Removal of Dye Basic Black 7 (BB7) from Tannery Wastewater Using Convenient Modified Graphene Oxide (MGO)

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Abstract- Thedye containing wastewater originating from leather industries contains huge amount of unreacted dyes which have great influence on water ecosystemdue to carcinogenic effects.In this experiment, modified graphene oxide was synthesized using convenient modified Hummars method, for adsorption of cationic dye Basic Black7 (BB7) in water. The functional groups,morphology and elemental compositionof MGO were analyzed by Fourier transform infrared spectrometer (FTIR), Scanning electron microscope (SEM) and Energy dispersion x-ray spectroscopy (EDX). Functional groups such as-COOH, OH, -C=O, C-O-C were examined, which would adsorb cationic dyes. The surface particles were appeared rough, porous with clear edge.The adsorption studies were carried out based on several factors such as adsorbent dose, time, pH and initial concentration of dye. However, The removal efficiency of BB7 was found to be 100% of the dye concentration upto 600 ppm by using 10 mg (0.1g/L) adsorbent MGO at pH~7 within 6 minutes. The MGO material was very effective to remove BB7 and it might be used for the treatment of organic dye containing tannery wastewater.
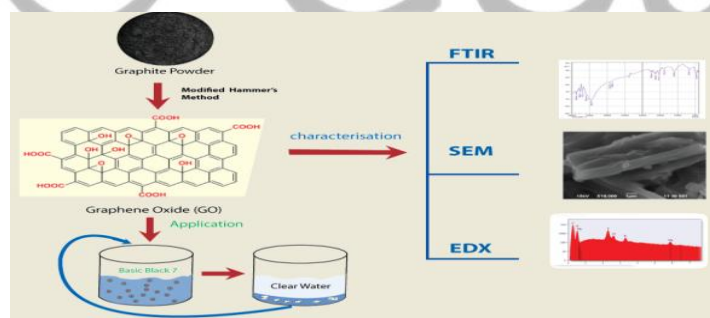
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I. Introduction

The pollution of water bodies is mainly due to direct discharge of contaminated and untreated industrial effluents into water reservoirs such as rivers, lakes and other wetlands which influence the water quality. The contamination of surrounding water bodies is unsafe to living organisms that directly and indirectly used water. Wastewater from leather and textile dyeing processes consists of different organic dyes, which have a great influence on human health and environment because of their toxicity and aesthetic aspects [1]. It has been approximated that more than 7×10^5 tons of around 10,000 different commercial dyes and pigments are manufactured in the global annually [2].It has been also reviewed that in a particular dyeing process 10-15% / 10-20% of dyestuffs is generally lost directly to the effluent [3-4].The dyestuffs that are discharged without treatment causes potential danger to the aquatic environment. There are many approaches that have been developed, for example adsorption,

chemical oxidation, flocculation, coagulation, membrane filtration, biological and electrochemical treatments of dyes containing wastewater, amongst which adsorption is considered a promising route for water purification process[5].

Carbon based materials have been preferred by many researchers for adsorption experiments due to their inherent large surface area. Graphene oxide (GO) is considered to be the most known carbon based material which is an oxidized product of graphite. GO is a compound having a hexagonal carbon lattice bonded to oxygen containing groups such as carboxyl (-COOH), hydroxyl (-OH), carbonyl (-C=O) and epoxy (C-O-C). Graphene oxide (GO) has been considered widely as a prominent and a starting material for the synthesis of different process-able material[6-7].Graphene oxides are used as a potential adsorbent because of π-π rich electron interaction structure [8]. Dyeing is the process of adding colour to leather fibres and other materials in such a way that the colouring materials becomes an integral part of materials rather than a surface coating[9] .Basic black 7 (BB7) is a dye of the azine class which is soluble in water and this dye is mostly made to obtain black and green. BB7 is mostly used in leather dyeing process as a cationic dye. The molecular formula of BB7 is $C_{28}H_{25}Cl_2N_5O$ and molecular weight (m.w) is 518.44g[10].

In this work, we synthesized modified graphene oxide (MGO)by oxidation process of graphite and evaluated the removal efficiency of cationic dye. Basic Black 7 was elected as model dye. The adsorption studies were carried out based on several factors such as adsorbent dose, time, pH and initial concentration of dyes. Finally, we have investigated the reusability of modified graphene oxide as an adsorbent for the removal of BB7 from tannery wastewater.

II. Materials and Method
2.1. Materials

Analytical grade of chemicals and reagents were used for all the experimental purposes and used further without any purification. The principle raw materials graphite powder (98% extra pure) for the study was purchased from LobaChemie Pvt. Ltd. The cationic dye (Basic black 7, CAS Number 6363-84-4, Linear formula $C_{28}H_{25}Cl_2N_5O$, M.W: 518.44g) was collected from Stahl India private limited. The other important chemicals and reagents for the synthesized of graphene oxide were Magnesium nitrate $(Mg(NO_3)_2)$, Potassium permanganate $(KMnO_4)$,

Sulfuric acid 98% (H_2SO_4), Hydrogen peroxide (H_2O_2), Hydrochloric acid (HCl).

2.2. Instruments and Accessories

Modified graphene oxide was synthesized and analyzed using the following instruments and accessories; Digital balance (XB 220A, Precisa), Hotplate with magnetic digital stirrer (PA 1180, LK LAB Korea), Hot air oven, pH meter (HANNA instruments), chilly bin (10^0 C), Fourier transform infrared spectrophotometer (FTIR) (Model IRPrestige21, Shimadzu Corporation, Kyoto Japan), Scanning electron microscopy (SEM,JSM-6490LA, JEOL), Energy dispersion X-ray spectroscopy (EDX JSM-6490LA, JEOL). Filter paper (102 qualitative, medium speed, pore 20-30μm), petri dishwere necessary to prepare the modified graphene oxide.UV-visible spectrometer (Model Spractro UV-Vis duel beam, uvs-2700, Labomed, Inc.) was used to find out the adsorption efficiency.

2.3. Synthesis of Modified Graphene Oxide (MGO)

Modified graphene Oxide (MGO) has been synthesized from natural raw materials graphite powder (98% extra pure) followed by Hummer's Method [11] in convenient modified way. In details, 2.5 gm of graphite powder was added in 100 ml of sulfuric acid (H_2SO_4). The mixture was continuously stirred (60 rpm) for 2 hours. Then the mixture was cooled in ice bath (below 20 ^{0}C) and was slowly added an oxidizing agent $KMnO_4$ (5 gm) with continuous stirring for 1.30 hours. After the reaction completed, 100 ml of distilled water was added to the above mixture by keeping continuous stirring at the temperature around 98 ^{0}c for 1.30 hours. Then the heater was turned off and 200 ml of distilled water was added and stirred for an hour. 10 ml of hydrogen peroxide (H_2O_2) (30%) was added to the mixture to remove the extra potassium per magnetite. In the end, the mixture was washed with HCl (5%) to remove metal ions and rinsed with distilled water several times. The prepared solid sample was dried in vacuum oven at 70 ^{0}C.

2.4. Adsorption Study

The experiment of adsorption of BB7 on modified graphene oxide was conducted using UV-visible spectrometer analysis at λ_{max}= 660 nm. The experimental parameters were adsorbent dose (5-12 mg), pH(2-12), contact time (0-6 minutes) and concentration of BB7 dye (200 to 1000 ppm). The

experiments were conducted in beakers for a fixed volume (100 mL) of 200 ppm (200 mg L^{-1}) dye concentration. The percentage dye of removal efficiency of BB7 was estimated using the equation,

$$\%R = \frac{A_0 - A_t}{A_0} \times 100\%$$, where A_0 is the initial

absorbance (at λ_{max}) and A_t is the final absorbance at time t in the dye solution respectively.

III. Results and Discussion

3.1. Characterization of MGO
3.1.1. FTIR Analysis

The FTIR analysis of MGO was carried out at wavelength ranges of 400 cm^{-1} to 4000 cm^{-1}. The spectra represented the wavelength and intensity which have the characteristics of specific types of molecular vibration and stretching that help to identify functional groups of MGO. Figure 1 illustrated the FTIR spectrum and the broad peak at 3448 cm^{-1} is attributed for O-H stretching vibration of C-OH groups and peak at 1749 cm^{-1} confirmed the carbonyl group (C=O). The peak centered at 1629 cm^{-1} is mainly from stretching vibration of C=C bond indicating the presence of sp^2 hybridized carbon. The spectrum shows peak at 1103 cm^{-1} is indicated as C-O stretching and C-OH bending is also attributed at wavelength 1531 cm^{-1}.
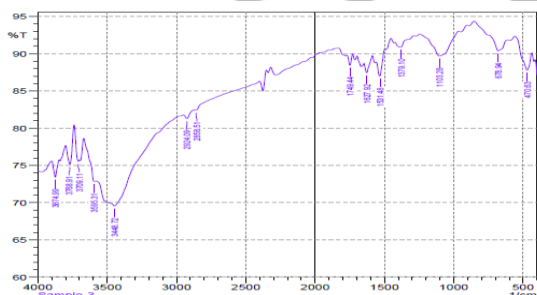

Figure 1: FTIR spectrum of Convenient Modified Graphene Oxide (CMGO)

Table 1: FTIR bands of Convenient Modified Graphene Oxide (CMGO)

Frequency (cm^{-1})	Functional groups
3448	OH (alc./water)
1749	C=O (carbonyl)
1627, 1531	C=C (sp^2 hybrid)
1379	C-OH (deformed)
1103	C-O (alkoxy)/sulfonatd

3.1.2. SEM Analysis

The surface morphological study of MGO material was examined with scanning electron microscope (JSM-6490LA, JEOL). Figure 2 depicted the SEM images of at low (a-left) and high magnification (b-right) of MGO. At low magnification as shown in the first one, the particles are appeared with clear edges. Additionally, the sample was taken at high magnification to observe the morphological surface clearly and observed that the surface is completely rough and porous.
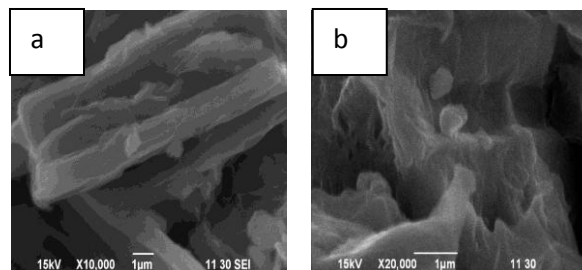

Figure 2: SEM images of Modified Graphene oxide (MGO)

3.1.3. EDX Analysis

The energy dispersive X-ray spectroscopy was investigated with analytical scanning electron microscope (JSM-6490LA, JEOL) within the range of 0-12 kV; to find out the elemental composition of the prepared sample. Figure 3 illustrated the EDX spectrum of MGO and showed the peaks corresponding to C, O, Mn, S, Cl and K. The EDX of the synthesized MGO showed the carbon/oxygen atomic ratio of 3.12:1 which is almost same to typical value [12]. This is the confirmation that modified graphene oxide was actually formed.
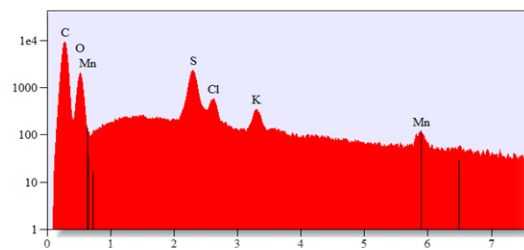

Figure 3: EDX spectrum of Modified Graphene oxide (MGO)

The elemental composition including percentage of weight and atoms are displaced in table 2. It is found that the presence of carbon atom in the prepared sample around 69.60% which is the highest amount. Manganese present very small amount and that is 0.57%.

Table 2: Elemental compositions of Modified Graphene oxide (MGO)

Elements	Weight %	Atom %

C	56.66	69.60
O	24.20	22.32
S	11.73	5.40
Cl	3.11	1.30
K	2.16	0.81
Mn	2.14	0.57
Total	100.00	100.00

3.2. Adsorption Experiment of BB7 on MGO

3.2.1. Effect of adsorbents dose

The effect of different adsorbent dose on the adsorption of BB7 in aqueous solution was carried out by varying the adsorbent dose from 5 to 12 mg shown in figure 4.The doses are added to a series of 100 mL BB7 dye solution of 200 ppm concentration, pH~7 at room temperature and stirred for 10 minutes at 120 rpm to get the optimum dose of adsorbent. From the graph 4, it is clearly seen that the adsorption efficiency increased with increasing in adsorbent dose due to the higher number of available active binding sites for cations in dye solution. At the beginning, the adsorption efficiency was 71% for a very low amount of adsorbent dose of 5 mg and 94.58% for 9 mg of adsorbent dose then it increased up to 100% with 10 mg adsorbent dose. The result suggested that the visible constant value of adsorption efficiency (100%) after 10 mg of adsorbent dose. So, the optimum dose for the removal of BB 7 was considered to be 10 mg (0.1g/L) of MGO and used for further adsorption studies.
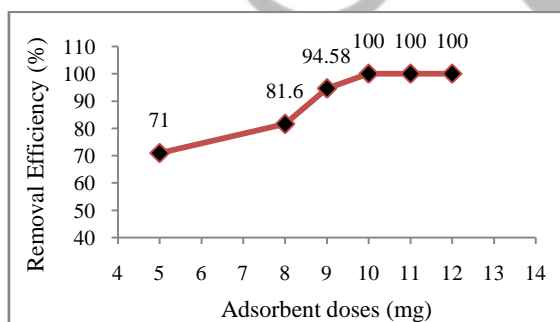

Figure 4: The effect of adsorbent doses vs. removal efficiency (%) of BB 7 on MGO with an initial dye concentration of 200 ppm at room temperature and pH~7

3.2.2. Effect of pH

The effect of pH on adsorption was carried out at room temperature by altering the pH at acidic and basic conditions from 2 to 12, initial BB7 dye solution concentration of 200 ppm and adsorbent dose 10 mg. The pH of the solution was adjusted by adding a suitable volume of 0.1M HCl and 0.1M NaOH. The pH plays an important role in a solution containing ions as it affects the electrostatic interaction between adsorbent and adsorbate. From figure 5, it is noticeable that the increases in pH lead to increasing the removal efficiency. It is also manifested that cationic dyes completely removed at pH range 6 to 12 but at pH 2 it removes up to 81.96% and at pH 4 it removes up to 83.37%. Lower pH leads to protonation of adsorbent surface; therefore, adsorption efficiency is low due to electrostatic repulsion of the cationic dye molecules with the adsorbent surface [13]. With the increase pH, the negative charges increase with slow de-protonation of surface groups associated with the MGO, thus, increasing the electrostatic interactions with cationic dye. Hence, the optimum pH value for the adsorption of BB7 was found at pH 6 to 12. So we considered the pH~7 for adsorption studies.
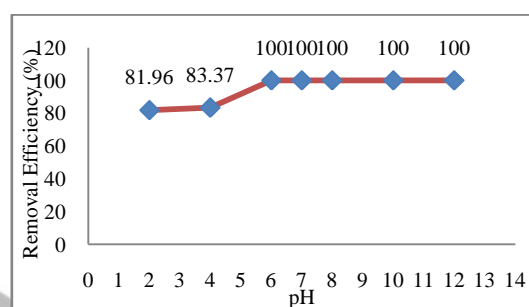

Figure 5: The effect of pH vs. removal efficiency (%) of BB 7 on MGO with an initial dye concentration of 200 ppm, adsorbent dose 10 mg (0.1 g/l) at room temperature

3.2.3. Effect of contact time

The effect of contact time on the removal of BB7 by the MGO was observed with 100 mL of 200 ppm dye solution, 10 mg adsorbent dose at pH~7 and room temperature by varying the contact times. At the beginning, the mixture was stirred for 15 minutes at 120 rpm then supernatant was collected every 1 minute of intervals. It was found from the % of removal versus time graph that adsorption efficiency was 100%, this might be due the available active binding sites for cationic dyes. The rapid adsorption rate was mainly attributed to the electrostatic interaction of oppositely charged adsorbate-adsorbents species along with their π-π interaction [14] .

Again, to find out the effect of contact time for removal of BB 7 by MGO; keeping other parameters constant, the stirring time has reduced from 15 to 5 minutes and collected the supernatant every 1 minute interface. The figure 6shows that removal efficiency increased rapidly with contact time for cationic dye BB7 and it was found that after 5 minutes stirring, it removed almost 90% impurities. It can be assumed that initially the rate of binding is

high because of higher numbers of open active sites and get saturated with increasing the stirring time. And after 6 minutes, the removal efficiency reached to 100%.
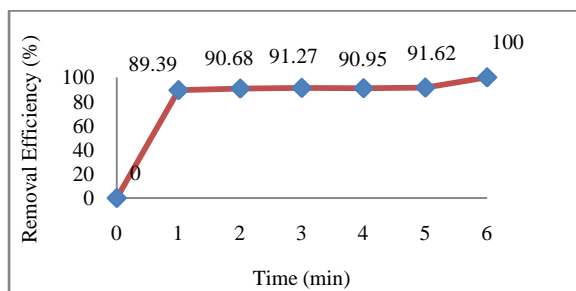

Figure 6: The effect of contact time vs. removal efficiency (%) of BB7 on MGO with an initial dye concentration of 200 ppm, adsorbent dose 10 mg (0.1 g/l) at room temperature and pH~7

3.2.4. Effect of initial dye concentration

The experiments were performed to manifest the effect of initial BB7 dye concentration on adsorption onto adsorbent MGO. For this experiment the initial concentration of dye was varied from 200 ppm to 1000 ppm with optimum adsorption dose, time and pH. It is noticeable from the result that the adsorption efficiency of BB7 remained constant up to 600 ppm of dye concentration. Therefore, from figure 7, it is observed that the removal efficiency decreased from 100% to 64.64%; this is due to the lack of available active binding sites required for the high concentration of BB7 dye solutions. The results also indicated that the higher uptake of dye at low concentration of adsorbent may be attributed to the availability of more active binding sites on the surface of adsorbent MGO for a lesser number of adsorbate species.
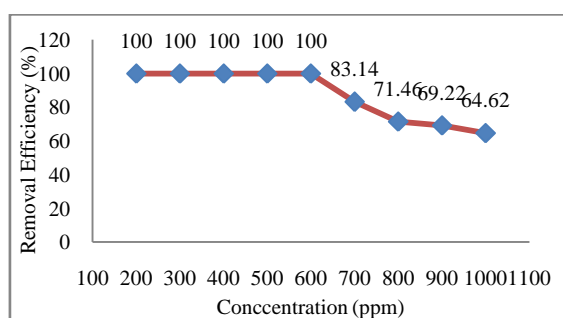

Figure 7: The effect of initial concentrations of BB7 vs. removal efficiency (%) by MGO

3.3. Reusability of MGO

The MGO was dried in an oven at 70 ^{0}C for 3 hours after single using. Then the adsorbent was reused for the removal of BB7. The adsorption study was conducted like as before by maintaining same factors. The removal efficiency of adsorbent was found 100% like previous experiments upto the three cycled.

IV. Conclusion

Modified graphene oxide was synthesized from graphite powder and it was used as adsorbent of Basic Black 7 (BB7). Because of the presence of oxygen containing functional groups, MGO exhibited good ability to remove cationic dye BB7 fromcolored water.The removal of BB7 was found to be 100% of the dye concentration upto 600 ppm by using 10 mg (0.1g/L) adsorbent MGO at pH~7. Moreover, MGO can be recycled without losing it adsorbing capabilityand BB7 is easily adsorbed into the adsorbent. The study suggested that synthesized MGO could be used as potential adsorbent to remove cationic dyes from tannery wastewater.

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