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Experimental Studies on Decolorisation of Malachite Dye using Continuous Photocatalytic Reactor

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Abstract

Textile industry consumes large quantity of water during dyeing and finishing process which discharges the toxic and hazardous chemical to the environment. Therefore, suitable treatment process has to be carried out for the degradation of organic dye. By choosing the desired catalyst and suitable light source, degradation can be potentially effective and develops an eco friendly environment. In this paper, Heterogeneous Photo-catalysis under Visible light is employed as an effective method for the degradation and decolorisation. Sol–gel technique has been taken as one of the adaptable method for the preparation of metal doped nano crystalline TiO_2. The parameters considered for this study are pH, initial concentration of dye, flow rate of dye and light intensity. Malachite green is used for experimental study. Photo decolorisation is increased with a decrease in flow rate of reactant and by increasing the light intensity. The color removal of MG is very effective by maintaining pH at 9 respectively. It has been found that as the initial concentration of dye increases, the rate of color removal decreases.

Keywords: Sol gel method, doped nano crystalline TiO_2, malachite green, color removal.

Introduction

Treatment of waste water is emerging as one of the major hazardous environmental problem throughout the world. Improper treatment of industrial as well as "hazardous" waste have been polluting groundwater, streams, lakes and rivers causing vast damage to aquatic system. The increasing population, growth of industries, energy intensive life style, and lack of environmental protection leads to water pollution. Hence, the rate of generation of effluent keeps on increasing in daily basis. The discharged effluent may have undesirable color, odor, turbidity, heavy metals, hazardous and toxic chemicals etc. In order to avoid the consequence of water pollution on human and other living organisms, some standards/rules have been advised for discharged effluent by authorities like Central pollution Control Board of India, World Health Organization (WHO) etc.

In common textile industry consumes large quantity of water during dyeing and finishing process which discharges the toxic chemicals to the environment. The release of these dyes is polluting our water resources severely. Various physical, chemical treatment methods such as coagulation, sedimentation, membrane filtration, adsorption techniques and disinfection are available techniques for the degradation of the organic matter. In all these methods the toxic chemicals are transferred from one place to another. Such pollution transfer is not an adequate one. Hence, conventional wastewater treatment processes are challenged due to the finding of more and more toxic chemicals which reduces the availability of water resources.

In 1972, Fujishima and Honda discovered that photochemical splitting of water into hydrogen and oxygen which proved heterogeneous photocatalysis as a promising photo catalyst. The semiconductor TiO_2 is well known environmental friendly photo catalyst applied for waste water treatment, because of its low cost, excellent stability, non toxicity, high photo catalytic activity. The photoreaction is initiated by the light source with semiconductor material. Both oxidation and reduction reaction are carried out all together with the help of catalyst.

Here organic matters are degraded by the action of highly oxidizing agent hydroxyl radical and converted into small molecules like H_2O, CO_2 etc. Therefore sludge disposal problem can be avoided. The catalyst itself is unchanged during the process, so the catalyst can be used repeatedly. The water treatment cost can be saved and provides a cleaner environment.

Mechanism of Photocatalysis: Electrons and holes are produced by irradiating UV light on TiO_2 catalyst. By absorbing light, the electron present in the valence band of TiO2 is energized and promoted to conduction band thereby creating an electron hole pair. This is known as photo excitation state of semiconductor. The generated electrons react with oxygen molecule to form superoxide radical anions (O_2^-) and the holes react with the water molecule or hydroxyl ion (OH^-) to form hydroxyl radicals ($OH^\bullet$). After fluorine, the hydroxyl radical is the second strongest known oxidant having an oxidation potential of 2.8 eV. It has an ability to oxidize the organic pollutant and yielding H_2O, CO_2 molecules. The reaction steps are shown below;

$TiO_2 + hv \Rightarrow TiO_2 (e^-_{cb} + h^+_{vb})$ (1)
$TiO_2 (e^-_{cb} + h^+_{vb}) + H_2O_{ads} \Rightarrow TiO_2 + OH^- + H^+$ (2)
$e^-_{cb} + O_{2ads} \Rightarrow O_2^-$ (3)
$O_2^- + H_2O \Rightarrow OH^{\cdot}$ (4)
$h^+_{vb} + OH^- \Rightarrow OH^{\bullet}$ (5)
$OH^{\bullet} + Organics \Rightarrow H_2O, CO_2, etc$ (6)

The difference in energy among the conduction band and valence band is known as the Band Gap. Band gap energy of TiO_2 is 3.2ev. If it is decreased, the photo catalytic activity can be increased due to the fast movement of electron from valence band to conduction band. The energy of excitation is the energy of wave length of light. Wavelength of light required for photo excitation is given by:

$$\frac{1240(h)}{Band\ gap\ energy} = \lambda\ (nm) \quad (7)$$

Where, h => Plank's constant, λ => Wavelength of light.

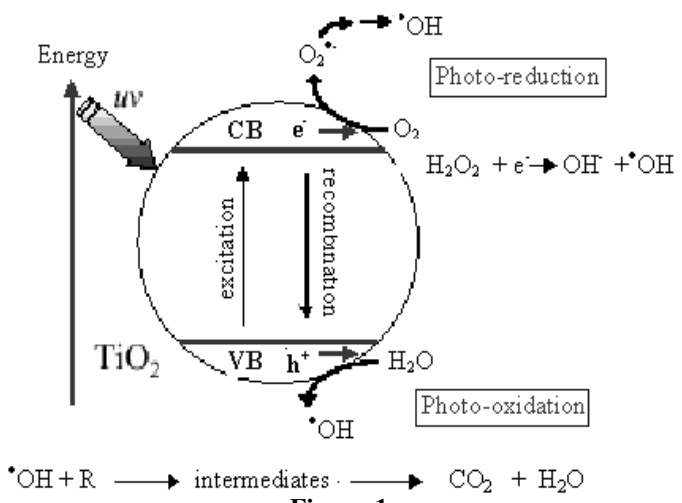

Figure-1
Photo catalytic process of TiO_2

According to the equation (7) by reducing the band gap energy of semiconductor, the wave length of light increases, it shifted from UV region to visible region. So the demand for usage of sunlight (visible light) activated photo catalytic systems is increasing rapidly.

Material and Methods

Materials Required: Metal Alkoxide (Titanium tetra iso propoxide), Absolute alcohol (Glacial acetic acid), Metal Nitrate ($MgNO_3$), Poly Vinyl Alcohol (PVA), Malachite Green (MG).

SOL-GEL Process: Sol–gel method is used for the preparation of metal doped nano crystalline TiO_2. This method is a solution process, so we have to control the compositional homogeneity, size and morphology of the catalyst particle. In sol-gel method, titanium alkoxide is used as starting material, which undergoes hydrolysis and poly-condensation reaction by the addition of acid. It is then formed as sol-like system, containing solid and liquid phase. Drying process is done to remove the remaining liquid (solvent) phase. The rate of removal of solvent can be determined by the distribution of porosity in the gel. Structural properties of compound are influenced by this phase changing process. Afterwards, undergoes firing process for improving mechanical properties and structural stability. This method is able to control the product's chemical composition.

Catalyst Preparation: N. Venkatachalam et al[1] described the method of preparation of alkaline earth metal doped TiO_2 nano catalyst. Doped TiO_2 photo catalyst preparation method is as follows:18.5 ml of Titanium (IV) isopropoxide mixed with 35.8 ml of glacial acetic acid in a beaker at 0^0C. 395 ml of water was added to this solution and 1gm of $MgNO_3$ was added dropwise and vigorously stirred for 1 h using magnetic stirrer. The solution undergoes continuous stirring for another one hour to form a clear solution. The resulting solution was kept in dark during the night and then the solution was kept in an oven at a temperature of 70 ^{0}C for gelation process for 12 hrs. The gel was dried at 100^0C and then calcined in a muffle furnace at 500^0C.

Immobilization of Catalyst on Glass Column: The prepared doped TiO_2 nano particle is mixed with deionized water and Poly Vinyl Alcohol (PVA) was consequently added into the TiO_2 suspension with continous mechanical stirring at 95^0C for 1 hr. The mixture of the solution was constantly stirred at 60^0C for 3 hrs. The solution must be free from air bubbles by resting in the air and allowed the solution to cool at room temperature. The obtained viscous mixture was coated onto a clean glass column and allowed to evaporate throughout the night at room temperature.

Continuous Flow Photo Reactor: The annular type continuous flow photo catalytic reactor is shown in figure 2. It has been made to immobilize the photo catalyst to the outer surface of inner glass column. The visible lamp was installed at the centre of the inner glass column. The light source emits visible light (500 watts), which activate the doped TiO_2 catalyst and thereby creating hydroxyl radicals. The experiment was started by filling the dye solution to the inlet tank and was pumped through the reactor by varying the flow rate of dye to analyze the decolorisation efficiency of doped catalyst.

Results and Discussion

Effect of Flow Rate: Flow rate is one of the important parameter for analyzing the rate of decolorisation of dye solution flowing through the photo reactor. Hung-Yee Shu, et al [2] studied effect of flow rate on degradation rate in continuous reactor. The color removal efficiency of MG had been analyzed by varying the flow rate of dye solution from 0.25 ml/s - 3.0 ml/s. Effect of the flow rate on decolorisation of MG at (Light intensity-500 watts, pH 9, and initial concentration of dye 100

ppm) is shown in figure 3. From graph, it could be analyzed that by increasing flow rate 0.25 ml/sec – 3.0 ml/sec, color removal efficiency decreases. It was observed that flow rate and concentration are inversely related. The highest color removal efficiencies for MG obtained as 88.9 % at 0.25 ml/s. In the plug flow reactor residence time is defined as the ratio of reactor volume (V) to volumetric flow rate (v).It is expressed as

$$\tau = V/v \quad (8)$$

Decolorisation (%) of MG Vs Residence time (sec) in the presence of Mg doped: TiO_2 is shown in figure 4. The graph depict that longer residence time enhances degradation rate effectively. It has been observed that the reactor operating at lowest flow rate the residing time for the reactant molecule in the reactor is increased. This is due to the fact that the adsorption rate of dye molecule on catalyst increases the active surface area; thereby reaction rate can be enhanced.

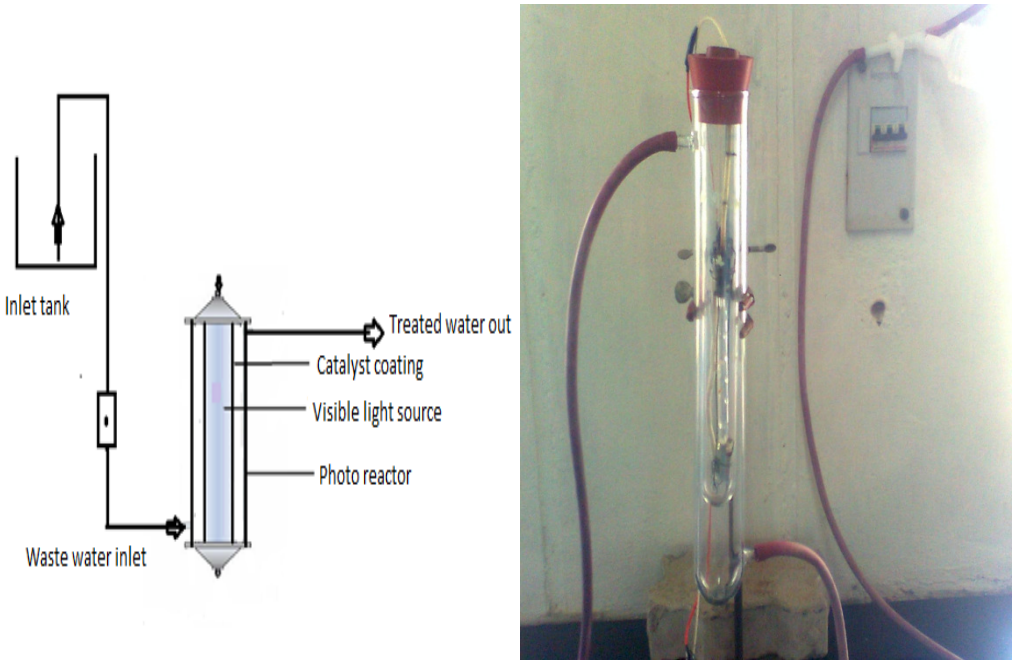

Figure-2
Photo-catalytic continuous reactor

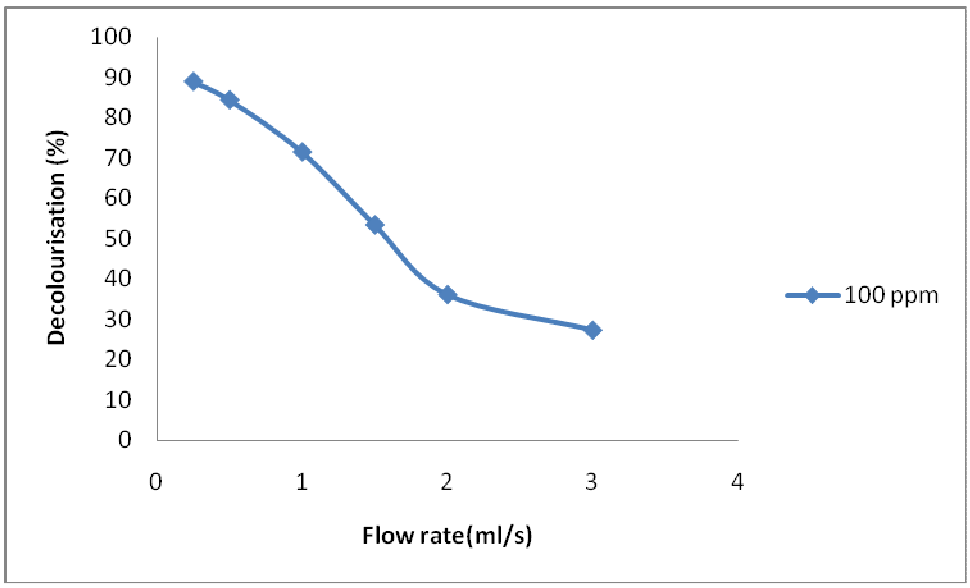

Figure-3
Decolourisation (%) of MG at various flow rate (ml/s) in presence of Mg doped -TiO_2

Effect of pH: Many of the literature revealed that pH played an important role in photo catalytic degradation process. Chung-Shin Lu et al[3] investigated the effect of the pH variation on decolorisation rate. It influences many physico-chemical properties like adsorption-desorption reaction, photo catalyst surface charge etc. The point of zero charge in physical chemistry, describes the state, when the electrical charge density on the surface is zero. At isoelectric point the protonated and deprotonated groups are equal. When the pH of the solution is higher than doped TiO_2, iso electic point of TiO_2 surface is negatively charged and vice versa. So TiO_2 surface charge can be varied with pH variation, which affect the adsorption of molecule on catalyst surface and influence the degradation rate effectively. So the experiments were conducted to find out optimal pH of reaction mixture for the decomposition of MG in water. The examined range of pH was 3-11. The experimental result indicated that decolorisation of MG in water were greatly influenced by pH. The percentage of decolorisation of 100 ppm MG as a function of flow rate is shown in figure 5. The result showed that photo decolorisation rate was found to increase along with an increase in pH for MG.

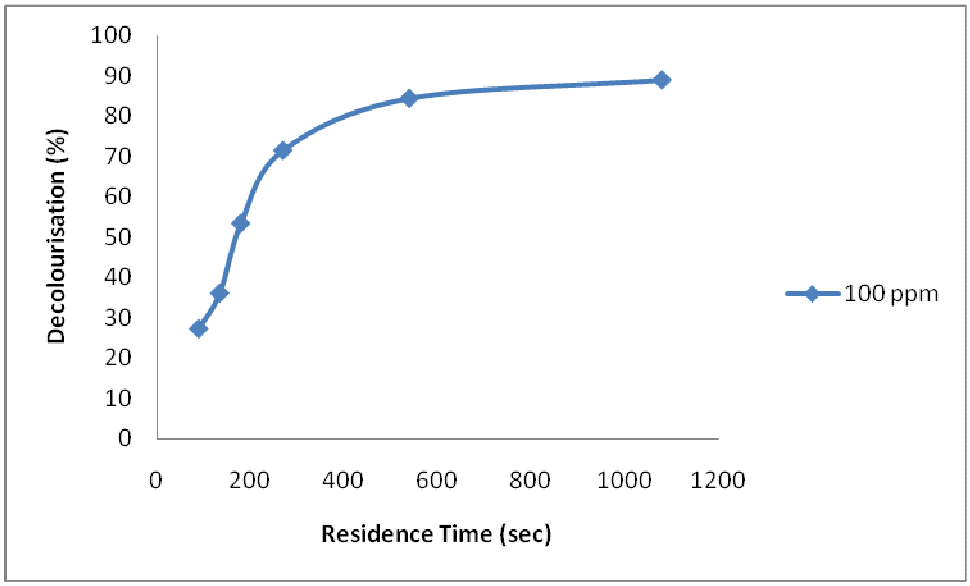

Figure-4
Decolorisation (%) of MG Vs Residence time (sec) in presence of Mg doped -TiO_2

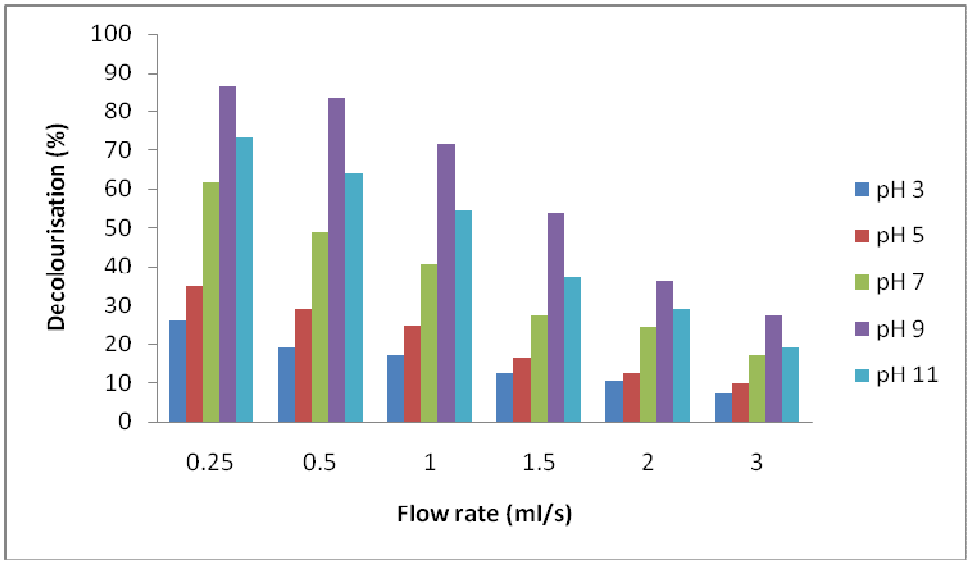

Figure-5
Decolorisation (%) of MG (100ppm) in various pH

The rate of decolorisation in basic pH range (at 9) was found to be higher than the acidic pH. Under acidic condition the adsorption rate of MG dye on TiO_2 surface is low, so the generation of hydroxyl radical is in low concentration. So there is an electrostatic attractive force between the cationic MG dye and negatively charged TiO_2 surface. When the pH is too high, large number of MG molecule get adsorbed on the TiO_2 active surface, therefore the path length of photon entering the solution decreases.

Effect of Initial Dye Concentration: The initial dye concentration is one of the important parameter in determining decoloristion efficiency of photo catalytic system. N. Modirshahla, et al[4] and Djebbar Kamel et al[5] anlaysed the influence of initial reactant concentration on degradation rate. The experiments were conducted by varying initial concentration from 100 ppm to 300 ppm, at constant pH of 9 for Mg. The absorbance of dye was measured using UV spectrophotometer. It was found that at 100 ppm dye concentration, percentage of decolorisation was 88.9%, at 300 ppm dye concentration, the percentage of decolorisation was reduced to 67.7 %. It can be seen that degradation rate decreases when increasing the dye concentration and was presented in figure-6. Percentage of decolorisation as a function of residence time for MG is shown in figure 7.

The inverse effect is explained that if the dye concentration increases in the treating solution, large amount of dye molecules are adsorbed on catalyst surface active site. The catalyst surface area available will help to increase the degradation efficiency, but with further increasing dye concentration active sites of catalyst occupied by dye molecule and there is no space for the formation of hydroxyl radical. So ultimately there is a reduction in degradation efficiency. Hydroxyl radical is the strongest oxidizing agent promoting the degradation rate. According to beer-Lambert law, as the initial dye concentration increases, the path length of photon entering the solution decreases ,therefore resulting lower photo degradation rate.

Effect of Light Intensity: Light intensity is an important parameter that influences photo catalytic reactions. The experiments were conducted by varying light intensity in the range of (100watts – 500watts) by maintaining initial concentration of dye as 100ppm and pH 9 for MG. The experimental result showed that the percentage removal of color increases steadily with an increase in light intensity .It can be seen that color removal percentage at 100,250 and 300 watts are 46.1 %, 75.7% and 95.6% respectively. This was due to the increase in the probability of excitation of catalyst particle and also re-excitation of recombined electrons. The result showed that the lamp power had considerable effect on the degradation rate. When increasing the light intensity the generation rate of hydroxyl radical increased gradually. The reactive hydroxyl radical oxidised the dye molecules effectively and thereby degradation rate was greatly enhanced under higher light intensity was shown in figure-8 and 9.

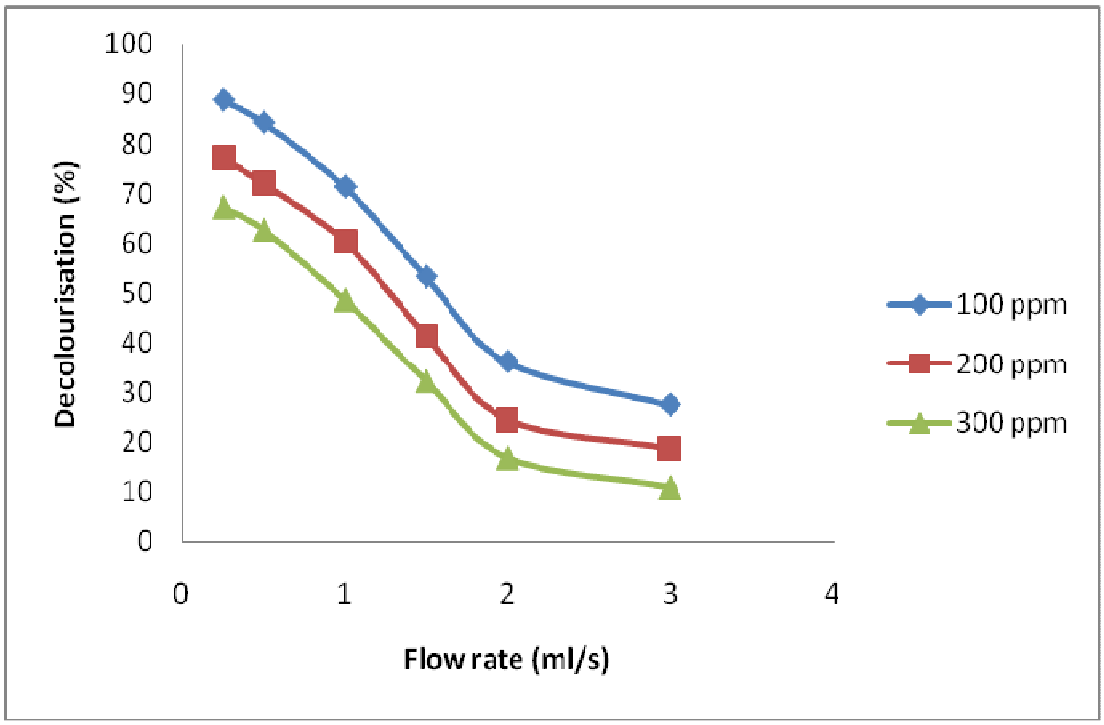

Figure-6
Decolourisation (%) of MG in various initial dye concentration

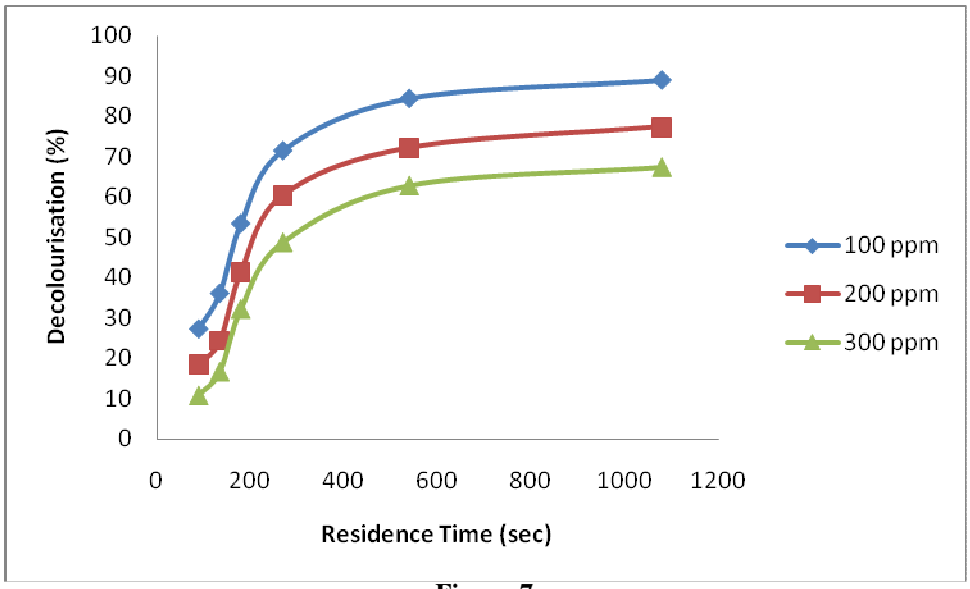

Figure-7
Decolorisation (%) of MG Vs Residence Time (sec)

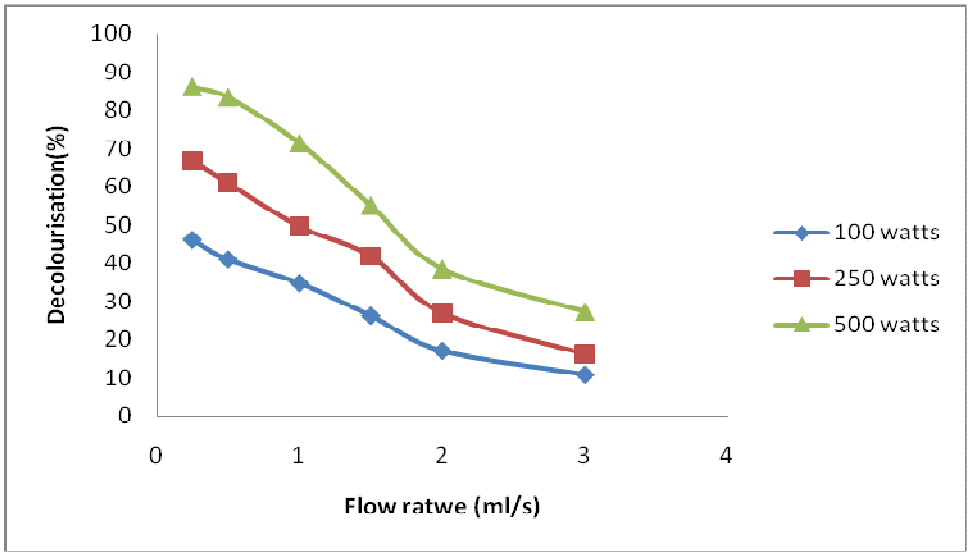

Figure-8
Decolorisation (%) of MG by varying light intensity

Conclusion

Heterogeneous photo catalysis process is eco-friendly way to reduce the organics load of wastewater. This process has proved its superiority to other conventional methods of wastewater treatment. It leads to complete destruction of contaminants present in waste water. Treatment of dyes has been carried out by varying the parameters like pH, flow rate, initial concentration of dye and light intensity. The photo catalyzed degradation of malachite green in doped TiO_2 nano particle carried out using visible lamp source. The observation of these investigations clearly reveal the importance of choosing the optimum degradation parameters to obtain a high decolorisation rate, which is essential for any practical application of photo catalytic oxidation processes using photo catalyst (Doped TiO_2). Heterogeneous photo catalytic oxidation process using visible light, could be efficiently applied for the degradation of dyes.

Experimental results indicate that the decolorisation of dye is effective in the presence of catalyst. Efficiency of Photo decolorisation is increased with an decrease in flow rate of reactant and by increasing the light intensity. The color removal of MG is very effective by maintaining pH at 9. It is found that the rate of color removal decreases with an increase in initial concentration of dye.

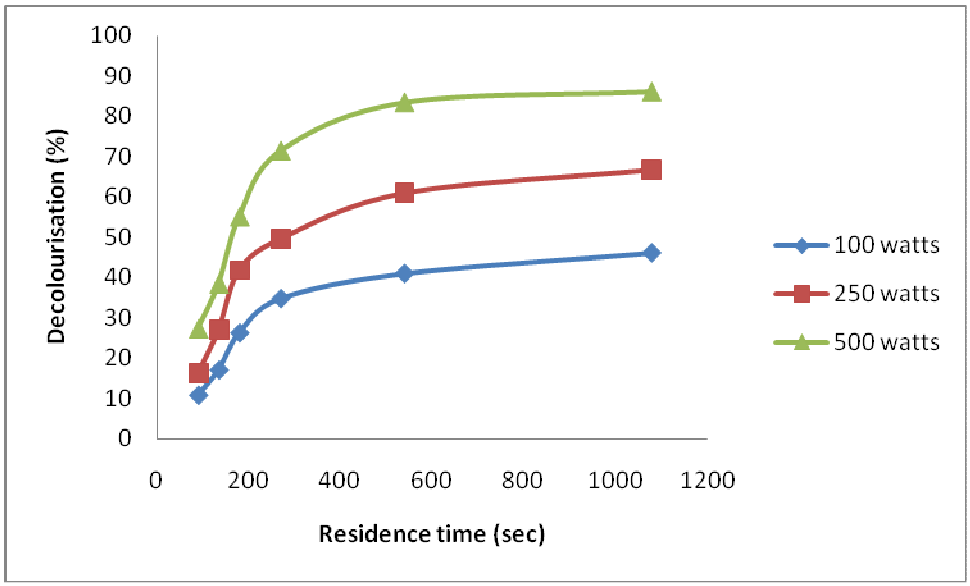

Figure-9
Decolorisation (%) of MG by varying light intensity

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