2015-01-01

Novel Engineered Nanomaterials For Water Remediation And Gas Adsorption: Graphene Oxide And Carbon Nanotubes Decorated With Metal-Organic Frameworks And Magnetic Nanoparticles

Vahid Jabbari

University of Texas at El Paso, vahid_jabbari.azeri@yahoo.com

Follow this and additional works at: https://digitalcommons.utep.edu/open_etd

Part of the Environmental Engineering Commons, Materials Science and Engineering Commons, Mechanics of Materials Commons, and the Nanoscience and Nanotechnology Commons

Recommended Citation

https://digitalcommons.utep.edu/open_etd/864

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact lweber@utep.edu.
NOVEL ENGINEERED NANOMATERIALS FOR WATER REMEDIATION AND GAS ADSORPTION: GRAPHENE OXIDE AND CARBON NANOTUBES DECORATED WITH METAL-ORGANIC FRAMEWORKS AND MAGNETIC NANOPARTICLES.

VAHID JABBARI,
Department of Chemistry

APPROVED:

__________________________
Dino Villagrán, Ph.D, Chair

__________________________
Jorge Gardea-Torresdey, Ph.D, co-Chair

__________________________
Juan C. Noveron, Ph.D

__________________________
Yirong Lin, Ph.D

__________________________
Charles Ambler, Ph.D.
Dean of the Graduate School
Dedication

Dedicated to my dear family, my mother’s pure soul, and Hazrat Vali-e-Asr.
NOVEL ENGINEERED NANOMATERIALS FOR WATER REMEDIATION AND GAS ADSORPTION: GRAPHENE OXIDE AND CARBON NANOTUBES DECORATED WITH METAL-ORGANIC FRAMEWORKS AND MAGNETIC NANOPARTICLES

by

VAHID JABBARI, B.S.

THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Chemistry
THE UNIVERSITY OF TEXAS AT EL PASO
December 2015
Acknowledgements

First and foremost, I would like to dedicate my deepest thank to my advisors Dr. Dino Villagrán and Dr. Jorge Gardea-Torresdey for their tremendous mentoring, guidance, and patience.

I would also like to acknowledge my committee members Dr. Juan C. Noveron and Dr. Yirong Lin for their contribution toward the research as well as their valuable advices and comments.

Special thanks to my fellow lab-mates in Dr. Villagran’s and Dr. Gardea’s labs for their tremendous support. Furthermore, I would also like to dedicate my special thanks to Jose M. Veleta from Dr. Villagran’s lab for his assistance in running BET and TGA measurements, Edison Castro from Dr. Echegoyen’s lab for running Raman analyses, Dr. Maryam Zarei-Chaleshtori for training and helping me with SEM, EDAX, and XRD measurements, and college of engineering at UTEP for allowing access to their SEM, EDAX, and XRD instruments.

Dr. Peter Cooke from New Mexico State University (NMSU) and Dr. Jing Wu from Texas A&M University are highly appreciated for their great help on TEM and XPS analyses.

Finally I would like to thank all the graduate students, faculty and staff from the UTEP’s chemistry department, especially Dr. Michael and Dr. Narayan for their valuable advice and support.
Abstract

In the current study, a series of novel magnetic and non-magnetic hybrid nanocomposites based on metal-organic frameworks (MOFs) of $\text{M}_3(\text{BTC})_2$ (M: Ni, Cu, Zn, and Cd), graphene oxide (GrO), and carbon nanotubes (CNTs), and Fe$_3$O$_4$ magnetic nanoparticles (MNPs) were developed via a green, simple and versatile solvothermal method at which GrO and CNT were used as platform to grow the MOFs and Fe$_3$O$_4$ MNPs over them. The as-synthesized nanocomposites were characterized by XRD, SEM, TEM, XPS, IR, Raman, TGA, and $\text{N}_2$ adsorption/desorption isotherms. Morphological analysis confirmed successful growth of nano-size Fe$_3$O$_4$ MNPs and $\text{M}_3(\text{BTC})_2$ MOFs over GrO and CNT platforms. XRD results exhibit highly crystalline structure for the prepared hybrid nanocomposite. Chemical and elemental analysis verified chemical structure and successful compositing of the parent materials. TGA experiments further confirm successful loading of Fe$_3$O$_4$ MNPs and $\text{M}_3(\text{BTC})_2$ MOFs over GrO and CNT substrates. It was also found that presence of GrO and CNT platforms during synthesis of the MOFs have several benefits for the MOFs: different physicochemical properties, increasing dispersive forces during MOFs formation, suppression of MOFs aggregation, different morphology and smaller size, and formation of small pores between MOF and the platforms. Furthermore, adsorption capacity of the prepared magnetic and non-magnetic hybrid nanocomposites was examined over methylene blue (MB) as model organic pollutant and a large improvement in adsorption capacity of the hybrid composites compared to that of parent materials was recorded. The improved adsorption capacity is attributed to synergetic effect of parent materials. Overall, it is proposed that due to promising features of the synthesized nanocomposites, they can be excellent candidates for environmental applications such as water remediation and pollutant adsorption.
# Table of Contents

Acknowledgements........................................................................................................ iv

Abstract .................................................................................................................................. v

Table of Contents .................................................................................................................. vi

List of Tables ........................................................................................................................ vii

List of Figures ........................................................................................................................ viii

Chapter 1: Introduction........................................................................................................... 1

Chapter 2: Synthesis, Characterization and Pollutant Adsorption Capacity of Ni$_3$(BTC)$_2$ MOF-based Hybrid Nanomaterials........................................................................................................ 8

Chapter 3: Synthesis, Characterization and Pollutant Adsorption Capacity of Cu$_3$(BTC)$_2$ MOF-based Hybrid Nanomaterials ........................................................................................................ 21

Chapter 4: Synthesis, Characterization and Pollutant Adsorption Capacity of Zn$_3$(BTC)$_2$ MOF-based Hybrid Nanomaterials ........................................................................................................ 39

Chapter 5: Synthesis and Characterization of Cd$_3$(BTC)$_2$ MOF-based Hybrid Nanomaterials ....53

Chapter 6: Conclusion .......................................................................................................... 65

Chapter 7: References ......................................................................................................... 67

Vita ........................................................................................................................................... 70
List of Tables

Table 1.1 Labelling the prepared materials.

Table 2.1 Measured MB dye adsorption capacities of the hybrid nanocomposites and the corresponding parent materials.

Table 3.1 BET specific surface area ($S_{BET}$), pore volume ($P_{vol}$), average pore diameter ($P_{diam}$), and particle size ($P_{size}$) of the prepared 2, 9, 13, 14, and 19.

Table 3.2 MB adsorption capacity of the prepared absorbents.

Table 4.1 Comparison of capacities of adsorption of MB on different adsorbents.
List of Figures

Figure 2.1 XRD patterns of the prepared 3 and 4-7 hybrid nanomaterials with different ratio between 1 and 3.

Figure 2.2 SEM images of 3 (a,b), 2 (c,d), 1 (e,f), and 4 (g,h).

Figure 2.3 TEM images of 2 (a,b), 1 (c,d), 4 (e,f), and 8 (g,h).

Figure 2.4 XPS results of the prepared 8 hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, (d): Fe2p, and (e): Ni2p.

Figure 2.5 IR spectra of 1, 3, and 4-6 hybrid nanomaterials with different ratio between 1 and 3.

Figure 3.1 XRD patterns of the prepared (a) 10-13 and (b) 16-19 hybrid nanomaterials with different ratio between the parent materials.

Figure 3.2 SEM images of 9 (a,b), 1 (c,d), 10 (e,f), 14 (g,h), 15 (i,j), and 16 (k,l).

Figure 3.3 TEM images of 9 (a,b), 10 (c,d), 14 (e,f), 16 (g), and 20 (h).

Figure 3.4 XPS result of the prepared 14 hybrid nanocomposites. (a): survey, (b): C1s, (c): O1s, (d): Fe2p, and (e): Cu2p.

Figure 3.5 IR spectra of 1, 9, and 10-13 hybrid nanocomposites with different ratio between 1 and 9.

Figure 3.6 Raman spectra of (a): 9 and 10, and (b): 15 and 16.

Figure 3.7 TGA results of 1, 2, 9, 11 and 14 hybrid nanocomposites.

Figure 4.1 XRD patterns of the prepared (a) 22-25 and (b) 27-30 hybrid nanomaterials with different ratio between the parent materials.

Figure 4.2 SEM images of 21 (a,b), 22 (c,d), 26 (e,f), and 27 (g,h).

Figure 4.3 TEM images of 22 (a,b), 26 (c,d), and 27 (e,f).
Figure 4.4 XPS result of the prepared 26 hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, (d): Fe2p, and (e): Zn2p.

Figure 4.5 IR spectra of 1, 21, and 22-25 hybrid nanocomposites with different ratio between 1 and 21.

Figure 4.6 Raman spectra of (a): 22 and 26 and (b): 15 and 27.

Figure 4.7 TGA curves of 1, 2, 21, 22, 25 and 26.

Figure 3.8 N2 isotherms of parent 9 and hybrid nanocomposites of 13 and 19.

Figure 5.1 XRD patterns of the prepared (a) 33-36 and (b) 37-40 hybrid nanocomposites.

Figure 5.2 SEM and TEM images of 32 (a,b), 33 (c-f), and 37 (g,h).

Figure 5.3 XPS spectra of the prepared 33 hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, and (d): Cd3d.

Figure 5.4 XPS spectra of the prepared 37 hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, and (d): Cd3d.

Figure 5.5 IR spectra of 33-36 hybrid nanocomposites and their parent materials.

Figure 5.6 Raman spectra of 15 and 37.
Chapter 1: Introduction

Due to vast population growth resulting in a large increase in air and water contaminants over the past few decades, environmental remediation has become one of the main concerns of our society\(^1\)-\(^3\). Present environmental concerns move us to search for greener energy sources and processes with better waste management. Examples of such efforts are production and utilization of biogas along with improvement in wastewaters treatment systems\(^4\)-\(^7\). On this regard, over the past two decades, an explosion in the research and development of new porous materials for gas- and liquid-phase pollutants adsorption was experienced, of which the spearhead are the highly porous metal-organic frameworks (MOFs)\(^8\)-\(^11\). MOFs are a new class of highly porous materials fabricated through linking metal clusters or ions with organic molecules by strong covalent bonds\(^12\). MOFs own ordered structures, high porosity, and large surface area can be fabricated by various functional groups which due to these properties, they have been found useful in many applications such as catalysis, gas storage and separation, gas adsorption, sensor, biomedicine, energy, and water remediation\(^13\)-\(^18\). For instance, linkage of copper (Cu) with benzene tricarboxylic acid (BTC) (Cu-BTC, also known as HKUST-1, MOF-199, or Cu\(_3\)(BTC)\(_2\)) was reported by Chui et al.\(^11\) which due to its large pore volume, high surface area, high chemical stability, and its ability to coordinate with water molecules, was successfully applied in catalytic gas separation and storage, and pollutants removal\(^19\)-\(^22\).

Adsorption technique has received more interest every year due to its superiority compared to other techniques in hazardous materials removal such as gas and water purification. Due to the necessity of low temperatures operating conditions, adsorption is less energy consuming and comparatively, a lower cost process. Other advantages of adsorption include design simplicity, ease of operation, broad range of applications, and less harmful byproducts. MOFs are well-
known for their application in adsorption which owes numerous advantages such as high specific surface area and large number of pore openings\textsuperscript{23,24}. Furthermore, MOFs own special functional groups are beneficial for selective adsorption of various species\textsuperscript{10-16}.

MOF materials have been implemented to both liquid and gas phase adsorptions. Adsorptions in gas phase are mainly performed for toxic gas removal\textsuperscript{25-27}. Over the past two decades, an increase in the field of research and development of new porous materials for adsorption of toxic gases and molecules was witnessed, at which the spearhead is being porous MOFs\textsuperscript{12,28,29}. Lately, Hamon et al., reported H$_2$S toxic gas adsorption over various MOFs of MIL-53(Al,Cr,Fe), MIL-47(V), MIL-101(Cr) and MIL-100(Cr)\textsuperscript{30}. While all the MOFs were capable of adsorbing toxic gas, decent reversible adsorption was only observed in MIL-47(V) and MIL-53(Al,Cr). Regarding to MIL-53(Fe), MOF destruction occurred which was ascribed to H$_2$S reactive adsorption resulting in the formation of FeS\textsuperscript{30}. In the case of MIL-100(Cr) and MIL-101(Cr), porosity of the MOFs was partially recovered and partial decomposition of the MOFs and reactive adsorption between the MOFs and the gas was hypothesized\textsuperscript{30}. Adsorptions in liquid phase using MOFs have also been reported and water remediation using MOF materials is attracting increased attention every year. Recently, Haque et al., reported potential application of a Cr-based MOF as absorbent for removal of methylene orange (MO)\textsuperscript{31}. Due to negative charge of the dye, they found that MOFs with positive charge show significant adsorption capacity and rapid uptake of the dye\textsuperscript{31}, which suggests presence of charge-charge interaction between MOF and dye. They have also reported application of iron terephthalate MOF (MOF-235) in the adsorption of MO as anionic dye and MB as cationic dyes and the same mechanism of charge-charge interaction was proposed\textsuperscript{32}. Zhang and his coworkers have also investigated MB dye adsorption by MIL-100(Fe) MOF\textsuperscript{33}.
Although MOFs themselves demonstrate promising chemical and physical properties for a variety of applications, their properties can be further enhanced by modifying their physicochemical nature and structure in many ways. These methods include substituting organic linkers, grafting with active functional groups, impregnating them with appropriate materials, and making composites of them with different materials. Among the above mentioned techniques, the concept of MOFs composites is a relatively new idea, and only a few studies have been recently reported on successful synthesis along with promising applications. By making MOF’s composites with appropriate smart materials, synthesis kinetics, physicochemical properties, and morphology, the potential applications of MOFs can be considerably improved. Also the procedure to synthesize the composites is sometimes simple and easy, compared to synthesis of sole MOFs.

GrO can be easily obtained through oxidation and exfoliation of graphene layers of graphite. Graphite, which is abundant and very cheap source of carbon, is made of graphene layers owning five and six member rings of carbon with sp² hybridization. Another derivative of graphene, CNTs are made of rolled graphene layers in tube morphology with diameter in nanosize. Due to their excellent electrical conductivity, high mechanical strength, durability and tunable surface chemistry of these carbon nanostructures, GrO and CNTs are vastly applied in various fields, especially structural composite materials. Owning large dimension in the XY plane which reaches few micrometers and significantly thin thickness (nanometer scale) in Z-axis, GrO and CNTs have huge surface area and tunable surface chemistry and are great candidates to act as platform for loading various nanoparticles.

The advantages of using GrO and CNTs in the MOFs formation and growth include: (i) an increase in dispersive forces within MOFs. In the other words, pure MOFs structure are full of
void and free spaces due to weak dispersive forces, which is adverse for the retention of small molecules. On the other hand, GrO has a non-porous structure with arrays of layers. Consequently, by combining the positive features of these two materials, MOF/GrO composites are developed and hence MOFs with higher surface area and much less inter-MOFs void space are created which make them promising materials with high potential in various fields.\(^{42}\) (ii) It has also been hypothesized that graphene layers in GrO and CNTs also have the role of structure directing in MOFs synthesis, and (iii) controlling MOF’s structure, morphology and size during its formation and growth over the platforms\(^{51,52}\).

A vast enhancement in gas-phase and liquid-phase pollutant adsorption capacity of MOFs has been found in composites of MOF, GrO and CNT in comparison to that of the parent materials\(^{52-55}\). Recent reports exhibit successful application of MOFs@GrO hybrid composites in various gas adsorption e.g. H\(_2\)S, NH\(_3\), NO\(_2\)\(^{53-55}\). They have reported that there is around 10% for NH\(_3\) and 30% for H\(_2\)S gas adsorption improvement which was due to synergetic effect between the parent materials, and a little improvement in NO\(_2\) adsorption was found\(^{55}\). Petit et al., also studied adsorption behavior of gas adsorption over composite of MOF (HKUST-1) and graphite oxide (GO)\(^{54}\). They have reported that making composite of these two species result in formation of small pores which are beneficial in gas adsorption. They justified this phenomenon by dispersive forces between Cu\(_3\)(BTC)\(_2\) MOF and GrO and the fact that GrO helps Cu\(_3\)(BTC)\(_2\) MOF to prevent such forces. They have also suggested that physisorption and reactive adsorption are the main mechanism of H\(_2\)S retention, at which H\(_2\)S molecules bind chemically to copper metal centers of Cu\(_3\)(BTC)\(_2\) MOF\(^{54}\). A copper-based MOF@GrO was synthesized and tested for toxic gas removal under ambient conditions\(^{53}\). Compared to the parent materials, considerable improvement in gas adsorption was found, which was ascribed to the
physiosorption in the MOFs pore space with strong dispersive forces. Reactivity adsorption was also found as the main mechanism of retention. Huang et al., reported the preparation of Zn$_3$(BTC)$_2$ MOF@GrO for small gas adsorption. They found that physicochemical features of the developed composites were very dependent on GrO content in the prepared composites, and in comparison to the parent MOF, enhanced gas adsorption was recorded over the composites. Xiang and his coworkers found that decoration of Cu$_3$(BTC)$_2$ over CNT surface largely improve the gas separation capacity of Cu$_3$(BTC)$_2$ MOF of CO$_2$/CH$_4$ mixture. Yang et al. reported fabrication of MOF@CNT at which MOF-5 was used as the MOF. They showed that the porosity of the composites was higher than the parent materials and that this led to an enhancement in the hydrogen uptake.

However, synthesis and applications of MOF@GrO and MOF@CNT composites are still a new idea, in comparison to their ample potential prospective applications and there are vast areas of research to find new ways of synthesis and applications of these composites. Besides, superparamagnetic iron oxide magnetic nanoparticles (Fe$_3$O$_4$ MNPs) are not just helpful in magnetic separation of absorbent materials and recovery, but also due to hydroxyl functional groups over their surface, they can be very useful in water remediation and decontamination. Hence, due to highly magnetic and surface chemistry properties of Fe$_3$O$_4$ MNPs and due to synergic effect, its loading over MOF@GrO or MOF@CNT can enhance pollutant adsorption capacity of the hybrid nanocomposites. In addition, there are no previous report regarding to synthesis of Fe$_3$O$_4$/MOF@GrO and Fe$_3$O$_4$/MOF@CNT hybrid nanocomposites and their applications in adsorption of organic pollutants.

As it is mentioned, preparation and application of MOFs, GrO, CNT and Fe$_3$O$_4$ MNPs hybrid nanocomposites is still a new idea, compared to their potential applications. Hence, new
investigations can be helpful in developing new physical and chemical procedures in the synthesis and applications of these hybrid nanocomposites. Further reasons that support the intellectual merit of the project are: (1) in previous studies, MOFs have played the main component in the composites, whereas here we use GrO and CNT as main components along with the addition of various types of $M_3$(BTC)$_2$ MOF; (2) here we present comprehensive instrumental-study over magnetic and non-magnetic MOF@GrO and MOF@CNT hybrid nanocomposites which is missing in many of the previous works. Hence, this study, which uses water and ethanol as solvents, deals with a green, simple and versatile method to synthesize $M_3$(BTC)$_2$@GrO, $M_3$(BTC)$_2$@CNT, Fe$_3$O$_4$/M$_3$(BTC)$_2$@GrO and Fe$_3$O$_4$/M$_3$(BTC)$_2$@CNT nanomaterials to reintroduce and also to generalize concept of magnetic and non-magnetic MOF@GrO and MOF@CNT hybrid nanomaterials by investigating their common physicochemical attributes and features.

In the other words, non-magnetic hybrid nanocomposites based on $M_3$(BTC)$_2$ MOF (M: Ni, Cu, Zn, and Cd) decorated over GrO ($M_3$(BTC)$_2$@GrO) and CNT ($M_3$(BTC)$_2$@CNT) along with magnetic hybrid nanocomposites of Fe$_3$O$_4$/M$_3$(BTC)$_2$@GrO and Fe$_3$O$_4$/M$_3$(BTC)$_2$@CNT are synthesized. The resulting materials were synthesized via a simple green solvothermal method and were characterized by XRD, SEM, TEM, IR, Raman, XPS, TGA, and BET. The as-synthesized smart GrO- and CNT-based nanomaterials were applied as absorbents in removal of methylene blue (MB) as model organic pollutant. Authors believe the current study draw useful criteria in preparation of new class of magnetic and non-magnetic MG and MC hybrid nanomaterials toward specific applications in various pollutants adsorption. This work should also provide a comprehensive knowledge and understanding in terms of the formation of
magnetic and non-magnetic MG and MC compounds and can be used as reference in designing other kind of MOF-based hybrid nanocomposites.

In order to ease following up the synthesized materials, they are labeled by number as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>GrO</td>
<td>1</td>
</tr>
<tr>
<td>Fe₃O₄ MNPs</td>
<td>2</td>
</tr>
<tr>
<td>Ni₆(BTC)₂ MOF</td>
<td>3</td>
</tr>
<tr>
<td>Ni₆(BTC)₂@GrO (ratio 1:2 w/w)</td>
<td>4</td>
</tr>
<tr>
<td>Ni₆(BTC)₂@GrO (ratio 1:1 w/w)</td>
<td>5</td>
</tr>
<tr>
<td>Ni₆(BTC)₂@GrO (ratio 2:1 w/w)</td>
<td>6</td>
</tr>
<tr>
<td>Ni₆(BTC)₂@GrO (ratio 5:1 w/w)</td>
<td>7</td>
</tr>
<tr>
<td>Fe₃O₄/Ni₆(BTC)₂@GrO</td>
<td>8</td>
</tr>
<tr>
<td>Cu₃(BTC)₂ MOF</td>
<td>9</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@GrO (ratio 1:2 w/w)</td>
<td>10</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@GrO (ratio 1:1 w/w)</td>
<td>11</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@GrO (ratio 2:1 w/w)</td>
<td>12</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@GrO (ratio 5:1 w/w)</td>
<td>13</td>
</tr>
<tr>
<td>Fe₃O₄/Cu₃(BTC)₂@GrO</td>
<td>14</td>
</tr>
<tr>
<td>Fe₃O₄@CNT</td>
<td>15</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@CNT (ratio 1:2 w/w)</td>
<td>16</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@CNT (ratio 1:1 w/w)</td>
<td>17</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@CNT (ratio 2:1 w/w)</td>
<td>18</td>
</tr>
<tr>
<td>Cu₃(BTC)₂@CNT (ratio 5:1 w/w)</td>
<td>19</td>
</tr>
<tr>
<td>Fe₃O₄/Cu₃(BTC)₂@CNT</td>
<td>20</td>
</tr>
<tr>
<td>Zn₃(BTC)₂ MOF</td>
<td>21</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@GrO (ratio 1:2 w/w)</td>
<td>22</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@GrO (ratio 1:1 w/w)</td>
<td>23</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@GrO (ratio 2:1 w/w)</td>
<td>24</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@GrO (ratio 5:1 w/w)</td>
<td>25</td>
</tr>
<tr>
<td>Fe₃O₄/Zn₃(BTC)₂@GrO</td>
<td>26</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@CNT (ratio 1:2 w/w)</td>
<td>27</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@CNT (ratio 1:1 w/w)</td>
<td>28</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@CNT (ratio 2:1 w/w)</td>
<td>29</td>
</tr>
<tr>
<td>Zn₃(BTC)₂@CNT (ratio 5:1 w/w)</td>
<td>30</td>
</tr>
<tr>
<td>Fe₃O₄/Zn₃(BTC)₂@CNT</td>
<td>31</td>
</tr>
<tr>
<td>Cd₃(BTC)₂ MOF</td>
<td>32</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@GrO (ratio 1:2 w/w)</td>
<td>33</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@GrO (ratio 1:1 w/w)</td>
<td>34</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@GrO (ratio 2:1 w/w)</td>
<td>35</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@GrO (ratio 5:1 w/w)</td>
<td>36</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@CNT (ratio 1:2 w/w)</td>
<td>37</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@CNT (ratio 1:1 w/w)</td>
<td>38</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@CNT (ratio 2:1 w/w)</td>
<td>39</td>
</tr>
<tr>
<td>Cd₃(BTC)₂@CNT (ratio 5:1 w/w)</td>
<td>40</td>
</tr>
</tbody>
</table>
Chapter 2: Synthesis, Characterization and Pollutant Adsorption Capacity of Ni$_3$(BTC)$_2$ MOF-based Hybrid Nanomaterials

1. Introduction

Novel hybrid nanocomposites based on GrO (1), Fe$_3$O$_4$ MNPs (2) and Ni$_3$(BTC)$_2$ MOF (3) were synthesized, characterized, and implemented as absorbent for organic pollutant adsorption. A simple, versatile, and green solvothermal process using water and ethanol was used for synthesis of the nanomaterials. In this regard, 2 and 3 are decorated over a platform of 1. XRD results confirmed crystallinity of the prepared nanomaterials and successful decoration of 3 over substrate 1. It was also found that intensity of the XRD signals of the hybrid nanocomposites is proportional to the MOF content. Morphological studies show successful formation and growth of needle-shape crystals of 3 over 1. Formation of spherical shape particles of 2 over 1 was also shown by morphological analysis. Chemical studies carried out with IR, Raman and elemental analysis conducted by XPS further verified the successful loading of 2 and 3 over the platform of 1. The prepared hybrid nanomaterials were used as absorbents to remove toxic small molecules, in which MB was used as model organic dye. MB adsorption on the hybrid composites was higher than the parent materials of 1, 2 and 3. The improved dye adsorption capacity of the prepared nanocomposites compared to their parent materials were attributed to synergetic effect of several parameters: suppression of dispersive forces in MOF formation, well dispersion of nanosize scale MOF over a platform of 1, formation of small pores between 3 and the platform. This findings show that the newly developed magnetic and non-magnetic nanocomposites own high capacity of liquid-phase pollutant removal and can be considered as promising candidates for water remediation and small molecules adsorption.
2. Experimental

2.1. Chemicals

The reagent grade quality chemicals were purchased from Acros, Alfa Aesar, Sigma-Aldrich, Fisher, and Tokyo Chemical Industry Companies and were used as received without further purification. Ultrapure water was obtained from Milli-Q® instrument, Millipore Corporation.

2.2. Synthesis of GrO (1)

Compound 1 was prepared from graphite powder via a method previously reported. The chemical and elemental characteristic of the prepared compound are as follows: IR: 1739 cm\(^{-1}\) (C=O stretch), 1615 cm\(^{-1}\) (C=C stretch), and 1229 cm\(^{-1}\) (C-O vibration).

2.3. Synthesis of Fe\(_3\)O\(_4\) MNPs (2)

Compound 2 were synthesized by using chemical co-precipitation method with some modifications. FeSO\(_4\).7H\(_2\)O (5.59 g), FeCl\(_3\) (6.22 g), and hydrochloric acid (12 M, 1.7 mL) were dissolved into 50 mL ultrapure water under N\(_2\) gas flow at ambient temperature. The resulting mixture was added dropwise into a 500 mL NaOH solution (1.5 M) under N\(_2\) atmosphere. After addition of NaOH solution, Fe\(_3\)O\(_4\) NPs precipitate and later were separated from the reaction medium with the help of an external magnetic field. The resulting solid materials were rinsed three times with ultrapure water.

2.4. Synthesis of Ni\(_3\)(BTC)\(_2\) MOF (3)

To synthesize the compound 3, First, NiCl\(_2\).6H\(_2\)O (1.000g, 0.0042mole) was dissolved into deionized water (10 mL) and was mixed with benzene-1,3,5-tricarboxylic acid (BTC) (0.500g, 0.0024mole) dissolved into ethanol (10 mL). The resulting mixture was placed into a glass reactor and tightly sealed. The glass reactor was heated to 383 K for 48 h in an oven. Afterward, the glass reactor was cooled to room temperature. Green solids of 3 were collected and washed.
with ethanol three times. Finally, the resulting solid was dried in a vacuum oven for 12 h and a fine green powder of 3 was obtained. The chemical and elemental characteristic of the prepared compound are as follows: IR: 2980 cm\(^{-1}\) (C-H of the aromatic rings), 1645 and 1614 cm\(^{-1}\) (asymmetric vibrations in -CO\(_2\)-), 1110 cm\(^{-1}\) related to C–O–Ni.

2.5. Synthesis of Ni\(_3\)(BTC)\(_2\)@GrO Hybrid Nanocomposites (4-7)

To fabricate 4-7 hybrid nanostructures, the following procedure was carried out: first, a suspension of 1 in an ethanol:water mixture with ratio of 2:1 (v/v) was prepared via vigorous sonication for 1 h in an ice bath. A solution of NiCl\(_2\).6H\(_2\)O and BTC in an ethanol:water mixture with ratio of 2:1 (v/v) was prepared separately. Afterwards, the nickel solution was added to the suspension of 1 and sonicated in a 500W horn sonicator for 15 min to place metal ions onto the 1 sheets. Then, the BTC solution was added to the above solution and sonicated for 10 min. The resulting mixture was placed into glass reactor and then was sealed. Then, the glass reactor was heated to 383 K for 48 h in an oven. Afterward, the glass reactor was cooled to room temperature. Black solids of 1- and 3-based hybrid nanomaterials were collected and washed with ethanol three times. Finally, the resulting solids were dried in a vacuum oven for 12 h and fine dark black powders were obtained. Four different types of 1- and 3-based hybrid nanocomposites were synthesized depending on 1 and 3 weight ratio as follows: 1:2 (4), 1:1 (5), 2:1 (6) and 5:1 (7).

2.6. Synthesis of Fe\(_3\)O\(_4\)/Ni\(_3\)(BTC)\(_2\)@GrO Hybrid Nanocomposite (8)

The synthetic procedure for 8 hybrid nanostructure is as follows: first, a suspension of 5 (5 mg/ml) was prepared by sonication of the powder in deionized water at room temperature for 1 h in an ice bath. Then, the suspension was purged under N\(_2\) gas for 30 min to remove oxygen from the suspension. Then, a solution made of FeCl\(_3\).6H\(_2\)O (0.5 g) and FeCl\(_2\).4H\(_2\)O (0.25 g) dissolved
into 20 mL deionized water was added to the 5 suspension under purging with N$_2$ gas. After stirring for 30 min, 3 ml of 25% NH$_4$OH solution was quickly and in one portion injected into the mixture and followed by stirring for 30 min at room temperature. The black solid precipitate of 8 was collected by an external magnet, washed three times with deionized water and dried in vacuum oven at room temperature overnight.

2.7. Characterization of the Prepared Samples

Crystalline powder of the prepared samples was analyzed 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). The IR spectroscopy was performed on PerkinElmer® Universal ATR instrument, which data were collected in range of 650–4000 cm$^{-1}$. XPS test was monitored by Omicron XPS/UPS system with Argus detector which uses Omicron's DAR 400 dual Mg/Al X-ray source. The extent of MB after its treatment with the absorbents was measured through on a Shimadzu UV-1800 UV-vis spectroscopy.

2.8. Pollutant Adsorption Experiments

Dye adsorption experiments were conducted on a cationic dye methylene blue (MB) as model organic pollutant. For this purpose, 5 mg of the absorbents were treated with 10 ml of MB and the resulting mixture was sonicated in a 400W horn sonicator for 30 min. The non-magnetic absorbents were centrifuged and the magnetic absorbents were magnetically separated from the suspension. The remaining MB concentration was analyzed by UV-vis spectroscopy to monitor the extent of dye absorption.

The adsorption capacity (Q$_e$) of the prepared hybrid nanomaterials was calculated using Eq. 1 as follows:
\[
Q_e = (C_0 - C_e/m) \times V 
\]

(1)

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

3. Results and Discussion

3.1. Crystalline Structure

XRD patterns of the prepared hybrid nanocomposites of 4-7 with various 1 and 3 content are shown in Fig. 2.1. The peak around \(2\theta = 11-13\) is attributed to 1 and the distance between carbon layers in graphene (9.5Å), as determined using Bragg’s law\(^{47}\), which overlap with some 3 signals in this area.

![Figure 2.1 XRD patterns of the prepared 3 and 4-7 hybrid nanomaterials with different ratio between 1 and 3.](image)

The corresponding peaks of the 4-7 hybrid nanomaterials is consistent with compound 3 pattern\(^{59,60}\), which verifies successful formation and growth of 3 over a platform of 1. These results prove that a platform of 1 does not prevent formation of 3 by blocking the linkage of
nickel dimers and the BTC organic linker. This findings illustrate that hybrid nanomaterials with higher MOF content show relatively higher intensity in signals\textsuperscript{52-54}, which derives from higher 3 formation and loading over 1. Additionally, a shift in the position of the peaks was found meaning that chemical bonding between the precursors exist\textsuperscript{55,56}.

### 3.2. Morphological Characteristic

Morphology of the prepared hybrid nanomaterials and their parent materials are characterized by SEM and TEM electron microscopes, which the corresponding images are shown in Fig. 2.2 and Fig. 2.3, respectively. The prepared compound 3 show uniform needle-shape structure, (Fig. 2.2a and b)\textsuperscript{62} while 2 has particles in a spherical shape with slight agglomeration (Fig. 2.2c and d)\textsuperscript{61}. SEM micrographs show successful synthesis of 1 nanolayers through exfoliation of graphite oxide (Fig. 2.2e and f)\textsuperscript{47}, where the exfoliated layers are stacked together in the dried sample. Regarding the hybrid 4 nanocomposite, SEM images demonstrate successful formation and growth of the 3 nanoparticles over the 1 platform, as the particles are decorated over the platform (Fig. 2.2g and h).

Furthermore, TEM images confirm successful synthesis of 4 and 8 hybrid nanomaterials and their parent materials as shown in Fig. 2.3. SEM morphological findings of 2 are verified by TEM images which show slightly agglomerated spherical nanoparticles (Fig. 2.3a and b). Images related to 1 show successful synthesis and exfoliation of nanolayers, in which very thin nanolayers are formed (Fig. 2.3c and d). Successful formation of growth of 3 over the platform of 1 is also observed by TEM (Fig. 2.3e and f) which confirm XRD and SEM results.
Figure 2.2 SEM images of 3 (a,b), 2 (c,d), 1 (e,f), and 4 (g,h).
Figure 2.3 TEM images of 2 (a,b), 1 (c,d), 4 (e,f), and 8 (g,h).
Well dispersed needle-shape nanoparticles are formed and decorated over 1. Presence of 1 layers during the 3 formation and growth leads to nano-sized 3 which may be beneficial for small molecule adsorption due to increased dispersive forces in the MOFs caused by the presence of 1, suppressing MOF aggregation and formation of small pores between 1 and 3 (Fig. 2.3e and f). It is hypothesized that due to in situ formation of 3 through the precursors of Ni and BTC, 3 is formed and grew over 1 layers through chemical bonding between the functionalities of 3 and 1, which result is separation of the layers of 1 and prevent their stacking\textsuperscript{52-54}. Furthermore, TEM findings (Fig. 2.3g and h) show successful loading of 2 over the substrate 1.

3.3. Elemental Analysis

Elemental composition of the prepared hybrid nanocomposite of 8 was investigated via XPS analysis, the corresponding results are shown in Fig. 2.4, where the corresponding signals related to C, O, Fe, and Ni are observed as follows: C1s at 285 eV, O1s at 531 eV, Fe2p\textsubscript{3/2} at 711 and 725 eV, and Ni2p\textsubscript{3/2} at 851, 856, 861, and 873eV\textsuperscript{48,59,63}. Observations of these peaks show successful synthesis and decoration of 2 and 3 over the platform 1. XPS findings are also in agreement with XRD pattern and morphological results and successful compositing of the parent materials.
Figure 2.4 XPS results of the prepared hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, (d): Fe2p, and (e): Ni2p.
3.4. IR Analysis

To further verify successful synthesis and decoration of 3 nanoparticles over 1 platform and the chemical properties of the bonds, chemical analysis was done by IR (Fig. 2.5). Characteristic signals of 1 are observed at around 3195 cm\(^{-1}\), 1739 cm\(^{-1}\), 1615 cm\(^{-1}\), and 1229 cm\(^{-1}\) related to O-H, C=O, C=C and C-O vibrations, respectively\(^{47}\). 3 show peaks at around 3396 cm\(^{-1}\) (O-H); 2980 cm\(^{-1}\) (C-H of the aromatic rings); 2976 cm\(^{-1}\) (asymmetric CH in -CH\(_2\)-); 2945 cm\(^{-1}\) (symmetric CH in -CH\(_2\)-); 1645 and 1614 cm\(^{-1}\) (asymmetric vibrations in -CO\(_2\)-); 1440 and 1370 cm\(^{-1}\) corresponding to the asymmetric and symmetric stretching vibrations of the BTC carboxylate groups, respectively, 1110 cm\(^{-1}\) related to C–O–Ni vibration in 3, and 775 and 722 cm\(^{-1}\) related to the nickel substitution in BTC’s benzene groups\(^{50}\). The presence of these characteristic peaks provides clear evidence of the successful formation of the MOF and its loading over 1 platform. Chemical bonding between the parent materials in the hybrid nanocomposites was confirmed by the relative shift of the signals. Intensities of the peaks at 1645/1614 cm\(^{-1}\) and 1440/1370 cm\(^{-1}\) are changed in the hybrid nanomaterials which might be due to variation of the environment of the BTC’s carboxylate ligands. An explanation for this phenomenon can be the interactions between BTC ligands and functional groups of 1 platform, as well as distortion in the structure of 3 deriving from the introduction of 1. It is also found that increase in the concentration of 3 in the 4-7 hybrid nanocomposites result in intensified corresponding signals of the MOF.
Figure 2.5 IR spectra of 1, 3, and 4-6 hybrid nanomaterials with different ratio between 1 and 3.

3.5. Methylene Blue (MB) Adsorption

Dye adsorption capacity of the newly developed 4 and 8 hybrid nanocomposites and the corresponding parent materials was tested over adsorption of MO as a model organic dye. The adsorption results are shown in Table 2.1.

Based on these findings, the 4 hybrid nanocomposite show superior pollutant removal compared to that of the parent materials. In this respect, the MB adsorption capacity of 4 was several times higher than that of 3 and 1. The magnetic 8 hybrid nanocomposite shows a relatively high dye adsorption capacity. Enhanced dye adsorption capacity of the hybrid nanomaterials compared to the parent materials derives from the synergetic effect of mixing them. In overall, our findings show that the newly developed 5 and 8 can be synthesized through
a simple and versatile green synthetic method and are a promising candidate for water remediation and adsorption of small molecules.

Table 2.1 Measured MB dye adsorption capacities of the hybrid nanocomposites and the corresponding parent materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Q_e$ (mg g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
<td>This work</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
<td>This work</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>This work</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>This work</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>31</td>
<td>66</td>
</tr>
<tr>
<td>Cu$_3$(BTC)$_2$</td>
<td>30</td>
<td>67</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@Cu$_3$(BTC)$_2$</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>MOF-235</td>
<td>187</td>
<td>32</td>
</tr>
<tr>
<td>MIL-101</td>
<td>21</td>
<td>68</td>
</tr>
</tbody>
</table>

4. Conclusion

Compound 3 with different concentration and 2 were successfully decorated over layers of 1 through chemical bonding. Crystalline structure of the prepared hybrid nanomaterials was confirmed through XRD patterns. Morphological investigations also verified successful loading of 2 and 3 over the 1 platform. Chemical studies showed chemical interaction and bonding between the parent materials in the 4-7 hybrid nanocomposites. The prepared hybrid nanocomposites showed a very promising dye removal adsorption capacity which derives from synergetic effect of compositing 1, 2, and 3.
Chapter 3: Synthesis, Characterization and Pollutant Adsorption Capacity of Cu$_3$(BTC)$_2$ MOF-based Hybrid Nanomaterials

3.1 Introduction

In the current study, hybrid nanocomposites based on Cu$_3$(BTC)$_2$MOF (9), Fe$_3$O$_4$ MNPs (2), GrO (1), and CNTs (15) were developed via a simple solvothermal method in which 1 and 15 were used as platforms to grow nanostructured 2 and 9. The as-synthesized nanocomposites were characterized by XRD, SEM, TEM, IR, Raman, XPS, TGA and BET techniques. Morphological analysis confirmed successful growth of 2 and 9 nanoparticles over platforms of 1 and 15. XRD results exhibit highly crystalline structure for the prepared hybrid nanocomposite. Chemical and elemental analysis verified chemical structure and successful compositing of the parent materials. N$_2$ absorption-desorption isotherms showed high specific surface area for 9. TGA experiments further confirm successful loading of 2 and 9 over 1 and 15 substrates. Furthermore, the adsorption capacity of the prepared hybrid nanocomposites was examined over methylene blue (MB) as a model organic pollutant. A large improvement in adsorption capacity of the hybrid composites compared to that of parent materials was recorded. The improved dye adsorption capacity of the prepared nanocomposites were attributed to synergetic effect of parent materials combining which lead to different physicochemical properties of the MOF, suppression of aggregation and dispersive forces in MOF formation, different morphology, smaller size of the MOF, and formation of small pores between MOF and the platforms. In overall, it is proposed that due to promising features of the synthesized nanocomposites, they can be excellent candidates for a variety of potential applications in environmental applications such as water remediation and gas purification.
3.2 Experimental

3.2.1 Chemicals

The reagent grade quality chemicals were purchased from Acros, Alfa Aesar, Sigma-Aldrich, Fisher, and Tokyo Chemical Industry Companies and were used as received without further purification. Ultrapure water was obtained from Milli-Q® instrument, Millipore Corporation.

3.2.2 Synthesis of GrO (1)

The procedure to synthesize compound 1 is explained in the second chapter.

3.2.3 Synthesis of Fe₃O₄ MNPs (2)

Synthetic procedure of compound 2 is explained in the second chapter.

3.2.4 Synthesis of Cu₃(BTC)₂ MOF (9)

To synthesize the compound 9, Cu(NO₃)₂·3H₂O (1.000g, 0.0041mol) was dissolved into deionized water (10 mL) and was mixed with benzene-1,3,5-tricarboxylic acid (BTC) (0.500g, 0.0024mol) dissolved into ethanol (10 mL). The resulting mixture was placed into a glass reactor and sealed. The glass reactor was heated to 383 K for 48 h in an oven. Afterward, the glass reactor was cooled to room temperature. Blue solids of 9 were collected and washed three times with ethanol. Finally, the resulting solid was dried in a vacuum oven for 12 h and a fine blue powder of 9 was obtained. The chemical and elemental characteristic of the prepared compound are as follows: IR: 1739 cm⁻¹ (C=O stretch), 2980 cm⁻¹ (C-H of the aromatic rings); 1640 and 1590 cm⁻¹ (asymmetric vibrations in -CO₂-); 1110 cm⁻¹ related to C–O–Cu vibration.

3.2.5 Synthesis of Cu₃(BTC)₂@GrO Hybrid Nanocomposites (10-13)

To synthesize the 10-13 hybrid nanostructures, the following procedure was carried out: A suspension of 1 in ethanol:water mixture with ratio of 2:1 (v:v) was prepared via sonication in a 500W horn sonicator for 1 h in an ice bath. Second, a solution of Cu(NO₃)₂·3H₂O and BTC was
prepared separately in an ethanol:water mixture with ratio of 2:1 (v:v). The copper solution was added to the suspension of 1 and sonicated for 15 min to place metal ions onto the sheets of 1. Then, the BTC solution was added to the above solution and sonicated for 10 min. The resulting mixture was placed into glass reactor and sealed. The glass reactor was heated to 383 K for 48 h in an oven. Subsequently, the glass reactor was cooled to room temperature. Black solids of 1- and 9-based hybrid nanocomposites was collected and washed three times with ethanol. Finally, the resulting solid was dried in a vacuum oven for 12 h and fine dark black powder of 1- and 9-based hybrid nanocomposites were obtained. Four different types of 1- and 9-based hybrid nanocomposites were synthesized depending on 1 and 9 ratio: 1:2 (10), 1:1 (11), 2:1 (12) and 5:1 (13).

3.2.6 Synthesis Cu₃(BTC)₂@CNT Hybrid Nanocomposites (16-19)

The same procedure for the preparation of 10-13 was followed with the exception that instead of 1, functionalized CNTs (15) were used. 15 were prepared by treatment of pristine CNTs by H₂SO₄:HNO₃ 3:1 mixture at room temperature for 6 h. Four different types of 9- and 15-based hybrid nanocomposites were synthesized depending on 9 and 15 ratio: 1:2 (16), 1:1 (17), 2:1 (18) and 5:1 (19).

3.2.7 Synthesis Fe₃O₄/Cu₃(BTC)₂@GrO Hybrid Nanocomposite (14)

The synthesis procedure of 14 hybrid nanostructure is as follows: first, a suspension of 10 (5 mg/ml) was prepared by sonication of 10 in deionized water at room temperature for 1 h in an ice bath. Then the suspension was purged under N₂ gas for 30 min to remove oxygen from the solution. Then a solution containing FeCl₃.6H₂O (0.5 g) and FeCl₂.4H₂O (0.25 g) dissolved into 10 mL deionized water was added to the 10 suspension under N₂ gas purging. After stirring for 30 min, 3 ml of 25% NH₄OH solution was quickly and in one portion injected into the mixture
and stirred for 30 min at room temperature. The black solid precipitates of 14 were collected by an external magnet and washed three times with deionized water and dried in vacuum oven at room temperature overnight.

### 3.2.8 Synthesis Fe₃O₄/Cu₃(BTC)₂@CNT Hybrid Nanocomposites (20)

To prepare 20, the same procedure for preparation of 14 was used followed with the exception that 10 was replaced by 16.

### 3.2.9 Characterization of the Prepared Samples

Crystalline phases of the prepared samples were analyzed by X-ray powder diffractometer (XRD, Bruker D8 Discover X-ray Diffractometer). The morphology was studied 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). The IR spectroscopy was performed on a PerkinElmer® Universal ATR instrument in the 650–4000 cm⁻¹ range. Raman spectra of the samples were collected from DXR™ Raman Microscope, Thermo Scientific. Thermogravimetric Analysis (TGA) data was obtained by using Q50 TGA instrument, Universal V4.5A TA Instruments. Pore volume and Brunauer–Emmett–Teller (BET) surface area of the materials were analyzed through N₂ adsorption/desorption isotherms with micromeritics surface area and porosity analyzer (ASAP 2020). XPS test was monitored by Omicron XPS/UPS system with Argus detector which uses Omicron's DAR 400 dual Mg/Al X-ray source. The extent of MB after its treatment with the absorbents was measured through on Shimadzu UV-1800 UV-cis spectroscopy.

### 3.2.10 Pollutant Adsorption Experiments

Dye adsorption experiments were conducted on methylene blue (MB) as an organic pollutant model. In this regard, 5 mg of the absorbents were treated with 10 ml of MB with known
concentration and the resulting mixture was sonicated in a 400W horn sonicator for 30 min. The non-magnetic absorbents were centrifuged and the magnetic absorbents were magnetically separated from the suspension. The remaining MB concentration was analyzed by UV-vis spectra in order to monitor the amount of dye absorption.

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

$$Q_e = (C_0 - C_e/m) \times V$$

(1)

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

### 3.3 Results and Discussion

#### 3.3.1 Crystalline Structure

Crystalline structure of the synthesized hybrid 10-13 and 16-19 hybrid nanocomposites was determined by XRD technique as shown in Fig. 3.1. According to our findings, the relative intensities and position of all the peaks are consistent with the standard XRD pattern of 1, 9 and 15, also highly crystalline structure of the synthesized hybrid nanomaterials are observed. Diffraction peaks for 16-19 samples show that the sketch of the 9 and 15 crystals are retained, since almost all the diffraction signals of 9 and 15 can be readily indexed, which show successful synthesis of the nanocomposites. In the case of 10-13 hybrid nanocomposites, the d002 peak related to 1 is not observed for the hybrid nanocomposites. Reason for this phenomenon might correspond to high exfoliation and dispersion of 1 during the nanocomposites preparation. It was also found that presence 1 and 15 did not disturb formation of 9, and hence, we can hypothesize that 1 and 15 do not prevent formation of the MOF through linkage of copper dimers and BTC as
an organic linker. We also found that the intensity of the peaks in 9 become slightly weaker as the 1 and 15 content of the samples raise\textsuperscript{54}.

**Figure 3.1** XRD patterns of the prepared (a) 10-13 and (b) 16-19 hybrid nanomaterials with different ratio between the parent materials.
3.3.2 Morphological Characteristic

The morphology of the synthesized 1-, 9- and 15-based hybrid nanocomposites was characterized by SEM and TEM microscopies, the resulting images are illustrated in Fig. 3.2 and Fig. 3.3, respectively. According to the SEM and TEM images, the synthesized compound 9 (Fig. 3.2a and b and Fig. 3.3a and b) is made of large pyramid-shape particles in size of tens of microns. Results indicate that in situ synthesis of 9 in presence of 1, very small MOF nanoparticles form and load over the platform as shown in Fig. 3.2e and f and Fig. 3.3c and d. Presence of layers of 1 during the formation of 9 leads to nano-size 9 which may be beneficial for small molecules adsorption as result of increased dispersive forces in the MOFs due to the presence of 1, suppressing the MOF aggregation and formation of small pores between 1 and 9. Furthermore, we found that in situ synthesis of 9 over 1 prevent formation of distorted layers and densely packed 1 agglomerates, which is in accordance with XRD results. We hypothesize that there is alternation between MOF units and graphene layers, which due to presence of MOF precursors and in situ formation of MOF over 1. Copper ions in the solution can either react with oxygen-containing groups in BTC ligands or in 1 to form crystals of 9. Additionally, due to steric hindrance, charge-charge interaction as well as presence of intercalation, 1 layers coated with MOF are well-exfoliated which is very beneficial for small molecules adsorption. Furthermore, it is noteworthy to compare bare 9, in-situ synthesis of 9 in presence of 1 platform results in formation of the MOF with nanoscale size. Presence of 1 and 15 platforms help 9 to prevent aggregation plus to forming in nanosize, which in overall lead to the MOF with higher pore volume (next section) which is very important for the application of MOF as absorbent.
**Figure 3.2** SEM images of 9 (a,b), 1 (c,d), 10 (e,f), 14 (g,h), 15 (i,j), and 16 (k,l).

Fig. 3.2k and l and Fig. 3.3g show that like 10, in situ synthesis of 9 in presence of 15 result in the formation of 9 nanoparticles decorated over 15 platform\(^4\). Furthermore, we found that addition of 2 to 10 and 16 through co-precipitation method, leads to decoration of 1 and 15 platforms with 2 and successful synthesis of 14 (Fig. 3.2g and h and Fig. 3.3e and f) and 20 hybrid nanomaterials (Fig. 3.3h).
Figure 3.3 TEM images of 9 (a,b), 10 (c,d), 14 (e,f), 16 (g), and 20 (h).
3.3.3 Elemental Analysis

XPS measurement was carried out to confirm elemental composition of the surface of the newly developed 14 hybrid. The corresponding results are shown in Fig. 3.4. The signals observed at around 931, 941, 953, and 962 eV correspond to electrons in Cu2p3/2 \(^{48}\). The binding energy for O1s is observed at around 530 eV which corresponds to O\(^{2+}\) ions in crystalline network of the samples \(^{48}\). The peak at 285 eV corresponds to C 1s and Fe signals at 711 and 725 eV are related to Fe2p3/2 \(^{63}\). Our findings are in good agreement with previous results \(^{71}\) and suggest successful decoration of 2 and 9 over 1 platform.
Figure 3.4 XPS result of the prepared 14 hybrid nanocomposites. (a): survey, (b): C1s, (c): O1s, (d): Fe2p, and (e): Cu2p.
3.3.4 Chemical Studies: IR & Raman

Fig. 3.5 demonstrates IR spectra of the prepared hybrid nanomaterials 1, 9, and 10-13 with different ratio between the starting materials.

The characteristic peaks of 1 are 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 vibration).\(^{47}\) Compound 9 exhibits major signals of 3392 cm\(^{-1}\) (O-H or –OH deriving from coordinated or absorbed water molecules); 2980 cm\(^{-1}\) (C-H of the aromatic rings); 2950 cm\(^{-1}\) (asymmetric CH in -CH\(_2\)-); 2890 cm\(^{-1}\) (symmetric CH in -CH\(_2\)-); 1730 cm\(^{-1}\) (C=O stretch); 1640 and 1590 cm\(^{-1}\) (asymmetric vibrations in -CO\(_2\)-); 1455 and 1370 cm\(^{-1}\) corresponding to the asymmetric and symmetric stretching vibrations of the BTC carboxylate groups, respectively, 1110 cm\(^{-1}\) related to C–O–Cu vibration in 9, and 729 and 760 cm\(^{-1}\) related to metal copper substitution in BTC’s benzene groups\(^{37,38}\). The presence of these characteristic peaks provides clear evidence of the successful synthesis of 9.

IR spectra of the hybrid nanocomposites of 10-13 with different ratio of 1 to 9, show characteristic peaks of both the MOF and the platform do exist in the spectra, which confirm successful synthesis of the hybrid nanocomposites\(^{53}\). The changes in the intensities of the peaks at 1640/1590 cm\(^{-1}\) and 1455/1370 cm\(^{-1}\) can be ascribed to variations in the environment of the BTC’s carboxylate ligands. A feasible explanation for this phenomenon can be the interactions between these ligands and functional groups of 1, as well as distortion in the structure of 9 resulting from introduction of 1. As it is obvious in Fig. 3.5, the characteristic peaks of all the components in the prepared 10-13 hybrid nanocomposites exist in the final hybrid product, which confirms successful synthesis of them (Fig. 3.5). Additionally, we found that by increasing the
concentration of the MOF, the intensity of relevant signals for increases which leads to this conclusion that more MOFs are loaded over the platform at higher concentration of the MOF.

![Figure 3.5](image)

**Figure 3.5** IR spectra of 1, 9, and 10-13 hybrid nanocomposites with different ratio between 1 and 9.

**Fig. 3.6** shows the Raman spectra of the prepared 9, 10, 15, and 16. Spectrum of the MOF shows characteristic peaks of 9 as previously reported. Compound 1 and 15 show double peaks of the D and G bands around 1350 and 1600 cm\(^{-1}\), and 450 and 790 cm\(^{-1}\), respectively. The G band is typically assigned to E\(_{2g}\) phonon of sp\(^2\) carbon atoms, whereas D band is attributed to κ-point phonons of A\(_{1g}\) symmetry. In other words, G-band is a characteristic attribute of graphitic layers which corresponds to carbon atoms tangential vibration, and D-band is typical sign of defect in graphitic structure. According to **Fig. 3.6**, spectra of the hybrid nanocomposite not only
retain major characteristic peaks of 9, but also contain G band and D band of 9 and 15. The resulting magnetic and non-magnetic 10 and 16 hybrid nanocomposites retain 1 and 15 double peaks with some shift due to presence of 2 and 9, which is a good evidence of successful synthesis of those nanocomposites.

![Raman spectra](image)

**Figure 3.6** Raman spectra of (a): 9 and 10, and (b): 15 and 16.

### 3.3.5 Thermogravimetric Analysis (TGA)

TGA provide useful information regarding to thermal stability of materials, which can be linked to the chemistry of the materials. The TGA curves for the parent materials and the composites are presented in Fig. 3.7. There is a sharp weight drop in the samples at around 110 °C, which is related to dehydration of the absorbed moisture and/or coordinated water molecules. TGA analysis undertaken for the 10-13 and 14 hybrid nanocomposites, are very similar to those of their parent materials except to absence of epoxy groups. In fact, this phenomenon may be related to the binding of the MOF through metal centers to the epoxy groups of 1 and 15. In the case of 14, after small mass loss, the curve remains steady and a large portion of the original
mass remains undecomposed, this mass is attributed to 2. In overall, TGA analysis further support successful loading of 2 and 9 over the 1 platform.

![TGA results of 1, 2, 9, 11 and 14 hybrid nanocomposites.](image)

**Figure 3.7** TGA results of 1, 2, 9, 11 and 14 hybrid nanocomposites.

### 3.3.6 N<sub>2</sub> Adsorption/Desorption Isotherms

N<sub>2</sub> isotherms, surface area and pore volume analysis of the prepared samples were also performed and the results are shown in Fig. 3.8 and in Table 3.1. Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore size of 13, 14 and 19 hybrid nanocomposites and their parent materials were determined and the corresponding results are shown in Table 3.1. According to the resulting data, 2 shows BET surface area of 50 m<sup>2</sup>g<sup>-1</sup>, which is a good surface area for metal-oxide nanoparticles. A specific surface area of ~508 m<sup>2</sup>g<sup>-1</sup> and 123 m<sup>2</sup>g<sup>-1</sup> was found for 13 and 19, respectively, which is relatively high compared to the parent materials. The
data also shows that hybrid nanocomposites were successfully made and they are not physical mixture of the parent materials.

![Figure 3.8](image)

**Figure 3.8** N$_2$ isotherms of parent 9 and hybrid nanocomposites of 13 and 19.

Additionally, we found that the 13 hybrid nanocomposites show higher pore volume (P$_{vol}$) than that of bare 9. The large surface area and high porosity of the prepared hybrid nanomaterials provide many channels for the pollutants and favor their migration into the hybrid nanomaterials which consequently higher adsorption capacity is expected for the hybrid nanomaterials compared to that of their parent components.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S$_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>P$_{vol}$ [cm$^3$ g$^{-1}$]</th>
<th>P$_{diam}$ [nm]</th>
<th>P$_{size}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>55.770</td>
<td>0.072</td>
<td>3.90</td>
<td>107.6</td>
</tr>
<tr>
<td>9</td>
<td>856.00</td>
<td>0.031</td>
<td>2.55</td>
<td>7.000</td>
</tr>
<tr>
<td>13</td>
<td>507.70</td>
<td>0.048</td>
<td>4.20</td>
<td>11.80</td>
</tr>
<tr>
<td>14</td>
<td>176.14</td>
<td>0.360</td>
<td>8.31</td>
<td>34.10</td>
</tr>
<tr>
<td>19</td>
<td>123.25</td>
<td>0.081</td>
<td>4.05</td>
<td>48.70</td>
</tr>
</tbody>
</table>

**Table 3.1** BET specific surface area ($S_{BET}$), pore volume ($P_{vol}$), average pore diameter ($P_{diam}$), and particle size ($P_{size}$) of the prepared 2, 9, 13, 14, and 19.
3.3.7 Methylene blue (MB) Adsorption

Pollutant adsorption capacity of the prepared hybrid nanomaterials was tested through MB dye adsorption (Table 3.2). The newly developed hybrid nanocomposites of 10 and 14 illustrate significantly higher dye adsorption capacity in comparison to their parent materials. The vast improvement of the newly developed hybrid nanocomposites was attributed to the small size of the 9 particles, suppression of dispersive forces and well-separation of the MOFs, preventing distortion and bundling in 1 and 15, and to the synergetic effect of combining the parent materials. We also propose that due to the functional groups of the prepared composites which carry negative charge in neutral environment and positive charge of MB, adsorption mechanism between MB and the composite nanomaterials to be hydrophobic and/or π-π interactions, which is in agreement with previous literature\(^{50}\).

Table 3.2 MB adsorption capacity of the prepared absorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Qe (mg g(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
<td>This work</td>
</tr>
<tr>
<td>9</td>
<td>58</td>
<td>This work</td>
</tr>
<tr>
<td>10</td>
<td>163</td>
<td>This work</td>
</tr>
<tr>
<td>14</td>
<td>88</td>
<td>This work</td>
</tr>
<tr>
<td>15</td>
<td>144</td>
<td>This work</td>
</tr>
<tr>
<td>17</td>
<td>89</td>
<td>This work</td>
</tr>
<tr>
<td>20</td>
<td>29</td>
<td>This work</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>31</td>
<td>66</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>Cu(_3)(BTC)(_2)</td>
<td>30</td>
<td>67</td>
</tr>
<tr>
<td>Fe(_3)O(_4)@Cu(_3)(BTC)(_2)</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>MOF-235</td>
<td>187</td>
<td>32</td>
</tr>
<tr>
<td>MIL-101</td>
<td>21</td>
<td>68</td>
</tr>
</tbody>
</table>

3.4 Conclusion

The purpose of the current project was to make hybrid composites of 1, 2, 9, and 15, to fabricate novel nanomaterials of 10-14 and 16-20 with high potential MB pollutant removal. In this regard, a series of 2 and 9 were loaded over 1 and 15 surface via a simple solvothermal process accompanied with a co-precipitation method and the prepared hybrid nanocomposites
are characterized by XRD, SEM, TEM, IR, Raman, XPS, TGA, and BET. XRD results show highly crystalline structure of 10-13 and 16-19 nanocomposites. Morphological, elemental and chemical studies confirmed presence of 1, 2, 9, and 15 in the hybrid nanomaterials. BET surface area analysis verifies highly porous nature of 10 and 16 hybrid nanomaterials with ample improvement in the $V_m$ of 9. Removal of MB as model organic pollutant was considerably higher on the hybrid nanocomposites than their parent materials. Significantly improved dye adsorption capacity of the composite nanomaterials was ascribed to the small size of the particles of 9, suppression of dispersive forces and well-separation of the MOFs, preventing stacking and bundling in 1 and 15, and to the synergetic effect. In total, we found that the newly developed hybrid nanocomposites of 1, 2, 9, and 15 parent materials have great potential for wastewater purification with large unexplored environmental applications.
Chapter 4: Synthesis, Characterization and Pollutant Adsorption Capacity of 
Zn₃(BTC)₂ MOF-based Hybrid Nanomaterials

1. Introduction

A series of hybrid nanocomposites of Zn₃(BTC)₂ MOF (21) decorated GrO (1) and CNTs (15) are synthesized via a simple solvothermal method. The prepared nanomaterials are used as absorbents for organic pollutant adsorption. Furthermore, in order to easily separate absorbent from liquid media through an applied external magnetic field, Fe₃O₄ MNPs (2) were loaded over above-mentioned hybrid nanocomposites and the novel hybrid nanomaterials of 26 and 31 were developed. The as synthesized hybrid nanocomposites were characterized by XRD, SEM, TEM, IR, Raman, XPS, and TGA techniques. XRD results confirmed high crystalline structures of the prepared samples. Morphological and elemental studies also verified successful decoration of 2 and 21 over platforms of 1 and 15. Chemical analysis collected through IR and Raman, and thermal analysis monitored through TGA technique showed the presence of all the components in the hybrid nanomaterials. Methylene blue (MB) was used as model organic pollutant to analyze potential application of the prepared hybrid nanomaterials as absorbent. The enhanced adsorption was observed in the case of hybrid nanomaterials compared to that of parent 21, which the reason for this might be due to new 21 features: different physicochemical properties, suppression of aggregation, increased dispersive forces, different morphology, smaller size, and the formation of small pores between MOF and the platforms. In overall, the newly developed adsorbents combine the advantages of 1, 2, 15 and 21 and due to low cost, large adsorption capacity, and easy separation of the adsorbents (solid phase) can be good candidates for water remediation.
2. Experimental

2.1. Chemicals

The reagent grade quality chemicals were purchased from Sigma-Aldrich, Fisher, and Tokyo Chemical Industry Companies and were used as received without further purification. Ultrapure water was obtained from Milli-Q® instrument, Millipore Corporation.

2.2. Synthesis of GrO (1)

Synthetic procedure of 1 is explained in the second chapter.

2.3. Synthesis of Fe₃O₄ MNPs (2)

Synthetic procedure of 2 is explained in the second chapter.

2.4. Synthesis of Zn₃(BTC)₂ MOF (21)

To synthesize 21, Zn(NO₃)₂·6H₂O (1.000g, 0.004mole) was dissolved into deionized water (10 mL) and was mixed with benzene-1,3,5-tricarboxylic acid (BTC) (0.500g, 0.0024mole) dissolved into ethanol (10 mL). The resulting mixture was placed into a glass reactor and sealed. Then, the glass reactor was heated to 383 K for 48 h in an oven. Afterwards, the glass reactor was cooled to room temperature. White solids of 21 were collected and washed three times with ethanol. Finally, the resulting solid was dried for 12 h and a fine white powder of 21 was obtained. The chemical and elemental characteristic of the prepared compound are as follows: IR: 3370 cm⁻¹, 1739 cm⁻¹, 1615 cm⁻¹, and 1229 cm⁻¹ deriving from vibration of O-H, C=O, C=C, and C-O, respectively.

2.5. Synthesis of Zn₃(BTC)₂@GrO Hybrid Nanocomposites (22-25)

To synthesize 22-25 hybrid nanostructures, the following procedure was carried out: A suspension of 1 in ethanol:water mixture with ratio of 2:1 (v:v) was prepared via sonication in a 500W horn sonicator for 1 h in ice bath. A solution of Zn(NO₃)₂·6H₂O and BTC was prepared
separately in ethanol:water mixture with ratio of 2:1. Afterward, zinc solution was added to a suspension of 1 and vigorously sonicated for 15 min to place metal ions onto sheets of 1. Then, the BTC solution was added to the above solution and sonicated for 10 min. The resulting mixture was placed into glass reactor and sealed. The glass reactor was heated to 383 K for 48 h in an oven. Afterward, the glass reactor was cooled to room temperature. Black solids of 1- and 21-based hybrid nanomaterials were collected and washed three times with ethanol. Finally, the resulting solid was dried in an oven for 12 h and a fine dark black powder of 1- and 21-based hybrid nanomaterials was obtained. Four different types of 1- and 21-based hybrid nanomaterials were synthesized depending on 1 and 21 ratio: 1:2 (22), 1:1 (23), 2:1 (24) and 5:1 (25).

2.6. Synthesis of Zn$_3$(BTC)$_2$@CNT Hybrid Nanocomposites (27-30)

The same procedure for preparation of 22-25 was followed except instead of 1, functionalized CNTs (15) were used. Compound 15 was prepared by treatment of pristine CNTs by H$_2$SO$_4$:HNO$_3$ 3:1 mixture at room temperature for 6 h$^5$. Four different types of 15- and 21-based hybrid nanocomposites were synthesized depending on 15 and 21 ratio: 1:2 (27), 1:1 (28), 2:1 (29) and 5:1 (30).

2.7. Synthesis of Fe$_3$O$_4$/Zn$_3$(BTC)$_2$@GrO Hybrid Nanocomposite (26)

The synthesis procedure for 26 nanostructure was as follows: first, a suspension of 22 (5 mg/ml) was prepared by sonication of 22 powder in deionized water at room temperature for 1 h in an ice bath. Then the suspension was purged under N$_2$ gas for 30 min to remove oxygen from the solution. Then a solution made by dissolving FeCl$_3$.6H$_2$O (0.5 g) and FeCl$_2$.4H$_2$O (0.25 g) into 10 mL deionized water was added to a of 22 suspension under purging with N$_2$ gas. After stirring for 30 min, 3 ml of 25% NH$_4$OH solution was quickly injected in one portion into the mixture and followed by stirring for 30 min at room temperature. The black solid precipitate of
were collected by an external magnet, washed three times with deionized water and dried in a vacuum oven at room temperature overnight.

2.8. Synthesis of Fe₃O₄/Zn₃(BTC)₂@CNT Hybrid Nanocomposite (31)

To prepare 31, the same procedure for preparation of 26 was used followed except 27 was used instead of 22.

2.9. Characterization of the Prepared Samples

Crystalline phases of the prepared samples were analyzed 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). IR spectroscopy was performed on a PerkinElmer® Universal ATR instrument; data was collected in the range of 650–4000 cm⁻¹. Raman spectra of the samples were collected with a DXR™ Raman Microscope, Thermo Scientific. Thermogravimetric Analysis (TGA) data was obtained by using Q50 TGA instrument, Universal V4.5A TA Instruments. XPS test was monitored by Omicron XPS/UPS system with Argus detector which uses Omicron’s DAR 400 dual Mg/Al X-ray source. The extent of MB after its exposure to the absorbents was measured through Shimadzu UV-1800 UV-vis instrument.

2.10. Pollutant Adsorption Experiments

Dye adsorption experiments were conducted on cationic dye methylene blue (MB) as model organic pollutant. In this regard, 5 mg of the absorbents were treated with 10 ml of MB solution and the resulting mixture was vigorously sonicated with a 400W horn sonicator for 30 min. Then, the non-magnetic absorbents were centrifuged and magnetic absorbents were magnetically separated from the suspension and remaining MB concentration was analyzed by UV-vis instrument to monitor the amount of dye absorption.
Adsorption capacity ($Q_e$) of the prepared hybrid nanomaterials is calculated (Eq. 1) as follows:

$$Q_e = (C_0 - C_e/m) \times V$$

(1)

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

3. Results and Discussion

3.1. Crystalline Structure

X-ray diffraction (XRD) patterns were collected to identify the crystalline structure of the prepared hybrid nanomaterials. According to the XRD results (Fig. 4.1), highly crystalline 21 are successfully formed and grew over 1 and 15 platforms at which the characteristic peaks of the 21 appear on the spectrum$^{48,56,73-75}$. In other words, 21 crystalline pattern is in agreement with previous reports, suggesting successful decoration of 21 over the platforms. In the case of 22-25 hybrid nanocomposites, at low 21 content, very weak signal of 1 at 2$\theta$ of ~12 is observable, but at high MOF content there are no evident peaks representing 1, which the reason may be due to higher surface coverage of the MOFs over the 1 substrate$^{73,75}$. Regarding the 27-30 hybrid nanocomposites, a sharp signal at 2$\theta$ of ~25 relate to 15 substrate present in all the prepared samples, however, in higher content of the MOF, the signals related to the MOF raises drastically$^{5,49}$. No peak corresponding to impurities was detected, which shows successful synthesis and compositing of the 1, 15 and 21 parent materials. It was also verified that the prepared composites are binary hybrid 22-25 and 27-30 nanocomposites rather than physical mixture of 21 with 1 and 15.
Figure 4.1 XRD patterns of the prepared (a) 22-25 and (b) 27-30 hybrid nanomaterials with different ratio between the parent materials.
3.2. Morphological Characteristic

Morphological study of the prepared hybrid nanocomposites and their parent components are carried out through SEM and TEM microscopies, which the corresponding results are shown in Fig. 4.2 and Fig. 4.3. SEM images show needle-shape morphology for parent 21 (Fig. 4.2a and b).  

Figure 4.2 SEM images of 21 (a,b), 22 (c,d), 26 (e,f), and 27 (g,h).
Electron microscopy images of and 26 (Fig. 4.2e and f and Fig. 4.3c and d) and 27 (Fig. 4.2g and h and Fig. 4.3e and f) show successful decoration of 21 nanoparticles and 2 over graphene layers of 1 and 15 substrates. In total, the morphological findings show that 2 and 21 are successfully decorated over 1 and 15 surfaces.

Figure 4.3 TEM images of 22 (a,b), 26 (c,d), and 27 (e,f).
3.3. Elemental Analysis

To verify successful synthesis of the hybrid nanocomposites, XPS test was carried out to show presence of the elements in the samples. All the elements of C, O, Fe, and Zn present in the prepared 26 hybrid nanomaterial (Fig. 4.4). The characteristic signals of C1s and O1s related to 1 and BTC ligand appear at 285 eV and 530 eV, respectively\textsuperscript{47,67}. The peak at 711 eV and 725 eV is related to Fe 2p\textsubscript{3/2} of sample 2\textsuperscript{78}. Zn 2p\textsubscript{3/2} deriving from Zn metal content of the 26 hybrid nanocomposite show signals at 1020 eV, which is in agreement with previous literatures\textsuperscript{78}.

![Figure 4.4 XPS result of the prepared 26 hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, (d): Fe2p, and (e): Zn2p.](image-url)
3.4. Chemical Studies: IR & Raman

Chemical structure of the prepared 22-25 hybrid nanocomposites and their parent components was investigated by IR and Raman spectroscopies. In IR spectra (Fig. 4.5), 1 show peaks at around 3370 cm\(^{-1}\), 1739 cm\(^{-1}\), 1615 cm\(^{-1}\), and 1229 cm\(^{-1}\) deriving from stretching vibration of O-H, C=O, C=C, and C-O, respectively\(^{47}\). The prepared 21 show the characteristic peaks of OH group at 3408 cm\(^{-1}\) deriving from coordinated or absorbed water molecules, C-H vibrations at 2981 cm\(^{-1}\), carbonyl stretch at 1725 cm\(^{-1}\), asymmetric vibrations in -CO\(_2\)- at 1628 and 1570 cm\(^{-1}\), 1455 and 1376 cm\(^{-1}\) deriving from asymmetric and symmetric vibrations of carboxylate groups of BTC, respectively, C–O–Zn vibration at 1105 cm\(^{-1}\), and 762 and 740 cm\(^{-1}\) related to metal zinc substitution in BTC’s benzene groups\(^{53,74}\). The characteristic signals related to the parent materials appear in the IR spectra of the 22-25 hybrid nanocomposites verify successful hybridization of the parent materials\(^{53,56}\). Additionally, there is a change in intensities of the peaks at 1628/1570 cm\(^{-1}\) and 1455/1376 cm\(^{-1}\) in the hybrid nanocomposites which can correspond to a variation in the environment of the BTC’s carboxylate ligands, or in other words, interactions between BTC ligands of the MOF and functional groups of 1\(^{5,56}\). Furthermore, it is observed that loading of higher MOF content in the hybrid nanomaterials result in higher intensities of the 21 signals.
Figure 4.5 IR spectra of 1, 21, and 22-25 hybrid nanocomposites with different ratio between 1 and 21.

Raman results (Fig. 4.6) of the 22 and 26 hybrid nanomaterials show the D and G bands of 1 around 1350 and 1590 cm\(^{-1}\), respectively, which confirm successful fabrication and decoration of 2 and 21 over 1 platform\(^{22,28}\). It is also found that there is shift in 1 bands in the hybrid nanocomposites which confirm successful decoration of MOF and magnetic nanoparticles over 1 platform\(^{13,22,38}\). In the case of bare 15 and 27 hybrid nanocomposite, two peaks corresponding to 15 appear at around 455 and 795 cm\(^{-1}\), which belong to 15 and there is also considerable shift in position and intensity of the signals in the hybrid nanomaterials compared to the parent 15, which further verify successful loading of the 21 over 15. Chemical structure studies further
confirm successful loading of 2 and 21 over 1 and 15 platforms and fabrication of the hybrid nanocomposites, which is in agreement with crystalline and morphological analysis.

![Figure 4.6 Raman spectra of (a): 22 and 26 and (b): 15 and 27.](image)

### 3.5. Thermogravimetric Analysis (TGA)

To further verify successful synthesis of 22-25 and 26 hybrid nanocomposites, TGA analysis was carried out which the corresponding TGA curves of these hybrid nanocomposites and are shown in Fig. 4.7. The TGA curve of 21 show signals related to mass loses at around 110 °C related to dehydration and around 250 °C which deriving from removal of decomposition of excessive water and decomposition of 21 and organic linker.\textsuperscript{48,75} Our findings show that the hybrid nanocomposites of 22-25 show very similar pattern to their parent materials.\textsuperscript{48,75} It was also observed that at higher MOF content of the composites, their spectra are very similar to the spectra of parent 21. In the case of 26, after a small mass loss at around 110 and 250 °C, the curve remain steady and large portion of the original mass remain undecomposed, which this mass is ascribed to 2.
3.6. Methylene blue (MB) Adsorption

Dye adsorption capacity of the prepared hybrid nanomaterials are tested through MB dye adsorption which the results are collected in Table 4.1. The newly developed hybrid nanocomposites of 22, 26, 27, and 31 illustrate significantly higher dye adsorption capacity in comparison to their single parents. The higher small molecule adsorption capacity of the newly developed hybrid nanocomposites is ascribed to the synergetic effect of the parent materials which present in the composites, which might be due to suppression of dispersive forces and aggregation as well as well-separation of the MOFs, preventing distortion and bundling in 1 and 15, and controlled morphology and size of the 21 particles. Besides, according to previous literature (Table 4.1), the prepared hybrid nanomaterials show significant dye adsorption. Due to functional groups of the prepared composites which carry negative charge in neutral environment and positive charge of MB, adsorption mechanism between MB and the composite nanomaterials
was suggested to be hydrophobic and/or $\pi-\pi$ interactions, which is in agreement with previous literature$^{67}$.

Table 4.1 Comparison of capacities of adsorption of MB on different adsorbents.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$Q_e$ (mg g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
<td>This work</td>
</tr>
<tr>
<td>21</td>
<td>negligible</td>
<td>This work</td>
</tr>
<tr>
<td>22</td>
<td>176</td>
<td>This work</td>
</tr>
<tr>
<td>26</td>
<td>87</td>
<td>This work</td>
</tr>
<tr>
<td>15</td>
<td>144</td>
<td>This work</td>
</tr>
<tr>
<td>27</td>
<td>110</td>
<td>This work</td>
</tr>
<tr>
<td>31</td>
<td>53</td>
<td>This work</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>31</td>
<td>66</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>Cu$_3$(BTC)$_2$</td>
<td>30</td>
<td>67</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@Cu$_3$(BTC)$_2$</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>MOF-235</td>
<td>187</td>
<td>32</td>
</tr>
<tr>
<td>MIL-101</td>
<td>21</td>
<td>68</td>
</tr>
</tbody>
</table>

4. Conclusion

Present work deals with fabrication of novel high efficient magnetic and non-magnetic hybrid nanomaterials of 22-25, 26, 27-30, and 31 as absorbents for water remediation through adsorption process. In this respect, MB dye was used as model organic dye pollutant. Morphological analysis indicates successful decoration of 2 and 21 over 1 and 15 platforms. To investigate crystalline and chemical structure of the prepared samples, XRD, IR and Raman measurements were undertaken and the measurements show all the signals related to the parent materials in the developed hybrid nanocomposites. Additionally, elemental and thermal analysis carried out with XPS and TGA respectively, confirm presence of all the parent materials in the hybrid nanomaterials. In addition, we found that the composite nanomaterials show considerably higher MB absorption capacity compared to that of parent materials. In total, our findings show that the newly developed hybrid nanomaterials have promising potential and can be good candidates for environmental applications such as water and wastewater purifications.
Chapter 5: Synthesis and Characterization of Cd₃(BTC)₂ MOF-based Hybrid Nanomaterials

1. Introduction

Here and for the first time, we report synthesis and characterization of a series of hybrid nanocomposites based on GrO (1) and CNTs (15) decorated with Cd₃(BTC)₂ MOF (32) via a simple, versatile, and green one-pot solvothermal method. The as-synthesized nanocomposites were characterized by XRD, SEM, TEM, IR, Raman, and XPS techniques. Morphological analysis illustrates successful formation and growth of very well-dispersed needle-shape 32 over 1 and 15 platforms. XRD results demonstrate highly crystalline structure for the prepared 33-36 and 37-40 hybrid nanomaterials. It was observed that the higher MOF content in the nanocomposites, the more intense the MOF signals are, which not just prove successful loading of 32 over the platforms, but also show higher loading for higher 32 content. The chemical and elemental structures of the hybrid nanocomposites were also explored by IR, Raman, and XPS techniques, which they have confirmed successful growth of the MOF over the 1 and 15 platforms. It is proposed that presence of 1 and 15 during the MOF formation benefit its formation through number of ways such as suppression of dispersive forces, inhibits aggregation, formation of small pores between MOF and the platforms, less inter-MOFs voids, smaller size of the MOF, and improved physicochemical characteristic. In total, we think that due to the excellent features deriving from synergetic effects, these newly developed hybrid nanocomposites can be promising candidates for various MOF-based applications.
2. Experimental

2.1. Chemicals

The reagent grade quality chemicals were purchased from Acros, Alfa Aesar, Sigma-Aldrich, Fisher, and Tokyo Chemical Industry Companies and were used as received without further purification. Ultrapure water was obtained from Milli-Q® instrument, Millipore Corporation.

2.2. Synthesis of GrO (1)

Synthetic method of sample 1 is described in chapter 2.

2.3. Synthesis of Cd₃(BTC)₂ MOF (32)

To synthesize 32, First, Cd(OOCCH₃)₂·2H₂O (1.000g, 0.0037mole) was dissolved into deionized water (10 mL) and mixed with benzene-1,3,5-tricarboxylic acid (BTC) (0.500g, 0.0024mole) dissolved into ethanol (10 mL). The resulting mixture was placed into a 500ml glass reactor and sealed. Then, the reactor was heated to 383 K for 48 h in an oven. Afterward, the glass reactor was cooled to room temperature and white solids of 32 were collected and washed three times with ethanol and deionized water. Finally, the resulting solid was dried in an oven for 12 h and fine bright white powder of 32 was obtained. The chemical and elemental characteristic of the prepared compound are as follows: IR: 1749 cm⁻¹ (C=O stretch), 1635 cm⁻¹ (C=C stretch), and 1236 cm⁻¹ (C-O vibrations).

2.4. Synthesis of Cd₃(BTC)₂@GrO Hybrid Nanocomposites (33-36)

To fabricate 33-36 hybrid nanocomposites, the following procedure was carried out: first, a suspension of 1 in ethanol:water mixture with ratio of 2:1 (v:v) was prepared via sonication in a 400W horn sonicator for 1 h in an ice bath. Second, solutions containing Cd(OOCCH₃)₂·2H₂O and BTC were prepared separately in ethanol:water mixture with ratio of 2:1 (v:v). Afterward, cadmium solution was added to the 1 suspension and sonicated for 15 min to place metal ions
onto the 1 sheets. Then, the BTC solution was added to the above solution and sonicated for another 15 min. The resulting mixture was placed into a glass reactor and sealed. The reactor was heated to 383 K for 48 h in an oven. Afterward, the reactor was cooled to room temperature. Black solids of 1- and 32-based hybrid nanocomposites were collected and washed three times with ethanol and then deionized water. Finally, the resulting solid was dried in an oven for 12 h and fine dark black powder of 1- and 32-based hybrid nanocomposites was obtained. Four different types of 1- and 32-based hybrid nanocomposites were synthesized based on mass ratio between Cd₃(BTC)₂ MOF and GrO: 1:2 (33), 1:1 (34), 2:1 (35) and 5:1 (36).

2.5. Synthesis of Cd₃(BTC)₂@CNT Hybrid Nanocomposites (37-40)

The same preparation procedure of 33-36 hybrid nanocomposites was followed with the exception that instead of 1, the compound 15 was used. The compound 15 was prepared by acid-treatment of pristine CNTs using H₂SO₄:HNO₃ 3:1 mixture at room temperature for 6 h²⁶,²⁷. Four different types of 15- and 32-based hybrid nanocomposites hybrid nanocomposites were synthesized based on mass ratio between 15 and 32: 1:2 (37), 1:1 (38), 2:1 (39) and 5:1 (40).

2.6. Characterization of the Prepared Samples

Crystalline phases of the prepared samples were analyzed 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). The IR spectroscopy was performed on PerkinElmer® Universal ATR instrument, which data were collected in range of 650–4000 cm⁻¹. Raman spectra of the samples were collected from DXR™ Raman Microscope, Thermo Scientific. Thermogravimetric Analysis (TGA) data were obtained by using Q50 TGA instrument, Universal V4.5A TA
Instruments. XPS test was monitored by Omicron XPS/UPS system with Argus detector which uses Omicron's DAR 400 dual Mg/Al X-ray source.

3. Results and Discussion

3.1. Crystalline Structure

The crystalline structure of the prepared 33-36 and 37-40 hybrid nanocomposites was collected using x-ray diffraction patterns, as shown in. Fig. 5.1. XRD results show that the prepared hybrid nanomaterials have very high crystallinity and the position of the peaks is in accordance with the parent materials, which confirms successful formation of highly crystalline 32 over 1 and 15 platforms, which is in agreement with previous reports. Furthermore, it is found that presence of 1 and 15 platforms do not prevent formation and growth of 32 through linking between metal and BTC ligand. In the 32-36 samples, there is no peak indicative of 1. However, in case of 37-40 samples, there is a sharp signal of 15 in the hybrid nanocomposites especially in the nanocomposites with lower content of 32. In addition, it was found that there is a pattern for the hybrid nanocomposites with different MOF content and the increases of the signals of 32 crystallites is proportional to its content in the samples.
Figure 5.1 XRD patterns of the prepared (a) 33-36 and (b) 37-40 hybrid nanocomposites.
3.2. Morphological Characteristic

Morphology of the prepared samples was investigated by SEM and TEM microscopies. SEM and TEM micrographs of prepared hybrid nanocomposites along with their parent materials are shown in Fig. 5.2. According to Fig. 5.2, nanocomposite of 32 is made of large needle-shape particles (Fig. 5.2a and b). Nanocomposite of 33 shows that in presence of 1, nanostructured 32 particles are formed and decorated over exfoliated 1 layers (Fig. 5.2c and d). TEM images of the 33 (Fig. 5.2e and f) and 37 (Fig. 5.2g and h) hybrid nanocomposites and their parent materials is in agreement with SEM findings and confirm successful formation and growth of nanostructured 32 over the 1 and 15 platforms\textsuperscript{44,69}. Furthermore, it is noteworthy that compared to pure 32, in-situ synthesis of 32 in presence of 1 and 15 platforms results in formation of nano-sized 32 with increased dispersive forces of the MOFs and suppressed aggregation and inter-MOFs voids\textsuperscript{44,69}, which in overall leads to 32 with higher micro-pore volume which is very important for MOFs applications such as in catalysis, gas separation and purification, gas adsorption, etc.
Figure 5.2 SEM and TEM images of 32 (a,b), 33 (c-f), and 37 (g,h).
3.3. Elemental Analysis

XPS measurement was performed over 33 and 37 hybrid nanomaterials to confirm the elemental composition of the surface of the newly developed hybrid nanomaterials. As shown in Fig. 5.3, the signals observed for 33 at around 406 and 412 eV correspond to electrons in Cd3d\textsubscript{3/2} and Cd3d\textsubscript{5/2}, respectively. The binding energy for O1s is observed at around 533 eV which corresponds to O\textsuperscript{2+} ions in crystalline network of the sample (Fig. 5.3)\textsuperscript{48}. The peak at 285 eV corresponds to C 1s\textsuperscript{67}. The same results were found in respect to 37 with Cd3d\textsubscript{3/2} and Cd3d\textsubscript{5/2}, O1s and C1s signals at around 406 and 413 eV, 533 eV and 285 eV, respectively (Fig. 5.4). Our findings suggest successful decoration of 32 over 1 and 15 platforms.

![XPS spectra](image)

**Figure 5.3** XPS spectra of the prepared 33 hybrid nanocomposite. (a): survey, (b): C1s, (c): O1s, and (d): Cd3d.
3.4. Chemical Studies: IR & Raman

IR spectra (Fig. 5.5) of the synthesized 33-36 hybrid nanocomposites with different content of 32 along with the parent materials are recorded and the functional groups are identified in each sample. The characteristic peaks of 1 are found to be: double peak at 3230 and 3390 cm\(^{-1}\) (O-H stretch), 1749 cm\(^{-1}\) (C=O stretch), 1635 cm\(^{-1}\) (C=C stretch), and 1236 cm\(^{-1}\) (C-O vibrations).\(^{47}\) 32 exhibits major signals of around 3410 cm\(^{-1}\) (O-H or –OH deriving from coordinated or absorbed water molecules); 3150 cm\(^{-1}\) (C-H of the aromatic rings); 1760 cm\(^{-1}\) (C=O stretch); 1611 and 1548 cm\(^{-1}\) (asymmetric vibrations in -CO\(_2\)-); 1443 and 1373 cm\(^{-1}\) corresponding to the asymmetric and symmetric vibrations of the BTC carboxylate groups, respectively, 1118 cm\(^{-1}\) related to C–O–Cd vibration in 32, and 740 cm\(^{-1}\) related to metal
cadmium substitution in BTC’s benzene groups\textsuperscript{75,80}. The presence of these characteristic peaks provides clear evidence of the successful synthesis of \textbf{32}.

IR spectra of the hybrid nanocomposites of \textbf{33-36} show characteristic peaks related to both the MOF and the platforms parent materials with some shifts compared to the parent materials, which confirm successful synthesis of the hybrid nanocomposites. The changes in the intensities of the peaks at 1611/1548 cm\textsuperscript{-1} and 1443/1373 cm\textsuperscript{-1} can be ascribed to variation in environment of the BTC’s carboxylate ligands. A feasible explanation for this phenomenon can be the interactions between these ligands and functional groups of \textbf{1}, as well as distortion in \textbf{32} structure resulting from introduction of \textbf{1}\textsuperscript{53,84}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{IR_spectra.png}
\caption{IR spectra of \textbf{33-36} hybrid nanocomposites and their parent materials.}
\end{figure}
Raman spectra of the prepared 15 shows two peaks at around 445 cm\(^{-1}\) and 780 cm\(^{-1}\), verifying chemical composition of 15 (Fig. 5.6).\(^{22,28,38,47}\) G band is typically assigned to \(\text{E}_{2g}\) phonon of sp\(^2\) carbon atoms, whereas D band is attributed to \(\kappa\)-point phonons of \(\text{A}_{1g}\) symmetry.\(^{47}\) No peak observed for 32. Besides, it is found that after decoration of 15 with 32, the resulting 37 hybrid nanocomposite retain 15 double peaks with some shift due to presence of 32, which is a good evidence of successful synthesis of the hybrid nanocomposites.\(^{37}\) In fact, observation of chemical shifts in the hybrid nanocomposites compared to their parent materials verifies the assumption of chemical bonding between functional groups of the MOF and the platform.

![Figure 5.6 Raman spectra of 15 and 37.](image)

The findings draw the conclusion of chemical bonding between the MOF functionalities and functional groups of CNT surface.\(^{84}\) In this respect, carboxyl groups of BTC in the MOF react with functional groups of surface of the platforms, and then under reaction in the reactor the MOF grows and forms 3D structure.\(^{84}\)
4. Conclusion

In the present study, which is done for the first time, a series of novel hybrid nanocomposites of 33-36 and 37-40 were developed through a simple and versatile solvothermal method, using 1 and 15 as platforms for formation and growth of 32. It was found that the prepared 33-36 and 37-40 hybrid nanomaterials are highly crystalline and with raising 32 content in the nanocomposites, the intensities of the peaks rise, which draw the conclusion of higher MOF loading at higher MOF content. Morphological studies show that nanostructured needle-shape 32 is formed and decorated over the 1 and 15 platforms. Elemental studies carried out with XPS verify presence of C, O, and Cd elements and successful synthesis of the hybrid nanocomposites. IR findings illustrate presence of all the functional groups belonging to the parent materials in the hybrid nanocomposites and Raman analysis exhibit retaining 15 double bands with some shift after decoration 32. In total, we found that presence of 1 and 15 during the 32 formation are beneficial in the suppression of inter-MOFs voids through raising dispersive forces, inhibiting aggregation of the MOF, along with formation of small pores between the MOF and the platform, and controlling morphology and size of the MOF.
Chapter 6: Conclusion

A series of hybrid nanocomposites based on M₃(BTC)₂ MOFs (M: Ni, Cu, Zn, and Cd) decorated GrO (M₃(BTC)₂@GrO) and CNTs (M₃(BTC)₂@CNT) were synthesized via a simple and facile green solvothermal method using a metal salts and benzentricarboxylic acid (BTC), GrO, and CNTs as precursors. The prepared nanomaterials were used as absorbent for pollutant adsorption and removal. Furthermore, in order to easily separate absorbent from liquid media through an applied external magnetic field, Fe₃O₄ MNPs were loaded over M₃(BTC)₂@GrO and M₃(BTC)₂@CNT and for the first time novel hybrid nanomaterials of Fe₃O₄/M₃(BTC)₂@GrO and Fe₃O₄/M₃(BTC)₂@CNT were developed. The as synthesized hybrid nanocomposites were characterized by XRD, SEM, TEM, IR, Raman, XPS, TGA, and N₂ adsorption/desorption isotherms techniques.

XRD results confirmed high crystalline structure of the prepared hybrid nanomaterials. In addition, we found that signal intensity of the XRD patterns is proportional to the MOF content of the composites and higher MOF content results in higher peak intensities. In addition, it is noteworthy to mention that the position of the signals of the MOFs were retained after compositing them with GrO and CNT which means presence of the platforms does not prevent formation and growth of the MOFs.

Morphological and elemental studies also verified successful decoration of M₃(BTC)₂ MOF and Fe₃O₄ MNPs over GrO and CNT platforms. SEM and TEM images show successful formation and growth of nanostructured MOFs over the platforms. Morphological analysis also illustrated that bare MOFs are in micron size and presence of GrO and CNT platforms leads to well-dispersed nano-sized MOFs. XPS study further confirmed presence of all the elements in the hybrid nanocomposites and successful loading of MOFs and Fe₃O₄ MNPs over the platforms.
Chemical analysis collected through IR and Raman further verified successful formation and loading of MOFs and Fe$_3$O$_4$ MNPs over the platforms, at which characteristic peaks of all the parent components did present in the hybrid nanomaterials.

Thermal analysis monitored through TGA technique showed presence of all the components in the hybrid nanomaterials. There was also a direct relationship between the MOF content and position of the TGA curves. N$_2$ adsorption/desorption isotherms demonstrated higher micro-pore volume for the hybrid nanocomposite compared to that of pure MOF, which comes from formation of new pores between the MOF and the platform.

Methylene blue (MB) was used as model organic pollutant to analyze potential application of the prepared hybrid nanomaterials as absorbent. Dye adsorption measurements exhibit strong interaction between MB and the hybrid nanomaterials with vast improvement in the adsorption compared to that of the parent materials, which was also significant compared to the previous literatures. Improved pollutant adsorption capacity of the hybrid nanomaterials in comparison to their parent materials was ascribed to synergetic effect of positive features of the MOFs over the platforms including different physicochemical properties, well-dispersion, enhanced dispersive forces, different morphology and smaller size, and formation of small pores between the MOFs and platforms.

In overall, it is proposed that the newly developed adsorbents combine the advantages of M$_3$(BTC)$_2$ MOFs, GrO, CNT and Fe$_3$O$_4$ MNPs and due to low cost, large adsorption capacity, and easy separation of the adsorbent (solid phase), can be good candidates for environmental applications such as water remediation and gas adsorption.
Chapter 7: References

(8) Li, Wei-Jin.; Gao, Shui-Ying.; Liu, Tian-Fu.; Han, Li-Wei.; Lin, Zu-Jin. et al., Langmuir 2013, 29, 8657.
(16) Li, Wei-Jin.; Gao, Shui-Ying.; Liu, Tian-Fu.; Han, Li-Wei.; Lin, Zu-Jin. et al., Langmuir 2013, 29, 8657.
Vahid Jabbari, born in Rasht-Iran, is from an Azeri ethnicity of an Iranian family. He received his Bachelor degree in Chemistry from Arak University and a Master degree in NanoScience and Nanotechnology-NanoChemistry from University of Kashan. His research covers vast range of science and technology including Nanomaterials, Polymers, Carbon Nanostructures, Metal-Organic Frameworks (MOFs), Solar Energy, and Water Remediation. He has published over 40 papers in peer-reviewed journals, international conferences, and several book chapters. He has been serving as member of technical, scientific, and organizing committee of numerous international conferences, symposiums and expos, and as editor and reviewer of numerous prestigious scientific journals. He is also member of several prestigious scientific associations such as ACS, AASCIT, IIE, and ISALS.