

An Innovative Approach To Remove Microorganic Pollutant From Waste Water

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Abstract: A cost effective Graphene/TiO₂ nanocomposite having photocatalytic properties has been prepared for the removal of aspirin from the aqueous solution. The quantity of TiO₂ was varied (1:0.04, 1:0.1, and 1: 0.2 GO-TiO₂) in the composite and effect on adsorption as well as photo degradation efficiency was observed. The 1:0.1 GO-TiO₂ composite has been found to be best one for aspirin degradation, confirmed by pseudo first order rate constant i.e. 0.006 min⁻¹. By performing kinetic experiments, the pseudo-first-order kinetic model provided the best fit for TMP adsorption onto GO-TiO₂ Nano composite. The influence of various parameters, namely pH (3-11) initial concentration (8, 17, 30 ppm), dose (5 – 150mg) on the removal efficiency of TMP by the composite has been analyzed. The characteristics of GO-TiO₂ nanocomposite were analyzed using AFM, FT-IR, analysis. The maximum TMP removal efficiency was found to be 39% for pure TiO₂, 83% for GO, and 96% for 100mg of 1:0.1 GO-TiO₂ nanocomposite for 30 ppm aspirin solution.

Keyword: Nano Composite ,FTIR.

I. INTRODUCTION

Photocatalysis employs a light source and a catalyst to bring about a chemical reaction and generate highly reactive hydroxyl radicals (OH[•]) which then attack the organic pollutants in solution. However, the reaction only occurs when the catalyst absorb the sufficient light with energy equal to or higher than their corresponding band gap. When a TiO₂ particle absorbs adequate energy from a photon light, an electron of TiO₂ is promoted from the valence bond to the conduction band [1][2]. This moment of electron leaves a hole the valence bond. These generated electrons and holes can either recombine, dissipating energy, or be available for Redox reactions with electron donor or acceptor species adsorbed on the surface of Tio₂ or nearby in the electrical double layer in the surrounding the catalyst. The holes are suggested to the main species responsible for degrading organic pollutants, either directly by oxidising organics adsorbed on the Tio₂ surface indirectly or generating hydroxyl radicals to attack organics reacting with water or OH[•] In this reaction, oxygen is introduced to react with the generated electrons to minimise recombination of hole and electron [3]. In addition it is, suggested that the superoxide radicals may also participate in photo oxidation

mechanism. Such highly reactive species are able to effectively degrade a wide range of organic compounds including, aromatics and Aliphatic, dyes, pesticides and herbicides [4].

In general, photocatalytic degradation takes place by electron transfer reaction. The oxidation mechanisms can vary depending up on the physical and chemical properties of the organic compounds to be degraded by either the highly reactive OH species and active hole or both. In case where the reactive hydroxyl radicals becomes the predominant species, a high concentration of H₂O and OH molecules adsorbed on the catalyst surface is essential [5]. This water adsorption potential can be promoted by the super hydrophilicity of Tio₂ [6].

Nanotechnology has become one of the most significant technologies of the 21 century. It encompasses a broad range of tools, techniques and applications based on structure size between 1 and 100 nm. A unique aspect of nanotechnology is the enormously increased ratio of surface area to volume presented in many nanoscale materials, leading to new possibilities in surface based science. Due to their small size and well organized structure, nonmaterial offers an alteration of physico-chemical properties of the corresponding bulk material properties. E.g. colour, strength and thermal resistance etc., providing opportunities to be exploited in many industrial facets. Nonmaterial considered as new functional materials used in industry based techniques and processes, such as cleaning up industrial contamination and improving energy production and uses.

A. Photocatalysis and TiO₂

The term photocatalysis is defined as "a catalytic reaction involving production of catalyst by absorption of light". In 1972, Honda and Fujishima discovered photocatalytic water splitting and after that heterogeneous catalysis by TiO₂ came into picture.

After then heterogeneous catalysts are widely used because they are,

- (1) Inexpensive
- (2) Non-toxic
- (3) Having high surface area
- (4) Having broad absorption spectra
- (5) Having tunable properties i.e. doping, size reduction etc

(6) Can be recovered by filtration.

When TiO₂ is irradiated with UV light, it absorbs the energy and when this energy exceeds its band gap energy, electron shifts from its valence band to conduction band and forms hole in the valence band[7][8]. These holes and electron go through many oxidation and reduction reactions with any species and degrade them to simple compound like CO₂ and water molecules.

Following conditions should be full-filled,

(1)Band gap energy should be larger than desired for reaction.

(2) The Redox potential of generated electron and hole should be suitable for redox process on TiO₂ surface.

(3)The rate of reaction should be faster than electron hole recombination rate.

If the rate of Redox reaction is lower than recombination, electron and hole will recombine before they degrade any of the organic material.

Certain properties of good semiconductor catalyst are,

(1)Absorb photons efficiently

(2)Generate electron-hole pairs

(3)Avoid electron-hole recombination

Semiconductor band gap energy There are many catalysts available in the market. Few of them are represented in table with their band gap energies,

Table 1: Different Semiconductors and Their Band Gap Energies

Semiconductor	E _g (eV)
TiO ₂ (Rutile)	3.0
TiO ₂ (Anatase)	3.2
CdS	2.4
Fe ₂ O ₃	2.3
ZnO	3.2
ZnS	3.6
WO ₃	2.8

B. Graphene

Graphene is a substance composed of pure carbon, with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one-atom thick sheet. It is very light, with a 1-square-meter sheet weighing only 0.77 milligrams. Graphene discovered in 2004 and the doors for thousands of applications. It is having the combination of excellent properties which were never found out in any of the material till date [9].properties like high chemical stability, very high surface area (theoretical:2600m²/g), high mobility of charge carriers (2000 m²v⁻¹sec⁻¹), high young modulus (1Tpa) and optical transparency which are favourable in many fields and photo catalysis is one of them. Graphene is easily be produced by oxidizing graphite by Hummers method and then reduced chemically to obtain reduced graphene oxide which is chemically prepared Graphene. Graphene oxide made by hummer’s method is directly used to make graphene oxide-TiO₂ nanocomposite [10].

C. Water Quality Insurance

The obtained water via desalination using graphene nanocomposite has been tested chemically and biologically. All chemical testing has been carried out according to the standard international protocols in order to determine water quality such as: Salinity, pH, dissolved oxygen test, hardness, heavy metal content, and the total amount of phosphate, sulphate and carbonate ions [11]. The result indicates that the obtained water is totally pure and free from all salts, metal ions and heavy metals.

Table 2: Quality Standards after Using Graphene

Water quality	Our obtained desalinated water	Drinking water
p ^H	7	6.8
Calcium content	Zero	50 ppm
Chlorine content	Zero	100 ppm
Oxygen	1.5%	2.2%
Sulphate ions	Zero	20 ppm
Mg ions	Zero	30 ppm
Salinity	Zero	0.03%
Hardness	Zero	3%

In recent years, Graphene oxide (GO), which is considered to have a one-atom thick, two-dimensional, closely packed honeycomb lattice, has attracted extensive attention for its Remarkable electrical,

physical, and mechanical properties[12]. Much research is ongoing to investigate the applications of GO for nanoelectronic devices, transparent conductors, and composite materials.

II. EXPERIMENTAL

A. Materials

TiO₂ nanoparticles, H₂SO₄, KMnO₄, NaNO₃, and H₂O₂ were obtained from Merck, India. Graphite powder (200 mesh) was purchased from Qualikems, India. All the above chemicals were of analytical purity and used without further purification.

B. Synthesis of Graphene Oxide

Modified hummer's method was used to prepare graphene oxide. In this method, concentrated H₂SO₄(69 ml) was added to a mixture of graphite powder(200 mesh siz3 gm,1 eq.wt.) and NaNO₃(1.5gm,0.5 eq.wt.),and it was cooled to 0°C by using an ice bath.KMnO₄(9 gm 3 eq.wt.) was added slowly in parts to keep the reaction temperature less than 20 °C.After adding KMnO₄ The reaction temperature was taken to 35°C and stirred for 30min.Then,exothermic condition of around 98 °C was created by adding 138 ml of water slowly and kept the temperature constant at 98 °C for 15 min by providing external heat. Later reaction was cooled using water bath for 10min.Additional 420ml of water and 30% H₂O₂ were added, for producing second exothermic condition. After cooling, mixture was washed by milliQ water several times until pH 7 is obtained [13].These multiple washes and centrifugation gives graphene Oxide suspended in water. Finally, it is freeze dried to give solid powder of graphene Oxide (GO).

C Synthesis of GO-TiO₂ Nanocomposite

GO-TiO₂ composite was prepared by simple sonication process. First of all, GO/ TiO₂(w/w) ratio of 1:0.04,1:0.2,1:0.1/ml basis was taken. GO-actone suspension was prepared by 1gm/ml basis. Now GO (1:0.04,1:0.,1:0.1) were sonicated for 1 hour to get completely exfoliated GO sheets in acetone[14].Then, TiO₂ powder was added according to decided ratios and further sonicated for 1 h to get GO-TiO₂ nanocomposite[15][16].Finally it was dried in oven at 70 °C.

D. Photocatalytic Measurements

Photocatalytic activity was measured by degrading aspirin drug at various parameters like concentration, pH, dosing, percentage of GO. Water cooled mercury lamp (125 watt) was used throughout the experiments. Mixture was stirred in the dark for 1 h to establish adsorption-desorption equilibrium. 5 ml of aliquots were taken at certain time intervals. To remove the catalyst from sample .For kinetic study of aspirin drug degradation, pseudo first order kinetics was followed.

III. METHODS

A. Characterization

FT-IR absorption spectra of the samples were recorded in Perkin-Elmer FT-IR spectrometer (Model-FT-1730).Powdered X-ray diffraction was carried out in a Philips X'pert MPD system using Cu K α radiation. Thermo gravimetric analysis (TGA) was carried out in Mettler TGA/SDTA 851e and the data were processed using star software, in flowing air at a flow rate of 60ml/min and at a heating rate of 5 °C/min. Ntegra Aura atomic force microscope (NT-MDT, Russia) in semi contact mode using an NSG-01 Silicon probe was used to take the images.

IV. RESULT AND DISCUSSION

A. Characterization of GO and GO-TiO₂ Nanocomposite

B. FT-IR Analysis

Fourier transform method was employed to characterizing the material. In infrared spectroscopy, IR radiations are passed through the sample. The resulting spectrum represents the absorption and transmission of the sample and creates a molecular finger print. Fourier transform infrared (FT-IR) spectra were recorded in this study on Bruker IFS 88 Fourier transform infrared spectrophotometer with KBr pellets in the 500-4000cm⁻¹ region.

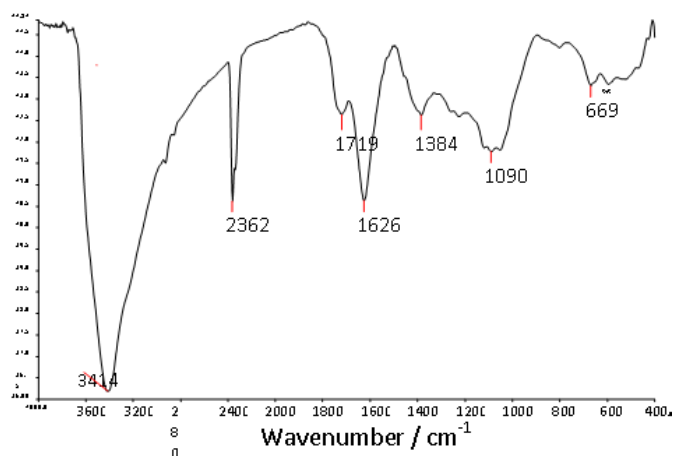


Figure 1: FT-IR spectra of Graphene oxide

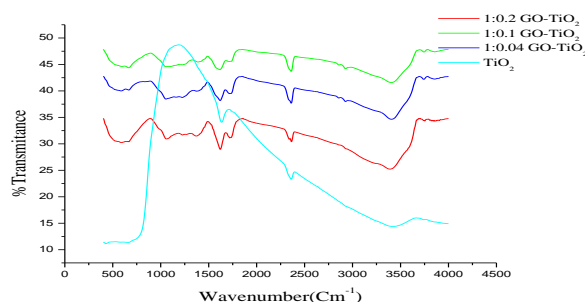


Figure 2: FT-IR of Varying Quantity of TiO₂ in GO-TiO₂ Nano composite

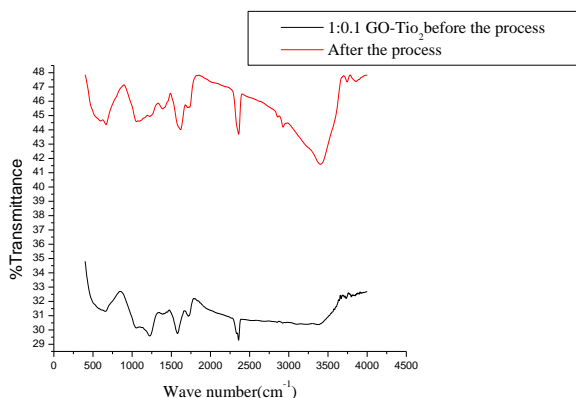


Figure 3: FT-IR spectra of 1:0.1 GO-TiO₂ Nano Composite Before and After The Process

Wavenumber	Functional group	Description
3414	C-OH	Hydroxyl stretching due to -COOH and water content
1719	C=O	Carbonyl/carboxyl group
1626	C=C	Due to an oxidized graphite skeletal ring vibration
1384	C-O	-OH deformation vibrations
1090	C-O	Alkoxy group vibrations
669	C = C R R	Cis vibrations

The FT-IR spectrum of the GO in Figure shown Several peaks: a peak at 3414 originated from O-H stretching vibration indicates abroad and intense absorption a peak at 1719 cm⁻¹ due to the C=O stretching of carboxylic groups placed at the edges of GO sheets stretching vibration peaks of C-O(epoxy) and C-O (alkoxy) are observed at 1384 cm⁻¹ and 1626 cm⁻¹ respectively. The peak at 1626 cm⁻¹ can be attributed to in plane C=C bands and skelital vibration of the graphene sheets that confirming the successful oxidation of graphite[17][18]. From figure, one can identify that, all oxygen functionalities are present in the GO-TiO₂ nanocomposite. Composite is having strong peak at 730cm⁻¹ and 690cm⁻¹ which is observed in all the composites which is a signature of pure TiO₂. Functional groups like alkoxy, carboxy, carbonyl, hydroxyl and most importantly skeletal vibrations of graphitic domain in the composite clearly indicate presence of graphene oxide[19]. So, GO-TiO₂ composite exhibits all functional groups that are present in both GO and TiO₂.

Aspirin Drug degradation results

Pseudo first order reaction

For the experimental conditions, degradation data are decent agreement with pseudo first order reaction.

$$-(dC/dt) = k \cdot C$$

After integration we get,

$$\ln(C_0/C) = K \cdot t$$

Hence, by plotting ln(C₀/C) versus irradiation time, straight line was obtained and its slope gives rate of degradation.

C. Drug Degradation By Varying TiO₂ Quantity

In this experiments, percentage of GO were varied and effect on adsorption as well as photo degradation efficiency was noted. In this case, 1:0.04, 1:0.2, 1:0.1 GO-TiO₂ composites were used. 100mg/l of catalyst loading and 30ppm initial concentration of drug gives the results shown in figure below.

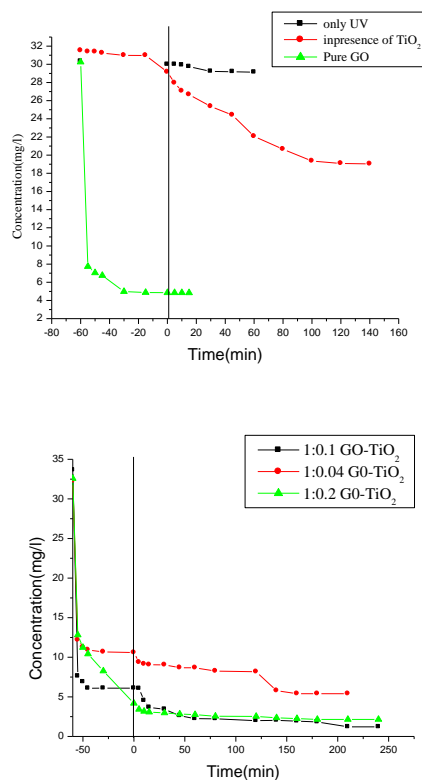


Figure 4: Drug Degradation By Pure TiO₂, GO and Varying Quantity of TiO₂

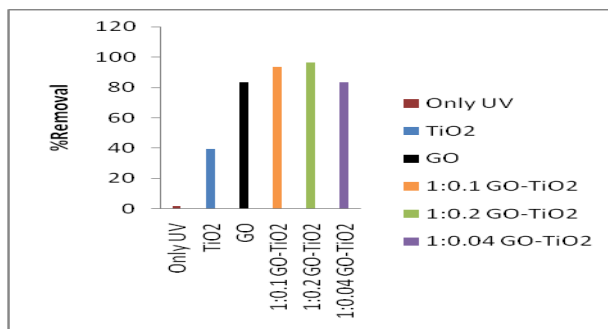


Figure 5

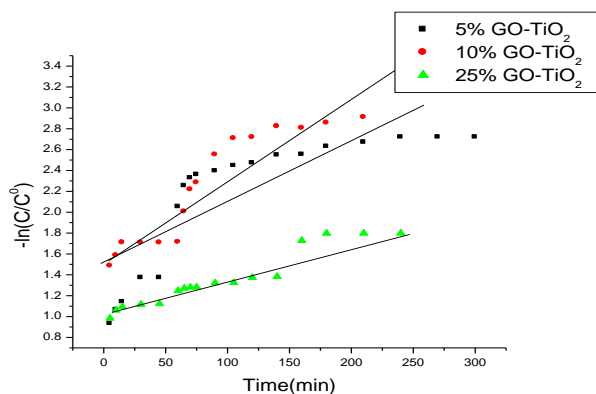


Figure 6

Figure 4.5: Figure 4.6: Kinetics Of Aspirin Drug Degradation For Different Proportions Of GO-TiO₂ Nanocomposite

Interesting result that can be seen in dark adsorption part is; by using pure GO 83% removal of TMP from the aqueous solution takes place. For GO-TiO₂ nanocomposites 1:0.1 is just right content because agglomeration of TiO₂ nanoparticles is significantly prevented and drug is adsorbed on TiO₂ as well as GO which provides active sites. For 1:0.04 GO-TiO₂ nano composite adsorption capacity is high but photo degradation efficiency decreases which are confirmed by results. For this, k value is 0.005min⁻¹, 0.006min⁻¹, 0.003min⁻¹ for 1:0.2, 1:0.1 and 1:0.04 GO-TiO₂ respectively. It was noted that, the K value is highest for 1:0.1 GO-TiO₂.

D. Drug Degradation at Different Concentrations

Drug degradation carried out by varying concentration with a regular interval of 10ppm. 100mg/100ml catalyst loading was used for each experiment. Catalyst used was 1:0.1 GO-TiO₂ nanocomposite.

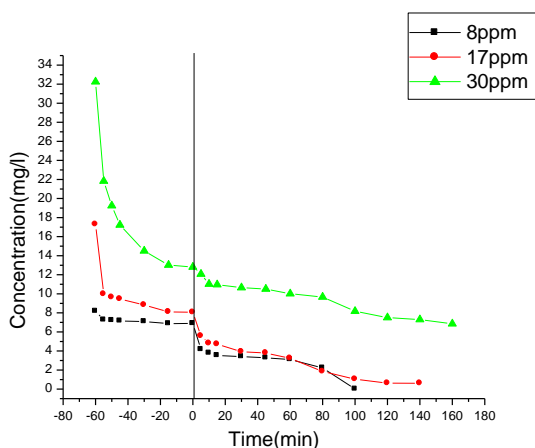


Figure 7: Photo degradation by Varying Drug Concentration

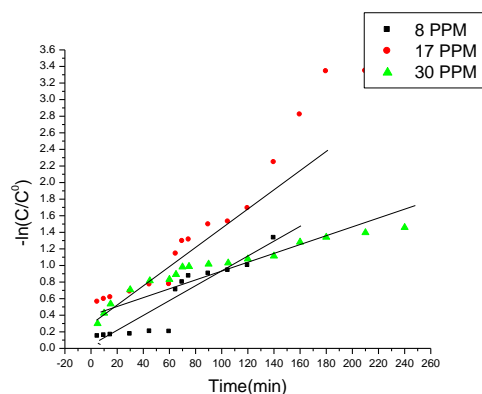
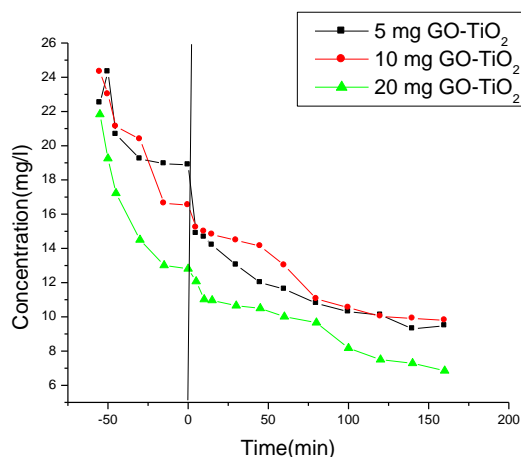


Figure 8: Kinetics of Aspirin Degradation By Varying Concentration (Linear transformation $\ln(C_0/C)$ vs t

As concentration is increased, more and more drug is adsorbed on the GO-TiO₂ surface. If the concentration is too high, then photo activity decreases by two reasons. Firstly, whole surface is covered by drug molecules, thus, UV light cannot reached to the catalysts surface and secondly high concentration itself hinders light intensity in the solution. So as concentration increases, photo activity decreases. K values for 8ppm, 17ppm, and 30ppm solution are 0.009 min⁻¹, 0.005 min⁻¹ and 0.004 min⁻¹ respectively.

E. Drug Degradation at Different Catalyst Loading

Photo degradation of aspirin drug is carried out by varying catalyst loading to study the effect on degradation kinetics. Here catalyst load is varied from 5mg/100ml to 100mg/100ml. Initial concentration 30ppm and catalyst loading 1:0.1 GO-TiO₂ was constant throughout the experiments. Increases in catalyst loading will give excellent result for adsorption and photo degradation. Here higher and higher catalyst loading will lead to efficient removal of drug from the solution taken place.



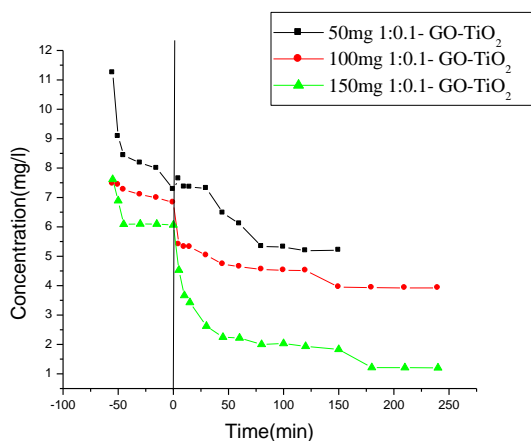


Figure 9: Photo Degradation by Varying Catalyst Loading

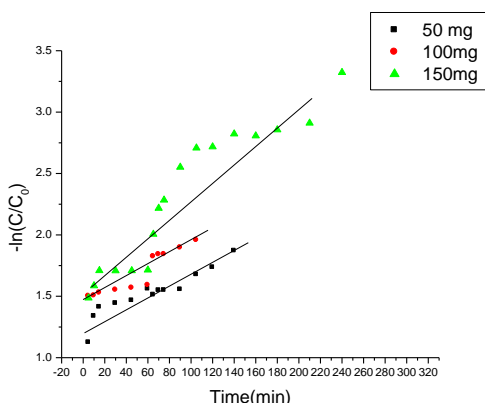
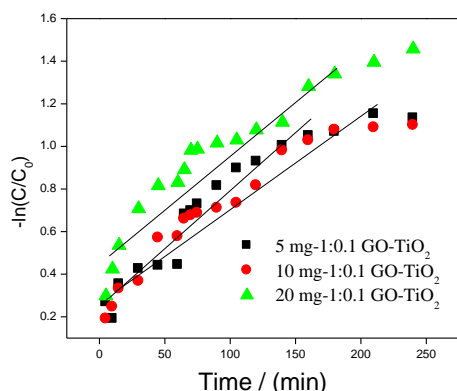


Figure 10: Kinetics of aspirin degradation by Varying Catalyst Dose (Linear transformation $\ln(C_0/C)$ vs. T

Interesting results that can be observed from varying the catalyst amount i.e; as the catalyst dosage increases from 5mg to 20mg/100ml photo catalytic activity is most predominant than the adsorption. But further increases in dosage cause adsorption to be more predominant than photocatalysis. This is because as the dosage increases more number of active sites that are available for adsorption which leads to increase in adsorption capacity. The decreases in photo catalytic activity is due

to whole surface being covered by drug molecules, thus, UV light cannot reach the catalysts surface. Results revealed that, with for low catalyst loading photocatalytic activity is more efficient and for high catalyst loading adsorption is more efficient for the removal of drug from the solution. Rate of reaction also gets affected in the same manner. For 5mg/100ml it was 0.0042 min^{-1} , for 10mg/100ml it was 0.0045 min^{-1} and 0.0048 min^{-1} for 15mg/l. For 50mg/100ml it was 0.005 min^{-1} , for 100mg/100ml it increases and becomes 0.006 min^{-1} . After that decreases to 0.003 min^{-1} for 150mg/100ml. The optimized value from the amount of adsorbent studies was clearly around 100mg/100ml.

Effect of PH on drug degradation

It was observed that pH is one of the most important factors for degradation studies. Photo degradation is carried out by varying pH at 3, 5, 8.5 and 10. Initial concentration (30ppm) with catalyst loading of 100mg/100ml and using 1:0.1 GO-TiO₂ as a catalyst was constant through the experiments. GO-TiO₂ surface is negatively charged in alkaline medium and positively charged in acidic medium. Aspirin when dissolved in methanol gives an initial pH of 8.5, from the results it is clearly observed that at this pH the photocatalytic change is high, though the percentage adsorption is higher when pH is either increased or decreased. In acidic medium, the possibility of H₂O⁺ from -OH in graphene oxide, and also the -COOH functional groups could tend to interact better with the amine and -N-functional groups of aspirin. Similarly when coming to basic medium, the only change could be assumed to happen is in the structure of graphene oxide where the carboxylic acid functional group would change to -COO(-), still giving a possibility for a fast formation of hydrogen bonding between these groups, looking at the structures mentioned in the report, it's clearly evident that there are 7 possibilities, from the side of aspirin to form hydrogen bond with graphene oxide. Also, since there are TiO₂ molecules, under UV radiation, we see an increase in the %removal because of by increase in adsorption causes more number of drug molecules are trying to contact with free radicals formed by the excitation of TiO₂.

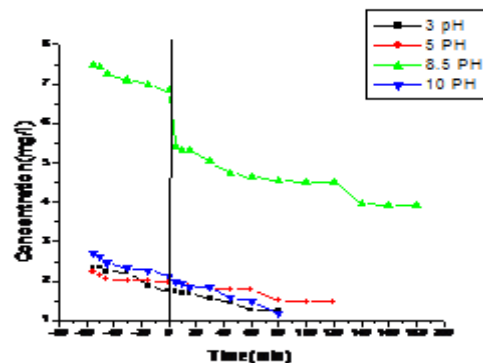


Figure 11: Photo degradation by varying P^H

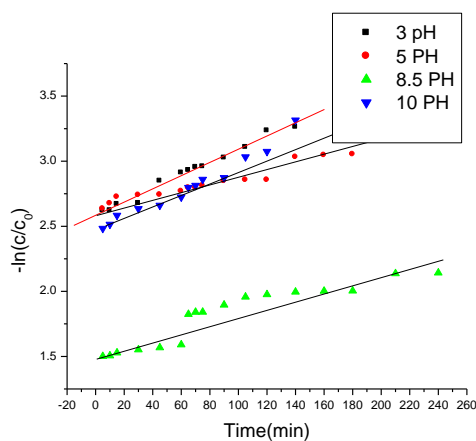


Figure 12: Kinetics of Aspirin Degradation By Varying Catalyst Dose (Linear transformation $\ln(C_0/C)$ vs t)

F. Reusability of the Catalyst

Catalyst was used repeatedly to check the variation in its photo activity. Same catalyst was used three times and after each cycle it was washed with acetone and dried in oven at 70°C . Loss of catalyst can be minimized by lowering the volume of drug solution. Here drug concentration was 30ppm and catalyst loading is 100mg/100ml.

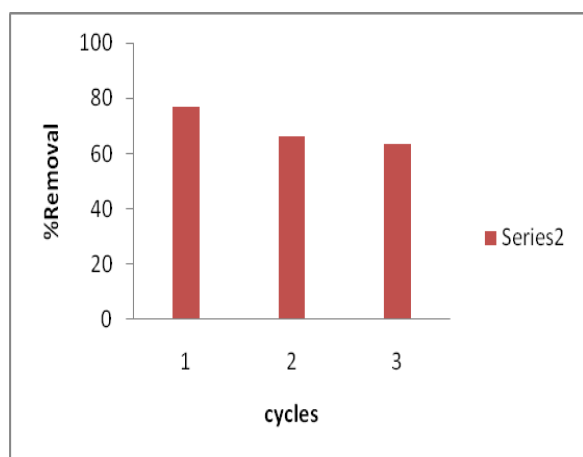


Figure 13: Regeneration of The Catalyst

CONCLUSIONS

Successful preparation of GO was done by using Modified Hummer's method. Simple sonication method was employed to synthesis GO-TiO_2 which is an excellent adsorbent used in Photo catalysis. 1:0.1 of Graphene oxide was found to be an appropriate amount for composite preparation and gives best results to remove aspirin drug from the water. For photo degradation, pseudo first order kinetics was performed. For the low catalyst loading adsorption capacity is less while the photo catalytic degradation is more. As the amount of catalyst increases adsorption capacity increases and photo reaction decreases. After one cycle, the efficiency decreases very slightly it indicates that the

prepared catalyst is regenerated. Furthermore, due to great thermal stability and physical strength of the catalyst it can sustain extreme conditions. Therefore, prepared catalyst is perfectly acceptable for real world application.

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