Kinetic studies on the photocatalytic decolourisation of water-soluble crown dyes using Fe$^0$ and Zn$^0$ catalysts

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Photodecolourisation of crown dyes with Fe$^0$ and Zn$^0$ as catalysts is discussed. Effects of pH and concentration of catalyst on the decolourisation and kinetics for degradation etc have been studied.

Zero-valent iron (Fe$^0$) is one of the most abundant metal on the earth and promising reactive medium of degrading contaminants$^1$. These methods have recently been used for rapid degradation of organic materials$^2,3$.

In the present investigation, the photocatalytic degradation of newly synthesized crown dyes have been studied with zero valent iron and zinc in the presence of sunlight and UV light. The purpose of this work is to investigate the feasibility of discoulouration of the dyes by the UV/Fe$^0$ system and the effects of sunlight and UV light on the discoulouration efficiencies.

Experimental Procedure

Chemicals and reagents

The chemicals used were of A.R. grades of E. Merck or B.D.H.

Synthesis of the dyes

The dyes were synthesized by the diazotization of trans-diaminodibenzo-18-crown-6 and coupling with H-acid, γ-acid and K-acid, respectively as described elsewhere$^4$. A brief synthesis is described below.

Bis(2-chloro ethyl)ether and dibenzo-18-crown-6-ether(DB18C6) were synthesised from diethylene glycol$^5$ and catechol$^6$, respectively. Nitration of DB18C6 gave tran-DB18C6. The transientaminodibenzo-18-crown-6) [BADBC] was synthesized by reduction of trans-DB18C6 with Raney nickel and anhydrous ethanol. The crown dyes were prepared by reacting BADBC with NaNO$_2$ in HCl at -5°C and coupling with H-acid (3, 6-disulfonic acid), γ-acid (7-amino-1-naphthol-3-sulphonic acid) and K-acid (8-amino-1-naphthol-3, 5-disulphonic acid) in NaOH$^7$ to obtain 4, 4'-bis(1-hydroxy-8-amino-3,6-disulfo-2-naphthylazo)-2, 3, 11, 12 dibenzo-1, 4, 7, 10, 13, 12-hexaoxyacyclo-octadeca-2, 11-dyne (H-ADBC), 4, 4'-bis(1-hydroxy-7-amino-3-sulfo-2-naphthylazo)-2, 3, 11, 12-dibenzo-1, 4, 7, 10, 13, 16-hexaoxyacyclo-octadeca-2, 11-dine (γ-BADBC) and 4, 4'-bis (1-hydroxy-8-amino-3, 5-disulfo-2-naphthyl)-2, 3, 11, 12-dibenzo-1, 4, 7, 10, 13, 16-hexaoxyacyclo-octadeca-2, 11-dine (K-BADBC), respectively.

Apparatus

BET surface area of the catalysts was determined by using Micromeritics Pulse Chemisorb - 2700 system Shimadzu Particle Size Analyser (SALD). UV experiments were performed in a specially designed double-walled reactor vessel made up of pyrex glass fitted with low pressure mercury ultra-violet lamp (8 watts Spectroline Penray Lamp, UV Products, Inc., California) emitting light through a quartz envelope with the wavelength maximum at 253.9 nm with power supplier (230 v, 50 Hz, Spectronic Corporation, New York, U.S.A.) (Fig. 1). Other experiments were performed in an open reactor system.

The intensity of sunlight and UV radiation was measured using a digital Lux-meter LX-101.

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Method

Dye solutions were stirred with an agitator to keep the catalyst suspended. Either HCl or NaOH was used to adjust the pH 2-6 of the solution. Samples were withdrawn at the intervals of 15 or 30 min and centrifuged at 4000 rpm. The absorbance of the solutions was measured at 550 nm, 545 nm and 410 nm for H-BADBC, γ-BADBC and K-BADBC, respectively.

Results and Discussion

BET surface area of Fe⁰ and Zn° was found to be 7.47 m²/g, and the particle size was 0.44 microns. The intensities of the UV and sunlight were found to be 74 and 7-10 × 10⁴ Lux, respectively.

To examine the effect of the sunlight and UV irradiation, control experiments for decolouration of all the dyes were conducted under (a) dark, (b) sunlight, (c) UV, (d) sunlight + Fe⁰, (e) UV + Fe⁰, (f) sunlight + Zn° and (g) UV + Zn° conditions (Fig. 2).

The photodecolourisation of H-BADBC, γ-BADBC and K-BADBC, under different conditions is shown in Figs 2-5. The data show that there was no significant decolourisation in the absence of catalyst and light, which suggested that decolourisation of all the three dyes was purely photocatalytic. Exposure of the dyes in UV irradiation results almost in no decolourisation. However, in the presence of Fe catalyst, an increased photodecolourisation was observed. Both the catalysts were found to be more efficient when the dyes were exposed to sunlight. Almost 100% decolourisation of dyes with Fe⁰ and Zn° in presence of UV light was attributed to the fact that the bandgap of catalysts was favourable for UV light.

Effect of pH on t₁/₂ values

The photocatalytic reactions were carried out at the different pH 2-11. The t₁/₂ values (time taken to degrade 50% of initial concentration) were determined for a particular concentration of each dye at the pH values ranging from 2 to 11. The (t₁/₂) values were plotted against the pH for each dye (Fig. 3). It reveals that increase in pH from 2 to 6 increases the t₁/₂ values. At high pH (>6) the photodecolourisation did not occur. Hence, the optimum pH for the photocatalytic reaction is lower e.g. (pH < 2.0).

![Fig. 3—Effect of pH on the photodecolourisation of the dyes in presence of catalyst Fe⁰ and Zn° under UV radiation.](image)

![Fig. 2—Effect of time and amount of catalysts on the photodecolouration under (a) dark, (b) sunlight, (c) UV, (d) sunlight + Fe⁰, (e) UV + Fe⁰, (f) sunlight + Zn° and (g) UV + Zn° conditions.](image)
Table 1—Rate of decolouration of the crown dyes in UV radiation

<table>
<thead>
<tr>
<th>Dyes</th>
<th>K 0.5 mol⁻¹min⁻¹</th>
<th>Zn⁺⁺</th>
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<tbody>
<tr>
<td>H-BADBC</td>
<td>0.024</td>
<td>0.019</td>
</tr>
<tr>
<td>γ-BADBC</td>
<td>0.034</td>
<td>0.023</td>
</tr>
<tr>
<td>K-BADBC</td>
<td>0.036</td>
<td>0.032</td>
</tr>
</tbody>
</table>

where $K'$ is the apparent rate constant of the photocatalytic decolourisation. When $t = t_{1/2}$ and $C_0/C = 0.5$, then $t_{1/2} = (0.5C_0)/K + 0.693/K'$.

The rate of decolourisation of the dyes with the iron and zinc catalysts is given in Table 1. From these results it can be seen that the molecular structure of the dyes containing an azo bond is an important factor for decolourisation. The plots of $C/C_0$ versus time (min) (Fig. 4) show that higher the initial concentration, the smaller is the decolourisation ratio. The comparison of the decolourisation efficiencies under the UV/Fe⁺ and Fe⁰ system is given in Table 2. In the 2-6 pH range the decolourisation is enhanced with the UV light alongwith Fe⁰ and Zn⁺⁺ expressed by ΔDE with a maximum value of 9.10 for K-BADBC with Fe⁰ while with Zn⁺⁺ the maximum value 11.47 for γ-BADBC. The order of decolourisation has been obtained as ΔDEFe⁰ K-BADBC > H-BADBC > γ-BADBC and order of ΔDEZn⁺⁺ γ-BADBC > K-BADBC > H-BADBC.

Optimisation of catalyst weights

The weight of catalyst was varied from 0.4 to 1.0 g/L for studies using UV radiation keeping the volume and concentration of dyes constant. The concentration of each dye obtained at different intervals of time was found out and their $t_{1/2}$ and K (rate constant) were calculated. The $t_{1/2}$ values were plotted against the amount of catalyst (Fig. 5).

It can be seen from Fig. 4 that with increase in the amount of iron and zinc the $t_{1/2}$ values decreases in all the cases. This is due to the exposed surface area of Fe⁰. However, after the 0.8 g of catalyst the $t_{1/2}$ values did not reduce and beyond 1.0 g the $t_{1/2}$ values were almost constant since the saturation point might have been reached and there is no increase in the surface area of the catalyst. The Figs 3-5 shows that 0.8 g/L of the Fe⁰ and Zn⁺⁺ catalysts are needed to decolourise the dyes, under UV radiation.

References