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 CO\textsubscript{2} and water [1]. Most researches has been focalized on the heterogenic systems based on high dispersion TiO\textsubscript{2} with a crystalline modification of anatase (Degussa P25, Hombriot 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 TiO\textsubscript{2} (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 MO\textsubscript{2} (M= CeO\textsubscript{2}, ZrO\textsubscript{2}, SnO\textsubscript{2}), M'\textsubscript{2}O\textsubscript{3} (M'=\alpha-Fe\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}...), 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, so that 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 charge carriers 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\textsubscript{2ads}•–), hydroperoxide (HO\textsubscript{2ads}) radicals and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2ads}) Equation (2-4), while the photogenerated holes can oxidize either the organic compound directly Equation (5) or both hydroxylic and water molecules adsorbed on the photocatalyst surface Equation (6-7) forming the organic cation-radicals (R\textsuperscript{+ads}) and hydroxyl radicals (HO\textsubscript{ads}). The stepwise photocatalytic mechanism is illustrated below:

\begin{align}
\text{ZnO} + \text{hv} &\rightarrow \text{ZnO} (\text{e}^-_{(CB)} + \text{h}^+_{(VB)}) \\
\text{O}_{2ads} + \text{e}^- &\rightarrow \text{O}^-_{2ads} \\
\text{O}^-_{2ads} + \text{H}^+ &\rightarrow \text{HO}_2ads \\
\text{O}^-_{2ads} + 2\text{H}^+ + \text{e}^- &\rightarrow \text{H}_2\text{O}_{2ads} \\
\text{R}_{ads} + \text{h}^+ &\rightarrow \text{R}^+_{ads} \\
\text{HO}_{ads} + \text{h}^+ &\rightarrow \text{OH}_{ads}^+ \\
\text{H}_2\text{O}_{ads} + \text{h}^+ &\rightarrow \text{OH}_{ads}^+ + \text{H}^+ 
\end{align}

The hydroxyl, 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 charge carriers, the amphoteric properties of photocatalyst, pH, temperature, nature of pollutant, photocogeners, 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...
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 m²/g and particle size D=60 nm, 99.99%), TiO₂ (anatase 99.99%), Al₂O₃ (99.99%), CeO₂ (99.99%), and Fe₂O₃ (99.99%), were obtained from Merck, and were used without further purification. Congo red (C.I. 22120, MW = 696.67 g mol⁻¹, C₃₂H₂₄N₆O₆S₂.2Na, λ max = 497 nm and pKa=4) and benzopurpurine 4B (C.I.23500, MW =724.74 g mol⁻¹, C₃₄H₂₆N₆O₆S₂Na₂ λ max=500 nm and 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 was 15 cm. The experiments were 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/ cm² as well as band gap of semiconductors by replacing ZnO with TiO₂, Al₂O₃, CeO₂, and Fe₂O₃ nanoparticles.

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/ cm² as well as band gap of semiconductors by replacing ZnO with TiO₂, Al₂O₃, CeO₂, and Fe₂O₃ nanoparticles.

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 λ = 497 and 500 nm for CR and BP4B respectively, as a function of irradiation time.

The data obtained from the photocatalytic degradation experiments were then used to calculate the degradation efficiency η (%) of the substrate which was estimated by Equation (11):

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

where Cᵢ: dye initial concentration (mg·L⁻¹) and Cᵢ : dye residual concentration after certain intervals (mg·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):

\[
E(eV) = \frac{hc}{\lambda j}
\]

where h is Planck’s constant (6.626 × 10⁻³⁴ J s); c is the speed of light (3 × 10⁸ m/s); and j is the number of electro-volt per joule (joule=1.6 × 10⁻¹⁹ electro-volt). The corresponding light energy at UV-A (365 nm) wavelength was estimated to E_{UV-A} = 3.4 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]:

\[
\frac{dC_i}{dt} = \theta = \frac{K_s C_i}{1 + K_s C_i}
\]

where Kₛ is a specific rate constant that changes with photocatalytic activity, Kₛ the adsorption equilibrium constant, and Cᵢ 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):

\[
\frac{1}{K_s C_i} = \frac{1}{K_s} + \frac{C_i}{K_s}
\]
Thus, a plot of reciprocal of the apparent first order rate constant \( \frac{1}{K_{app}} \) against initial concentration of the dye \( C_0 \) should be a straight line with a slope of \( \frac{1}{K_1} \) and an intercept of \( \frac{1}{K_1K_2} \). 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):

\[
\frac{1}{C} = \frac{1}{K_1K_2} - \frac{1}{K_1}K_2 t + \ln \frac{C_0}{C}
\]  

(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):

\[
\ln \frac{C_0}{C} = \frac{1}{K_1K_2}t
\]  

(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 \( \ln \frac{C_0}{C} \) against irradiation time \( t \) should give straight lines, whose slope is equal to \( \frac{1}{K_1} \). The half-life of dye degradation at various process parameters was raised from Equation (14):

\[
t_{1/2} = \frac{0.5C_0}{K_1K_2} + 0.693
\]  

(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 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 to10, 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
nanoparticles can undergo photo-corrosion through self-oxidation of the BP4B dye, but to catalyst behavior under strong acid pH. ZnO efficiency cannot be ascribed to the photocatalytic oxidation of the reducing species to the CR and BP4B reduction kinetics. However, adsorption affects strongly the accessibility of the surface active centers on the catalyst surface and consequently 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 increase in the absorption of the light quanta by the catalyst and consequently in the active centers on the catalyst surface, which results in decrease in 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):

\[
\text{pH} < \text{pH}_{zpc} \quad \text{ZnO} + 2\text{H}^+ (\text{VB}) \rightarrow \text{Zn}^{2+} + \frac{1}{2}\text{O}_2
\]

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 negativity charged RC and BP4B dye anions results in electrostatic repulsion electrostatic.

Moreover, the stability of ZnO may not be guaranteed at this high pH value lower than 4 Equation (17) In particular, ZnO can be photo-oxidized with decreasing the pH Equation (18)

\[
\text{ZnO} + 2\text{H}^+ (\text{VB}) \rightarrow \text{Zn}^{2+} + 1/2\text{O}_2
\]

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.

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\[
\text{ZnO} + 2\text{OH}^- \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O} \quad \text{(acidic dissolution)}
\]

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.

**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=365 nm and I=90j/cm²).

<table>
<thead>
<tr>
<th>Initial pH solution (pH)</th>
<th>Experimental results</th>
<th>Pseudo-first order model</th>
<th>Experimental results</th>
<th>Pseudo-first order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CR</td>
<td>BP4B</td>
<td>CR</td>
<td>BP4B</td>
</tr>
<tr>
<td></td>
<td>ADS / %</td>
<td>PCD /%</td>
<td>ADS /%</td>
<td>PCD /%</td>
</tr>
<tr>
<td>RC</td>
<td>6</td>
<td>18.19</td>
<td>70.25</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>16.13</td>
<td>75.68</td>
<td>0.025</td>
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<tr>
<td></td>
<td>8</td>
<td>10.50</td>
<td>95.02</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>14.94</td>
<td>89.38</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11.81</td>
<td>86.339</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Figure 6 illustrates the effect of initial dye concentration on the photocatalytic 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 hydroxyl 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 1 g/L of ZnO for CR and BP4B respectively is found to be 20 mg/L. Similar trend was observed in the photocatalytic degradation of Reactive Black 5 and Reactive Orange 4 dyes using ZnO and TiO2 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 lnC/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 Kapp.

On the other hand, the effect of initial concentrations of both dyes
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 ($1/K_2$) respectively. The values of $K_1$ and $K_2$ were found to be 0.048 L/g and 0.085g/L.min for CR and 0.073L/g and 0.068 min –1 for CR and BP4B respectively which represent the product of $K_1K_2 = 0.004$ and 0.006 min. This results suggest that the photocatalytic degradation 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 $K_{app} = 0.004$ and 0.006 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 suggests 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 $K_{app}$ for low initial concentrations of dye and is in agreement with the experimental results obtained from (Equation 13) for BP4B. This suggests 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 $K_{app}$ for low initial concentrations of dye and is in agreement with the experimental results obtained from (Equation 13) for BP4B. 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energy of the semiconductor (hv ≥ Eg), 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, hydroxyl ions, and most of organic compounds below of reducing photogenerated holes within a wide interval of the pH due to which the formation of hydroxyl 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 (Eg = 3.2 and 3.3 eV for ZnO and TiO₂ respectively) are slightly equal to that of the 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 (lnC₀/C against t) yielding to a straight line. The regression coefficients for the fitted lines were calculated to be R² = 0.881 and 0.956 for CR and BP4B respectively. The apparent rate constants, Kₚ, and the half-life time, t½, 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 Zn₅O 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

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Pseudo-first order model</th>
<th>Experimental results</th>
<th>Pseudo-first order model</th>
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</thead>
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<td></td>
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<td>BP4B</td>
<td>CR</td>
<td>BP4B</td>
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<td></td>
<td>CR</td>
<td>BP4B</td>
<td>CR</td>
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<td>0.001</td>
<td>693.15</td>
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</table>

R²: 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, λ =365 nm).

**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]=[BP4B]=20mg/L, pH =8, T=298K, λ =365 nm and I=90/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 (hν ≥ Eg), 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 O₂ on the ZnO photocatalyst particle sites, reducing it to a superoxide radical anion O₂− 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 ‘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 valance band. The photogenerated electrons react with the adsorbed oxygen molecules to form O−+ ads, species, while the photogenerated holes that are able to migrate to the hydroxylated surface can create a highly reactive and short-lived hydroxyl radicals •OH. These processes could be represented in the following equations:

\[ \text{ZnO} + \text{hv} \rightarrow \text{ZnO} (e^- + h^+) \]  
(21)

\[ \text{O}^{-}_{\text{ads}} + e^- \rightarrow \text{O}^{-}_{\text{ads}} \]  
(22)

\[ h^+ + \text{OH}^- \rightarrow \text{OH} \]  
(23)

**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 ZnO usually is too fast (in the range of tens of femtoseconds). Further active oxygen molecule formed in Equation (27) subsequently reacts with H₂O to generate •OH radicals Equation (28) and peroxyde Equation (29).

The formed species oxidize the dye molecules, as follows:

\[ \text{Dye} + \text{hv} \rightarrow \text{Dye}^+ \]  
(24)

\[ \text{Dye}^+ \rightarrow \text{Dye}^+ + e^- \]  
(25)

\[ \text{ZnO} + e^- \rightarrow \text{ZnO}^- \]  
(26)

\[ \text{ZnO}^- + \text{O}_2 \rightarrow \text{ZnO} + \text{O}^2^- \]  
(27)

\[ \text{O}^2^- + 2\text{H}_2\text{O} + e^- \rightarrow 2\text{H}_2\text{O}_2 \]  
(28)

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH} + \text{OH}^- \]  
(29)

These •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).

\[ \text{•OH} + \text{Dye} \rightarrow \text{degradation of the dye} \]  
(30)

These observations clearly demonstrate the involvement of holes (h+), hydroxyl (OH−) and superoxide anion (O₂−) 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 oxidents involved in the photodegradation reactions were identified as holes (h+), hydroxyl radicals (•OH) and superoxide anion radicals (O₂−). 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**

We greatly acknowledge the material support obtained from DR T.M. University.

**References**


