Preparation of Perovskite Nanocomposites and Photochemical Degradation Kinetics of Acid Yellow 199

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(Received 05 Apr. 2012; Final version received 21 Sep. 2012)

Abstract
In this study PbZrO₃ was prepared as a matrix by the sol-gel process and is characterized by XRD and SEM techniques. The particle size of the synthesized nanocomposite is evaluated about 43 nm. The Lead Zirconate is then doped with Ce³⁺/TiO₂ in different ratios. Nanocomposites are added in the reaction in a photoreactor with a pollutant (an Azo dye) and as a result the degradation percentage is obtained. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique. Kinetic studies on these nanocomposites are carried out based on the related models and the reaction order is evaluated. Finally, Surface adsorption of the pollutants on the nanocomposite surface is measured through IR technique.

Keywords: Lead Zirconate, Photoreactor, Acid Yellow 199.

Introduction
Water bodies consisting of both polluted wastewaters and groundwater from the seas, rivers and lakes are of special concern to people working in water purification and the environment in general. Organic dyes came up as one of the many new chemicals which could be used in many industrial activities. Due to the extensive use of these dyes in industries, they have become an integral part of industrial effluent [1]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem [2]. Various methods have been suggested to handle the dye removal from water including the biodegradation, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process [3–8]. Among these techniques, the advanced oxidation processes [9] appears to be a promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils, because

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they can provide an almost total degradation. The various AOPs include the following:

**Introduction**

(1) Photolysis (UV or VUV)

(2) Hydrogen peroxide (this includes the $\text{H}_2\text{O}_2 + \text{UV}$, Fenton: $\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+}$, Fenton-like reagents: $\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+}$, Fenton-like reagents:

(3) Ozone (this includes ozonation, photo-

ozonation, ozonation + catalysis and $\text{O}_3 + \text{H}_2\text{O}_2$

and $\text{O}_3 + \text{Fe}^{2+}/\text{Fe}^{3+}$)

(4) Photocatalysis (this includes heterogeneous
catalysis and photocatalysis and $\text{TiO}_2 + \text{CdS} +$

combinations).

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**Figure 1.** Schematic diagram showing the generation of oxidative species in a photocatalytic study.

Photocatalytic degradation is a part of AOP which has proven to be a promising technology for degrading organic compounds. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this process, an electron–hole pair is produced.

$$\text{Catalyst} + \h^+ \rightarrow \text{e}^- + \text{h}^+ \ (1)$$

Where, $\text{e}^-_{\text{cb}}$ and $\h^+_{\text{vb}}$ are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases $\h^+_{\text{vb}}$ can react easily with surface bound $\text{H}_2\text{O}$ to produce \(\cdot\)OH radicals, whereas, $\text{e}^-_{\text{cb}}$ can react with $\text{O}_2$ to produce superoxide radical anion of oxygen:

$$\text{H}_2\text{O} + \h^+_{\text{vb}} \rightarrow \cdot\text{OH} + \text{H}^+ \ (2)$$

$$\text{O}_2 + \text{e}^-_{\text{cb}} \rightarrow \text{O}_2^- \ (3)$$

This reaction prevents the combination of the electron and the hole which are produced in the first step. The \(\cdot\)OH and $\text{O}_2^-$ produced in the above manner can then react with the dye to form other species and is thus responsible for the discoloration of the dye [10].
O₂−• + H₂O → H₂O₂  \hspace{1cm} (4)
H₂O₂ → 2•OH  \hspace{1cm} (5)
•OH + dye → dye_{ox} (k= 10^{9} M^{-1} s^{-1}) (6)
Dye + e_{cb} → dye_{red}  \hspace{1cm} (7) \cite{11}

Organic dyes came up as one of the many new chemicals which could be used in many industrial activities. An ideal photocatalyst should exhibit the following features: (i) high reaction rate under band gap (or higher) irradiation; (ii) photostability; (iii) chemical and biological inactivity; and (iv) accessibility and low cost. Titanium dioxide mediated photocatalytic oxidation have been examined and used as photocatalysts for the degradation of environmental pollutants in water. A schematic presentation of the mechanisms of generation of oxidative species in a photocatalytic study is shown in Figure 1 \cite{12}.

**Photodegradation Kinetics**

The pseudo first order equations are presented as equations 8 and 9. The experimental kinetics data were further analyzed using the pseudo second order kinetic model 10 \cite{13}:

- Lagergern: \( \ln (q_e - q_t) = \ln q_e - kt \) \hspace{1cm} (8)
- Elovich: \( q_t = 1/\beta \ln (a\beta + 1/\beta \ln t) \) \hspace{1cm} (9)
- Blanchard: \( t/q_t = 1/k_2 q_e^2 + t/q_e \) \hspace{1cm} (10)

**Experimental**

**Preparation of PbZrO₃**

In this work, the PbZrO₃ was prepared by the sol–gel process. Lead acetate trihydrate \( \text{Pb(CH}_3\text{COO)}_2\cdot3\text{H}_2\text{O} \), acetic acid and zirconium (IV) acetylacetonate \( \text{Zr(C}_2\text{H}_4\text{COCHCOCH}_3\text{)}_4 \) were selected as starting materials. In a typical synthesis procedure, 25 ml isopropanol was mixed with zirconium (IV) acetylacetonate \( \text{Zr(C}_2\text{H}_4\text{COCHCOCH}_3\text{)}_4, 0.0156 \text{mol} \) dissolved in 8 ml of acetic acid. Lead acetate trihydrate \( \text{Pb(CH}_3\text{COO)}_2\cdot3\text{H}_2\text{O}, 0.0309 \text{ mol} \) dissolved in 10 ml acetic acid was then added to the above precursor solution under vigorous stirring. At first sol was prepared then it was exchanged to gelatinized by heating treatment. Precursor solution was dried at 120°C to produce dried gels then ground and calcined at 650°C for 4 h to obtain PZ(PbZrO₃) nanocrystal powder \cite{14-19}.

**Doping PbZrO₃ with Ce³⁺/TiO₂**

0.37, 0.92, 1.33, 1.64 and 1.895 g Ce(NO₃)₃ added to 3.63, 3.07, 2.66, 2.35 and 2.105 g TiO₂ anatase respectively, then each of them mixed with 1 g PbZrO₃ and 40-50 ml tert-Butanol. Precursor solution was dried at 120°C to produce dried then ground and calcined at 700°C for 4 h to obtain respectively PZ- Ce³⁺/ TiO₂ \( \text{Ce}^{3+}/\text{TiO}_2=0.1, 0.3, 0.5, 0.7 \) and 0.9.

**Photodegradation Procedure**

3g PZ- Ce³⁺/ TiO₂ (Ce³⁺/ TiO₂ =0.1, 0.3, 0.5, 0.7 and 0.9) is added to 200 ml Acid yellow 199 \( 10^{-4} \) M with 20 ml H₂O₂ 0.5 M in photoreactor and the initial and final absorptions were studied at some intervals by monitoring the change in substrate concentration employing UV spectroscopic analysis technique.
Results and discussion

SEM analysis of PZ is shown in Figure 2. The particle size of the synthesized nanocomposite is evaluated to be about 43 nm. The weight percent results obtained from EDXA analysis is in total agreement with PbZrO₃ structure.

Degradation efficiency

TiO₂ is known to be active only under irradiation of UV light. With the advancement of experimental techniques, various catalysts have been tested for their efficiencies towards dye degradation. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique. The photocatalysed degradation of Acid Yellow 199 was investigated in aqueous suspensions of (PZ-Ce⁺³/TiO₂) and PZ. The photocatalytic activity was examined in the oxidation process by using TiO₂ and Ce⁺³-doped PbZrO₃ (PZ- Ce⁺³/ TiO₂) and PbZrO₃ with different ratios of Ce⁺³/ TiO₂ (0.1, 0.3, 0.5, 0.7 and 0.9) and H₂O₂.

Degradation efficiency = \[(\text{initial absorption} - \text{absorption in time } t)/ \text{initial absorption}\] × 100

Result of degradation efficiency, initial and final (different time 1, 2, 3h) for (PZ- Ce⁺³/ TiO₂) and PZ are shown in Tables 1 and 2 respectively.

Table 1. Degradation % of Acid yellow 199 with PZ - Ce⁺³/ TiO₂.

<table>
<thead>
<tr>
<th>Sample: PZ - Ce⁺³/ TiO₂</th>
<th>t=1 hr</th>
<th>t=2 hr</th>
<th>t=3 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>43.23</td>
<td>52.75</td>
<td>59</td>
</tr>
<tr>
<td>0.3</td>
<td>64</td>
<td>75.81</td>
<td>76.27</td>
</tr>
<tr>
<td>0.5</td>
<td>76.03</td>
<td>79.67</td>
<td>81.67</td>
</tr>
<tr>
<td>0.7</td>
<td>78.49</td>
<td>82.98</td>
<td>87.31</td>
</tr>
<tr>
<td>0.9</td>
<td>82.11</td>
<td>89.90</td>
<td>97.46</td>
</tr>
</tbody>
</table>

Table 2. Degradation % of Acid yellow 199 with PZ.

<table>
<thead>
<tr>
<th>Sample: PZ</th>
<th>t=1 hr</th>
<th>t=2 hr</th>
<th>t=3 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ</td>
<td>21.05</td>
<td>32.92</td>
<td>39.29</td>
</tr>
</tbody>
</table>
Surface adsorption of the pollutant on the nanocomposite surface is studied with IR technique. The results are shown that the pollutant decomposed completely but not adsorbed on nanocomposite surface. The decomposition of the pollutant increases with increasing the time of reaction. The result of three kinetic models (Laguerren, Elovich, Blanchard) for PZ are shown in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kinetics Study</th>
<th>( R^2 ) (Correlation Coefficient)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ</td>
<td>( \ln(q_e - q_t) = \ln q_e - k_1 t ) ( y = -0.015x - 13.01 )</td>
<td>0.855</td>
<td>-</td>
</tr>
<tr>
<td>PZ</td>
<td>( q_t = \frac{1}{\beta} \ln(q_\beta) + \frac{1}{\beta} \ln(t) ) ( y = -0.015x - 13.01 )</td>
<td>0.897</td>
<td>pseudo first order reaction</td>
</tr>
<tr>
<td>PZ</td>
<td>( k_2 q_e^2 + (1/q_e) \cdot \int \frac{t}{q_e} = 6(10)^{-7}x - 2(10)^{-6} ) ( y = 32262x + 5(10)^7 )</td>
<td>0.789</td>
<td>-</td>
</tr>
</tbody>
</table>

Based on the values of correlation coefficient for each model, it was found that PZ nanocomposite reaction obeys from pseudo-first order reaction rate. The corresponding plots are presented in Figures 3, 4 and 5 respectively.

**Figure 3.** Laguerren kinetic plot obtained for PZ.

**Figure 4.** Elovich kinetic plot obtained for PZ.
Results of three kinetic models (Lagergern, Elovich, Blanchard) for PZ- Ce$^{3+}$/TiO$_2$ with different doping ratios are shown in Table 4. Based on the values of correlation coefficient for each model, it was found that in all cases Ce$^{3+}$ Photocatalysts obey from pseudo-second order kinetic that plots of kinetic models (Lagergern, Elovich, Blanchard) for PZ- Ce$^{3+}$/TiO$_2$ (Ce$^{3+}$/TiO$_2$=0.1) are presented in Figures 6, 7 and 8 respectively. Figure 9 shows the effect of irradiation time on absorption spectra of AY199.

![Figure 5. Blanchard kinetic plot obtained for PZ.](image)

![Figure 6. Lagergern kinetic plot obtained for PZ- Ce$^{3+}$/TiO$_2$ (Ce$^{3+}$/TiO$_2$=0.1).](image)

![Figure 7. Elovich kinetic plot obtained for PZ- Ce$^{3+}$/O$_2$ (Ce$^{3+}$/TiO$_2$=0.1).](image)
IR spectrum of Acid yellow 199 is compared with PZ- Ce⁴⁺/TiO₂ catalyst before and after interaction in the photoreactor that represents the dye was decomposed and didn’t adsorb on surface photocatalyst. The comparison of IR spectrum of PZ- Ce⁴⁺/TiO₂ catalyst before and after interaction in the photoreactor indicates that they are almost same and there is no Acid yellow 199 IR peak in the IR spectrum of it.

**Table 4.** Results of kinetic studies for photodegradation of dye on PZ- Ce³⁺/TiO₂.

<table>
<thead>
<tr>
<th>PZ- Ce³⁺/TiO₂</th>
<th>Kinetics Study</th>
<th>R² (Correlation Coefficient)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>ln(q₀-q)= lnq₀ - k₁t y = -0.00x – 1098</td>
<td>0.987</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>qₜ=1/β ln(αβ)+1/β ln(t) y = 4(10)^{7}x -3(10)^{-7}</td>
<td>0.977</td>
<td>-</td>
</tr>
</tbody>
</table>
Conclusion

The experimental results indicate that PbZrO₃ had semiconducting properties and under UV irradiation, photocatalytic properties are shown and electron-hole pairs produced. After spending time degradation percentage of Acid yellow 199 are increased. Increasing degradation percentage of Acid yellow 199 by PZ-Ce³⁺/TiO₂ indicates that photocatalytic property of PbZrO₃ are improved in the new PZ-Ce³⁺/TiO₂ composite which is a result of more convenient electron-hole pairs and radicals generation in comparison with PZ alone.

References


