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태양광과 UV-A 빛 하에서 ZnO을 이용한 Reactive Black 5의 광분해작용

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Photomineralisation of Reactive Black 5 with ZnO using Solar and UV-A Light

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요 약. 태양광과 UV-A빛 조건하에 수용액 속에서 디아조염료의 광 촉매분해반응에 대해 조사를 해보았다. 염료의 광 촉매 분해반응에는 염료의 농도, 촉매 량, 그리고 pH와 같은 여러 가지 영향 요소들이 존재한다. 과산화수소, ammonium persulphate와 isopropanol 등의 첨가는 분해비율에 대해 큰 영향을 미친다. Langmuir-Hinshelwood model에 근거한 광 분해반응의 동역학적분석은 광분해반응은 대략적으로 pseudo first order kinetics을 따름을 알 수 있다. 광분해산물로 이산화탄소, 질산염, sulphate 이온 등이 증명되었다. 광 촉매, ZnO는 태양광 하에서보다 UV-A빛 하에서 더욱 효율적임을 발견하였다.

주제어: 광 촉매, Reactive Black 5, 아연산화물, 동력학적 분석, UV-A빛(300-400 nm), 태양광

ABSTRACT. The photocatalytic degradation of a textile diazo dye in aqueous solution has been investigated under Solar and UV-A light. The effect of various parameters such as concentration of dye, amount of catalyst and pH on the degradation of dye has been studied. Addition of hydrogen peroxide, ammonium persulphate and isopropanol strongly influences the degradation rate. Kinetic analysis of photodegradation reveals that the degradation follows approximately pseudo first order kinetics according to the Langmuir-Hinshelwood model. Carbon dioxide, nitrate and sulphate ions have been identified as mineralisation products. The photocatalyst ZnO was found to be more efficient in UV-A light than in Solar light.

Keywords: Photocatalysis, Reactive Black 5, Zinc Oxide, Kinetic Analysis, UV-A Light (300-400 nm), Solar Light

INTRODUCTION

The reactive azo dyes are extensively used in the textile industries because of its simple dying procedure. The release of textile industry wastewater in natural environments is very problematic to aquatic life and mutagenic to human.[1,2] The semiconductor mediated heterogeneous photocatalyst has been of great importance over the last few years due to its potential to destroy a wide range of organic compounds in water and air at ambient temperature.[3-5] Heterogeneous photocatalyst uses air rather than ozone or hydrogen peroxide, which renders it a very attractive and green technology for wastewater treatment. Experimental observations indicate almost complete oxidation of most of the organic compounds to carbon dioxide via photocatalytic process. The quantitative forma-

tion of carbon dioxide is of great importance in water treatment because it provides unequivocal evidence for the total destruction of organic pollutants present in water. The other advantages of photocatalytic oxidation are (i) mild operating conditions (ii)it can be carried out using solar light, thus reducing significantly the electric power required and therefore the operating costs.

The photocatalytic degradation of Reactive Black 5 (RB 5) using TiO_2-P25 had been reported in detail.[6,7] Heterogeneous photocatalysis using semiconductors such as TiO_2, ZnO is an attractive advanced oxidation process as it has several advantages.[8,9] Though TiO_2 is the most commonly used and effective photocatalyst for a wide range of organic compounds degradation, ZnO, is also found to be a suitable alternative to TiO_2 since its photodegradation mechanism has been proven to be similar to that of TiO_2.[10] ZnO has been reported to be more efficient than TiO_2 in some of the processes such as the advanced oxidation of pulp mill bleaching wastewater,[11] the photooxidation of phenol[12] and photocatalysed oxidation of 2-phenyl phenol.[13] Furthermore the optimum pH reported for ZnO process is close to neutral, whereas the optimum pH for TiO_2 mostly lies in acidic region. Hence the ZnO process is more economical for the treatment of industrial effluents. According to Kormann *et al*,[14] the quantum yield of H_2O_2 production in illuminated aqueous suspension of ZnO was found to be one order of magnitude higher than the corresponding value for TiO_2.

Since solar light is abundantly available natural energy source, its energy can be conveniently exploited for the irradiation of semi-conducting materials. In photocatalytic process, electron-hole recombination is a major problem to circumvent. Addition of oxidants (electron acceptors) reduces electron-hole recombination and increases the degradation rate. In our laboratory we had carried out the degradation of dyes using various advanced oxidation processes.[15-20]

In the present work we have undertaken a detailed study on the photodegradation of toxic reactive azo dye RB 5 employing ZnO as a photocatalyst in aqueous solution under solar and UV light sources examining the impact of various experimental parameters. This dye was chosen because (i) it is a representative refractory chemical due to relatively high consumption rate for reactive dyeing as well as the fact that up to 50% of fiber reactive dyes remain in the exhausted dye bath as nonrecoverable hydrolyzed form (ii) its degradation using TiO_2 was previously investigated in our laboratory.

EXPERIMENTAL

Materials

The commercial azo dye RB 5 (C.I. No. 20505, Trade Name: Remazol Black 5) obtained from Jaysynth Dye Chem. Ltd., Pondicherry, India was used as such. The photocatalyst ZnO was purchased from E.Merck (99% purity), has a particle size 0.1-4 nm and surface area 10 m^2/g. Analar grade H_2O_2 (30 w/w%), $(NH_4)_2S_2O_8$ (Merck) and isopropanol (SD fine chemicals, India) were used as received. The pH of the solutions was adjusted using H_2SO_4 and NaOH. The chemical structure and absorption spectra of dye are presented in *Fig.* 1.

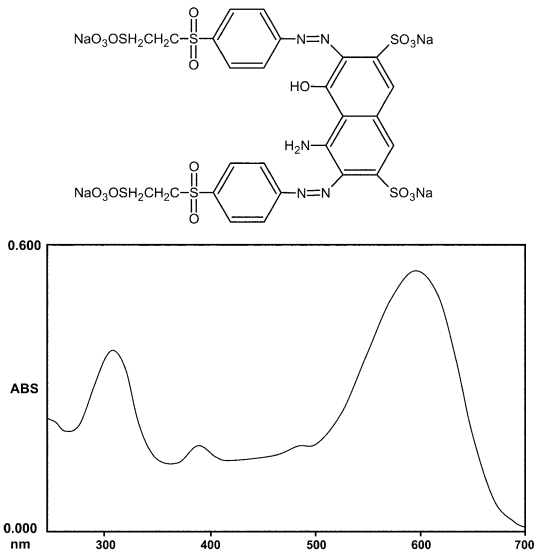

Fig. 1. The chemical structure and absorption spectra of RB 5.

Procedure

For the degradation by UV-A light (365 nm) a Heber Multilamp-photoreactor HML MP 88 was used. This model consists of eight 8W medium pressure mercury vapor lamps set in parallel and have emission maximum at 365 nm. It has a reaction chamber with specially designed reflector made of highly polished aluminium and built in cooling fan. It is provided with a magnetic stirrer and 50 ml capacity reaction glass tubes with B_{14} joints. The light exposure length is 330 mm. The irradiation was carried out using four parallel 8W medium pressure mercury lamps.

The solar experiments were carried out in the reaction tubes of 50 ml capacity and CO_2 free air was passed into the solution. The whole set up was placed in solar light between 10 AM and 2 PM. The intensity of solar light was measured using Lux meter and the intensity (1100×100 lux) was nearly constant.

Analysis

In all cases 50 ml of the RB 5 solution containing appropriate quantity of the semiconductor powder was magnetically stirred during the illumination while the solution was purged with carbon dioxide free air. At specific time intervals, 2 ml of sample was withdrawn and ZnO particles were removed by centrifugation. The change in the concentration of RB 5 was monitored from its characteristic absorption at 296 nm using UV-visible spectrophotometer. After complete mineralization, the presence of inorganic ions such as sulphate, nitrate was tested by the reported procedure.[31] The evolution of CO_2 was tested by passing the evolved gas during the reaction in to lime water.

RESULTS AND DISCUSSION

Photodegradability of RB 5

The photocatalytic degradability of RB 5 was carried out under following conditions (i) dye solution with UV and Solar light (ii) dye solution with ZnO in dark (iii) dye solution with UV light and ZnO (iv) dye solution with Solar light and ZnO. The results are shown in *Fig.* 2. Dye is resistant to self-photolysis by UV and solar light and no photodegradation was observed. In the presence of ZnO without UV irradiation, about 8.68% decrease in concentration was observed from absorbance measurements. This is due to the adsorption of dye molecule on the surface of ZnO. It was found that 99.91% degradation of dye took place in the presence of UV light whereas only 55.25% degradation occurred under solar light after 80 mins of irradiation. This reveals that the degradation of RB 5 is much faster in the presence of UV-A light as compared to solar light.

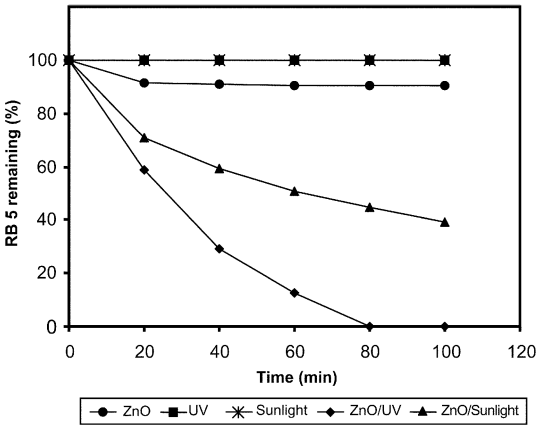

Fig. 2. Photodegradability of RB 5 [RB 5] 5×10^{-4} M; [ZnO] 2 g/L; pH 7.0 + 0.1; I 1.381×10^{-3} einstein $L^{-1}s^{-1}$; air-flow rate = 8.1 ml. s^{-1}. Error range = ±0.2%.

Effect of catalyst loading

A series of experiments were carried out to assess the optimum catalyst loading by varying the amount of catalyst from 0.5 to 4 g/L. *Fig.* 3 shows the percentage degradation of RB 5 as a function of catalyst concentration under UV-A and solar light. It is interesting to note that the percentage degradation of RB 5 under UV-A light source increases with increase in catalyst concentration from 0.5 to 2 g/L and then decreases. Similarly highest efficiency is observed at 3 g/L, which slowly decreases with further addition of catalyst under solar light. The enhancement of removal rate is due to (i) increase in the amount of catalyst

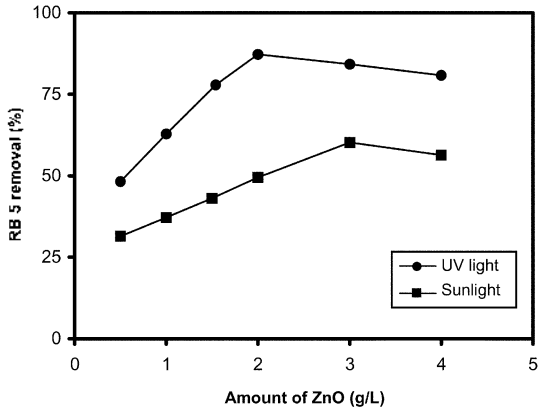

Fig. 3. Effect of catalyst loading [RB 5]=5×10^{-4} M; pH=7.0 ±0.1; irradiation time = 60 min; $I = 1.381\times10^{-5}$ einstein $L^{-1}s^{-1}$; airflow rate = 8.1 mL s^{-1}. Error range = ±0.2%.

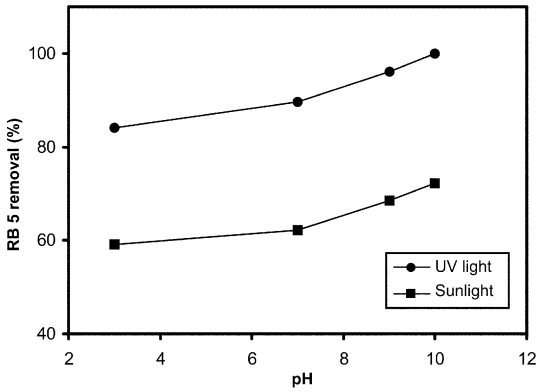

Fig. 4. Effect of solution pH [RB 5]=5×10^{-4} M; [ZnO]=2 g/L (UV), 3 g/L (Solar); irradiation time = 60 min; $I = 1.381\times10^{-5}$ einstein $L^{-1}s^{-1}$; airflow rate = 8.1 mL s^{-1}. Error range = ±0.2%.

amount, which increases the number of dye molecules adsorbed, (ii) the increase in the density of catalyst particles in the area of illumination. Higher concentration of catalyst above 3 g/L leads to decrease in the removal efficiency of RB 5 due to the enhancement of light reflectance. Similar results have been reported for the photocatalysis by TiO_2 and ZnO in the degradation of various dyes.[22,23]

Effect of solution pH

The amphoteric behavior of most semiconductor oxides influences their surface charge. The role of pH on the photocatalytic degradation of RB 5 with ZnO was studied in the pH range of 3 and 10 under UV and solar light sources. The results are shown in *Fig.* 4. In this pH range, there was no significant change in UV spectra of the dye. It is pertinent to mention here that the pH of the solution was adjusted initially before irradiation and it was not maintained throughout the reaction. It was observed that both light sources increased the removal efficiency of RB 5 with increase in pH from 3 to 10. Sakthivel *et al.*[24] had observed a similar trend in ZnO photocatalysis of acid brown 14 commenting that acid-base property of the metal oxide surfaces could have considerable implications upon their photocatalytic activity. The zero-point charge for ZnO is 9.0 and above this value, ZnO surface is negatively charged by the adsorbed OH^- ions. The presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of $OH^\bullet$ radical, which is the principal oxidizing species for the dye degradation process. Many investigators have found that textile processes using reactive dyes produce effluents with high pH, suitable for the use of ZnO as a catalyst.[23,24]

Effect of substrate concentration

It is important both from mechanistic and application point of view to study the dependence of photocatalytic degradation on the substrate concentration. Hence the effect of substrate concentration on the RB 5 degradation was studied at different concentrations such as 3, 5, 7 and 9×10^{-4} M. *Fig.* 5 shows that the increase of substrate concentration from 3 to 9×10^{-4} M decreases percentage of removal from 99.1 to 48.5% for UV light and 74.9 to 30% for solar light in 40 minutes.

The results reveal that the degradation is less in solutions of higher initial dye concentration when compared to the degradation at lower concentration. The rate of degradation relates to the probability of $^\bullet OH$ radical formation on catalyst surface and probability of $^\bullet OH$ radical reacting with dye molecule. For all initial dye concentrations, the catalyst, oxidant and UV power are same. Since

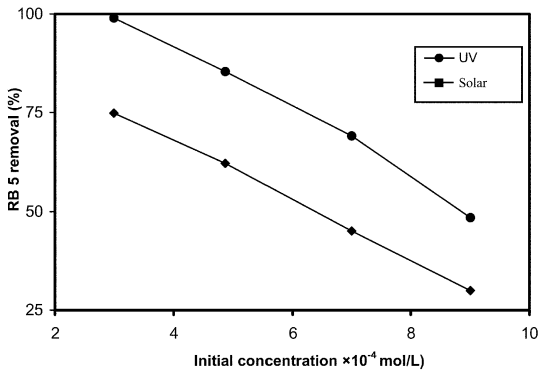

Fig. 5. Effect various initial dye concentration [ZnO]=2 g/L (UV), 3 g/L (Solar); irradiation time = 60 min; $I = 1.381\times10^{-3}$ einstein $L^{-1}s^{-1}$; airflow rate = 8.1 mL s^{-1}. Error range = ±0.2%.

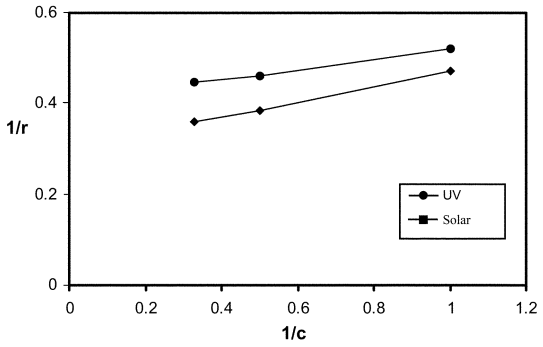

Fig. 6. Linearised reciprocal kinetic plot of the photodegradation of RB 5 [ZnO]=2 g/L (UV), 3 g/L (Solar); irradiation time = 60 min; $I = 1.381\times10^{-3}$ einstein $L^{-1}s^{-1}$; airflow rate 8.1 mL s^{-1}. Error range ±0.2%.

the generation of hydroxyl radical remains constant, the probability of dye molecule to react with hydroxyl radical decreases. At high initial dye concentrations the path length of photon entering into the solution decreases, and also the amount of dye adsorbed on catalyst surface increases. These processes affect the activity of the photocatalyst.

The influence of the initial concentration of RB 5 on the photocatalytic degradation rate of most organic compounds is described by *pseudo*-first order kinetics (eqn. 1).

$$\ln\left[\frac{C_0}{C}\right] = k't \qquad (1)$$

In this equation, k' is the *pseudo*-first order rate constant, C_0 is the equilibrium concentration of dye and C is the concentration at time't'. The eqn.1 was rationalized in terms of modified Langmuir-Hinshelwood model to accommodate reaction occurring at solid liquid interface (eqn.2).

$$r = \frac{K_1K_2[\text{Dye}]_0}{1 + K_1[\text{Dye}]_0} \qquad (2)$$

This equation can be modified as equation 3.

$$1/r = \frac{1}{K_1K_2[\text{Dye}]_0} \cdot \frac{1}{K_2} \qquad (3)$$

Where $[\text{Dye}]_0$ is the initial concentration in mol/L, K_1 is the constant related to adsorption and K_2 is to the reaction properties of dye. The applicability of L-H equation for the photodegradation has been confirmed by the linear plot obtained by plotting reciprocal of initial rate (1/r) against reciprocal of initial concentration (1/C) (*Fig.* 6). The values K_1 and K_2 are found to be 0.0165 $(mg/L)^{-1}$ and 3.168 (mg/L) m^{-1} for UV and 0.0116 $(mg/L)^{-1}$ and 2.4331 (mg/L) m^{-1} for Solar processes respectively.

Effect of oxidants

One practical problem in using semiconductor oxide as a photocatalyst is the undesired electron-hole recombination, which leads to low quantum yield. Hence the prevention of electron-hole recombination becomes very important. This can be achieved by adding oxidants such as H_2O_2 and $(NH_4)_2S_2O_8$ which can behave as electron acceptors.[25,26] Generally molecular oxygen is used as an electron acceptor in heterogeneous photocatalysed reaction. Besides the addition of molecular oxygen, the electron-hole recombination can be reduced by the addition of irreversible electron acceptors H_2O_2 and $(NH_4)_2S_2O_8$. The addition of these oxidants enhances the degradation rate by several ways (i) preventing the electron-hole recombination by accepting the conduction band electron, (ii) increasing the hydroxyl radical production, (iii) generating other oxidizing species such as $SO_4^{-\bullet}$ to accelerate the intermediate compounds oxidation rate.

The degradation percentages of RB 5 in the presence of H_2O_2 and $(NH_4)_2S_2O_8$ are shown in

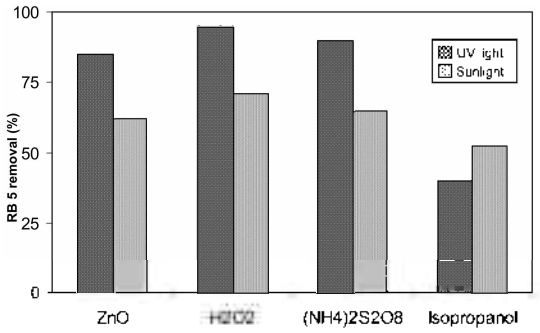

Fig. 7. Effect of oxidants and isoprpanol [RB 5]=5×10^{-4} M; [ZnO] = 2 g/l. (UV), 3 g/l. (Solar); irradiation time = 60 min; H_2O_2 = 0.05 M; $I = 1.381\times10^{-3}$ einstein $L^{-1}s^{-1}$; airflow rate = 8.1 mL s^{-1}.

Fig. 7. Both the oxidants showed a beneficial effect on the degradation of dye under UV light and solar light according to the following equations (eqns.4-8).

$$H_2O_2 + e^-_{(CB)} \longrightarrow {}^{\bullet}OH + OH^- \quad (4)$$

$$H_2O_2 \xrightarrow{h\nu} {}^{\bullet}OH + {}^{\bullet}OH \quad (5)$$

$$S_2O_8^{2-} + e^-_{(CB)} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (6)$$

$$SO_4^{\bullet} - e^-_{(CB)} \longrightarrow SO_4^{2-} \quad (7)$$

$$SO_4^{\bullet-} - H_2O \longrightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \quad (8)$$

Mechanism of photodegradation

Earlier studies on photocatalytic degradation by ZnO have indicated that the main oxidizing species involved in photodegradation are hydroxyl radicals. The positive holes and super oxide ion radical are found to play a minor role.[27,28] The results on the effects of H_2O_2 and $(NH_4)_2S_2O_8$ in this degradation also indicate that the main oxidizing species in the photocatalysis is hydroxyl radical. This is further confirmed by the effect of isopropanol on the photocatalytic degradation. The addition of isopropanol, a known hydroxyl radical quencher, decreases the photodegradation efficiency (*Fig.* 7).

Based on the experimental results and from the earlier reports on dye degradation by photocatalysis, we propose a dual hole-radical mechanism qualitatively for the photooxidation of this dye. According to this mechanism, direct h^+ oxidation of the ethyl sulphonic and sulphonic groups takes place in combination with $OH^{\bullet}$ attack of benzene and naphthalene rings. The $OH^{\bullet}$ radicals attack the azo linkage-bearing carbon atoms. The resulting $OH^{\bullet}$ breaks down to produce a substituted phenyldiazene and naphthalene radical. Phenyldiazine can be readily oxidized to phenyl radicals and nitrogen.[29] This may reduce the concentration of nitrate. The naphthalene radicals under continuous attack of $OH^{\bullet}$ and oxygen leads possibly to naphthaquinone and phthalic acid derivatives and finally to carbon dioxide.[30,31]

The formation of CO_2, sulphate ions and trace amounts of NO_3^- ions shows that there is a total destruction of organic compound in this process. So the overall equation after a long irradiation time in this process can be presented as (eqn.9&10).

$$C_{26}H_{21}O_{19}N_5S_6Na_4 + 38O_2 \longrightarrow \text{intermediates} \rightarrow 26CO_2 + 5NO_3^- + 6SO_4^{2-} + 13H^+ + 4Na^+ + 4H_2O \quad (9)$$

$$R \xrightarrow{{}^{\bullet}OH} \text{Intermediates} \longrightarrow CO_2 + NO_3^- + SO_4^{2-} + H^+ + Na^+ + H_2O \quad (10)$$

CONCLUSIONS

ZnO can efficiently photocatalyse the textile azo dye RB 5 with UV-A and Solar light as radiation sources. The investigation clearly demonstrates the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which is essential for any practical application of photocatalytic degradation process. The best degradation condition depends strongly on the kind of pollutant. Though the UV irradiation can bring better efficiency in the degradation of textile dye, solar energy can be an alternative and cost effective light source because of its abundance and non-hazardous nature.

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