2D and 3D graphene-based nanomaterials for environmental remediation

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Certificate

This is to certify that this dissertation entitled **"2D and 3D graphene-based nanomaterials for environmental remediation"** towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by **Shubham Kumar** at CSIR-National Chemical Laboratory, Pune under the supervision of **Dr Kaliaperumal Selvaraj**, Senior Scientist, Catalysis Division, CSIR-NCL, Pune during the academic year 2017-18.

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Declaration

I hereby declare that the matter embodied in the report entitled "**2D and 3D graphene-based nanomaterials for environmental remediation**" are the results of the work carried out by me at the Catalysis division, CSIR-National Chemical Laboratory Pune, under the supervision of **Dr Kaliaperumal Selvaraj** and the same has not been submitted elsewhere for any other degree.

Shubham Kumar

Dr K Selvaraj

Acknowledgement

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20-03-2018   Shubham Kumar

                                                                       IISER Pune

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1. Abstract

Waste water treatment has become a major problem in 21st century. Dyes are the major component of the effluents released by industries. Many techniques are used today to remove dyes from water but adsorption has been considered as the best option due to ease of handling, good dye removal efficiency and low cost. The objective of this work is to explore dye adsorption capabilities of various graphene forms and see the effect of dimensionality and surface properties on their dye adsorbing capacities. Six materials were chosen for this study with 2D and 3D dimensions. Graphite, Graphene oxide(GO), reduced GO(rGO), holey rGO are considered as 2D carbon materials whereas GO hydrogel(GOH) and Holey GO hydrogel(HGOH) are considered as 3D materials. Out of these, GO outperformed others due to the cumulative effect of better electrostatic interaction, hydrogen bonding, π-π stacking and large surface area.

2. Introduction

2.1. Dyes

Dyes are coloured compounds which are used in cosmetics, plastics, textiles, printing, leather industries to colour their compounds resulting in the generation of a large amount of coloured wastewater [1]. Earlier, dyes were mainly derived from natural sources such as plants, animals and minerals without any chemical treatment [2]. But today they are manufactured via chemicals, making them synthetic. Among the dye using industries, textile industries are placed in position one to use dye to colour fabrics [3]. Modern reactive dyes have been found to cause adverse effects on workers in textile factories and on the environment. Today, the production of commercial dyes is >7 x10^5 tons per year and more than 100000 dyes (in total) are known, to date [4-8]. Even the acute presence of dyes (<1 mg/L for some dyes) in the water, which are highly visible, affects the aerobic levels seriously. It also affects the transparency of lakes, rivers and other water bodies, leading to damage to the aquatic environment. On irrigation, it pollutes the soil too. Therefore, a major area of basic and applied science works on the dye removal from the industrial wastewater.

2.2. Use of various dyes in industries

Dyes are basically classified as cationic, anionic and non-ionic. Dyes can also be classified in terms of their chemical structure and their application. According to their structures, dyes are classified as azo, nitro, nitroso, indigoid etc (Table 1). According to application, dyes can be categorized as reactive, acid, direct, disperse, vat and basic dyes (Table 2).

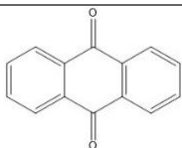Table 1: Classification of dyes based to their chemical structure [9]
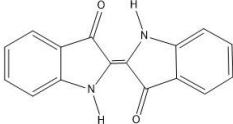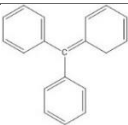
Class	Chemosphere	Examples
Azo		Reactive blue 5
Anthraquinone		Reactive blue 4
Nitroso		Nitroso green, Acid green 1
Nitro dyes		Picric acid, Acid yellow 24
Indigoid		Acid blue 27
Triarylmethane		Phenolphthalein, Basic red 9

Table 2: Classification of dyes based on their chemical nature [10]

Class	Method of application	Substrate	Examples
Direct	Usage from neutral or slightly alkaline baths which contains additional electrolyte	Nylon, paper, leather, rayon and leather	Azo, oxazine, phthalocyanine, stilbene
Acid	From acidic to neutral bath	Wool, inks, silk, and leather	Triphenyl methane, anthraquinone, nitro and azo
Basic	Used from acidic dye bath	Inks, paper, polyacrylonitrile and polyester	Acridine, azo, diphenylmethane xanthene, triarylmethane, cyanine azine, oxazine, and anthraquinone

Reactive	Functional group on fibre reacts with the reactive sites on dyes to bind dye covalently under the influence of heat and pH.	Cotton, wool, nylon and silk	Azo, anthraquinone, phthalocyanine, oxazine, basic and formazan.
Disperesed	Often applied by lowering the temperature of fine aqueous dispersions; dye then padded on fixed cloth.	Acrylic polyester, acetate, plastics and ployamides	Azo, benzodifuranone, nitro, styryl, and anthraquinone.
Sulphur	Vatted substrate along with sodium sulphide(reoxidized) to form insoluble sulfur-containing products on fibre.	Cotton and rayon	Indeterminate structures

Dye are commonly used by textile, leather, rubber, plastic, printing, cosmetics etc to colour their products. Out of all dye using industries, textile industries are polluting the environment most. Azo dyes are the most used dye. Among others, Methylene blue(MB), which is a basic dye, is also a commonly used dye. This dye is generally used to dye jute, acrylic fibres etc.

2.3. Hazards of dye polluted water

Quality of water has degraded over time due to the emission of organic pollutants from textile industries. Worldwide, the total consumption of dye by the textile industries is greater than 10,000 tones/year and approx. 100 tone/year is discharged into water streams [11]. In the textile industries, almost 10% of the dyes are lost in the dying process and about 2% is directly discharged in the environment as aqueous effluent. In the absence of suitable treatment, these compounds persist their chemical structure and colour even in contact with sunlight thereby effecting aquatic life badly. Major impacts are prevention of sunlight penetration which inhibits the growth of algae and photosynthesis in plants. These residual dyes can be very toxic to fish and aquatic organisms [12].

2.4. Separation of dyes from water

An ideal dye removal water treatment should satisfy:

1) Separation of dye wastes from water environment.
2) At least partial or complete degradation or mineralisation of waste organic dye.

Separation can be established on the principles of fluid mechanics such as sedimentation, centrifugation, flotation and filtration. It can also be based on separation techniques via membrane such as Nano, ultra or micro-filtration and reverse osmosis. Physio-chemical processes such as adsorption, ion exchange, chemical precipitation, flocculation and coagulation are also used for separating solid, emulsified and dissolved components from waste water [13,14,15].

Partial and complete mineralisation or degradation can also be achieved by using chemical and biological processes. Biological processes are used in combination with activated sludge and bioreactors. Chemical process includes oxidation of dyes using oxidants such as ozone, H_2O_2 etc under UV irradiation [16].

2.4. (a) Chemical methods:

1. Irradiation:

One of the most effective alternative for the treatment of wastewater is radiation processing. Irradiation processing has many advantages:

1) Safe and efficient reduction of pathogens [17].
2) Organic pollutants which are lethal and hazardous like pesticides, herbicides etc can be oxidised and converted into degradable substances [18].
3) Odour irritation elimination is also expected during irradiation processes [17].
4) Safe, easy and efficient way of sludge treatment [17].

2. Oxidation

Chemical oxidation is the conversion of pollutants by an oxidant. Modern textile dyes are resistant toward mild oxidation processes therefore more powerful oxidants such as ozone, chlorines, fenton reagents, UV/ozone, UV/peroxide etc have to be employed for efficient dye removal [19]. Peroxide treatment can decolorize most of the aromatic dyes from water. Preparation of hydroxy radical involves advanced oxidation processes [20]. Peroxidases can catalyse aromatic dye degradation either by ring opening or precipitation. H_2O_2/O_3 are reported for removing cyanide for drinking water [21]. Electrochemical oxidation is also a promising technique because the electrons deliver as an efficient, cost-effective, easily automatable, safe and clean reagent for wastewater treatment [22]. Disadvantages includes need of massive space, risk of overdose and partial oxidation which may produce more toxic impurity.

3. Ozonation

Ozone has been used for more than a decade in the treatment of wastewater. One of the most crucial features of ozone in the treatment of industrial wastewater is its ability to convert bio-refractory compounds into less poisonous compounds which can be easily degraded via biological processes [23]. Disadvantage of ozonation includes its short lifetime (approx. 1200 secs), getting destabilised in the presence of salts, pH, temperature, and the additional costs of installation an ozonation plant [24].

2.4. (b) Physical methods:

1. Adsorption

The accumulation of a substance at the interfaces between two phases (solid-liquid or gas-solid) is termed as adsorption. The substance that gets accumulated is called an adsorbate and the material on which adsorption happens is called an adsorbent. There are two types of adsorption i.e. chemical (chemisorption) and physical (physisorption). Chemical adsorption is illustrated by the development of a chemical association between adsorbate and adsorbent. In physical adsorption, reversible weak intraparticle bonds are formed [25]. Major physical forces in physisorption are Vander Waal's forces, polarity, hydrogen bonding, dipole-dipole π-π interactions etc [26].

The adsorption process for dye removal has been widely used. From ancient times carbon adsorption has been used for water purification. Adsorption was first observed by C.W Scheele in 1773 (gases exposed on carbon) [27], followed by Lowitz in 1785 making an observation of the reversible elimination of colour and odour producing compound (wood charcoal) from water.

2. Ionic exchange

Ion exchange is a process in which one or more undesirable substance is removed from water in exchange with a less or non-objectionable material [28]. Heavy metals are effectively removed from wastewater using ion exchange. Recovery and reuse of the ion exchange resins can be easily done using regeneration processes [29]. Ion exchanged in this process are not chemically changed. Recovery of valuable metals, selectivity and low volume of sludge production are the main advantages of this process [30].

3. Membrane processes

Filtration via membranes has been used for colour removal, polyvinyl acetate recovery, salt reduction and many others. This process can also be combined with other effluent treatment processes. This method is temperature resistant. High cost, clogging and frequent replacement of membrane are the major disadvantages of this process. Types of membrane filtration includes micro, ultra, nano filtration and reverse osmosis(RO) [31]. Micro filtration is suitable for separating suspended solids and colloids using macromolecules with pore size of 0.1-1 micron. Ultra-filtration is used to separate polymers from salts and low molecular weight materials with pore size of 0.001-0.1 microns. Nano-filtration(NF) has its ability to remove colour from solutions with a pore size of 1-2 nm. NF systems are highly sensitive to fouling by filtrate materials such as polymers, colloidal macromolecules etc, thereby extensive pre-treatment is required [19]. RO is used to remove mineral salts, ionic compounds (most kinds) and hydrolysed reactive dyes [32].

4. Coagulation and flocculation

This is one of the most used technology for the treatment of wastewater. Coagulation flocculation involves clumping of small and destabilized particle into a larger aggregate by addition of a polymer thereby making their easy removal from water [33]. The terms 'Coagulation' describes the initial process of destabilization of original colloid dispersion, typically by charge neutralization and the term 'Flocculation' defines the subsequent process in which the destabilised colloids (in the micron and sub-micron size range) undergo aggregation and particle grows into millimetre-sized flocs [34].

Out of all the methods mentioned above, adsorption is considered as the most preferred and effective method to remove dye from aqueous solution due to several advantages such as its low cost, ease of operation, simplicity in design and insensitivity towards toxic and reactive pollutants that reduces its activity [35]. Hence, adsorption-based dye removal is heavily being explored in the recent years.

2.5. Materials used for dye removal

To remove dyes, many materials have been studied such as $Ti-O_2$, magnetite, zeolites (in membranes), $Ag/Ti-O_2$ (commonly used in the process of disinfection), Nano $Ti-O_2$ and fullerene derivative (as photocatalytic agents), alumina, silica gels, Nanofibers, metal oxide etc. Few of them such as Nanofibers, metal oxides are advantageous over others because of their high surface area, easy reuse etc. But carbon materials get an edge over other materials due to their large specific surface area, high stability, different structural variety and pore size modification [35,36].

2.6. Graphene for dye adsorption:

Soon after its discovery, Graphene has become a novel material in adsorption and catalytic technologies. To date, many carbon materials have been used for removing water pollutants such as activated carbon [38], carbon nanotubes [39] etc. But recently, graphene has come out as a star material as an efficient material for removing organic and inorganic pollutants from water. Magnificent adsorption capacity, excellent catalytic performance and abundant availability are the key factors which makes this material a suitable alternative to control environmental pollutant especially in terms of the removal of water pollutants [40]. However, the influence of

various factors of graphene such as chemical reactivity, surface availability, structural features on the adsorption of polluting dyes are hardly examined. Hence in the present work, we study the effect of some of such influencing factors on the adsorption of dyes by choosing various forms of graphene and graphene-based materials.

2.7. Purpose and Scope of this work

Purification of water bodies is of paramount importance to us, one aspect of which is dye removal from industrial waste water, before releasing the waste onto the drainage system. The research work carried out in this project introduces effective dye separation schemes.

The objective of this work is to understand the effect of having an extra dimension and different surface characteristics on material's dye removal capabilities. In order to do that, six forms of graphene-based nanomaterials are designed, developed and then analysed to understand the responsible factors for their dye removal capabilities. Out of six, four materials (Gr, GO, rGO and HrGO) can be classified as 2D materials and two materials (GOH, HGOH) as 3D materials. This work is done on the belief that an extra dimension (when comparing 2D and 3D) will help in more dye adsorption. In continuation, holes have been created in rGO and GOH (called as HrGO and HGOH respectively) assuming they will increase the quantity of oxygen functional groups in the basal plane thereby leading to an increase in dye adsorption capacity (discussed in section 4.3). These all six materials are also different from each other in terms of functional groups present on their surfaces. Gr, rGO and HrGO are supposed to have lesser number of oxygen functional groups compared to GO, GOH and HGOH. Methylene blue(MB) has been used as the dye in this study because it is commonly used in textile industries. In context to chemistry, it serves as a good adsorbate since it has a ring structure which can interact with graphene material via π-π interactions. MB being a positively charged dye, it can have an electrostatic interaction with graphene adsorbent making it as a good adsorbate for this study.

It is important to note that the present work reports the real-time analysis of MB adsorption by graphene-based materials using an *in-situ* UV -visible experimental setup (as described in the following sections) for the first time.

3. Materials and methods

3.1. Materials

Liquid form of pure dye i.e MB is used in this work which was bought from external sources. Graphite was bought from Sigma Aldrich and GO was prepared as well as bought from Platonic nanotech Pvt Ltd. Both sodium hydroxide(NaOH) and hydrogen peroxide (H_2O_2) were bought from Finar limited.
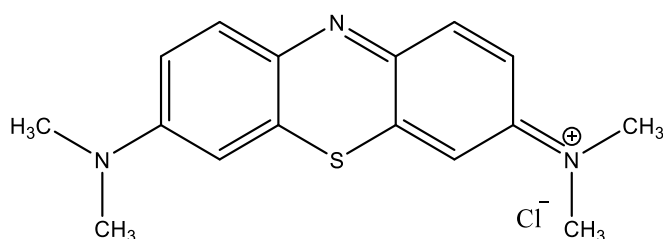

Figure 1: Structure of Methylene Blue

3.2. Synthesis

Graphene oxide (GO)

GO is prepared using Modified Hummer's method [41]. In a typical procedure graphite powder is stirred with $NaNO_3$ and H_2SO_4 at low temperature and $KMnO_4$ (strong oxidant) is added slowly in small amounts with stirring. After stirring for another two hours, Millipore water and H_2O_2 are added to obtain bright yellow colour suspension. It is washed with HCl and water and dried to obtain GO.

Reduced graphene oxide (rGO)

rGO is synthesized via hydrothermal treatment of GO suspension. In this procedure, GO is added to 70 mL of Millipore water and is sonicated for 2 h. Then while stirring, NaOH solution (2 mol/L) is added dropwise. Whole suspension is then transferred into a Teflon-lined hydrothermal reactor and heated at 180 °C for 6 h and then washed with millipore water followed by drying.

Holey reduced graphene oxide (HrGO)

Holey rGO is prepared via hydrothermal treatment. GO suspension (in millipore water) is prepared using sonication. While sonicating, 0.3% H_2O_2 is added into GO suspension and again sonicated for 4 h followed by addition of NaoH solution. In the end, whole solution is sealed in an autoclave and kept for heating for 6 h at 180 °C and dried.

Graphene oxide hydrogels (GOH)

3-D self-assembled GO hydrogel is synthesized by hydrothermal treatment of GO dispersion [42]. GO dispersion is prepared by adding GO to 240 ml of Millipore water and sonicated for 2 h. The GO dispersion is then poured into a 100 mL Teflon-lined hydrothermal reactor and kept at 180 °C for 6 h. Obtained hydrogels is then freeze dried for ~17 h.

Holey Graphene oxide hydrogels (HGOH)

GO dispersion is made using Millipore water and sonicated it for 2 h. H_2O_2 solution (0.3%) is added to the GO dispersion and then again kept for sonication for 1 h. The resulting suspension is then transferred into a Teflon-lined hydrothermal reactor and heated at 180 °C for 6 h and the as prepared Holey GOH is then freeze dried for ~16 h [39].

3.3. Adsorption parameters

Each MB solution for this study is made new. Each ppm value is converted into volume of pure MB solution in Millipore water. The formula used to calculate adsorption capacity and efficiency are:

Adsorption capacity = $[(C° - C) \times V]/ m$ ....Eqn. 1

where

C° = initial conc. of the dye solution, C = conc. of dye left after adsorption experiment, V = volume of total solution in litres, m = mass of adsorbent in grams

Efficiency =   [(C° - C)/ C°] x 100 %   ……………………….. Eqn. 2

where

C° = initial conc. of the dye solution, C = conc. of dye left after adsorption experiment

Calibration plots

For each sample, separate calibration plot is made, by measuring the UV-Vis absorbance for the same MB solution used for adsorption study. Using the calibration plot, each absorbance value at the end of the experiment is converted into concentration and then used for further calculations (using Eq. 1 and Eq.2).

3.4. Dye adsorption study

Adsorption experiments are carried out using Perkin Elmer Lambda 465 spectrometer, with a MB concentration of ~1500 ppm and a total volume of 15 mL in all the experiment with a catalyst concentration of 0.33 g/L. In the sample vial, MB solution and catalyst are continuously stirred using a magnetic bead and in-situ UV measurements were taken after every 3 mins. The setup consists of a glass vial, which is connected to the UV-Vis spectrometer using flexible Teflon tubes. In order to make sure no catalyst reaches the UV cuvette inside the spectrometer, a tube with smaller diameter (washed and obtained from empty gel pen refill) is used as a connector between UV tubes and MB solution, which had cotton plugged at the end. Before adding the catalyst, a blank trial was run with all the setup except the catalyst in order to make sure that there was no absorption from the setup when UV absorption for solution with catalyst was measured. The setup used is shown in Fig.2.
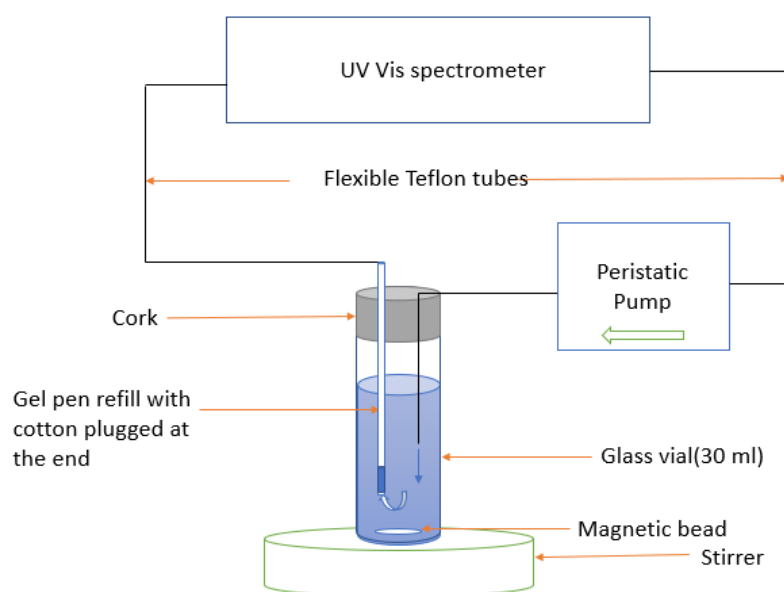
Figure 2: Experimental setup for *in-situ* adsorption studies

4. Results and Discussions

4.1. Physicochemical characterisation techniques used

Raman spectroscopy is considered to be a powerful technique to study carbon materials especially graphene and its derivatives. Raman analysis is done for the samples on LabRAM Horiba JY HR-800 micro Raman spectrometer. XRD patterns are collected using PAN analytical X'pert Pro dual goniometer diffractometer. Transmission Electron Microscopy (TEM) images are taken using an FEI TECNAI F20 electron microscope operating at 200 kV. Field Emission Scanning Electron Microscopy (FESEM) images are taken using FEI Nova NanoSEM 450. EDS analysis is done using EDAX analyser attached to Environmental Scanning Electron Microscope, FEI Quanta 3D.

4.2. Structural aspects of 2D and 3D graphene materials

Figure 3: FESEM images of (a) Gr, (b) GO, (c) rGO, (d) HrGO, (e) GOH and (f) HGOH

Fig. 3 shows FESEM images of six different graphene-based materials. (a) and (b) represents Gr and GO respectively. Images show that graphite being highly 2 dimensional in nature and that a simple oxidation has not made huge change in the graphitic structure with exfoliated 2D graphene oxide sheets. (c) and (d) represents rGO and HrGO which have irregular surface compared to the precursor GO which happens due to hydrothermal treatment at alkaline conditions. (e) and (f) represents GOH and HGOH having 3D porous structure obtained by making hydrogels of GO and making them porous using hydrothermal conditions much different from that given to (c) and (d) as discussed in section 3.2.
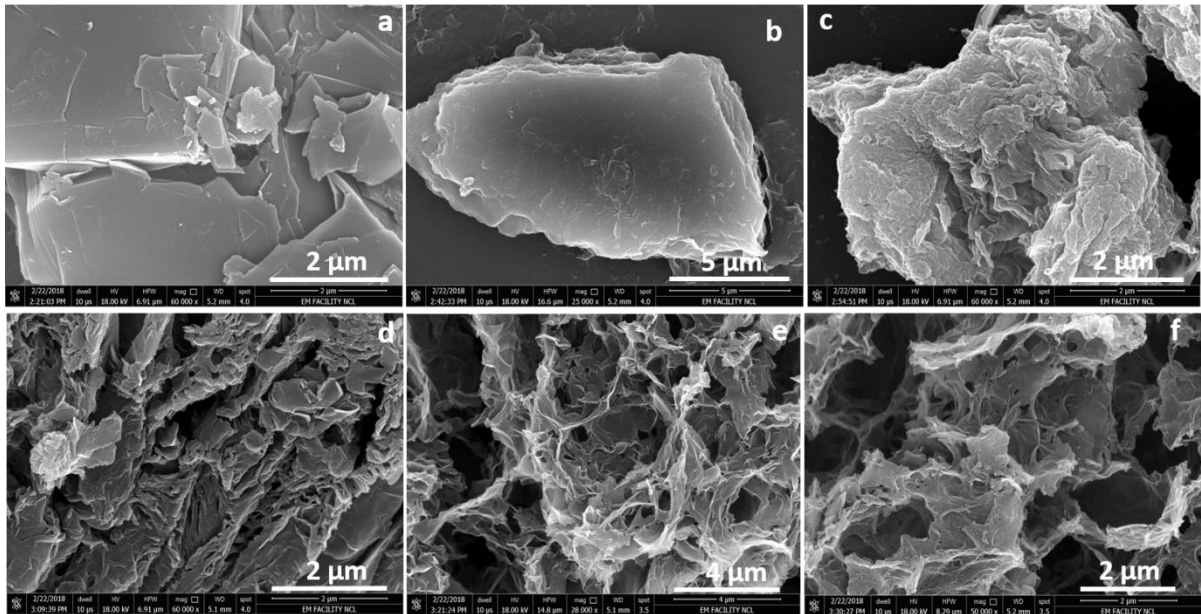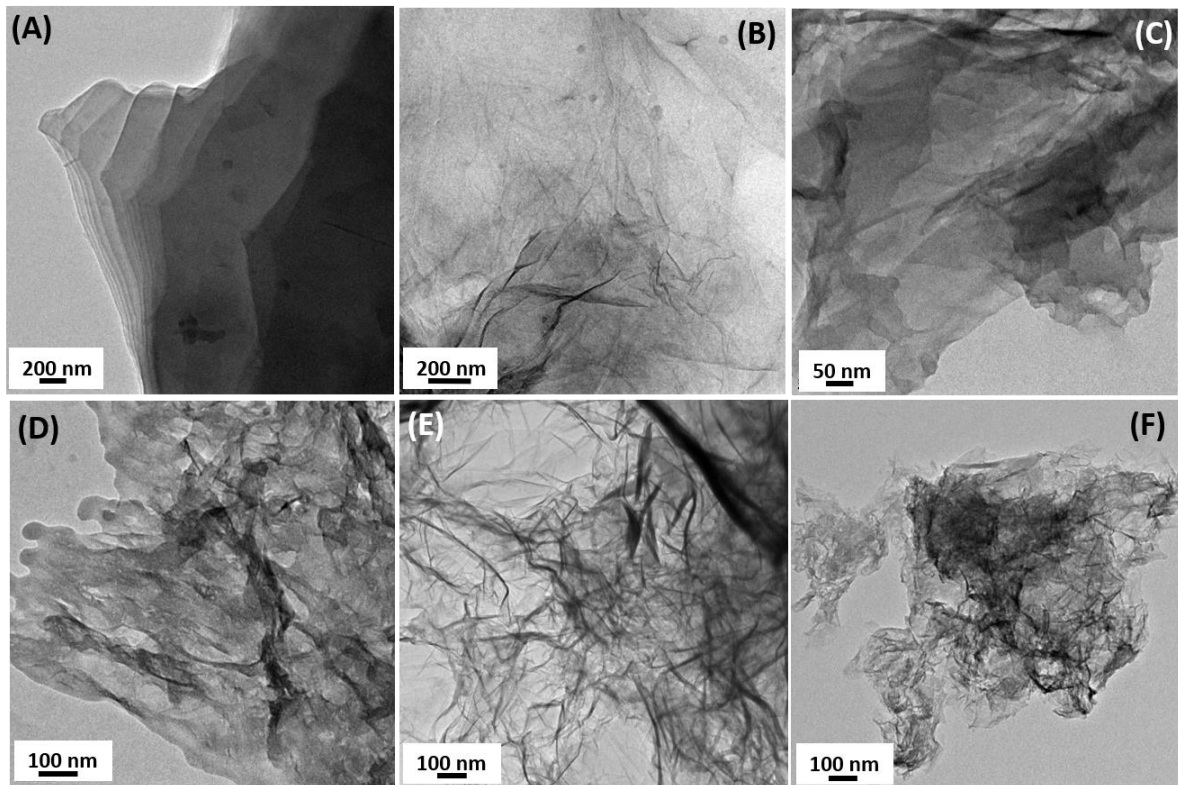
Figure 4: TEM images of (A) Gr, (B) GO, (C) rGO, (D) HrGO, (E) GOH and (F) HGOH

TEM images of six different graphene-based materials is shown in Fig. 4. In Gr as seen in Fig4. (A), a lot of sheets are stacked (represented by dark colour) with different shades of grey indicating their contrast with increasing number of sheets which is not so prominent in case of GO. Wrinkles can be seen in GO Fig4. (B) due to the scrolling of sheets. This is due to the addition of high degree of oxygen containing functional groups (such as epoxy and hydroxyl etc.,) on the basal plane of exfoliated 2D graphene sheets during oxidation. Fig4. (C) represents rGO which has multiple shades indicating the probability of re-staking graphene sheets due to the removal of oxygen containing groups during reduction. Fig4. (E) shows GOH with many GO sheets intertwined, giving an irregular and a 3D morphology. Fig4. (D) and Fig4. (F) represents HrGO and HGOH respectively, in which very fine holes can be seen as a light shaded (almost) circles on the darker sheets. Holes are large in number but small in size in both the cases. This may also be observed in their corresponding FESEM images (Fig. 3.d and 3.f).
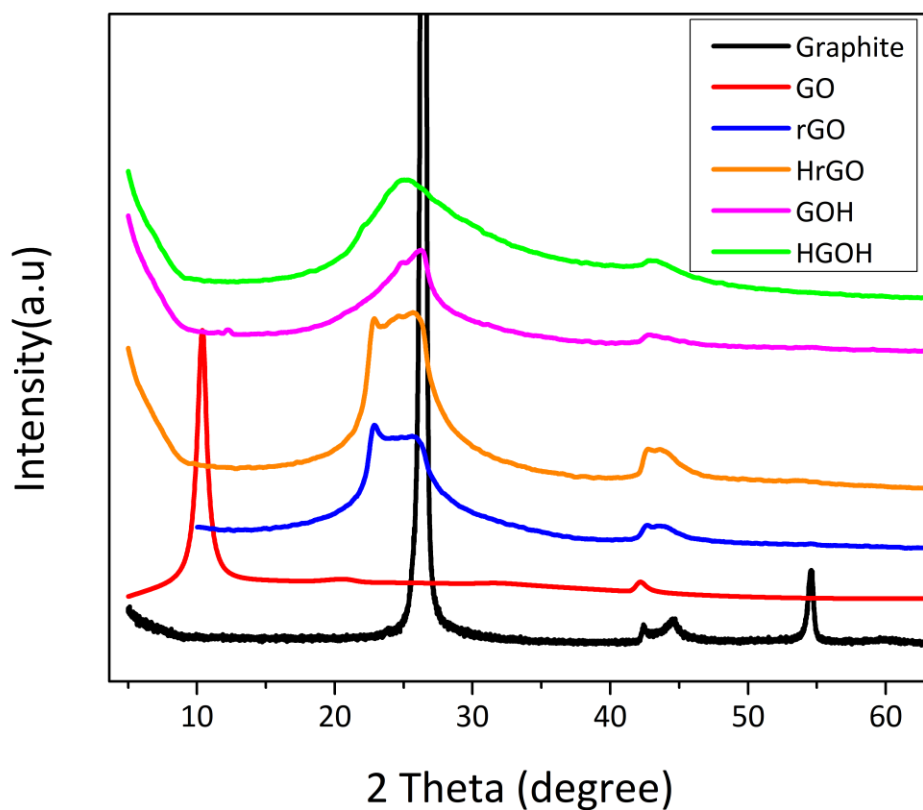
Figure 5: XRD pattern Gr, GO, rGO, HrGO, GOH and HGOH

Figure 5 represents the XRD profiles of six different graphene-based materials. Graphite shows a sharp peak at 27° which corresponds to a characteristic graphitic (*001*) reflection corresponding to an interlayer spacing of 0.16nm, which is shifted down to 11° in case of GO due to the intercalation of oxygen atoms in between the layers, consequently increasing the interlayer spacing to 0.43nm. With the rest of the materials, there is no peak at 11° corresponding to GO but a broad peak around 26° which corresponds to the reduction of all oxygen groups as expected with a little shift towards lower 2 theta value indicating a slight increase in the interlayer spacing [43].
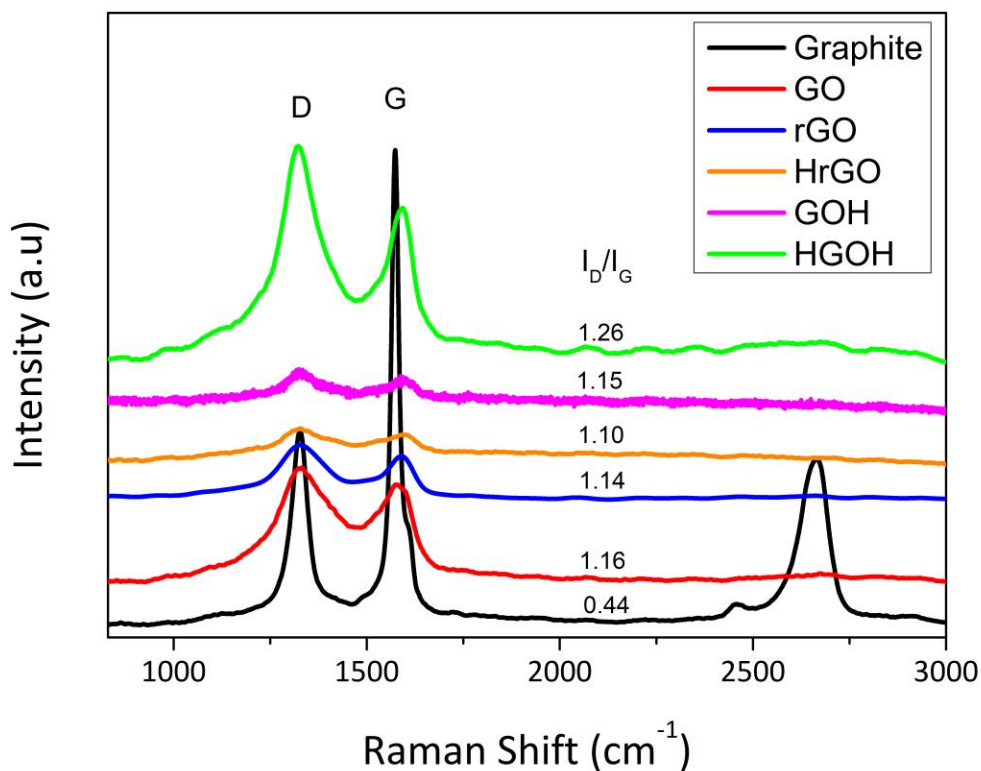
Figure 6: Raman spectra of Gr, GO, rGO, HrGO, GOH and HGOH

Figure 6 shows the Raman spectra of six different graphene-based materials. The G band corresponds to the arrangement of graphitic carbon which is generally assigned to sp^2 carbon atoms. Whereas, the D band represents local defects and disorder. In the Raman spectrum of GO, there is an increase in I_D/I_G ratio with respect to graphite indicating a higher degree of disorder. In case of rGO and HrGO, due to reduction in number of oxygen functional groups, there is a decrease in I_D/I_G ratio with respect to GO, the starting precursor. The increase of I_D/I_G ratio for HGOH compared to that of GOH is due to the formation of nano-porous holes in the basal plane thereby increasing defects.

Elemental Analysis

Energy Dispersive X-ray Spectroscopy (EDS) is an analytical technique for understanding the changes in the chemical or elemental nature of the samples during

various steps of chemical processes. All graphene-based materials are analysed for their carbon and oxygen content. Results of the analysis are shown in Table 3.

S. No	Sample	Carbon (atomic %)	Oxygen (atomic %)
1	Graphite	90.13	9.86
2	GO	48.08	51.96
3	rGO	76.00	34.00
4	HrGO	80.66	19.33
5	GOH	69.18	30.18
6	HGOH	38.82	61.17

Table 3: EDS for six different samples

As expected, Graphite has least atomic percentage of oxygen atoms. As we oxidise graphite using Modified Hummer's method (section 3.2), number of oxygen functional groups increases which is reflected perfectly in Table 3 with GO having an oxygen atomic percentage of 51.96. GO is taken as a precursor for the synthesis of remaining graphene-based samples. GO is treated with NaOH under the influence of hydrothermal conditions to produce rGO and HrGO (with extra addition of H_2O_2 for HrGO). This procedure is expected to reduce oxygen functional groups present on the GO, leading to its reduction which is further confirmed by Table 3(Oxygen at% in rGO and HrGO < Oxygen at% GO). Among the 3D forms of GO, GOH has less atomic percentage of oxygen compared to precursor GO because the high temperature hydrothermal treatment tends to reduce the oxygen functional groups generating H_2O and CO_2[44]. However, in the case of HGOH oxygen atomic percentage has increased compared to GO (precursor) due the addition of H_2O_2 (used for creating holes) which also partially oxidises the carbon atoms leading to an increase in oxygen functional groups around the nanopores [39].

4.3. Dye adsorption using graphene-based carbon materials

Literature Background

In general, Graphene is considered to be a good adsorbent due to its high surface area as well as planar structure. Dye removal capabilities of graphene-based nanomaterials are judged by their nature of interactions (chemical or physical) with dye molecules, surface area available for interaction, nature of dye etc. GO is considered to be an excellent adsorbent for cationic dyes due to the presence of enormous amount of oxygen functionalities thereby establishing electrostatic interaction with the dye molecule [45]. However, Minitha C.R. et al is suggesting that rGO is considered to be a good adsorbent for both cationic and anionic dyes [46]. According to the said report, the presence of large number of defects, remaining oxygen functional groups, π electron domains in the planar structure are the factors which promise the potential of rGO as a better adsorbent than GO. Apart from this dichotomy, adding a third dimension at nanoscopic levels to the graphene-based materials (3D GO/rGO) is thought to increase the adsorption capacity for dye molecules due to an expected increase in the surface area with porous networks [47]. This sets a perfect background for the specific objectives of the present research work. In this work, various representative samples of the entire above said scenario are examined for their dye adsorption capabilities so that clarity can be brought out in this respect.

Dye removal study

The discussion followed in this thesis is considering the following most possible factors that could play critical role in the dye removal at any given scenario:

1) Electrostatic interactions between the dye molecules and the adsorbent
2) π-π stacking between dye molecules and the adsorbent
3) Hydrogen bonding
4) Surface area
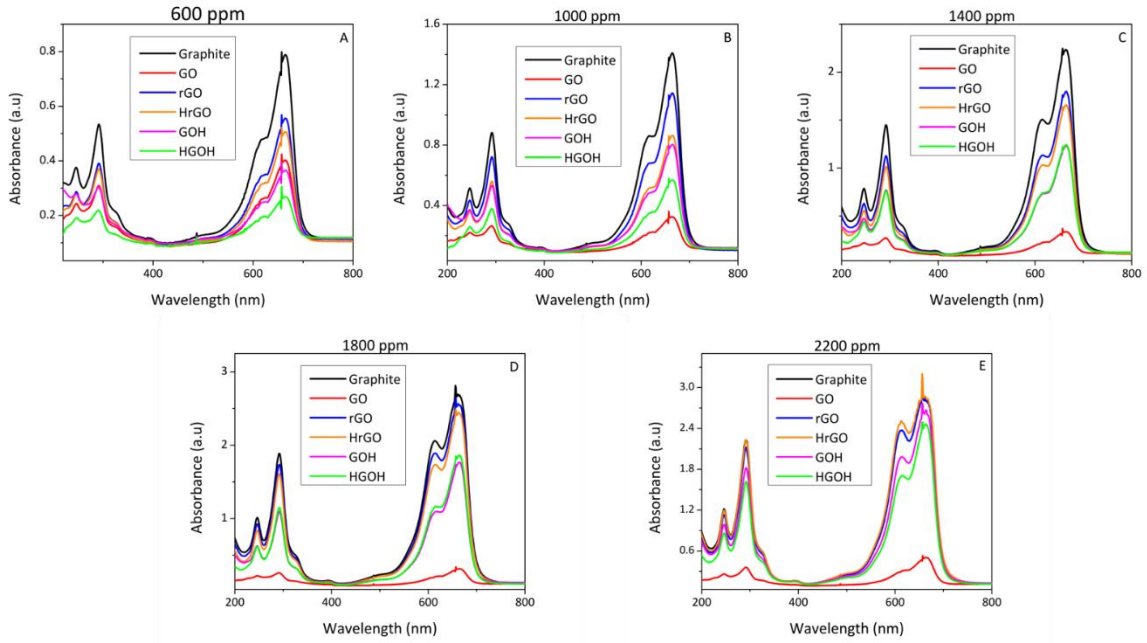
Figure 7: Multiplots of UV-Vis spectrum collected for six different graphene-based samples at MB concentrations (A) 600 ppm, (B) 1000 ppm, (C)1400 ppm, (D) 1800 ppm and (E) 2200 ppm

Using the equations (Eq. 1 & 2) as provided in section 3.3. the dye adsorption capacities and efficiencies of various materials are calculated from the absorbance values collected from UV-Vis spectral data as shown in Fig. 7.
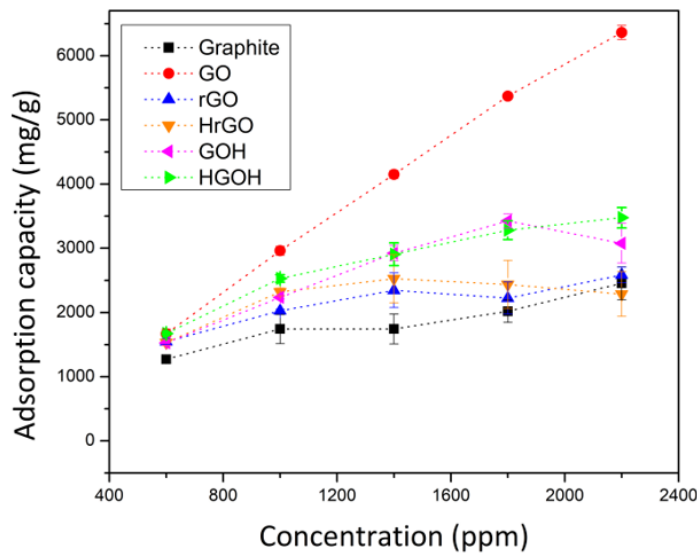
Figure 8: Adsorption capacity for six different samples against concentration.

Conc. (ppm)	Graphite	GO	rGO	HrGO	GOH	HGOH
600	1272.23	1666.89	1547.70	1530.76	1525.26	1673.52
1000	1741.34	2961.91	2027.63	2319.30	2236.13	2529.88
1400	1741.85	4149.36	2346.17	2525.84	2924.59	2907.06
1800	2019.12	5370.34	2224.44	2436.02	3426.67	3280.74
2200	2453.97	6362.70	2586.38	2286.90	3078.26	3475.79

Table 4: Adsorption capacity (mg/g) for six different samples
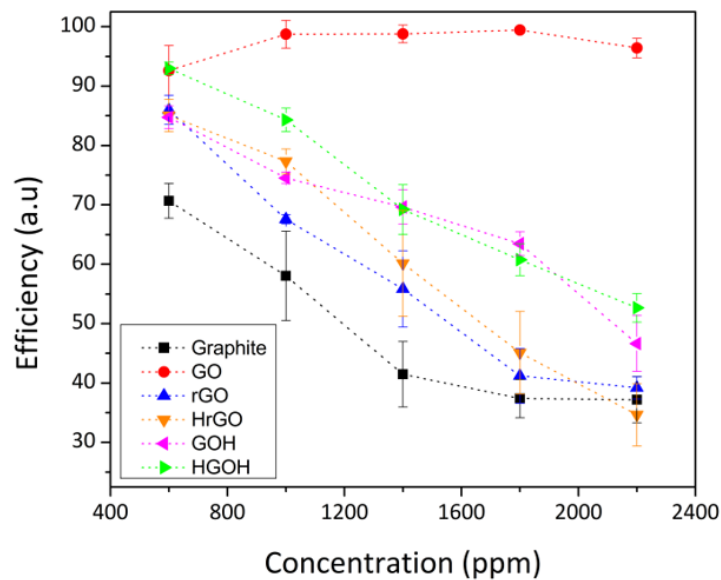
Figure 9: Efficiencies for six different samples against concentration.

Conc. (ppm)	Graphite	GO	rGO	HrGO	GOH	HGOH
600	70.67	92.60	85.98	85.04	84.73	92.97
1000	58.04	98.73	67.58	77.31	74.53	84.32
1400	41.47	98.79	55.86	60.13	69.63	69.21
1800	37.39	99.45	41.19	45.11	63.45	60.75
2200	37.18	96.40	39.18	34.65	46.64	52.66

Table 5: Efficiency (%) for six different samples

As seen in Table 5, out of all six materials, GO performed the best giving an efficiency of > 92%. Rest of the five materials follow almost a similar trend as can be seen in the Fig. 9. In Fig 8, adsorption capacity for GO keeps on increasing with the increase in the concentration whereas other five materials do not follow the same trend. They get almost saturated at higher concentrations of MB. Similarly, efficiency (Fig. 9) of GO is stable within the range of >92% for all concentrations whereas in other materials, it decreases gradually with the increase in concentration.

Theoretically, there could be two strong interaction modes possible between graphene-based materials and the dye molecule, methylene blue viz., (a) π-π interactions between the aromatic rings present in both entities and (b) other non-covalent interactions between the functional groups present in GO (and materials based on it) and the MB molecules.

In our study, GO performed the best compared all other five materials while graphite's performance was the poorest. Graphite being a highly stalked material without much surface area available, its poor performance is understandable. This directly proves the importance of surface area of any material in dye adsorption. Hence exfoliated free standing graphene or graphene oxide materials should be able to perform better compared to graphite. This is exactly observed in the present study. However, when

one compares between GO and rGO, the former is invariably much superior. Chemically the difference between them is in terms of the available oxygen containing functional groups. rGO contains less oxygen containing functional groups compared to that of GO (Elemental analysis data as shown in Table 3) and rGO adsorbs less dye than GO. This is once again directly correlating the dye adsorption with the availability of oxygen containing functional groups. It is also interesting to note that the chances of π-π interactions between MB and rGO is quite high than that between MB and GO. However, it is observed that GO adsorbs 200% more dye than rGO adsorbs even at higher concentration levels of MB (Fig 8).

Much larger number of oxygen containing functional groups present in GO gives it a net negative charge whereas MB (Fig. 1) being a cationic molecule naturally gets attracted towards GO and thus facilitating the adsorption. This also seems to help in the formation of hydrogen bonds with the dye molecule [35].

Both graphene especially rGO and MB have several aromatic rings with conjugated double bonds, there is certainly a good chance for π-π interactions. If π-π staking is predominant, rGO should adsorb better than GO, which is not the case in our study. This shows in the case of graphene-based materials and dye such as MB, other non-covalent (electrostatic, hydrogen bonding) interactions are more favourable than π-π interactions.

Between HGOH (with nano-holes) and GOH (without holes), HGOH performs better. This could be due to the fact that HGOH contains fine nano-holes (Fig. 4(E & F) representing GOH and HGOH respectively). It is well known in general that the edges of graphene sheets are more reactive and accessible for interaction than the central basal plane. Thus the edges of the holes in HGOH that tend to accommodate more oxygen containing functional groups (hydroxyl and carboxyl) attract more MB molecules towards it, resulting in more dye adsorption. It is also possible that the nano-holes in the holey-systems (such as HGOH and HrGO) facilitate the MB flow across the graphene sheets resulting in a better adsorption. This explanation is doubly validated by comparing the adsorption performances of rGO and HrGO. Between them, HrGO performs better due to the mentioned reasons again (Fig. 4(C & D) representing rGO and HrGO respectively).

It was thought that adding 3rd dimension to the graphene 2D sheets might help in improving dye adsorption. For instance, both Raman (I_D/I_G ratio) and EDS data suggest that HGOH (3D) has more functional groups than GO (2D). However, 3D hydrogels viz., GOH & HGOH performed poorly than their 2D counter parts however outperformed the 2D but reduced GO viz., rGO and HrGO. Although HGOH has one dimension more compared to GO, not all of the surface area is accessible for dye adsorption since some part of it gets buried inside during the formation of hydrogel. Presence of oxygen functional groups can be expected in these inaccessible regions which will have less electrostatic interactions with the dye molecule resulting in less dye adsorption whereas in GO all functional groups will present on basal plane as well as on the edges hence available directly for interaction.

This brings out an interesting and deeper understanding that having more 'accessible functional groups' has a greater priority than adding extra dimensionality and bringing more 'functional groups'. For instance, among GO and HGOH, HGOH has higher number of oxygen functional groups but still GO performs better. However HGOH is adsorbing better compared to HrGO and rGO.

The overall MB adsorption order among the materials under study is as follows:

GO > HGOH > GOH > HrGO > rGO> Graphite

5. Conclusion

Six different types of graphene based nano-materials are designed and developed to represent distinct variations among the factors that can influence the dye adsorption properties. Methylene blue is chosen and used as a model adsorbate in this study because of its common usage in textile industries thereby considered as a fair contributor in water pollution. This project is aimed at understanding the effect of dimensionality as well as surface properties of a material on its dye adsorption capabilities. Materials considered in this project differ both in dimensionality as well as surface properties. Materials are characterized by SEM, TEM, XRD, Raman, and EDS to understand their physical and chemical distinctions. All materials are compared among each other using the collected data. Among all the materials, 2D GO performed

the best, having with an average efficiency of > 92% at more or less in a wide range of MB concentrations. Though synergic effects among electrostatic interactions, hydrogen bonding, π-π stacking and surface area available for adsorption are thought to be influencing the dye adsorption, the study provided (along with clear proof) with the following major and deeper understandings.

- exfoliated free standing graphene or graphene oxide materials perform better compared to graphite.
- 2D GO performed the best, with an average efficiency of >92% at more or less in a wide range of MB concentrations.
- Electrostatic interactions are more favourable than π-π for adsorbing dye such as MB using graphene-based materials.
- Having more 'accessible functional groups' has a greater priority for better dye adsorption than adding extra dimensionality and bringing more 'functional groups'.

6. Future scope

Since GO came out as an excellent material for MB adsorption, improving it to have enhanced adsorptions can be explored using the work that can provide a deeper understanding at molecular level. The ability of dye adsorption could be dye specific. Hence the similar studies on various highly industrially polluting dyes can benefit to have more generalised understanding about the materials. To progress with viability of the application, adsorption abilities should also be examined with real samples such as polluted industrial waste water.

References

1. Ravi Vital Kandisa, Narayana Saibaba KV, Khasim Beebi Shaik and R Gopinath. Dye Removal by Adsorption: A Review. Journal of Bioremediation & Biodegradation, 2016, 7(6), 1-4.

2. Kadolph, Sara, Delta Kappa Gamma Bulletin. Natural Dyes: A Traditional Craft Experiencing New Attention. Delta Kappa Gamma Bulletin, Fall 2008.

3. Marc S. Reisch. Asian Textile Dye Makers are a Growing Power in Changing Market. Chem. Eng. News, 1996, 74 (3), 10–12.

4. Chao-YinKuo, Chung-HsinWu, Jane-YiiWu. Adsorption of direct dyes from aqueous solutions by carbon nanotubes: Determination of equilibrium, kinetics and thermodynamics parameters. Journal of Colloid and Interface Science, 2008, 327(2),308-315.

5. BetinaRoyer, Natali F.Cardoso, Eder C.Lima, Julio C.P.Vaghetti, Nathalia M.Simon, TatianaCalvete, Renato CataluñaVeses. Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions—Kinetic and equilibrium study. Journal of Hazardous Materials, 2009, 164 (2–3), 1213-1222.

6. B.H.Hameed, D.K.Mahmoud, A.L.Ahmad. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. Journal of Hazardous Materials, 2008, 158(1), 65-72.

7. Mohamad M Ayad, Ahmed Abu El-Nasr. Anionic dye (acid green 25) adsorption from water by using polyaniline nanotubes salt/silica composite. Journal of Nanostructure in Chemistry, 2012, 3(3), 1-9.

8. Siew-Teng Ong, Pei-Sin Keng, Seok-Theng Ooi, Yung-Tse Hung and Siew-Ling Lee. Utilization of Fruits Peel as a Sorbent for Removal of Methylene Blue. Asian Journal of Chemistry, 2012, 24(1), 398-402.

9. Mustafa T.Yagub, Tushar KantiSen, SharmeenAfroze, H.M.Ang. Dye and its removal from aqueous solution by adsorption: A review. Advances in Colloid and Interface Science, 2014, 209, 172-184.

10. M. Rajabi, K. Mahanpoor and O. Moradi. Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups: critical review. RSC Adv., 2017,7, 47083-47090.

11. Yagub, M. and Sen, T. and Ang, M. Equilibrium, Kinetics, and Thermodynamics of Methylene Blue Adsorption by Pine Tree Leaves. Water, Air and Soil Pollution: an international journal of environmental pollution. 2012, 223 (8), 5267-5282.

12. Green Chemistry for Dyes Removal from Waste Water: Research Trends and Applications, published by Wiley, 2015.

13. B. Ramesh Babu, A.K. Parande, S. Raghu, and T. Prem Kumar. Cotton Textile Processing: Waste Generation and Effluent Treatment. The Journal of Cotton Science, 2007, 11(3), 141–153.

14. Shahid Naveed, I. Bhatti. Membrane Technology and its suitability for treatment of textile waste water in Pakistan. Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan. 2006, 17(3), 155-164.

15. Carmen, & Daniela. Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview. Published by Intech, ISBN 978-953-307-917-2.

16. Udo Wiesmann, In Su Choi, Eva-Maria Dombrowski. Fundamentals of Biological Wastewater Treatment. Published by Wiley, ISBN: 978-3-527-31219-1.

17. Wang Jianlong, Wang Jiazhuo. Application of radiation technology to sewage sludge processing: A review. Journal of Hazardous Materials, 8 May 2007, 143(1–2), 2-7.

18. S.I.Borrely, A.C.Cruz, N.L.Del Mastro, M.H.O.Sampa, E.S.Somessari. Radiation processing of sewage and sludge. A review. Progress in Nuclear Energy, 1998, 33(1–2), 3-21.

19. Cao Guomin, Yang Guoping, Sheng Mei, Wang Yongjian. Chemical industrial wastewater treated by combined biological and chemical oxidation process. Water Science & Technology, 2009, 59(5), 1019-1024.

20. William H. Glaze , Joon-Wun Kang & Douglas H. Chapin. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. The Journal of the International Ozone Association. 1987, 9(4). 335-352.

21. UrszulaKepa, Ewa Stanczyk-Mazanek, Longina Stepniak. The use of the advanced oxidation process in the ozone + hydrogen peroxide system for the removal of cyanide from water. Desalination. 2008 ,223(1–3), 187-193.

22. Smita Venkatesh, A. R. Quaff, N. D. Pandey & Kumar Venkatesh. Impact of Ozonation on Decolorization and Mineralization of Azo Dyes: Biodegradability Enhancement, By-Products Formation, Required Energy and Cost. The Journal of the International Ozone Association. 2015, 37(5), 420-430.

23. Jon P Scott, David F. Ollis. Integration of chemical and biological oxidation processes for water treatment: Review and recommendations. Environmental Progress & Sustainable Energy, 1995, 14(2), 88–103.

24. West Virginia University, National Small Flows Clearinghouse: Ozone Disinfection U.S. Environmental Protection Agency: Ozone.

25. S. J. Allen, B. Koumanova. Decolourisation of water/wastewater using adsorption. Journal of the University of Chemical Technology and Metallurgy, 2005, 40(3), 175-192.

26. Mustafa T. Yagub, Tushar Kanti Sen, Sharmeen Afroze, H.M.Ang. Dye and its removal from aqueous solution by adsorption: A review. Advances in Colloid and Interface Science, 2014, 209, 172-184.

27. Charles Letnam Mantell, Adsorption, Published by McGraw Hill, 1951.

28. Ion Exchange Treatment of Drinking Water, Environmental fact sheet, 2009.

29. Sawsan Abo-Farha, Ahmed Abdel-Aal, Isaac A. M. Ashour, S E Garamon. Removal of some heavy metal cations by synthetic resin purolite C100. Journal of hazardous materials, 2009,169(1-3), 190–194.

30. I-Hsien Lee, Yu-Chung Kuan, Jia-Ming Chern. Equilibrium and kinetics of heavy metal ion exchange. Journal of the Chinese Institute of Chemical Engineers, 2007, 38(1), 71–84.

31. Y. Anjaneyulu, N. Sreedhara Chary, D. Samuel Suman Raj. Decolourization of Industrial Effluents – Available Methods and Emerging Technologies – A Review, 2005, 4(4), 245–273.

32. Fraser C. Kent, Khosrow Farahbakhsh, Basuvaraj Mahendran, Magdalena Jaklewicz, Steven N. Liss, Hongde Zhou. Water reclamation using reverse osmosis: Analysis of fouling propagation given tertiary membrane filtration and MBR pretreatments. Journal of Membrane Science, 2011, 382(1-2), 328–338.

33. Jia-Qian Jiang, The role of coagulation in water treatment, Current Opinion in Chemical Engineering, May 2015, 8, 36-44.

34. Akshaya Kumar Verma, Rajesh Roshan Dash, Puspendu Bhunia. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. Journal of Environmental Management, 2012, 93(1), 154-168.

35. Yanhui Li, Qiuju Du, Tonghao Liu, Xianjia Peng, Junjie Wang, Jiankun Sun, Yonghao Wang, Shaoling Wu, Zonghua Wang, Yanzhi Xia, Linhua Xia. Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. Chemical engineering research and design, 2013, 91(2), 361–368.

36. M. T. Amin, A. A. Alazba, and U. Manzoor, A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials, Advances in Materials Science and Engineering, 2014, 2014(825910), 1-25.

37. Yuxi Xu, Zhaoyang Lin, Xing Zhong, Xiaoqing Huang, Nathan O. Weiss, Yu Huang & Xiangfeng Duan. Holey graphene frameworks for highly efficient capacitive energy storage. Nature Communications, 2014, 5(4554), 1-8.

38. Yue Chen, Yanchao Zhu, Zichen Wang, Ying Li, Lili Wang, Lili Ding, Xiaoyan Gao, Yuejia Ma, Yupeng Guo, Application studies of activated carbon derived from rice husks produced by chemical-thermal process—A review, Advances in Colloid and Interface Science, 2011, 163(1), 39-52.

39. Ren XM, Chen CL, Nagatsu M, Wang XK. Carbon nanotubes as adsorbents in environmental pollution management: A review. Chemical Engineering Journal, 2011, 170(2–3), 395-410.

40. Hou Wang, Xingzhong Yuanab Yan Wu, Huajun, Huangab, XinPeng, Guangming Zengab, Hua Zhong Jie Liang, MiaoMiao Ren. Graphene-based materials: Fabrication, characterization and application for the decontamination of wastewater and wastegas and hydrogen storage/generation. Advances in Colloid and Interface Science, 2013, 195–196, 19-40.

41. Leila Shahriary, Anjali A. Athawale. Graphene Oxide Synthesized by using Modified Hummers Approach. International Journal of Renewable Energy and Environmental Engineering, 2014, 02(01), 58-63.

42. Yuxi Xu, Kaixuan Sheng, Chun Li and Gaoquan Shi. Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process. ACS Nano, 2010, 4 (7), 4324–4330.

43. Pei Tang, Gang Hu, Yongjun Gao, Wenjing Li, Siyu Yao, Zongyuan Liu & Ding Ma. The microwave adsorption behavior and microwave-assisted heteroatoms

doping of graphene-based nano-carbon materials, Scientific reports,2014, 4(5901), 1-7.

44. Stacey Indrawirawan, Hongqi Sun, Xiaoguang Duan and Shaobin Wang. Low temperature combustion synthesis of nitrogen-doped graphene for metal-free catalytic oxidation, Journal of Materials Chemistry A, 2015, 3, 3432-3440.

45. G.K.Ramesha, A.Vijaya Kumara, H.B.Muralidhara, S.Sampath. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes, Journal of Colloid and Interface Science, 2011, 361(1), 270-277.

46. Minitha C.R., Lalitha M., Jeyachandran Y.L., Senthilkumar L., Rajendra Kumar R.T. Adsorption behaviour of reduced graphene oxide towards cationic an anionic dyes: Co-action of electrostatic and π-π interactions, Materials Chemistry and Physics, 2017, 194, 243-252.

47. Kanika Gupta, Om P. Khatri, Reduced graphene oxide as an effective adsorbent for removal of malachite green dye: Plausible adsorption pathways, 2017, 501, 11-21.