2.2 were determined. According to the linear relationships, the parameter

which obtained based on the following equations: ln KC = ?S − ?H R RT

KC can be calculated as the ratio between the equilib- rium concentration on the solid phase (Ca, mg/L) and in the solution (Ce, mg/L)[47]. ΔG was calculated using the equation below: ?G = −RTln(Kc) The calculated values of ΔH, ΔS, and ΔG are given in Table 3. The negative ΔH of the adsorption systems denote that the heat was released during the process and that the adsorption occurred exothermically[48]. The nega- tive ΔS implies the decrease in the degree of freedom of the molecules due to the fact that the bonded adsorbate molecules have less freedom of movement than when they are free in solution. Compared to the MB system, the less negative of ΔS value for the CR system can be attributed to the softer binding potential in this system[49]. The negative ΔG values of MB and CR adsorption indicate the thermodynamic favorability and spontaneous nature of the adsorption process[50]. Figure 7. Characterization of post-adsorption CuGA 90–2.2. (a) FTIR spectra of MB-loaded CuGA (MB@ CuGA) and CR-loaded CuGA (CR@CuGA). (b) XRD crystallography of CuGA after 5 adsorption–desorption cycles. (c) and (d) SEM image of MB@CuGA (c) and CR@CuGA (d). Dye Adsorbent CuGA 90–2.2 Adsorption capacities (mg/g) 124.64 Temp (°C) 30 Ref This work UiO-66 91.00 30 39 MB MIL-101 21.79 25 40 Fe3O4@MIL-100 56.15 35 41 NH2-MIL-88B 61.46 25 42 CuGA 90–2.2 344.54 30 This work Glu-Cu2+ (MOFs) 77.60 37 43 CR Chitosan/UiO-66 246.21 25 44 ZIF-8@CoFe2O4 64.48 30 45 Fe3O4/Bi2S3 MSs 92.24 55 46 Table 2. Adsorption capacities of various adsorbents for MB and CR removal. Dye MB ΔH (kJ/mol) ΔS (J/mol) − 19.3517 − 50.2856 ΔG (kJ/mol) 303 K − 4.2442 313 K − 3.3373 323 K − 3.2561 CR − 10.5147 − 16.0269 − 5.6700 − 5.4106 − 5.3851

CuGA 90–2.2. Figure 8. Effect of recycle number of Cu-GA MOF

capacity. Reusability. Adsorbents with high reusability can benefit from the aspects of process-cost savings, environ- mental friendliness, and practicality[51]. Ethanol was employed as the desorption agent for the regeneration of CuGA. The CuGA showed excellent recyclability, retaining high adsorption efficiency (> 90%) after five adsorp- tion–desorption cycles (Fig. 8). After fifth adsorption–desorption cycles, the efficiency of CuGA is 94.96% and 93.82%

removal of 115.51 mg/g and 310.67 mg/g, respectively. To confirm the stability of CuGA 90–2.2 after 5 adsorption–desorp- tion cycles, the PXRD patterns of the CuGA were recorded. As shown in Fig. 7b, there

is no significant change in the PXRD pattern of the adsorbent before and after 5 cycles of dye removal. Conclusion An aqueous synthesis method of CuGA MOF has been developed to replace the conventional synthesis method. Two important conditions in the synthesis that affect the successful formation of CuGA MOF are the synthesis temperature and the molar ratio of NaOH to GA. A proper amount of NaOH addition is important in promot- ing the formation of CuGA MOF while preventing metal oxide formation. A synthesis temperature of 90 °C was found to facilitate the formation of CuGA with stable coordination. Synthesis temperature also profoundly affected the adsorption ability of the resulting CuGA MOF for dye removal. Compared to other extensively studied MOFs, the aqueous-synthesized CuGA MOF possesses higher adsorption capacity for MB and CR. The CuGA MOF showed high reusability with adsorption efficiency decreased less than 10% after 5 adsorp- tion–desorption cycles. Materials and methods Materials. Copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, CAS 10125-13-0, ≥ 99% purity) and gallic acid ($C_7H_6O_5$, CAS 149-91-7, ≥ 97.5% purity) were obtained from Sigma-Aldrich (St Louis, MO). Sodium hydroxide (NaOH, CAS 1310-73-2, ≥ 97% purity)

> 3**was obtained from Fisher Scientific** (Leicestershire, **UK**

). CR (C.I. 22,120, CAS 573-58-0) was supplied by Alfa Aesar (China). MB (C.I. 52,015, CAS 7220-79-3, ≥ 95% purity) and hydro- chloric acid (HCl, CAS 7647-01-0,

> 3**37%) were purchased from Acros Organics (New Jersey, USA**

). All chemicals were used directly as obtained without any further purification. Synthesis of CuGA MOF. For CuGA MOF synthesis, 2.5 mmol (0.425 g) of GA was dissolved in 5 mL NaOH solution at certain molar concentration (Table 4). Into the GA solution, 2.5 mmol (0.426 g) $CuCl_2 \cdot 2H_2O$ solution in 5 ml DI water was added dropwise. This mixture was then stirred for 2 h at constant temperature. The dark brown solids obtained from the reaction were collected then rinsed with DI water 5 times. Finally, the solids were freeze-dried using a Labconco freeze dryer for 24 h. The as-synthesized solids were referred to as CuGA T-X (T refers to the reaction temperature; X refers to the molar ratio of NaOH to GA, as listed in Table 4). Characterization of CuGA MOF. Elemental analysis of the complex was carried out using a Thermo Flash 2000 CHNS/O Analyzers. The crystallinity pattern was determined by using a Powder X-Ray Diffraction (PXRD, Bruker D2 PHASER XE-T XRD) operated at 30 kV; 10 mA using Cu-Kα radiation (λ = 0.154060 nm) at 3° PSD opening, 0.5 times per step and 2Theta from 5° to 60°. The surface functional group analysis was performed by using a

> 5**Fourier-Transform Infrared Spectroscopy (FTIR**, SHIMADZU Tracer-100); **the** analysis **was carried out in the range of** 400–4000 **cm−1**

wavenumbers and KBr pellets were applied as the background. Thermogravimetric analysis (TGA,

> 3**TA instruments/TGA 550**) was carried out **at temperature range**

30–650 °C with a heating rate of 10 °C/min. The isotherms of N_2 adsorption–desorption were measured

> 4**at 77 K using a BELSORP-max analyzer. The samples were degassed for** 4 **h at** 383 **K before** analyzing. **The specific surface area was calculated from the**

adsorption branch using the Brunauer–Emmett–Teller (BET) model. The pHPZC and

zeta potential measurement were done according to the previous report34,52. Sample name CuCl2.2H2O Concentration (M) GA NaOH Temp pHmeasured First optimization step 60–1.1 0.5 0.5 0.55 60 3.71 ± 0.13 60–2.2 0.5 0.5 1.10 60 4.64 ± 0.37 60–3.3 0.5 0.5 1.65 60 7.30 ± 0.05 60–4.4 0.5 0.5 2.42 60 8.53 ± 0.13 Second optimization step 30–2.2 0.5 0.5 1.10 30 4.51 ± 0.08 90–2.2 0.5 0.5 1.10 90 4.13 ± 0.14 Table 4. Conditions used to synthesize CuGA MOF. Adsorption experiment. CuGA MOF powder (20 mg) was mixed with 2 mL dye solution. CR and MB were chosen as the model adsorbate in this work at a respective initial concentration of 500–4500 mg/L and 10–2000 mg/L. The adsorption was carried out

3in a shaking incubator for 24 h, at 200 rpm, under a constant tem- perature of 303

, 313, and 323 K. The remaining dyes were then separated from CuGA MOFs by centrifugation (Smart 15 Plus Micro Centrifuge) at 15,000 rpm (21,055 g) for 20 min. A UV–visible spectrophotometer (Shi- madzu UV 2600) was used to determine the concentration of the remaining CR or MB left in the supernatant (Ce). The adsorption isotherm data were then plotted as Ce vs Qe. Qe

23were calculated by the following equation: $Qe = \frac{(C_0 - C_e) V}{W}$ where Qe (mg/g) is the equilibrium amount of

adsorbate adsorbed,

15C0 and Ce (mg/L) represents the initial and final (post-adsorption) concentrations of dye, respectively, V (L) is the volume of dye solution, and W (g) is the weight of

CuGA MOF. Adsorption modeling. SigmaPlot 12.5, a Systat software, was used for adsorption data modeling and fit- ting. The models used include 2-parameters model (i.e., Langmuir, Freundlich) and 3-parameters Sips models. The Langmuir model can be expressed as: $Qe = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$ where KL (L/g)

21is the Langmuir affinity constant related to the energy of adsorption, and Qmax (mg/g) is the maximum adsorption capacity

of the CuGA MOF with assumption of monolayer surface coverage53. Freundlich isotherm model was used to describe the multilayer adsorption with the interaction of adsorbent and adsorbed molecules. Freundlich model is represented by the following equation: $Qe = K_F C_e^{1/n}$ where

20KF((mg/g)(L/mg)−1/n) is the Freundlich constant related to the adsorption capacity of the adsorbent, and n (dimensionless) is the

heterogeneity and adsorption intensity of adsorbent[54].

> [8]**Sips isotherm model is a combined form of Langmuir and Freundlich expressions** designed **for predicting the heterogeneous adsorption systems** while evading **the limitation of rising adsorbate concentration**

. At low adsorb- ate concentrations, it

> [19]**reduces to Freundlich isotherm**; and **it predicts monolayer adsorption**, a **characteristic of the Langmuir isotherm, at high adsorbate concentrations**

. Sips isotherm model is represented by following equation: $Q_e = \dfrac{Q_{ms}K_SC_e^\beta}{1 + K_sC_e^\beta}$ where Q_{ms}(

> [16]**mg/g) is the Sips maximum adsorption capacity** of the adsorbent, **K_s (L mg^{-1})** is **the Sips equilibrium constant, and β is the Sips model exponent**

,

> [13]**which can also be employed to describe the system's** heterogene- ity **when is between 0 and 1. When β = 1, the Sips equation reduces to the Langmuir equation** which **implies a homogeneous adsorption**

process[34].

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