

ZnO-Assisted Photocatalytic Degradation of Congo Red and Benzopurpurine 4B in Aqueous Solution

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Abstract

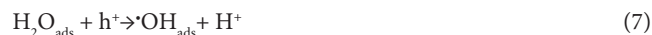
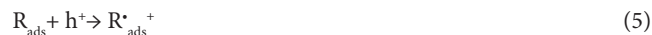
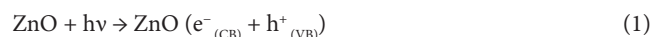
The photocatalytic degradation of two commercial azo dyes Congo red (CR) and Benzopurpurine 4B (BP4B) in aqueous solution was investigated under UV-A light at different operating conditions, including irradiation time, pH solution, initial dye concentration, amount of catalyst, light intensity as well as band gap of other semiconductor groups by UV-spectrophotometric monitoring. The highest decomposition were obtained at pH 8 as a result of 95.02 and 97.24 % degradation efficiencies of CR and BP4B for 60 and 80min of irradiation time respectively. Photodecomposition reactions of both dyes were correlated with pseudo-first-order kinetic model. For BP4B, the degradation data were satisfactory described by Langmuir-Hinshelwood (L-H) mechanism, whereas those of CR were not sufficient to conclude that the L-H mechanism is the most suitable one to describe the photocatalytic process of CR. These findings can support the design of remediation processes and also assist in predict their fate in the environment.

Keywords: Photocatalysis; Zinc oxide; Congo red; Benzopurpurine 4B; Langmuir-Hinshelwood (L-H)

Introduction

Heterogeneous photocatalysis oxidations performed with light irradiated semiconductors dispersions has been extensively investigated owing to their highly efficiency to completely mineralize the harmful organic and inorganic ions species to CO₂ and water [1]. Most researches has been focalized on the heterogenic systems based on high dispersion TiO₂ with a crystalline modification of anatase (Degussa P25, Hombriat UV-100, Aldrich, etc.) as a result of their high photocatalytic activity and widespread uses for large-scale water treatment. However, the relatively elevated intrinsic band gap of anatase TiO₂ (3.2 eV), limited their efficiencies under solar light, so that the effective utilization of solar energy is limited to about 4% of total solar spectrum. In order to meet the requirement of future environment and energy technologies, it is necessary to develop highly efficient, non toxic and chemically stable photocatalyst. Various semiconductor catalysts such as MO₂ (M= CeO₂, ZrO₂, SnO₂), M'₂O₃ (M'=α-Fe₂O₃, Bi₂O₃, Al₂O₃, Sb₂O₃ ect...) metal oxide and DS (D=Zn, Cd, Bp) metal chalcogenide groups were investigated, but their practical uses have been constrained by their low photocatalytic activity under solar light, short-term stability against photo- and chemical corrosion as well as potential toxicity [2]. Many attempts have been made to study ZnO-mediated photocatalytic degradation of organic compounds [3-6]. Semiconductor, on irradiation with photon of sufficient energy, greater than or equal to the band gap energy of the semiconductor ($h\nu \geq E_g$), a free electron (e⁻) and electronic vacancy-a hole (h⁺) are generated and recombine or migrate in the semiconductor surface being partially localized on structural defective centers of its crystalline lattice Equation (1). The photogenerated electrons take part in the reduction reaction with dissolved oxygen, producing superoxide anion (O⁻_{2ads}), hydroperoxide (HO_{2ads}) radicals and hydrogen peroxide (H₂O_{2ads}) Equation (2-4), while the photogenerated holes can oxidize either the organic compound directly Equation (5) or both hydroxylic ions and water molecules adsorbed on the photocatalyst surface Equation (6-7) forming the organic cation-radicals (R⁺_{ads}) and hydroxylic radicals

(HO[•]_{ads}). The stepwise photocatalytic mechanism is illustrated below:



The hydroxylic, peroxide and hydroperoxide radicals are the main oxidizing agents in the heterogeneous photocatalytic systems used in the water treatment technologies. The heterogeneous photocatalytic processes substantially depend on a variety of environment conditions such as surface charge and electronic structure of catalyst, the nature of surface-active center, the localization degree of photogenerated charges, the amphoteric properties of photocatalyst, pH, temperature, nature of pollutant, photocongeners, crystalline structure, synthesis method and photoreactor dimension [7].

Aggregation is one of the features of dyes in solution. Based on literature, Congo red dye tends to aggregate in aqueous and organic

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solutions leading to dimer formation and sometimes even higher order aggregates due to hydrophobic interactions between aromatic rings of dye molecules. This aggregation phenomenon is more noticed for high Congo red concentrations, at high salinity and/or low pH. The formed aggregates (micelles) separate and precipitate onto solid surfaces.

In the present work, the potential ability of ZnO-assisted photocatalytic degradation of Congo red (CR) and benzopurpurine 4B (BP4B) was assessed in terms of evolution of the photodecomposition efficiency at different operating parameters such as, irradiation time, pH solution, initial dye concentration, amount of catalyst, light intensity and as well as band gap of other semiconductor groups. The experimental data were quantified by applying the pseudo-first order kinetic and Langmuir-Hinshelwood (L-H) model to accommodate reactions occurring at a solid-liquid interface.

Materials and Methods

Nanoparticle semiconductors ZnO (BET surface area, $S = 10 \text{ m}^2/\text{g}$ and particle size $D = 60 \text{ nm}$, 99.99%), TiO_2 (anatase 99.99%), Al_2O_3 (99.99%), CeO_2 (99.99%), and Fe_2O_3 (99.99%), were obtained from Merck, and were used without further purification. Congo red (C.I. 22 120, MW = 696.67 g mol^{-1} , $\text{C}_{32}\text{H}_{24}\text{N}_6\text{O}_6\text{S}_2\cdot 2\text{Na}$, $\lambda_{\text{max}} = 497 \text{ nm}$ and $\text{pKa} = 4$) and benzopurpurine 4B (C.I.23500, MW = 724.74 g mol^{-1} , $\text{C}_{34}\text{H}_{26}\text{N}_6\text{O}_6\text{S}_2\cdot \text{Na}_2$, $\lambda_{\text{max}} = 500 \text{ nm}$ and $\text{pKa} = 6.8$). The molecular structure of the dye is illustrated in Figure 1. Distilled water was used for preparation of various solutions.

Photocatalytic reactions were carried out inside a (BLX-E365) photoreactor equipped with 6UV-A lamps with an emission maximum at λ of 365 nm. The suspension was irradiated perpendicularly to the surface of solution, and the distance between the UV source and vessel containing reaction mixture was fixed at 15 cm. The experiments were performed at 298K. In all photocatalytic degradation experiments, 300mL CR solution of appropriate concentration was taken in photocatalytic reactor vessel of 600 ml capacity. A known quantity of semiconductor was added and mixture was stirred to obtain uniform suspension. The suspension pH values were previous adjusted using $\text{NaOH}/\text{H}_2\text{SO}_4$ solutions via pH meter (HANNA HI 83141).

Before irradiation, photocatalyst/substrate suspension was stirred in the dark for 30 minutes at 298K to ensure the adsorption equilibrium was established. Next, the lamp was switched on to initiate the photocatalytic degradation reaction. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. The suspension was sampled at regular intervals of time and immediately centrifuged using (EBA-Hetlich) at 3500 rpm for 15 min to completely remove photocatalyst particles. The residual concentration of the solution samples was monitored using UV-Vis Spectrophotometer (Shimadzu UV mini-1240) at $\lambda = 497$ and 500 nm for CR and BP4B respectively, as a function of irradiation time.

The effect of initial pH on the photocatalytic degradation of Benzopurpurine 4B was researched over a range of pH values from 2 to 10. But for Congo red, the experiments were only conducted from pH 6 to 10 for avoiding dye aggregation. The experiments were also performed by varying the initial dye concentration from 20 to 60 mg/L, amount of photocatalyst from 0.25 to 3 g/L and light intensity from 50 to 90 J cm^{-2} as well as band gap of semiconductors by replacing ZnO with TiO_2 , Al_2O_3 , CeO_2 and Fe_2O_3 nanoparticles.

The data obtained from the photocatalytic degradation experiments were then used to calculate the degradation efficiency η (%) of the substrate Equation (8):

$$\eta(\%) = \left[\frac{C_i - C_f}{C_i} \right] 100 \quad (8)$$

where C_i : dye initial concentration ($\text{mg}\cdot\text{L}^{-1}$) and C_f : dye residual concentration after certain intervals ($\text{mg}\cdot\text{L}^{-1}$).

To calculate the corresponding energy at UV-A wavelength. The energy of an electro-volt, E (eV), at a given wavelength, λ (nm), is given by Equation. (9):

$$E(\text{eV}) = \frac{hc}{\lambda j} \quad (9)$$

where h is Planck's constant ($6.626 \cdot 10^{-34} \text{ J s}$); c is the speed of light ($3 \cdot 10^8 \text{ m/s}$); and j is the number of electro-volt per joule (joule = $1.6 \cdot 10^{-19}$ electro-volt). The corresponding light energy at UV-A (365 nm) wavelength was estimated to $E_{\text{UV-A}} = 3.4 \text{ eV}$.

The photocatalytic degradation efficiency of ZnO catalyst for the degradation of CR and BP4B was quantified by measurement of dyes apparent first order rate constants under operating parameters and Langmuir-Hinshelwood modified kinetic analysis to accommodate reactions occurring at a solid-liquid interface. Surface catalyzed reactions can often be adequately described by a monomolecular Langmuir-Hinshelwood mechanism, in which an adsorbed substrate with fractional surface coverage θ is consumed at an initial rate given as follow Equation (10) [8]:

$$-\left[\frac{dC}{dt} \right] = r_0 = K_{\text{app}} \theta = \frac{K_1 K_2 C_0}{1 + K_1 C_0} \quad (10)$$

where K_1 is a specific rate constant that changes with photocatalytic activity, K_2 the adsorption equilibrium constant, and C_0 is the initial concentration of the substrate (Congo Red and Benzopurpurine 4B in our cases). Inversion of the above rate equation is given by Equation (11):

$$\frac{1}{K_{\text{app}} C_0} = \frac{1}{K_1 K_2} + \frac{C_0}{K_1} \quad (11)$$

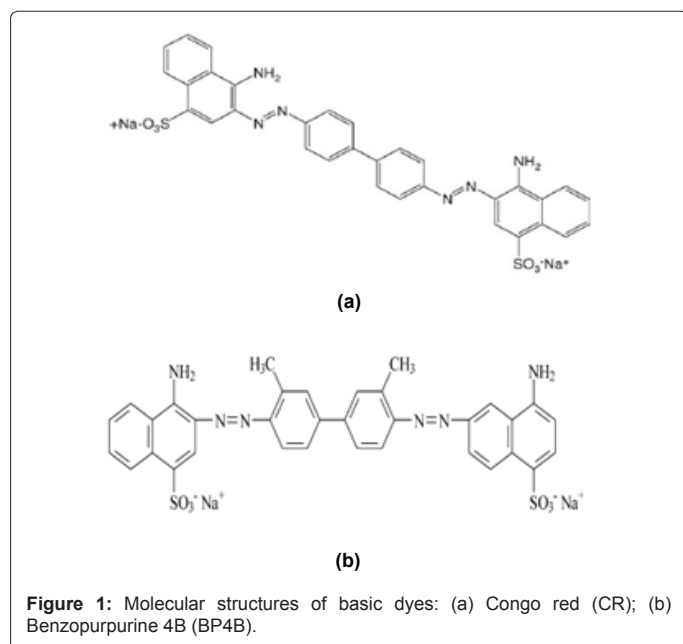


Figure 1: Molecular structures of basic dyes: (a) Congo red (CR); (b) Benzopurpurine 4B (BP4B).

Thus, a plot of reciprocal of the apparent first order rate constant $1/K_{app}$ against initial concentration of the dye C_0 should be a straight line with a slope of $1/K_1$ and an intercept of $1/K_1K_2$. Such analysis allows one to quantify the photocatalytic activity of ZnO catalyst through the specific rate constant K_1 (with larger K_1 values corresponding to higher photocatalytic activity) and adsorption equilibrium constant K_2 (K_2 expresses the equilibrium constant for fast adsorption-desorption processes between surface of catalyst and substrates). The integrated form of the above equation (Equation 10) yields to the following Equation (12):

$$t = \frac{1}{K_1K_2} \ln \frac{C_0}{C} + \frac{1}{K_2}(C_0 - C) \quad (12)$$

where t is the time in minutes required for the initial concentration of the dye C_0 to decrease to C . Since the dye concentration is very low, the second term of the expression becomes small when compared with the first one and under these conditions the above equation reduces to Equation (13):

$$\ln \frac{C_0}{C} \approx K_1K_2t = K_{app}t \quad (13)$$

where k_{app} is the apparent pseudo-first order rate constant, C and C_0 are the concentration at time ' t ' and ' $t=0$ ', respectively. The plot of $\ln C_0/C$ against irradiation time t should give straight lines, whose slope is equal to K_{app} . The half-life of dye degradation at various process parameters was raised from Equation (14):

$$t_{1/2} = \frac{0.5C_0}{K_2} + \frac{0.693}{K_1K_2} \quad (14)$$

where half-life time, $t_{1/2}$, is defined as the amount of time required for the photocatalytic degradation of 50% of the RC and BP4B dyes in aqueous solution by ZnO catalyst.

Results

Effect of UV light and catalyst

Figures 2 and 3 illustrate the photocatalytic degradation kinetics of 20 mg/L of dyes in aqueous solution under three different experimental conditions through UV-A alone, dark/ ZnO and UV-A/ZnO. The degradation rate was found to increase with increase in irradiation time

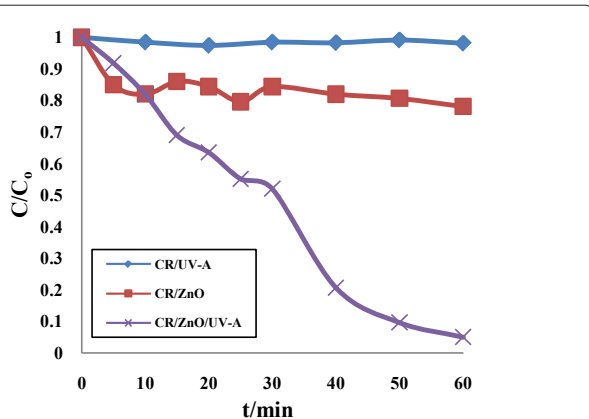


Figure 2: Photocatalytic degradation of CR under different experimental conditions ($[ZnO]=0.5g/L$, $[CR]=20mg/l$, natural pH =8, $T=298K$, $\lambda_{max}=365$ nm and $I=90j/cm^2$).

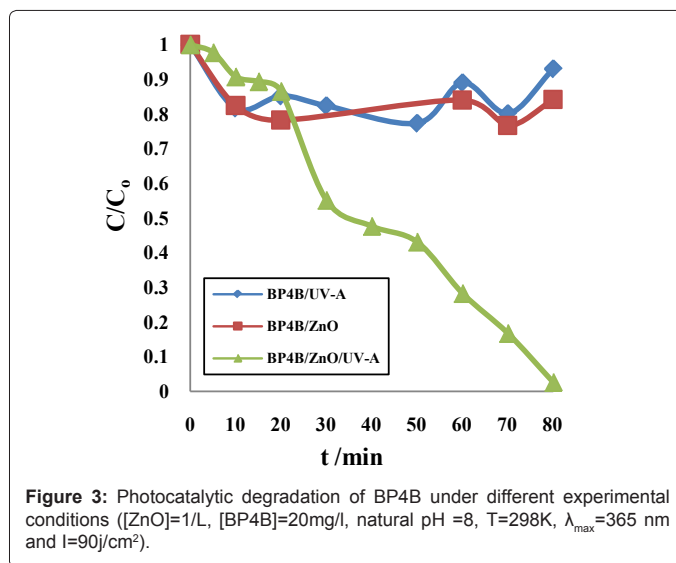


Figure 3: Photocatalytic degradation of BP4B under different experimental conditions ($[ZnO]=1/L$, $[BP4B]=20mg/l$, natural pH =8, $T=298K$, $\lambda_{max}=365$ nm and $I=90j/cm^2$).

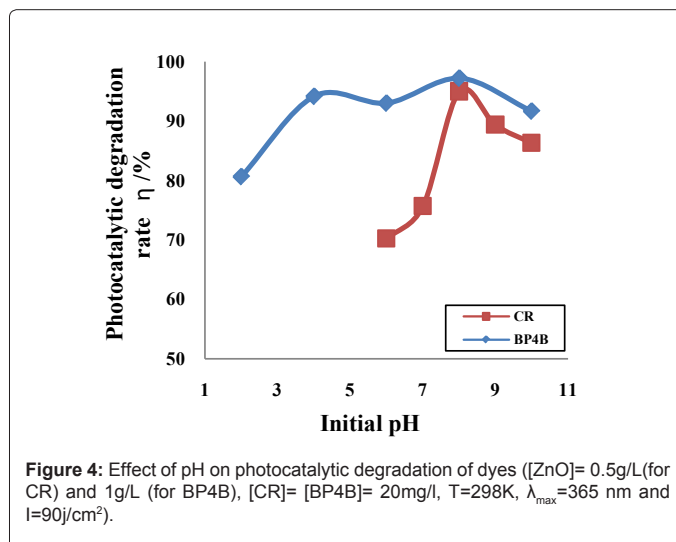


Figure 4: Effect of pH on photocatalytic degradation of dyes ($[ZnO]=0.5g/L$ (for CR) and $1g/L$ (for BP4B), $[CR]=[BP4B]=20mg/l$, $T=298K$, $\lambda_{max}=365$ nm and $I=90j/cm^2$).

and 95.02 and 97.24% of degradation were achieved within 60 and 80 min for CR and BP4B respectively (curve Dye/ZnO/UV-A). When 20 mg/L of both dyes along with ZnO were magnetically stirred for the same optimum irradiation times in the absence of light, lower (20.78 and 13.17 %) degradation were observed (curve Dye/ZnO) for CR and BP4B respectively, whereas, disappearance of dyes was negligible (0.49% for CR and 4.45% for BP4B) in the direct photolysis (curve Dye/UV-A) indicating that the observed high decomposition of both dyes in the UV/ZnO process is exclusively attributed to the photocatalytic reaction of the semiconductor particles. Similar results have been reported for ZnO-assisted photocatalytic degradation of azo dyes such as Congo red [9] and Reactive Black 5 [10].

Effect of pH solution

In order to study the effect of initial pH on the degradation efficiency of ZnO catalyst on photodecomposition of both dyes, experiments were carried out at various pH, ranging from 2 to 10, except for CR, where tests were done from 6 to 10 for avoiding dye aggregation. The results showed that the pH significantly affected the degradation efficiency for both dyes. As shown in Figure 4 and Table

Experimental parameters		Experimental results				Pseudo-first order model			Experimental results		Pseudo-first order model		
		CR							BP4B				
Initial pH solution (pH)	RC	BP4B	ADS / %	PCD /%	$k_{app} / \text{min}^{-1}$	$t_{1/2} / \text{min}$	$R^2 / \%$	ADS /%	PCD /%	$k_{app} / \text{min}^{-1}$	$t_{1/2} / \text{min}$	$R^2 / \%$	
	6	2	18.19	70.25	0.014	49.511	79.8	86.09	80.70	0.023	9.57	32.2	
	7	4	16.13	75.68	0.025	27.726	96.8	41.51	94.19	0.037	14.29	98.3	
	8	6	10.50	95.02	0.041	16.906	88.1	32.84	93.07	0.035	128.36	98.0	
	9	8	14.94	89.38	0.038	18.241	79.0	3.89	97.24	0.026	26.45	95.6	
	10	10	11.81	86.339	0.035	19.804	74.7	24.84	91.69	0.036	144.40	88.0	

R^2 : Regression coefficient, ADS: Adsorption and PCD: Photocatalytic degradation

Table 1: Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as a function of pH ([ZnO]=0.5g/L (for CR) and 1g/L (for BP4B), [CR]=[BP4B]=20mg/L, T=298K, λ_{max} =365 nm and I=90j/cm²).

1, for CR, the degradation rate increased from 70.25 to 95.02% as the pH value was increased from 6 to 8, and then decreased to 86.34% at pH 10, whereas, for BP4B, the degradation activity raised from 80.70 to 97.24% when the pH was increased from 2 to 8 and then decreased to 91.69 % at pH 10. The maximum degradation rate of CR (95.02%) and BP4B (97.24%) were achieved at pH 8. For this reason, for both dyes, the pH 8 was selected for subsequent experiments.

It is commonly accepted that in photocatalyst/aqueous systems, the potential of the surface charge is determined by the activity of ions (e.g. H⁺ or pH). A convenient index of the tendency of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net charge (pH zpc) [11,12]. pH zpc is a critical value for determining the sign and magnitude of the net charge carried on the photocatalyst surface during adsorption and photocatalytic degradation process. Most of the semiconductor oxides are amphoteric in nature, can associate (Equation 15) or dissociate (Equation 16) proton. To explain the relationship between the layer charge density and the adsorption, so-called Models of Surface Complexation (SCM) was developed [13], which consequently affects the sorption-desorption processes and the separation and transfer of the photogenerated electron-hole pairs at the surface of the semiconductor particles. In the 2-pK approach we assume two reactions for surface protonation.

The zero point charge pH zpc for ZnO is 9.0. For pH values lower than the pH zpc of ZnO, the surface becomes positively charged, according to the following reaction Equation (15):

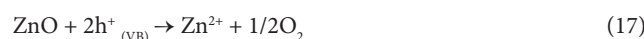


ZnO surface becomes negatively charged for pH values higher than pH_{zpc} , given by the following reaction Equation (16):



The experimental data revealed that higher degradation rate of BP4B was observed in acidic medium. Since BP4B is an anionic dye, its adsorption mainly performed via an electrostatic interactions between the positive ZnO surface and BP4B anions, leading to a maximum extent at pH 2. Thus, a strong adsorption can lead to a drastic decrease in the active centers on the catalyst surface, which results in decrease in the absorption of the light quanta by the catalyst and consequently to a reducing of the kinetic reaction. As a result, the high degradation efficiency cannot be ascribed to the photocatalytic oxidation of the BP4B dye, but to catalyst behavior under strong acid pH. ZnO nanoparticles can undergo photo-corrosion through self-oxidation

at pH lower than 4 Equation (17) In particular, ZnO can be photo-oxidized with decreasing the pH Equation (18)



Photocatalytic activity of anionic dyes (mainly sulfonated groups) such as CR and BP4B reaches a maximum value in lower pH zpc (i.e. pH =8). At alkaline mediums, excess of hydroxyl anions facilitate photogeneration of ·OH radicals which is accepted as primary oxidizing species responsible for photocatalytic degradation, resulting in enhancement of the efficiency of the process. Furthermore we found that, where the adsorption of dyes was weak, degradation scarcely occurred. The adsorption affects strongly the accessibility of the surface reducing species to the CR and BP4B reduction kinetics. However, adsorption is not the only factor that controls the photocatalytic degradation of dyes. Although the adsorption extents of both dyes were lower, the degradation rates were in the reverse order.

At pH higher than pH zpc value (i.e. pH =10), a dramatically decrease in the degradation efficiency could be explained on the basis of amphoteric behaviors of ZnO catalyst. The negatively surface of ZnO catalyst (highly concentration of hydroxide ions) and the great negatively charged RC and BP4B dye anions results in electrostatic repulsion electrostatic.

Moreover, the stability of ZnO may not be guaranteed at this high

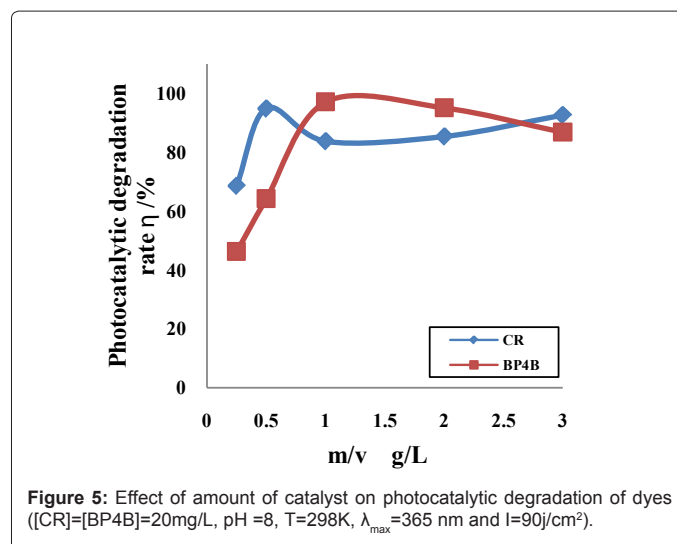


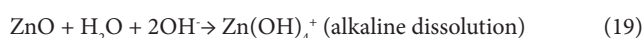
Figure 5: Effect of amount of catalyst on photocatalytic degradation of dyes ([CR]=[BP4B]=20mg/L, pH =8, T=298K, λ_{max} =365 nm and I=90j/cm²).

Experimental parameters		Experimental results		Pseudo-first order model			Experimental results		Pseudo-first order model				
		CR						BP4B					
		ADS / %	PCD / %	$k_{app} / \text{min}^{-1}$	$t_{1/2} / \text{min}$	$R^2 / \%$	ADS / %	PCD / %	$k_{app} / \text{min}^{-1}$	$t_{1/2} / \text{min}$	$R^2 / \%$		
Catalyst amount ZnO/g/L	0.25	8.93	68.73	0.030	23.105	82.6	38.31	46.29	0.014	49.511	46.1		
	0.5	10.50	95.02	0.041	16.906	88.1	2.34	64.21	0.018	38.508	68.4		
	1	33.59	83.80	0.037	18.734	93.0	3.89	97.24	0.026	26.456	95.6		
	2	41.98	85.45	0.040	17.329	79.0	35.54	95.26	0.037	18.734	96.7		
	3	53.40	92.68	0.048	14.441	93.0	60.85	86.97	0.026	26.660	96.2		

R^2 : Regression coefficient, ADS: Adsorption and PCD: Photocatalytic degradation

Table 2: Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as a function of amount of photocatalyst ($[\text{CR}] = [\text{BP4B}] = 20 \text{ mg/L}$, $\text{pH} = 8$, $T = 298 \text{ K}$, $\lambda_{\text{max}} = 365 \text{ nm}$ and $I = 90 \text{ J/cm}^2$).

pH due to possibility of alkaline dissolution of ZnO Equation (19):



Effect of the amount of catalyst

The effect of the amount of catalyst (m/v) on photocatalytic degradation of dyes was conducted over a range of catalyst amount from 0.25 to 3g/L. As observed in Figure 5 and Table 2, the degradation rate of CR increased from 68.73 to 95.02 % in CR and from 46.29 to 97.24% in BP4B when the ZnO amount was raised from 0.25 to 0.5 g/L for CR and from 0.25 to 1g/L for BP4B respectively. This increase in degradation rate with the photocatalyst amount can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension as a result of increased screening effect and scattering of light. Further increase in the catalyst amount beyond of 0.5 g/L for CR and 1g/L for BP4B, the rate of degradation remains nearly constant for CR, but it slightly decreased for BP4B due to overlapping of adsorption sites as a result of overcrowding of adsorbent and deactivation of activated catalyst particles owing to collision with ground state catalyst as shown below Eq. (20) [14]:



where ZnO^* is ZnO with active species adsorbed on its surface; $\text{ZnO}^\#$ deactivated form of ZnO^* shielding by ZnO may also take place. The adsorbent dose of 0.5 and 1 g/L for CR and BP4B were used in all other parameter experiments.

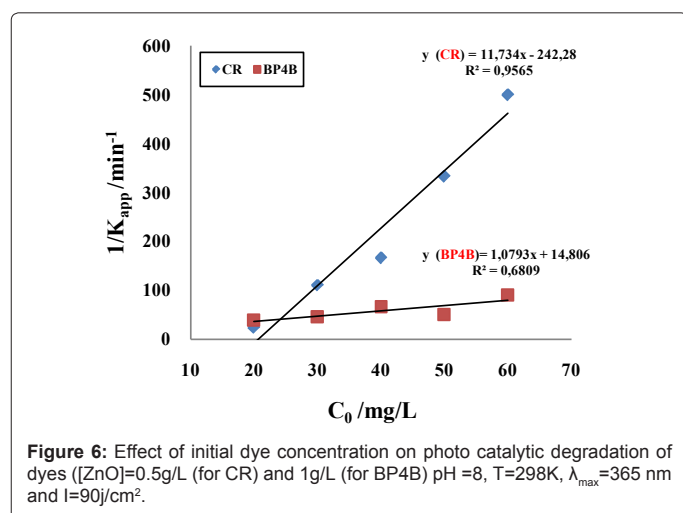


Figure 6: Effect of initial dye concentration on photo catalytic degradation of dyes ($[\text{ZnO}] = 0.5 \text{ g/L}$ (for CR) and 1 g/L (for BP4B) $\text{pH} = 8$, $T = 298 \text{ K}$, $\lambda_{\text{max}} = 365 \text{ nm}$ and $I = 90 \text{ J/cm}^2$).

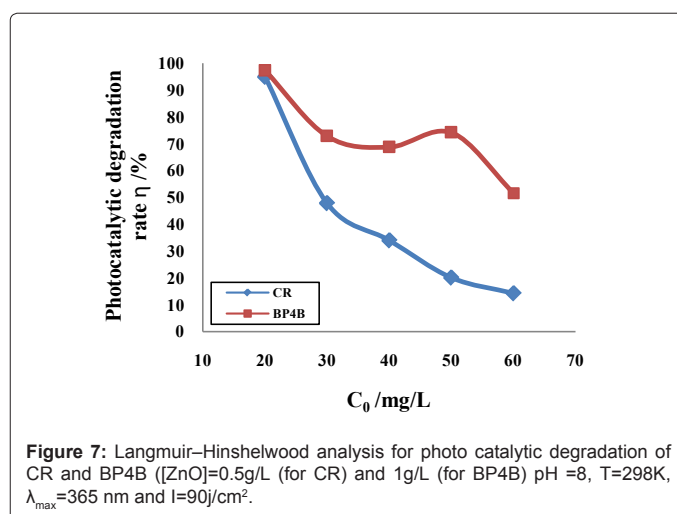


Figure 7: Langmuir-Hinshelwood analysis for photo catalytic degradation of CR and BP4B ($[\text{ZnO}] = 0.5 \text{ g/L}$ (for CR) and 1 g/L (for BP4B) $\text{pH} = 8$, $T = 298 \text{ K}$, $\lambda_{\text{max}} = 365 \text{ nm}$ and $I = 90 \text{ J/cm}^2$).

Effect of initial dye concentration

Figure 6 illustrates the effect of initial dye concentration on the photo catalytic degradation rate of dyes in the range of 20 to 60 mg/L. As it can be observed, disappearance rate was found to be inversely affected by initial concentration of dyes. The drastic decrease in the degradation activity with dyes concentration is ascribed to the increase in the local concentration of CR as well as BP4B on the ZnO surface, while the UV light irradiation time and photocatalyst amount are kept constant, leading to the formation of dimer and higher order aggregates owing to hydrophobic interactions between aromatic rings and hence the rate formation of hydroxylic and superoxide anion radicals are dramatically reduced thereby decreasing rate of degradation. The maximum concentration of both dyes that could be degraded by 0.5 and 1g/L of ZnO for CR and BP4B respectively is found to be 20mg/L. Similar trend was observed in the photocatalytic degradation of Reactive Black 5 and Reactive Orange 4 dyes using ZnO and TiO_2 as photocatalysts [15]. Thus 20 mg/L CR and BP4B was selected as optimum concentration for the study of other experiments.

The photocatalytic degradation process profiles of both dyes by ZnO catalyst at low dye concentrations and under pH solution, amount of catalyst and initial dye concentration follow apparently pseudo-first-order kinetics. The linear plot of $\ln C_0/C$ against irradiation time t (Table 1, 2 and 3) should give a straight line with relatively high regression coefficients, whose slope is equal to the apparent first order rate constant K_{app} .

On the other hand, the effect of initial concentrations of both dyes

Experimental parameters		Experimental results		Pseudo-first order model			Experimental results		Pseudo-first order model		
		CR		CR			BP4B				
		ADS / %	PCD / %	$k_{app} / \text{min}^{-1}$	$t_{1/2} / \text{min}$	$R^2 / \%$	ADS / %	PCD / %	$k_{app} / \text{min}^{-1}$	$t_{1/2} / \text{min}$	$R^2 / \%$
Initial dye concentration Dye/mg/L	20	10.50	95.02	0.041	16.906	88.1	3.89	97.24	0.026	26.456	95.6
	30	20.93	47.87	0.009	77.016	91.0	11.25	72.85	0.022	31.651	82.6
	40	15.26	34.10	0.006	115.525	91.0	2.12	68.87	0.015	45.904	98.2
	50	1.95	20.15	0.003	231.049	95.0	1.18	74.24	0.020	34.485	81.9
	60	3.86	14.25	0.002	346.574	86.00	33.11	51.71	0.011	62.446	95.9

R^2 : Regression coefficient, ADS: Adsorption and PCD: Photo catalytic degradation

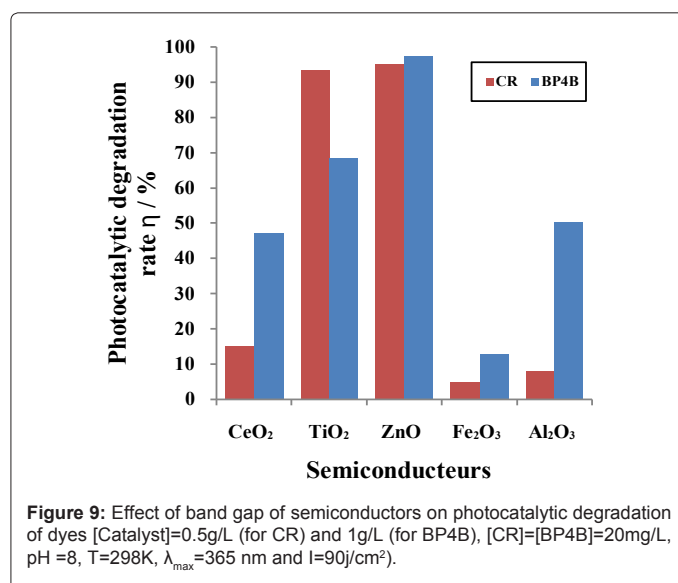
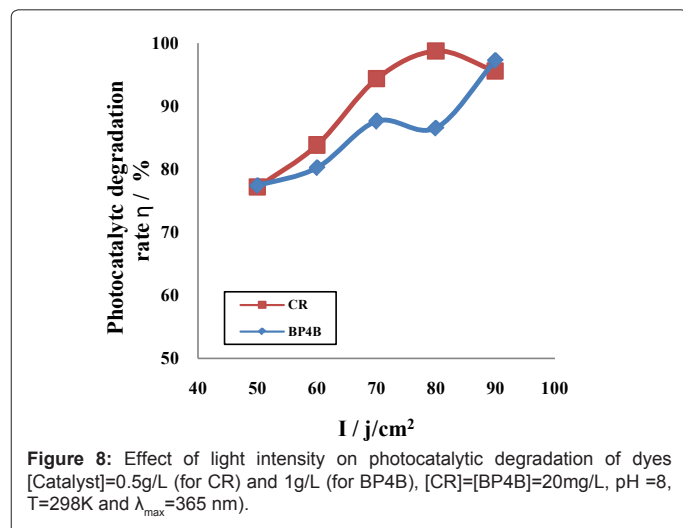
Table 3: Kinetic parameters of photo catalytic degradation of dyes in aqueous solution as a function of initial dye concentrations. ([ZnO]=0.5g/L (for CR) and 1g/L (for BP4B), pH =8, [CR]=[BP4B]=20-60mg/L, $P^H = 8$ T=298K, $\lambda_{max} = 365$ nm and $I = 90$ j/cm²).

in the photocatalytic degradation rate can be assessed in terms of the Langmuir–Hinshelwood (LH) kinetic model modified.

The plot of $1/K_{app}$ against C_0 (Figure 7) should yield a straight line with high regression coefficients ($R^2=0.96$ and 0.68 for CR and BP4B respectively). The K_1 and K_2 values were calculated from the slope ($1/K_1$) and the intercept ($1/K_1K_2$) respectively. The values of K_1 and K_2 were found to be 0.048 L/g and 0.085 g/L.min for CR and 0.073 L/g and 0.927 g/L.min for BP4B respectively. The product of $K_1K_2 = 0.004$ and 0.068 min⁻¹ for CR and BP4B respectively which represent the apparent rate constant K_{app} for low initial concentrations of dye and is in agreement with the experimental results obtained from (Equation 13) for BP4B. This results suggest that the photocatalytic degradation data were satisfactorily described by Langmuir–Hinshelwood (LH) kinetic model in a wide range of dye concentration. However, that of CR are not sufficient to conclude that the L-H mechanism is the most suitable one to describe the photocatalytic process of CR, since the calculated K_{app} ($K_{app} = K_1K_2$) value deduced from pseudo-first-order kinetic equation was much different compared with experimental K_{app} , despite its regression coefficient is higher than of BP4B.

Effect of the UV-A light intensity

Intensity of the irradiation has been reported to be an important parameter influencing the degradation of organic chemicals by photo catalytic activity. The effect of light intensity on the rate of photo catalytic degradation of dyes was investigated by varying the light intensity of UV-A between 50 and 90 j / cm². Results reported in Figure



8 and Table 4, depicts that the degradation efficiency of BP4B increased linearly with the light intensity, whereas that of CR it increased up to 70j/cm² and after no changes are observed. The linear increase of the degradation efficiency for CR and BP4B at light intensity, ranging from 50 to 70 j/cm² and from of 50 to 90 j/cm² for CR and BP4B respectively is assigned by more photons would be available for excitation at the semiconductor surface and in turn more electron hole pairs will be generated. Thus this resulted in enhanced rate of degradation. The value of k_1 was found to increase with the increase in light intensity, a typical characteristic of a photo catalytic reaction. At a higher light intensity than 70 j/cm² for CR, there is no effect on degradation activity on further increase in light intensity. The results indicate that maximum numbers of photons which are required for excitation are available in specific constant range of irradiating light intensity. Further increase in light intensity no significant changes are observed in photocatalytic degradation efficiency because all photo catalyst particles are excited, so, the rate of degradation remains unchanged [16].

Effect of the band gap of semiconductors

The photocatalytic degradation reactions were further performed in four other semiconductors having different band gap values (Figure 9 and Table 5). It is evident that the photocatalytic degradation of dyes greatly depends on the electronic structure and properties of semiconductor surface/solvent. Generally, semiconductor on irradiation with light energy greater than or equal to band gap

energy of the semiconductor ($h\nu \geq E_g$), a free electron (e^-) and electronic vacancy-a hole (h^+) are formed and recombine or migrate in the semiconductor surface. Probability of electron transfer in the semiconductor/adsorbate system is determined by a relative position of the valence band, the photocatalyst conductance band and the value of the oxidation-reduction potential (ORP) of the oxidant and the substrate. The photogeneration of electrical charge is in dynamic equilibrium with their recombination substantially reducing the quantum yield of the photocatalytic process. The ORP of water oxidation, hydroxylic ions, and most of organic compounds below of reducing photogenerated holes within a wide interval of the pH due to which the formation of hydroxylic radicals and organic cation-radicals of photocatalyst surface are thermodynamically possible processes. It has already reported that semiconductors such as ZnO and TiO₂ having band gaps larger than 3 eV are excellent photocatalysts. Obviously, ZnO and TiO₂ semiconductors exhibit a higher degradation activity than that of the other systems because their band gaps ($E_g = 3.2$ and 3.3 eV for ZnO and TiO₂ respectively) are slightly equal to that of UV-A irradiation source ($E_{UV-A} = 3.4$ eV). The photogenerated electron (e^-)-hole (h^+) pairs can be easily separated and transferred to the semiconductor/adsorbate interface efficiently, consequently improving the photocatalytic activity [17].

On the other hand, Al₂O₃ and Fe₂O₃ catalysts showed lower activity for the photocatalytic activity of dyes than ZnO and TiO₂, since their conductance bands of 5.6 and 3.7 eV respectively, are much higher than of the E_{UV-A} light irradiation source as a result of low light energy conversion efficiency, so the photogenerated electrical charge in semiconductor cannot efficiently transfer in the surface and are lost due to recombination.

The minimum energy required for excitation of an electron from the valence band to conductance band for the semiconductor such as CeO₂ is 2.7 eV. The photodecomposition process of both dyes in CeO₂

system was much lower than ZnO and TiO₂ catalysts, although its band gap being smaller than of E_{UV-A} light energy. The CeO₂ system might reduce the life of electron-hole pairs, and enhance the opportunities of their recombination. The order of the photocatalytic degradation efficiency is ZnO > TiO₂ > CeO₂ > Al₂O₃ > Fe₂O₃. Consequently, the photocatalytic ability of semiconductor is significantly dependent on their band gap values.

Table 4 and 5 record the kinetic parameters of photocatalytic degradation of CR and BP4B in aqueous solution.

The results show that the photocatalytic decolorization of both the dyes in aqueous solutions under light intensity and band gap of catalysts can be described by the pseudo-first-order kinetic model. The semi-logarithmic plots of the experimental data under optimized conditions ($\ln C_0/C$ against t) yielding to a straight line. The regression coefficients for the fitted lines were calculated to be $R^2 = 0.881$ and 0.956 for CR and BP4B respectively. The apparent rate constants, K_{app} and the half-life time, $t_{1/2}$ were calculated to be 0.041 min⁻¹ and 16.906 min for CR and 0.026 min⁻¹ and 26.46 min for BP4B.

Table 4 and 5 report the kinetic parameters of the photo decomposition of both dyes in aqueous solution using ZnO catalyst at low dyes concentration and under light intensity and band gap of catalysts.

Mechanism

Photocatalytic degradation schemes for an azo-dye are characterized by nitrogen to nitrogen double bonds (N=N) that are usually attached to two radicals of which at least one but usually both are aromatic groups (benzene or naphthalene rings). The color of azo-dyes is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo-dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron

Experimental parameters		Experimental results		Pseudo-first order model			Experimental results		Pseudo-first order model			
		CR						BP4B				
		ADS / %	PCD / %	k_{app}/min^{-1}	$t_{1/2}/\text{min}$	$R^2/\%$	ADS/%	PCD/%	k_{app}/min^{-1}	$t_{1/2}/\text{min}$	$R^2/\%$	
Light Intensity I / J/cm ²	50	12.20	77.11	0,029	16.906	83.7	50.65	77.35	0.022	31.364	92.8	
	60	11.19	83.78	0.027	12.603	64.7	32.41	80.24	0.022	31.364	96.9	
	70	17.93	94.33	0.045	15.403	98.6	34.95	87.57	0.032	21.661	75.2	
	80	24.07	98.69	0.055	12.603	83.1	26.14	86.52	1.032	0.672	75.2	
	90	10.50	95.02	0.041	16.906	88.1	3.89	97.24	0.026	26.456	95.6	

R^2 : Regression coefficient, ADS: Adsorption and PCD: Photocatalytic degradation

Table 4: Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as a function of light intensity ([ZnO]=0.5g/L (for CR) and 1g/L (for BP4B), pH =8, [CR]=[BP4B]=20-60mg/L, pH =8, T=298K and λ_{max} =365 nm).

Experimental parameters		Experimental results		Pseudo-first order model			Experimental results		Pseudo-first order model			
		CR						BP4B				
		ADS / %	PCD / %	k_{app}/min^{-1}	$t_{1/2}/\text{min}$	$R^2/\%$	ADS/%	PCD/%	k_{app}/min^{-1}	$t_{1/2}/\text{min}$	$R^2/\%$	
Band gap of catalyst [Eg] (eV)	Zn O	10.50	95.02	0.041	16.906	88.1	3.89	97.24	0.026	26.456	95.6	
	Ti O ₂	13.47	93.34	0.045	15.40	98.5	28, 52	68.54	0.002	346.57	78.2	
	Ce O ₂	8.00	14.93	0.003	231.05	49.0	25, 59	47.19	0.033	20.94	70.7	
	Al ₂ O ₃	4.21	7.91	0.001	693.15	88.7	13, 73	50.21	0.011	63.01	46.4	
	Fe ₂ O ₃	5.15	4.72	0.001	693.15	34.0	1, 74	12.77	0.018	38.08	95.0	

R^2 : Regression coefficient, ADS: Adsorption and PCD: Photocatalytic degradation

Table 5: Kinetic parameters of photocatalytic degradation of dyes in aqueous solution as a function of band gap of semiconductors. ([Catalyst]=0.5g/L (for CR) and 1g/L (for BP4B), [CR]=20mg/l, pH =8, T=298K, λ_{max} =365 nm and I=90J/cm²).

in the conduction band. The cleavage of N=N bonds leads to the decoloration of dyes [18].

When a semiconductor is irradiated with light having energy equal to or more than band gap energy ($h\nu \geq E_g$), a heterogeneous photocatalytic reaction occurs at the photocatalyst/adsorbate interface. The conduction band electrons (e^-) and valence band holes (h^+) are formed Equation (21). A part of the photogenerated charge carriers recombines in the bulk of the semiconductor, while the rest transfer in the photocatalyst surface, where the holes as well as the electrons act as powerful oxidants, respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the ZnO photocatalyst particle sites, reducing it to a superoxide radical anion $O_2^{\cdot-}$ Equation (22), while the photogenerated holes can oxidize either the dye molecule directly or the OH^- ions and the water molecules adsorbed the ZnO surface to $\cdot OH$ radicals Equation (23).

In the photocatalytic oxidation process, the generation of hydroxyl radicals occurs in two different pathways.

First pathway: In the first pathway, where U.V light is used in the photocatalytic reaction, electrons in the semiconductor are excited from the valence band to the conduction band leaving positive holes in the valence band. The photogenerated electrons react with the adsorbed oxygen molecules to form $O_2^{\cdot-}$ species, while the photogenerated holes that are able to migrate to the hydroxylated surface can create a highly reactive and short-lived hydroxyl radicals $\cdot OH$. These processes could be represented in the following equations:



Second pathway: In the second pathway where a solar radiation is used a photosensitization process takes place. In this process, the dye molecules act as a sensitizer by the absorption of UV light in the visible range to yield an excited state of the sensitizer Equation (24). The dye radicals inject electrons to the conduction band of the ZnO photocatalyst Equation (25-26) in where it is scavenged by O_2 to form active oxygen molecule as shown in Equation (27). The electron transfer from the excited dye molecule to the conduction band of ZnO usually is too fast (in the range of tens of femtoseconds). Further active oxygen molecule formed in Equation (27) subsequently reacts with H_2O to generate $\cdot OH$ radicals Equation (28) and peroxide Equation (29).

The formed species oxidize the dye molecules, as follows:



These $\cdot OH$ radicals formed on the illuminated semiconductor surface via either a photoexcitement of semiconductor or photosensibilization of dye are highly effective oxidizing agent

which have been shown to be the primary cause of organic matter mineralization (Equation 30).



These observations clearly demonstrate the involvement of holes (h^+), hydroxyl (OH^\cdot) and superoxide anion ($O_2^{\cdot-}$) radicals as highly oxidizing agents in the ZnO-mediated photocatalytic oxidation of Congo red as well as Benzopurpurine 4B.

Conclusion

Congo red dye tends to aggregate in acidic aqueous solutions leading to dimer and higher order aggregates due to hydrophobic interactions between aromatic rings of dye molecules. Degradation photocatalytic of CR and BP4B was negligible when ZnO catalyst and UV light were used on their own, whereas, the observed high decomposition in the UV/ZnO process is exclusively attributed to the photocatalytic reaction of the semiconductor particles. The degradation kinetics of both dyes were fast with maximum efficiencies of 95.02% for CR and 97.24 % for BP4B have been achieved within 60 and 80 min using 0.5 and 1g/L of ZnO catalyst for CR and BP4B respectively at a pH of 8 and 298K. The degradation rate of dyes was obviously affected by the operating parameters (illumination time, initial dye concentration, and amount of photocatalyst, light intensity, pH and the band gap of semiconductors). L-H mechanism is the most suitable to describe the photocatalytic process of BP4B, so the oxidants involved in the photodegradation reactions were identified as holes (h^+), hydroxyl radicals ($\cdot OH$) and superoxide anion radicals ($O_2^{\cdot-}$). However the present kinetic data are not sufficient to conclude the validity of the L-H model in interpreting the results of heterogeneous photocatalysis of CR dye.

Acknowledgments

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