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# Indirect oxidation of *o*-chlorotoluene to *o*-chlorobenzaldehyde

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Ex-cell synthesis of *o*-chlorobenzaldehyde from *o*-chlorotoluene was carried out using $Mn^{3+}$ in sulfuric acid as a mediator. Reaction conditions were optimized to obtain maximum oxidation efficiency for the aldehyde. Reuse of the spent mediator requires its regeneration; however, this results in low current efficiency. Thus, electrolyte containing the mediator was treated by different techniques to maintain the current efficiency of catalyst regeneration, during recycle, at the initial value.

Keywords: *ex-cell synthesis*, *o-chlorobenzaldehyde*, *indirect oxidation*, *$Mn^{3+}$ regeneration*, *optimization*

## 1. Introduction

Selective oxidation of ring substituted toluenes to aromatic aldehydes is one of the most important reactions in the chemical industry. These aldehydes are key intermediates for the production of a variety of fine and specialty chemicals such as pharmaceutical intermediates and dyestuffs. Chlorobenzaldehydes in particular are used in the production of dyes, optical brighteners, agricultural chemicals, pharmaceuticals etc.; for example, *o*-chlorobenzaldehyde (OCB) is used as an intermediate for manufacturing Basic Blue-1 and pigment Blue-9, triphenylmethane manufacture and in zinc electroplating [1]. OCB is conventionally produced by chlorination of *o*-chlorotoluene (OCT) to form *o*-chlorobenzal chloride, followed by hydrolysis to give the aldehyde. The mediated or indirect oxidation of OCT using a redox mediator in a suitable electrolyte can be a good alternative to this chemical route. Different redox mediators–electrolyte systems have been used in the past for oxidation of substituted toluenes to the corresponding aldehyde. Ibl *et al.* [2] have used $Ce^{4+}$ in $HClO_4$ for the oxidation of toluene to benzaldehyde. Kramer, *et al.* [3] have reported the oxidation of OCT using $Ce^{4+}$ in $HClO_4$. Wendt and Schneider [4] have studied the oxidation of *p*-nitrotoluene and *p*-chlorotoluene to the corresponding aldehyde using $Mn^{3+}$ in $H_2SO_4$ electrolyte. Millington and Dalrymple [5] have studied oxidation of *p*-chlorotoluene, 2,4 dichlorotoluene and *p*-xylene using the $Mn^{3+}$–$H_2SO_4$ system. Also, optimum conditions for $Mn^{3+/2+}$–$H_2SO_4$ in a filterpress electrolyser have been identified. Vaudano [6] and Vaudano *et al.* [7] have recently shown that regeneration of $Mn^{3+/2+}$ in sulfuric acid can be carried out on industrial scale. Kreh *et al.* [8] have used $Ce^{4+}$ in methanesulfonic acid for the oxidation of OCT to OCB. The preparation of these partially oxidized chemicals has generally relied on the high selectivity of transition metal oxidants used for oxidizing organic substrates. Mediated or indirect electrochemical synthesis is a cyclic process involving electrochemical generation of the redox agent, use of the same to effect a chemical reaction and again its regeneration for the next use. The stoichiometric use and disposal of these mediators is undesirable from economic and environmental viewpoints. As a result, there has been much recent interest in the electrochemical recycle of these oxidants. However, after oxidizing the organic substrate, when the mediator is reoxidized in the electrolyser for reuse, lower current efficiencies have been obtained [9]. This is mainly because of the presence of dissolved organic compounds in the electrolyte containing the redox mediator. During electrochemical regeneration of the spent redox mediator, electrical charge is consumed preferentially for oxidation of dissolved organics, thereby decreasing the current efficiency for the regeneration of the spent mediator [9]. Therefore, removal of dissolved organics from the electrolyte containing the spent mediator is necessary to maintain the current efficiency of the electrochemical step at maximum (initial) value.

Previous studies report the use of $Ce^{4+/3+}$–$HClO_4$ [3] and $Co^{3+/2+}$–$H_2SO_4$ [4] for the oxidation of chlorotoluenes to the corresponding aldehydes. Comninellis *et al.* [10] have used $Mn^{3+/2+}$–$H_2SO_4$ for oxidizing OCT to OCB. However, their work is related to the calculation of current efficiency losses during regeneration of spent mediator and reaction conditions have not been optimized for maximum efficiency for OCB. Use of $Mn^{3+}$ is advantageous due to its low solubility in acid electrolyte. Being insoluble in acid electrolyte, its reduction at the cathode is prevented, thus, an undivided electrolyser can be used for its generation. $Mn^{3+/2+}$–$H_2SO_4$ is used in the present work, for the oxidation of chlorotoluenes,

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which is safer than $Ce^{4+/3+}$–$HClO_4$ and more selective than $Co^{3+/2+}$–$H_2SO_4$. In addition, optimization of the process parameters for maximum efficiency for OCB has also been carried out. Different techniques for removal of organics present in the aqueous electrolyte containing the spent mediator have also been explored to improve the current efficiency during its recycle.

## 2. Experimental details

### 2.1. *Electrolyser*

Experiments were carried out in an FM01-LC laboratory process package with the electrolyser configured for undivided operation. The details of the electrolyser set-up were given previously [11, 12]. $Mn^{2+}$ oxidation was carried out with $PbO_2/Pb$ and Pt/Ti electrodes (0.0064 $m^2$) as anode and a stainless steel electrode (0.0064 $m^2$) as cathode with the inter-elecrode gap maintained at 6 mm.

### 2.2. *Chemical reactor*

Chemical oxidation of OCT using $Mn^{3+}$ generated in the electrolyser was carried out in a standard fully baffled glass reactor equipped with a motor driven impeller. The reactor was placed in a constant temperature water bath.

### 2.3. *Materials*

Analytical grade OCT was procured from E. Merck, Germany. Analytical grade sulfuric acid, hydroxyl amine hydrochloride, sodium hydroxide, manganese sulfate, ferrous ammonium sulfate, were supplied by Loba Chemie, India.

### 2.4. *Conditions of electrolysis*

Electrochemical oxidation of $Mn^{2+}$ is a widely studied process and reported conditions for maximum current efficiency of $Mn^{3+}$ are as follows: acid concentration 49.7–55 wt %, temperature 35–40 °C and $Mn^{3+}$ concentration less than 0.15 M and current density about 1000 A $m^{-2}$ [5]. Manganese sulfate was dissolved in 55 wt % sulfuric acid and electrolysed galvanostatically to manganic sulfate at a current density of 781.25 A $m^{-2}$ and temperature of 33 °C. The reaction mixture from the flask was pumped into the electrolyser with a magnetically driven PTFE pump at the maximum obtainable flow rate of 2.6 L $min^{-1}$.

### 2.5. *Condition of ex-cell synthesis*

$Mn^{3+}$ generated in the electrolyser was placed in the glass reactor. After the required temperature was attained, 3.96 mmol of OCT were added to the reactor and the reaction was started. Experiments were carried out at a speed of agitation of 50 $s^{-1}$. Conversion of OCT was found to be independent of speed of agitation in the range 33 to 55 $s^{-1}$. $Mn^{3+}$ concentration was measured at regular time intervals to follow the progress of the reaction.

### 2.6. *Analysis*

$Mn^{3+}$ in the reaction mixture was estimated by titration with 0.05 N ferrous ammonium sulfate [13]. Aldehyde was estimated by the oxime method [14].

## 3. Results and discussions

### 3.1. *Electrochemical oxidation of $Mn^{2+}$*

Oxidation of $Mn^{2+}$ to $Mn^{3+}$ was carried out at a $PbO_2/Pb$ anode in 55 wt % sulfuric acid. Thus, 600 ml. 0.11 molar $MnSO_4$ in sulfuric acid was electrolysed to give a current efficiency of 43%. The current efficiency was found to be independent of change in acid concentration (44–55 wt %), current density (156.25–937.5 A $m^{-2}$) and temperatures (33–60 °C). However, it was found to be dependent on the nature of the electrode surface. It was found to decrease from 43% to 21% when the smooth $PbO_2$ electrode became rough after use, due to corrosion in the acid solution. This phenomenon is probably due to the deposition of $Mn_2(SO_4)_3$ on the electrode surface since $Mn^{3+}$ has poor solubility and a rough $PbO_2$ surface is likely to favour deposition and growth of $Mn^{3+}$ on its surface. This deposition of $Mn^{3+}$, which inhibits oxidation of $Mn^{2+}$, was visually observed. The rate of corrosion of $PbO_2$ depends on the composition of the lead alloy, which is the base material. In the present case it became rough after 40 h of electrolysis. The results are shown in Fig. 1.

Due to the limitation posed by the $PbO_2/Pb$ electrode, it was decided to carry out further experiments with platinized titanium DSA. Electrochemical oxidation of $Mn^{2+}$ to $Mn^{3+}$ carried out under similar experimental conditions gave a maximum current efficiency of 40%. However, with decreasing acid concentration from 55 to 44 wt %, the current efficiency increased marginally to 45%. Also, for increase in temperature from 33 to 60 °C, an increase in current efficiency from 40 to 45% was obtained. No effect of change in current density from 400 to 937.5 A $m^{-2}$ was observed on the current efficiency. Increase in the current efficiency with decreasing acid concentration and increasing temperature is due to decreased diffusion resistance as the solution viscosity decreases. A relatively low current efficiency of 33% and 40% obtained indicates that the reaction is mass transfer controlled, as reported earlier [5], and rest of the current is utilized for oxygen evolution.

### 3.2. *Ex-cell synthesis of OCT*

Manganic sulfate generated in the electrolyzer was used for the ex-cell synthesis of OCB. Different parameters were investigated to obtain maximum 'oxidation efficiency' of $Mn^{3+}$ for OCB at significant

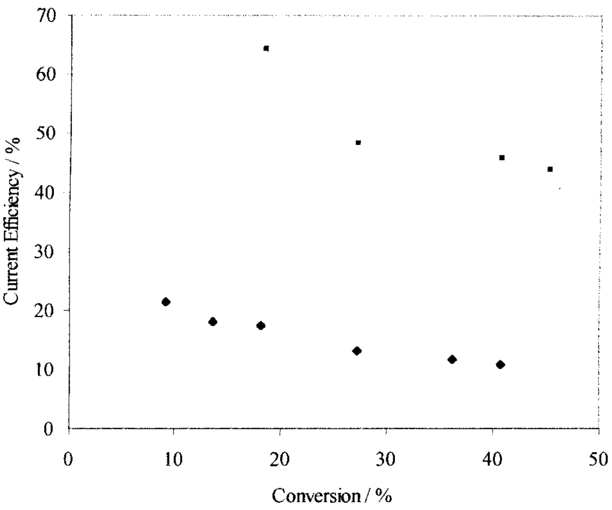

Fig. 1. Electrochemical oxidation of $Mn^{2+}$ at $PbO_2$ anode: effect of nature of the electrode surface on the current efficiency. Key: (■) oxidation at smooth $PbO_2/Pb$ anode; (◆) Oxidation at rough $PbO_2/Pb$ anode. *Conditions of reactions:* $Mn^{2+}$ 6.2 mmol in 55 wt% sulfuric acid; flow velocity 2.6 L min$^{-1}$; current density 781.25 A m$^{-2}$; charge passed 1.78 A h; temperature 33 °C. Electrode became rough after 40 h of electrolysis.

conversion level. Oxidation efficiency is defined as the ratio of the moles of $Mn^{3+}$ used for forming OCB to the total moles of $Mn^{3+}$ consumed.

*3.2.1. Stability of $Mn^{3+}$.* The Stability of $Mn^{3+}$ was evaluated by carrying out experiments as described in Section 2.5 except without OCT. No change in $Mn^{3+}$ concentration (error in measurement ≤2%) was observed at 70 and 85 °C for 49.7 and 55 wt% acid concentration up to 6 h. No variation in $Mn^{3+}$ concentration was observed at 100 °C for 49.7 and 55 wt % acid concentrations up to 3 h. The stability of $Mn^{3+}$ obtained was found to be adequate, since the time taken for all the OCT oxidation experiments was less than 5 h at 70 °C, 2 h at 85 °C and 1 h at 100 °C for acid concentrations of 49.7 and 55 wt %.

*3.2.2. Effect of $Mn^{3+}$ to OCT molar ratio on oxidation efficiency.* Experiments were carried out with different $Mn^{3+}$ to OCT mole ratios, or at different stoichiometric conversions. Stoichiometric conversion refers to the ratio of the moles of OCT that would be oxidized by the moles of $Mn^{3+}$ employed for the reaction to give OCB assuming 100% oxidation efficiency to the moles of OCT taken at the start of the reaction. With increasing stoichiometric conversion or increasing molar ratio, the oxidation efficiency was found to decrease. An oxidation efficiency of 100% was obtained at a mole ratio (or stoichiometric conversion) of 0.37 (18%). A molar ratio of 0.85 (42%) was found to be optimum giving an oxidation efficiency of 96%. The results are shown in Fig. 2.

*3.2.3. Effect of acid concentration on oxidation efficiency.* Oxidation of OCT with $Mn^{3+}$ generated in sulfuric acid concentration of 49.7 and 55 wt % was carried out at different molar ratio of $Mn^{3+}$/OCT. These experiments showed no change in oxidation efficiency.

*3.2.4. Effect of temperature on oxidation efficiency.* Experiments carried out with increasing reaction temperature from 70 to 100 °C at different mole ratio of $Mn^{3+}$/OCT showed no effect of temperature on oxidation efficiency.

## 4. Regeneration of the spent mediator

The most attractive features of mediated electrosynthesis are the use of nonstoichiometric quantities of redox mediator and its recycle. The former makes it economically attractive and the latter makes it environment friendly since recycle of electrolyte results in a '*zero effluent*' process. However, regeneration of the mediator gives poor current efficiencies for reasons described earlier. For removal/destruction of the dissolved organics present in the electrolyte, two techniques were considered. These were (i) extracting the dissolved organics from the aqueous electrolyte containing spent mediator with organic solvent and (ii) treating aqueous electrolyte containing spent mediator with activated carbon to remove dissolved organics. Kreysa and Medin [13] and Tzedakis and Savall [15] have used solvent extraction of dissolved organics in electroregeneration of redox mediator. Regeneration experiments were carried out under the same conditions as that of $Mn^{2+}$ oxidation using Pt/Ti DSA.

After oxidation of OCT, redox agent was regenerated without purification of the aqueous electrolyte. The regeneration efficiency, that is, the ratio of the current efficiency for obtaining $Mn^{3+}$ from spent mediator (electrolyte containing dissolved organics) to the current efficiency for obtaining $Mn^{3+}$ from fresh mediator of 33%, was obtained.

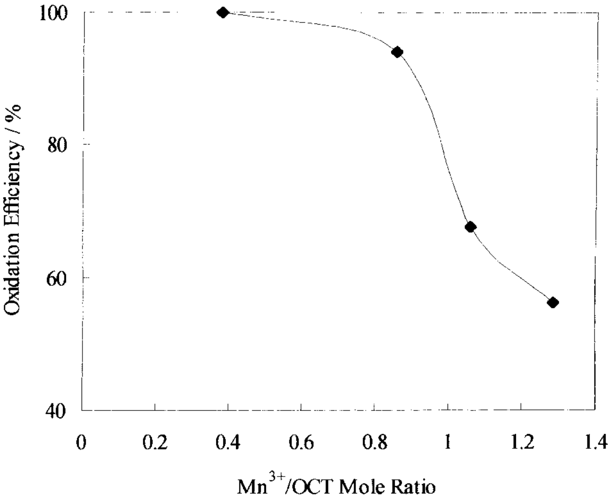

Fig. 2. Effect of molar ratio of $Mn^{3+}$ to OCT on oxidation efficiency. *Conditions of reactions*: OCT 3.968 mmol, $Mn^{3+}$ generated in 55 wt % sulfuric acid; temperature 70 °C; agitation speed 50 s$^{-1}$.

### 4.1. *Extraction of dissolved organics with solvent*

After OCT oxidation, the electrolyte containing $Mn^{2+}$ was subjected to single stage solvent extraction with 1,2-dichloroethane (DCE) to remove traces of organics. After solvent extraction of the acid electrolyte, when spent mediator was regenerated, a regeneration efficiency of 93% was obtained. This shows that the electrolyte still contains traces of organics which are responsible for the loss in current efficiency.

### 4.2. *Treatment of electrolyte containing spent mediator with activated carbon*

After OCT oxidation, activated carbon was added to the electrolyte containing $Mn^{2+}$, and equilibrated to adsorb the dissolved organics. A carbon loading of 8% (w/v), that is, 8 g of carbon per 100 ml of electrolyte containing spent mediator was used. No effect of different parameters such as time of adsorption and carbon loading was investigated. A current efficiency for regeneration of $Mn^{3+}$ similar to that obtained with fresh mediator was obtained. Activated carbon is a well-known adsorbent for organic compounds. Thus, it is expected to remove the dissolved organics from the spent electrolyte and thereby restore the regeneration efficiency. Generally for adsorption of complex mixtures such as the present the activated carbon can be regenerated using a known technique and can be reused. The results are given in Table 1.

## 5. Conclusions

Oxidation of OCT to OCB with $Mn^{3+/2+}$–$H_2SO_4$ is a more versatile process compared to one that involves hazardous $HClO_4$ as electrolyte or $Co^{3+/2+}$ as mediator, which offers poor selectivity for OCB. A $Mn^{3+}$/OCT mole ratio of 0.85 was found to be optimum, giving an oxidation efficiency of 96% at a sufficiently high conversion level of 42%.

*Table 1. Regeneration efficiency for spent mediator*

$Mn^{2+}$ 6.2 mmol in 55 wt % sulfuric acid; flow velocity 2.6 L min$^{-1}$; current density 781.25 A m$^{-2}$; charge passed 1.78 A h; temperature 33 °C

| *Acid electrolyte containing spent mediator* | *Regeneration Efficiency /%* |
|---|---|
| Untreated Electrolyte | 33 |
| Extraction with DCE | 93 |
| Adsorption on Carbon | 100 |

Extracting the electrolyte with suitable solvent, or treating it with activated carbon, can eliminate the problem of low current efficiency during regeneration of the spent mediator. Solvent extraction gave a regeneration efficiency of 93% and treatment with activated carbon resulted in regeneration efficiency of 100%.

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