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Influence of Various Inorganic Cations and Anions on Photocatalytic Degradation of Indigo Carmine

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The effect of various inorganic cations and anions on photocatalytic degradation of indigo carmine at optimum conditions have been studied. For achieving optimum conditions several parameters such as pH and the amount of TiO_2 on photocatalytic degradation have been investigated. In addition, the effects of UV and TiO_2 have been discussed. The maximum efficiency of dye decomposition was achieved at acidic pH of 2 and with 0.4 g of TiO_2. The experiments showed that TiO_2 and UV light had a negligible effect when used without the addition of the catalysts. It was found that in acidic media addition of various cations and anions resulted in reduction of degradation process.

Key Words: Photocatalyst, Advance oxidation technology, Recalcitrant Pollutants, Indigo carmine.

INTRODUCTION

Liquid effluents containing various complex hydrocarbon ring structures are commonly produced in a variety of industrial processes such as dye and pesticide. They are environmentally persistent, as they do not break down rapidly through natural processes[1]. The conventional treatment methods for eliminating dyes from the waste stream include flocculation with lime, adsorption on activated charcoal and biotreatment. Lime treatment and charcoal adsorption generate large amounts of solid wastes which require costly disposal and regeneration methods. Biotreatment processes rely on indigenous soil microorganisms to degrade dye compounds. Since the synthetic dyes are resistant to aerobic biodegradation, this process is likely to be insufficient. Thus, there is a need for developing treatment technologies that are more effective in eliminating dyes from waste stream at its source. In recent years, great efforts have been made using widely-called advance oxidation technologies (AOT) for treatment of these recalcitrant pollutants to more biodegradable molecules or mineralization into CO_2 and other inorganics[2–5]. In AOT, materials with photocatalytic function could be used. The semiconductors such as SnO_2, WO_3, Fe_2O_3, ZnO, TiO_2, CdSe, CdS and ZnS are known to have photocatalytic function. Among these, TiO_2 has been noted for photochemical reaction, since TiO_2 is an effective, easily available, relatively inexpensive and chemically stable photocatalyst.

In addition to the application of photocatalysts in eliminating organic compounds from waste streams, they are used in other cases such as air cleaners[6, 7], self-cleaning windows[7–9], self-cleaning glass[10–15], super hydrophilic surfaces[16–18] and energy conversion[7, 19, 20]. Recently, it has found especial application in cancer treatment[21]. In this paper, indigo carmine which is used in a functional kidney test in colouring nylon surgical sutures and present in waste streams was selected and its decomposition was investigated and discussed by AOT.

Concept of photocatalytic degradation on TiO_2 particles

Heterogeneous photocatalysis is a process in which the illumination of an oxide semiconductor usually anatase or rutile, produces photo-excited electron (e^-) and positive charged holes (h^+). The photo-excitation of the semi-conductor particles by UV light changes the energy state of the electrons from the valence band of the solid to the conduction band. The band gap energy of TiO_2 is 3.2 eV with the lower level being –0.4 eV and the upper level being 2.8 eV, relative to the reduction potential of hydrogen. The reduction potential of water lies between the lower and upper levels. The water, thus, can be photochemically decomposed by TiOa catalyst[22]. The complete degradation of many organic pollutants is shown by the following mechanism:

Absorption of efficient photons $h\nu \geq E_G = 3.2$ eV by titania:

$$(TiO_2) + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \qquad (1)$$

Oxygen ionosorption:

$$(O_2)_{ads} + e^-_{CB} \longrightarrow O_2^{\bullet -} \qquad (2)$$

Neutralization of OH^- groups into $OH^\bullet$ radical by photo holes:

$$(H_2O \longleftrightarrow H^+ + OH^-)_{ads} + h^+_{VB} \longrightarrow H^+ + OH^\bullet \qquad (3)$$

Oxidation of the organic reactant *via* successive attacks by $OH^\bullet$ radicals:

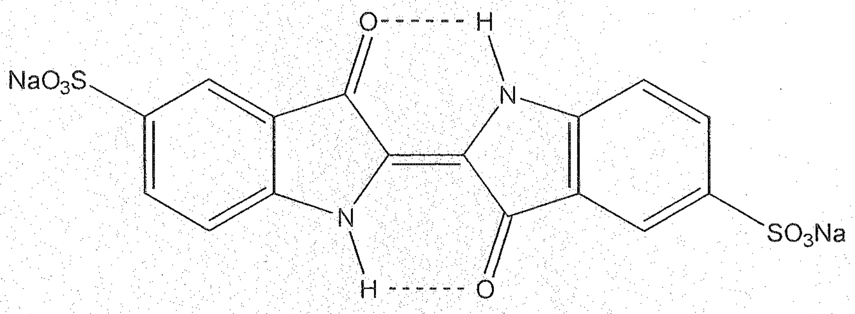
$$\text{Reactant} + OH^\bullet \longrightarrow R'^{\bullet} + H_2O$$

By direct reaction with holes:

$$\text{Reactant} + h^+ \longrightarrow R^{+\bullet} \longrightarrow \text{degradation products}$$

EXPERIMENTAL

Indigo carmine, the molecular formula of which is given below, was supplied by Merck.



Titanium dioxide of analytical grade was supplied by Merck (99%). Powder solution of dye (1000 mg/L) was prepared with distilled water and further diluted during the experiment. All the other chemicals used in this study were of analytical reagent grade. The salts of $CaCl_2$, KCl, $SnCl_4$, $AlCl_3$, $CuCl_2$, $CrCl_3$, $NaNO_2$, $NaSO_4$, NaCN, $NaBiO_3$, $NaNO_3$ and CH_3COONa were also supplied by Merck.

The apparatus used were UV-Vis spectrophotometer (Biotek 922 model), pH-meter (Horiba-f-12) with sensitivity ±0.02 and centrifuge (KoKusan H-108N).

Procedure: The effect of pH on photocatalytic degradation of the dye sample: 100 mL aliquots of aqueous dye solutions (10 ppm each) were previously adjusted to fixed pHs (2.0, 7.0 and 10.0) by addition of 1.00 M H_2SO_4 or 1.00 M NaOH solution and controlled with a pH-meter. The concentration change in the sample solutions was examined in presence of TiO_2 (0.2 g) and irradiation from UV lamp (sunlamp, ultraviolet radiation, Philips 40W) individually and together contemporaneously. Aliquots of 5 mL were collected at regular time intervals (0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5, 25, 27.5, 30, 40, 50 and 60 min). The dye adsorbed on catalyst surface without any reaction with UV rays was described as the initial corresponding adsorption (t = 0 and at approximately 30 s time intervals during which the dye mixed with the catalyst). Then, in the next step, the obtained sample solutions were separated from TiO_2 catalyst by centrifuging for 15 min at 4500 rpm. The concentration of dye in supernatant was determined using UV-Vis spectrophotometer at 609 nm. The percentage of degradation was calculated by the following equation:

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is the initial dye concentration (mg/L) and C is the dye concentration (mg/L) after the treatment.

The effect of amount of TiO_2 on photocatalytic degradation of the dye sample: For achieving optimum amount of photocatalyst, different quantities of TiO_2 were added to the solutions. The experiments were carried out as described above.

The effect of presence of various ions in photocatalytic degradation of the dye sample: The effect of cations and anions on photocatalytic degradation efficiency at optimum conditions was also studied. The effect of cations was investigated by adding various salts. Therefore, 300 mg/L of Cl-salts of various cations were added into the dye samples. The effects of anions were also investigated similarly by adding Na-salts of various anions into the dye sample solutions.

RESULTS AND DISCUSSION

The concentration characteristics of dye effluents are generally affected by pH which gives rise to modification of the physical properties (including charge) of molecules with ionizable functional groups which is an important factor for improving irradiation time. The amount of photocatalyst also plays an important role in optimizing irradiation. It was found that the presence of cations and anions of the selected salts decreased and increased the photocatalytic degradation efficiency of indigo carmine, respectively. Thus, these parameters have been investigated and discussed separately.

UV-Vis spectra changes: The absorption spectra obtained for the degradation of indigo carmine with TiO_2/UV system at wavelength between 190–790 nm are shown in Fig. 1 (at time intervals of 0–60 min), at pH = 2 and with 0.2 g of TiO_2 in UV-Vis region.

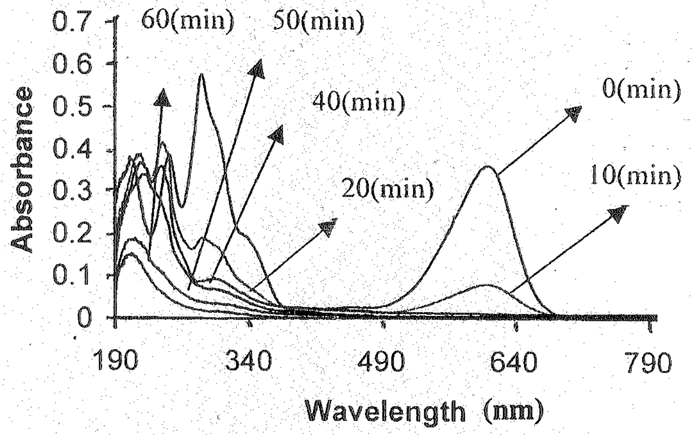


Fig. 1. The change of absorption with irradiation time in UV-Vis region

As can be seen from Fig. 1, the absorption peak at 609 nm decreased with irradiation time which indicated that the dye compound decomposed rapidly by TiO_2/UV system. From Fig. 1, it can be observed that at initial step of the degradation, the polyaromatic rings of indigo carmine were decomposed and, therefore, generated aromatic single rings which as a result led to increasing absorbance in UV region. After 60 min of irradiation only a small peak is observed. Thus, these results demonstrate that indigo carmine and all of its intermediates are decomposed and mineralized into CO_2 and other inorganics.

Effect of pH on the photocatalytic degradation of the dye sample: The results of pH effect on photocatalytic degradation of indigo carmine are shown in Figs. 2, 3 and 4 at pHs of 2, 7 and 10, respectively.

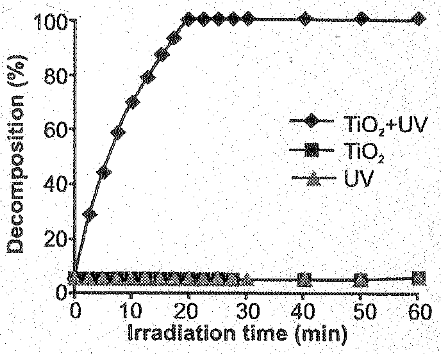


Fig. 2. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2

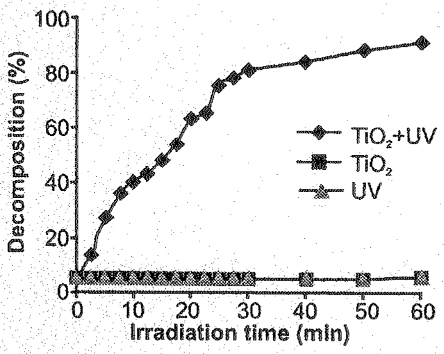


Fig. 3. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 7

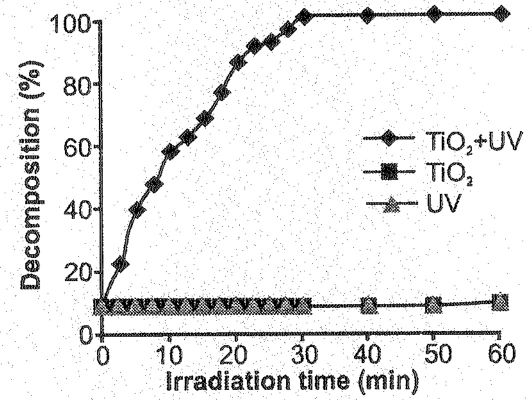


Fig. 4. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 10

As can be seen from Figs. 2–4, the optimum pH, which provided the best degradation ratio, was found to be 2 for dye sample. The effect of pH on degradation efficiency depends upon the hypothesis that sulphonate groups in indigo carmine solution have negative charge and that the surface of TiO_2 particles has positive charge in acidic pH. Therefore, it may be concluded that the electrostatic force can result in adsorption of indigo carmine on TiO_2 surface and hence lead to the reduction of time required for the degradation of dye sample. However, the presence of UV and TiO_2 is also shown in Figs. 2–4. It can be seen that they had little effect on photocatalytic degradation and based upon these results, the acidic pH 2 and TiO_2/UV system were selected as the optimum conditions.

The effect of amount of the photocatalyst on the degradation of dye sample: The amount of TiO_2 on irradiation time is shown in Fig. 5.

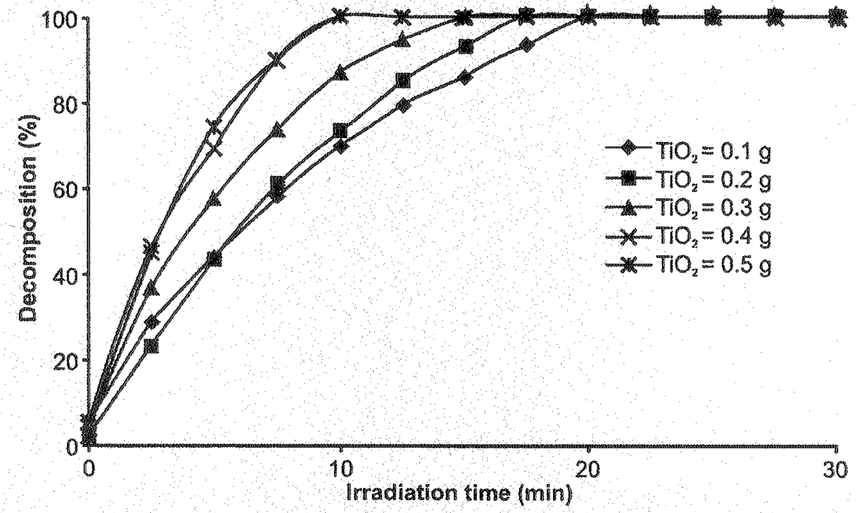


Fig. 5. The change of decomposition value (%) of indigo carmine sample with irradiation time with variable amount of TiO_2 at pH = 2

As can be seen from Fig. 5, as amount of TiO_2 increases from 0.1 g to 0.4 g, irradiation time for complete degradation of indigo carmine decreases. From Fig.

5, it can be seen that on increasing the amount of TiO_2 from 0.4 to 0.5 g, the irradiation time has not changed. The reason for this is thought to be due to the fact that when all dye molecules are adsorbed on TiO_2 surface, any further addition of TiO_2 could have no effect on the degradation efficiency. Therefore, 0.4 g of TiO_2 was considered to be the optimum value.

Photocatalytic degradation of dye sample in presence of various cations: The effects of various cations such as Ca^{2+}, K^+, Cr^{2+}, Cu^{2+}, Sn^{4+} and Al^{3+} on photocatalytic degradation of dye sample were studied as a function of degradation percentage *vs.* irradiation time. The results obtained are shown in Figs. 6 to 11, respectively.

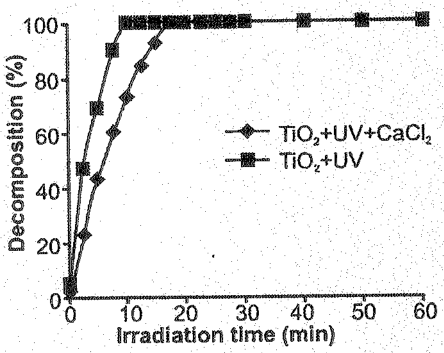


Fig. 6. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $CaCl_2$

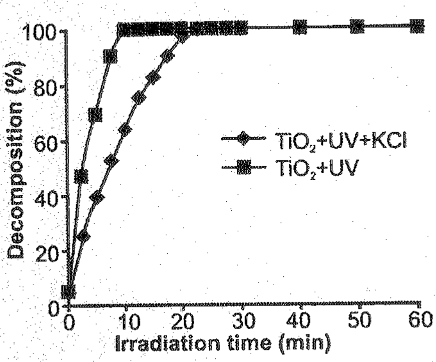


Fig. 7. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of KCl

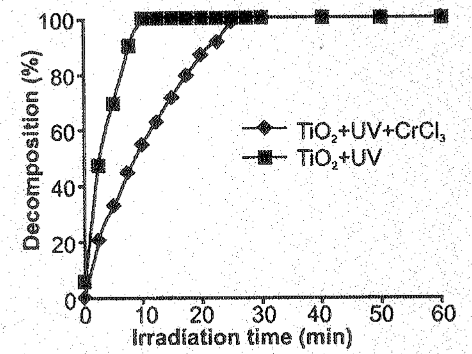


Fig. 8. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $CrCl_3$

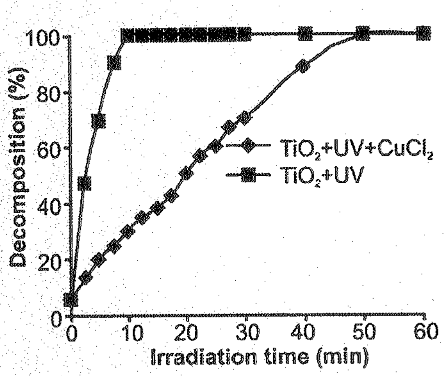


Fig. 9. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $CuCl_2$

As can be seen from Figs. 6–11, all cations decreased the degradation efficiency with increasing time of irradiation. This may be due to the fact that cations have trapped the electron-hole pair more easily than the dye molecules.

The order of cations decreasing the degradation efficiency of dye sample are as follows:

$$Ca^{2+} < K^+ < Cr^{3+} < Al^{3+} < Cu^{2+} < Sn^{4+}$$

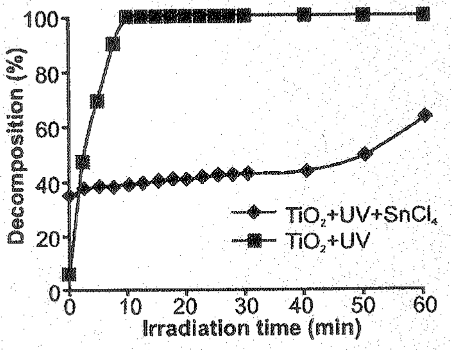


Fig. 10. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $SnCl_4$

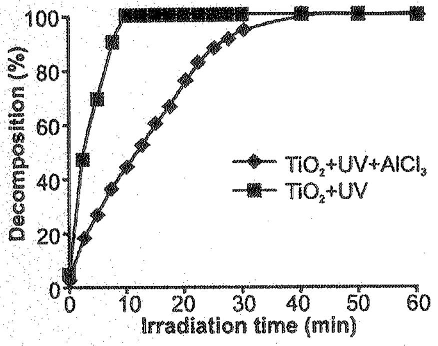


Fig. 11. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $AlCl_3$

From Fig. 10, it can be seen that addition of Sn^{4+} resulted in approximately 40% decomposition of the dye sample prior to the irradiation. This may be due to the fact that indigo carmine is more sensitive to the oxidizing reagent; therefore, even without using the UV irradiation, sample solution was decomposed and Sn^{+} reduced to Sn^{2+} after oxidation of indigo carmine. Due to the fact that Sn^{2+} is a much stronger reducing reagent (relative to indigo carmine), even after 40 min from time of irradiation, decomposition of indigo carmine was not observed.

Photocatalytic degradation of dye sample in presence of various anions: The effect of various anions on photocatalytic degradation of dye sample was also investigated and the results obtained are shown in Figs. 12 to 16.

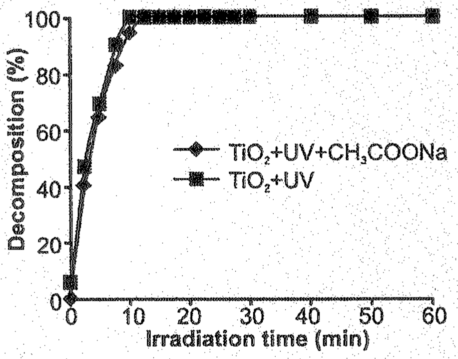


Fig. 12. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of CH_3COONa

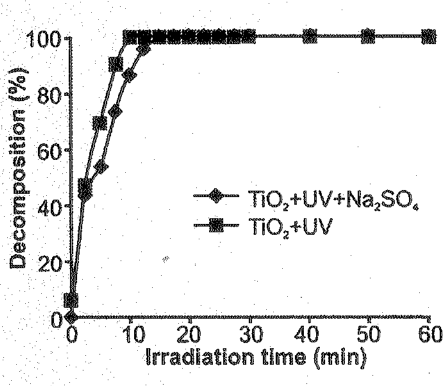


Fig. 13. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of Na_2SO_4

As can be seen from Figs. 12 and 13, the effects of CH_3COO^- and SO_4^{2-} anions on the degradation efficiency were insignificant. But when CN^- anion was added to the dye sample, the effect of TiO_2/UV system was significant in reducing the degradation efficiency (Fig. 14). This can be correlated to the CN^- anion competing with $^\circ OH$ according to the following reaction:

$$A_+^- \, {}^\circ OH \longrightarrow A_+^\circ \, {}^- OH$$

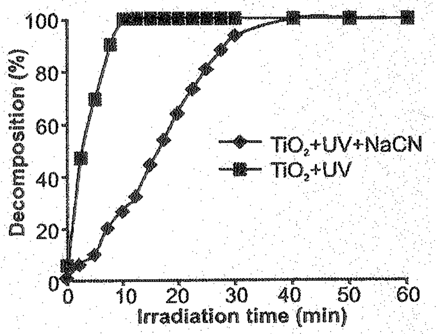


Fig. 14. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of NaCN

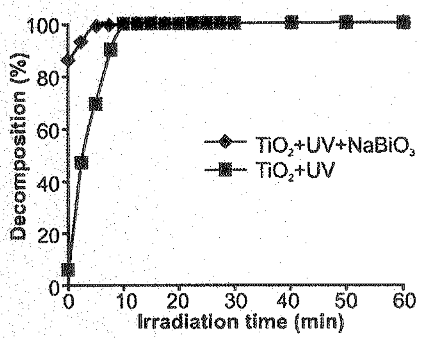


Fig. 15. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $NaBiO_3$

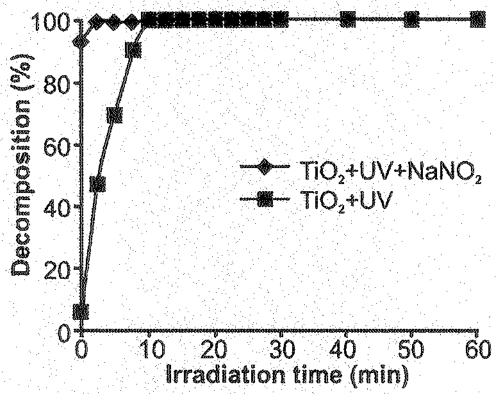


Fig. 16. The change of decomposition value (%) of indigo carmine sample with irradiation time at pH = 2 in presence of $NaNO_2$

As the reactivity of $\overset{\circ}{A}$ is thought to be less than that of OH, therefore, this may have caused the reduction of degradation efficiency. The photocatalytic degradation was also increased when BiO_3^- and NO_2^- anions were added to the dye sample solutions as shown in Figs. 15 and 16, respectively. These anions have greater oxidation activity, therefore, before the dye sample solutions were irradiated with UV light, a large amount of dye had already been decomposed and hence degradation efficiency was increased.

Conclusions

Photocatalytic degradation of indigo carmine with various parameters was investigated and the results are summarized as follows:

1. In presence of TiO_2, indigo carmine decomposed readily by a photocatalytic reaction.
2. Parameters, such as pH and the amount of photocatalyst have been found to play an important role in the degradation process. By increasing the amount of TiO_2 from 0.1 g to 0.4 g, degradation efficiency was increased, but further addition of TiO_2 had no effect on the degradation efficiency.

3. Using only UV and TiO_2 system has shown to have a negligible effect when used without the addition of catalysts.
4. Parameters such as various cations and anions have shown to play an important role in the degradation process. It was found that in acidic media all cations decreased the degradation process with different efficiency. It was also found that in acidic media all anions decreased the degradation efficiency, but the effect was more significant with CN^- anions.

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