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Photodegradation and Adsorption of Methyl Orange and Methylene Blue Dyes on TiO_2

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Abstract: ***Dyes are extensively used in the textile industry and a considerable amount of water is consumed during dyeing and finishing operations. These wastewaters are discharged in rivers or public sewerage treatment plants and are highly coloured and contaminated. This creates a major environmental problem primarily due to substantial amounts of unfixed dyes released in wastewater. These dyes are characterized by low biodegrability which makes them a source of pollution. In this research work, using two model dyes (Methyl Orange and Methylene Blue) the possibility of degrading the dye wastewaters is investigated with the objective of their effective removal from wastewaters. Photocatalytic degradation was used for dye removal.*** TiO_2 ***was used as a photocatalyst. As a source of UV light, UV tubes were used and a UV/Vis spectrophotometer was used to monitor the changes in dye concentrations. From the changes in concentration during irradiation, the rate of degradation was determined. After irradiation, the amount of Methyl Orange adsorbed on the surface of*** TiO_2 ***catalyst was determined for the various concentrations. The results showed that*** TiO_2 ***photocatalyst shows a high activity for (Methyl Orange /Methylene Blue) degradation under UV irradiation. Amount of adsorbed Methyl Orange increases with dye concentration and for concentrations higher than*** 1×10^{-4} ***M it increases only slightly. It means that there is a direct relation between amount adsorbed and degradation rate and thus Photodegradation of dyes using*** TiO_2 ***can be used for treatment of colored industrial effluents containing dyes. In place where we have plenty of sunlight solar radiation can be used for degradation.***

Keywords: Photodegradation, Photocatalyst, Irradiation

1. Introduction

Background of the Study

In our world today, there is an increasing need in many countries to access clean and safe water both for domestic use and other purposes (Cosgrove & Rijsberman, 2014). The demand for clean water surpasses its supply. This means that water emitted out of industries should be recycled, purified and later used for other purposes (Clark, 1999). The pollution that accompanies the dye industry is of great significance and importance. This is particularly because of the non-biodegradable nature of the dyes as well as due to the presence of Acid/Alkali toxic trace metals/carcinogenic aromatic amines in the effluent (Balakrishnan et al., 2008). In addition to effluent, gaseous emissions such as sulphur dioxide, nitrogenous gases, ammonia/hydrochloric and solid wastes in the forms of iron sludge, gypsum and sludge from treatment facilities are generated. More than 15% of the total world production of dyes is lost during the dyeing process and is released as a source of textile pollution (Houas et al., 2001). Wastewater is known to contain considerable amounts of non-fixed dyes, especially azo dyes, and huge amounts of inorganic salts. It is well known that some azo dyes and degradation products such as aromatic amines are carcinogenic (Lachheb et al., 2002).

Titanium dioxide (TiO_2) as a semi-conductor has been successfully used as a photo catalyst for the oxidative degradation of organic compounds including dyes. Anatase form is the most practical for photo catalytic environmental applications such as water purification, wastewater treatment and water disinfections (Fox & Dulay, 1993). It is biologically and chemically inert, stable with respect to photo-corrosion and chemical corrosion and inexpensive. Its disadvantage is however, too high band gap energy (about 3.2eV) that enables titanium dioxide to absorb only UV light with wavelength lower than 388 nm thus reducing the solar harvesting efficiency down to 5% (Han et al., 2009).

Occurrence of Dyes

Dyes are an abundant class of coloured organic compounds that represent an increasing environmental danger. During dye production and textile manufacturing processes a large amount of wastewater containing dyestuffs with intensive colour and toxicity can be introduced into aquatic systems (Beydoun et al., 1999).

Removal of dyes

Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation (Robinson et al., 2001). This has led to the study of other methods and recent studies have demonstrated that photocatalytic degradation can be used to destroy dye compounds using semi-conductors such as TiO_2 and UV light irradiation. This technique has been developed to a useful process for the reduction of water pollution caused by dying compounds because of mild conditions required and their efficiency in mineralization (Umebayashi et al., 2003).

Mechanistically, it is now commonly accepted that the photocatalyst TiO_2 is first excited by UV light and subsequently initiates the photodegradation process. However, only light of wavelengths below 400nm can be absorbed by TiO_2 particles (e.g., 3.2eV approx. 388nm)

(Woan et al., 2009). Artificial light and TiO_2 particles tend to be somewhat expensive and the UV component in sunlight reaching the earth surface and available to excite TiO_2 is relatively small (ca. 3-5%) (Hasnat & Siddiquey, 2005). Therefore efforts have been focused on exploring means to utilize the sunlight and artificial inexpensive UV or visible light sources and degrading agents for treating polluted water.

Organic pollutants like dyestuffs have the ability to absorb visible light (Chatterjee & Dasgupta, 2005). The electron transfer process from dye to semiconductor, especially TiO_2 has been found to be very effective. The visible light mechanism suggests that the light excites the dyestuff. The excited dye injects an electron to the conduction band of TiO_2 where it is scavenged by O_2 to form active oxygen radicals. These active radicals drive the photodegradation or mineralization of organic compounds (Umebayashi et al., 2003).

Principles of Photodegradation

The important property of semiconductors is that the valence and conduction band are not on the same energy level (Xu & Schoonen, 2000). Ultra violet light in the form of a photon with energy hv greater than band gap energy, Eg, promotes an electron from the valence band to the conducting band leaving a hole behind. Oxidation by OH radicals is not selective and high number of intermediates is produced The formation of holes allows adsorbed water to be oxidized to strong OH radicals .OH radicals are very strong oxidative species (2.8V vs. SHE) and are able to oxidize almost all organic molecules. These organic intermediates are further oxidized by molecular oxygen and or OH radicals and finally mineralized to carbon dioxide and water. In order to close up the circuit, electrons react with the dissolved oxygen on the TiO_2 surface to form super oxide radicals. If the degradation is performed in acidic media the superoxide radical anion protonates to give hydroperoxide radical. These radicals then form molecular oxygen and hydrogen peroxideas shown in figure 1 below (Houas et al., 2001).

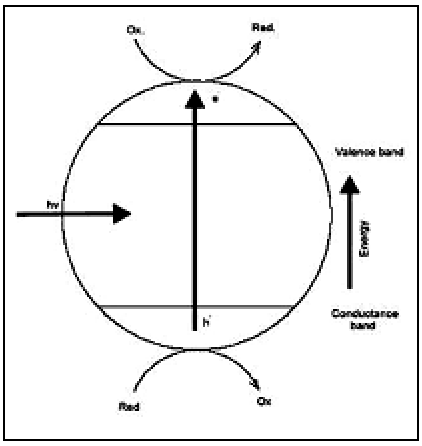

Figure 1: The scheme of TiO_2 activity in the solution containing oxidative and reductive factors

Photocatalytic Oxidation

The first step in photocatalytic process is absorption of UV light ($\lambda < 400$nm) in TiO_2 and the production of electrons and holes in conduction band and valence band (Li et al., 2007). The photogenerated holes that escape direct recombination reach the surface of TiO_2 and react with surface adsorbed hydroxyl groups or water to form trapped holes. The trapped hole is usually described as a surface-bound or adsorbed hydroxyl radical. Hydroxyl radicals generated at the surface of semiconductor leaves the surface to bulk solution to form free hydroxyl radicals. If electron donors are present at the TiO_2 surface, electron transfer may occur. In aerated systems, oxidative species, such as hydrogen peroxide generate from the reduction site (Mills & Lee, 2002).

Photosensitized oxidation

Photosensitized oxidation, a photodegradation mechanism in the presence of VIS light ($\lambda > 400$ nm) is somewhat different. In this oxidation process, dye absorbs light ($\lambda > 400$ nm) and inject e^- on to the conduction band of TiO_2. Excited dye converts to cationic dye radicals ($Dye^{\bullet +}$) and e^- in TiO_2 leads to the formation of oxidation species ($O_2^{\bullet -}$, $HO_2^{\bullet}$ or $HO^{\bullet -}$) (Wrona et al., 2003).

2. Photocatalytic Degradation of Dyes

Decolorization

Decolorization is monitored by an UV-Vis spectrophotometer. Experiments conducted show that decolorization of dyes with photocatalytic methods is feasible (Bizani et al., 2006; Hasnat & Siddiquey, 2005).

The relationship between adsorption and photodegradation

Studies show that those organics with better adsorption on the surface are more likely to be degraded in the photocatalytic process. Organics easily adsorbed on the surface of TiO_2 would have more chances to be oxidized by photo generated hole. In general TiO_2 photocatalysis occurs at specific active sites on TiO_2 (Fujishima et al., 2000).

3. Materials and Methods

The Photodegradation of the two test dyes using TiO_2 photocatalysis was done using the methodology of Bizani et al. (2006). After bleaching, the optical density (OD) of these solutions was measured using UV-Vis spectrophotometer and the final concentrations (C_2) obtained from the standard graph. The extent of removal of the dye in terms of percentage removal was calculated using the extinction coefficient derived from Lambert-Beer law.

4. Results and Discussions

Extinction Coefficients

The extinction coefficient was derived from Lambert- Beer law when the concentration of the dye solution and the length of the cuvette used are known.

If the transmission through a sample is given by T, then the absorbance A is

$A = -\log_{10} T$

The ideal absorbance of a dilute solute in a transparent solvent follows the Beer's law

$A = \varepsilon c d$

where ε (dm^3 mol^{-1} cm^{-1}) is the molar extinction coefficient of the solute at the wavelength of measurement, c (mol/dm^3) is the molarity of the solute, and d is the optical path length (cm). The linear dependence of A on c may not hold if there are concentration-dependent effects, e.g., aggregation or acid-base dissociation of the solute

Extinction coefficient Methyl Orange

To determine the extinction coefficient of Methyl Orange at 485 nm the following concentrations of dye solutions were prepared. (1×10^{-5}M, 2.5×10^{-5}M, 5×10^{-5}M, 7.5×10^{-5}M, 1×10^{-4}M). Using a cuvette of 1 cm and a spectrophotometer CE 2021, absorbance was measured at wavelength 485 nm. Using the data obtained a calibration curve is plotted yielding a value of 20178 $mol^{-1}dm^3$ cm^{-1}, which is quite close to the literature value of $2.1\times10^4 mol^{-1}dm^3cm^{-1}$ (485 nm) (Brown & Darwent, 1984).

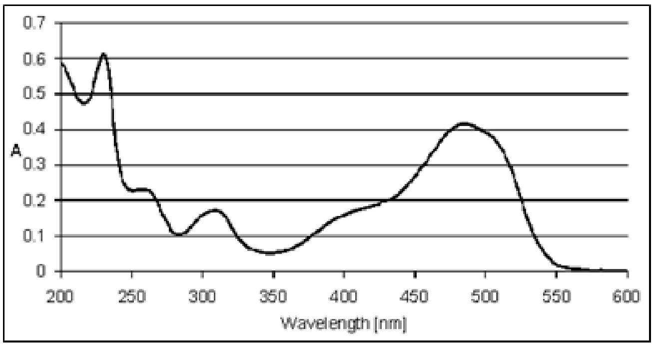

Figure 2: Methyl Orange dye UV/VIS spectrum of aqueous solution c (1×10^{-5}M)

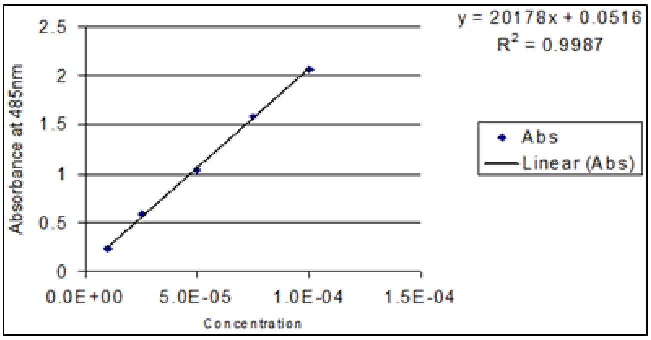

Figure 3: Calibration curve methyl orange dye different concentrations

Extinction coefficient Methylene Blue

Figure 4 shows the UV/VIS spectrum of aqueous solution of MB concentration (1.5×10^{-5}M). The spectrum shows that MB has a peak absorbance at wavelength 660, 2 nm.

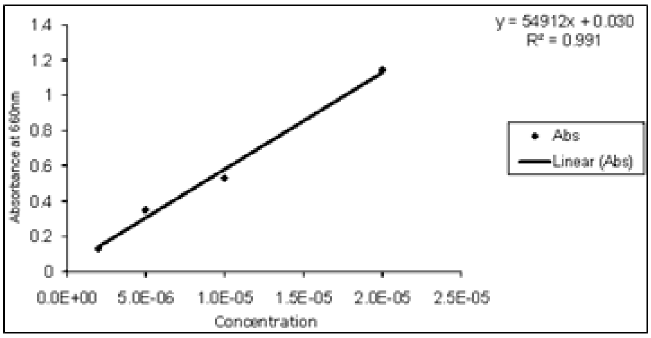

Figure 4: UV/VIS spectrum of aqueous solution of MB, concentration (1×10^{-5}M).

In determining the extinction coefficient of Methyl Blue the following concentrations of dye solutions were used (1×10^{-5}M, 2×10^{-5}M, 5×10^{-5}M, 2×10^{-6}M). Using a cuvette of 1 cm and a spectrophotometer, absorbance was measured at wavelength 660 nm. A calibration curve is plotted yielding a value of 54912 $mol^{-1}dm^3cm^{-1}$ as shown in figure 5 below.

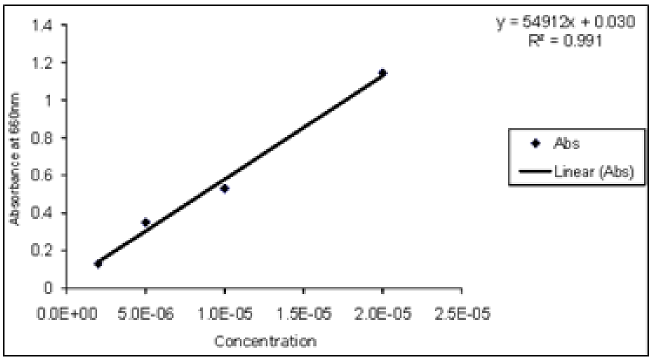

Figure 5: Calibration curve for Methylene Blue

Adsorption of Methyl Orange

Several dye solutions of Methyl Orange of various concentrations were used in the adsorption experiment. Bottles were filled each with 20 ml of various dye concentrations and addition of 0.1g TiO_2 P25 powder. Three bottles of the same starting concentrations were used in each case. Shaking is then performed for two hours after which centrifugation are done for at least 10 minutes. The clear suspension was the filtered and the solution then stored in small bottles. The absorbance of the dye solutions was then measured using a spectrophotometer. The absorbance values were then used to calculate the equilibrium and the amount of dye adsorbed in (mol/g). The plot is shown below (figure 6).

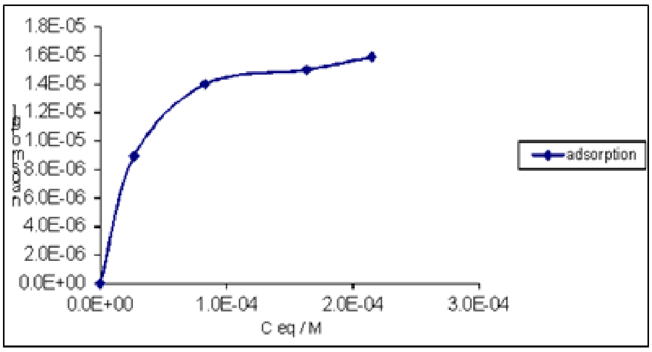

Figure 6: Adsorption of dye Methyl Orange on TiO_2 photocatalyst

Degradation of Methyl Orange dye

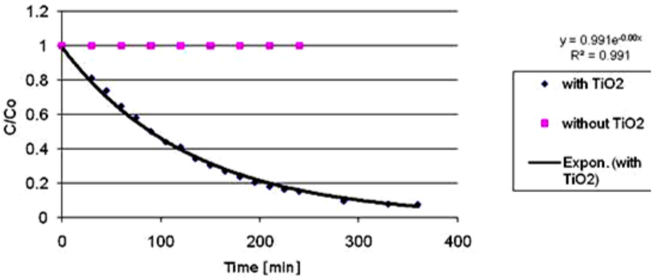

Figure 7: Graph showing photocatalytic degradation of dye Methyl Orange c (2.5×10^{-5}M)

The graph shows a systematic decline in dye concentrations with time when dye Methyl Orange is irradiated with UV light in the presence of TiO_2. However experiment conducted without TiO_2 catalyst showed no change in concentration. This proves that photocatalytic degradation is a viable means of dye removal from wastewaters.

Degradation of Methylene Blue dye

The results of Photodegradation of methylene blue are hereby presented and discussed.

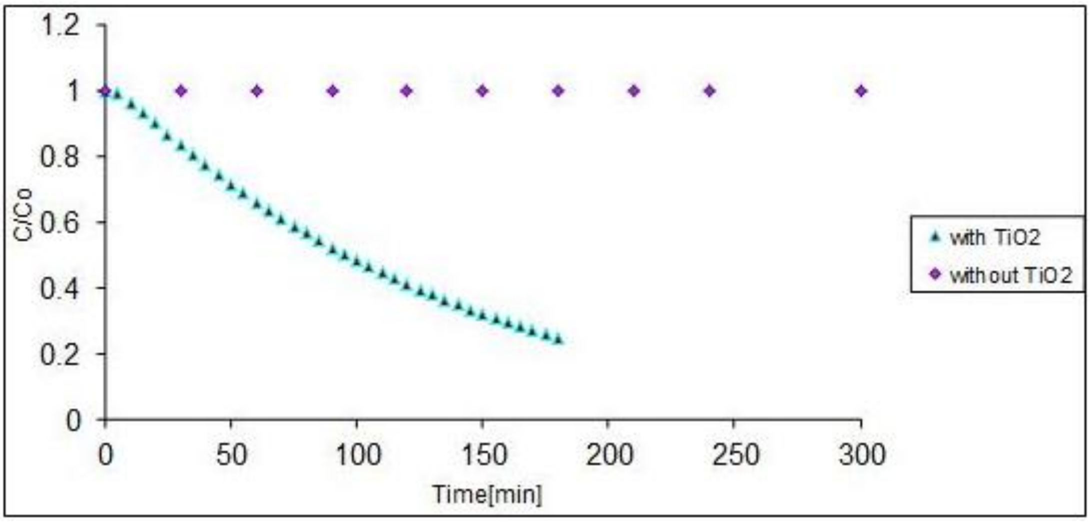

Figure 8: Graph showing photocatalytic degradation of dye Methylene Blue c (2.5×10^{-5}M)

The graph shows a systematic decline in dye concentrations with time when dye Methyl Orange is irradiated with UV light in the presence of TiO_2. However experiment conducted without TiO2 catalyst showed no change in concentration. This proves that photocatalytic degradation is a viable means of dye removal from wastewaters.

5. Conclusions

TiO_2 photocatalyst shows a high activity for (Methyl Orange /Methylene Blue) degradation under UV irradiation.

Amount of adsorbed Methyl Orange increases with dye concentration and for concentrations higher than 1×10^{-4} M it increases only slightly. It means that there is a direct relation between amount adsorbed and degradation rate and thus Photodegradation of dyes using TiO_2 can be used for treatment of colored industrial effluents containing dyes. In place where we have plenty of sunlight solar radiation can be used for degradation.

6. Recommendations

In future, researchers should focus on the development of novel nanomaterials/nanocomposites with a high surface area, sufficient surface functional groups and high sorption ability, for the removal of different heavy metalions and organic dyes.

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List of Symbols

A	Absorbance
ε	Extinction Coefficient (mol^{-1}dm^{3}cm^{-1})
c^o	Initial Concentration (mol/dm^3)
A	Irradiated surface area (m^2)
c	Molar Concentration (mol/dm^3)
d	Optical Path (cm)
SHE	Standard Hydrogen Electrode (volts)
TOC	Total Organic Carbon (ppm)
t	Time (min)
T	Transmittance
UV	Ultra violet (nm)
V	Volume of dye solution used for degradation (dm^3)
Λ	Wavelength (nm)