Abstract

The copper mustard and soyabean surfactants have been synthesized and characterized by IR and NMR spectroscopic techniques. The photo catalytic degradation of copper mustard and soyabean surfactants have been carried out by zinc oxide in non-aqueous solutions. Various factors such as effect of concentration, dose of ZnO, light intensity and solvent polarity were varied to achieve the optimum rate of photo degradation. Both copper surfactants were degraded successfully by using ZnO under UV light. The disappearance of copper surfactants follows a pseudo-first-order kinetics according to the Langmuir-Hinshelwood (L-H) model.

Keywords: Zinc oxide; Photo catalytic degradation; Semiconductor; Copper mustard and soyabean surfactants.

1. Introduction

Surfactants are materials that tend not only to accumulate at the surface, but also, by their presence, change the properties of surfaces [1-2]. They are capable of making a transition from a state of molecular disintegration to a colloidal state [3]. The use of surfactants as wood preservatives, water proofing & repellences agents, and in various industries of rubber, paints and varnishes etc. are relatively newer applications [4-5]. Survey of literature shows that copper soaps and their complexes with nitrogen and sulphur containing ligands play a vital role in various applications [6-8]. Surfactant derived from different fatty acids and edible oils with transition metal like copper (II) and exact information about their thermal degradation will play a vital role in its selection in specific applications in various fields of agro chemistry and pharmacology and in their selection as herbicides, fungicides, pesticides and insecticides [9-12]. Hence it is important to find out some advanced methods for the degradation of surfactants due to these are less biodegradable.

Zinc oxide work as a semiconductor for various applications [13-14]. Photodegradation of various dyes i.e naphthol green B [15], methylene blue [16-17] textile waste water [18], enhancing photocatalytic activity by natural pigment [19], rhodamine B [20], commercial dyes [21], some of pharmaceuticals [22], tetracycline [23] have been reported. Therefore, we plan to first synthesize and characterization of copper mustard and soyabean surfactants. The photo catalytic degradation of copper mustard and soyabean surfactants has been carried out by zinc oxide in non-aqueous solutions. Various factors such as effect of concentration, dose of ZnO, light intensity and solvent polarity were varied to achieve the optimum rate of photo degradation. The developed method is easy due to its simple operation, and low cost.
2. Materials and methods

2.1 Synthesis

Firstly, copper mustard and soya bean surfactants were prepared by direct metathesis of corresponding potassium surfactant [24]. The synthesized compounds are denoted by CM and CS. The physical & analytical data of CM and CS surfactants are given in Table-1.

\[
\text{RCOOH} \xrightarrow{\text{KOH, EtOH}} \text{RCOOK} \xrightarrow{\text{Cu (II), Benzene}} (\text{RCOO})_2\text{Cu}
\]  

(1)

3. Results and Discussion

3.1 Photo-chemical degradation studies:

The photo-catalytic degradation has been carried out by reported method [25]. The calculation of degradation efficiency \(\psi\) was made by the relation.

\[
\text{Degradation \% } = \frac{A^0 - A}{A^0} \times 100
\]  

(2)

Here \(A^0\) is initial absorbance, and \(A\) is absorbance after degradation of copper surfactants at time \(t\). The rate constant, \(k\) was calculated by using the expression:

\[
k = 2.303 \times \text{slope}
\]  

(3)

The effects of the various parameters such as concentration of soap, amount of semiconductor, effect of light intensity, effect of polarity of solvent on the rate of photocatalytic degradation are as follows:

3.1.1 Effect of Concentration of Surfactants

The rate of photocatalytic degradation of CM and CS is likely to be affected by change in concentration of the surfactant and therefore, the concentration of CM and CS was varied from 0.40-0.96 g l\(^{-1}\). The results are graphically presented in Fig.1 with RSD \(\pm 0.2\%\). The rate of photocatalytic degradation was found to increase with increasing concentration of CM, CS surfactant up to 0.6 g l\(^{-1}\). Further increase in the surfactant concentration resulted in a decrease the rate of degradation (Table 2) which was also coincide by rate constant \(k\) (Fig.2). The increase in the rate may be due to the fact that as the concentration of copper surfactant was increased more surfactant molecules were available for excitation and energy transfer and The decrease in the rate may be attributed to the fact that the surfactant molecules will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles [26].

Table 1: Analytical and Physical Data of Copper Surfactants Derived from Mustard / Soyabean Oil

<table>
<thead>
<tr>
<th>Name of Surf.</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>Metal Content</th>
<th>S.V.</th>
<th>S.E.</th>
<th>Av. M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CM</td>
<td>Green</td>
<td>90</td>
<td>95</td>
<td>11.176</td>
<td>9.075</td>
<td>175.80</td>
<td>319.10</td>
</tr>
<tr>
<td>CS</td>
<td>Green</td>
<td>102</td>
<td>94</td>
<td>9.144</td>
<td>9.966</td>
<td>194.80</td>
<td>287.83</td>
</tr>
</tbody>
</table>
Figure 1: Plot of $2 + \log A$ versus time on effect of concentration of copper surfactant derived from mustard and soyabean oils (Light intensity-34mW cm$^{-2}$, solvent- benzene, amount of ZnO - 0.04 g.)

Table 2: Effect of concentration of copper surfactant on degradation efficiency

<table>
<thead>
<tr>
<th>Concentration of surfactants [g l$^{-1}$]</th>
<th>Degradation efficiency % (CM)</th>
<th>Degradation efficiency % (CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>16.27</td>
<td>22.18</td>
</tr>
<tr>
<td>0.48</td>
<td>31.15</td>
<td>34.32</td>
</tr>
<tr>
<td>0.56</td>
<td>54.42</td>
<td>40.56</td>
</tr>
<tr>
<td>0.64</td>
<td>72.74</td>
<td>49.80</td>
</tr>
<tr>
<td>0.72</td>
<td>35.96</td>
<td>30.67</td>
</tr>
<tr>
<td>0.80</td>
<td>29.31</td>
<td>28.42</td>
</tr>
<tr>
<td>0.88</td>
<td>26.88</td>
<td>25.59</td>
</tr>
<tr>
<td>0.96</td>
<td>19.82</td>
<td>13.90</td>
</tr>
</tbody>
</table>

Light intensity-34mW cm$^{-2}$, solvent-benzene, amount of ZnO-0.04 g
3.1.2 Selection of suitable catalyst:

The rate of photo catalytic degradation was carried out on three different catalysts i.e. ZnO, TiO$_2$, ZnS. It was found that higher rate constant $k$ observed for ZnO, therefore for present study ZnO was taken (Fig. 3).

Figure 3: Selection of suitable catalyst for degradation of copper surfactant derived from edible oils. (Catalyst= 0.04 g, light intensity-34mW cm$^{-2}$, solvent- benzene, concentration of CS, CM = 0.4 g l$^{-1}$)
3.1.3 Effect of amount of Semiconductor (ZnO)

The amount of semiconductor is also likely to affect the process of surfactant degradation and hence, different amounts of photocatalyst were used ranging from 0.01 g to 0.06 g. The results are graphically presented in Fig. 4 with RSD ±0.2%. A perusal of the results indicates that the rate of photo degradation of copper surfactant increase with an increase in the amount of semiconductor and then ultimately, it becomes almost constant after a certain amount. The rate was found to be maximum at 0.04 g (Table 3) which was also coinciding by rate constant k (Fig. 5). This may be attributed to the fact that as the amount of semiconductor was increased, the exposed surface area also increases but after a certain limit, if the amount of semiconductor was further increased, then there will be no increase in the exposed surface area of photocatalyst [27].

![Figure 4: Plot of 2 + log A versus time on effect of amount of semiconductor on copper surfactant derived from mustard and soyabean oil. (Light intensity-34mW cm\(^{-2}\), solvent- benzene, concentration of CS, CM = 0.4 g l\(^{-1}\)](image)

**Table 3: Effect of amount of semiconductor on degradation efficiency of copper surfactants**

<table>
<thead>
<tr>
<th>Amount of ZnO (g)</th>
<th>Degradation efficiency % (CM)</th>
<th>Degradation efficiency % (CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>25.90</td>
<td>24.96</td>
</tr>
<tr>
<td>0.02</td>
<td>31.58</td>
<td>25.73</td>
</tr>
<tr>
<td>0.03</td>
<td>36.61</td>
<td>35.19</td>
</tr>
<tr>
<td>0.04</td>
<td>48.39</td>
<td>53.30</td>
</tr>
<tr>
<td>0.05</td>
<td>48.43</td>
<td>53.26</td>
</tr>
<tr>
<td>0.06</td>
<td>48.16</td>
<td>53.14</td>
</tr>
</tbody>
</table>

Light intensity-34mW cm\(^{-2}\), solvent- benzene, concentration of CS, CM = 0.4 g l\(^{-1}\)
Arun Kumar Sharma et al. / Langmuir–Hinshelwood kinetic expression and kinetic studies of photo catalytic degradation of copper surfactants derived from edible oils by semiconductor Zinc Oxide

![Figure 5](image)  
**Figure 5:** Plot of rate constant $k$ versus amount of semiconductor on copper surfactant derived from mustard and soyabean oils. (Light intensity-34mW cm$^{-2}$, solvent- benzene, concentration of CS, CM = 0.4 g l$^{-1}$)

### 3.1.4 Effect of Light Intensity

The effect of light intensity on the photocatalytic degradation of copper surfactant was also studied. The light intensity was varied from 18 mWcm$^{-2}$ to 46 mWcm$^{-2}$. The results are graphically presented in Fig. 6 with RSD ±0.2%.

![Figure 6](image)  
**Figure 6:** Plot of $2 + \log A$ versus time on effect of light intensity on copper surfactant derived from mustard and soyabean oils. (Solvent- benzene, amount of ZnO - 0.04 g, concentration of CS,CM = 0.4 g l$^{-1}$)
The data indicate that the rate of photocatalytic degradation of CM was found to increase with increasing light intensity up to 34 mWcm$^{-2}$ while for CS up to 38 mWcm$^{-2}$ (Table 4) which was also coincide by rate constant $k$ (Fig. 7). Further increase in the light intensity resulted in a decrease in the rate of degradation. As the number of photons striking per unit area of semiconductor powder increases with the increase in light intensity, there is a corresponding increase in the rate of photocatalytic degradation of soap. The rate of photocatalytic degradation was found to decrease with a further increase in the light intensity due to thermal side effects [28].

Table 4: Effect of Light Intensity on degradation efficiency of copper surfactants

<table>
<thead>
<tr>
<th>Light Intensity (mW cm$^{-2}$)</th>
<th>Degradation efficiency % (CM)</th>
<th>Degradation efficiency % (CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>15.97</td>
<td>21.16</td>
</tr>
<tr>
<td>22</td>
<td>24.81</td>
<td>24.53</td>
</tr>
<tr>
<td>26</td>
<td>28.83</td>
<td>29.83</td>
</tr>
<tr>
<td>30</td>
<td>35.56</td>
<td>40.58</td>
</tr>
<tr>
<td>34</td>
<td>42.81</td>
<td>51.00</td>
</tr>
<tr>
<td>38</td>
<td>51.37</td>
<td>30.92</td>
</tr>
<tr>
<td>42</td>
<td>40.19</td>
<td>29.24</td>
</tr>
<tr>
<td>46</td>
<td>23.50</td>
<td>28.27</td>
</tr>
</tbody>
</table>

Amount of ZnO- 0.04 g, solvent- benzene, concentration of CS, CM = 0.4 g l$^{-1}$

Figure 7: Plot of rate constant $k$ versus effect of light intensity on copper surfactant derived from mustard and soyabean oils. (Solvent- benzene, amount of ZnO - 0.04 g, concentration of CS, CM = 0.4 g l$^{-1}$)
3.1.5 Effect of Solvent

The rate of photocatalytic degradation of copper surfactant is also affected by the change in solvent. The percentage of methanol was varied from 20% to 80%. The results are graphically presented in Fig. 8 with RSD ±0.2%

![Figure 8: Plot of 2 + log A versus time on effect of solvent on copper surfactant derived from mustard and soyabean oils. (Light Intensity-34mW cm⁻², amount of ZnO - 0.04 g, concentration of CS, CM = 0.40 g l⁻¹)](image)

It was observed that the rate of degradation continuously decreases with increase in the polar solvent such as methanol. In the case of copper surfactants degradation, it has been clearly observed that rate decreases with the increase in polarity of solvent (Table 5) which was also coinciding by rate constant k (Fig. 9). It may be suggested from the above observations that the polarity inhibits the reactivity of the surfactant molecule [29].

Table 5: Effect of Solvent polarity on degradation efficiency of copper surfactants

<table>
<thead>
<tr>
<th>Polarity of solvent (%)</th>
<th>Degradation efficiency % (CM)</th>
<th>Degradation efficiency % (CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>62.75</td>
<td>57.75</td>
</tr>
<tr>
<td>30</td>
<td>49.34</td>
<td>53.72</td>
</tr>
<tr>
<td>40</td>
<td>46.96</td>
<td>49.64</td>
</tr>
<tr>
<td>50</td>
<td>41.48</td>
<td>42.53</td>
</tr>
<tr>
<td>60</td>
<td>30.51</td>
<td>35.76</td>
</tr>
<tr>
<td>70</td>
<td>23.82</td>
<td>30.09</td>
</tr>
<tr>
<td>80</td>
<td>20.53</td>
<td>20.24</td>
</tr>
</tbody>
</table>

Amount of catalyst- 0.04 g, Concentration of CS, CM = 0.4 g l⁻¹, Light Intensity-34mW cm⁻² solvent-benzene.
3.2 Mechanism

A tentative mechanism for the photocatalytic degradation may be proposed as [30-32].

SC $\overset{h\nu}{\rightarrow}$ SC$^*$  \hspace{1cm} \text{(4)}

SC$^*$ $\rightarrow$ SC [h$^+$ (VB) + e$^-$ (CB)] \hspace{1cm} \text{(5)}

$^1$Surfactant $\rightarrow$ h$\nu$ $^1$Surfactant$^*$  \hspace{1cm} \text{(6)}

$^1$Surfactant $\rightarrow$ ISC $^3$Surfactant  \hspace{1cm} \text{(7)}

$^3$Surfactant $\rightarrow$ Degraded Products  \hspace{1cm} \text{(8)}

As the surfactant molecule possesses a $\sigma$ C=O moiety which may undergo degradation initially through the homolytic cleavage. Norrish type I and II reactions may be possible as $\sigma$ and $\gamma$ hydrogen’s are present in the molecule. The reaction is slow and may be the excited state of molecule involved in the reaction is a sufficiently long lived species capable of waiting for different possible steps of degradation, it may be suggested that it should be a triplet species rather than a singlet species [33-34].

3.3 Langmuir Isotherm

Langmuir represented the following equation:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0C_e} \hspace{1cm} \text{(9)}$$
Where $C_e$ is the equilibrium concentration of the adsorbate, $q_e$ is the amount adsorbed, and $Q^*$ and $b$ is Langmuir constants related to maximum adsorption capacity and energy of adsorption relatively. When $1/q_e$ is plotted agents $1/C_e$, L shape graph is obtained (Fig. 10) which shows that there is no strong competition between the solvent and the surfactant to occupy the ZnO surface sites [35].

Figure 10: Copper surfactants isotherm on ZnO at concentration 0.4 g/l, temperature 30 ± 0.1°C.

4. Conclusion

The photocatalytic efficiency for copper mustard observed higher than that of copper soyabean it is suggested that CM has higher molecular weight compare to CS which co-related by higher rate constant $k$ for CM compare to CS catalyst was examined by using it for the photocatalytic degradation of CM and CS surfactants. The optimum reaction conditions of copper surfactants degradation with ZnO were experimentally determined. The photochemical degradation of copper surfactants follows pseudo first-order kinetics. Experimental results indicate that the CM surfactant degrades best at concentration 0.64 g l$^{-1}$ with light intensity 38 mWcm$^{-2}$ and catalyst loading 0.04 g, 20 % methanol polarity with degradation efficiency 72.25 %. Similarly, CS surfactant degrades best at concentration 0.64 g l$^{-1}$ with light intensity 34 mWcm$^{-2}$ and catalyst loading 0.04 g, 20 % methanol polarity with degradation efficiency 49.85 %.

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