Green Synthesis of Magnetic MOF@GO and MOF@CNT Hybrid Nanocomposites with High Adsorption Capacity towards Organic Pollutants

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Abstract

Hybrid nanocomposites based on Cu-BTC MOF, graphene oxide (GO), carbon nanotubes (CNTs), and Fe₃O₄ magnetic nanoparticles (MNPs) were developed via a simple green solvothermal method, at which GO and CNT were used as platforms to load nanostructured Cu-BTC MOF and Fe₃O₄ MNPs. The as-synthesized hybrid nanocomposites were characterized by XRD, SEM, TEM, XPS, IR, Raman, TGA, and BET techniques. XRD measurements show highly crystalline structures for the prepared hybrid nanocomposites. Morphological analyses carried out by SEM and TEM also confirm successful growth of Fe₃O₄ MNPs and nanoparticulate Cu-BTC MOF over the carbon-based platforms. Chemical, elemental, and TGA analyses verify chemical bonding and successful compositing of the parent materials. Nitrogen isotherms show a cumulative pore volume of 0.360 cm³g⁻¹ for the hybrid nanocomposite of Fe₃O₄/Cu-BTC@GO compared to 0.030 cm³g⁻¹ of the sole Cu-BTC MOF, which suggests potential uses towards small molecule adsorption. We have found that use of GO and CNT substrates (i) diminish the aggregation and increases dispersive forces within the MOFs, (ii) lead to MOFs with different morphology and size, and (iii) result in formation of small pores between the MOF and the platforms. Adsorption capacity of the prepared nanomaterials was examined over methylene blue (MB) as a model organic pollutant. The developed hybrid nanomaterials show enhanced pollutant adsorption capacity compared to that of the parent materials. The improved adsorption capacity is attributed to the synergetic effect of covalent bonding between the parent materials as well as to the unique features of the nanoscale MOF. Overall, these novel materials may be considered as excellent candidates towards a variety of environmental applications such as water remediation.

Keywords: Fe₃O₄; MOFs; CNTs; Graphene Oxide; Adsorption; Water Remediation

1. Introduction

Over the past few decades, and due to fast population growth and rapid industrial expansion, emission of contaminants into the environment has sharply increased [1-3]. This has made environmental remediation a major global concern [3]. Thus, current global environmental problems require greener energy sources and better liquid, solid and gas waste management. Dye containing effluents are considered major sources of water pollution with adverse effects on human and wildlife health [4,5]. Textile, paper, printing, pulp mill, electroplating, food, and cosmetic industries are among the major consumers of dyes which produce vast amounts of coloured wastewater. Complex structures and xenobiotic characteristic of some dyes make them difficult to degrade [6]. Methylene blue (MB) is an ionic organic dye that is used in dyeing wool, silk, and cotton. It has detrimental effects on human health such as eye damage upon contact, nausea, and mental confusion [5]. Techniques for decolouration of MB include adsorption, membrane filtration, precipitation, and ion exchange separation [7-9].

Adsorption technique has advantages of being low cost, easy to implement, consuming low energy, and producing safe by-products. Therefore, these advantages make adsorption technique superior over the other pollutant removal techniques [10-12]. Indeed, several types of absorbents have been developed to remove MB [4,5]. However, current and traditional absorbents have some limitations such as low adsorption capacity and difficulty in separation of the absorbents after the reaction. Hence, there is a need to design high-efficiency and low cost absorbents that can also be easily separated from the contaminated media. In this respect, development of new porous materials has attracted great attention, at which the spearhead is metal-organic frameworks (MOFs) [13-15].

MOFs are a class of highly porous materials fabricated through linking metal clusters or ions and organic linkers through covalent bonds. MOFs have crystalline and highly ordered structures, high porosity, large surface areas, and are currently being used in various applications such as catalysis, gas storage and separation, sensor, biomedicine, energy, and water remediation [16-21]. In fact, due to their high-porosity and high specific surface area, MOFs are excellent adsorption materials [10,11]. MOFs have been used for both liquid and gas phase adsorption applications. Gas adsorption techniques have been developed for the removal of hazardous gases [22,23]. For instance, Hamon et al., report the adsorption of H₂S over various MOFs including MIL-53 (Al, Cr, Fe), MIL-47 (V), MIL-101 (Cr) and MIL-100 (Cr) [23]. MOFs have also been used in wastewater treatments. For instance, Haque et al., report potential application of a Cr-based MOF as absorbent for removal of methylene orange (MO) [24]. Due to the anionic nature of MO, cationic MOFs show increased adsorption capacity and rapid dye uptake [24]. MOF-235 and MIL-100 (Fe) have been used to remove cationic methylene blue (MB) through similar charge-charge mechanism [25,26].

Although MOFs show promising chemical and physical properties for a variety of adsorption applications, their properties can be further enhanced by modifying their physicochemical nature and structure by substituting organic linkers [27], grafting with active functional groups [28], impregnating them with appropriate materials [29], and making composites of them with different materials [30-32]. Among the above mentioned techniques, MOFs composites are relatively new [33-36]. However, finding appropriate complementary materials and synthetic pathways are crucial to make MOF-based composites [37-39]. Graphene oxide (GO) and carbon nanotubes (CNTs) are among the most suitable materials for synthesis of MOF composites [18,31,37]. They improve MOF formation by increasing the dispersive forces within the MOFs,

suppressing their aggregation, and controlling MOF's physicochemical properties such as structure, morphology, and size [40-46]. For instance, Petit and Bando report the synthesis of MOF-5@GO composites and they have found that compared to that of sole MOF, presence of GO during formation of the MOF results in improved N₂ gas adsorption [31]. They also report that nanocomposites of Cu-BTC@GO and MOF-5@GO show similar porosity and chemical structure in comparison to the parent MOFs [40]. In addition, they have tested adsorption of toxic gases (H₂S, NH₃, and NO₂) over Cu-BTC@GO. 10% and 30% improvement in adsorption of NH₃ and H₂S, respectively, with little enhancement in NO₂ adsorption was reported [40,43]. Huang et al., have showed that Zn-containing MOFs-loaded GO increase H₂S adsorption compared to that of sole MOF [44]. In addition, Cu- and Zn-containing MOFs loaded over CNT substrate show improved gas selectivity toward CO₂/CH₄ as well as enhanced H₂ uptake [45,46]. Moreover, the incorporation of superparamagnetic iron (III) oxide nanoparticles (Fe₃O₄ MNPs) to the MOF@GO or MOF@CNT hybrid nanocomposites can be engineered for the magnetic separation and recovery of the absorbents [47-49].

In this work we describe (1) the synthesis of several novel hybrid nanocomposites based on water stable Cu HKUST-1 MOF, GO, and CNT, having covalent nature of interactions between the MOFs, GO and CNT as opposed to simple admixtures in previous reports; (2) the strategy of using the GO and CNT substrates as the main components of the composites to grow nanoscale MOFs; (3) the implementation of magnetic properties by incorporation of Fe₃O₄ MNPs to make recyclable absorbents; (4) applying the prepared hybrid nanocomposites as adsorbent. Hence, in the current study magnetic and non-magnetic hybrid nanocomposites of Cu-BTC@GO, Cu-BTC@CNT, Fe₃O₄/Cu-BTC@GO and Fe₃O₄/Cu-BTC@CNT were synthesized using a simple, facile, and green solvothermal method. The synthesized materials were characterized by XRD,

SEM, TEM, XPS, IR, Raman, TGA, and BET, and were used as absorbents in removal of MB as model organic pollutant. Authors believe that this study provides useful criteria in synthesis of magnetic and non-magnetic copper-containing MOF@GO and MOF@CNT hybrids and can also be used as reference in designing of other kinds of MOF-based hybrid nanocomposites.

2. Experimental

2.1. Chemicals

Reagent-grade chemicals of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, benzene-1,3,5-tricarboxylic acid (BTC), ethanol, H_2SO_4 , HNO_3 , KMnO_4 , and H_2O_2 were purchased from Acros, Alfa Aesar, and Fisher Scientific. Graphite powder (Sigma-Aldrich) and carbon nanotubes (20-40 nm in diameter, 5-15 μm in length, Tokyo Chemical Industries Co.) were used as received without further purification. Deionized water was obtained from Milli-Q® instrument, Millipore Corporation.

2.2. Synthesis of the Materials

Graphene oxide (GO). GO was prepared from graphite powder via a method reported in the literature [50].

Functionalized Carbon nanotubes (F-CNTs). F-CNTs were prepared by acid-treatment of pristine CNTs [5,51].

Fe_3O_4 Magnetic Nanoparticles (Fe_3O_4 MNPs). The Fe_3O_4 MNPs were synthesized via chemical co-precipitation method according to the previous report [49].

Cu-BTC MOF. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.0 g, 0.004 mmol) was dissolved into deionized water (10 mL) and mixed with benzene-1,3,5-tricarboxylic acid (H_3BTC) (0.5 g, 0.0024 mmol) dissolved into ethanol (10 mL). The resulting mixture was placed in glass reactor which was then sealed.

The glass reactor was heated to 383 K for 48 h in an oven. Afterwards, the glass reactor was cooled to room temperature. Blue solids of Cu-BTC MOFs were collected and washed three times with ethanol. Finally, the resulting solid was dried under vacuum for 12 h resulting in a fine blue powder of Cu-BTC MOFs. XRD: the observed signals are in agreement with the previous reports [31,43]. IR: 1739 cm^{-1} (C=O stretch), 2980 cm^{-1} (C-H of the aromatic rings); 1640 and 1590 cm^{-1} (asymmetric vibrations in $-\text{CO}_2^-$); 1110 cm^{-1} related to C–O–Cu stretch. XPS: $\text{Cu}2\text{p}_{3/2}$ at 931, 941, 953, and 962 eV, O1s 530 eV, C1s at 285 eV [45].

Cu-BTC@GO (CuG) Hybrid Nanocomposites. A suspension of 1 mg/ml GO in an ethanol:water mixture with ratio of 2:1 (v:v) was prepared via vigorous sonication for 1 h in an ice bath. Then, solutions containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.0 g, 0.004 mmol) and H_3BTC (0.5 g, 0.0024 mmol) were prepared separately in 10 ml of an ethanol:water mixture with ratio of 2:1 (v:v). Afterwards, the copper solution was added to the GO suspension and vigorously sonicated for 15 min. Then, the H_3BTC solution was added to the above solution and sonicated for another 15 min. The mixture was placed into glass reactor and sealed. The glass reactor was heated to 383 K for 48 h in an oven. The reactor was then cooled to room temperature. Black solids of CuG hybrid nanocomposites were collected and washed three times with ethanol and deionized water. Finally, the resulting solid was dried in an oven for 12 h and a fine dark black powder of CuG was obtained. Four different types of CuG hybrid nanocomposites were synthesized according to the ratio between Cu-BTC MOF and GO: 1:2 (CuG12), 1:1 (CuG11), 2:1 (CuG21) and 5:1 (CuG51). The instrumental analyses such as XRD, IR, and XPS confirm presence of the signals corresponding to all the parent materials.

Cu-BTC@CNT (CuC) Hybrid Nanocomposites. The same procedure for preparation of CuG was followed except that instead of GO, F-CNTs were used. Four different types of CuC hybrid

nanocomposites were synthesized according to the Cu-BTC MOF and CNT ratio: 1:2 (CuC12), 1:1 (CuC11), 2:1 (CuC21) and 5:1 (CuC51). The instrumental analyses such as XRD, IR, and XPS confirm presence of the signals corresponding to all the parent materials.

Magnetic Hybrid Nanocomposite of Fe₃O₄/Cu-BTC@GO (FCuG). First, a 100 ml suspension of CuG (5 mg/ml) was prepared by sonication of CuG powder in deionized water at room temperature for 1 h in ice bath. Then, the suspension was purged under N₂ gas for 30 min to remove oxygen from the solution. Afterwards, a solution made of dissolving FeCl₃.6H₂O (0.25 g) and FeCl₂.4H₂O (0.15 g) in 10 mL deionized water which was then added to the CuG suspension under purging with N₂ gas. After stirring for 30 min, 3 ml of a 25% NH₄OH aqueous solution was quickly injected into the mixture in one portion followed by stirring for 30 min at room temperature. The black precipitates were collected by applying an external magnet, washed three times with deionized water and dried in a vacuum oven overnight. The instrumental analysis of XPS confirms presence of the signals corresponding to all the parent materials.

Magnetic Hybrid Nanocomposite of Fe₃O₄/Cu-BTC@CNT (FCuC). To prepare FCuC, the same procedure for preparation of FCuG was used except instead of CuG, CuC was used.

A schematic view of formation of Cu-BTC MOFs and Fe₃O₄ MNPs over the graphene layer of the substrates is shown in [Fig. 1](#).

Fig. 1.

2.3. Characterization of the Prepared Samples

Crystalline phases of the prepared samples were analysed by x-ray powder diffractometer (XRD, Bruker D8 Discover x-ray Diffractometer). The morphology was revealed by a transmission electron microscope (TEM, Hitachi H-7650) and scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive x-ray detector (EDAX). Infrared (IR) spectroscopy

was performed on a PerkinElmer® Universal ATR instrument, and data were collected in the range of 650–4000 cm^{-1} . Raman spectra of the samples were collected on a DXR™ Raman Microscope, Thermo Scientific. Thermogravimetry Analysis (TGA) data were obtained by using a Q50 TGA instrument, Universal V4.5A TA Instruments. Pore volume and Brunauer–Emmett–Teller (BET) surface area measurements of the synthesized materials were analysed through N_2 adsorption/desorption isotherms with a Micromeritics Surface Area and Porosity Analyser (ASAP-2020). XPS tests was monitored by Omicron XPS/UPS system with Argus detector which uses Omicron's DAR 400 dual Mg/Al X-ray source from the Materials and Characterization Core facility at Texas A&M University, in College Station TX. The extent of MB adsorption was measured by UV-Visible spectroscopy and measured by a Varian Cary® 50 UV-Vis Spectrophotometer.

2.4. Pollutant Adsorption Experiments

Pollutant adsorption experiments were conducted on methylene blue (MB) as model organic pollutant. In this regard, 5 mg of the absorbents were treated with 20 ml of a 50, 100, and 1000 ppm MB solution and the resulting mixture was sonicated for 10 min followed by shaking for 12 h to complete the reaction. Then, the non-magnetic absorbents were centrifuged and magnetic absorbents were magnetically separated from the suspension and the remaining MB concentration was analysed by adsorption spectroscopy at the 665 nm wavelength to monitor the extent of the removal.

Adsorption capacity (Q_e) of the prepared nanomaterials is calculated (Eq. 1) as follows:

$$(1)$$

Where C_0 and C_e are initial and equilibrium concentration of the pollutant (mgL^{-1}), respectively, m is the adsorbent mass (gr) and V is the mixture volume (L).

3. Results and Discussions

3.1. X-ray Diffraction Patterns

The crystalline structure of the synthesized CuG and CuC hybrid nanocomposites with different MOF content was determined by XRD which the corresponding results are shown in Fig. 2 and Fig. S2, respectively. According to our findings, the hybrid nanocomposites show highly crystallinity and the relative intensities and position of all the peaks are consistent with the standard pattern of the parent materials [5,40,48]. Diffraction peaks for CuC samples (Fig. S2) show preservation of the crystallinity of the CNT and Cu-BTC MOF parent materials. All the diffraction signals of the parent materials can be readily indexed, which confirms the synthesis of the nanocomposites [4,46]. In the case of CuG hybrid nanocomposites (Fig. 2), the d002 peak related to GO is not observed for the hybrid nanocomposites [40-43]. This is due to the high exfoliation and dispersion of GO during the nanocomposites preparation [52]. It also was found that the presence of CNT and GO do not prevent the formation of the MOF [48]. We also found that the intensity of the Cu-BTC MOF peaks in the hybrid nanocomposites decreases as the content of CNT and GO substrates increases. This is attributed due to the lower concentration of MOFs crystals vs the substrate, and to the higher concentration of CNT and GO which impose additional constraints on degrees of freedom and growth of the Cu-BTC MOF crystals during *in situ* synthesis of the Cu-BTC MOF in the hybrid nanocomposites [41-43,46].

Fig. 2.

3.2. Morphological Characteristic

Morphology of the synthesized hybrid nanocomposites are characterized by SEM and TEM microscopies. The corresponding SEM images are illustrated in Fig. 3 and Fig. S2, and the corresponding TEM images are shown in Fig. 4 and Fig. S3. According to the SEM and TEM findings, GO nanosheets (Fig. 3a, 3b and Fig. S3a, S3b) are successfully synthesized by exfoliation of graphite oxide, which is in agreement with previous studies [40,41]. Fig. 3e and 3f show that the F-CNTs are well-dispersed and retain the tube structure of the pristine CNTs after acid-treatment (Fig. S3c, S3d). The synthesized Cu-BTC MOF (Fig. S2c, S2d and Fig. S3g, S3h) has morphology of pyramid in size of tens of microns. The bare Fe₃O₄ MNPs are made of slightly agglomerated spherical-shape particles with size ranging from 5-20 nm (Fig. S2a, S2b and Fig. S3e, S3f).

Fig. 3.

Furthermore, it is noteworthy that compared to the pure Cu-BTC MOF, *in situ* synthesis of Cu-BTC MOF in the presence of GO platforms result in the formation of nanoscale Cu-BTC MOF compared to the sole Cu-BTC MOF obtained at the micronscale scale as shown in Fig. 3c, 3d and Fig. 4a, 4b. We also found that the *in situ* synthesis of Cu-BTC MOF in presence of GO substrate prevents the formation of distorted layers and densely packed GO agglomerates, which is in accordance with XRD results. Since Cu ions in the solution can either react with oxygen-containing groups of BTC ligands or GO, we have hypothesized *in situ* formation of the MOF over GO leads to alternation between MOF units and graphene layers [44]. Additionally, due to steric hindrance and charge-charge interactions, GO layers decorated with MOF are well-exfoliated and also new pores are formed between the substrate and the MOF, which are very beneficial for adsorption of small molecules [41-43].

Regarding the CNT-based nanomaterials, Fig. 3g, 3h and Fig. 4e, 4f show that similar to the MOF@GO, *in situ* synthesis of Cu-BTC MOF in the presence of F-CNTs result in the formation of Cu-BTC MOF decorated over the CNT platform [46,53]. Furthermore, we found that coprecipitation of Fe₃O₄ MNPs in the presence of CuG12 and CuC12 hybrid nanocomposites leads to the formation of Fe₃O₄ MNPs over GO and CNT platforms and successful synthesis of magnetic FCuG (Fig. S2c and S2d) and FCuC (Fig. S3g and S3h) hybrid nanomaterials.

Fig. 4.

3.3. Elemental Study by XPS

XPS measurements were performed to confirm the elemental composition of the developed FCuG hybrid nanocomposite, which the corresponding results are shown in Fig. 5. The signals observed at around 931, 941, 953, and 962 eV correspond to electrons in Cu2p_{3/2} [45]. The binding energy for O1s is observed at around 530 eV, deriving from O²⁺ ions in crystalline network of the sample [45]. The peak at 285 eV corresponds to C 1s, and Fe signals related to Fe2p_{3/2} are observed at 711 and 725 eV [48]. These findings confirm successful decoration of the Cu-BTC MOF and Fe₃O₄ MNPs over the GO platform.

Fig. 5.

3.4. Chemical Properties: IR and Raman Studies

Fig. 6 shows IR spectra of the prepared hybrid nanomaterials and of the corresponding parent materials. The characteristic peaks of GO are observed as follows: double peak at 3195 and 3370 cm⁻¹ (O-H stretch), 1739 cm⁻¹ (C=O stretch), 1615 cm⁻¹ (C=C stretch), and 1229 cm⁻¹ (C-O stretch) [50]. The Cu-BTC MOF exhibits signals at 3392 cm⁻¹ (O-H or -OH deriving from coordinated or absorbed water molecules); 2980 cm⁻¹ (C-H stretch of the aromatic rings); 2950 cm⁻¹ (asymmetric CH in -CH₂-); 2890 cm⁻¹ (symmetric CH in -CH₂-); 1730 cm⁻¹ (C=O stretch);

1640 and 1590 cm^{-1} (asymmetric vibrations in $-\text{CO}_2^-$); 1455 and 1370 cm^{-1} corresponding to the asymmetric and symmetric stretch of the BTC carboxylate groups, respectively, 1110 cm^{-1} related to C–O–Cu vibration in the MOF [31,41].

IR spectra of the hybrid nanocomposites of CuG with a different ratio between the Cu-BTC MOF and GO show the characteristic peaks of both parent materials [41,43], confirming the successful synthesis of the hybrid nanocomposites. Additionally, we found that increasing the MOF content in the hybrid nanocomposites, increases the intensities of the MOF-related signals. The changes in the intensities of the peaks at 1640/1590 cm^{-1} and 1455/1370 cm^{-1} can be ascribed to variation in environment of the BTC's carboxylate ligands.

Fig. 6.

Fig. S4 shows Raman spectra of the prepared F-CNT and CuC12. The Raman spectra of F-CNT shows double peaks of the D and G bands around 450 and 790 cm^{-1} , respectively. The G band is typically assigned to E_{2g} phonon of sp^2 carbon atoms, whereas the D band is attributed to κ -point phonons of A_{1g} symmetry [40,54-56]. In the other words, G-band is characteristic of graphitic layers which correspond to carbon atoms tangential vibration, and the D-band is a typical sign of defects in the graphitic structure. According to Fig. S4, spectra of the hybrid nanocomposites retain the major characteristic peaks of the parent materials which means the chemical structure of the parent materials remain intact after compositing them.

3.5. Thermogravimetric Analysis (TGA)

TGA provide useful information for the thermal stability of materials. The TGA curves for the parent materials and the corresponding hybrid nanocomposites are shown in Fig. 7. In the case of GO, two major weight drops are observed. The first is around 100 $^{\circ}\text{C}$ attributed to dehydration.

The second signal around 170 °C is related to decomposition of the GO functional groups [50]. The TGA pattern of the parent Cu-BTC MOF illustrates a small drop at around 110 °C, which is ascribed to dehydration. Coordinated water molecules are released at around 210 °C. The complete decomposition of the Cu-BTC MOF is observed at around 350 °C, which is in agreement with previous reports [41]. TGA curves for the hybrid nanocomposites are similar to those of the parent materials. The higher the content of the Cu-BTC MOF in the hybrid nanocomposites, the higher the resemblance of the TGA to the parent MOF. Importantly, the hybrid nanocomposites show higher thermal stability compared to the parent materials which is likely due to the chemical bonding between the MOF and the substrate platforms.

Fig. 7.

3.6. N₂ Adsorption/Desorption Isotherms

The porosity of the prepared materials was investigated via nitrogen adsorption-desorption isotherms (Fig. 8). Brunauer–Emmett–Teller (BET) specific surface area, cumulative pore volume (P_{vol}), average pore diameter (P_{diam}), and particle size (P_{size}) of Cu-BTC MOF, CuG51, and CuC51 hybrid nanocomposites were measured and the corresponding results are shown in Table 1. Pore size distribution of these samples were also analysed using the Barrett–Joyner–Halenda (BJH) method (Fig. S5-S7 and Tables S1-S3).

Fig. 8.

According to the results, a relatively high specific surface area was found for CuG51 ($\sim 508 \text{ m}^2\text{g}^{-1}$) compared to that of the sole Cu-BTC MOF ($856 \text{ m}^2\text{g}^{-1}$). Surprisingly, it was found that hybrid nanocomposites show significantly higher P_{vol} in comparison to the sole MOF. It is hypothesized that formation and growth of the MOF over GO surface through chemical bonding results in formation of micro-pores which are beneficial for small molecules adsorption [31]. The large

surface area and high porosity of the prepared hybrid nanomaterials provide many channels for pollutants **adsorption** and favour their immigration into the pores [31]. The data also shows that hybrid nanocomposites rather than physical admixtures of the parent materials are made through this synthetic methodology.

Table 1. BET specific surface area (S_{BET}), cumulative pore volume (P_{vol}), average pore diameter (P_{diam}), and particle size (P_{size}) of the prepared samples.

Sample	S_{BET} [m^2g^{-1}]	P_{vol} [cm^3g^{-1}]	P_{diam} [nm]	P_{size} [nm]
Fe ₃ O ₄ MNPs	55.770	0.072	3.90	107.6
Cu-BTC MOF	856.00	0.031	2.55	7.000
CuG51	507.70	0.048	4.20	11.80
FCuG	176.14	0.360	8.31	34.10
CuC51	123.25	0.081	4.05	48.70

3.7. Pollutant **Adsorption** Capacity

Pollutant **adsorption** capacity of the prepared hybrid nanomaterials and their parent materials were tested through **adsorption** of MB dye, which the results are shown in Fig. 9 and Table 2. The **adsorption** experiments were carried out at two different MB concentrations of 50, 100 ppm to monitor the effect of pollutant concentration on the **adsorption** capacity of the prepared samples. Further studies for MB **adsorption** using a 1000 ppm solution of MB was tested on CuG11, CuG21, and CuG51 composites (See Table 2). It was found that the **adsorption** capacity of the absorbents increases as the extent of the pollutant increases which is in agreement with the previous reports [24-26,57].

Fig. 9.

The developed hybrid nanocomposites show higher dye adsorption capacity when compared to the parent materials. In the case of GO-based hybrid nanocomposites (Fig. 9a), MB adsorption of magnetic FCuG was found to be the highest among the samples and several times higher than that of the parent materials of Cu-BTC MOF, Fe₃O₄ MNPs, and GO. Regarding to the non-magnetic hybrid nanocomposites, it was observed that higher loading of the MOF results in higher MB adsorption. However, MOF overloading has adverse effect on the adsorption capacity of the pollutant due to the presence of free Cu-BTC MOF along with the hybrid nanocomposites. Treatment of MOF@GO hybrid composites with 1000 ppm MB solution shows higher adsorption capacities compared to the 50 and 100 ppm MB adsorption. Samples CuG11, CuG21, and CuG51 show adsorption capacities of 1087, 193, and 545 mg g⁻¹ respectively (See Table S4). An increase in adsorption capacities is expected when using high concentrations of the pollutant, due the fact that there is less competition between solvent molecules to occupy the pores in MOFs.

Results for MB adsorption using CNT-based hybrid nanocomposites are shown in Fig. 9b. A similar trend is observed, where overloading of the Cu-BTC MOF decreases dye adsorption. It should be noted that the measured dye adsorption of the magnetic hybrid nanocomposite of FCuC is slightly lower than that of non-magnetic CuC hybrid nanocomposites. The reason might be due to filling the pores formed between the MOF and the substrate by Fe₃O₄ MNPs and suppression of MB trapping in those pores. Another reason can be related to disrupting the connection between the parent materials after loading of Fe₃O₄ MNPs.

Table 2. MB adsorption capacities of the prepared hybrid nanocomposites and the corresponding parent materials at room temperature.

Material	Q_e (mg g ⁻¹) (20-30 ppm)	Q_e (mg g ⁻¹) (50 ppm)	Q_e (mg g ⁻¹) (100 ppm)	Ref.
Fe ₃ O ₄ MNPs	-	62	80	This work
GO	-	71	94	This work
F-CNT	-	110	125	This work
Cu-BTC MOF	-	46	67	This work
CuG12	-	48	128	This work
CuG11	-	88	96	This work
CuG21	-	32	152	This work
CuG51	-	28	40	This work
FCuG	-	166	136	This work
CuC12	-	90	108	This work
CuC11	-	78	160	This work
CuC21	-	130	172	This work
CuC51	-	136	132	This work
FCuC	-	112	152	This work
carbon nanotubes	65	-	-	5
graphene oxide	40	-	-	9
activated carbon	20	25	30	11
MOF-235	160	170	180	11
Fe ₃ O ₄ @Cu ₃ (BTC) ₂	25	-	-	48
Cu ₃ (BTC) ₂	29.5	-	-	48

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The improvement in the MB adsorption capacity of the hybrid nanocomposites is attributed to the synergetic effect of the parent materials, nanoscale size of the Cu-BTC MOF particles, suppression of dispersive forces, well-separation of the MOFs, inhibition of distortion and

bundling in GO and CNT [40,41]. Besides, high P_{vol} of the hybrid nanocomposites is also an important factor contributing to their high dye adsorption capacity. In fact, the increased pore volume provides more pores for adsorption of MB molecules. In addition, due to presence of unsaturated bonds and also negative charge of the prepared hybrid composites (coming from carboxylate groups) and positive charge of MB dye, adsorption mechanism between MB and the composite nanomaterials to be hydrophobic and/or π - π as well as charge-charge interactions, which is in agreement with previous literatures [25,48].

Overall, we found that due to the excellent features of the synthesized hybrid nanocomposites these materials can be candidates for water and wastewater treatments with many other unexplored environmental remediation applications.

4. Conclusion

The purpose of the current study was to make highly efficient absorbents for the removal of organic dye pollutants. In this respect, a series of hybrid nanocomposites based on the Cu-BTC MOF, Fe₃O₄ MNPs, GO, and CNTs were synthesized via a facile, versatile, and green solvothermal method. The prepared hybrid nanocomposites were characterized by XRD, SEM, TEM, XPS, IR, Raman, TGA, and BET. XRD results show highly crystalline nature of the hybrid nanocomposites. Morphological, elemental and chemical studies confirmed formation of nanoscale Cu-BTC MOF and Fe₃O₄ MNPs over GO and CNTs substrates. BET surface area analysis verifies highly porous nature of the hybrid nanomaterials. Pollutant adsorption tests were conducted over MB dye as model organic pollutant. It was found that pollutant adsorption was considerably higher on the hybrid nanocomposites compared to that of the parent materials. A significant improvement in adsorption capacity of the composite nanomaterials was ascribed

to the positive features deriving from compositing the parent materials. In this respect, we found that synthesis of the MOF in presence of GO and CNT platforms benefit their formation and functionality through number of ways such as increased dispersive forces, preventing aggregation, less inter-MOFs voids, different morphology and size. In addition, in situ formation of the Cu-BTC MOF leads to suppression of stacking and bundling of the substrates as well as formation of small pores between the MOF and platforms.

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Figures Caption:

Fig. 1. Schematic view of formation of Cu-BTC MOF and Fe₃O₄ MNPs over the graphene layer.

Fig. 2. XRD patterns of CuG12, CuG11, CuG21, and CuG51 hybrid nanocomposites.

Fig. 3. SEM images of GO (a,b), CuG12 (c,d), F-CNTs (e,f), and CuC12 (g,h).

Fig. 4. TEM images of CuG12 (a,b), FCuG (c,d), CuC12 (e,f), and FCuC (g,h). Scale lines shown represent 100, 10, 50, 50, 200, 200, 500, and 200 nm for a-h, respectively.

Fig. 5. XPS spectra of the prepared FCuG hybrid nanocomposite.

Fig. 6. IR spectra of Cu-MOF@GO hybrid nanocomposites and the corresponding parent materials.

Fig. 7. TGA curves of the prepared hybrid nanocomposites and their parent materials.

Fig. 8. Nitrogen isotherms of the Cu-BTC MOF (a), CuG51 (b), and CuC51 (c).

Fig. 9. MB removal through adsorption over the (a) GO- and (b) CNT-based magnetic and non-magnetic hybrid nanocomposites.

Fig. 1. Schematic view of formation of Cu-BTC MOF and Fe₃O₄ MNPs over the graphene layer.

Fig. 2. XRD patterns of Cu-BTC@GO₁₂, Cu-BTC@GO₁₁, Cu-BTC@GO₂₁, and Cu-BTC@GO₅₁ hybrid nanocomposites.

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