Photodegradation study of Congo Red in Aqueous Solution using ZnO/UV-A: Effect of pH And Band Gap of other Semiconductor Groups

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Abstract

The photocatalytic degradation of Congo red in aqueous solution was investigated under UVA light at different operating conditions, including irradiation time, pH solution and band gap of MO2 (M=Ti4+ and Ce4+) and M’2O3 (M’=Al3+ and Fe3+) semiconductor groups by UV-spectrophotometric monitoring. The results showed slight stability of 597nm-band of CR over the pH range of 6-7, while, it almost completely disappeared at pH higher than 7. Maximum photodegradation was obtained at pH 8 as a result of 95.02% degradation efficiency of CR for 60 min of irradiation time. The photo decomposition efficiency of MO2 (M=Ti4+ and Ce4+) semiconductor group was higher, compared to that of M’2O3 (M’=Al3+ and Fe3+). Photodecomposition reactions correlated with pseudo-first-order kinetic model. These findings can support the design of remediation processes and also assist in predict their fate in the environment.

Keywords: Kinetics; Photocatalysis; Congo red; Zinc oxide

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 have been focalized on the heterogeneous systems based on high dispersion TiO2 with a crystalline modification of anatase (Degussa P25, Hombrit 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) and M’2O3 (M’=α-Fe2O3, Bi2O3, Al2O3, Sb2O3 etc…) metal oxides and DS (D=Zn, Cd, Pb ect…) 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 (hv ≥ Eg), a free electron (e−) and electronic vacancy-a hole (h+) are generated, 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 (O2−ads), hydroperoxide (HO2ads) radicals and hydrogen peroxide (H2O2ads) Equation (2-4), while the photo generated holes can oxidize either the organic compound directly Equation (5) or both hydroxyl ions and water molecules adsorbed on the photo catalyst surface Equation (6-7) forming the organic cation-radicals (R+ads) and hydroxylic radicals (HO2ads). The stepwise photo catalytic mechanism is illustrated below:

\[ZnO + hv → ZnO (e−_{CB}) + h^+ (VB)\]  \hspace{1cm} (1)

\[O_2 + e− → O_2−_{ads}\]  \hspace{1cm} (2)

\[O_2−_{ads} + H^+ → HO_2_{ads}\]  \hspace{1cm} (3)

\[O_2−_{ads} + 2H^+ + e− → H_2O_{2ads}\]  \hspace{1cm} (4)

\[R_{ads} + h^+ → R_+\hspace{1cm} (5)\]

\[HO_2_{ads} + h^+ → OH_2_{ads}^+\]  \hspace{1cm} (6)

\[H_2O_{ads} + h^+ → •OH_{ads} + H^+\]  \hspace{1cm} (7)

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 charges, the amphoteric properties of photocatalyst, pH solution, temperature of system, nature of pollutant, photocongerens, crystalline structure, synthesis method and photoreactor dimension [7]. Aggregation is one of the features of dyes in solution. Based on literature, Congo red 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.

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Received March 19, 2011; Accepted May 10, 2011; Published May 13, 2011


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In the present study, the stability of optical properties of the Congo red (CR) in aqueous solutions and upon photodegradation process was investigated at various pH values using UV spectroscopic monitoring. The potential ability of ZnO-assisted photocatalytic degradation of CR, was assessed in terms of evolution of the adsorption and photodecomposition efficiency at different operating parameters such as, pH solution and band gap of MO (M=Ti+4 and Ce+4) and M′2O3 (M′=Al+3 and Fe+3) semiconductor groups as a function of irradiation time. The experimental data were quantified by applying the pseudo-first order kinetic.

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 Sigma-Aldrich. Photocatalytic reactions were carried out inside a (BLX-E365) photoreactor equipped with 6 UV-A lamps with an emission maximum at λ of 365 nm. The suspension pH values were previous adjusted using NaOH/H₂SO₄ solutions via pH meter. 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 (BEA-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 nm as a function of irradiation time.

The effect of initial pH on the photocatalytic degradation of Congo red was researched over a range of pH values from 6 to 10 for avoiding dye aggregation. The experiments were also performed by replacing ZnO catalyst by MO₂ (M=Ti+4 and Ce+4) and M′₂O₃ (M′=Al+3 and Fe+3) semiconductor groups. The data obtained from the photocatalytic degradation experiments were then used to calculate the degradation efficiency η (%) of the substrate Equation (8):

$$\eta(\%) = \frac{(C_i - C_f)}{C_i} \times 100$$  

where $C_i$: dye initial concentration (mg.L⁻¹) and $C_f$: dye residual concentration after certain intervals (mg.L⁻¹).

The photocatalytic degradation efficiency of ZnO catalyst for the degradation CR was quantified by measurement of dye apparent first order rate constants under operating parameters.

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]:

$$\frac{dC}{dt} = \frac{h\nu}{\lambda j}$$

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

The photodegradation efficiency of ZnO catalyst for the degradation CR was measured by dye apparent first order rate constants under operating parameters.

Thus, a plot of reciprocal of the apparent first order rate constant 1/Kapp against initial concentration of the dye C₀ should be a straight line with a slope of 1/K′ and an intercept of 1/K₀K′. Such analysis allows one to quantify the photocatalytic activity of ZnO catalyst through the specific rate constant Kₜ, the adsorption equilibrium constant, and C₀ is the initial concentration of the substrate (Benzopurpurine 4B in our case). Inversion of the above rate equation is given by Equation (11):

$$\ln \frac{C_0}{C} = K_1 K_2 t = K_{app} t$$

where $t$ is the time in minutes required for the initial concentration of the dye C₀ 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).

$$\ln \frac{C_0}{C} = K_1 K_2 t = K_{app} t$$

where \( k_{\text{app}} \) 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 \( \ln \frac{C}{C_0} \) against irradiation time \( t \) should give straight lines, whose slope is equal to \( k_{\text{app}} \).

The half-life of dye degradation at various process parameters was raised from Equation (14).

\[
\frac{t_{1/2}}{2} = \frac{0.5C_0}{K_2} + \frac{0.693}{K_1K_2}
\]  

(14)

where \( t_{1/2} \) is defined as the amount of time required for the photocatalytic degradation of 50% of CR dye in an aqueous solution by ZnO catalyst.

**Results**

**Effect of UV irradiation and ZnO nanoparticle**

Figure 2 illustrated the photocatalytic degradation kinetics of 20 mg/L of CR in aqueous solution under different experimental conditions under UV-A alone, dark/ ZnO and UV-A/ZnO. The degradation rate was found to increase with increase in irradiation time and 95.02% of degradation were achieved within 60 min at pH of 8 (curve CR/ZnO/ UV-A). When 20 mg/L of both dye along with ZnO were magnetically stirred for the same optimum irradiation times in the absence of light, lower (20.78 %) degradation was observed (curve CR/ZnO), whereas, disappearance of dyes was negligible (0.49%) in the direct photolysis (curve CR/UV-A) indicating that the observed high decomposition of the dye 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**

**Qualitative study:** The evolution of maxima absorption bands of CR in aqueous solution and upon ZnO-mediated photocatalytic degradation under UV-A light at various pH: Figure 3 illustrated UV visible spectra of CR in aqueous solution at various pH solutions. The position and the evolution of the maxima absorption bands of CR in aqueous solution and upon ZnO-mediated photocatalytic degradation of substrate CR in aqueous solution were displayed in Table 1. Congo red in aqueous solution exhibited a main band at 497 nm (\( C_0=20 \) mg/L and natural pH=8), assigned to the absorption band of anionic monomer, and associated with two absorption bands in the ultraviolet region at 235 and 347 nm, attributed to the benzoic and naphthalene rings, respectively. As seen in Table 1, the CR monomers have nearly constant absorption bands and absorbance intensities over a range of pH values of 6 to10, while they are most sensitive to the pH solution under acidic medium (pH=6). The main band of CR monomer at 497 nm (in aqueous solution) gradually shifted to the longer wavelengths, almost reaching 595.5 and 537.5 nm at pH 2 and 4 respectively. The intensity decrease and red shift of CR monomer bands are attributed to the partially self-association of CR monomers as anionic dimers in face-to-face arrangement to minimize their hydrophobic interaction with water. For that reason, the adsorption and photocatalytic degradation conditions were conducted only within neutral and alkali pH range.

The adsorption equilibrium of CR on ZnO catalyst in dark for 30 min at different pH values (Table 1) showed that CR monomers have nearly constant absorption bands, while a slight decrease in the absorbance intensities over the pH values in the range of 6 and 10 was observed.

On the other hand, the behavior of the maxima absorption bands of CR during the ZnO-mediated photocatalytic degradation as a function of pH solution differ in certain aspects from those of CR in aqueous solution and adsorbed on ZnO catalyst surface. As elucidated Table 1, the photodecomposition profile of CR was accompanied by a blue shift of the main bands of CR monomers, compared to those in aqueous solutions.

The maxima bands became visible at 497, 481, 492, 481 and 488 nm at pH 6, 7, 8, 9 and 10 respectively as the light illumination time was increased up to 40 minutes. However, they remained nearly constant at pH 6 and 7 and completely disappeared within 60 minutes of irradiation time at pH beyond of 7. The shift does not exceed 10 nm over the pH in the range of 6 and 10. These results are consistent with the destruction of CR chromophoric structure in the vicinity of the azo-linkage. Additionally, this shift was accompanied by a parallel decrease in the intensities of bands in the ultraviolet region located at 235 and 347 nm, ascribed to the benzoic and naphthalene rings, respectively. No new absorption bands appeared in either the visible or the ultraviolet spectra regions.
Photonically degradable rate of CR in aqueous solution by ZnO under UV-A irradiation at various pH: 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) for ZnO is 9.0. For pH values lower than the pH ZPC of ZnO, the surface becomes negatively charged for pH values higher than pH ZPC.

Quantitative study: The evolution of photocatalytic degradation rate of CR in aqueous solution and during the ZnO-mediated photocatalytic degradation of dye as a function of pH (\([\text{ZnO}] = 0.5\, \text{g/L}, [\text{CR}] = 20\, \text{mg/L}, \lambda_{\text{max}} = 365\, \text{nm}, \lambda = 90\, \text{J/cm}^2\) and irradiation time = 60min).

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Adsorption (CR/ZnO)</th>
<th>Photocatalytic degradation (CR/ZnO/UV-A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Species ((\lambda) nm)</td>
<td>AE (%)</td>
</tr>
<tr>
<td></td>
<td>(CR(_1))</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.359</td>
<td>595.5</td>
</tr>
<tr>
<td>4</td>
<td>0.986</td>
<td>537.5</td>
</tr>
<tr>
<td>6</td>
<td>0.83</td>
<td>497</td>
</tr>
<tr>
<td>8</td>
<td>0.628</td>
<td>497</td>
</tr>
<tr>
<td>10</td>
<td>0.83</td>
<td>497</td>
</tr>
<tr>
<td>12</td>
<td>0.83</td>
<td>496</td>
</tr>
</tbody>
</table>

CR and (CR\(_1\)): Monomer and dimer anion forms of Congo red respectively; A: Absorbance; AE: Adsorption efficiency; PDE: Photocatalytic degradation efficiency; D: Disappearance

**Table 1:** The position of the absorption bands of CR in aqueous solution and during the ZnO-mediated photocatalytic degradation of dye as a function of pH (\([\text{ZnO}] = 0.5\, \text{g/L}, [\text{CR}] = 20\, \text{mg/L}, \lambda_{\text{max}} = 365\, \text{nm}, \lambda = 90\, \text{J/cm}^2\) and irradiation time = 60min).

At pH higher than pH ZPC value (i.e. pH=9-10), 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 CR dye anions results in electrostatic repulsion electrostatic.

Moreover, the stability of ZnO may not be guaranteed at this high pH due to possibility of alkaline dissolution of ZnO Equation (19):

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

Photocatalytic activity of anionic dyes (mainly sulfonated groups) such as CR reaches a maximum value (95.02%) in lower pH ZPC (i.e. pH=8). At alkaline mediums, excess of hydroxyl anions facilitate photogeneration of \(\cdot\text{OH}\) 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 dye was weak, degradation scarcely occurred. The adsorption affects strongly the accessibility of the surface reducing species to the CR reduction kinetics. However, adsorption is not the only factor that controls the photocatalytic degradation of dye. Although the adsorption extents of the dye were lower, the degradation rates were in the reverse order (Figure 4 and Table 2).

At pH higher than pH ZPC value (i.e. pH=9-10), 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 CR dye anions results in electrostatic repulsion electrostatic.

The linearity of the plots of \(\text{InC}/\text{C}_0\) against irradiation time \(t\) for the photocatalytic degradation process of CR by ZnO catalyst at low dye concentration.

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

**Figure 4:** Adsorption and photocatalytic degradation of CR as a function of initial pH (\([\text{ZnO}] = 0.5\, \text{g/L}, [\text{CR}] = 20\, \text{mg/L}, \lambda_{\text{max}} = 365\, \text{nm}, \lambda = 90\, \text{J/cm}^2\)).
concentrations and under various pH solutions adsorption (Figure 5, Table 2) suggest that the adsorption data were satisfactorily described by pseudo-second order model (R²=0.747-0.968).

**Effect of band gap of semiconductor**

The photocatalytic degradation reactions were further performed in two semiconductor groups MO₂ (M=Ti⁴⁺ and Ce⁴⁺) and M'₂O₃ (M'=Al³⁺ and Fe³⁺) having different band gap values. Figure 5 depict the plot of Cₐ/C₀ versus irradiation time CR on ZnO catalyst. It is evident that the photocatalytic degradation of dye greatly depends on the electronic structure and properties of semiconductor surface/solvent. The results exposed in Figure 6 shows that the highest degradation efficiency of 95.02% was obtained for ZnO catalyst. The photo decomposition process profiles under the same optimized conditions (pH=5, C=20 mg/L CR, m/v=0.5g/L ZnO and irradiation time of 60min) were different for both MO₂ and M'₂O₃ semiconductor groups in comparison with that of ZnO catalyst. As elucidated Figure 5, the best result of photocatalytic degradation process was observed for MO₂ group. TiO₂ catalyst exhibited high degradation efficiency of 93.34 %, whereas, only 14.95% of CR was degraded for CeO₂ semiconductor. On the other hand, the M'₂O₃ (M'=Al³⁺ and Fe³⁺) semiconductors group showed lower (4.20 and 5.15 % for Al₂O₃ and Fe₂O₃ respectively) best result of photocatalytic degradation process was observed for MO₂ in comparison with that of ZnO catalyst.

**Table 2:** Kinetic parameters of the photocatalytic degradation of CR as a function of initial pH ([ZnO]= 0.5g/L; [CR]= 20mg/L, T=298K, λ_max=365 nm and I=90 J /cm²).

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Adsorption efficiency (%)</th>
<th>Photocatalytic degradation efficiency (%)</th>
<th>K_app (min⁻¹)</th>
<th>t₁/₂ (min)</th>
<th>R² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=6</td>
<td>8.000</td>
<td>14.928</td>
<td>0.003</td>
<td>231.049</td>
<td>49.0</td>
</tr>
<tr>
<td>pH=7</td>
<td>7.905</td>
<td>6.723</td>
<td>0.001</td>
<td>693.147</td>
<td>88.7</td>
</tr>
<tr>
<td>pH=8</td>
<td>7.905</td>
<td>14.928</td>
<td>0.003</td>
<td>231.049</td>
<td>49.0</td>
</tr>
<tr>
<td>pH=9</td>
<td>8.000</td>
<td>14.928</td>
<td>0.003</td>
<td>231.049</td>
<td>49.0</td>
</tr>
<tr>
<td>pH=10</td>
<td>7.905</td>
<td>14.928</td>
<td>0.003</td>
<td>231.049</td>
<td>49.0</td>
</tr>
</tbody>
</table>

**Table 3:** Kinetic parameters of photocatalytic degradation of CR as a function of band gap of semiconductors ([CR]= 20mg/L, [Catalyst]= 0.5g/L, pH=8, T=298K, λ_max=365 nm and I=90 J /cm²).

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Adsorption efficiency (%)</th>
<th>Photocatalytic degradation efficiency (%)</th>
<th>K_app (min⁻¹)</th>
<th>t₁/₂ (min)</th>
<th>R² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO₂ (M=Ti⁴⁺)</td>
<td>10.510</td>
<td>95.018</td>
<td>0.044</td>
<td>15.753</td>
<td>94.4</td>
</tr>
<tr>
<td>MO₂ (M=Ce⁴⁺)</td>
<td>13.479</td>
<td>93.342</td>
<td>0.045</td>
<td>15.403</td>
<td>98.5</td>
</tr>
<tr>
<td>M'₂O₃ (M'=Al³⁺)</td>
<td>4.207</td>
<td>7.905</td>
<td>0.001</td>
<td>693.147</td>
<td>88.7</td>
</tr>
<tr>
<td>M'₂O₃ (M'=Fe³⁺)</td>
<td>5.151</td>
<td>4.723</td>
<td>0.001</td>
<td>693.147</td>
<td>34.0</td>
</tr>
</tbody>
</table>

**Figure 5:** Pseudo first order kinetics of photocatalytic degradation of CR as a function of initial pH ([ZnO]= 0.5g/L; [CR]= 20mg/L, T=298K, λ_max=365 nm and I=90 J /cm²).

**Figure 6:** Photocatalytic degradation kinetics of CR as a function of band gap of semiconductors ([CR]= 20mg/L, [Catalyst]= 0.5g/L, pH=8, T=298K, λ_max=365 nm and I=90 J /cm²).
The photodegradation rate of MO$_2$ (M=Ti$^{+4}$ and Ce$^{+4}$) semiconductor group was higher, compared to that of M'$_2$O$_3$ (M'=$Al^{+3}$ and Fe$^{+3}$). Photodecomposition process profiles were satisfactory correlated with pseudo-first-order kinetic model. These findings suggest that the degradation of Congo Red mainly occurred by the attack of OH radical [15].

**Acknowledgments**

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

**References**


