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Photo Catalytic Degradation of Azure A Using Nanoscale ZNO in the Presence of Visible and Solar Light Radiations

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Abstract:

Heterogenous photocatalytic oxidation is an effective method to remove low concentrations of organic dyes. The present work incorporates the study of efficiency of ZnO for photocatalytic degradation of Azure A dye. The disappearance of the dye has been monitored spectrophotometrically, followed pseudo-first order kinetics, according to Langmuir-Hinshelwood model. The effect of some factors such as catalyst dose, concentration of salt and pH etc., on degradation of the dye was examined. 95% of dye was degraded by the ZnO upon exposure to solar and visible light irradiation for 90 min. The reduction in COD values and increase in CO_2 values indicates the complete mineralization of Azure A dye.

Key words: Advanced oxidation technologies (AOTs), Destruction of organic dyes, Hydrogen peroxide and hydroxyl radical

Introduction:

The oxidative decolorization techniques of dye have several limitations, e.g., biological oxidation, oxidation with H_2O_2 take a long time for the effluent to reach the required standards and produce a large quantity of sludge, which normally cannot be reused and oxidation with ozone is costly[(1)].

Advanced oxidation processes (AOPs) have been attracting substantial interest due to it's effectiveness and sustainability in the long term [(2)]. Advanced oxidation processes (AOPs) involves the generation of highly reactive hydroxyl radicals (HO•) [(3)] at near ambient temperature and pressure.

In the phenothiazine class of dyes an atom of sulphur replacing oxygen in the heterocyclic ring. These dyes have phenazonium nucleus as chromophore with amino group's para to the ring nitrogen as auxochromes. They have color range from green to blue and have been used for coloring paper, tannin mordant cotton and silk. Fastness to light is usually only fair. Azure A is a type of of phenothiazine class

Kinetics of photocatalytic degradation of dyes:

Langmuir-Hinshelwood theory is the most commonly used kinetic model for describing photocatalytic behaviors. In Langmuir–Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics.

The values of order of reaction and rate constant have been calculated to find the net degradation rate of selected dyes. However, for the simplification of analysis, it is assumed that there is a rate-determining step within all the reactions and k represents the rate constant of this slowest one.

Materials used:

Azure A solution: Stock solution of Azure A 1.0 × 10-3 mol dm-3 was prepared by dissolving 0.0291 gm of Azure A in 100 ml double distilled water.

Sodiuum carbonate saolution: Stock solution of Na2CO3 1.0 × 10-2 mol dm-3 was prepared by dissolving 0.106 g of Na2CO3 in 100 mL distilled water.

Sodium chloride solution: Stock solution of NaCl 1.0 × 10-2 mol dm-3 was prepared by dissolving 0. 058 g of NaCl in 100 mL distilled water.

Photoreactor design for experiment:

The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor. The pyrex glass vessel equipped with magnetic stirrer was surrounded by thermostatic water circulation arrangement to keep temperature in the range of 30±0.30C. The irradiation was carried out using 500 W halogen lamps (Philips India) surrounded with aluminum reflectors in order to avoid loss of irradiation. Decolorization was studied by spectrophotometrically. Beer's law was valid for the measurement under the experimental conditions considered. No apparent interference from the other reagents, intermediates or products had been noticed. Experiments were performed at room temperature, with a constant lamp power of 500 W and a fixed distance between the photoreactor and the lamp housing (50 cm). Experimental conditions that directly affect the degradation of dyes through photocatalytic oxidation processes include the initial concentration of dyes, light intensity, amount of photocatalyst, effect of NaCl, and Na_2CO_3 on the rate of reaction, effect of pH and effect of temperature on degradation rate. Standard analytical methods for identification of mineralized products were used.

Kinetics of photocatalytic degradation of Azure A

The photocatalytic degradation of Azure A dye followed pseudo first order kinetics. The detection was realized at 600 nm. The results for typical run are given in Fig. 1. The absorbance of Azure A dye decreased with an increase in irradiation time. The plot of log absorbance versus time followed pseudo first order kinetics with correlation co-efficient of 0.98, rate constant of 2.53×10^{-4} s^{-1} and half life time of 2.73×10^{3} s.

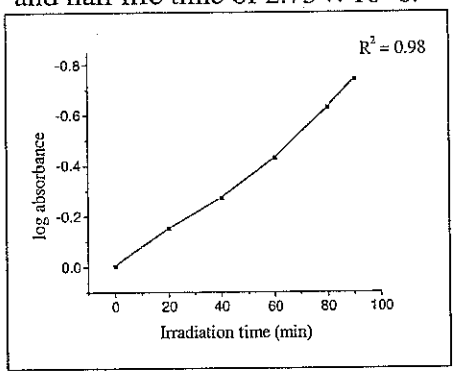

Fig. 1: Pseudo first order kinetics: [Azure A] = 5.0×10^{-5} mol dm^{-3}, pH = 8.0
ZnO = 200 mg/100 mL, Light intensity = 27×10^{3} lux
Temperature = 30 ± 0.3 ^{0}C.

Result and Discussion

Effect of Catalyst loading:

The observation indicated that beyond the optimum catalyst concentration, other factors affect the degradation of dyes. It is clear that the rate of degradation did not increase linearly with the increase in the amount of the catalyst in the reactor, and that a limiting rate was achieved when high amounts of ZnO are used (Table 1). This could be explained on the

fact that when low amount of ZnO was used, the rate of reaction on the ZnO surface area was limited and the reaction rate was proportional to the amount of ZnO particles. The attainment of limiting value and further decreased in the reaction rate with increase in the amount of catalyst might be due to (i) aggregation of ZnO particles at high concentrations causing decrease in the number of surface active sites and (ii) increase in opacity and light scattering of ZnO particles at high concentration leading to decrease in the passage of irradiation through the sample [4].

Table 1: Effect of catalyst loading: [Azure A] = 5.0×10^{-5} mol dm^{-3}, pH = 10.0
ZnO = 200 mg /100 mL, Light intensity = 27×10^{3} lux
Temperature = 30± 0.3 ^{0}C.

ZnO mg /100mL	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^{3}$ s
50	1.07	6.47
100	1.52	4.55
150	2.1	3.30
200	2.53	2.73
250	1.81	3.28
300	1.45	4.88

Effect of dye concentration:

The rate constant (k) for the degradation of Azure A first increased from 1.91×10^{-4} s^{-1} to 2.53×10^{-4} s^{-1} with the increase in substrate concentration and reached to highest efficiency at the concentration of 5.0×10^{-5} mol dm^{-3}. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of ZnO [5]. The degradation rate at this concentration reached more than double its value in comparison to the 1.0×10^{-5} mol dm^{-3} concentration. Table 2 shows that the further increase of the concentration, ZnO produced no significant improvement in the degradation rate and this phenomenon has three possible explanations [6]: (i) First, a significant quantity of visible light may be absorbed by the highly concentrated dye molecules rather than by the ZnO particles, thereby reducing decolorization efficiency. The dye therefore has a visible light-screening effect, fewer photons reach the ZnO surface as dye concentration increases, slowing the formation of OH radicals. (ii) Second, as the initial concentration of dye increased, the ZnO surfaces adsorbed additional dye molecules, which inhibited direct contact between the dye molecules and photogenerated holes and which also suppressed the generation of hydroxyl radicals at the ZnO surface as dye molecules covered active surface sites. (iii) Third, the increased amounts of dye and reaction intermediates competed with both hydroxyl radicals and active reaction sites at the ZnO surface. Hence, the fraction of hydroxyl radicals that attacked the dye molecules and its reaction intermediates declined as the dye concentration increased. In contrast, considering the Beer–Lambert law, as the initial dye concentration increased, the path length of the photons entering the solution decreased, resulting in lower photon absorption on catalyst particles and accordingly lower photodegradation rate [7-10].

Table 2: Effect of dye concentration: [Azure A] = 5.0 × 10-5 mol dm-3, pH = 10.0

ZnO = 200 mg/100 mL, Irradiation intensity = 27 × 103 lux
Temperature = 30± 0.3 0C.

[Azure A] × 10^{-5} mol dm^{-3}	k × 10^{-4} s^{-1}	$t_{1/2}$ × 10^{3} s
1.0	1.91	3.62
3.0	2.12	3.26
5.0	2.53	2.73
7.0	2.01	3.44
9.0	1.65	4.20

Role of pH:

The deradation efficiency increased from 1.30 × 10^{-4} s^{-1} to 2.53 × 10^{-4} s^{-1} with increase in pH from 5.0 to 10.0 (Table 3). At high pH values adsorb OH^- ions on the surface of the photocatalyst particles act as efficient traps for the photogenerated holes [11]. On further increasing the pH value, the rate constant decreased up to 1.92 × 10^{-4} s^{-1}. On increasing the pH above 5, the increased in reaction rate may be due to the preferential adsorption of H^+ ions on the photocatalyst surface as compared to the cationic dye molecule. In the high basic medium, the rate of degradation was found to decrease due to competition between the OH^- groups to attach to the active site of catalyst. The rate of attachment of OH^- groups thus decreases with a resultant decrease in formation of $^{\bullet}OH$ free radicals decreased. [12]

Table 3: Effect of pH: [Azure A] = 5.0 × 10-5 mol dm-3, ZnO = 200 mg/100 mL
Light intensity = 27 × 103 lux, Temperature = 30± 0.3 0C.

pH	k × 10^{-4} s^{-1}	$t_{1/2}$ × 10^{3} s
5	1.30	5.33
6	1.54	4.50
7	1.92	3.60
8	2.13	3.25
9	2.22	3.12
10	2.53	2.73
11	2.11	3.28
12	1.92	3.60

Effect of NaCl and Na_2CO_3:

The effect of addition Na_2CO_3 on the photocatalytic degradation of Azure A is shown in Table 4. The degradation percentage of the dye gradually decreased from 2.53 × 10^{-4} s^{-1} to 1.03 × 10^{-4} s^{-1} with increasing carbonate ion concentration. This is due to the hydroxyl scavenging property of carbonate ion.The free hydroxyl radical which is a primary source for the photocatalytic degradation decreases gradually with increase in the carbonate ion concentration resulting in the ultimate decrease in the percentage degradation of the dye significantly. Similarly, the results of the studies carried out with the addition of NaCl revealed that the degradation percentage of the dye decreased from 2.53 × 10^{-4} s^{-1} to 1.07 × 10^{-4} s^{-1} with increase in the amount of chloride ion.

Table 4: Effect of salt: [Azure A] = 5.0 × 10-5 mol dm-3, pH = 10.0
ZnO = 200 mg/100 mL, Irradiation intensity = 27 × 103 lux
Temperature = 30± 0.3 0C.

[Salt] × 10^{-5} mol dm^{-3}	NaCl		Na_2CO_3	
	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s
0.0	2.53	2.73	2.53	2.73
1.0	2.32	2.98	2.17	3.19
3.0	2.11	3.28	2.01	3.44
5.0	1.76	3.93	1.65	4.20
7.0	1.43	4.84	1.33	5.21
9.0	1.30	5.33	1.20	5.77
11.0	1.07	6.47	1.03	6.72

Effect of light intensity:

The rate constant values found to be increased from 1.60×10^{-4} s^{-1} to 3.80×10^{-4} s^{-1} on increasing light intensity from 10×10^3 lux to 36×10^3 lux. This was because at higher intensity electron hole separation competes with electron hole recombination and resulted high reaction rate [13,14]. The effect of light intensity and rate constant on photo catalytic degradation showed in Table 5.

A linear dependence would be expected at low light intensities. It was reported that the change in kinetic constant is a function of the square root of the radiation entering at high light intensities, while this change can be linear with light intensity of incident radiation low light intensities. The effect of light intensity on the kinetics of the photocatalytic degradation of dye as follows:(i) At low light intensities (0–20 mW/cm^2), the rate of photocatalytic degradation is proportional directly with light intensity (first order).(ii) At high light intensities (25 mW/cm^2), the rate of photocatalytic degradation is proportional directly with the square root of the light intensity (half order) (iii) At high light intensities the rate of photocatalytic degradation is independent of light intensity (zero order) [15-19].

Table 5: Effect of light intensity: [Azure A] = 5.0 × 10-5 mol dm-3, pH = 10.0
ZnO = 200 mg/100 mL, Temperature = 30± 0.3 0C.

Light intensity × 10^3 lux	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s
10	1.60	4.33
19	2.0	3.46
24	2.31	3.0
27	2.53	2.73
32	3.23	2.14
36	3.80	1.82

Effect of temperature:

The rate constant increased from 2.53 × 10^{-4} s^{-1} to 3.12 to 10^{-4} s^{-1} with increase in temperature from 30-40 ^{0}C (Table 6). High temperatures may have a negative impact on the concentration of dissolved oxygen in the solution and consequently, the recombination of holes and electrons increases at the surface of photocatalyst [20].

Table 6: Effect of temperature: [Azure A] = 5.0 × 10-5 mol dm-3, pH = 10.0
ZnO = 200 mg/ 100 mL, Light intensity = 27 × 103 lux.

Temperature (^{0}C)	k × 10^{-4} s^{-1}	$t_{1/2}$ × 10^3 s
30	2.53	2.73
35	2.70	2.56
40	3.12	2.22
45	2.50	3.23
50	2.11	3.28
55	1.67	4.14

Chemical oxygen demand (COD) and free CO_2 measurement during photo degradation process:

The dyes are not directly mineralized, but transformed in intermediate photoproducts. These generated photoproducts may submit other cycles of degradation to complete total mineralization. The photodegradation is precursor to the mineralization in most of the AOPs. COD and free CO_2 measurement were carried out to record the extent of mineralization of the organic molecule under consideration over ZnO suspension, COD test allowed the measurements of waste in terms of the total quantity of oxygen required for the degradation of organic matter to CO_2 and inorganic ions. After 8 hours of irradiation, COD values decreased from 360 mg/L to 4.5 mg/L, while there was an increased in CO_2 values and inorganic ions (Table 7). An increase in conductivity of solution was observed with increase in the extent of degradation.

Table 7: COD and free CO_2 measurement during photodegradation process:
[Azure A] = 5 × 10^{-5} mol, ZnO = 200 mg/100 ml, pH = 10.0
Light intensity = 27 × 10^3 lux, Temperature = 30± 0.3 ^{0}C.

Time (h)	COD (mg/L)	CO_2 (mg/L)	Efficiency (%)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Conductivity (mS/cm)
0	360	12.5	0	0	0	0.140
1	322	24	10	5	2.4	0.143
2	267	44.4	25	11.3	4.3	0.156
3	200	68.5	44	14.5	9.4	0.189
4	156	89.5	56	18	13.0	0.234
5	82	134	77	18.3	13.6	0.346
6	45	155	87	19.0	16.2	0.378
7	16	179.4	95	23.8	21.4	0.432
8	4.5	230.5	98	30.4	25.6	0.478

Conclusion:

The organic dye degradation kinetics by ZnO suspension was experimentally studied. The findings suggested that various operating parameters such as amount of photocatalyst, reaction temperature, visible light intensity, amount of catalyst, initial pH of the reaction medium,

chloride and carbonate ions etc. could significantly influence the photocatalytic degradation rate of Azure A. According to the experimental resultsit is revealed that the degradation rate was function of pH of the system. The degradation rate is much faster at alkaline pH. The lowering of the degradation rate at high pH levels can be explained by the adsorption-desorption effect. It is also evident that the effect of photodegradation efficiency and decolorization reaction became faster when increased with an increase in the amount of photo catalyst was increased and the results indicated that initial rate of photodegradation increased with increase in catalyst dose up to an optimum loading, when the ZnO dosage was further increased, a shielding effect of excess particles occurred and resulted in a reduced performance. The enhancement of degradation efficiency of dyes with increasing light intensity was attributed to there being more light energy to be used for the photo catalytic degradation. The reduction in COD values and increase in CO_2 values indicates the photodegradation of treated dye solution. The reduction in the estimated COD value and increase in CO_2 value indicated the photodegradation of treated dye solution. A decrease in pH value and increase in conductivity of solution was observed with increase in the extent of mineralization. The peaks in the UV region at got decreased with the passage of time, thereby confirming the complete mineralization of the dye. This has been concluded that heterogeneous photocatalysis can be used as an efficient and environmental friendly technique for effluent treatment of industrial wastewater containing organic compounds and dyes from textile industry.

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