ISSN: 0973-3469, Vol.20, No.(1) 2023, Pg. 60-74

Material Science Research India

www.materialsciencejournal.org

Preparation and Characterization of Nanohybrids Made of Graphene Oxide as Super Adsorbents

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Abstract

Adsorption is considered one of the best methods for the removal of heavy metal ions from an aqueous solution. However, the synthesis of adsorbents with desired selectivity and performance remains a key challenge in the battle of water decontamination. Recently, carbon-based and metal-oxide based nanomaterials have emerged as promising candidates for the adsorption of heavy metals due to their high specific surface area, high aspect ratio, and concentrated pore size distribution. Here, in this work five adsorbents ie. Graphene Oxide (GO), Magnetic Graphene Oxide (MGO), Titanium Dioxide (TiO_2), and their composites GO-TiO_2 and MGO-TiO_2 were synthesized. The prepared samples were characterized via high-resolution imaging, BET-N_2 adsorption-desorption analysis, and spectroscopic techniques. TEM results revealed the nanoscale structures of the synthesized nanomaterials. The approximate sizes of MGO and TiO_2 nanoparticles found under TEM studies were about 24.58 and 35.51 nm respectively. The presence of desired functional groups was very well deciphered by FT-IR spectroscopy. Results of N_2 adsorption-desorption studies revealed that the prepared GO was macro-porous while all other samples were mesoporous. MGO was found to have the highest BET surface area of about 108.375 m^2/g. These results indicate that the prepared nanomaterials may serve the purpose of effectively adsorbing the heavy metal ions from an aqueous solution.

Article History

Received: 24 January 2023

Accepted: 14 March 2023

Keywords

Adsorption;
Graphene Oxide;
Heavy Metals;
Nanomaterials;
Titanium Dioxide.

Introduction

The discharge of heavy metals into aquatic ecosystems has raised global concerns over the past few decades. These contaminants are introduced into water bodies through effluents from various industries, including paper and pulp, petrochemicals, automobiles, and battery manufacturing. While several methods, such as precipitation, ion exchange,

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Doi: http://dx.doi.org/10.13005/msri/200107

reverse osmosis, and membrane filtration, have been employed to remove heavy metals. Most of these methods have drawbacks, such as high cost, low efficiency, and sludge generation (Kumar *et al.*, 2019). Additionally, they fail to meet the demand for water resources, particularly for large volumes. Adsorption, on the other hand, is a simple, economical, and adaptable method in terms of unit design. Natural and synthetic adsorbents, such as clay, activated carbon, mesoporous silica, and resin, have been used to treat heavy metal-contaminated water. However, separating and regenerating these adsorbents from wastewater poses a significant challenge. Therefore, there is a need to develop novel adsorbents with high adsorption capacity and quick separation from large volumes of water (Almomani *et al.*, 2019). Recently, nanomaterials, particularly carbon-based and metal oxide-based ones, have emerged as promising adsorbents for heavy metal ions due to their high specific surface area, surface-to-volume ratio, and concentrated pore size distribution (Khan *et al.*, 2013; Qu *et al.*, 2015). Among these, graphene oxide (GO), a carbon-based nanomaterial, has received widespread attention (Yan *et al.*, 2014, Majumder P, Gangopadhyay R. 2022). GO consists of a hexagonal network of covalently bonded carbon atoms with oxygen-containing functional groups, such as hydroxyl, epoxy, lactone, quinone, phenol, anhydride, carbonyl, ether, and carboxyl groups, attached to various sites, which facilitate the binding of positively charged metal ions to its surface (Guerrero-Fajardo *et al.*, 2020; Zhao *et al.*, 2011). However, GO's hydrophilicity and tendency to agglomerate during its application and storage make it challenging to separate, even after saturation adsorption (Liu *et al.*, 2015; Sun *et al.*, 2015). To address these issues, GO can be magnetized, for example, with iron oxides. Nano-sized iron oxides exhibit super-paramagnetism, low toxicity, chemical inertness, and the ability to immobilize various adsorbents on their surface (Jawed *et al.*, 2020). The magnetized GO can be easily separated using an external magnetic field (Lingamdinne *et al.*, 2019). Another category of nanomaterials that has shown favourable adsorption towards heavy metals is nano-sized metal oxides (Hua *et al.*, 2012). Functionalizing GO with metal oxides largely increases the electronegative charge on its surface thereby improving metal removal efficiency (Jawed *et al.*, 2020). The inclusion of active materials such as manganese dioxide (Xiang *et al.*, 2018), iron oxide (Tian *et al.*, 2017), and titanium dioxide (Liu *et al.*, 2016) have sparked a profound interest in the field of adsorption as the metallic compounds could improve the adsorption performance by providing more active sites (Lai *et al.*, 2020). Titanium dioxide nanoparticles are widely used as an adsorbent for heavy metal ions due to their low cost, stability, and non-toxicity towards human beings and the environment (Seidlerová *et al.*, 2016). Here in this work the synthesis of adsorbents such as Graphene Oxide (GO), Magnetic Graphene Oxide (MGO), Titanium Dioxide (TiO_2), and their composites GO-TiO_2, and MGO-TiO_2 has been reported. GO-TiO_2 is synthesized keeping in view the favourable properties of both GO and TiO_2. MGO-TiO_2 nanocomposites are synthesized aiming at integrating the advantages of all the components – GO, TiO_2 along with magnetic properties of iron oxide for the added advantage of easier regeneration of adsorbents and improve the overall adsorption efficiency.

Material and Methods

Graphite fine powder extra pure of size 10-30 nm was procured from Loba Chemicals, sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), ferrous ammonium sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2.6H_2O$], ammonium ferric sulfate dodecahydrate [$(NH_4\ Fe(SO_4)_2).10H_2O$], aqueous ammonia ($NH_4OH$) (weight 25%), hydrogen peroxide (H_2O_2), isopropyl alcohol (IPA), titanium isopropoxide (TTIP), isopropanol, HCl, and anhydrous ethanol were procured from Molychem, and were of analytical grade and used without any further purification.

Synthesis of Adsorbents

GO was prepared by the modified Hummer's method. Graphite powder was added into a mixture of concentrated H_2SO_4 and H_3PO_4 in the ratio of 9:1 under continuous stirring followed by the addition of KMnO4 to bring about the oxidation. The mixture was stirred continuously till the color changed to purple. Then the mixture was cooled down to room temperature and an ice water mixture and H_2O_2 were added to stop the reaction. A yellow-colored solution was obtained which was then sonicated to bring about the complete exfoliation of graphite oxide. Then the solution was centrifuged once with HCl and many times with distilled water until a neutral pH was obtained. Finally, solid GO was

obtained by vacuum drying in an oven and grinding using a pestle and mortar (Kaur and Jeet 2017). The observations recorded during the synthesis of GO are given in figure 1.

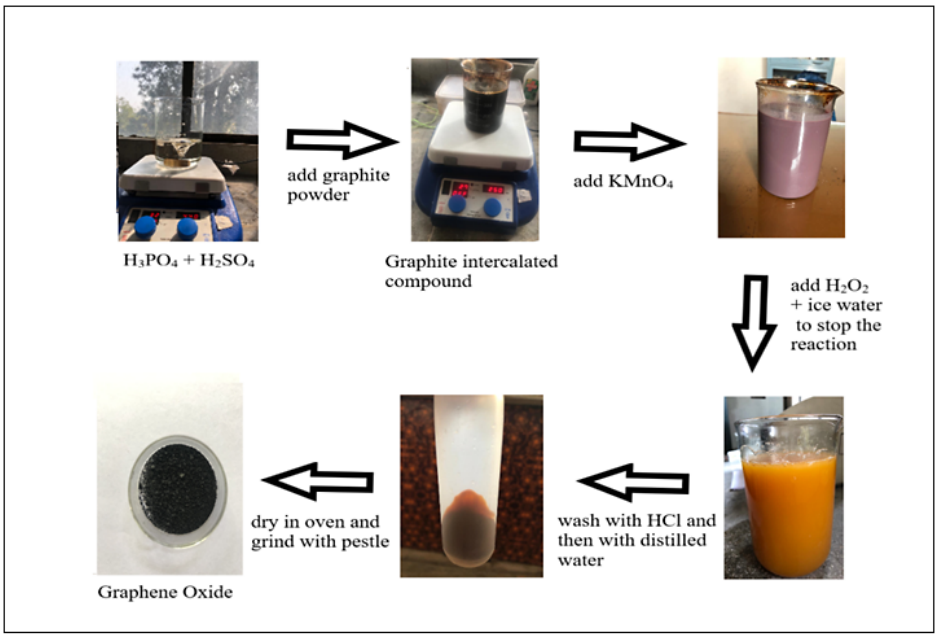

Fig. 1: Observations recorded during the synthesis of Graphene Oxide

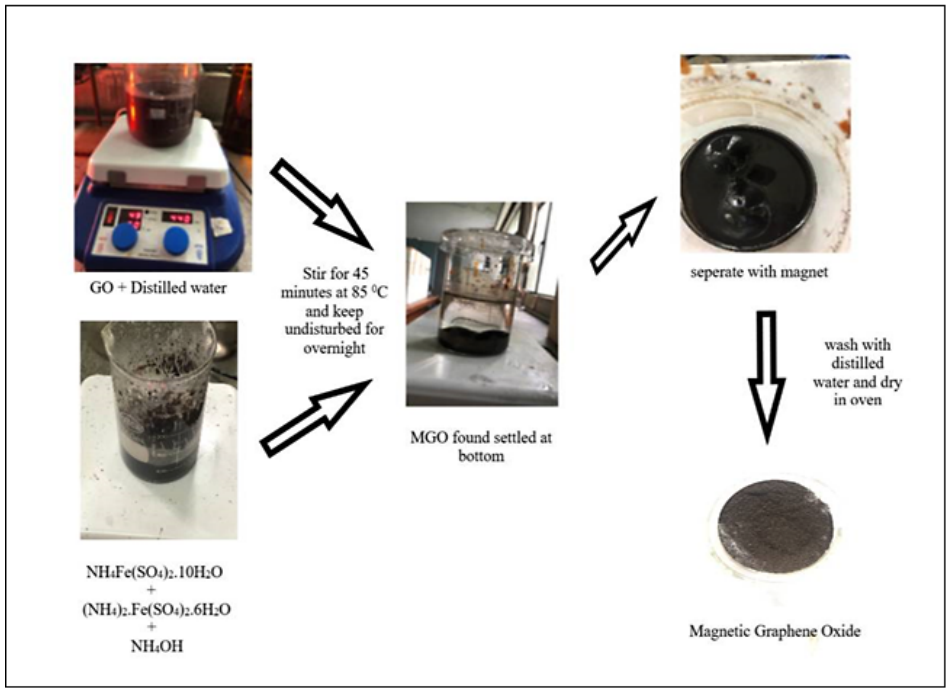

Fig. 2: Observations recorded during the synthesis of MGO

MGO was prepared by the co-precipitation of iron oxide nanoparticles on the surface of GO. A dispersion of GO was prepared by adding a small amount of prepared GO in 100 ml of double-distilled water and sonicating it for an hour. Then, 10.7 g of ferric ammonium sulfate and 5.8 g of ferrous ammonium sulfate were added to 100 ml of double-distilled water followed by the rapid addition of 10 ml of aqueous ammonia. The solution was then kept under stirring and GO suspension was slowly added to this solution after that the stirring was continued for about 45 minutes at 85 0C and then the solution was kept undisturbed overnight. Finally, MGO was separated with a magnet and washed thrice with distilled water and anhydrous ethanol respectively. Subsequently, MGO was kept in an oven at 70 0C for drying (Deng *et al.*, 2013, Yi *et al.* 2021). The observations recorded during the synthesis of MGO are given in figure 2.

Titanium Dioxide was prepared by a wet chemical method. 10 ml of TTIP was added into a solution containing ethanol and double distilled water in the ratio of 7:1 under constant stirring. The stirring was further continued at room temperature until a thick paste with lots of nanoparticles was obtained, which were then separated by centrifugation with distilled water. The nanoparticles were then calcined and stored in an airtight container (Tamilselvi *et al.*, 2016, MironyukI *et al.* 2020). The observations recorded during the synthesis of TiO_2 are given in figure 3.

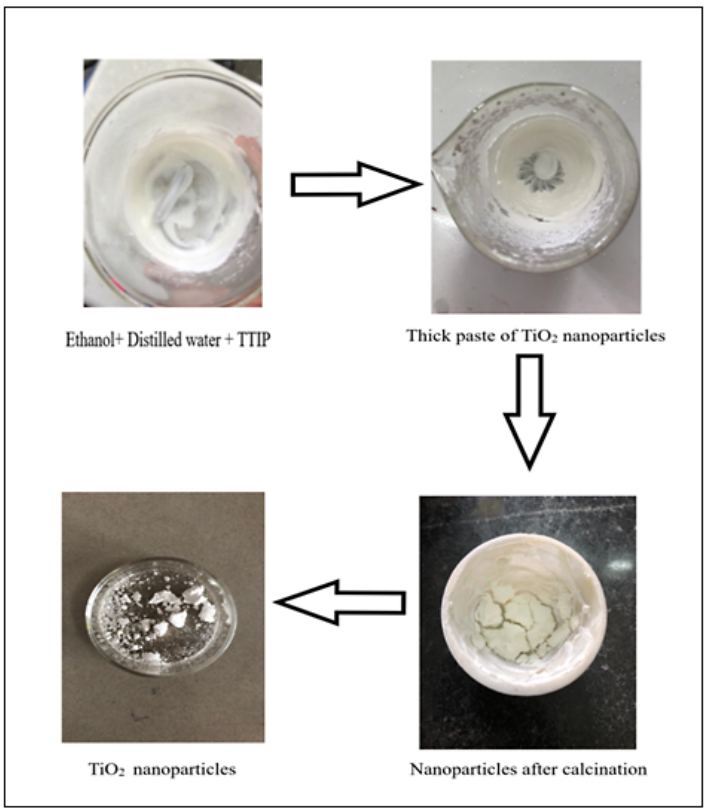

Fig. 3: Observations recorded during the synthesis of TiO_2

GO-TiO_2 nanocomposite was prepared by the sol-gel process. A small amount of the prepared GO was added into the double distilled water and was sonicated to re-exfoliate GO. Afterward, a mixture of isopropanol and TTIP in the ratio of 4:1 was dropped into the GO solution under continuous stirring for the crystallization of TiO_2 Nanoparticles. The precipitates were washed, filtered with water and ethanol, and dried in the oven. Finally, GO-TiO_2 nanohybrids were obtained by calcination at 400^0C (Sakulpaisan *et al.*, 2016). The observations recorded during the synthesis of GO-TiO_2 are given in figure 4.

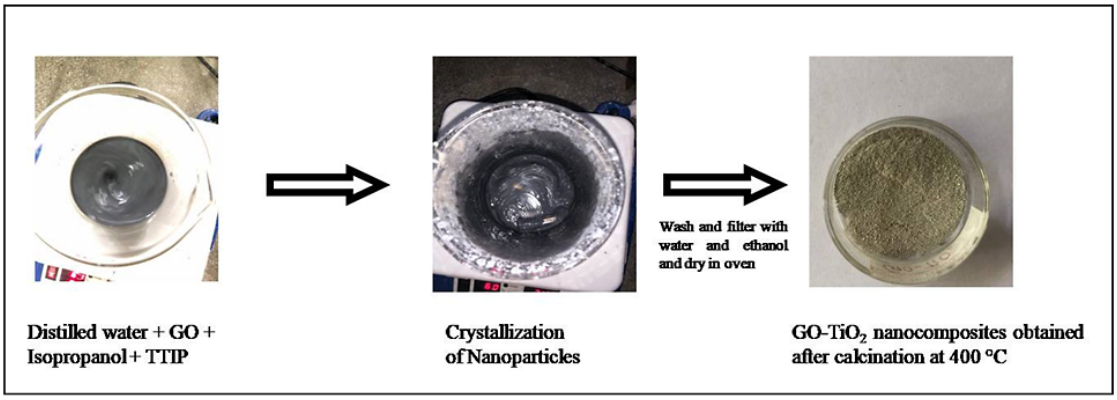

Fig. 4: Observations recorded during the synthesis of GO-TiO_2

For the preparation of MGO-TiO_2 nanocomposite, the prepared GO and TiO_2 nanoparticles were separately dispersed in double-distilled water and were sonicated for about an hour. Then $(NH_4)_2Fe(SO_4)_2.6H_2O$ and $(NH_4Fe(SO_4)_2).10H_2O$ were dispersed in distilled water and 10 ml of aqueous ammonia was quickly added to this solution, as in the preparation of MGO. Afterward, this solution and TiO_2 dispersion were simultaneously added to the GO dispersion under vigorous stirring. The stirring was further continued at 850C for 45 minutes and kept overnight at room temperature. The rest of the procedure of obtaining nanoparticles was the same as that in the case of MGO (Chang *et al.*, 2015). The pictorial representation of MGO-TiO2 synthesis is given in figure 5.

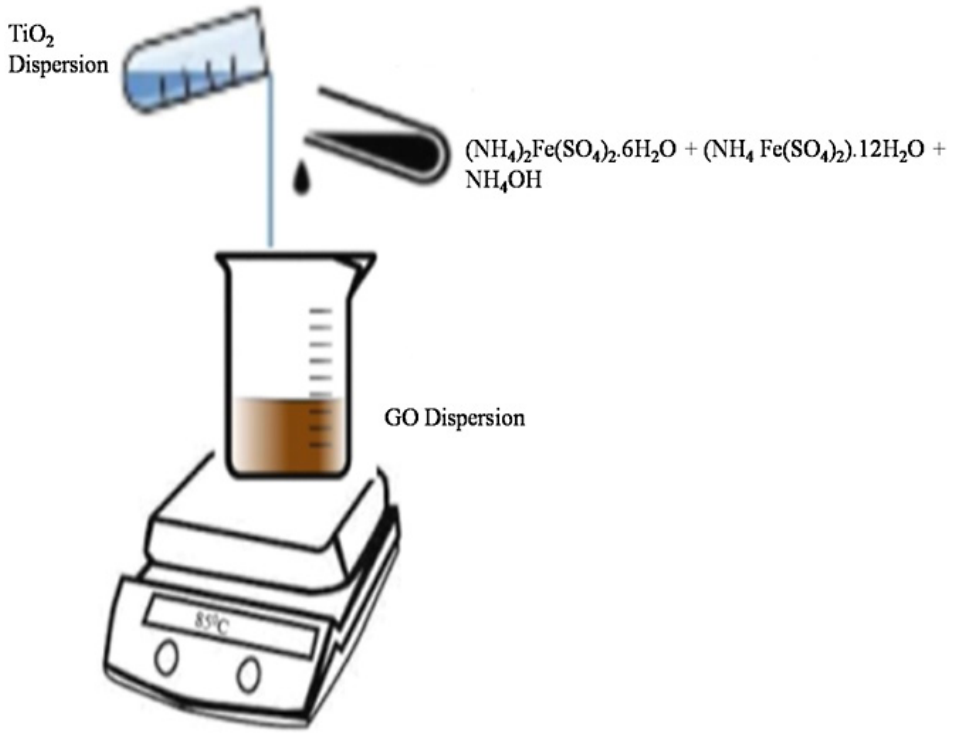

Fig. 5: Pictorial representation of MGO-TiO_2 synthesis

Characterization

The surface area of the prepared nanomaterials was examined by BET N_2 adsorption-desorption analysis using Micromeritics ASAP 2020 volumetric adsorption analyzer installed at Emerging Life Sciences, Guru Nanak Dev University, Amritsar, Punjab, India. Before each analysis, each sample was degassed for 4-6 hours at 2000C. For the determination of the elemental composition and functional groups present the prepared samples were analyzed using Perkin Elmer Fourier Transform Infrared Spectrometer installed at Central Instrumentation Facility, Lovely Professional University, Phagwara, Punjab, India. The prepared samples were viewed under Transmission Electron Microscopy (TEM) installed at the Electron Microscopy and Nanoscience Lab, Punjab Agricultural University, Ludhiana, Punjab, India, to study their structural and morphological properties.

Results and Discussions

BET N_2 Adsorption-Desorption Analysis

Magnetic Graphene Oxide was found to have the largest surface area of 108.3750 m^2/g. The magnetization of GO appeared to increase its surface area, as evidenced by the larger surface area of MGO compared to GO. The surface areas of both the nanocomposites ie. GO-TiO_2 and MGO-TiO_2 were less than that of MGO which showed that the substitution of graphene oxide with titanium dioxide decrease its surface area. Due to the agglomeration of individual nanoparticles, the surface area of TiO_2 nanoparticles was only 4.42 m^2/g. The extremely high calcination temperature may have contributed to the high average particle size of TiO_2 particles. As a result, the individual TiO_2 nanoparticles were agglomerated which was also evident from the TEM micrograph of TiO_2 nanoparticles. The pore diameters of the synthesized samples confirmed the presence of mesopores as per the IUPAC classification except for GO which was found to be macroporous (Thommes *et al.*, 2015). The BET surface areas, pore sizes, and pore volume distribution of the synthesized samples are given in Table 1.

Table 1: BET surface areas, pore sizes, and pore volume distribution of the synthesized samples

Adsorbent	BET surface area (m^2/g)	Pore width (nm) By BET method	Pore volume (cm^3/g) By BET method	Average particle size (nm)	BJH adsorption average pore diameter (nm)
Graphene Oxide (GO)	35.8220	31.97	0.286316	167.4947	51.7066
Magnetic Graphene Oxide (MGO)	108.3750	9.77	0.264600	55.36	9.67
Titanium Dioxide (TiO_2)	4.4288	268.67	0.297472	1354.76	46.755
GO-TiO_2	106.1106	16.89	0.448001	56.545	13.91
MGO-TiO_2	81.3364	19.71251	0.400836	73.77	23.63

Transmission Electron Microscopy

Figure 6 shows the TEM micrographs of the prepared samples. The TEM micrograph of GO captured at 500 nanometers (Figure 6a) reveals a layered-wrinkled structure with many folds on it, which may be attributed to various oxygen-containing functional groups (Liu *et al.*, 2015; Deng *et al.*, 2013, Nhlane *et al.* 2021). The TEM micrograph of MGO (Figure 6b) was captured at 100 nm and depicts the homogeneous distribution of iron-oxide nanoparticles on the surface of GO. The average diameter of MGO nanoparticles determined using Image J software was found to be 24.58 nm (Deng *et al.*, 2013). The TEM micrograph of TiO_2 nanoparticles (Figure 6c) reveals that the formed TiO_2 nanoparticles are almost spherical and are aggregated to some extent. The average diameter of TiO_2 nanoparticles was found to be 35.51 nm. The TEM micrograph of GO-TiO_2 nanocomposite (Figure 6d) shows the successful deposition of TiO_2 nanoparticles on the layered structure of GO (Ibrayev *et al.*, 2019). The TEM images of the MGO-

TiO_2 nanohybrid (Figure 6e) depict the presence of iron-oxide nanoparticles, some iron rods, and TiO2 nanoparticles on the surface of GO, showing the successful stacking of all the components. The crumpled structure of GO sheets enables the binding of nanoparticles onto their surface (Chang *et al.*, 2015; Jo & Selvam, 2015).

Fig. 6a): TEM micrograph of GO

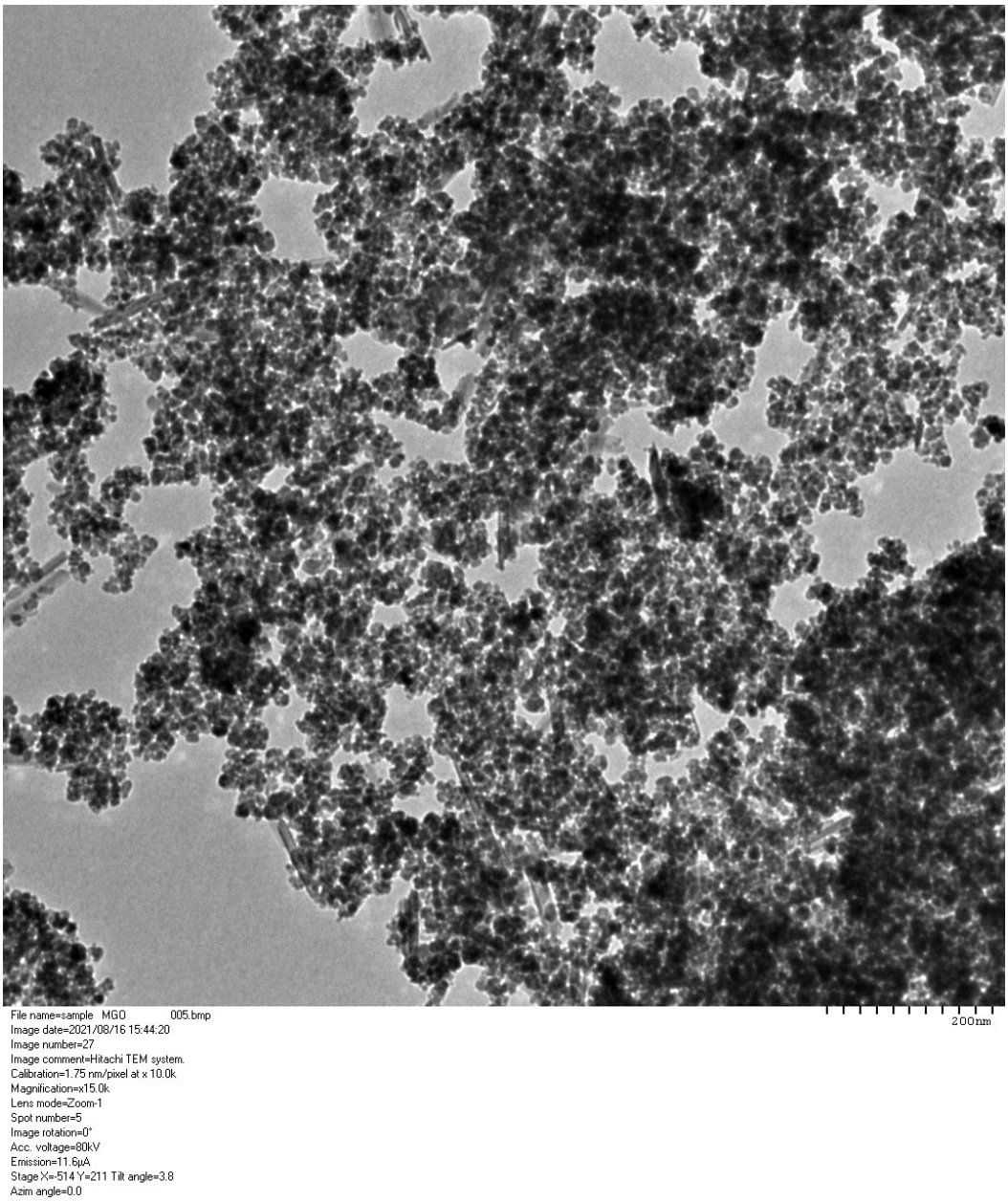

Fig. 6b): TEM micrograph of MGO

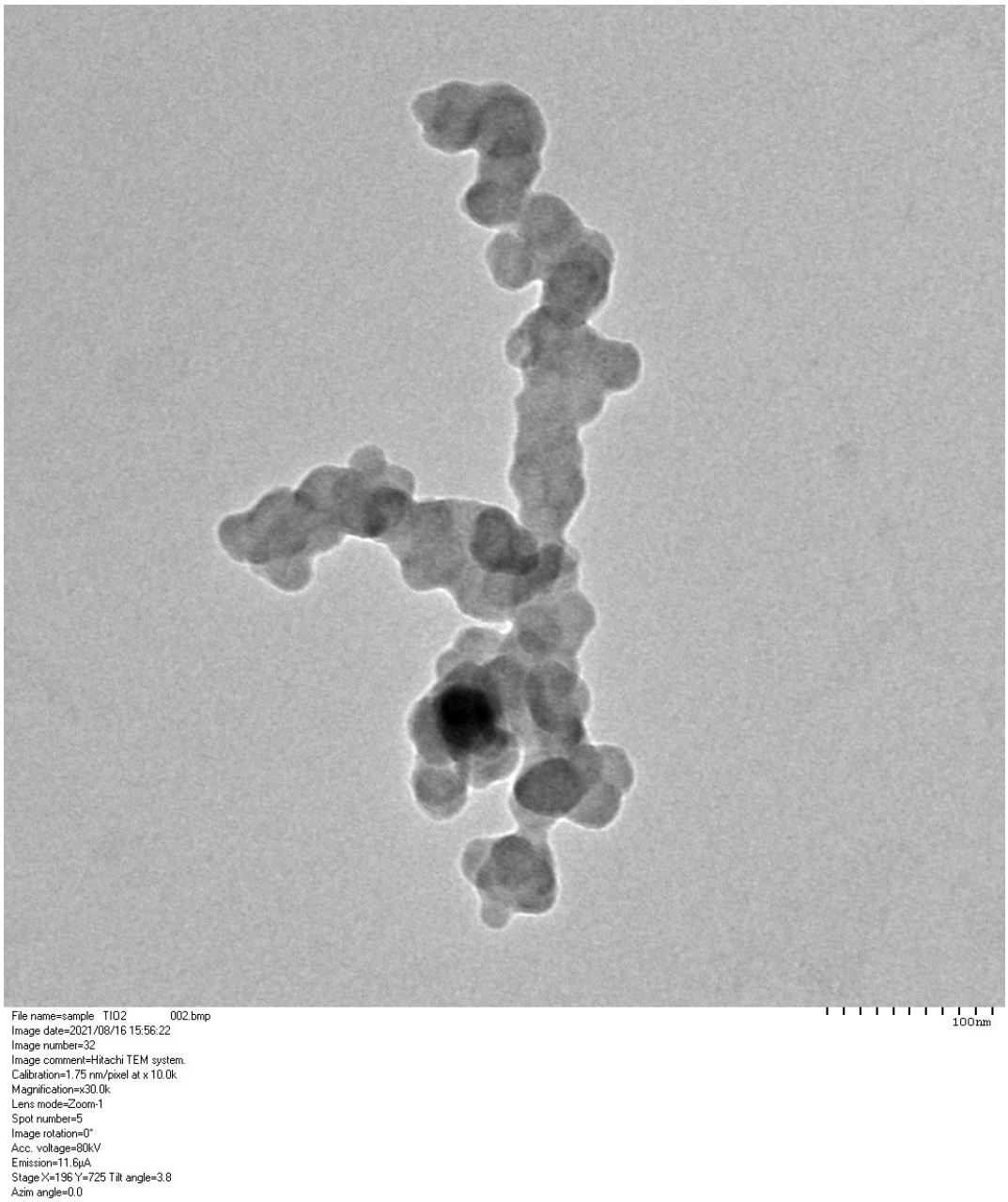

Fig. 6c): TEM micrograph of TiO2

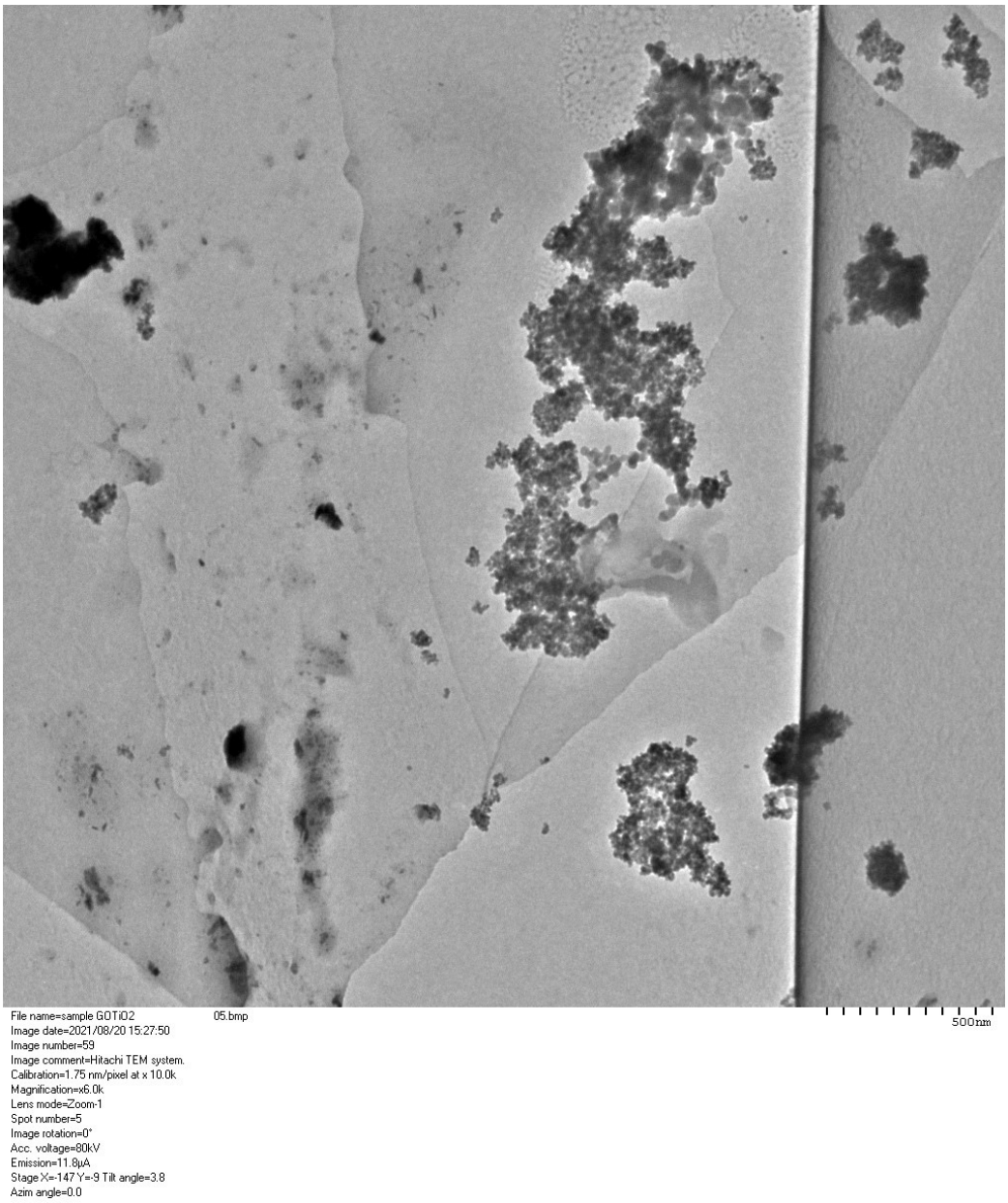

Fig. 6d): TEM micrograph of GO-TiO_2

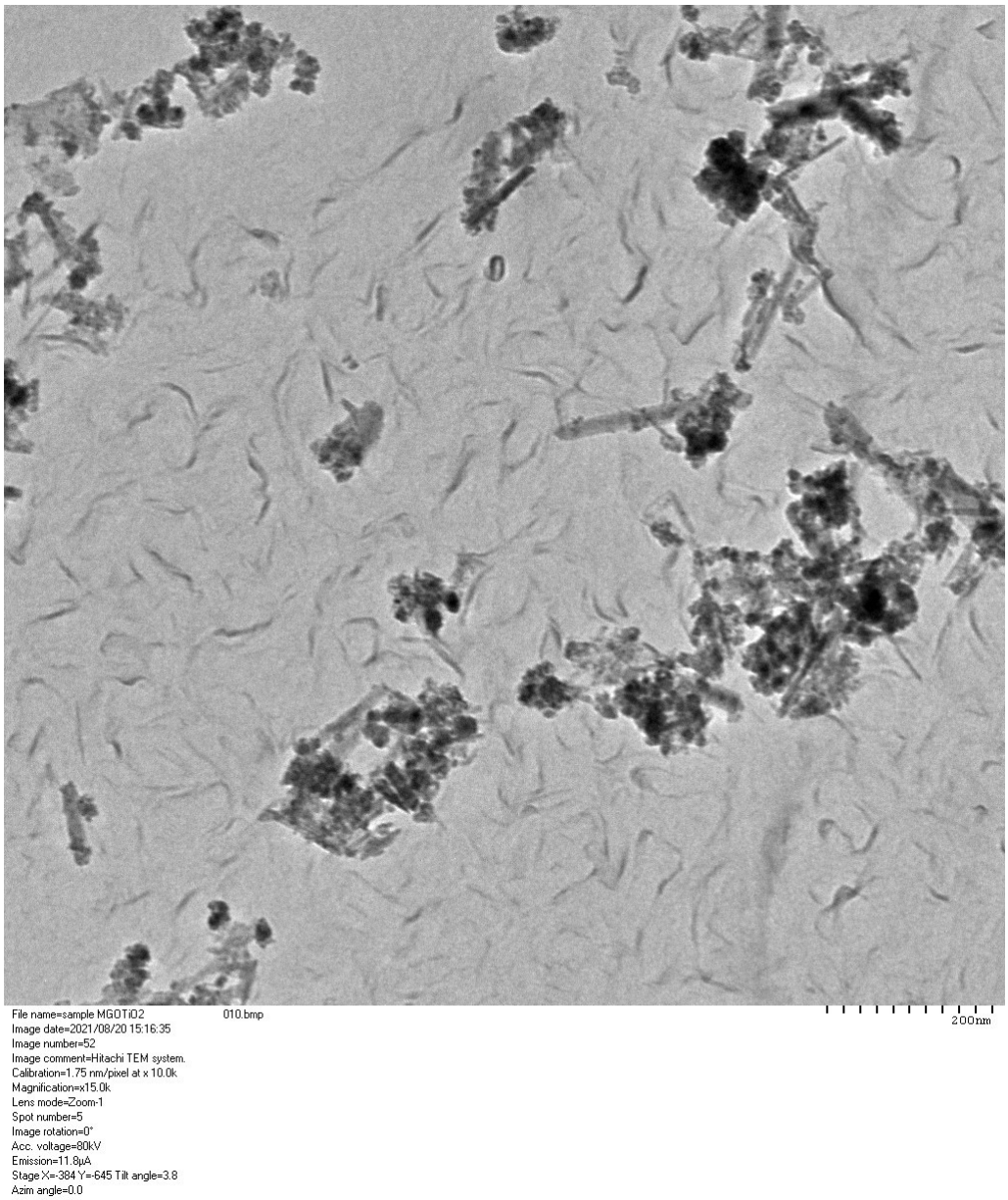

Fig. 6e): TEM micrograph of MGO-TiO_2

FT-IR Spectroscopy

The FT-IR spectra of the prepared samples are presented in Figure 7. The FT-IR spectrum of GO displayed a broad band at 3225.37 cm-1, which can be attributed to the presence of water adsorbed on the surface of GO or to the structural hydroxyl groups (-COH and -COOH) of GO. Additionally, a band at 1722.77 cm-1 was observed, which is characteristic of the vibrations of the C=O group, and a band at 1046.22 cm-1 was due to C-O stretching vibrations of the alkoxy group (Sitko *et al.*, 2013).

The FT-IR spectrum of MGO exhibited a band at 3203.39 cm-1, which can be attributed to the O-H

stretching vibrations. Additionally, a band at 551.62 cm-1 was observed, which is due to Fe-O stretching vibrations. The band at 890.95 cm-1 supports the deposition of iron nanoparticles on the surface of GO (Liu *et al.*, 2015; Sun *et al.*, 2018).

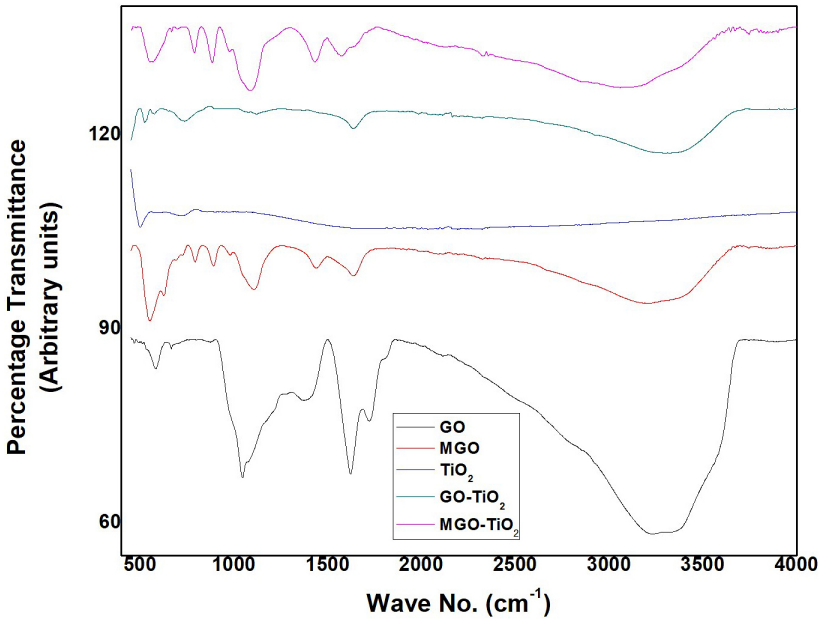

Fig. 7: FT-IR spectra of the prepared samples

The FT-IR spectrum of TiO2 exhibited only one major peak at 499 cm-1, which is characteristic of Ti-O-Ti bonds (Bok-Badura *et al.*, 2017). The FT-IR spectrum of GO-TiO2 showed bands at 1635.26 cm-1 and 3387 cm-1, which are characteristic of aromatic groups and O-H stretching vibrations, respectively. Additionally, a band at 523.51 cm-1 was observed, which corresponds to the Ti-O-Ti vibrations (Sakulpaisan *et al.*, 2016; Kurniawan *et al.*, 2020).

The FT-IR spectrum of MGO-TiO2 displayed bands at 3058 cm-1, 1578 cm-1, 1086 cm-1, and 788 cm-1, which are attributed to the adsorbed water content on the GO surface, C=C vibrations, C-O vibrations, and C-O-Ti vibrations, respectively. The band at 884 cm-1 can be attributed to the covalent bonding of Fe3O4 nanoparticles on the GO surface. The lowering of the carbonyl band of GO to 1431 cm-1 indicates the successful deposition of TiO2 and Fe3O4 nanoparticles on the GO surface (Zhang *et al.*, 2015).

Conclusion

The morphologies and size of the prepared nanomaterials were determined using transmission electron microscopy. TEM micrograph of GO depicted the formation of the layered structure of GO with many folds which might be attributed to the presence of oxygen-containing functionalities, TiO_2 micrograph depicted the formation of large agglomerates of TiO_2 particles. MGO-TiO_2 revealed the deposition of iron oxide nanoparticles and TiO_2 nanoparticles on the surface of GO. From the TEM micrographs the approximate sizes of MGO and TiO_2 nanoparticles were found to be about 24.58 and 35.51 nm respectively. FT-IR spectra of the synthesized nanomaterials depict the presence of required functional groups on their respective surfaces. N2 adsorption-desorption studies exhibited that MGO was having the highest surface area (108.3750 m2/g), and the prepared GO was macroporous while all other samples were mesoporous. Thus, the successful preparation of the adsorbents was confirmed.

Transmission electron microscopy was used to measure the produced nanomaterials' sizes and morphologies. A TiO2 micrograph showed the formation of huge agglomerates of TiO2 particles, and a TEM image of GO showed the development of a layered structure with many folds that may be explained by the presence of oxygen-containing functionalities. TiO2 and iron oxide nanoparticles were found to have been deposited on the surface of GO by MGO-TiO2. The approximate diameters of MGO and TiO2 nanoparticles were determined from the TEM micrographs to be around 24.58 and 35.51 nm, respectively. The presence of necessary functional groups on the surfaces of the synthesized nanomaterials is shown in their FT-IR spectra. Studies on the N2 adsorption-desorption of several materials showed that MGO had the greatest surface area (108.3750 m2/g), and that the produced GO was macroporous whereas all other samples were mesoporous. Thus, the adsorbents' successful preparation was verified. The results of the study provide information about the functional groups present in nanomaterials, which further aids in determining the heavy metal contamination that can be eliminated from aqueous medium, making the study highly beneficial for the synthesis of real-time filters. Moreover, surface area-related information offers binding site-related information. Better adsorption capability is demonstrated by higher surface area. The usage of GO as an adsorbent indicated an increase in the strength of the filtration material.

Acknowledgments

We sincerely thank the Department of Science and Technology for providing us research grant under the Promotion of University Research and Scientific Excellence (PURSE) grant scheme for carrying out the research work of this manuscript.

Funding

Department of Science and Technology (DST) under research grant Promotion of University Research and Scientific Excellence (PURSE).

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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