

Research Article

Degradation of methylene blue using graphene oxide and aluminium oxide nanoparticles and nanocomposites

R. Caroline Jeba* and Manpreet Kour Kalsi

Department of Biotechnology, Dr.M.G.R Educational and Research Institute
(Deemed to Be University) Maduravoyal, Chennai-95, Tamil Nadu, India.

*Email: janeshjeba@gmail.com

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Abstract

Methylene blue dye was degraded by using graphene oxide and aluminium oxide nanoparticles and with their nanocomposites. Graphene oxide and aluminium nanoparticles were synthesized by using modified Hummers method, sol-gel method respectively. Degradation of methylene blue of different concentrations was determined using graphene oxide and aluminium oxide nanoparticles and the absorbance value was evaluated using UV spectrometer. Evaluation of methylene blue degradation and their characterization are analysed by using FTIR & SEM. The maximum degradation achieved by Graphene oxide nanoparticles is 99.6% and the maximum degradation achieved by Aluminium oxide nanoparticles is 95.9%. Comparing to Graphene Oxide and Alumina, Nano composites have the higher degradation efficiency of 99.8% at the initial concentration. The degradation of Methylene blue was examined using varied concentrations of dye, nanoparticles & nanocomposites. The degradation rate rises as the concentration of nanoparticles rises, according to the findings. Graphene oxide and Nanocomposites were shown to be more efficient at degrading methylene blue than Aluminium oxide, with a maximum efficiency of 99.9%. Nanocomposites

- Graphene oxide
- Aluminium oxide

Graphene oxide nanoparticles and aluminium oxide nanoparticles can be used for the removal of methylene blue dyes which poses severe threat to environment.

Key words: Methylene blue, graphene oxide, aluminium oxide, nanocomposites, UV spectrometer, FTIR, SEM

Introduction

Environmental pollution is one of the world's most severe and critical concerns today. Because of the huge volume of water used in fabric manufacturing, industries are the major pollutants, with the textile industry producing the most liquid effluent contaminants. Wastewaters of various compositions are developed in this industry, from which coloured water released during the dyeing of fabrics is the most problematic since even a trace of dye can remain highly visible. Other

industries such as paper and pulp mills, dyestuff, distilleries, and tanneries also produce highly coloured wastewaters. It is in the textile industry that the largest quantities of aqueous wastes and dye effluents are discharged from the dyeing process, with both strong persistent colour and a high biological oxygen demand (BOD), both of which are aesthetically and environmentally unacceptable. Amongst various techniques of water purification, adsorption and degradation are the mostly

commonly employed technique as it is cheap, easy to handle, can be utilized for elimination of various pollutants and it also produces a high – quality treated effluent[1]. Methylene blue dye (MBD) is a heterocyclic aromatic chemical compound with the molecular formula of $C_{16}H_{18}ClN_3S$ and molecular weight of 319.85 g/mol. Methylene blue is a formal derivative of phenothiazine. It is a dark green powder that yields a blue solution in water. The hydrated form has 3 molecules of water per unit of methylene blue. It is also called as Methylthioninium chloride or Swiss blue. It is a synthetic basic dye, when it is administered intravenously in low doses, it converts methaemoglobin to haemoglobin. It functions as a histological dye, tracer, acid-base indicator, neuroprotective agent, fluorochrome etc. MB is widely used in textile industries for dye processing, and upto 50% of the dyes consumed in textiles industries are azo dyes. In the past few years, several catalysts such as Titanium dioxide (TiO_2), Bismuth ferrite ($BiFeO_3$), Zinc sulphide (ZnS) and Zinc oxide (ZnO) have been used to degrade methylene blue[2]. The degradation reaction occurs by attacking the organic compounds with OH , which can be converted to small oxidized by-products, where the in-situ formed H_2O_2 oxidizing agent plays a substantial role in additional hydroxyl radical OH generation. Graphene oxide (GO) has more oxygen functional groups than reduced graphene oxide (rGO). GO has a surface area of 736.6 m^2/g [7] compared to 400 m^2/g [8] for graphite. Numerous chemical, thermal, microwave and microbial/bacterial methods have been used in the synthesis of GO [9]. Chemical exfoliation is preferable due to its large-scale production and low cost. Chemical exfoliation involves three steps, oxidation of graphite powder, dispersion of graphite oxide (GTO) to graphene oxide (GO) and GTO exfoliation by ultrasonication to produce graphene oxide (GO) [10].

Nanobiotechnology is a field in which nanotechnology techniques are created and used to investigate biological phenomena. In the recent decade, the utilization of nanoparticles for wastewater treatment has picked up the extraordinary consideration because of its property being profoundly gainful as adsorbents and for utilizing for filtration reason. The large surface area, modified surface properties, unique electron conduction properties, etc. offer nanomaterials with excellent performances in dye-contaminated wastewater treatment. Nanoparticles are usually distinguished from “microparticles” (1-1000 μm), “fine particles” (sized between 100 and 2500 nm), and “coarse particles” (ranging from 2500 to 10,000 nm), because of their smaller size they have very different physical or chemical properties, like colloidal properties and optical or electric properties[3]. Functionalized multi walled nanotubes was used for the adsorption of three azoic dyes namely Congo red, yellow and reactive green HE4BD[4]. Adsorption capacity was maximum in case of Congo red (148 mg/g) followed by reactive green (152 mg/g) and golden yellow (141 mg/g) and also investigated the adsorption capacity of graphene oxide for methylene blue removal from its aqueous solution and concluded that the concentrations lower than 250ppm, dye adsorption is very fast and efficient with 99% of dye removal. Removal process gives best results at higher pH and low temperature showing huge adsorption capacity of 714 mg/g. A study carried out was analysed the degradation capacity of silver nanoparticles to reduce safranin orange and methyl red[5]. A decrease in the dye concentration was observed by a decrease in UV peak intensity within 24 hours of incubation. Dye degradation rate constant of safranin orange and methyl red was calculated to be $1.03 \times 10^{-3} \text{ min}^{-1}$ and $1.03 \times 10^{-3} \text{ min}^{-1}$ respectively. The nanocomposite hydrogel was prepared in in-situ co-reduction of graphene oxide as well as silver acetate within hydrogel matrix to reduced graphene oxide and silver

nanoparticles composite hydrogel. Hydrogels were found to be very effective in dye degradation as 100% of RhB and MB were degraded in 70 minutes and 30 minutes respectively.

MATERIALS AND METHODS

PREPARATION OF METHYLENE BLUE DYE:

Methylene blue solution of different dilutions were prepared for making a standard curve and a working solution of 10ml was prepared for carrying out dye degradation experiments. A stock solution of 10000ppm was prepared by dissolving 50mg of dye in 10ml of distilled water. Various dilutions (100 μ L, 200 μ L, 300 μ L, 400 μ L, 500 μ L) were made. Absorbance at 668nm is taken by UV-Spectrophotometer.

SYNTHESIS OF GRAPHENE OXIDE NANOPARTICLES:

Graphene oxide was produced through the modified Hummer's method by oxidizing the graphite powder. Graphite powder (4.5g) was added to 120ml of sulphuric acid containing (2.5g) of Sodium nitrate (NaNO_3). Then, the solution was continuously cooled for 20 minutes at 0°C on an ice bath. Potassium permanganate (KMnO_4) was added dropwise to the solution with vigorous stirring, maintaining the temperature at 0°C . Then, the mixture was heated at 40°C for 2 hours with vigorous stirring until the colour of the slurry mixture turned to dark green. Distilled water (125ml) was added dropwise, maintaining the temperature below 50°C . Then, 20ml of Hydrogen peroxide (H_2O_2) was added dropwise to the mixture. The reaction solution starts to become brownish yellow, indicating the formation of the GO seeds. After 30 minutes, the mixture was centrifuged at 6000rpm for 10 minutes. Finally, the GO is formed, it is then separated from the mixture, and washed with 10% of HCl to remove ions from the solution, followed by washing with

distilled water. The dark brown paste was dried in hot-air oven at 50°C overnight, and then, a black GO solid is formed.

SYNTHESIS OF ALUMINIUM OXIDE NANOPARTICLES:

Alumina is produced by using sol-gel method. The raw materials used to synthesize aluminium oxide nanoparticles were Aluminium chloride (Al_2Cl_3), and 25% Ammonium solution. 1.34g of aluminium chloride was added in 100ml of methanol (0.1M alcoholic solution) in a beaker. The beaker was kept or stirring without heat under 400 rpm and 20ml of ammonium solution was added dropwise for 1 hour into beaker during continuous stirring and kept overnight. After overnight stirring, white precipitate of alumina was formed.[6]

Al_2O_3 NANOPARTICLE SOLUTION

The solution is then centrifuged at 4000rpm for 15 minutes. After centrifugation the supernatant was discarded and the pellet was washed for 2 times with distilled water and 2 times with methanol for remove ions and acids from the solution. The solution is then kept in hot-air oven, overnight at 40°C to dry until it gets into its crystal form.

PREPARATION OF NANOCOMPOSITES:

Graphene oxide and Aluminium oxide ($\text{GO-Al}_2\text{O}_3$) nanocomposites were made by mixing both the nanoparticles in equal amount by sol-gel process. Sol-gel is a viable alternative method to produce nanocrystalline elements and composite powders.

DYE DEGRADATION BY GRAPHENE OXIDE:

Dye degradation capacity of Graphene oxide was evaluated using the following procedure: 0.01g of Graphene oxide was added in different dilutions of methylene blue dye solution and the mixture was stirred vigorously. After stirring, the mixture was centrifuged at 5000rpm for 10 minutes to settle

down the graphene oxide with dye adsorbed on it and the absorbance of the supernatant was then recorded. The same was repeated with varying concentrations of GO i.e., in g and mg (0.03, 0.06, 0.09) with the MB concentrations of (50ppm, 100ppm, 150ppm, 200ppm, 250ppm, 300ppm, 400ppm, 500ppm, 600ppm, 1ml & 2ml), then the absorbance value of supernatant was recorded by using UV-Spectrophotometer.

DYE DEGRADATION BY ALUMINIUM OXIDE:

0.01g of Aluminium oxide was added in different dilutions of methylene blue dye solution and the mixture was stirred vigorously. After stirring, the mixture was centrifuged at 5000rpm for 10 minutes to settle down the alumina with dye adsorbed on it and the absorbance of the supernatant was then recorded. The same was repeated with varying concentrations of alumina i.e., in g and mg (0.03, 0.06, 0.09) with the MB concentrations of (50ppm, 100ppm, 150ppm, 200ppm, 250ppm, 300ppm, 400ppm, 500ppm, 600ppm, 1ml & 2ml), then the absorbance value of supernatant was recorded by using UV-Spectrophotometer.

DYE DEGRADATION BY NANOCOMPOSITES:

0.03g of Graphene oxide and Aluminium oxide ($\text{GO-Al}_2\text{O}_3$) nanocomposites was added in different dilutions of methylene blue dye solution and the mixture was stirred vigorously. After stirring, the mixture was centrifuged at 5000rpm for 10 minutes to settle down the nanocomposites with dye adsorbed on it and the absorbance of the supernatant was then recorded. The same was repeated with varying concentrations of nanocomposites i.e., in g and mg (0.03, 0.06, 0.09) with the MB concentrations of (50ppm, 100ppm, 150ppm, 200ppm, 250ppm, 300ppm, 400ppm, 500ppm, 600ppm, 1ml & 2ml), then the absorbance value of supernatant was recorded by using UV-Spectrophotometer.

Results and discussion

FORMATION OF GRAPHENE OXIDE NANOPARTICLES:

Graphene oxide was synthesized using modified Hummer's method following the methodology. Oxidation of graphite using, Sodium nitrate (NaNO_3), Sulphuric acid (H_2SO_4), Potassium permanganate (KMnO_4) resulted in thick brown coloured slurry (figure :1), which was a mixture of Graphene oxide, residues of un-oxidized graphite powder and unreacted oxidizing agents. The solution gave dark-green colour on adding, Hydrogen peroxide(H_2O_2), which was an indicative of successful oxidation of Graphite to Graphene oxide. Repeated centrifugation was done to remove the unwanted salts, acids and ions & un-oxidized graphite particles to obtain a pure suspension of Graphene oxide. The dried graphene oxide was made powdered by using mortar and pestle.



Figure:1 Formation of graphene oxideseeds

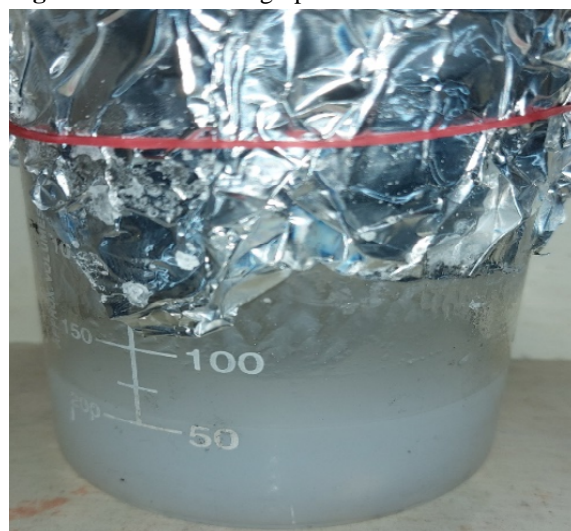


Figure:2 Formation of aluminium oxide nanoparticle solution

FORMATION OF ALUMINIUM OXIDE NANOPARTICLES:

Aluminium oxide was synthesized using sol-gel method following the methodology. The sol undergoes hydrolysis and polycondensation reactions to evolve gradually towards the formation of a gel-like network. During the process a mixture of Aluminium chloride (AlCl_3) containing the Ammonia solution (NH_3) was stirred continuously in a magnetic stirrer for 24 hours and the white-gel precipitate was formed (figure : 2). The precipitated solution was centrifuged many times by adding methanol and distilled water to

remove the acids, ions and salts from the alumina pellets. After obtaining the aluminium oxide paste, it is dried overnight in hot-air oven at 40°C . After drying the white crystalline powder of Alumina nanoparticles are obtained

UV-SPECTROSCOPY OF METHYLENE BLUE DYE:

The prepared Methylene blue dye solution (50mg/200ml) is monitored by using shimadzu UV-visible spectrophotometer at 668nm, to make the Standard curve, and to figure out the solute concentration of unknown samples.

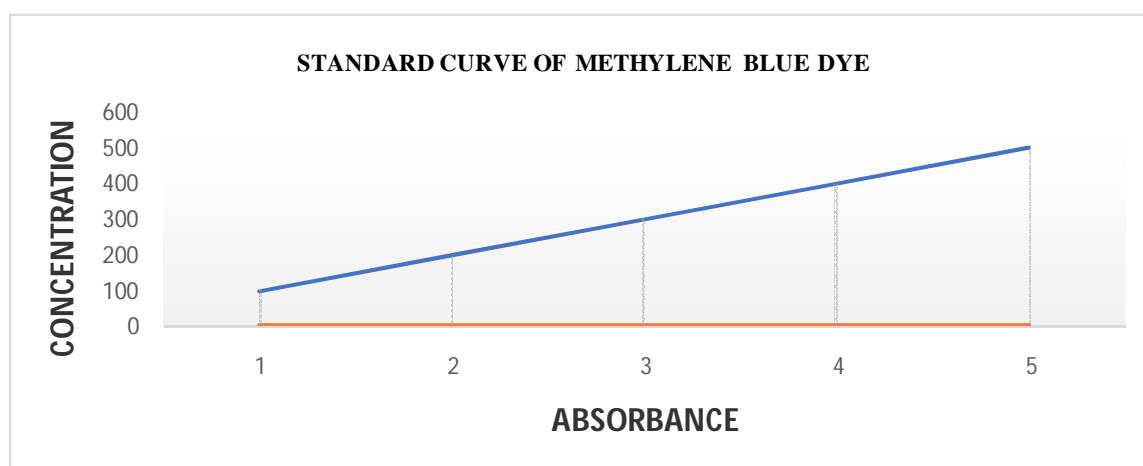


Figure 3: standard curve of methylene blue dye

Table 1: absorbance value of standard curve of MB dye

CONCENTRATION IN μl	ABSORBANCE VALUE
100	0.365
200	0.632
300	0.870
400	1.342
500	1.465

CHARACTERIZATION OF GRAPHENE OXIDE NANOPARTICLES:

UV-VISIBLE SPECTROPHOTOMETER:

The effect of Graphene oxide ranging 0.01g, checked on degradation of Methylene blue for the concentrations (50 μl , 100 μl , 150 μl , 200 μl , 250 μl , 300 μl , 400 μl , 500 μl , 600 μl). The MB dye solution changes its colour after 2 mins of stirring after the addition of 0.01g of Graphene oxide at room temperature. The figures below depict that GO is very good adsorbent of MB as 99.6% of degradation was achieved.

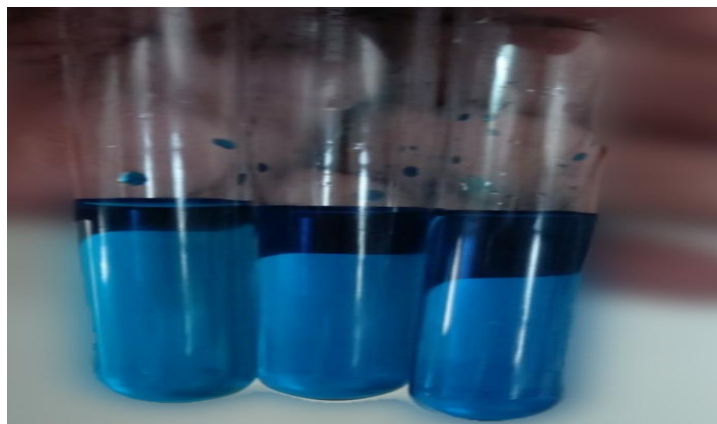


Fig 4 (a) Methylene Blue dye solution of (50 μ l, 100 μ l, 150 μ l)



Fig 4 (b) Degradation of methylene blue by graphene oxide nanoparticle



Fig 5 (a) Methylene blue dye samples

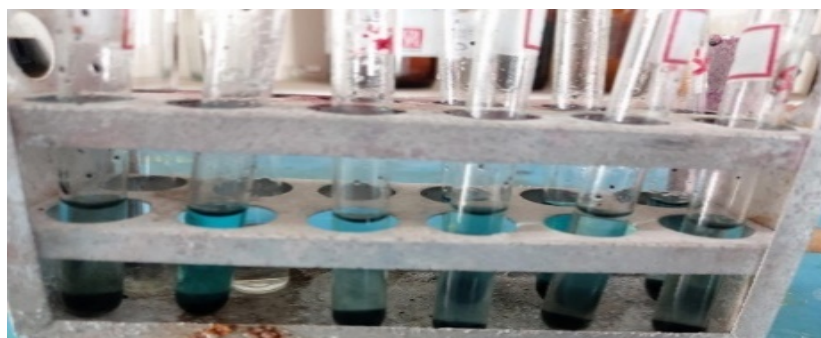


Fig 5(b) Degradation by graphemeOxide nanoparticle.

The figures:5(a & b) shows the degradation of Methylene blue dye by Graphene oxide in 30 minutes. The absorbance spectrum of the supernatant was subsequently measured using UV-Spectrophotometer with the wavelength of 668nm.

Percentage of dye degradation was estimated by the formula: $\% = \frac{C_0 - C}{C_0} \times 100$, Where, C_0 is the initial concentration of dye solution and C is the concentration of dye solution after degradation.

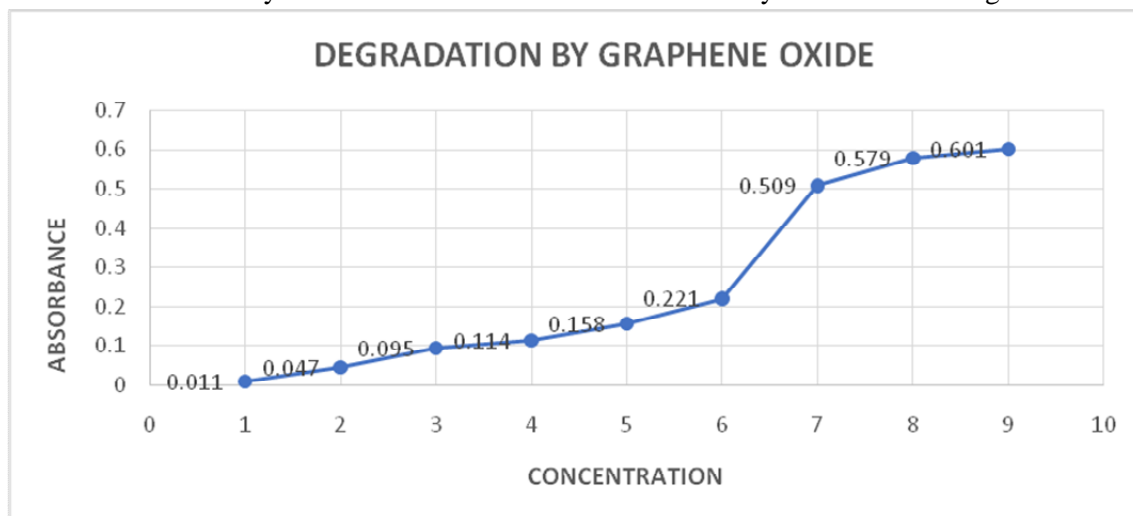


Fig 6: UV-Visible spectra of degradation by graphene oxide nanoparticle

Table 3: absorbance & percentage of mb dye degradation using graphene oxide nanoparticle

CONCENTRATION IN (μl)	ABSORBANCE VALUE	DEGRADATION PERCENTAGE (%)
50	0.011	99.2
100	0.047	99.6
150	0.095	99.7
200	0.114	99.6
250	0.158	99.6
300	0.221	99.6
400	0.509	99.5
500	0.579	99.5
600	0.601	99.6

Fourier – transform Infrared Spectroscopy (FTIR):

FTIR was done to examine the presence of oxygen-functional groups in the sample (GONP). Graphene Oxide stretching vibrations of OH functional groups were obtained at 3021.62, 3133.5, 3446.94, 3545.32, 3661.05, 3696.73, 3785.46 cm^{-1} . The peaks 425.32, 456.18, 478.37, 554.56, 600.85, 731.05, 756.13, 839.07, 873.79, 891.15, 941.3, shows the alkoxy C–O stretching of primary alcohol. The carbonyl group (C=O) stretching vibrations were seen at 1018.46, 1103.33, 1122.62, 1182.41, 1218.1, 1386.88, 1419.67, 1458.25, 1498.75, 1512.26, 1539.26, 1576.87, 1668.5, 1683.93. The CH– sp^3 stretching were seen at 2342.65, 2401.48, 2633.91, 2876.95, 2959. In the FTIR spectra of graphene oxide, the broad and the most intense peak between 3000–4000 cm^{-1} can be assigned to the superimposed stretching vibrations of O–H group of the carbonyl, alcoholic and the adsorbed water molecules. The other characteristic GO peaks are observed at 500–750 cm^{-1} assigned to C–O stretching vibrations of epoxy groups, 1750 cm^{-1} assigned to C=O stretching vibrations of COOH groups whereas the peak at 1500 cm^{-1} can be assigned to the H–O–H bending vibrations or adsorbed water molecules or to the skeletal vibrations of unoxidized C–C bonding. All the peaks related to the oxygen-containing functional groups indicate the oxidation of graphite.

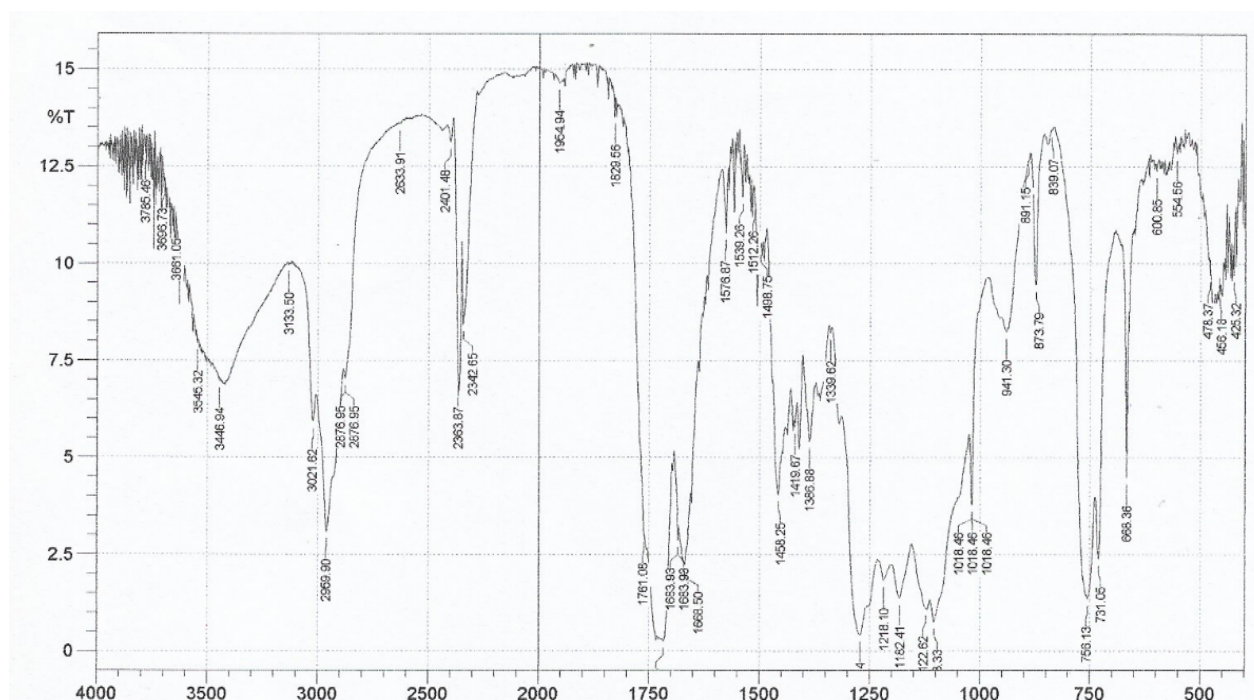


Fig 7: FTIR spectrum of graphene oxide

Table 4: Assignment of FTIR bands of graphene oxide nanoparticle

S.NO	WAVENUMBER	BAND ASSIGNMENT
1	≈3800	O–H stretching
2	≈2960	CH–sp ³ stretching
3	≈1700	C=O carbonyl stretching
4	≈1000	C–O stretching of primary alcohol

SCANNING ELECTRON MICROSCOPE (SEM):

SEM is used to characterize and describe the morphology of Graphene Oxide nanoparticles. The figure (8) shows the micrograph of Graphene oxide that were characterized at magnifications 10 Kx with accelerating voltage 30 kV. The electrons interact with atoms in the sample, producing various signals that contains information about the surface topography and composition of the sample. Oxidation of graphite is the use of strong oxidizing agents and their functionalities can expand the layer separation and also creates the material hydrophilic.

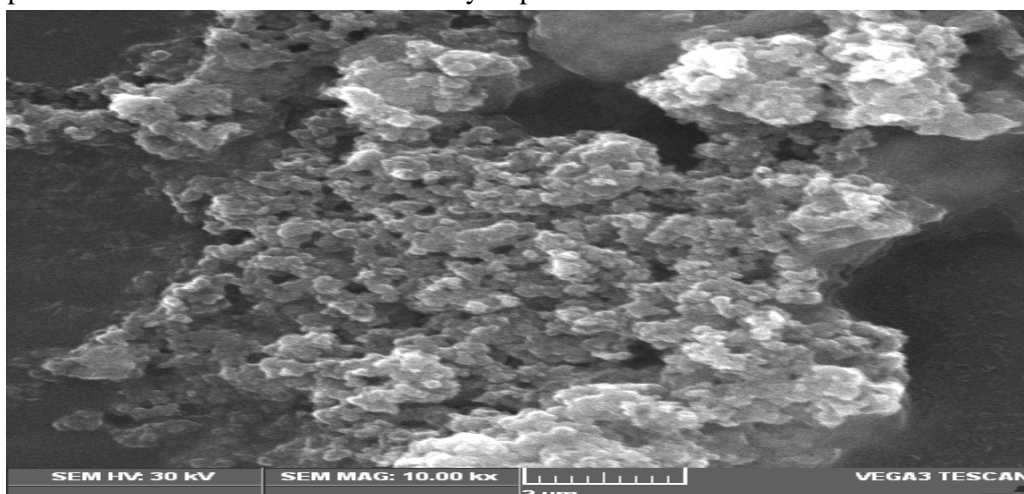


Fig 8: SEM image of graphene oxide nanoparticle

CHARACTERIZATION OF ALUMINIUM OXIDE NANOPARTICLES: UV-VISIBLE SPECTROPHOTOMETER:

The effect of Aluminium oxide ranging 0.01g, checked on degradation of Methylene blue for the concentrations (50 μ l, 100 μ l, 150 μ l, 200 μ l, 250 μ l, 300 μ l, 400 μ l, 500 μ l, 600 μ l). The MB dye solution changes its colour after 2 mins of stirring after the addition of 0.01g of Aluminium oxide at room temperature.

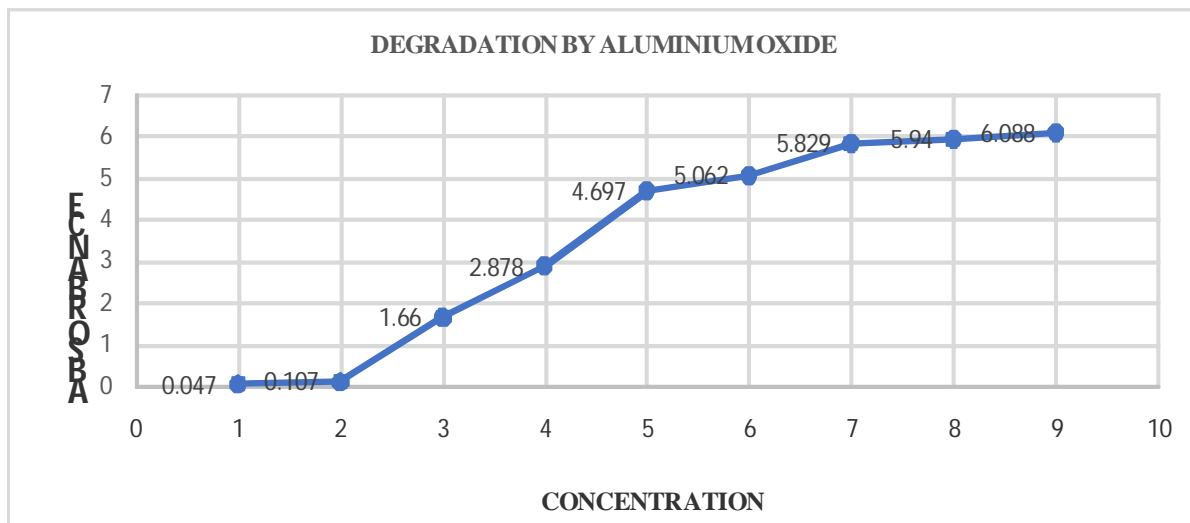


Fig 9: UV-Visible spectra of degradation by Aluminium oxide nanoparticle

Table 5: absorbance & percentage of MB dye degradation using AONP_s

CONCENTRATION IN (μ l)	ABSORBANCE VALUE	DEGRADATION PERCENTAGE (%)
50	0.047	99.2
100	0.107	99.2
150	1.660	95.4
200	2.878	94.2
250	4.697	91.8
300	5.062	93.7
400	5.829	94.1
500	5.940	95.2
600	6.088	95.9

Fourier – transform Infrared Spectroscopy (FTIR):

FTIR spectroscopy is useful in measuring the absorption of IR radiations by means of a sample, and the outcomes are verified with the useful resource of potential of a wavelength. The evaluation of the IR spectrum consists of the correlation of the absorption bands (vibrational bands) and the chemical compounds in the pattern. The peak at 877.65 is assigned to the aluminium oxide stretching. The peaks lie in the range of 400-900 cm^{-1} are assigned Al-O-Al stretching. The top value at 669 and 877 are assigned as aluminium oxide stretching. Vibrational peaks at 1039.68 cm^{-1} and 1170 cm^{-1} in the vary of 11901075 cm^{-1} are corresponding to C – O Stretching vibration of Sodium Carbonate. The Vibrational peaks at 1444.75 is prescribed to O – H bending vibration of solvent water. The vibrational peak at 3449.85 in the vary of 3300-2500 cm^{-1} are aligned to O – H Stretching vibration.

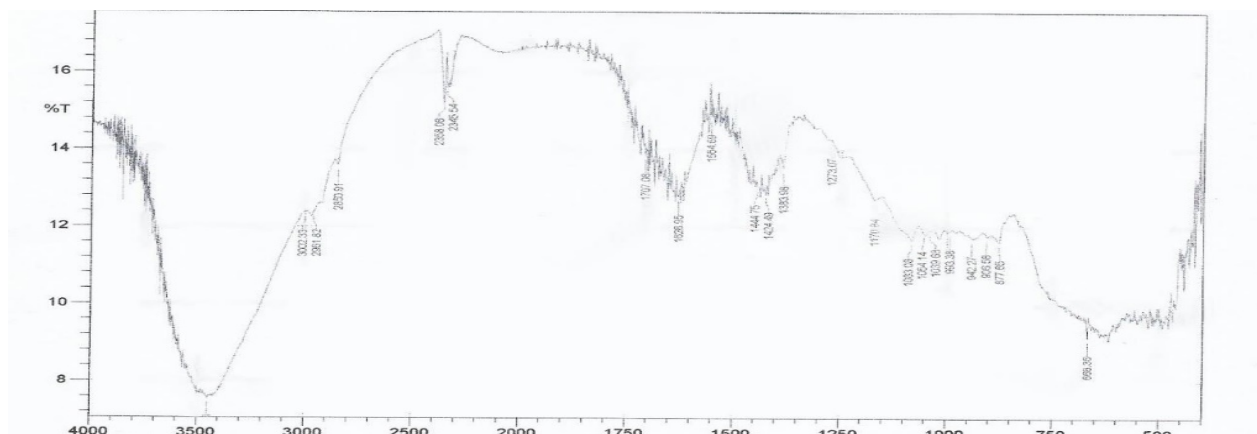


Fig 10: FTIR spectrum of Aluminium oxide

Table 5: assignment of FTIR bands of aluminium oxide nanoparticle

S.NO	WAVENUMBER	BAND ASSIGNMENT
1	669	Al – O - Al
2	877	
3	1039	C – O Stretching of Sodium Carbonate
4	1170	
5	1444	O – H bending vibration of solvent water
6	3449	O – H Stretching vibration

SCANNING ELECTRON MICROSCOPE (SEM):

SEM is used to characterize and describe the morphology of Aluminium Oxide nanoparticles. The figure (11) shows the micrograph of Aluminium oxide that were characterized at magnifications 50 x with accelerating voltage 30 kV.

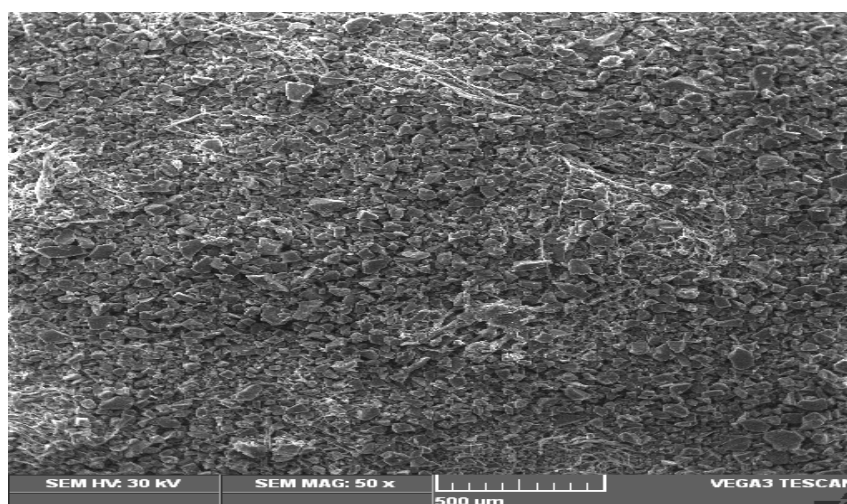


Fig 11: SEM image of Aluminium oxide nanoparticle

CHARACTERIZATION OF NANOCOMPOSITES:

UV-VISIBLE SPECTROPHOTOMETER:

The effect of (GO-Al₂O₃) nanocomposites ranging 0.01g, checked on degradation of Methylene blue for the concentrations (50 µl, 100 µl, 150 µl, 200 µl, 250 µl, 300 µl, 400 µl, 500 µl, 600 µl). The MB

dye solution changes its colour after 2 mins of stirring after the addition of 0.01g of nanocomposites at room temperature.

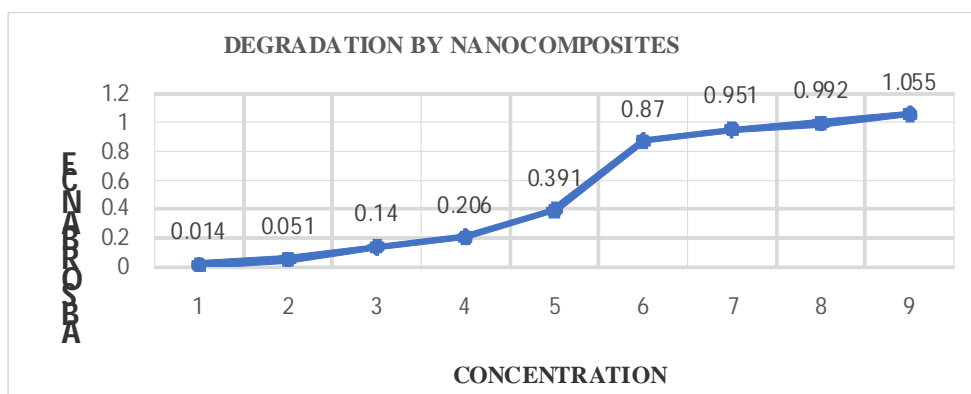


Fig 12: UV-Visible spectra of degradation by nanocomposites

Table 6: Absorbance & Percentage Of MB Dye Degradation Using Nanocomposites

CONCENTRATION IN (μl)	ABSORBANCE VALUE	DEGRADATION PERCENTAGE (%)
50	0.014	99.2
100	0.051	99.6
150	0.140	99.4
200	0.206	99.4
250	0.391	99.3
300	0.870	98.3
400	0.951	99
500	0.992	99.7
600	1.055	99.8

The effect of Graphene oxide, Aluminium oxide & Nanocomposites ranging 0.03g, 0.06g, 0.09g was checked for degradation of Methylene blue dye for the concentrations (50μl, 100 μl, 150 μl, 200 μl, 250 μl, 300 μl, 400 μl, 500 μl, 600 μl, 1ml, 2ml). Results showed that the degradation increases with increase in concentration of nanoparticles. The following figures depicts that GO, alumina and nanocomposites are a very good adsorbent of MB as 99.6%, 95.9% & 99.8% of degradation was achieved respectively.

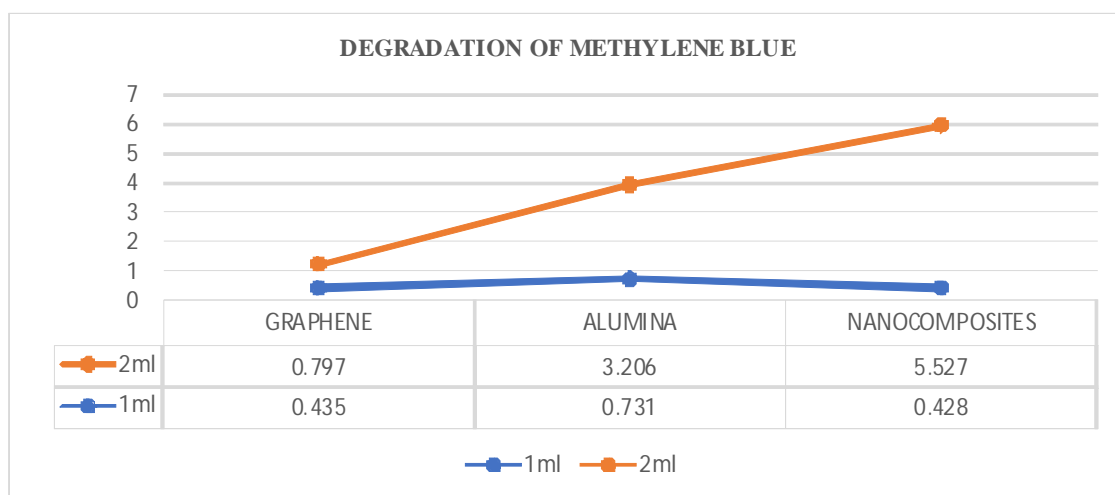


Fig 13: Degradation of methylene blue in 1ml & 2ml concentration with graphene oxide, aluminium oxide & nanocomposites.

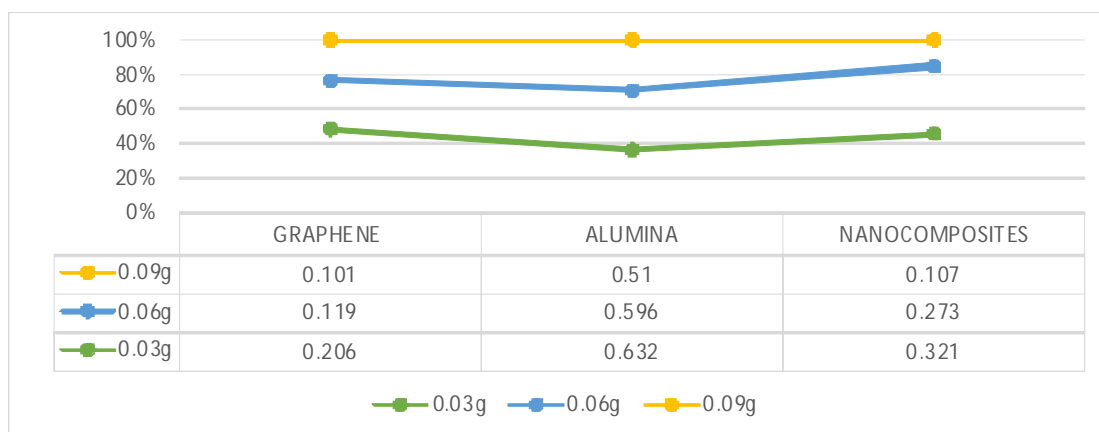


Figure 14: Degradation of methylene blue with different concentrations of nanoparticles

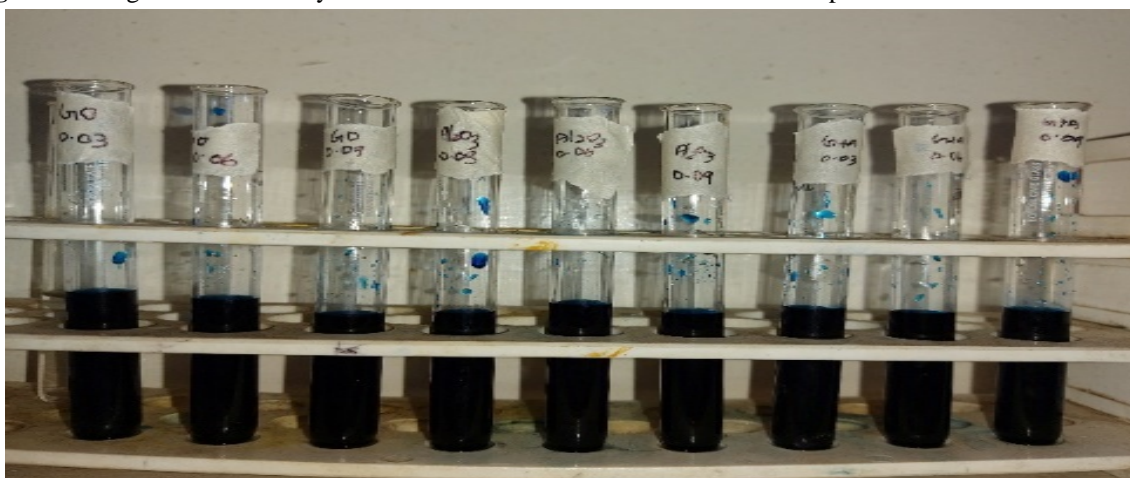


Figure 14(a)

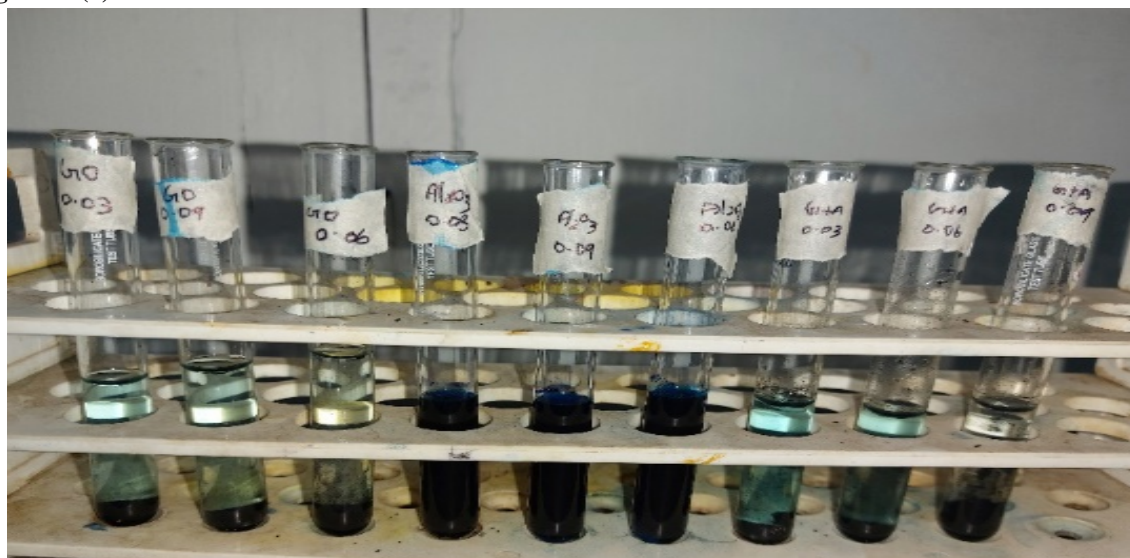


Figure 14 (b)

Figure 14 (a& b) shows the degradation by methylene blue by graphene oxide,aluminium oxide & nanocomposites at the varying concentrations of 0.09g,0.06g &0.03 g

CONCLUSION:

Graphene Oxide (GO) was prepared successfully by modified Hummers' method. The characterization results indicate that the

layer spacing of graphene oxide was longer than that of graphite. The crystal structure of graphite was changed. Graphite was oxidized to GO and lot of oxygen-containing groups

were found in the Graphene oxide. The maximum degradation achieved by Graphene oxide nanoparticles is 99.6% at the initial concentration of 0.01g of GONPs. Aluminium Oxide nanoparticles were prepared successfully by sol-gel method. The maximum degradation achieved by Aluminium oxide nanoparticles is 95.9% at the initial concentration of 0.01g. Comparing to GO and Alumina, Nanocomposites have the higher degradation efficiency of 99.8% at the initial concentration. The degradation of Methylene blue was examined using varied concentrations of dye, nanoparticles & nanocomposites i.e., (0.03g, 0.06g, and 0.09g) of nanoparticles in (50µl, 100µl, 150µl, 200µl, 250µl, 300µl, 400µl, 500µl, 600µl, 1ml, 2ml) of dye solution.

The degradation rate rises as the concentration of nanoparticles rises, according to the findings. Graphene oxide and Nanocomposites were shown to be more efficient at degrading methylene blue than Aluminium oxide, with a maximum efficiency of 99.9%.
Nanocomposites • Graphene oxide
• Aluminium oxide

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Conflicts of interest: Authors declared No conflict of interest.

REFERENCE:

1. A. K. Jain, V. K. Gupta, A. Bhatnagar & Suhas (2003) A Comparative Study of Adsorbents Prepared from Industrial Wastes for Removal of Dyes, *Separation Science and Technology*, 38:2, 463-481
2. Ehrampoosh, M., Moussavi, M., Rahimi (2011). Removal of methylene blue from textile stimulated sample using tubular reactor and TiO₂ /UV-C photocatalytic process. *Iranian journal of Environmental Health science and Engineering* 8(1):35-40
3. C. Buzea, I. I. Pacheco and K. Robbie, (2007) "Nanomaterials and Nanoparticles: Sources and Toxicity," *Biointerphases*, 2: 4 17-71.
4. Mishra AK, Arockiadoss T, Ramaprabhu S (2010). Study of removal of azo dye by functionalized multi walled carbon nanotubes. *Chemical Engineering Journal* 1623:1026-1034
5. Jyoti, K., & Singh. A (2016). Green synthesis of nanostructured silver particles and their catalytic application in dye degradation. *Journal of genetic engineering and biotechnology* 14:311-317
6. Giri, M. (2016). Degradation of disperse orange 3-an azo dye by silver nanoparticles. *Indian journal of chemical technology*. 22:3-4
7. Mohabansi, N.P.; Patil, V.B.; Yenkie, N. "A comparative study on photo degradation of methylene blue dye effluent by advanced oxidation process by using TiO₂/ZnO photo catalyst ," *Rasayan J. Chem.* 2011, 04, 814-819.
8. Navajas, P.M.; Asenjo, N.G.; Santamaria, R.; Menendez, R.; Corma, A.; Garcia, H. "Surface Area Measurement of Graphene Oxide in Aqueous Solutions ," *Langmuir*, 2013, 29, 13443–13448
9. Bianco, A.; Cheng, H.M.; Enoki, T.; Gogotsi, Y.; Hurt, R.H.; Koratkar, N.; Kyotani, T.; Monthieux, M.; Park, C.R.; Tascon, J.M.D.; et al. "All in the graphene family-A recommended nomenclature for two-dimensional carbon materials ," *Carbon* 2013, 65, 1–6.
10. Cao, N.; Zhang, Y. 2015 "Study of reduced graphene oxide preparation by Hummers' method and related characterization ," *J. Nanomater*, 13-17