ADSORPTION OF METHYLENE BLUE FROM WATER USING GOPANINANOCOMPOSITE

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A B S T R A C T

Methylene blue (MB) being disposed off as a waste in to water resources even in small quantity, poses certain hazards and environmental problems. The objective of this study is to investigate the adsorption of MB from aqueous solution onto hydrothermally synthesized graphene oxide polyaniline (GOPAni) composites. GOPAni composites are firstly characterized using, FTIR, XRD, AND SEM techniques. Batch adsorption experiments were conducted by using the UV-visible spectroscopy and by varying parameters namely: contact time, pH, initial dye concentration and adsorbent dose. The percentage of color removal decreased with increase of initial dye concentration. It was found that the percentage of dye removal was 97% for the GOPAni composite. The Freundlich and Langmuir models were applied to describe the equilibrium isotherms. Equilibrium data were fit to Langmuir isotherm. The Langmuir isotherm fits the MB adsorption data on GOPAni composite. Results obtained indicate that GOPAni composite could be employed as an efficient adsorbent similar to other conventional adsorbents for MB uptake.

Keywords: Adsorption, Methylene blue, GOPAni composites, X-ray diffraction Cationic dye

1. Introduction

Water pollution poses severe damages to the environment, thereby attracting much scientific attention to the removalof various pollutants from aqueous bodies [1]. The textile industry is one of the major contributions to the water pollution and causes major impact on available water quality through deliberate or inadvertent release of dye effluents into water bodies. Dyes have complex chemical structures that adhere to the surface of fabrics, thereby imparting colour to them. More than 100.000 chemically different dyes used in a wide variety of application such as textile [2], paper [3], tanning industries [4], plastic [5], printing [6], food processing [7], etc. Around 10,000 tons of synthetic dyes are used per year by textile industries alone, discharging nearly 100 tones of dyes in water bodies as effluents. As synthetic dyes are designed to resist breakdown with time and exposure to sunlight, water, soap, detergent and oxidizing agents[8, 9], they cannot be easily removed by conventional waste water treatment processes due to their complex structure and synthetic origin.

Methylene blue (MB), commercial dye used for various applications such as textile, papers, leathers, additives etc is heterocyclic aromatic compound having complex chemical structure and synthetic origin, owing to which it is resistant to biodegradation [10] and very stable to light [11] and oxidation [12]. This dye is highly carcinogenic, persisted, toxic and mutagenic in nature. Because of its cationic as well as aromatic nature it is easily soluble in aqueous or alcoholic medium and usually generates sulphur oxide and nitric oxide at higher temperature. On reduction, it reduces dissolved oxygen thereby modifies the

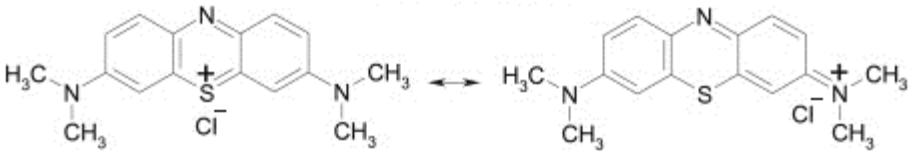
properties as well as characteristics of aqueous fluids and causes several damages to health such as breathing difficulties, nausea, vomiting, allergic dermatitis, skin irritation, cancer and mutations. Hence, for better environment, the removal of this noxious dye from aqueous environment is of a prime importance up to now several methods such as coagulation [13], biological treatment [14], chemical oxidation [15], membrane separation [16] and adsorption [17, 18] have been used to eliminate noxious dyes from aqueous environment. Amongst all these methods, adsorption provides attractive treatment due to its simplistic approach, economi9c consideration, greater efficiency and numerous benefits such as the capacity to remove dyes as a large scale, the ease of recovery and recyclability of adsorbents. Different classes of adsorbent such as activated carbon [19], polymeric materials [20], biomass [21], multiwall carbon nanotubes (MWCNT) [22] has been used to remove dyes form polluted water.

Conducting polymers attracted great interest in an academic and industrial level. The physical, chemical, electrical and optoelectric properties due to extended π- conjugated electron system make conducting polymers extensively explored materials. Conducting polymer such as polyphenelene, polypyrrole, polyacetelene, polythiophene and polyaniline have been extensively studied in multidisciplinary research areas like environment, elctronics, electromagnetic, thermoelectric, sensors, batteries, electroluminescence and electrochemical application [23, 24, 25, 26, 27, 28]. Polyaniline is considered to be one of the most promising classes of organic conducting polymers due to its unique electrochemical properties, higher environmental stability, easy synthetic methodology, cost effectiveness, efficient thermal stability, and wide variety of applications has been most intensively investigated by researchers [29]. However, due to poor stability, poor mechanical properties, lower effective surface area, it is of limited use in environmental applications [30]. In order to over their limitations, PAni is often polymerized in the presence of other materials to enhance its properties. Surface area and morphology plays an important role in increasing adsorption capacity of the polyanilinenanocomposite materials. Polyanilinenanocomposite have been widely used as adsorbent materials for the removal of dyes and other pollutants from waste water and hence, most favoured contender for various environmental applications [31].

Graphene is one-atom-thick plane of graphite and due to itsexcellent thermal and electrical conductivity, exceptional electronic transport and excellent chemical tolerance capacities as well as its large surface-to-volume ratio, it has attracted research interest [32, 33, 34, 35, 35]. One of the most important features of graphene is its large theoretical specific surface area (2630 m2g-1), which makes it a suitable adsorbent [36]. Because of these distinctive properties, it is often used for designing nanocompounds with polymers, metal organic frame work and metal nanoparticles etc [37, 38, 39, 40]. GOPAninanocomposites have showed enhanced physical and chemical properties compared with pure PAni or GO and have been exploited in many applications [41, 42, 43]. Besides GO, polyaniline based nanocomposites play a significant role in potential applications including photocatalytic, super capacitor, waste water treatment through adsorption etc owing to their low cost, facile synthesis, large surface area and physicochemical properties [44, 45, 46]. Various GO nanocomposite material with conducting polymers such as GO/polypyrrole, rGO/polypyrrole/Fe3O4 [47, 48] etc have been employed for the effective treatment of dye waste water. Therefore, GOPAninanocomposites can be explored for the synthesis of nanocomposite materials to address the present day issue of water pollution.

In the present study we reported the hydrothermal synthesis of GOPAninano-composites through a simple insitu oxidative polymerization technique for the adsorption of

cationic dye (MB). GO was synthesized by using modified Hummers method. Here grapheneoxide,due to the presence of oxygen containing functionalities, attains negative chargewhere aspolyaniline, due to presence of nitrogen containing functionalities (imine and amine), develops a positive charged backbone, thereby causing intensive electrostatic attraction between nanocomposites and dye molecules.



Structures of methylene blue

2. Experimental

Materials:

Graphite powder (99.9%), Potassium per-magnate (99.9%), Sodium nitrate(99.9%), Aniline (99.5 %), Ammonium persulfate (99.5 %) are procured from E. Merck. Aniline was distilled and stored in the dark before use. All supplementary chemicals such as Benzoic acid, Sulphuricacid, Hydrochloric acid, Ethanol, acetone, Hydrogen peroxide were used are of analytical grade and solutions were prepared with doubly distilled water. Methylene Blue (MB) was purchased from Sigma-Aldrich and was used without further purification.

Synthesis of GO:

GO was synthesized using modified hummers method [49]. In three-neck round bottom flask (500 mL), 120 mL concentrated sulphuric acid was added. The flask was immersed in ice-bath under continuous stirring at 500 rpm. Five gram of Graphite powder was added into ice-cooled sulphuric acid. Subsequently 2.5 g $NaNO_3$ and 15 g $KMnO_4$ was added to it. After a while, the flask was removed from ice-bath and the reaction mixture was stirred over night. When light Grey paste was obtained, 150 mL of de-ionized water were added to dilute the paste. The diluted paste was heated to 98 ^oC by continuous stirring for 2 hours. Then 50 mL H_2O_2 were added and reaction mixture was stirred for 30 minutes. The reaction mixture was then filtered and washed with 5% HCl until the filtrate becomes colorless. It was then washed with ethanol and subsequently with de-ionized water until the filtrate becomes neutral, and dried in an oven at 60 ^oC.

Preparation of Methylene Blue (MB) Solution:

weight 319. 85. Scheme 1 shows its molecular structure. It is water soluble dye, which is blue in color with /max 664 nm [50]. Methylene blue

Preparation of GOPAninanocomposite:

In 250 mL beaker, 2.3 g of prepared GO and doubly distilled Aniline (100 mL of 1M) were stirred for 18 hours for appropriate orientation of compounds. The Ammonium persulphate (100 mL of 1M) solution was then added slowly to the above mixture with continuous stirring at 30 ^oC. The whole reaction mixture was then transferred to Teflon inner container of the autoclave. The mixture was then diluted with de-ionized water up to 75% of the container. Teflon container was placed in hydrothermal autoclave and sealed with plumbing pliers. Autoclave was then transferred to oven, previously maintained at 125 ^oC. After 24 hours, autoclave was taken out of the oven and cooled at room temperature. The reaction mixture was centrifuged to get solid precipitate. The precipitate was washed with de-ionized water and ethanol to remove excess ions and monomers. The final product was dried in oven at 45 ^oC for 6 hours. This gave the bluish-black coloured GOPAni-1 composite with ratio 0.25:1. Similarly, other bluish-black coloured composite with ratio 0.50:1, 0.75:1 and 1:1were prepared.

Methylene Blue has a molecular formula C16H18N3ClS with molecular (stock) solution was prepared by dissolving appropriate quantity in a volume of distilled water. The required solutions were prepared by

further diluting the stock solution with distilled water to get appropriate concentration.

Characterization technique:

The surface morphological study of the synthesized nanocomposite was carried out using JSM-6390 LV Scanning electron microscope (JEOL Ltd., Tokyo, Japan) operated at 10 kV, from Indian Institute of Technology, Varanasi, U.P., India. The size and shape of obtained GOPAni composites were studied using a PHILIPS-CM200 Transmission electron microscope operated at 20-200 kV, from Indian Institute of Technology, Mumbai, M.S., India. X-ray diffraction (XRD) pattern were recorded using X"PER PRO X-ray diffractometer (PAN analyzed) from 2*= 10 o to 90 o using Cu- K< radiation at a scan rate 0.02 s-1, from Vishvesvaraya National Institute of Technology, Nagpur, M.S., India. Fourier Transform Infrared (FTIR) spectra of the powdered nanocomposite were recorded using BRUKER-ALPHA FT-IR ATR spectrophotometer in the range of 600-4000 cm-1 in spectral grade KBr plate, from Department of Chemistry, R.T.M. Nagpur University, Nagpur, M.S., India.

MB Adsorption Study:

The batch adsorption [51] study was carried out using MB dye in the water phase to investigate the adsorption ability of synthesized nanocomposite.Standard solutions of desired concentrations were prepared by diluting 1.0 g /L stock solution of MB. For adsorption, 0.25 g of GOPAni-1, GOPAni-2,GOPAni-3 and GOPAni-4 was added to 100 mL of different aqueous MB solutions having different concentrations ranging from 10 to 100 ppm (without adjusting pH). The solutions were stirred at constant speed of 300 rpm in continuous manner for 3 h. at 30 ± 0.2 ^{o}C. After equilibrium, dispersion was collected and filtered. The MB concentration was determined by monitoring absorbance at the maximum absorbency of MB (560 nm) using UV-VIS spectrophotometer (Shimadzu 1800). A calibration curve was prepared by plotting absorbance versus concentration and was used to determine the concentration of MB in the adsorption study.

The MB adsorption experiments were conducted at room temperature in a set of flasks by batch process to study the outcome of different parameters such as type of adsorbent (GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4), effect of contact time , effect of pH , and initial concentration of MB.

Effect of pH on MB removal

A series of 250mL flask were taken and each flask was added with 100 mL of MB solutionat the concentration of 30 mg/L, (C_o). All the flasks were maintained at 30°C and pH of MB solution was varied in the range of 5.0 to 10.0 with the help of reagent grade 0.1 M sodium hydroxide and 0.1 M hydrochloric acid. In each flask 0.25 g of GOPAni composites were added and shaked on rotatory shaker (300rpm) for about three hours. After agitation, all the samples were filtered through whatman no. 42 filter paper. The final concentration of MB in each flask was determined spectrophotometrically. The percentage adsorption of MB in each case was determined from initial and final concentration of MB. In each case graph of percentage removal of MB versus pH was plotted. From the graph, optimum pH required for maximum adsorption of MB was obtained and this value of pH was used in the further studies.

Effect of adsorbent dose on MB removal

At optimum pH of 8 and temperature 30°C, all experiment as mentioned earlier were carried out with various amount of adsorbents (i.e. GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4). The amount of adsorbent was varied from 0.7 to 4.0 g/L. In each case percentage adsorption was determined from initial and final concentration of MB in each flask. A graph of adsorbent dose in gram versus percentage removal of MB was plotted. From this graph maximum adsorbent dose was determined.

Effect of contact time on MB removal

The experiments were carried out at maximum pH (8), temperature (30°C) and by adding optimum adsorbent dose of GOPAni-1 (2.5 g), GOPAni-2 (2.0 g), GOPAni-3 (1.5 g) and GOPAni-4 (1.0 g). The contact time of MB onGOPAni composite was varied from 10 min to 180 min. The percentage adsorption of MB was calculated from initial and final concentration of MB. A graph of percentage removal of MB versus contact time was plotted. From this graph, optimum contact time for the maximum adsorption of MB was evaluated.

Effect of initial MB concentration

The experiments were carried out at the optimum, previously determined conditions, with the exception of concentration, MB. The concentration of MB in each case was a ranged from 10 mg/L to 100 mg/L. The percentage adsorption of MB was calculated from initial and final concentration of MB. A plot of percentage removal of MB versus concentration of MB was plotted. From this a maximum concentration of MBat which maximumpercentage of adsorption took place was calculated.

Study of adsorption isotherm

The 100 mL of ten solutions of the concentration10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L were prepared by a proper dilution of stock solution of MB. All previously determined optimum parameters were used for studying the adsorption isotherm. The equilibrium concentration (C_e) in each case was determined from initial concentration (C_o), initial absorbance (A_o) and adsorption of solution after optimum time (A_t) as below;

$$C_e = \left(\frac{C_0}{A_0}\right) A_t \quad \text{----------(1)}$$

In each case, amount of MB adsorbed (q_e) was evaluated by using the formula;

Langmuir equation related to the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. Langmuir equation is given in the subsequent form as;

$$q_e = \frac{q_{max}\, b\, C_e}{1 + b\, C_e} \quad \text{----------(5)}$$

The Langmuir adsorption equation is frequently written in the following linear form as;

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}} \quad \text{----------(6)}$$

Where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), q_{max} is adsorption efficiency and also called as maximum monolayer adsorption capacity (mg/g) and 'b' is the adsorption energy. 'b' is the reciprocal of concentration at which half saturation of the adsorbent is reached.

$$q_e = \frac{(C_0 - C_e)\, V}{m} \quad \text{----------(2)}$$

Where, $C_{o\ (mg/L)}$ is the initial concentration of MB, C_e is equilibrium concentration of MB, m is the mass of the adsorbent (GOPAni-composites) and V (mL) is the volume of MB solution.

Freundlich adsorption isotherm is capable of describing the adsorption of organic and inorganic compounds on the wide variety of adsorbents. The Freundlich adsorption equation can be written as;

$$\frac{x}{m} = q_e = k\ (C_e)^{1/n} \quad \text{----------(3)}$$

Taking the logarithm of both sides,

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad \text{----------(4)}$$

Where, 'q_e'is equilibrium adsorption capacity(mg/g), C_e is the equilibrium concentration of dye in the solution (mg/L) and 'k_f' and 'n' are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

From the above straight line equation and values of C_e and q_e, a plot of log q_e versus log C_e was plotted to verify the Freundlich adsorption isotherm.

From the above straight line equation and values of C_e and q_e obtained, another plot of ratio of C_e to q_e versus C_e was plotted to verify Langmuir adsorption isotherm.

The essential characteristic of Langmuir isotherm can be described by separation factor (R_L), which is given by the following equation;

$$R_L = \frac{1}{1 + b\, C_0} \quad \text{----------(7)}$$

where,$C_{o\ (mg/L)}$ is the initial concentration of the dye solution.

The value of separation factor (R_L),indicates the shape of the isotherm and nature of adsorption process to be either unfavorable (R_L >1), Linear (R_L =1),favorable (0< R_L <1) or irreversible (R_L =0).

3. Results and Discussion

Fourier Transform Infrared Spectral Analysis

Fig.1 shows the FT-IR spectra of graphene oxide, PAni and GOPAninanocomposites. The peak at 3740, 3362 and1503-1028 cm^{-1}

forgraphene oxide are attributed to the OH, C=O in COOH and C-O in COH/COC (epoxy) functional groups respectively [52,53,54]. Compared with the peaks of graphene oxide, the C=O Peak for GOPAni is downshifted to 1545-1569 cm^{-1}; the peaks of C-O in COH/COC (epoxy) are also red-shifted clearly. These indicate the carboxyl groups from graphene oxide are linked on the nitrogen of PAnibackbone. The spectral red- shift phenomena of chemically synthesized nanocomposite result from the π-π interaction and hydrogen bonding between the graphene oxide and PAni. Besides, there are large amount of oxygenous groups in the graphene oxide, which can easily interact with the nitrogen atoms in the -NH- group of PAnibackbone through –OH…N- and –O…H-N- hydrogen bonds.

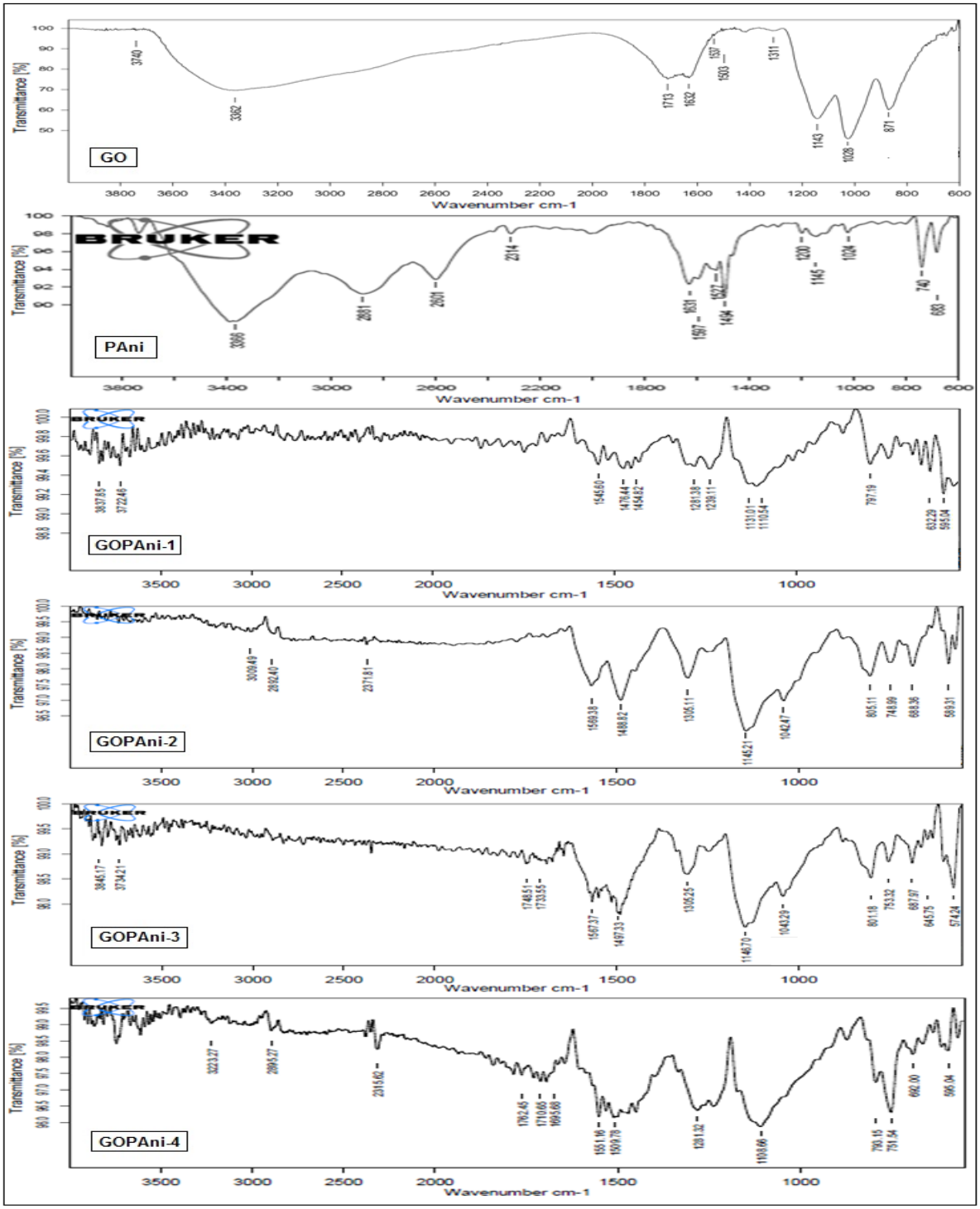


Fig. l FTIR spectra ofPAni, GO,GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

From the Fig. 1, it was also found that PAni existed in the composites owing to vibrational signals on benzoids and quinoids rings at 1537 cm^{-1} and 1503 cm^{-1} respectively [55]. The other signals found where at 3837.85 cm^{-1}, 3722.46 cm^{-1}, 3540 cm^{-1}, 3845.17 cm^{-1} and 3580 cm^{-1} due to the N-H streachingmode,the peak at 2800 cm^{-1}, 2892.40 cm^{-1}, 2883 cm^{-1} and 2895.27 cm^{-1} are due to the C-H bond.

The peaks observed at 1545.60 cm^{-1}, 1569.38 cm^{-1}, 1567.37 cm^{-1} and 1551.16 cm^{-1} are due to the benznoid ring respectively, similarly the peaks obtained in composites at 1476.44 cm^{-1}, 1488.82 cm^{-1}, 1497.33 cm^{-1} and 1509 cm^{-1} are due to quinoid structure respectively. The peaks appeared at 1454.82 cm^{-1}, 1450 cm^{-1}, 1350.50 cm^{-1} and 1440.25 cm^{-1} are due to the -N=Quinoid=N-. The peaks obtained in the figure at 1131.01 cm^{-1}, 1145.21cm^{-1}, 1146.70 cm^{-1} and 1108.66 cm^{-1} are ascribed to C-N+.

The major peaks for PAni in the spectrum of composites belongs to C-H vibration, C-N vibration, C=C vibration and C=N vibration and which are found in literature [56].The initial peak in GOPAni such as 624 cm^{-1} is due to aromatic ring deformation. The shift in GOPAni C-H, C-N, C=C and C=N vibrations are visible due to Graphene-polyaniline interaction

It was observed that GOPAninanocomposites shows similar peak to PAni and the peak intensities are also close to PAni. No additional peak is observed which indicates that crystal structure of PAni is maintained in the GOPAninanocomposites.

For GOPAninanocomposites, no GO peak is observed in the results and it is completely missing in GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4. It reveals that the layer of GO are completely exfoliated. This exfoliation of GOlayer helps to align thePAni chains and enhance the crystalline nature of GOPAninanocomposites.

X-ray diffraction analysis

Figure.2 depicts the x-ray diffraction pattern of the GO, PAni and samples of hydrothermally synthesized GOPAni-1,GOPAni-2,GOPAni-3 andGOPAni-4 nanocomposites. The XRD pattern of GO illustrated an intense and sharp peak centred at $2\Theta = 20°$, which corresponds to the inter planner spacing of GO sheets. The observed 2Θ for GO could be attributed to the (001) reflection plane, which is due to the process of synthesis and layers of water within inter planner space of GO [34, 42]. It is evident from Figure 2, the PAni exhibited diffraction peaks at 2Θ value 20° and 25°, which are characteristic, peaks of PAni. These peaks indicate the crystalline nature of PAni [57]. The peaks at angle 2Θ values of 20° and 25° shows the periodic repitation of benzoid and quinoid rings in PAni chains [58]. As per the XRD pattern of GOPAni-1,GOPAni-2,GOPAni-3 andGOPAni-4, the peak of GO has been reduced indicating that aggregation of GO diminished and was utilized by PAni to produce a nanocomposites material [42]. Characteristic GO and PAnipeaks can be seen clearly in the XRD spectrum of GOPAni-1,GOPAni-2,GOPAni-3 andGOPAni-4, which proves the uniform occurrence of GOPAninanocomposites. The peak at 20° becomes prominent as the concentration of GO increases in the nanocomposites. It is the indication of strong interaction of GO with benzene ring of PAni. Therefore, XRD investigation established the successful synthesis of GOPAninanocomposites and crystalline nature of these composites.

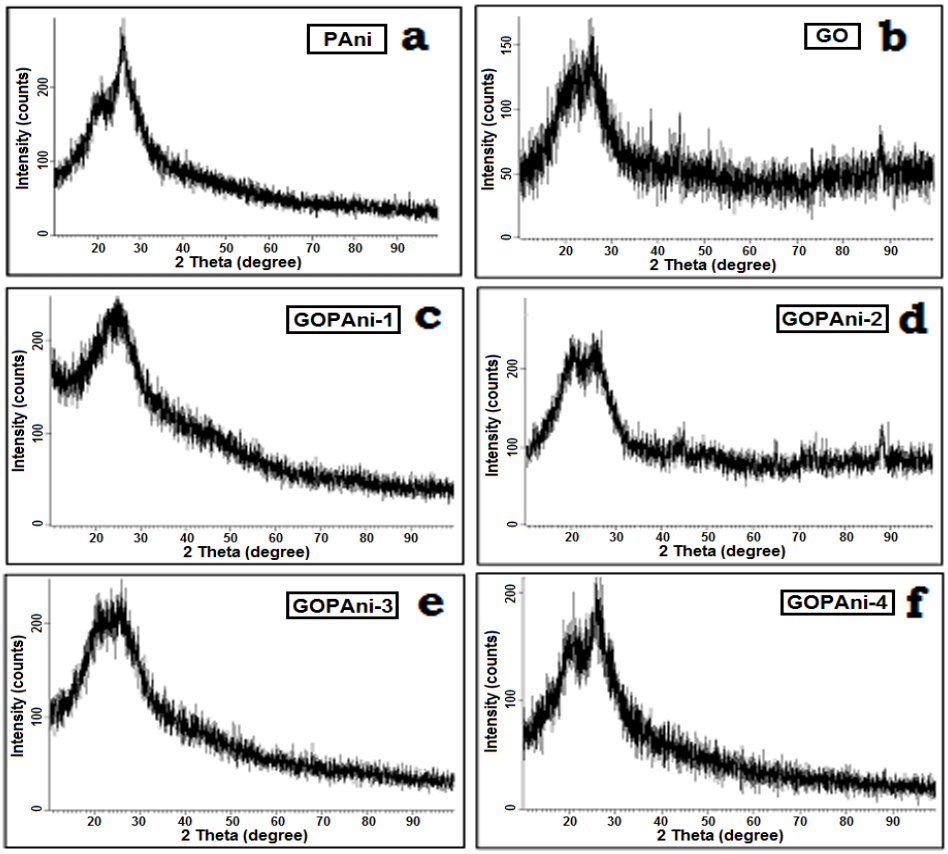


Fig. 2 XRD spectrum of PAni (a), GO (b), GOPAni-1 (c), GOPAni-2 (d), GOPAni-3 (e) and GOPAni-4 (f) nanocomposites

Scanning electron microscopy

The SEM images of PAni, GO and GOPAni composites are shown in Fig. 3. It reveals multilayer structure of GO with stack sheets and rod like structure of PAni.

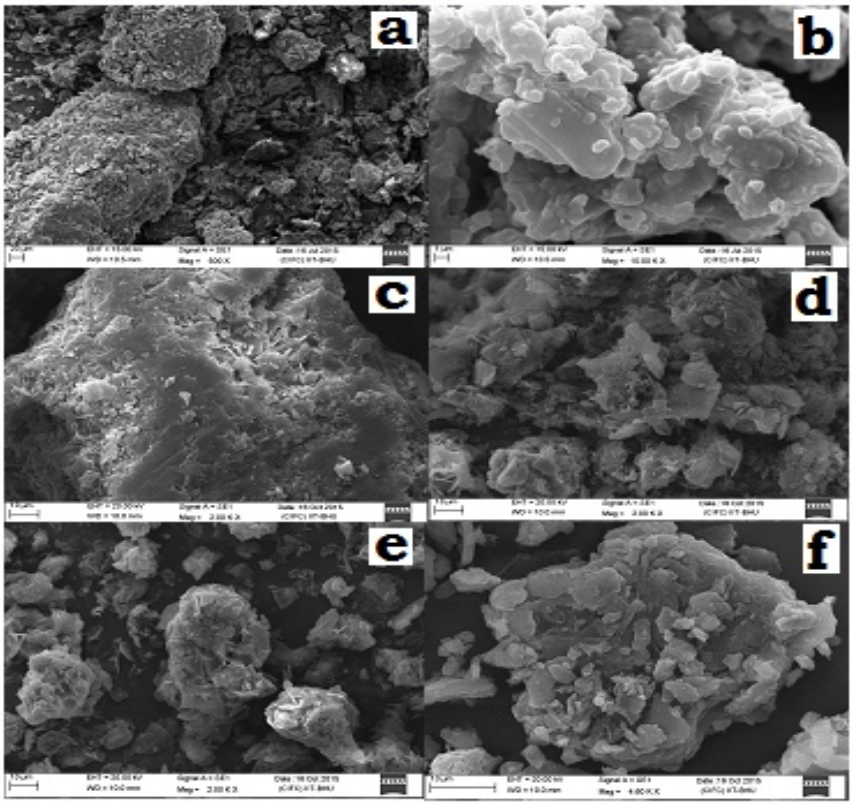


Fig. 3 SEM micrographs of PAni (a), GO (b), GOPAni-1 (c), GOPAni-2 (d), GOPAni-3 (e) and GOPAni-4 (f) nanocomposites

It can be seen that the morphology of GOPAninanocomposites is different from that of PAni and GO. GOPAninano composites show multiple shapes. The morphology is like flakes with fibres. The polymerization of aniline has been take place on the GO surface and results in flaky structures. The dispersion ofGO in PAnimatrix takes place in nanocomposites.

Transmission electron microscopy

The morphological structure of nanocomposites was established by transmission electron microscopy.

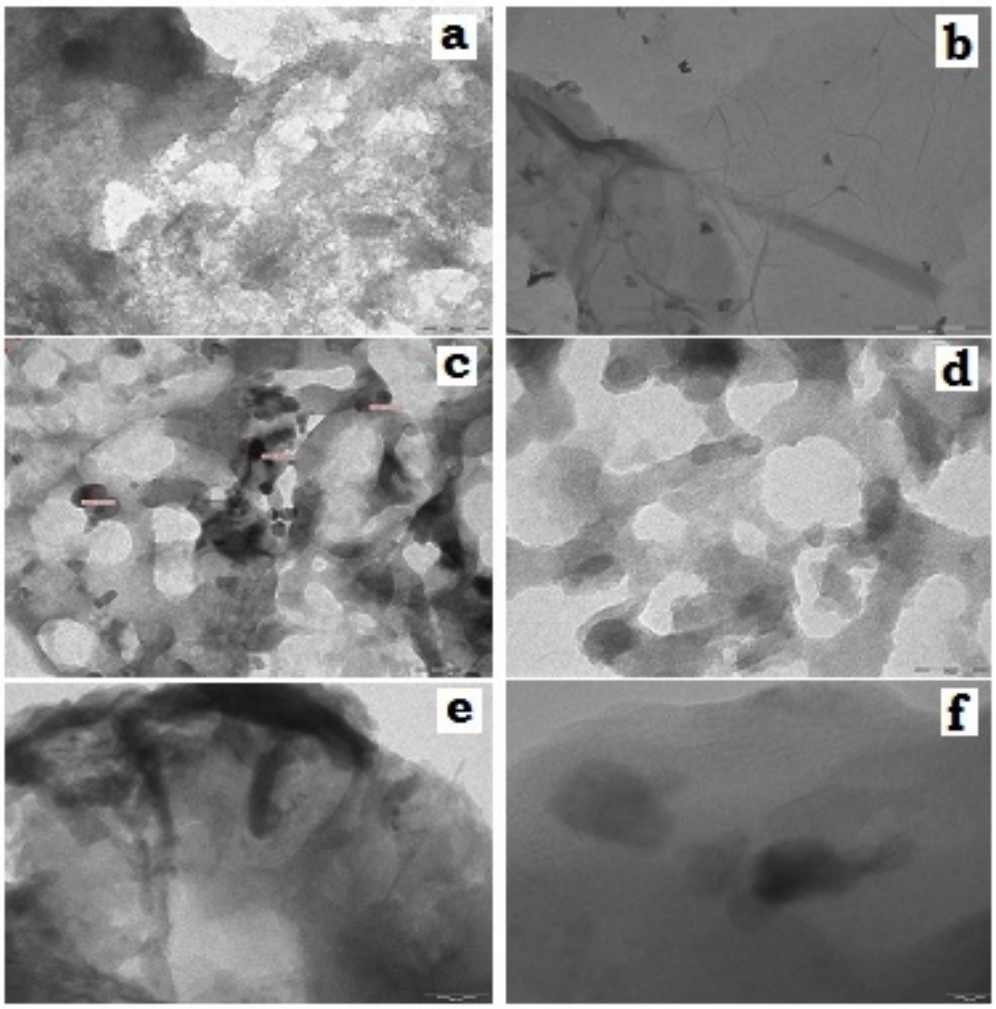


Fig. 4 TEM Images of PAni (a), GO (b), GOPAni-1 (c), GOPAni-2 (d), GOPAni-3 (e) and GOPAni-4 (f) nanocomposites

Fig. 4 Shows the TEM images of PAni, GO and GOPAninanocomposites. The morphology of pure PAni shows the tubular structure. However, the images obtained for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 with different concentration of GO, shows different morphology from PAni. This may be attributed to polymerization of aniline in presence of GOsheets. It is noted that GO get distributed in PAni and agglomeration of GOdoes not takes place.

The sizes of some molecules of nanocomposites are in range of 100-500 nm with tubular PAnistructure differed substantially among individual tubes of diameter in the range 50-200 nm and lengths 1-50 mm. [59]. TEM images also revealed morphological features and characteristics of GOPAni composites. TEM image indicates that a surface morphology of GOPAninanocomposite was irregular surface which is responsible for adsorption of MB.

Adsorption studies

Effect of pH of solution:

Generally the pH is an important factor affecting adsorption [60]. Many workers have suggested the pH dependency of dyes binding process on different materials [61, 62, 63, 64, 65]. The efficiency of adsorption is depends on solution pH, since variation in pH leads to the variation in degree of ionization of dye

molecule and surface property of adsorbent [66, 67]. Therefore, the removal of MB by GOPAni composites was examined at different pH value ranging from 5 to 10 at 30°C (50 mg of MB per Litre and equilibrated for three hours) and results are shown in Fig. 5. It is evident from the figure that all GOPAni adsorb MB dye in the higher pH value while the percentage removal of MB increases by increasing the pH value

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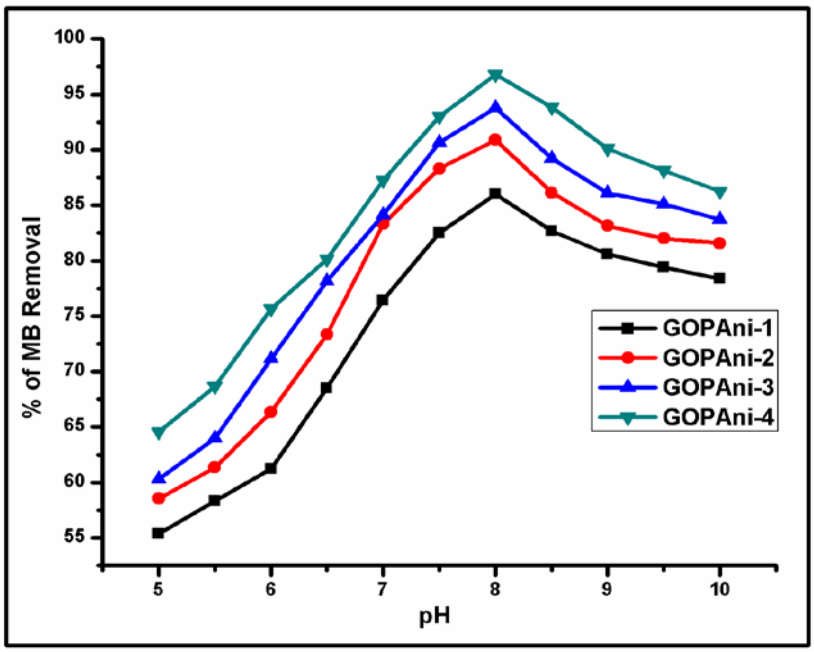

Fig. 5 Effect of pH on MB removal by GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

The results indicate that the composite show increasing removal capacity in pH 5.0 to 7.5. At pH 8.0, the removal of MB is maximum for all the composite. Further increase in pH up to 10, capacity decreases [68]. The percentage removal of MB for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 are 86.02%, 90.98%, 93.77% and 96.78% respectively. The removal by composites is in the following order,

GOPAni-1 < GOPAni-2 < GOPAni-3 < GOPAni-4

At higher pH(>8), the percentages removal found to decrease because the surface that the removal efficiencies of GOPAni-1 and GOPAni-2 were 85.98% and 90.41% respectively at 180 min by addition of 2.5 g /L and 2.0 g/L of GOPAni-1 and GOPAni-2 while removal efficiencies of GOPAni-3 and GOPAni-4 were found to be 93.55% and 96.42% respectively at 180 min by addition of 1.5 g/L and 1.0 g/L of GOPAni-3 and GOPAni-4 respectively.

area of the composite was more protonated and competitive adsorption takes place between H^+ and MB^+ ions. Therefore, H^+ ions react with $-COO^-$ groups on the surface of composites and results in blocking of the number of adsorbing sites for removal of MB.

Effect of adsorbent dose

Effect of adsorbent dose on adsorption of MB dye was varied by changing the adsorbent dose from 0.7 g/L to4.0 g/L with 50 mg/L MB solution. It was observed

In all the cases after addition of higher dose of respective adsorbents, the removal efficiency almost remains constant [69]. The effect of adsorbent upon removal of MB is shown in Fig. 6. The adsorption capacity of GOPAni composites are compaired with other adsorbents for removal of MB and are presented in Table.1.

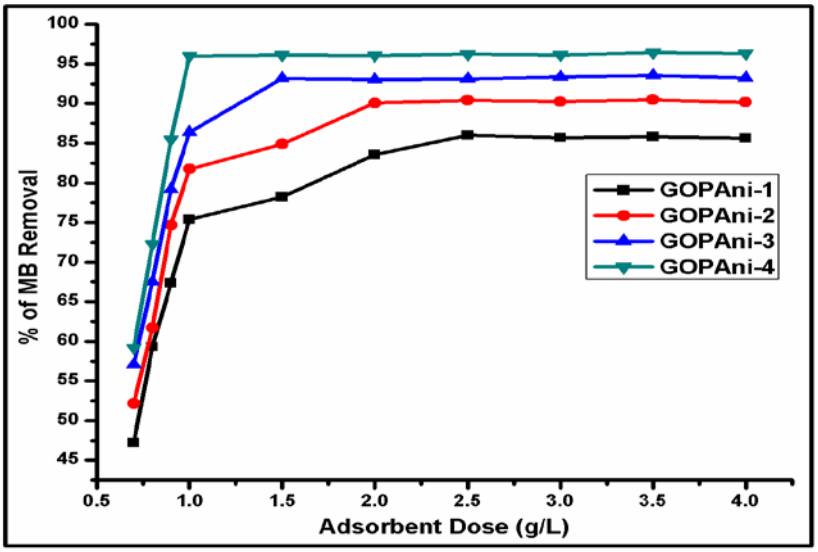

Fig. 6 Effect of Adsorbent dose on MB removal by GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

Table.1 Comparison of GOPAni composites with other adsorbents for removal of Methylene blue dye. (adsorption capacity, mg/g).

Adsorbents	**Adsorption capacity(q_m)**	**References**
Acid activated bentonite	20.16	[70]
Clay	58.2	[71]
Charcoal	62.7	[72]
Activated carbon	9.81	[73]
Pyrolysed furniture	80	[74]
Pitch	33	[75]
Activated date pits	12.9	[76]
Coir pith carbon	5.87	[77]
Zeolite	53.1	[78]
Amorphous silica	22.66	[79]
Raw kaolin	13.99	[80]
Glass wool	2.24	[81]
Posidoniaoceanica fibres	5.56	[82]
Living biomass	1.17	[83]
Coal fly ash	12.7	[84]
Fly ash (CFA)	6.04	[85]
Red mud	2.49	[86]
Coconut husk	99	[87]
Coffee husks	90.1	[88]
Walnut sawdust	59.17	[89]
Rice husk	40.59	[90]
Cotton waste	24	[91]
Orange peel	18.6	[92]
Wheat shells	16.56	[93]
GOPAni-1	24.89	Present study
GOPAni-2	31.34	Present study
GOPAni-3	42.51	Present study
GOPAni-4	64.15	Present study

Effect of Contact Time:

The equilibrium time between the adsobate and the adsorbent is of great importance in the removal of dyes by adsorption. For an adsorbent to be efficient in removal of dye, it needs to be able to a rapid uptake of the dye and reach the equilibrium in short time. Adsorption equilibrium time is determined as the time after which the uptake of the dye solution remained unchanged during the course of adsorption process. Fig.7 shows the effect of contact time on the percentage removal of MB by GOPAni composites.

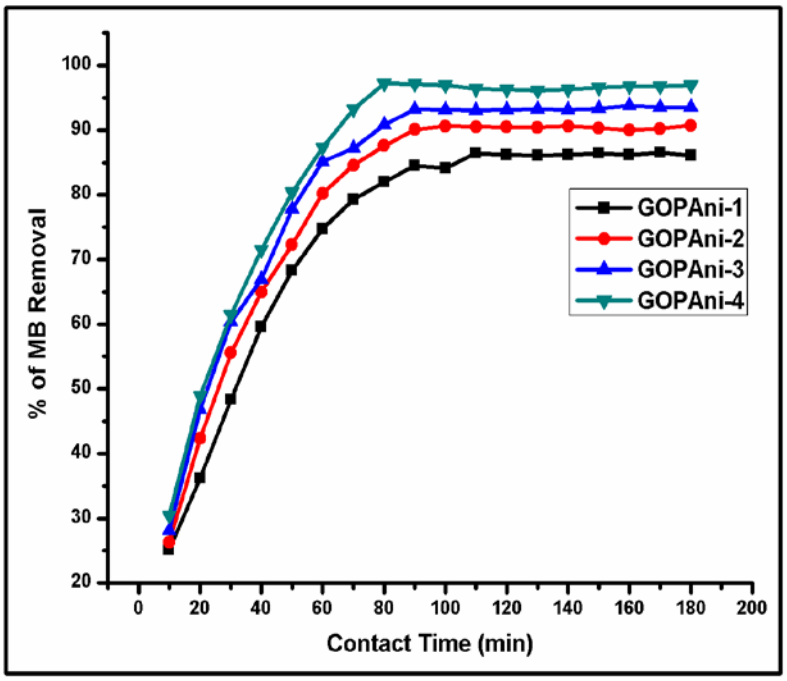

Fig. 7 Effect of Contact time on MB removal by GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

It can be seen that in all the nanocomposites, at initial stage percentage removal of MB was fast and then becomes slow and gets stagnated withincrease in time. In case of GOPAni-1 and GOPAni-2, percentage adsorption of MB increases from 25.13% to 86.42% and 26.33% to 90.62% respectively, by increasing the contact time from 10 min to 110 min and 100 min. Beyond this time it almost remain constant in both the cases.

In case of GOPAni-3 and GOPAni-4, the percentage removal increasesfrom 28.14% to 93.22% and 30.45% to 97.22% respectively, by varying the contact time from 10 min to 90 min and 80 min. Further increase in contact

After maximum contact time ability of each composite to adsorb MB almost remains constant. Thisisdue to complete saturation of MB on all the surface active sites [94, 95, 96, 97].

time does not increase the adsorption. The order of contact time for rate of removal of MB by GOPAni composites is,

GOPAni-1 (110 min) > GOPAni-2 (100 min) > GOPAni-3 (90 min) > GOPAni-4 (80 min)

The result shows that as the amount of GO increases in the composite, the contact time decreases. This is due to availability of more surface area and active sites for the adsorption of MB. Initial increase in the percentage of adsorption is due to the filling of active sites on the adsorbents (composites). At each optimum time, almost all the active sites on the composites are full of MB molecules. The amount of MB adsorbed by nanocomposites and it remained in the solution are in equilibrium.

Effect of initial dye concentration

The effect of initial dye concentration plays a significant role in the amount of dye adsorbed, and percentage dye removal. It depends on the immediate relation between the concentration of dye and available sites on the

adsorbed surface. The initial concentration of adsorbate in solution provides an important driving force in overcoming mass transfer resistance between the aqueous and solid phase [98, 99]. Equilibrium adsorption studies was performed and the equilibrium is established when the concentration of MB dye in the solution is in dynamic balance with that of surface of GOPAni composites. Effect of initial concentration on removal of MB was studied at different initial concentrations of MB (10mg/L to 100 mg/L) keeping all other parameters constant. The results are shown in Fig.8. The percentage of removal was varied according to the initial concentration of MB. It indicates that the initial MB concentration has an important influence on the adsorption capacity of GOPAni composites. At low concentration (10mg/L), maximum percentage removal was found to be 89.34% (GOPAni-1), 91.91% (GOPAni-2), 95.08% (GOPAni-3) and 97.07% (GOPAni-4) respectively. Increasing the concentration to 50 mg/L, the percentage removal was observed to be 83.69% (GOPAni-1), 86.26% (GOPAni-2), 88.43% (GOPAni-3), and 90.42% (GOPAni-4). However, further increase in concentration to 100mg/L, the percentage removal further decreases to 54.82% (GOPAni-1), 56.39% (GOPAni-2), 59.56% (GOPAni-3), and 60.55% (GOPAni-4) respectively.

The enhanced removal at low concentration could be due to faster movement of MB molecules in to the activated sites of the GOPAni composites. However, in higher concentration (100 mg/L) the percentage removal decreased due to saturation of absorption sites on the GOPAni surface. It may also be attributed to intraparticle diffusion of MB molecules to composite sites. In addition, steric repulsion between thesolute molecules could slow down the adsorption process and thereby decreases the removal [100,101].At lower concentrations, all MB present in the adsorption medium could interact with the binding sites on the surface of adsorbent [102, 103]. So, higher removal was obtained. Besides lower removal were observed at higher concentrations because of the saturation of the adsorption sites have take place [104].

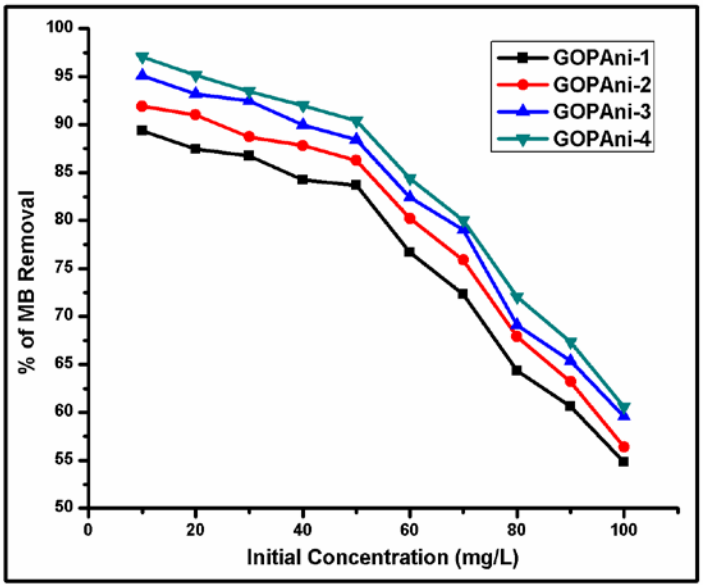

Fig. 8 Effect of Contact time on MB removal by GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

Adsorption isotherm

In order to establish the most appropriate correlation for an equilibrium data in the design of adsorption system, two common isotherm models were tested: Freundlich and Langmuir models. The applicability of the isotherm equations were compared by judging the square of correlation coefficient (R^2)[105, 106, 107, 108, 109, 110, 111].

Freundlichisotherm:

At a fixed adsorbent dose, different initial concentration of adsorbate was taken for equilibrium studies. Different adsorption isotherms were tested for the adsorption

process. It was found that the data fitted well into linearisedFreundlich adsorption isotherm whose mathematical expression is given in equation (4). The Freundlich equation suggests multilayer adsorption. Adsorption energy exponentially decreases on completion of the adsorption centers of an adsorbent. The plot of log qe versus log Ce forGOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 (Fig.9.) shows a linear curve and hence the adsorption obeys Freundlich isotherm.

Therefore, the parameters of k_f and 'n' were be estimated from the intercept and slope of the plots log qe versus log Ce. The calculated parameters at 30°C were presented in Table.2. The k_f values of all the adsorbents i.e. GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 were found to be 4.789, 7.140, 11.501 and 19.923 mg/g respectively, and indicates dominance of adsorption capacity. The Freundlich exponent 'n' were 2.170, 2.310, 2.533 and 2.743 for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 respectively, and indicates thefavourable adsorption.

The square of the correlation coefficient (R^2) values are 0.945,0.941, 0.949 and 0.958 for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 respectively, and shows well fitting of the Freundlich isotherm. The 'n' values are in between 1 to 10 and indicates the favorable adsorption of MB on GOPAni-1GOPAni-2, GOPAni-3 and GOPAni-4 (Table.2). The values of k_f clearly show the dominance of adsorption capacity. The intensity of adsorption (n) is indicative of the bond energies between MB and composites as well as the possibility of slight chemisorption rather than physisorption.

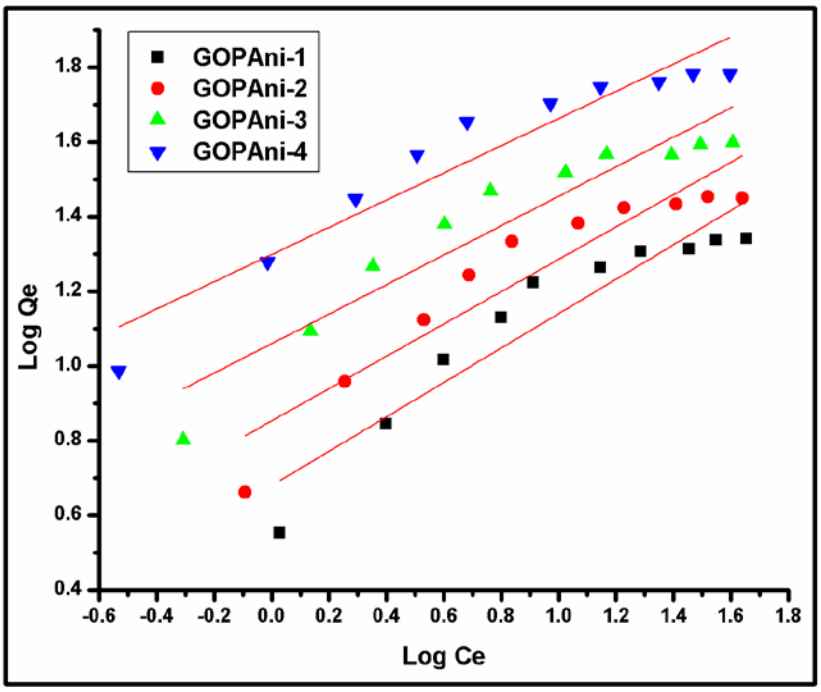

Fig. 9 Plot of Freundlich Adsorption Isotherm for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

Langmuir Isotherm:

The Langmuir adsorption isotherm suggests that, when the adsorbate occupies site, further adsorption cannot takes place at that site. All the sites are energetically equivalent and there is no interaction between molecules adsorbed on the neighboring sites [112].The equilibrium data also well fitted in Langmuir linear plot ofC_e/q_e versus $C_e$and it suggests the applicability of Langmuir isotherms. The values of adsorption efficiency $q_{max}$and adsorption energy 'b' were determined form the slope and intercept of the plots shown in Fig.10.The Langmuir monolayer adsorption capacity q_{max} gives the amount of the adsorbate required to occupy all the available sites per unit mass of the sample.

The values of q_{max} for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 were found to be 24.899, 31.342, 42.518 and 64.157

mg/g while values of 'b' were 0.185, 0.254, 0.341 and 0.455 respectively are presented in Table.2. This lower value of 'b' indicates the affinity between solute and adsorbent site which rules out the possibility of chemisorptions.

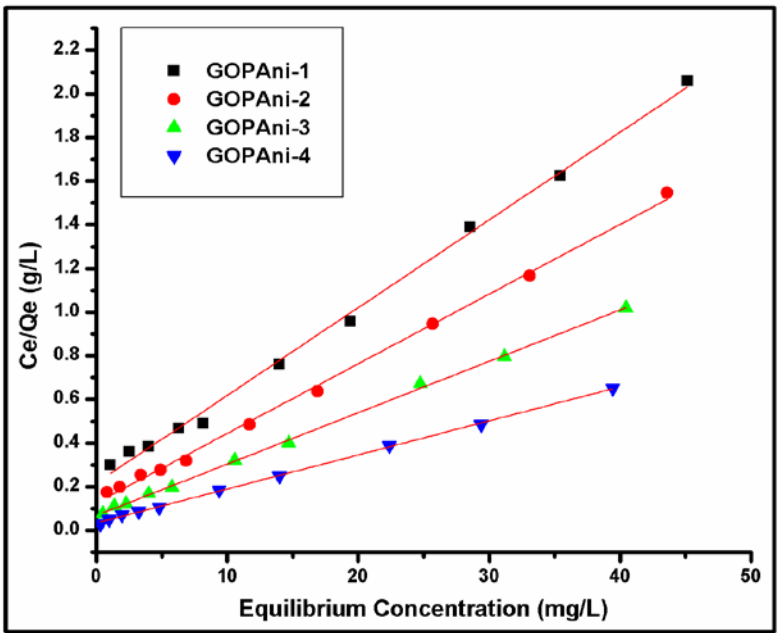

Fig. 10 Plot of Langmuir Adsorption Isotherm for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

To confirm the adsorptibility of the adsorption process, the equilibrium parameter also called separation factor (R_L) was computed for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 and found to be fractional in the range of 0 to 1, indicating that the adsorption process is favorable for these adsorbents for the removal of MB dye (Fig.11).

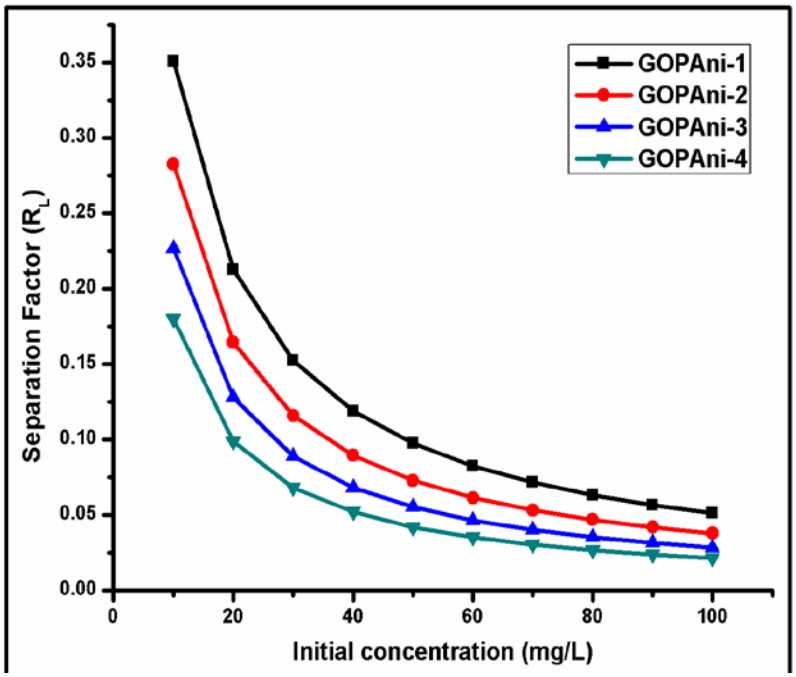

Fig. 11Plot of Separation Factor vs. Initial MB Concentration for GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 nanocomposites

Table.2: Freundlich and Langmuir isotherm parameters for adsorption of MB dye on GOPAni-1, GOPAni-2, GOPAni-3 and GOPAni-4 adsorbents

Adsorbent	Freundlich Isotherm Parameter			Langmuir Isotherm Parameter		
	R^2	n	k_f	R^2	b	*Qm*
GOPAni-1	0.945	2.170	4.789	0.999	0.185	24.899
GOPAni-2	0.941	2.310	7.140	0.999	0.254	31.342
GOPAni-3	0.949	2.533	11.501	0.999	0.341	42.518
GOPAni-4	0.958	2.743	19.923	0.999	0.455	64.157

The correlation coefficients of the Langmuir model were higher than that of Freundlich model suggestingfurtherresembling monolayer adsorption process. This adsorption study indicates that experimental results have been significantly fitted Langmuir adsorption systems.

4. Conclusion

GOPAninano composites have been hydrothermally synthesized by a simple insitu oxidative polymerization technique. The equilibrium studies for the adsorption of MB dye from aqueous solution on to GOPAninanocomposites were studied with variation in MB concentration. The uptake of the dye was studied using UV-Visible spectroscopy. The removal efficiency of MB was found to be pH dependent with maximum dye adsorption at pH 8. It is seen that MB adsorption onto nanocomposites is much more noticeable than the other adsorbents (Table.1). Adsorption rate increases in the following order; GOPAni-1 < GOPAni-2 <GOPAni-3 <GOPAni-4. This is probably due to the increase in surface area of nanocomposite substrates.

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