The degradation of 2,4 dichlorophenoxyacetic acid over zirconia doped photocatalysts

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Introduction

For many years, 2,4 dichlorophenoxyacetic acid (2,4-D) has been used as a herbicide to destroy wide leaf plants, which interfere with the growth of crops such as wheat and corn. It is mildly toxic [1] and its destruction using microbiological and chemical methods has yielded mixed results [2]. Heterogeneous photocatalysis is considered to be an oxidation technique used in the decontamination of water [3-6]. It has the promise of decreasing water treatment costs and has an advantage over other methods in that the catalyst can be regenerated. Although titania has been used nearly exclusively, it doesn’t have the same adsorption capacity for different molecules [7]. Zirconia, synthesized using sol-gel methods can behave as a semiconductor, which enables its use as a photocatalyst alternative to titania. In the current study, zirconia was doped with transition metals and tested in the photocatalytic degradation of 2,4-D.

Materials and Methods

The photocatalysts used in this study were prepared using a sol-gel method. Zirconium n-butoxide was used as the alcoxide with tertiary butanol as the solvent. The nitrates corresponding to the metals used as dopants were added to deionized water at a concentration of 1 mole % metal. The resulting gels were dried at 90°C for 12 hours followed by calcinations at 400°C for 12 hours. Surface areas and pore size distributions were performed using nitrogen adsorption measurements at 77K. A low pressure mercury lamp (254 nm) was used to irradiate the dispersed sample. The degradation was followed using UV in order to obtain concentrations as a function of time.

Results and Discussion

The adsorption-desorption isotherms for the pure oxide is shown in figure 1. Similar behavior was observed for all of the isotherms used in this study. They correspond to typical type IV isotherms with little or no adsorption-desorption hysteresis. For the pure oxide the hysteresis is practically non-existent suggesting very narrow pores. The photocatalytic results show that Mn and Fe increase the photoactivity of zirconia. These results are shown in Table 1. The photodegradation of 2,4-D increases from 65% to 85% for Mn/zirconia. The addition of Ni, Co or cu to zirconia show little or no improvement over pure zirconia.

Table 1. Percent degradation of 2,4-D for different photocatalysts following irradiation for a period of 2 hours.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>%</th>
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<tbody>
<tr>
<td>ZrO₂</td>
<td>65</td>
</tr>
<tr>
<td>Mn/ZrO₂</td>
<td>85</td>
</tr>
<tr>
<td>Fe/ZrO₂</td>
<td>80</td>
</tr>
<tr>
<td>Co/ZrO₂</td>
<td>65</td>
</tr>
<tr>
<td>Ni/ZrO₂</td>
<td>60</td>
</tr>
<tr>
<td>Cu/ZrO₂</td>
<td>60</td>
</tr>
</tbody>
</table>

Significance

Figure 1. Adsorption-desorption isotherm for pure ZrO₂ annealed at 400°C

References