Study the Photodegradation of Aniline Blue dye in Aqueous Phase by using Different Photocatalysts

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Abstract-- This study involves the photocatalytic degradation of Aniline blue (AB) dye, employing heterogeneous photocatalytic process. Photocatalytic activity of different semiconductors such as zinc oxide (ZnO), zinc sulfide (ZnS) and Tin dioxide (SnO₂) has been investigated. An attempt has been made to study the effect of process parameters through amount of catalyst, concentration of dye, pH of dye solution and temperature on photocatalytic degradation of AB solution. The experiments were carried out by varying pH (2-12), amount of catalyst (0.05–1.5 g), initial concentration of dye (25–100 ppm) and temperature range (293–323)K. The optimum catalyst dose was found to be (0.1, 0.5 g and 1) gL⁻¹ by using ZnO, ZnS and SnO₂ respectively. In the case of ZnO and SnO₂, maximum rate of photoreaction of AB solution was observed in acidic medium at pH 4, whereas the degradation of AB reached maximum at pH 5 when using ZnS catalyst. The performance of photocatalytic system employing ZnO/UV light was observed to be better than ZnS/UV and SnO₂/UV system. The complete degradation of AB was observed after 12 min with ZnO, whereas with ZnS, only 75% dye degraded and 24.5% with SnO₂ in 12 min. Photocatalytic degradation was found to increase with increasing temperature. Arrhenius plot shows that the activation energy is equal to 20.94 kJ mol⁻¹ with ZnO, 17.97 kJ mol⁻¹ with ZnS and 14.1 mol⁻¹ with SnO₂ catalyst. The thermodynamic parameters of the photodegradation of AB, like energy of activation, enthalpy of activation, entropy of activation and free energy of activation revealed the efficiency of the process.

Index Term-- Decolorization; Triphenylmethane; Aniline blue; Photocatalysis

1. INTRODUCTION

The treatments of industrial wastewater for aqueous waste effluents include different techniques such as biological treatment, reverse osmosis and activated carbon adsorption.¹ These techniques often utilize potentially hazardous or polluting materials and even most of them are non-biodegradable.² Therefore, the development of an effective treatment technique that can convert pollutants into non-toxic or less harmful materials is highly required.

Advanced oxidation processes are of ample interest currently for the effective oxidation of a wide variety of organics and dyes³. Advanced Oxidation Processes (AOP) are an attractive alternative for the treatment of contaminated ground, surface, and waste waters containing hardly-biodegradable anthropogenic substances as well as for the purification and disinfection of drinking waters⁴. Photocatalysis is a phenomenon that occurs when a reaction chain is taking place in the presence of light and solid catalyst in the solution⁵.

Photocatalyst is also called photochemical catalyst and the function is similar to the chlorophyll in the photosynthesis. In a photocatalytic system, photo-induced molecular transformation or reaction takes place at the surface of catalyst Schematic( 1). The initial step of photocatalysis is the adsorption of photons by a molecule to produce highly reactive electronically excited states. The photon needs to have energy of (hv) equal to or more than the band gap energy of the semiconductor. The energy absorbed will cause an electron to be excited from the valence band to the conduction band, leaving a positive hole in the valence band. This movement of electrons forms (e⁻/h⁺) or negatively charged electron/positively charged hole pairs. The positively charged holes in valence band are powerful oxidants, whereas the negatively charged electrons in conduction band are good reductants⁶.

Following are the reactions involving in photocatalysis:- Concerning photocatalysis with photocatalyst, electrons in conduction band (e⁻cb) and holes in the valence band (h⁺vb) are produced when the catalyst is irradiated with light energy higher than its band gap energy Ebg (hv>Ebg).

\[
\text{TiO}_2 + hv \quad (\text{UV}< 400\text{nm}) \rightarrow \text{TiO}_2 (e^-_{\text{cb}} + h^+_{\text{vb}})
\]

(1) h⁺cb + H₂O → h⁺ + HO₂⁻

(2) h⁺vb + HO₂⁻ → HO₂

(3)

Organic molecule + h⁺ → oxidation products

(4) e⁻cb + O₂ → O₂⁻

(5) O₂⁻ + h⁺ → HO₂

(6)

Organic molecule + e⁻cb → reduction products

(7) HO₂⁻ HO₂ + organic compounds → degradation products

(8)

Semiconductor compounds have drawn much attention during the last few years because of their novel optical and transport properties which have great potential for many optoelectronic applications.⁷
Among the listed semiconductors, TiO₂ has proven to be the most suitable for widespread environmental applications. ZnO also seems to be a suitable photocatalyst but it dissolves in acidic solutions it is a semiconductor material for various photonic and electrical applications. ZnO shows a unique set of physical and chemical properties, such as a wide band gap (3.2 eV), large exaction binding energy (60 meV) at room temperature, radiation hardess(9). Tin dioxide (SnO₂) is a n-type semiconductor with a large band gap (Eg = 3.9 eV ) which shows promise for a number of applications including transparent conductors. Zinc sulfide (ZnS) is a wide band gap and direct transition semiconductor(10). Zinc sulfide is an important semiconductor material with a wide direct band gap Eₙ = 3.68 eV (10).

Dyes are typically organic compounds that absorb light in specific areas of the visible spectrum. Aniline Blue dye it is water soluble dye (11), it is used for dyeing wool and cotton directly and widely used in dye industries therefore its presence in the industrial discharge water also contributes to environmental pollution (12). Due to its stability , it has long residence time in water. (13) Molecular structure of Aniline Blue has been illustrated in Fig. 1. Aniline Blue, also called acid blue 22, china blue, soluble blue 3M, and Marine blue. It is very soluble in water,  

![Fig. 1. structure of Aniline Blue dye](image)

Aniline Blue dye is a acidic dye belongs to triphenyl methane class of dye (15). Triphenylmethane dyes are those dyes in which a central carbon atom is bonded to two benzene rings and one p-quinoind group (chromophore)(16). The auxochromes are - NH₂, NR₂ and -OH(17). Triphenylmethane dyes are used extensively in the textile industries for dyeing of nylon, polyacrylonitrile, modified nylon, wool, silk and cotton.

In recent years, problem of wastewater became very important both for the sake of increasing amount and its variety . Removing color from waters is often more important than other colorless organic substances, because the presence of small amounts of dyes is clearly visible and influence the water environment considerably. This work reports an investigation of the photocatalytic degradation of aniline blue dye using different types of catalyst ZnO, SnO₂, and ZnS. The effect of different parameters was studied to estimate the best condition for degradation of aniline blue dye; and these parameters were the amount of catalyst, dye concentration, pH of dye solution and temperature of reaction and this is to prevent the expansion of colored pollution in our environments.

2. EXPERIMENTAL

A homemade photoreactor equipped with a Philips 250W, medium pressure mercury lamp as a source for UV radiation, was used to determine P.D.E. The reactor was consisted of graduated 1000 cm² Pyrex glass beaker and a magnetic stirring setup. The lamp was positioned perpendicularly above the beaker. The distance between the lamp and the graduated Pyrex glass was 15 cm. The whole photocatalytic reactor was insulated in a wooden box to prevent the escape of harmful radiation and minimized temperature fluctuations caused by draughts.

Zinc oxide with 99% purity were supplied by Fluka-Garantie, Zinc sulfide with 99.3% purity supplied by M.B.LTD Dagenham and Tin dioxide SnO₂ with 99% purity was supplied by Fluka-Garantie . Aniline blue dye (analytical grade) was purchased from (RDS-Hannover) and used without further purification. Solutions were prepared using double distilled water. In all experiments, the required amount of the catalyst was suspended in 200 cm³ of aqueous solutions of AB, using a magnetic stirrer. At predetermined times; 5 cm³ of reaction mixture was collected and centrifuged (3000 rpm, 15 min) in centrifuge. The supernatant was carefully removed by a syringe with a long pliable needle and centrifuged again at same speed and for the same period of time. This second centrifugation was found necessary to remove fine particles of catalysts. After the second centrifugation the absorbance at (309, 586) nm of the supernants was determined using ultraviolet-visible spectrophotometer, type UV-1650pc.

P.D.E. of AB was followed spectrophotometrically by a comparison of the absorbance, at specified interval times, with a calibration curve accomplished by measuring the absorbance, at λₘₐₓ (586) nm, with different concentrations of the dye solution.

\[
\%\text{Decolorization} = 100 \times \frac{(C₀ - C)/C₀}{100}
\]

where \( C₀ \) = initial concentration of dye solution, \( C \) = concentration of dye solution after photoirradiation. In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration from 0.05 to 1.5 g for dye solutions of 100ppm at natural pH (5.57). Similar experiments were carried out by varying the pH of the solution pH( 2–12) and concentration of dye(25,50,75,100) ppm. the reaction temperatures amounted to (293- 323)K.

3. RESULTS AND DISCUSSION

3.1. UV–vis spectra of dye

Results of the present study clearly show that the photocatalytic treatment of aqueous solution of aniline blue under UV light, leads to decolorization and degradation of dye. Figs.2 to 4 shows the typical time dependent UV-Vis spectrum of AB solution during photoirradiation with ZnO, ZnS andSnO₂ respectively. The rate of degradation was recorded with respect to the change in the intensity of absorption peak in ultraviolet region and visible region. The prominent peaks were observed at λₘₐₓ (586) nm which decreased gradually and finally disappeared indicating (18) that the dye had been degraded.
Fig. 2. Time dependent UV-Vis absorption spectra for degradation of aniline blue dye (100ppm) (0.1g) ZnO catalyst, time(min).

Fig. 3. Time dependent UV-Vis absorption spectra for degradation of aniline blue dye (100ppm) (0.5g) ZnS catalyst, time(min).

Fig. 4. Time dependent UV-Vis absorption spectra for degradation of aniline blue dye (100ppm) (1.0g) SnO_2 catalyst, time(hours).

Fig. 5. The change of P.D.E with irradiation time of different types of catalyst.

3.2 Degradation of AB solution Under Different Experimental Conditions

Degradation of AB solution was investigated under seven different experimental conditions through UV alone, UV + ZnS, UV + ZnO, UV + SnO_2, Dark + ZnS, Dark + ZnO and Dark + SnO_2. Fig. 6 depicts the photocatalytic degradation of AB solution under these experimental conditions. Initially blank experiments were performed under UV irradiation without addition of any catalyst (UV alone) and only 10% degradation was observed after 60min.

Thereafter the adsorption of the dye was observed with both catalysts, i.e., Dark + ZnS, Dark + SnO_2 and Dark + ZnO. Only 14.3%, 32% and 7.7% respectively adsorption of the dye was seen in the same time with both catalysts under dark conditions. Then photocatalytic experiments were carried out using all catalysts at fixed dye concentration (100ppm) and catalyst amount of 0.1g of ZnO, 0.5g of ZnS and 1g of SnO_2. When experiments were performed under UV irradiation with ZnO as photocatalyst (UV + ZnO), the complete degradation of dye was achieved after 12 min, whereas with ZnS as a photocatalyst (UV + ZnS), only 75%
Decolorization of AB solution was observed and only 24.3% byusing SnO2 in the same duration. It indicates that ZnO exhibits higher photocatalytic activity than other semiconductors for the decolorization of AB dye.

3.3 Degradation of Dye by ZnO, SnO2 and ZnS as photocatalysts

The experiments were carried out to study the degradation of AB solution employing ZnO, ZnS, SnO2 as catalysts under UV light. Various parameters which affect the degradation efficiency such as catalyst loading (0.05 – 1.5) g, pH (2-8), initial concentration of dye (25 – 100) ppm, and temperature (293-323)K of degradation were assessed under UV light.

3.3.1 Effect of Catalyst weight

Fig. 8 shows the effect of ZnO, ZnS and SnO2 catalyst amount on the degradation of AB solution at natural pH. It can be seen that initial slopes of the curves increase greatly by increasing catalyst weight from 0.05 to 0.1 g for ZnO, to 0.5g for ZnS, and to 1g for SnO2 thereafter the rate of degradation remains constant or decreases. Further increase in the dose of catalyst had no effect on degradation of dye. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface(18). At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases(24). Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering(25).

Fig. 7. Effect of ZnO, ZnS and SnO2 dose on degradation efficient of AB dye (at natural pH(5.57), and initial concentration of dye 100ppm),after (12min)

3.3.2 Effect of pH

Wastewater containing dyes is discharged at different pH; therefore it is important to study the role of pH on degradation of dye. In order to study the effect of pH on the degradation efficiency, experiments were carried out at various pH values, ranging from 2 to 12 for constant dye concentration (100) ppm and catalyst weight (0.1, 0.5 and 1 g for ZnO, ZnS and SnO2, respectively). Fig.8 shows the photodegradation efficiency of AB solution as a function of pH. It has been observed that by using ZnO and SnO2, the degradation efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 7. In the case of ZnS, the maximum degradation was observed at pH 5. Similar behavior has also been reported for the photocatalytic efficiency of ZnS for decolorization of acid dyes. The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task, because of its multiple roles. First, it is related to the acid base property of the metal oxide surface and can be explained on the basis of zero point charge(26). The adsorption of water molecules at sacrificial metal sites is followed by the dissociation of OH− charge groups, leading to coverage with chemically equivalent metal hydroxyl groups (M-OH)(27). Due to amphoteric behavior of most metal hydroxides, the following two equilibrium reactions are considered (Eqs. 9 and 10).

\[ M\cdot OH + H^+ \rightarrow M\cdot OH_2^+ \]  
\[ M\cdot OH \rightarrow M\cdot O^- + H^+ \]  

The zero point charge (zpc) for ZnO is 9 and 6.7 for ZnS, SnO2, surface is positively charged below this point and above this pH, surface is negatively charged by adsorbed OH ions(28). Photocatalytic activity of anionic dyes (mainly sulfonated dyes) such as AB dye reaches a maximum value in lower zero point charge. At pH > zpc, the surface is positively charged and the dye is anion(29). The experimental results revealed that higher degradation of AB solution was found to be in acidic conditions. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support(30).

3.3.3 Effect of Concentration of Dye

After optimizing the pH conditions and catalyst dose (pH 4 and catalyst dose 0.1 g for ZnO, pH 5 and catalyst dose 0.5 g for ZnS, pH 4 and catalyst dose 1 g for SnO2), the photocatalytic degradation of dye was carried out by varying the initial concentrations of the dye (25-100) ppm in order to assess the appropriate amount of catalyst dose. As the concentration of the dye was increased, the rate of photoreaction decreased indicating for either to increase the catalyst dose or time span for the complete removal. Fig.9 depicts the time-dependent graphs of degradation of AB dye.

Fig. 8. Effect of pH on degradation rate of AB dye (ZnO dose—0.1 g, ZnS dose—0.5 g and 1.0gSnO2 , dye initial concentration100ppm).

The zero point charge (zpc) for ZnO is 9 and 6.7 for ZnS, SnO2, surface is positively charged below this point and above this pH, surface is negatively charged by adsorbed OH ions(28). Photocatalytic activity of anionic dyes (mainly sulfonated dyes) such as AB dye reaches a maximum value in lower zero point charge. At pH > zpc, the surface is positively charged and the dye is anion(29). The experimental results revealed that higher degradation of AB solution was found to be in acidic conditions. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support(30).

Fig. 9.
solution at different concentrations of dye. The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration[31,32].

3.3.4 Effect of temperature:

The photocatalytic degradation was studied at various temperatures in the range (293–323)K and rate constant, $k$, was determined from the first-order plots. An increase in temperature helps the reaction to compete more efficiently with $e^-/H^+$ recombination[33]. The energy of activation, $E_a$, was calculated from the Arrhenius plot of $\ln k$ vs. $1/T$ (figure 10). Arrhenius plot shows that the activation energy for photocatalytic degradation of AB solution is equal to (20±1.17±1 and14±1) kJ mol$^{-1}$ by using ZnO, ZnS and SnO$_2$ respectively. The experimental activation energy was associated with the energy required to promote photoelectron from trapping centers into tin dioxide conduction band. the present value probably arises from the surface area and the purity of catalysts[34].

![Fig. 9. Effect of initial concentration of AB dye on photodegradation efficiency when using (ZnO dose 0.1g, pH 4, ZnS dose 0.5g and 1.0g SnO$_2$, pH 5.57)](image)

The other thermodynamic parameters such as Enthalpy of activation $\Delta H^\circ$, entropy of activation $\Delta S^\circ$ and free energy of activation $\Delta G^\circ$ were calculated from equations[29]:

$$\ln A = \ln B + \frac{\Delta S^0}{R}$$

(11)

$\ln A$= intercept

$K_B$: Boltzmann constant = 1.38066 10$^{-23}$ J K$^{-1}$

$R$: universal gas constant = 8.31441 J mol$^{-1}$K$^{-1}$

$h$: Planck constant = 6.6262 10$^{-34}$ J s

The Enthalpy of activation ($\Delta H^\circ$) was calculated from equation[35]:

$$\Delta H^\circ = E_a - RT$$

(12)

The free energy of activation($\Delta G^\circ$) was calculated from equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

(13)

The positive $\Delta H^\circ$ refer to endothermic reaction, the positive $\Delta G^\circ$ obtained indicate that the reaction is non spontaneous. Fairly high positive $\Delta H^\circ$ and $\Delta G^\circ$ this could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicals which is also supported by negative entropy of activation. In the present case the value of $\Delta S^\circ$ is negative as in Tables 1, 2 and 3, so that the complex formed is more ordered than the reactants. Initially the complex formed is unstable and degradation of the reactants into products is not very slow, but takes place rapidly under present experimental conditions[36].

![Fig. 10. Arrhenius plot for photocatalytic degradation of AB on ZnO, ZnS and SnO$_2$ catalysts.](image)
3.3.5 Kinetic Study

Figure 11 show the kinetics of disappearance of AB for an initial concentration of 100ppm under optimized conditions. The results show that the photocatalytic degradation of dye in aqueous ZnO, ZnS and SnO2 can be described by the first-order kinetic according to the Langmuir–Hinshelwood model \(^{(37,39)}\). In \((C/C_0) =ekt\), where \(C_0\) is the initial concentration and \(C\) is the concentration at any time, \(t\). The semi-logarithmic plots of the concentration data gave a straight line. The rate constants were calculated to be (0.338232, 0.165280 and 0.017087) \(min^{-1}\) for ZnO, ZnS, and SnO2 respectively.

4. Conclusion

The results of this study demonstrate that comparison of photocatalytic activity of different semiconductors has clearly indicated that the ZnO is the most active photocatalyst for degradation of aniline blue dye solution. Moreover, photocatalytic activity of ZnO is greater in the presence of UV light. The initial rate of photodegradation increased with the increase of the catalyst dose up to an optimum loading. Increasing weights of catalysts is attributed to the increase of the availability of photocatalysts sites further increase in catalyst dose showed no effect. As the initial concentration of dyes was increased, the rate of degradation decreased in dye due to the decrease of the concentration OH adsorbed on catalyst surface. The increasing of dye concentration increases the competitions between OH and dye to adsorb on active site of catalyst.

Photocatalytic activity of anionic dyes (AB) reaches a maximum value in lower zero point charge. At pH > zpc, the surface is positively charged and repels \(R-SO_3^-\) ions.

The photocatalytic decolorization and degradation followed pseudo-first order kinetics according to the Langmuir–Hinshelwood model.

The temperature is the factor that has the smallest effect on the photocatalytic degradation of AB solution. \(E_a\), which
was found to be smaller than 40 kJ mol\(^{-1}\). The results illustrate the decoloration of AB dye is mainly physical interaction. The thermodynamic parameters of the degradation of AB solution have been reported. The positive \(\Delta H^\#\) refer to endothermic reaction, the positive \(\Delta G^\#\) obtained indicate that the reaction is non spontaneous. Fairly high positive \(\Delta H^\#\) and \(\Delta G^\#\) this could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicals which is also supported by negative entropy of activation. Initially the complex formed is unstable and degradation of the reactants into products is not very slow, but takes place rapidly under present experimental conditions. The controlled experimental indicates that the presence of UV light, and catalyst are essential for the effective destruction of aniline blue solution.

Future research is needed for the development of more efficient catalysts for harnessing solar energy which are low cost and effective. Designing of reactors and solar collectors for photocatalytic treatment needs to be developed so that they can be used by both small and large scale textile industries in combination with the existing technology ultimately leading to recycling of water as large amount of water is utilized in textile industry.

5. SUGGESTED MECHANISM

Fig. 13. Suggested mechanism of photodegradation of Aniline blue dye.

**REFERENCE**


