Synthesis of Iron based Graphene (Fe$_2$O$_3$-GO) Nanocomposite for Removal of Dye in Aqueous Medium

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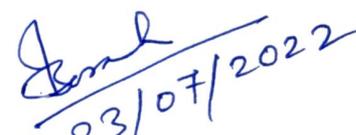Department of Chemistry
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It is my pleasure to forward the dissertation entitled "Synthesis of Iron based Graphene (Fe_2O_3-GO) Nanocomposite for Removal of Dye in Aqueous Medium" submitted by Prostuti Borah, student of B.Sc. 6th Semester of our College for the partial fulfillment of B.Sc. Degree in Chemistry (Core) under Dibrugarh University, Assam. Prostuti Borah Carried out the investigation under my constant supervision and guidance. The results enter incorporated in this dissertation have not been submitted to any university or institute for any purpose. The dissertation is in my opinion worthy of consideration for the paper DSE 601 of Chemistry core in accordance with the regulations of Dibrugarh University, Dibrugarh.

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With regards

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CONTENTS

Chapter

Abstract

In this study, Fe_2O_3 nanoparticles are synthesized to prepare composite material with graphene oxide (GO) nanosheets, which is characterized by XRD, SEM and TEM studies. The prepared Fe_2O_3-GO have been used for the adsorption of methyl orange (MO), dye from aqueous solution. Thus, the composite material can be predicted as a good adsorbent material for the adsorption of dyes. The adsorption of the MO onto the GO nanosheets has been carried out at different experimental conditions such as adsorption kinetics, concentration of adsorbate, pH, and temperature. The kinetics of the adsorption data was analyzed using kinetic models such as the pseudo second-order model to understand the adsorption behavior of MO onto the Fe_2O_3-GO nanocomposite and the mechanism of adsorption. The kinetics of adsorption result shows that the adsorption maximum was reached at 60 min and follows the linear form of pseudosecond-order kinetics.. The interaction of MO with Fe_2O_3-GO may be due to chemical bond formation or other electrostatic interactions.

1. Introduction:

Water pollution by various pollutants is nowadays a global environmental issue. Among the different types of water pollutants, dye represents a major polluting group. Organic dyes, a common water pollutant and highly used in industries such as textiles, paper, plastics, leather, food, cosmetics and printing industries [1-3]. The release of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation [4]. Dyes are mostly stable due to their complex molecular structure and as a result do not biodegrade readily. Synthetic dyes are usually toxic, carcinogenic and mutagenic and are stable to temperature, light and microbial attacks [5]. Dyes enter the food chain through water bodies and cause adverse effects on both human and animal health. So, these pollutants play a threatening role in terms of human health of 21st century.

Literature reveals different types of adsorbents for removal of dye in water in aquous medium. Aithough a number of processes are available for dye removal from aqueous system, adsorption is getting special interest from the researchers worldwide due to its high efficiency, cost effectiveness, and simple operation process. Therefore, it is an important research area for researchers to find new adsorbent materials, which are cost effective and practically viable. Most of the literature reveals that carbon-based materials are widely used for the dye removal process [6-9]. Reecent literature review focused on the use of the graphene or graphene oxide (GO) based materials as promising adsorbent materials for the removal of the dye molecule from the water. Researchers have reviewed the removal of dyes using adsorbents and environmental applications of graphene-based composites [10, 11]. However the composite materials have higher adsorption capacity than the component materials.

Graphene is made of single layer of carbon atoms which are closely packed into honeycomb two dimensional (2D) lattice [12]. Graphite is the basic material for preparation of individual graphene or GO nanosheets. Exfoliation of graphite oxide by ultrasonication results in single layered GO nanosheets. The large surface area, oxygen containing surface functionalities such as hydroxyl, carboxylic, carbonyl, and epoxide groups, and high water solubility makes GO a material of great interest in adsorption-based technologies as well as in other fields [13]

These composites of graphene with metal oxides, carbon derivatives, metal hybrids or polymers are synthesized mostly by solvo-thermal synthesis, hydrothermal process [14], microwave-assisted route [15], one-step sonochemical route, coprecipitation and ultrasonication route. The functionalization of graphene with magnetic iron oxide such as Fe_2O_3, Fe_3O_4, TiO_2, Ni and ZnO are reported in literature. Among them, magnetite (Fe_3O_4) nanoparticle functionalized GO has wide range of applications in catalysis, and dye adsorption [15] because of the excellent properties of Fe_3O_4 nanoparticles such as low toxicity, good biocompatibility and ferromagnetism. Simmilarly, hematite (α-Fe_2O_3) finds applications like waste water treatment. These attributes render graphene supported iron oxide based nanocomposites act as adsorbent for organic dye adsorption. The recent trend of research into graphene-based hybrid materials is due to their high surface area and high porosity. Therefore, efforts have been made on the studies on the removal of various classes of organic dyes from contaminated water using graphene-based composites is important in this case.

It is also reported that the cationic dyes were better adsorbed on the GO surface, while the anionic dyes were better adsorbed in the graphene surface. It is concluded that the charge–charge interaction is responsible for this adsorption behavior. In case of the cationic dyes, charge

transfer from negatively charged GO to the dye molecules takes place, while in case of the anionic dyes, charge transfer takes place from negatively charged dye molecules to graphene species.

1.1 Objectives:

Keeping the above views in mind following objectives points are pointed for the proposed work.

1. Synthesis of Fe_2O_3 nanoparticle by hydrothermal as well as microwave assisted green method

2. Synthesis of reduced graphene oxide (r-GO) by Hummers and Offeman method.

3. Preparation of Fe based iron based graphene (Fe_2O_3-rGO) composite material.

4. Adsorption studies of dye (e.g, Methyl orange, MO) on prepared Fe_2O_3-rGO composite material.

2. Experimental Section

2.1. Materials:

Graphite powder (<20 μm) (Sigma-Aldrich), Sulfuric acid (AR grade, Qualigens, India), hydrochloric acid (AR grade, Qualigens, India), H2O2 (30 %, Qualigens, India), potassium permanganate (> 99 %, NICE-Chemical, India), NaOH (99 %, Qualigens, India), and methyl orange (Loba Chemie, India), Sodium aceatate (Rankem, India), Ferric chloride (Sisco research lab, India), ethylene glycol are used for study and whole bench work is done in research

laboratory of Nanda Nath Saikia College, Titabar, Assam. All analytical grade reagents were used in the experiment.

2.2 Microwave assisted synthesis of iron oxide nanoparticle by using Hibiscus Rosasinensis:

Here the Hibiscus rosa sinensis flowers are collected from a local garden, washed several times, and rinsed with distilled water to remove dust particles. The washed flowers were dried in an oven at a temperature of 60^0C for 24 hours [16]. The dried flowers have been ground down, and 5g of ground hibiscus dissolved in 100 ml of doubled distilled-water. The mixture boiled for 5m minutes. After settling for an hour, the extract was filtered twice using Whatman No.1 filter paper. 0.02 gm of ferric chloride was dissolved in 100 ml of distilled water to prepare 1 mM of $FeCl_3$ solution. The synthesis of iron nanoparticles was achieved by mixing 1 mM $FeCl_3$ and Hibiscus rosa sinensis flower extract in three different volume ratios : 5mL of $FeCl_3$ and 5mL of extract (1:1) , 5mL of $FeCl_3$ and 10 mL of extract (1:2) and 5ml of $FeCl_3$ and 15 of extract (1:3). The mixtures were placed in a beaker. The mixtures of varying volume ratios were subjected to heat by microwave for different time durations. The best result was obtained when the mixture was exposed to heat for 20 seconds. Other volume ratios of larger extract volumes than the iron salt were used for synthesizing iron oxide nanoparticles. It was found that the ratio of 1 volume of to 2 vol $FeCl_3$ of the extract gives better results in the relation of surface plasmon resonance (SPR) peak and stability of the nanoparticles. The experiments were accomplished at pH 7, and no pH control was applied. Solution of 1 : 2 volume ratios was centrifuged at 3000 rpm for 30 minutes, the supernatant discarded, and the pellet washed with distilled water and centrifuged again. This process was repeated three times to remove any impurities. The synthesized Fe_2O_3 NPs powder was subjected to various characterizations.

2.3 Synthesis of Fe_2O_3 nanoparticles by hydrothermal approach :

Here the process involved dissolution of 0.85 mg of $FeCl_3.6H_2O$ in 100 mL of double distilled water in a 250 mL round bottom flask followed by magnetic stirring (at 800 RPM) for 45 min at 85^0C.And addition of 50 mL of NH_4OH was done to maintain the pH value of 11.The reaction mixture was then heated hydrothermally in a stainless steel Teflon lined parr Autoclave at $(160+-5)^0C$ for 12 hour. [18] Initially, the ferric-chloride Hexahydrate was yellow colored solid, and as the completion of reaction took place, it turns reddish brown similar to rust color. The color change was considered as the end point of the reaction and considered as an indicative of formation of Fe_2O_3-NP.

2.3 Preparation of graphene oxide GO

GO nanosheets were prepared from powder graphite using the Hummers and Offeman method.

2.4 Synthesis of GO-Fe_2O_3 nanocomposite:

The GO-Fe_3O_4 nanocomposite was synthesized [19] adopting the previously reported method. 25 mg GO nanosheets was dispersed in 20 ml deionized water by ultrasonication for 3 h. Then, 25% dilute NH_3 solution was added drop wise to the solution until the pH becomes 11. The mixture was then transferred to a round bottom flask (RB). To synthesizer GO-Fe_3O_4 nanocomposite of 5:1 ratio, 125 mg of $FeCl_3.4H_2O$ was added very slowly to the mixture with continuous magnetic stirring. After 3 h stirring, a black suspension of rGO-Fe_3O_4 nanocomposite was obtained. The rGO-Fe_3O_4 nanocomposite was separated by magnetic separation, washed with water and the residue was dried in a hot air oven for further use. The rGO-Fe_3O_4 nanocomposite of 1:10, 1: 20

ratios were synthesized adopting similar procedure by varying the initial amount of FeCl2 3H2O. rGO-Fe$_3$O$_4$ (1:20) nanocomposite was used to carried out all dye adsorption experiments.

2.5 Preparation of Methyl Orange solution and its callibration curve:

Prepare a 10 mM Methyl orange solution as a mother solution from which we make solutions of methyl orange having different concentrations e.g, 0.001 mM, 0.01 mM, 0.051mM etc. by dilution

Then using UV-visible spectrophotometer (Systronics 117) we measure the absorption maxima of methyl orange solution (0.05 mM) by scanning it in 200 nm to 800 nm range (c) After that we measure the absorbance of methyl orange solutions having different concentrations mM) using UV-Visible spectrophotometer to make a callibration curve by plotting the concentrations (mM) in X-axis Vs the absorbance in Y-axis

2.6 Adsorption Experiments:

To perform the adsorption experiments, first make a homogeneous mixture of Fe$_2$O$_3$-rGo Composite by taking 1 g of it in 80 ml deionised water and stirred it magnetically for about an hour maintaining the pH of the mixture at 5 by adding aqueous solutions of 0.1 M HCl on 0.1 M NaOH at temperature 25°C The total volume of the mixture should be 100 ml hence amount of 10 mM methyl orange required in 100 ml to become 0.05 mM solution is calculated which is about 05 ml (or 500 μl). Then we add the amount deionised water required to make the total volume of the mixture upto 100 ml. At last it is added the 0.5 ml tube placed in an ice bath to stop further adsorption. This same procedure is continued for upto 1 hour in the intervals of 10 minutes, and then these tubes are centrifuged in the centrifugation machine for 15 minutes and

after that we collect the clear solutions by decantation methyl orange solution (10 mM) to the mixture and at the same time we started the stopwatch.

After 5 minutes, taken a volume of 10 ml of the reaction mixture with the help of a syringe and transfer the solution to a centrifuge. These clear solutions are labeled with respect to their reaction time and then we measure the absorption of these supernatant liquid by using UV Visible spectrophotometer, from which we make a adsorption Vs time graph by ploting time.
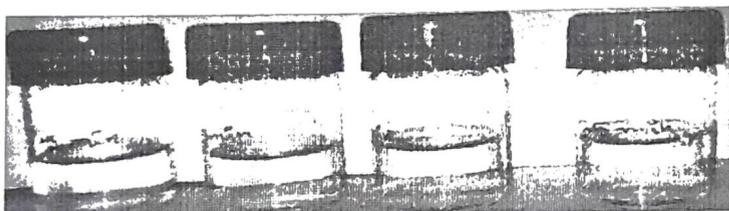

Fig. 2.1:Supernatent liquids after centrifugation

The adsorption kinetics was determined by the analysis of the adsorption capacity from the aqueous solution at different time intervals. For adsorption kinetics, M.O. solutions of fixed concentration were kept with the adsorbent under agitation until the equilibrium was achieved. The concentration of dye was determined at 466 nm for M.O using a UV-vis spectrophotometer, which is matched with literature [19]. The equilibrium adsorption capacity of M.O. onto the composite was evaluated by using the mass balance equation:

$$Q = (Co-C)V/m \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(i)$$

where Co is the initial concentrations and C, is the concentrations at time "t" of dye, m is the mass of the (Fe_2O_3-rGO) and V is the volume of solution.

3. Results and Discussion:

3.1 X-ray diffraction analysis:

X-ray diffraction is a conventional technique for determination of crystallographic structure and morphology. There is increase or decrease in intensity with the amount of constituent. This Technique is used to establish the metallic nature of particles, gives information on translational symmetry size and shape of the unit cell from peak positions and information on electron density inside the unit cell, namely where the atoms are located from peak intensities. The particle sizes were calculated from Deby-Sherrer formula given below

$$D = 0.9 \ \lambda/\beta \ \cos\theta$$

where (D) is the crystallite size, λ is the wave length of radiation, θ is the Bragg's angle, β is the full width at half maximum.
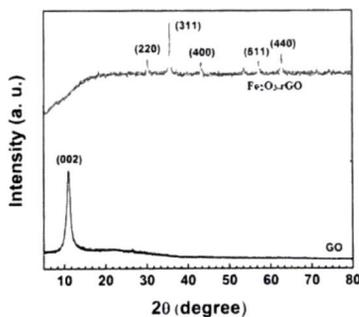

Fig. 3.1: XRD of GO and GO-Fe₂O₃

The GO-Fe$_2$O$_3$ sheets show a characteristic peak at $2\theta = 24.60°$ and $43.18°$ that disappear with the formation of Fe3O4 NPs on AG sheets. The characteristics peaks in the XRD pattern at 2θ values of about $30.24°$, $35.62°$, $43.16°$, $57.20°$ and $62.88°$ of the Fe$_3$O$_4$ NPs correspond to the

(221), (311), (400), (511) and (440) crystallographic planes, respectively [JCPDS card no. 01–075–0449]. The XRD pattern of GO/Fe$_3$O$_4$ nanocomposite has clearly established the formation of crystalline Fe$_3$O$_4$.

3.2 SEM (Scanning electron microscope) and TEM (Transmission electron microscopy analysis

The characterization of SEM and TEM analysis are employed to determine the size, shape & morphologies of formed nanoparticle. SEM gives high-resolution images of the surface of a desired sample. The SEM capable of magnifying images up to 200000 times. Measures the particle size) and characterization, Conductive or sputter coated sample involved and the sensitivity down to 1nm.
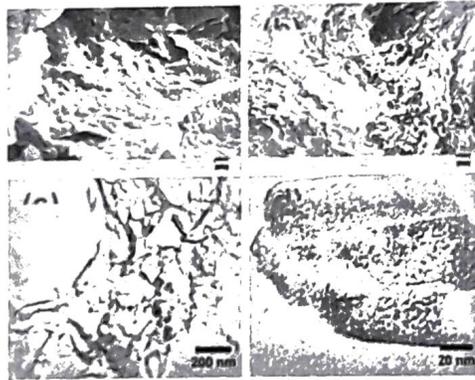

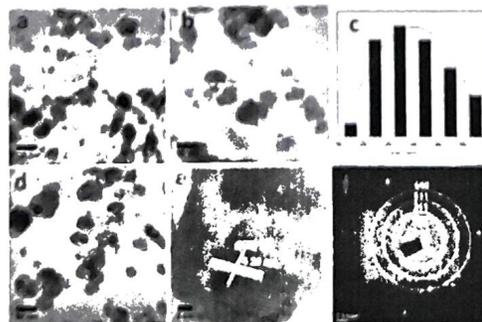Fig. 3.2 SEM, TEM and HRTEM images of rGO sheets

Fig.3.3 (a,b,d) TEM images of AG/Fe3O4 nanocomposite, (c) The particle size distribution curves, (e) HRTEM image of a single NP with lattice fringes for (220) plane of AG/Fe3O4 nanocomposite and (f) SAED pattern.

TEM analysis of the composite was performed to identify the morphology, shape and size of the NPs. Fig.3.2(a–e) show the TEM and HRTEM images of GO/Fe$_2$O$_3$ nanocomposite. It is clearly seen that the particles of Fe$_2$O$_3$ are spherical in shape and well dispersed on the GO surface.

3.3: UV-Visible spectrophotometer studies for absorption maxima of Methyl orange:

The absorption maxima of Methyl Orange dye is found to be 466 nm, which is almost similar to reported literature values [19] .
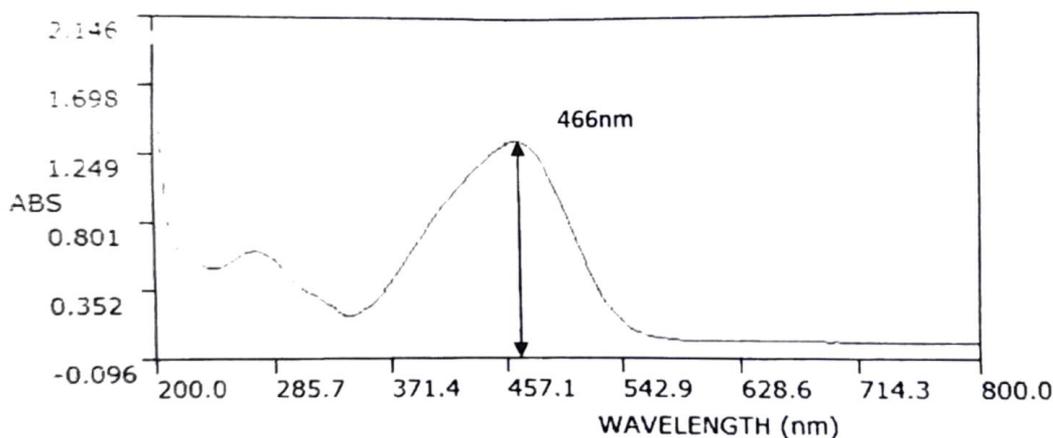

Fig. 3.4: UV-visible spectra of Methyl Orange dye (0.05mM)

3.4 Calibration curve of Methyl orange:

Callibration curve of Methyl Orange dye is used to determine the concentration of it in an unknown sample by comparing with standard samples of M.O of known concentrations. The different known concentration is plotted against absorbance values.

Table 1: Table for Absorbance of MO having different concentrations

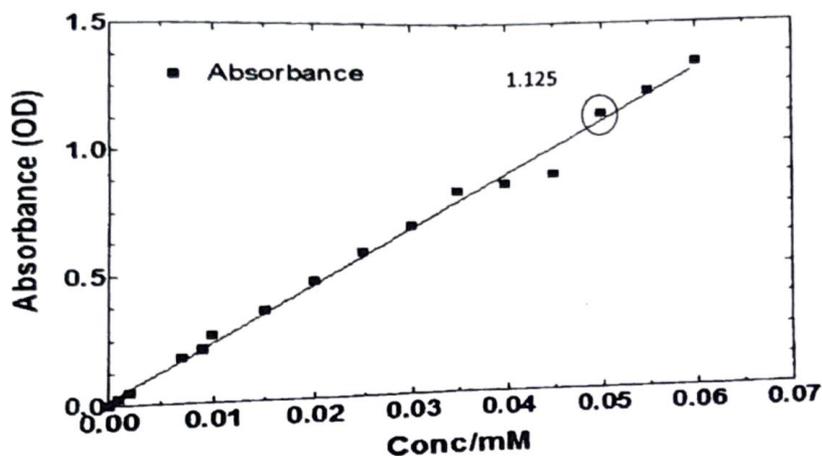| Sl No	Concentration, mM	Absorbance (OD)
1	0.001	0.026
2	0.005	0.135
3	0.01	0.265
4	0.015	0.356
5	0.02	0.463
6	0.025	0.572
7	0.03	0.676
8	0.035	0.816
9	0.05	1.125
10	0.055	1.218
11	0.06	1.336

Fig3.5: Callibration curve of Methyl Orange dye

3.5Adsorption Kinetics :

Adsorption kinetics provide a qualitative information on the capacity of the adsorbent as well as the nature of the solutesurface interection.Fig.6 Shows the adsorption kinetics of MO onto the GO/Fe_2O_3. The adsorption capacities of MO increased with increasing the reaction time. From the graph it is clear that the state of equillibrium is reached within 60 min. It gives an idea to carry to further adsorption isotherm studies.The experimental data is fitted with pseudo second order kinetics equation [9]

$$t/q_1 = 1/k_2q_e^2 + t/q_e$$

The value of k_2 is 0.3049 $mol^{-1}min^{-1}$

Table 2: Table shows the data of adsorption kinetics of MO onto GO/Fe$_2$O$_3$ composite

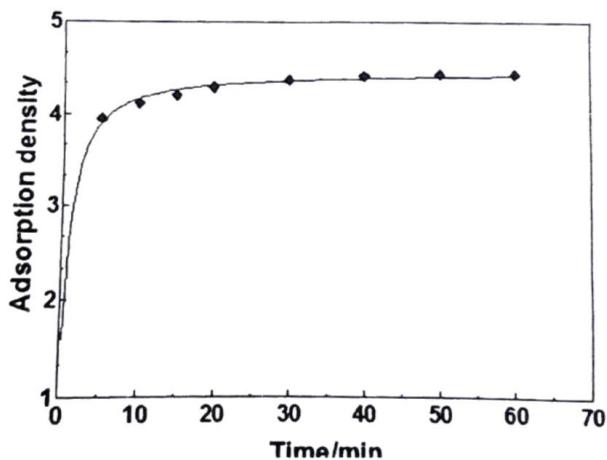| Sl No	Time(min)	Absorbance	Concentration	Adsorption density
1	5	0.246	0.0150	3.95
2	10	0.208	0.008	4.2
3	15	0.189	0.0079	4.12
4	20	0.169	0.007	4.3
5	30	0.153	0.0062	4.38
6	40	0.144	0.0058	4.42
7	50	0.140	0.0056	4.44
8	60	0.139	0.0056	4.44

Fig. 3.6 Adsorption kinetics of MO on GO/Fe$_2$O$_3$ composite

s4. Conclusion

The present shows that prepared Fe_2O_3/GO composite can be successfully utilized for the removal of dye from aqueous solution by the adsorption process with a removal efficiency > 75 %. The process is governed by chemical adsorption which is mainly due to electrostatic interaction of oppositely charged adsorbate–adsorbent species along with other electrostatic interactions. The removal efficiency is dependent on pH and temperature of the medium. It may be noted that preparative method for the synthesis of Fe_2O_3/GO composite is cost effective and good process for removal of methyl orange dye in aqueous medium.

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