



# Effect of inorganic anions and oxidizing agents on electrochemical oxidation of methyl orange, malachite green and 2,4-dinitrophenol



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## ABSTRACT

Electrochemical oxidation of methyl orange, malachite green and 2,4-dinitrophenol were performed in the presence of varying concentrations of inorganic anions and oxidizing agents. Methyl orange oxidation was positively affected by carbonate ( $<300 \text{ mg L}^{-1}$ ),  $\text{H}_2\text{PO}_4^-$  ( $100\text{--}500 \text{ mg L}^{-1}$ ),  $\text{H}_2\text{O}_2$  ( $<300 \text{ mg L}^{-1}$ ) and  $\text{S}_2\text{O}_8^{2-}$  ( $>400 \text{ mg L}^{-1}$ ). Carbonate ( $>400 \text{ mg L}^{-1}$ ), bicarbonate ( $100\text{--}500 \text{ mg L}^{-1}$ ), nitrate ( $>300 \text{ mg L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $>400 \text{ mg L}^{-1}$ ) inhibited the COD removal efficiency of methyl orange. Electrochemical oxidation of malachite green was inhibited by carbonate ( $100\text{--}500 \text{ mg L}^{-1}$ ), bicarbonate ( $100\text{--}500 \text{ mg L}^{-1}$ ), nitrate ( $>400 \text{ mg L}^{-1}$ ) and  $\text{H}_2\text{PO}_4^-$  ( $>400 \text{ mg L}^{-1}$ ), whereas nitrate ( $<300 \text{ mg L}^{-1}$ ),  $\text{H}_2\text{PO}_4^-$  ( $<300 \text{ mg L}^{-1}$ ),  $\text{H}_2\text{O}_2$  ( $<400 \text{ mg L}^{-1}$ ) and  $\text{S}_2\text{O}_8^{2-}$  ( $100\text{--}500 \text{ mg L}^{-1}$ ) increased the COD removal efficiency. The COD removal efficiency of 2,4-dinitrophenol was inhibited by bicarbonate ( $100\text{--}500 \text{ mg L}^{-1}$ ), nitrate ( $<300 \text{ mg L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $500 \text{ mg L}^{-1}$ ). A positive effect on the COD removal efficiency of 2,4-dinitrophenol was obtained in the presence of  $\text{H}_2\text{PO}_4^-$  ( $100\text{--}500 \text{ mg L}^{-1}$ ),  $\text{H}_2\text{O}_2$  ( $<400 \text{ mg L}^{-1}$ ) and  $\text{S}_2\text{O}_8^{2-}$  ( $100\text{--}500 \text{ mg L}^{-1}$ ). The degradation of 2,4-dinitrophenol was unaffected by the presence of carbonate. Addition of sulphate had no effect on the COD removal efficiency of all the three contaminants.

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## 1. Introduction

Electrochemical oxidation is an efficient technology used in the treatment of wastewater, especially recalcitrant organic wastewater. Hydroxyl radical is the main oxidant in the electrochemical oxidation technique and is produced by the anodic oxidation of water. Another pathway for degradation involves the action of active oxidants produced within the system, of which active chlorine species is one of the most common oxidants. Direct electron transfer is an additional mechanism by which the degradation is achieved in an electrochemical reactor. It is particularly helpful in the degradation of organics those that are unreactive towards hydroxyl radical [1,2]. The use of active oxidants (mainly active chlorine) is recommended in an electrochemical oxidation system to overcome the mass transfer limitations [3].

Electrochemical oxidation is widely studied for the treatment of complex wastewater including textiles, pharmaceuticals, and landfill leachate [4,5]. The major anions present in wastewater include carbonate, bicarbonate, chloride, sulphate, phosphate and nitrate [6]. Hussain et al. have also reported these anions to be present in textile industry wastewater [7]. These anions undergo series of reactions within the electrochemical system, affecting its performance. The role of inorganic anions and electron acceptors on the degradation of recalcitrant organic

contaminants using photocatalytic oxidation and photoelectrochemical oxidation has been reported [8,9]. Gupta et al. have demonstrated that photocatalytic oxidation of methyl red is inhibited by the presence of chloride ion, whereas nitrate, sulphate, and hydrogen phosphate did not affect the decolourization efficiency. Hydrogen peroxide was shown to be very effective in enhancing crystal violet degradation, while ammonium peroxydisulphate had more positive effect on methyl red [8]. These results indicate that the effects of these chemicals are dependent on the target contaminants. Zainal et al. have reported the positive effect of chloride on the photoelectrochemical degradation of methyl orange. Furthermore, the study showed that carbonate and sulphate affect the degradation efficiency negatively, whereas nitrate did not affect the degradation [9]. Arslan-Alaton has summarized the effect of various dye assisting chemicals on ozonation, Fenton's, ultrasonic, hydrothermal, photochemical and photo Fenton's oxidation [10]. However, the effect of these chemicals on electrochemical oxidation has not been studied.

In the present study the effects of bicarbonate, carbonate, sulphate, nitrate and dihydrogen phosphate on the electrochemical oxidation of dyes and phenol in the presence of NaCl were considered. Methyl orange, malachite green and 2,4-dinitrophenol were chosen as the target contaminants to understand the variation in effects of these anions with the contaminant treated. The effects of oxidizing agents (hydrogen peroxide and ammonium peroxydisulphate) on the electrochemical oxidation of these contaminants were also studied at varying concentrations of the electron acceptors.

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## 2. Materials and methods

### 2.1. Chemicals

Sodium bicarbonate, sodium carbonate, sodium sulphate, sodium dihydrogen phosphate (Merck India) and sodium nitrate (SD fine chem. limited) were used as the inorganic anions. Ammonium peroxydisulphate (Merck India) and hydrogen peroxide (6%) (Nice Chemicals, India) were used as the electron acceptors. Sodium chloride used as the supporting electrolyte was obtained from Merck India. All the chemicals were of analytical reagent grade and were of the highest purity available.

### 2.2. Instrumental

A high precision electronic balance (0.0001 g) was used for weighing and was obtained from Mettler Toledo (model AG 135), India. The magnetic stirrers used in the study were from Remi, India. pH was measured using pH meter manufactured by Toshniwal Inst. Mfg. Pvt. Ltd., India. DC power supplies with voltage range of 0 to 15 V and with current range of 0 to 5 A were used as the power source. Spectroquant TR 320 of Merck, was used for COD analysis using closed reflux colorimetric method (Method 5220 D) [11].

### 2.3. Experimental

Electrochemical reactions were carried out in a batch reactor mounted on a magnetic stirrer. Anode was prepared by electrodeposition of lead dioxide on mild steel from alkaline electrolyte bath and graphite was used as the cathode. The stability of the electrode and absence of lead leaching was tested and confirmed [12]. The detail of the setup is reported elsewhere [13]. Electrochemical oxidation of three recalcitrant pollutants viz. methyl orange, malachite green and 2,4-dinitrophenol were carried out in the presence of inorganic anions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ) and electron acceptors ( $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$ ) in a concentration range of 0–500  $\text{mg L}^{-1}$ . The oxidations were carried out at room temperature ( $26 \pm 2^\circ\text{C}$ ) at a current density of  $2.87 \text{ mA cm}^{-2}$  with an initial concentration of  $1 \text{ g L}^{-1}$  NaCl for methyl orange, at a current density of  $2.39 \text{ mA cm}^{-2}$  with  $2 \text{ g L}^{-1}$  of NaCl for malachite green and at a current density of  $1.44 \text{ mA cm}^{-2}$  with  $1 \text{ g L}^{-1}$  of NaCl for 2,4-dinitrophenol, which were the optimum conditions obtained from the uniparameter studies [13,14]. The working volume of the solution was 400 mL and the concentration of the pollutants was  $50 \text{ mg L}^{-1}$ . Samples were collected at 30 min interval and COD and pH were measured. COD measurement was carried out in duplicate. Pseudo-first order rate constants for the reactions were calculated using Eq. (1).

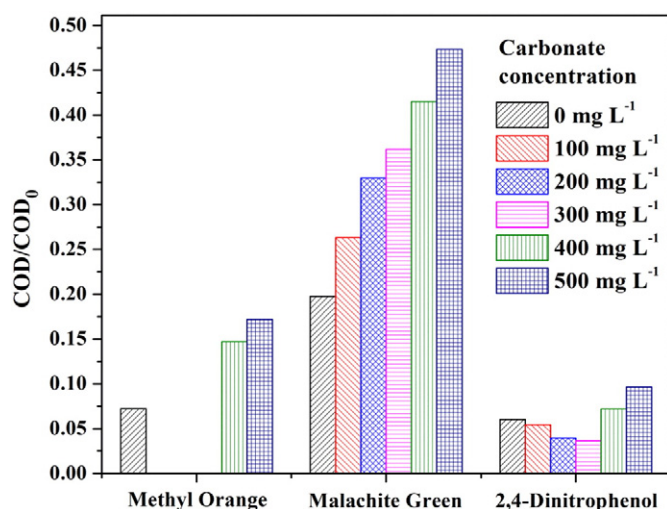
$$\ln(\text{COD}_t/\text{COD}_0) = k_{\text{app}} \times t \quad (1)$$

where,  $\text{COD}_0$  is the initial COD and  $\text{COD}_t$  is the COD at time  $t$ .

## 3. Results and discussion

### 3.1. Effect of carbonate

The effect on carbonate in the range of 0–500  $\text{mg L}^{-1}$  on electrochemical oxidation of methyl orange, malachite green and 2,4-dinitrophenol were studied (Fig. 1). The effect of carbonate at varying time is provided in supplementary material Fig. S1 a–c. Typical reactions of carbonate anion in an electrochemical system are as depicted in Eqs. (2)–(4). Carbonate is converted to percarbonate by anodic oxidation, which upon reaction with water yields  $\text{H}_2\text{O}_2$ . This reaction is initiated at a lower potential as compared to the generation of active chlorine species. Thus, percarbonate generation may supersede the generation of active chlorine species. Chlorate formation is also



**Fig. 1.** Comparison of effect of carbonate on electrochemical oxidation of methyl orange ( $2.87 \text{ mA cm}^{-2}$  current density,  $1 \text{ g L}^{-1}$  NaCl,  $26 \pm 2^\circ\text{C}$ ); malachite green ( $2.39 \text{ mA cm}^{-2}$  current density,  $2 \text{ g L}^{-1}$  NaCl,  $26 \pm 2^\circ\text{C}$ ) and 2,4-dinitrophenol ( $1.44 \text{ mA cm}^{-2}$  current density,  $1 \text{ g L}^{-1}$  NaCl,  $26 \pm 2^\circ\text{C}$ ) at 180 min.

enhanced by the buffering effect of carbonate. All these factors may contribute to a reduction in the COD removal efficiency, when carbonate is present in the electrolyte [15]. Another pathway is the generation of carbonate radical by the reaction of carbonate ion with hydroxyl radical (Eq. (4)) [16]. This scavenging of hydroxyl radical also may have an effect on the COD removal efficiency in hydroxyl radical limiting conditions.



Methyl orange degraded at a current density of  $2.87 \text{ mA cm}^{-1}$  with a NaCl concentration of  $1 \text{ g L}^{-1}$  in the presence of carbonate ( $100\text{--}500 \text{ mg L}^{-1}$ ), showed a marginal enhancement in the COD removal efficiency at a carbonate concentration of  $100\text{--}300 \text{ mg L}^{-1}$  (Fig. S1 a). Padmaja and Madison have determined the bimolecular reaction rate constant of carbonate radical with methyl orange to be in the order of  $2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is one order of magnitude higher than the bimolecular reaction rate constant of methyl orange with  $\text{Cl}_2^{\cdot-}$  and  $\text{Cl}^{\cdot}$  ( $3.7\text{--}6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) [10,16]. Furthermore, the bimolecular reaction rate constant of methyl orange with hydroxyl radical is reported as  $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , which is two order of magnitudes higher than that of the reaction of carbonate ion with hydroxyl radical ( $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) [16]. Thus, it is clear that mineralization of methyl orange by hydroxyl radical is favoured over scavenging of hydroxyl radical by carbonate. However, at higher carbonate concentration, the scavenging of hydroxyl radical by carbonate reduces the amount of hydroxyl radical available for the mineralization thus negatively affecting the COD removal efficiency. Hence, marginally better performance in COD removal efficiency of methyl orange is observed in the presence of sodium carbonate at a concentration range of  $100\text{--}300 \text{ mg L}^{-1}$  and an inhibition of mineralization is observed at sodium carbonate concentrations of  $400$  and  $500 \text{ mg L}^{-1}$ .

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