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WASTE WATER TREATMENT USING GRAPHENE OXIDE

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ABSTRACT

This paper discuss about the role of Graphene oxide [GO] in wastewater treatment. The increasing level of water consumption and water contamination by industrial sector is the big problem that needs to be solved. From different methods of wastewater treatment adsorption proved to be simple and economical. The properties and structure of GO are suitable for adsorption of contaminants. Different methods for synthesis of GO are available. Textile industry is primary target due to volume of discharge and contaminants present. Then performance of GO to treat effluent at different concentrations, different pH range and kinetic study. Next section focus on the applications of GO and the major challenges. Finally conclusion of research.

Key Words: Graphene oxide; adsorption; synthesis; effluent; pH; kinetic

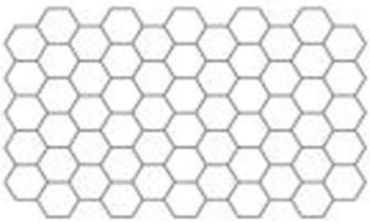
INTRODUCTION

Water is required for various purposes on earth from survival to essential use. In the old days, the extensive natural water available on Earth was sufficient for use, and the environmental cycle was tolerable for handling water management. But consider the recent scenarios, then the greater congestion of industries and man-made artificial things against the natural environment introduces more contamination in water bodies. This uncontrollable intrusion of water contamination needs to be controlled; otherwise it will affect the entire biodiversity leading to living on earth and destroying destructive things. To control pollution, major contaminant sources have to be reduced to avoid over-contamination. Such identified water-contaminated sources must take necessary measures to process their output by removing toxic and hazardous wastes from their sludge before being immersed in the watershed. This makes the water more suitable for domestic purposes, natural uses, ground water recycling and many other purposes.

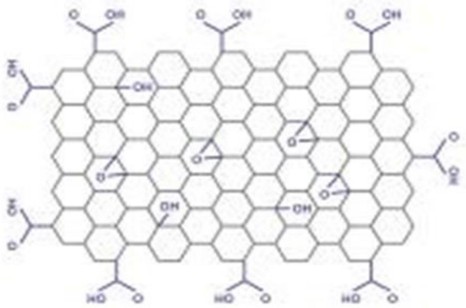
As water is extremely much important for all the living organisms and due to limited availability also as high demand, the research community intends to bring novel methodologies that can ensure the sustainability of water resources. There is great attraction towards the use of nanomaterial's on wastewater treatment. It has many potential properties, including higher surface area and higher efficient treatment due to better chemical properties. In addition, the availability of low cost, high reusability, and effective retrieval of nanomaterial's after their use made them more attractive. Today, many researches are aimed at using various forms of nanomaterial's which are used in treatment of wastewater.[1]
A wide range of environmentally friendly and high-cost Nano materials are tested by the research

community in the treatment of wastewater. These materials are developed with some specific functional and surface characteristics for the purification of surface water and ground water. In addition, these nanomaterial's were also used in the degradation of industrial wastes. In recent decades, nanoparticles have been studied as their potential as adsorbents. The size of nanoparticles is considered an important factor in determining chemical reactions such as adsorption. Graphene materials are being explored for a wide range of exciting applications, including electronics, sensors, and structural materials.
Graphene can be produced by several methods, including chemical vapor deposition, thermal decomposition of silicon carbide, or by exfoliation of graphite, and results in a strong lattice structure
Graphene oxide is a modified form of Graphene that has been treated to form oxide-based materials. It is produced by the oxidation of graphite and subsequent exfoliation, forming an imperfect, but still very useful, lattice. [2]

The oxidation treatment generally involves reactions in acids or combustion. The most commonly accepted oxidation treatment involves chemical process, using a sulphuric acid, sodium nitrate, and potassium permanganate mixture, known as the Hummer's method; however, other methods promising more complete oxidation have been developed. Oxidation of the graphite greatly improves the exfoliation process, which is why GO tends to be much less costly than Graphene



Graphene



Graphene Oxide

❖ Important of recycling waste water

Essential for all times , clean water is one of the foremost important natural resources on the world . Wastewater,which is essentially used water, is additionally a valuable resource, especially with recurring droughts and water shortages in many areas of the planet . However, wastewater contains many harmful substances and cannot be released back to the environment until it's treated. Thus, the importance of wastewater treatment is twofold: to revive the water system and to protect the earth from toxins.

Restoring the water system

Look at a worldwide drought map and you'll see that a lot of areas of the planet simply don't have enough water. All communities, especially areas with water scarcity, got to ensure they have good water treatment processes in situ so treated water can either be reused or returned to the water cycle, but never wasted.

Protecting the earth

Wastewater can include contaminants from both residential and commercial use. Untreated, the chemical compounds and pathogens in wastewater can harm the health of animals, plants and birds that live in or near the water. It can also contaminate crops and water, affecting human health. Wastewater treatment is essential to guard the health of the various different ecosystems. Wastewater, properly treated, is a source of water for several purposes. Good wastewater treatment allows more amount of water to be reused rather than getting to waste.

❖ HISTORY

For the primary time Graphene oxide was synthesized by Benjamin Brody in 1859 much prior to graphene was discovered. He invented method of constructing the graphite oxide. It consisted in oxidation and exfoliation of natural crystalline graphite and undoubtedly gave a plain amount of single layer graphene oxide. Unfortunately, at that point nobody knew about graphene. Only after over one and half century after "The rise of graphene" the old invention was recollected as an efficient and cheap way of creating the new interesting and promising material.

❖ PROPERTIES OF GRAPHENE OXIDE [GO]

1. Mechanical properties

Mechanical properties are physical properties that material exhibits upon application of forces. Examples of mechanical properties are modulus of elasticity, tensile strength, elongation, stiffness, and fatigue limits. The mechanical properties of pristine monolayer graphene are good as it has good strength to with stand load, temperature, etc. Somewhat similar properties graphene oxide possesses. Polymer Nano composites benefit greatly from the use of graphene oxide with fillers. In one example, the effects of graphene oxide were investigated in polyvinyl alcohol (PVA) films produced by solution casting. They found that a 20% graphene oxide filler material was able to increase the tensile strength of nano composite to 59.6MPa more than five times the strength of pure PVA film. The large-scale improvement in mechanical properties can be attributed not only to the strength of the graphene oxide filler but also to the strength of the matrix / filler interface; The single bond group of PVA and oxygen functions of graphene oxide led to high levels of hydrogen bonding.

2. Electrical properties

Graphene is an electrically conductive material with high electron mobility and electrical conductivity an atom thick consisting of 2D layers of sp2 carbon. Graphene has been shown to greatly improve the electrical conductivity of polymers at low filler content. In the general formulation of GO, the process results in the disintegration of sp2 bonding orbitals of graphene and addition of abundant electrical groups that inhibit its electrical conductivity, making GO an electrical resistor. As a results of this high resistivity, researchers have explored GO reduction techniques to provide RGO. When decreased, the electrical conductivity of GO can be greatly improved and tuned over several orders of magnitude with operations ranging from. Even after cutting, GO contains oxygen from residual sp3 bonded carbon, which disturbs the movement of the charge carriers through the rest of the sp2 groups. Electrical transport in GO occurs primarily by hopping, which is mechanically different from exfoliated graphene.

3. Thermal properties

Like its electrical conductivity, synthesized GO from graphite has a low thermal conductivity making it not an ideal option for most applications requiring good thermal properties. Graphene, on the other hand, has been shown to possess one among the very best in-plane thermal conductivities of known materials, with a thermal conductivity of. As a result, reduction of GO is critical for incorporation of GO into polymers to improve their thermal conductivity.

While for several applications it's useful to possess a high thermal conductivity, it's not the case for all situations. In some instances, it's useful to supply high thermal insulation properties like in-home insulation and in flame retardants. GO has recently been shown to be an effective filler to improve the flame retardant properties of various polymer nano composites.

MANUFACTURING METHODS OF GRAPHENE OXIDE

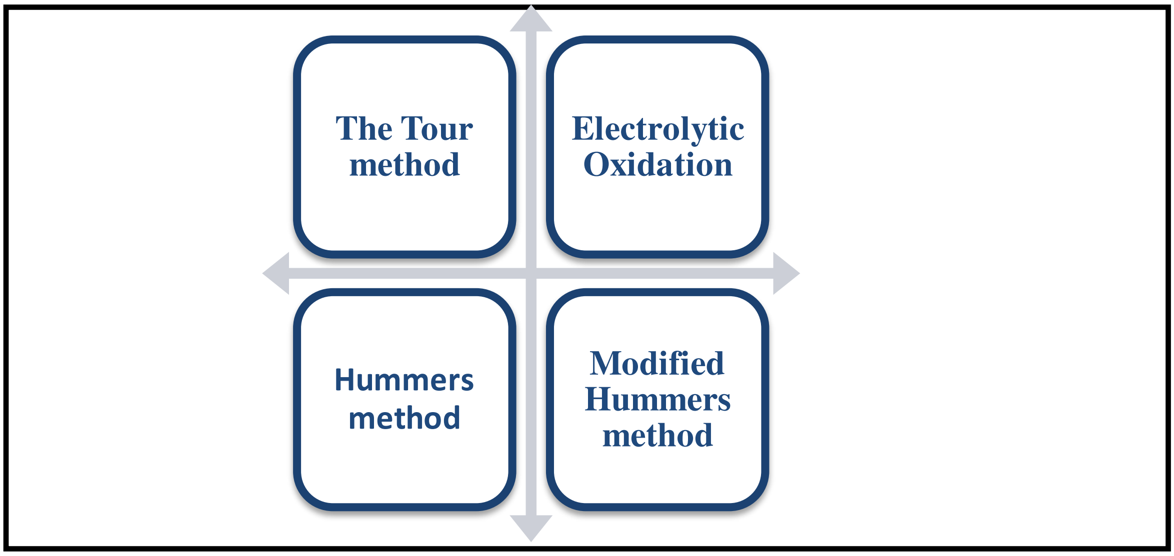


Table 1

➢ MODIFIED HUMMERS METHOD

The effective method use for making graphene oxide.This modified method of synthesis involves both oxidation and exclusion of graphite sheets due to thermal treatment of the solution.

Chemicals

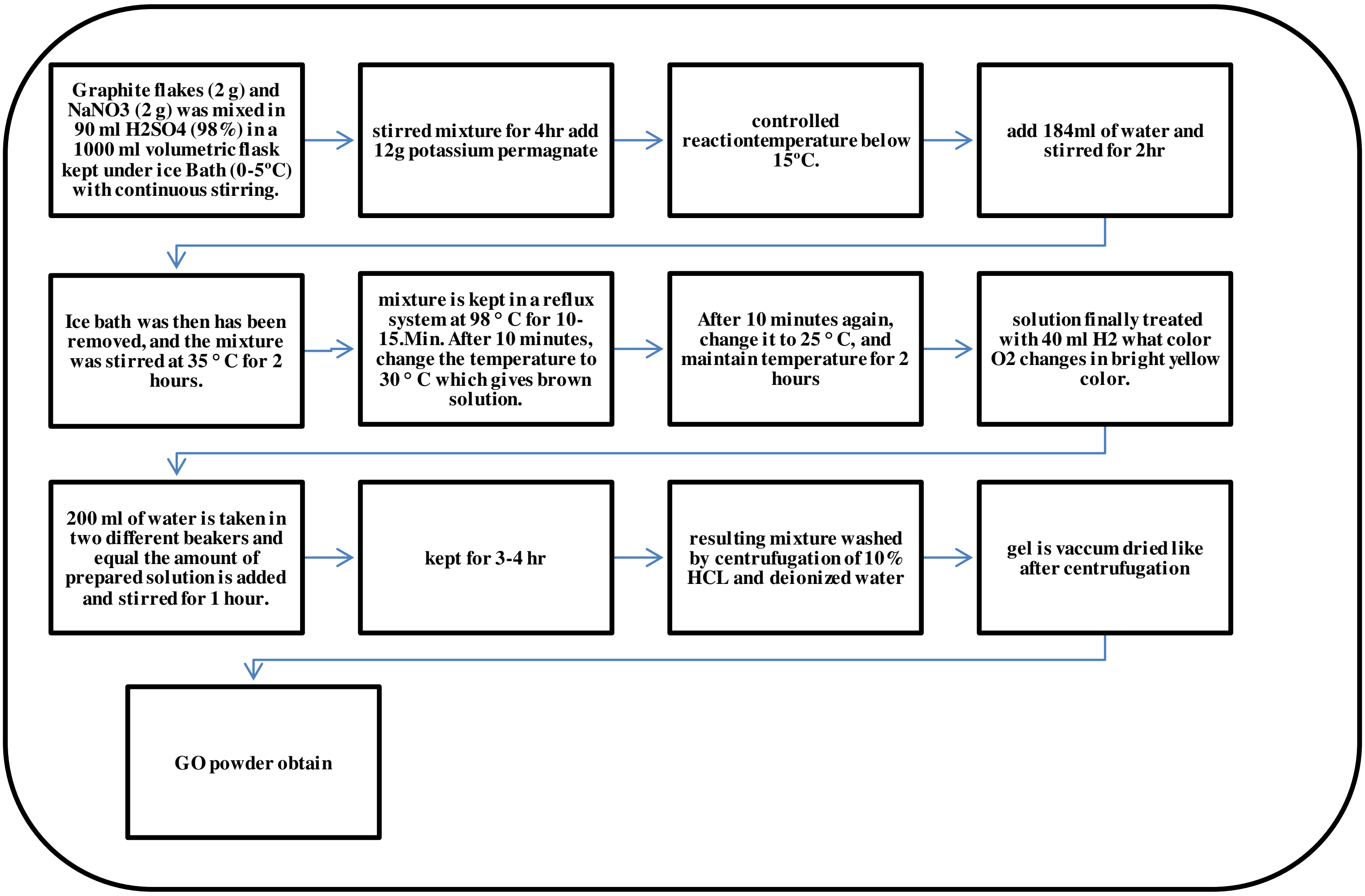
Graphite Flakes , Sodium nitrate , Potassium permanganate , Hydrogen peroxide , Sulphuric acid , Hydrochloric acid .

Procedure:

1. Graphite flakes (2 g) and $NaNO_3$ (2 g) was mixed in 90 ml H_2SO_4 (98%) in a 1000 ml volumetric flask kept under ice Bath (0-5℃) with continuous stirring.
2. At this temperature the mixture was stirred for 4 hours and Potassium permanganate (12 g) was added to the suspension very Slow. The rate of addition was carefully controlled keep reaction temperature below 15℃.
3. The mixture is diluted with a very slow addition of 184 ml.water and kept under stirring for 2 hours. Ice bath was then has been removed, and the mixture was stirred at 35 ° C for 2 hours.
4. The above mixture is kept in a reflux system at 98 ° C for 10-15.Min. After 10 minutes, change the temperature to 30 ° C which gives brown solution.

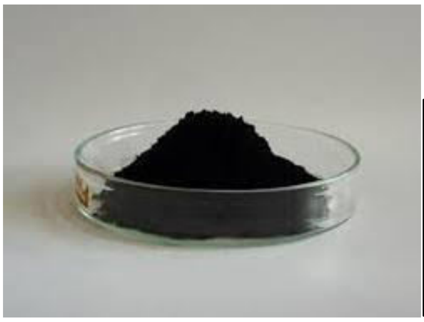
5. After 10 minutes again, change it to 25 ° C, and maintain temperature for 2 hours.
6. The solution is finally treated with 40 ml H2 what color O2 changes in bright yellow color.
7. 200 ml of water is taken in two different beakers and equal the amount of prepared solution is added and stirred for 1 hour.
8. It is kept without stirring for 3-4 hours, where the particles the bottom and the remaining water are added to filter.
9. The resulting mixture is repeatedly washed by centrifugation 10% HCl and then several times with deionized (DI) water
10. The gel is vacuum dried like a substance after centrifugation Go powder for 6 hours over 60 ° C.[3]

FLOW DIAGRAM



RESULT

Synthesis of graphene oxide was achieved by placing graphite in concentrated acid in the presence of an oxidizing agent. Hummer's method demonstrated a less hazardous and more efficient method for graphite oxidation. This and its modified versions are presently the most commonly used methods for the oxidation of graphite



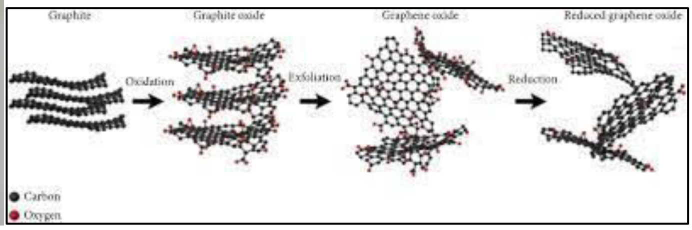


Fig 1 Fig 2

Result of textile industry

Textiles manufacturing is a large industry globally that generates significant quantities of wastewater, due to its high discharge volume, complexity, and recalcitrance.
Textilewastewater consider most polluting industrial effluents. Textile manufacturing industries consume high volumes of water every year. Water consumption varies with the process configuration, type of fibre, dyes characteristics, and equipment. Normally, to process 1 t of textiles, ~150 000 L of water is used in the dyeing and finishing stages. Textile wastewater characteristics are heterogeneous and therefore the variability of the many parameters, like colour, turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), and pH, are usually related to raw materials used during the processes, namely dyes, solvents, and surfactants. High concentrations of COD, BOD, and particulates promote a decrease in the dissolved oxygen concentration, interfering with the natural maintenance of aquatic environments. A high colour content in the waste water, attributed to the presence of dyes, is concerning because it is visible to the naked eye and the dyes are toxic. Synthetic dyes are difficult to degrade due to their stability in aqueous media, which is related to their complex aromatic structures.

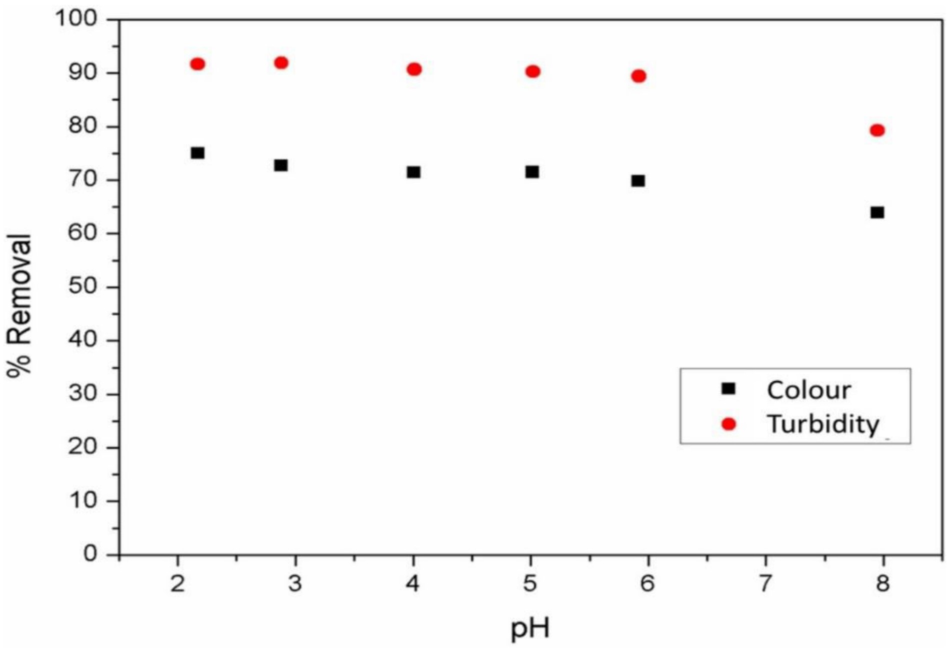
The sample is taken from a textile mill WWTP the colour of sample is dark blue in colour. The raw wastewater collection took place after the wastewater had passed through a screen for coarse particles separation. The raw wastewater sample was used in full concentration during the tests. Another sample of treated effluent coming from the last stages of the industrial laundry WWTP was also collected in order to compare it with the wastewater sample treated using GO. The initial characteristics of wastewater sample

Parameters	Sample
Temperature (°C)	35.0
pH	6.0
Apparent colour (Hazen)	485
Turbidity (NTU)	227
COD (mg O2/L)	715.4
BOD (mg O2/L)	270
Calcium (mg /L)	106
Potassium (mg L)	101

Sodium (mg/ L)	100
Chlorides (mg/ L)	78.1
Sulphates (mg /L)	24.1
Copper (mg/ L)	7.78
Manganese (mg/ L)	1.64
Zinc (mg /L)	0.12

Table 1

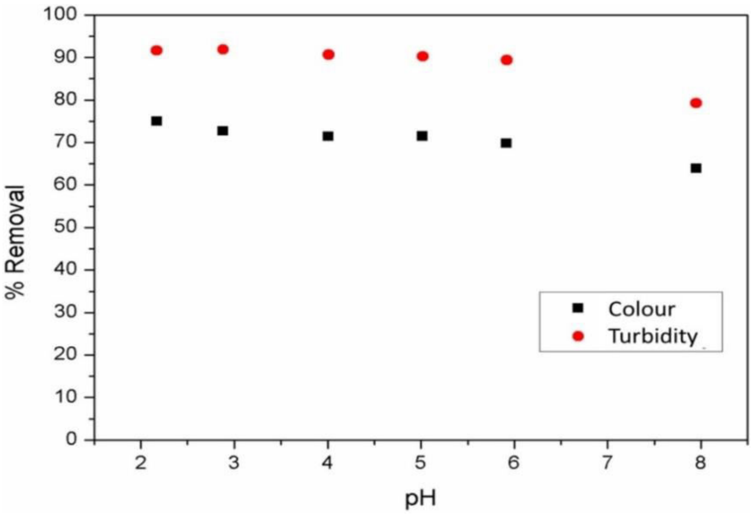
Dosage of the product used is one of the most critical parameters that has to be considered in wastewater treatment as it has an important effect on the treatment efficiency. Thus, to evaluate the effect of changing the volume ratios of GO suspensions and the effluent sample, GO/effluent ratios of 1:25, 1:30, 1:40, 1:50, 1:100, 1:150, 1:200, and 1:250 (mL mL−1) were used. Samples were placed under constant stirring for 1 hour at room temperature. It is possible to verify the variation within the removal efficiencies of apparent colour and turbidity consistent with the GO concentration within the medium.[4]



From the graph it can observed that the removal efficiencies of colour and turbidity increase when the GO dosage is increased. This occurs up to certain level when, as the adsorbent dosage is further increased, the percentages of removal increase slightly until they remain essentially constant. If the Go dosage increase was continued in the tests, the removal efficiencies would probably remain constant; however, the costs for the adsorbent would rise, which on a large scale would lead to higher operational costs. From an economic point of view, the study of the optimum dosage of adsorbent is useful when selecting the acceptable amount of adsorbent for industrial applications.

Effect of pH on wastewater treatment using GO

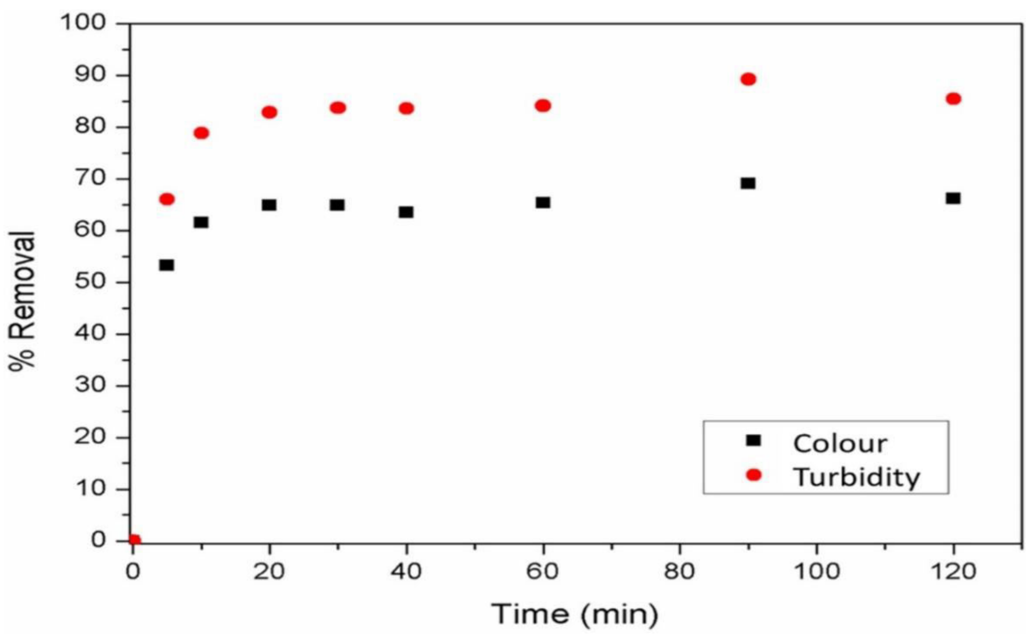
A graph showing the removal efficiencies of apparent colour and turbidity within the textile wastewater sample, and a range of initial pH, is given by . According to the results, it's observed that the removal efficiencies of apparent colour and turbidity remain essentially constant for pH values between 2-6. In this case when working with real textile wastewater, and taking into account that there are several dyes together, one still has to consider the presence of soaps, surfactants, and ions in the solution that may affect the process when changing the initial pH values. Therefore, considering the experimental results, and analyzing them from a cheap point of view, changing the pH during the method won't be necessary. Considering that up to a pH of ~6 (close to the raw textile wastewater) the apparent colour and turbidity removals were nearly 70% and 90%, respectively, it was decided not to proceed with pH correction.



[4]

Kinetics of contaminants removal using GO

To investigate adsorption kinetics, 30 mL aliquots of the textile wastewater sample were added to flask. Then, 1 mL of GO was added to every flask. The flasks were placed under constant stirring (300 rpm) at room temperature (28 ± 3°C) for different time intervals, namely 5, 10, 20, 30, 40, 60, 90, and 120 minutes. Apparent colour and turbidity at different time intervals were quantified in order to determine the removal efficiencies (% R).
The results of the kinetic study that evaluated contaminants removal from textile wastewater are given in, which shows the rise within the removal efficiencies of apparent colour and turbidity over time. As observed, there is a considerable increase in the percentage removal during the first 5 minutes. After that, increases within the removal efficiencies begin occurring gradually until they reach equilibrium. In general, the system reached steady-state in >1 hour. After 1 hour, the apparent colour removal efficiencies began oscillating around 66% and turbidity near 86%.



[4]

Wastewater sample	Parameters colour	%R colour	Turbidity	%R Turbity
Treated with GO and followed by decantation	150.5	66.0	25.8	88.4
Treated at the WWTP	279.0	36.9	27.5	87.7
Raw textile wastewater	442.0		223.0	

Table 2

Waste water sample	Parameters colour	%R colour	Turbidity	%R Turbidity	COD(mg L^{-1}	%R COD
Treat with GO and followed by centrifugation	103.5	76.6	23.5	89.5	283.3	60.9
Treate at the WWTP	279.0	36.9	27.5	87.7	370.7	48.9
Raw textile wastewater	442.0		223.0		724.8	

Table 3

APPLICATIONS OF GRAPHENE OXIDE

[5]The permeation of water through the membrane was attributed to inflammation between GO structures These oxides can also be used as action exchange membrane KCl, HCl, CaCl2, MgCl2, and BaCl2 solutions. There were also reports of membranes permeable by large alkaline ions because they are able to penetrate between the Go layers .There were also Go membranes was actively studied in the 1960s for application in desalination of water, but they were never used for practical applications. Retention More than 90% rates were reported in this study for NaCl solutions using stationary GO membranes in reverse osmosis setup. GO membranes can be used for seawater filtration.

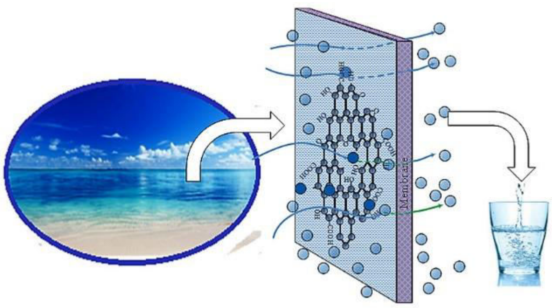


Fig 3

It is super Thin (just one atom thick), therefore the water just pops through "Very, very small holes within the graphene and release salt back. "GO film is 500 times thinner than the best filters on the market and stronger than B1000-fold steel, but has permeability more than the best competitive membrane on the market. Samples allow ions to pass through common salts filter but retain some larger ions.

- **Electronic Devices**

Many electronic devices have been designed using GO as a start ingredients for at least one component. Is one such tool Graphene-based field effect transistors (FETs) FETs using RGO have been used as chemical sensors and biosensor.FETs using functional RGOs as semi-conductors used as a biosensor to detect hormonal catecholamine molecules studied electrochemical glucose sensors using GO Activated with glucose oxidase after depositing on a electrode. One of the key areas where G.O. can be expected applications and uses of Graphene Oxide in the production of transparent conductive films after use is deposited on any substrate. Such coatings can be used in flexible Electronics, solar cells, liquid crystal devices, chemical sensors, and Touch screen device and also used GO as a transparent electrode light emitting diodes (LEDs) and solar cell equipment. Transparent the electrode GO / RGO has also been used as a hole transport layer Polymer Solar Cells and LEDs.

- **Biomedical**

GO is used in the biomedical field, especially in drug delivery system. GO is probably better than many other anticancer drugs because it does not target healthy cells, only tumors, and has low toxicity. Functional nano-GO (nGO) has been used in several studies on the targeted delivery of anticancer drugs. polyethylene Glycol (PEG) -functionalized nGO with SN38, a camptothecin derivative adsorbed on the surface (nGOPEGSN38) which was used as a source of drug soluble in water and serum soluble (Liu et al., 2008). In this study, nGOPEGSN38, was shown in three orders of irinotecan (CPT-11), more effective than the FDA-approved SN38 prodrug, on reducing cell viability of human colon cancer cell line HTC-116. The effectiveness of NGOPEGSN38 was similar to SN38 in DMSO. Melanoma Skin Cancer. Mice have been treated with a proximal laser and nGO using photothermal ablation therapy that was functionalized with PEG and hyaluronic acid and transdermally (Jung et al., 2014). In another the study, magnetite was advertised on GO loaded with anticancer drug doxorubicin hydrochloride for targeted delivery of the drug to specific sites using magnets studied various biomedical applications that specifically use GO / rGO in medicine distribution, cancer therapy and biological imaging.

- **Biosensors**

GO is a fluorescent material that can be used for bio sensing applications, for early disease detection, and even for the treatment of cancer and to aid in the detection of biologically relevant molecules. Go fluorescent-based biosensors have been successfully used for DNA and protein detection with promise of better diagnosisFor HIV. GO has been used as fluorescence quenching material biosensors using fluorescence resonance energy transfer (Fret) effect. used the FRET effect ATP is less than 10 µM as the fluorescein-labeled ATP aptamer denotes used single-stranded DNA (ssDNA) with a fluorescence tag and found that it is noncovalently bound to go together later fluorescence quenching of the tag. Add a complement ssDNA removes and restores tagged DNA from GO surface fluorescence. used folic acid-functionalized GO to detect human cervical cancer and human breast cancer cells.

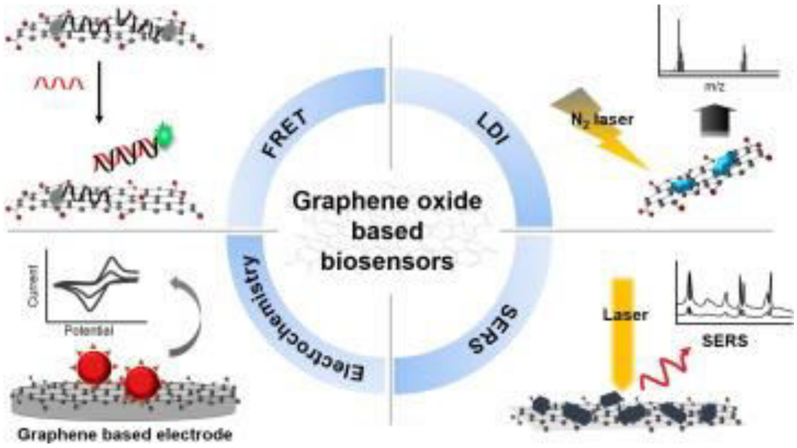


Fig 3

CONCLUSION

The Graphene is known as wonder material due to its properties. The derivatives of graphene like graphene oxide possesses near about similar properties. There is a need to clean up the waste generated during the process in industries and factories, which pollutes the water. Therefore, the search for cost-effective and highly efficient adsorbent. The study of GO adsorbents for heavy metal ion and its related pollutant dyes removal is still in the laboratory research stage. GO as an adsorbent still consists of many difficulties like complicated synthesis process, high-quality yield production, inadequate selectivity of heavy metal ion, unable to ensure its quality and supply, separation and purification after each cycle. However, the progress of economic applications of graphene or GO-based adsorbents remains at its beginning, and there are tremendous, and new approaches are constantly being explored. The research community considered GO to be an efficient and powerful alternative to next generation of filtration membranes. High price of Graphene and its derivatives is due to lack of manufacturers, but as researchers will progress the different ways GO can be used it will be produced in larger quantities. Graphene oxide membranes will replace polymer membranes due to properties they possess and will make a huge impact on wastewater treatment, water purification, desalination, etc. There seems to be a brighter future of graphene oxide in wastewater treatment field.

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