



ROLE OF ELECTRODES AND ELECTROLYTES ON THE EFFICIENCY OF ELECTROLYTIC DECONTAMINATION OF WATER FROM INDIGO CARMINE DYE POLLUTANT

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ABSTRACT Electrochemical Advanced Oxidation Processes (EAOP) using 'bismuth oxide doped titanium dioxide coated on titanium plate' ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$) as the anode, stainless steel plate (SS) as cathode and NaCl solution as the electrolyte ($\text{BiO}_x/\text{TiO}_2/\text{Ti}, \text{NaCl}, \text{SS}$) is found to be an efficient method for the decolorization of Indigo Carmine (IC) dye pollutant in water. However, this process does not lead to mineralization even after continued electrolysis for 10 hr. This is due to the formation of a number of stable organochlorine intermediates, as identified by LC/MS. Another system ($\text{BiO}_x/\text{TiO}_2/\text{Ti}, \text{Na}_2\text{SO}_4$, graphite) can lead to complete electrolytic mineralization and elimination of COD, even though the rate of decolorization is slower compared to ($\text{BiO}_x/\text{TiO}_2/\text{Ti}, \text{NaCl}, \text{SS}$). The effect of various reaction parameters on the efficiency of decolorization/mineralization of IC is investigated and optimized. Presence of salts/anions such as carbonate, bicarbonate, nitrate, etc. enhances the decolorization. The study illustrates that an electrolytic system which is highly efficient for the degradation of a pollutant need not necessarily be good for the mineralization. This observation is important in the design of appropriate electrolytic system for the efficient purification of wastewater so that it can be repeatedly recycled.

KEYWORDS : Electrocatalysis; Advanced oxidation process; Indigo Carmine, Water treatment

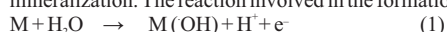
1. INTRODUCTION

Manufacture and use of synthetic dyes, especially in textiles, is a massive industry today. Around 30% of the dyes used in the textile industry does not get fixed on the target and are discharged in the respective factory effluent. Dyes are highly visible and even minor release into the water bodies may be unacceptable aesthetically as well as environmentally. Dyes can also obstruct light penetration into the water bodies, thus inhibiting the biological processes based on photosynthesis. Many of these dyes are also toxic, carcinogenic, mutagenic or teratogenic to various microbiological or animal species. Due to low biodegradability of dyes, the conventional treatment process is not very efficient for their removal from wastewater. Such techniques simply transfer the pollutants from one medium to another (water to water, water to soil and water to air) causing secondary pollution. In this context, advanced oxidation processes (AOP) are gaining importance as tertiary treatment techniques for the removal of even small concentration of chemical pollutants [1-6].

In recent years, electrochemical techniques have been gaining acceptance as powerful tools for wastewater remediation [7-9]. The advantage of this technology is its environmental compatibility because the main reactant is the electron which is not a pollutant [7]. Other advantages are related to its versatility, high energy efficiency, availability of automation, safety and mild reaction conditions. It can also be operated in combination with other techniques such as sonoelectrochemical [10], photoelectrochemical [11] processes etc.

Among the electrochemical methods, anodic oxidation is perhaps the most popular one for the treatment of wastewaters containing persistent organic pollutants (POPs). The pollutants are removed using high oxygen evolution potential anode which generates highly reactive hydroxyl radicals ($\cdot\text{OH}$) in situ [12,13]. These radicals instantly

interact with the pollutant leading to the degradation and eventual mineralization. The reaction involved in the formation of $\cdot\text{OH}$ is:



In presence of chloride, AOP oxidation of organic compounds proceeds through chlorinated intermediates. The organochlorine compounds (RCl) formed during the degradation of the pollutant have different genotoxic, carcinogenic and/or mutagenic effects depending on the chemical structure. Hence it is important that the chemistry of the pollutant and its possible interactions in chloride medium are verified before the electrolytic method is proposed for wastewater treatment.

Graphite, platinum, dimensional stable electrode (DSA), stainless steel (SS) and air diffusion electrode (ADE) are frequently used as cathodic materials. When graphite or ADE is used as cathode, it is often fed with air or pure oxygen to generate H_2O_2 through the electrochemical reduction of O_2 . This process which can be considered as anodic oxidation is normally termed as $\text{AO-H}_2\text{O}_2$. Use of Na_2SO_4 as the supporting electrolyte is usually preferred because: (i) it is relatively cheap, (ii) it could be oxidized into $\text{S}_2\text{O}_8^{2-}$ which also participates in the degradation of organics and (iii) it does not produce hazardous compounds during the process in most cases. Further, the presence of Na_2SO_4 is also reported to promote degradation of organics in many AOPs. [14, 15].

Indigo Carmine (IC, 5,5'-indigo disulfonic acid disodium salt, molecular weight: 466.36) which is used as the test pollutant in this study is a dark blue dye mainly used in the textile industry for the dyeing of polyester fibers and denim (blue jeans) [16]. IC is also used in food and cosmetics industry. Several processes have been suggested for removal of IC and other dyes from wastewater including

adsorption, photochemical, sonochemical and microwave processes [17-19]. In the present study, another AOP, i.e., electrolytic oxidation, is investigated as a potential method for the removal of small quantities of IC from water with special reference to the characteristics of the electrodes and electrolytes. The structure of Indigo Carmine is shown in figure 1.

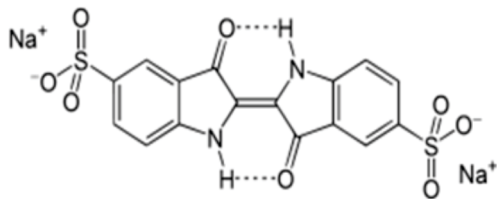


Fig. 1. Chemical structure of Indigo Carmine

2. MATERIALS AND METHODS

2.1. Materials

The Indigo Carmine dye used in the study was (99%) of AnalaR grade, from Sigma- Aldrich (India). Synthetic wastewater containing IC of desired concentrations was prepared by dissolving the dye in double distilled water. The Zinc oxide (99.9%) used was from Merck India. (BET surface area: $\sim 12\text{m}^2/\text{g}$) All other materials/chemicals used were of AnalaR grade or equivalent, unless indicated otherwise.

2.2. Electrodes used

The following electrodes used in the study were purchased from Titanium Tantalum Products limited Chennai, India:

- Ti Cathode – 50 x 25 x 1 (mm)
- Nb Cathode - 50 x 25 x 1 (mm)
- MMO/Ti-50 x25x1(mm) , MMO coating of 6 μ thickness, MMO: Mixed metal oxide
- Pt/Ti-50 x 25 x 1 (mm), Pt plating of 3 μ thickness
- Pt/Nb-50 x 25x1 (mm), Nb plating of 3 μ thickness

Further, the following electrodes were from in-house:

- Graphite rod (made by separating the electrode from a used dry cell)
- Bismuth oxide doped titanium dioxide, coated on titanium plate ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$) as the anode and Stainless steel plate (SS) as cathode are the same as described in previous studies [20-22]

2.3. Electrolysis Experiments

The experimental setup is shown in figure 2. Two single compartment electrolytic cells are used in parallel. The anode and the cathode were immersed vertically in an aqueous solution of the target IC pollutant mixed with 0.05M NaCl or Na_2SO_4 as the case may be. The height of the electrodes dipped in the solution was 3.5cm with an inter-electrode distance of 4.0 cm, unless indicated otherwise. A constant cell current (3.4V) was applied to the electrodes with a DC power supply. The samples were drawn periodically during the electrolytic process, filtered if needed and were analyzed for IC remaining in the system using UV/Vis spectrophotometry at a wavelength of 609 nm. The reaction intermediates were identified by using LC-MS (Q-TOF) instrument (Waters Xevo G2 Q-TOF). Open reflux method is used to determine the COD of the samples [23].

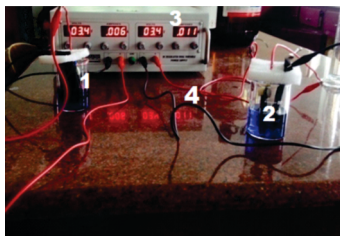


Fig 2: Electrolytic experimental setup

1, 2: Electrolytic cells, 3: Power supply unit, 4: Anode (red) and Cathode (black)

3. RESULTS AND DISCUSSION

Preliminary studies were made on the electrolytic oxidation of IC in water using different anode/cathode/electrolyte system. These include $\text{BiO}_x/\text{TiO}_2/\text{Ti}$, MMO/Ti, Pt/Ti or Pt/Nb as anode and SS, graphite, Ti or Nb as cathode. The electrolyte was NaCl or Na_2SO_4 . The anodes,

cathodes and electrolytes were used in different permutations and combinations. Most of the systems, except those listed in Table I were not efficient for the decolorization/degradation of IC and were hence not investigated further.

Table I: Preliminary results on potential electrolytic systems for the degradation of IC

[IC]: $1 \times 10^{-4}\text{M}$, [Electrolyte]: $5 \times 10^{-2}\text{M}$

| Anode | Cathode | Electrolyte | Preliminary electrolysis data |
|---------------------------------------|----------|--------------------------|-------------------------------|
| $\text{BiO}_x/\text{TiO}_2/\text{Ti}$ | SS | NaCl | Decolorization in 10min |
| $\text{BiO}_x/\text{TiO}_2/\text{Ti}$ | Graphite | NaCl | Decolorization in 10 min |
| $\text{BiO}_x/\text{TiO}_2/\text{Ti}$ | Graphite | Na_2SO_4 | Decolorization in 90 min |
| MMO/Ti | Graphite | Na_2SO_4 | Decolorization in 120 min |
| Pt/Ti | Graphite | NaCl | Decolorization in 10 min |
| Pt/Ti | Graphite | Na_2SO_4 | Decolorization in 90 min |

Based on the data presented in Table 1, three electrode-electrolyte systems, i.e., ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl, SS), ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl, graphite) and ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$, Na_2SO_4 , graphite) were selected for further investigation on the electrochemical degradation of IC. The efficiency of the system is determined from the time taken for the decolorization and total mineralization of the dye. The system with Pt/Ti anode, though efficient, is not investigated further, since it is relatively more expensive.

3.1. Electrolytic degradation of Indigo Carmine using $\text{BiO}_x/\text{TiO}_2/\text{Ti}$ anode and stainless steel (SS) cathode with NaCl as supporting electrolyte ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl, SS)

The degradation/decolorization of IC is tested using 50 mL of $1 \times 10^{-4}\text{M}$ solution of the dye. The supporting electrolyte (NaCl) concentration was 0.05 M. Potential applied was 3.4V. The length of the electrode dipped in the solution was 3.5 cm. Complete decolorization is obtained in 10 minutes as confirmed by UV/Vis spectrophotometry. Figure 3 shows the complete disappearance of the absorbance at 609 nm (which corresponds to IC), after 10 minutes of electrolysis.

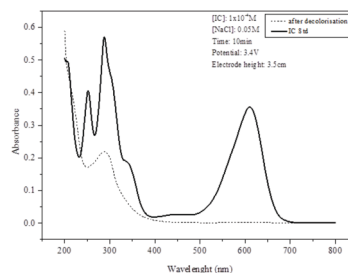


Fig 3: UV/Vis spectrum of IC: before and after decolorization ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl, SS)

The effect of various reaction parameters on the efficiency of the system is evaluated as follows:

3.1.1. Effect of pH on the degradation of IC

The effect of variation of initial pH on the time taken for decolorization of IC during electrolytic oxidation is shown in figure 4. The decolorization is faster in extreme acidic medium (pH \sim 2-3), probably because at low pH, the chlorine resulting from the Cl^- ions present in the solution forms hypochlorous acid, which has higher oxidation potential (1.63V) than hypochlorite (0.89V) [24]. Under comparable pH conditions and reaction times, the decolorization is very small and even negligible in the absence of electrolysis, as shown in the inset of the figure.

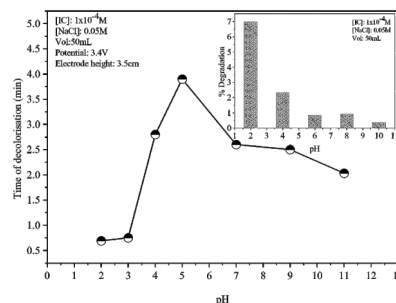


Fig 4: Effect of pH on the electrochemical degradation of IC ($\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl,SS)

[Inset]: % Degradation of IC at different pH without electrolysis

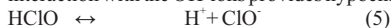
The reactions leading to the formation of HClO are;



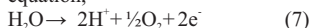
In the bulk solution, Cl_2 hydrolysis takes place as follows:-



Under alkaline medium, deprotonation of the HClO as well as the interaction with the OH^- ions provides hypochlorite (ClO^-) as follows:



At the anode, O_2 evolution competes with Cl_2 evolution according to the equation,



Acidity increases the efficiency of Cl_2 discharge and the rate of dye oxidation. The type and concentration of the active chlorine species present in solution is dependent on its pH [25]. The predominant species at various pH are: Cl_2 (pH<3), HClO (pH: 3-7.5) and ClO^- (pH>7.5). If the Cl^- concentration in solution is decreased, the pH interval for the predominance of the HClO species will extend further towards lower pH. For e.g., at very low $[Cl^-]$ of 0.005 mol L^{-1} at 25°C , the predominance of HClO occurs at pH ~1-7.5. However, extreme acidic pH may not be advisable for large scale applications and hence the natural pH of the system (~7.4) at which the degradation rate is still good is chosen for further studies. Moreover faster decolorization reactions do not guarantee the mineralization of the dye or reduction in toxicity, which is the yardstick for measuring the efficiency of the purification process.

3.1.2. Effect of Initial Concentration of IC

The influence of the initial concentration of IC on its decolorization was studied in the range of 2-60 mg/L. The time for decolorization increases with increase in concentration (figure 5). The rate of decolorization increases with increase in the concentration and is eventually stabilized or decreases thereafter (inset of figure 5). This is consistent with the variable kinetics with concentration, reported for many AOP degradation of organics [26,27]. With increase in concentration of the dye, there will be more number of interactions with the reactive free radicals and hence increase in the degradation. However at a particular concentration of the dye, the optimum number of molecules which can effectively utilize the reactive oxygen species (ROS) is

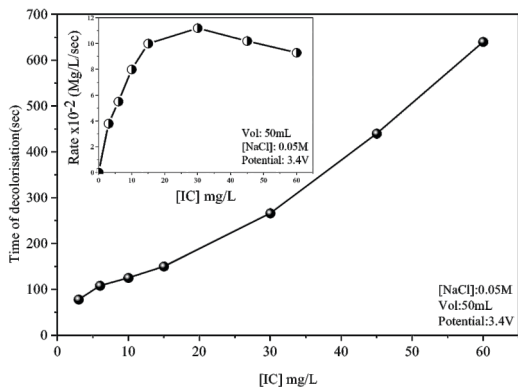


Fig 5: Effect of concentration of IC on its electrolytic degradation [$BiO_x/TiO_2/Ti$, NaCl, SS] {Inset: Conc. Vs Rate plot}

reached and the rate becomes constant. Above this optimum, increase in concentration will not lead to increased interaction. It is also possible that more and more intermediates are formed in the system especially at higher concentrations of IC and they will be competing with the substrate for the ROS. This will result in gradual decrease in rate of degradation of the parent compound. Also at higher concentration, the dye molecules tend to associate into larger molecules. This lowers the rate of diffusion of the dye to the anode surface with consequent decrease in the removal rate [28].

3.1.3. Effect of electrolyte (NaCl) concentration

Figure 6 shows the effect of concentration of NaCl electrolyte on the rate of the dye removal.

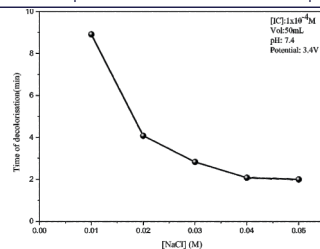


Fig 6: Effect of electrolyte (NaCl) concentration on the decolorization of IC [$BiO_x/TiO_2/Ti$, NaCl,SS]

Increased chloride concentration increases the rate of removal of the dye thereby reducing the time needed for decolorization. This enhancement can be attributed to the increased efficiency of Cl_2 discharge with increase in the concentration of NaCl. At the anode, O_2 evolution competes with Cl_2 evolution as in equation 7. As the concentration of NaCl increases, the discharge potential of Cl_2 will be less than that of O_2 and consequently the formation of the oxidant will be more and the decolorization of IC will be faster [29]. However, beyond an optimum concentration of NaCl, the potential applied being constant, the evolution of Cl_2 and O_2 as well as the formation of reactive species will be stabilized and the decolorization also levels off. At this stage, the decolorization can be enhanced probably by increasing the applied potential which is verified in the subsequent sections.

3.1.4. Effect of potential on the degradation of IC

The effect of applied potentials (1.0 – 3.4V) on the electrochemical degradation of IC is verified and the results presented in figure 7.

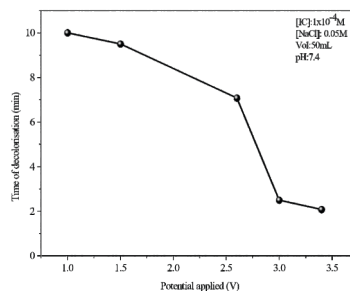


Fig 7: Effect of applied potential on the electrolytic degradation of IC [$BiO_x/TiO_2/Ti$, NaCl,SS]

The efficiency increases with increase in potential, as is reflected in decrease in the time taken for complete decolorization, and reaches an optimum at potential of 3.0 V. This can be attributed to increase in the evolution of Cl_2 and consequently of HClO generation resulting in increased degradation of IC. This also implies that with increase in the area of the electrodes immersed in the electrolyte, the generation of reactive species will also be increasing leading to increasing interaction with the dye and decrease in the time taken for decolorization. This is illustrated in the following section.

3.1.5. Effect of area/length of electrode immersed in the electrolyte

As the area of electrode immersed in the electrolyte is increased (by increasing the height of the electrode dipped in the solution), the time required for decolorization of IC decreases (figure 8).

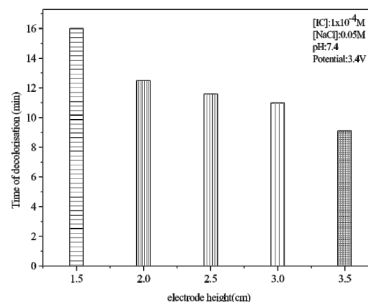


Fig 8: Effect of electrode height immersed in the electrolyte on the electrolytic degradation of IC [$BiO_x/TiO_2/Ti$, NaCl,SS]

With increase in the exposed area of the electrode more number of reactive Cl_2 , HOCl , Cl^- ions are generated in the solution leading to faster decolorization of IC.

3.1.6. Effect of inter-electrode distance

Another parameter which determines the efficiency of electrolytic process is the distance between the electrodes, i.e., inter-electrode distance. In this context, the effect of inter electrode distance on the efficiency of degradation of IC is verified. The results are shown in figure 9. Color removal efficiency is enhanced by reducing the distance between cathode and anode.

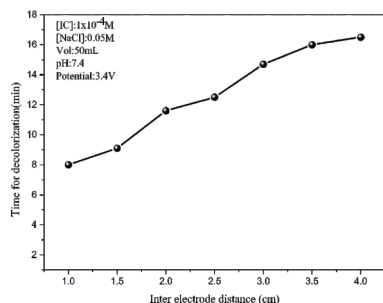


Fig 9: Effect of inter-electrode distance on the electrolytic degradation of IC
[$\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl , SS]

This can be explained based on the increase of electrical current with decreasing the inter-electrode distance and consequent increase in the frequency of collisions of the ions. Decrease of the space between anode and cathode leads to low resistance of the electrolyte which also in turn results in increased generation of reactive species and consequently increase in the reaction rate. In this study, the inter-electrode distance is optimized at 1.0 cm.

3.1.7. Effect of anions/salts

The wastewater from the dyeing process in textile industry will contain considerable amount of salts/anions naturally as well as from the chemicals used in various stages. They may also affect the efficiency of the electrolytic degradation of the dye in water. Hence, the effect of few individually added salts on the electrochemical degradation of IC is evaluated under the conditions standardized earlier. The results are plotted in figure 10.

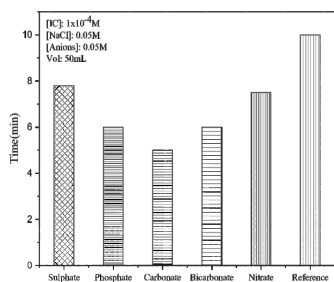
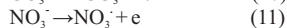
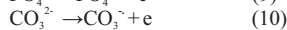
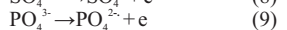
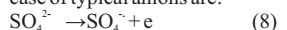


Fig. 10: Effect of anions on the electrolytic degradation of IC
[$\text{BiO}_x/\text{TiO}_2/\text{Ti}/\text{SS}/\text{NaCl}$]

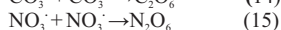
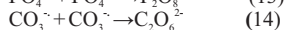
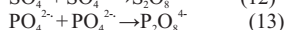
Sulfate, phosphate, carbonate, bicarbonate and nitrate anions are found to enhance the degradation. The enhancement is in the order: Carbonate > Phosphate > Bicarbonate > Nitrate > Sulphate

The enhancement of AOP degradation of organic pollutants in water by anions is explained based on the efficient and sustained formation of respective radical anions which do not get deactivated by recombination as in the case of OH^\cdot radicals [15, 30-33].

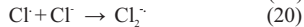
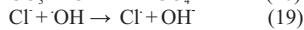
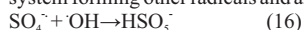
The anions are known to get oxidized at the anode surface followed by formation of radical anion species. Such species can continue to produce stable oxidants. Various possible reactions taking place in the case of typical anions are:



These radicals can combine forming stable peroxide salt oxidants as follows:

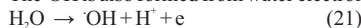


The oxidants can also interact with the OH^\cdot radicals present in the system forming other radicals and anions as follows:

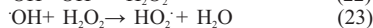


Thus many new types of oxidants/radicals are formed which can influence the degradation of IC.

The OH^\cdot is also formed from water electrolytically as:



However, photoluminescence study [34,35] does not reveal consistent increase in the concentration of OH^\cdot , probably due to the recombination/interaction of OH^\cdot to generate H_2O_2 or HO_2^\cdot ,



It is also possible that the effect of anions may be due to the change in the pH of the solution in their presence. Hence the pH of the reaction medium in presence of the anions is measured. It is observed that the pH remains practically unaffected by the anions except in the presence of PO_4^{3-} , CO_3^{2-} and HCO_3^- , where the pH varies in the range 5.5-8.5. The pH effect on the decolorization of IC in this range is the same as at the natural pH of IC solution in the absence of anions (7.4) (see inset of figure 4). Hence change in pH is not the cause of the anion effect at least at the concentration studied here.

3.1.8. Chemical Oxygen Demand/Mineralization

The efficiency of any AOP as a decontamination tool depends on its ability to mineralize the pollutants to harmless products such as CO_2 , H_2O , and salts, which is verified by the elimination of chemical oxygen demand (COD). In the current study also, the COD of the electrochemical system [$\text{BiO}_x/\text{TiO}_2/\text{Ti}$, NaCl , SS] is measured immediately after decolorization (10 min.) and after extended time (300 min.) of electrolysis. The COD remains unchanged even after 300 min. This suggests that electrolysis of the system leads to degradation/decolorization of IC to stable colorless compounds which cannot be degraded further. In this context, the reaction intermediates in the system after decolorization are analyzed by LC-MS. The identified intermediates are listed in table 2.

Table 2: Major intermediates formed during electrochemical degradation of IC under

| Mol. weight | Molecular formula | Molecular structure |
|-------------|---|---------------------|
| 163 | $\text{C}_8\text{H}_5\text{NO}_3$ | |
| 371 | $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_7\text{S}$ | |
| 454 | $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_{10}$ | |
| 198 | $\text{C}_7\text{H}_4\text{NSO}_4$ | |
| 226 | $\text{C}_8\text{H}_4\text{NSO}_5$ | |
| 454 | $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_{10}$ | |

| | | |
|-----|--|--|
| 523 | C ₁₆ H ₅ Cl ₂ N ₂ S ₂ O ₁₀ | |
| 472 | C ₁₆ H ₅ N ₂ ClS ₂ O ₉ | |

Some of the intermediates are chloro compounds which are relatively more stable and mineralize only slowly. The faster decolorization can be attributed to the transformation of IC into various chloro-compounds. However, some chloro compounds make mineralization slower. The source of chlorine is the electrolyte NaCl. Thus it is clear that the electrolysis system [BiO_x/TiO₂/Ti, NaCl,SS], which is highly efficient for the decolorization of IC, is not appropriate for its mineralization and hence for the purification of water.

The data in Table 1 shows that replacement of SS by graphite as the cathode gives same efficiency for decolorization of IC. Hence [BiO_x/TiO₂/Ti, NaCl, graphite] system is tested for mineralization efficiency. In this case also, the COD remains unchanged even after 300 min. of electrolysis thereby indicating that the system with NaCl as the electrolyte is not suitable for the mineralization of IC. In this context, another electrolyte Na₂SO₄ is used in place of NaCl and the experiments are repeated using the electrode system BiO_x/TiO₂/Ti and SS. The color of the dye remains unchanged even after 480 min. of electrolysis indicating that this system is not suitable for the degradation/decolorization of IC. When the cathode SS is replaced by graphite rod [BiO_x/TiO₂/Ti, Na₂SO₄, graphite] the decolorisation does take place and is complete in 90 minutes. Few more electrolytes other than NaCl, i.e. CO₃²⁻, HCO₃⁻, and PO₄³⁻ were also tested with the same electrode combination (BiO_x/TiO₂/Ti/ graphite). Of these, CO₃²⁻ has almost same efficiency for decolorisation (90 min.) as SO₄²⁻ while the other two electrolytes do not favor decolorization. Based on these observations, Na₂SO₄ is chosen as the convenient and safer electrolyte with BiO_x/TiO₂/Ti/graphite electrode system for further studies.

3.1.9. Studies with Na₂SO₄ as electrolyte

The efficiency of electrolytic decolorization of IC in the [BiO_x/TiO₂/Ti, Na₂SO₄, graphite] system is not affected by varying the concentration of SO₄²⁻ in the range of 0.25 to 0.60g/L, as is observed experimentally. In this case also, the degradation is more in the acidic pH with maximum in the range 2-4. Similarly, the decolorization is enhanced with increase in the area of the electrode exposed to the electrolyte and with decrease in the inter-electrode distance. Thus the optimized parameters for the decolorization of IC in the [BiO_x/TiO₂/Ti, Na₂SO₄, graphite] system are: [Na₂SO₄] = 0.05M, pH = 2-4, area of the graphite electrode dipped in the electrolyte: 7.2 cm², inter electrode distance: 1.0 cm.

Various intermediates formed during the electrolysis in this case (immediately after decolorization) as analyzed by LC-MS are listed in Table 3. There are no chloro-compounds and hence the mineralization is expected to be faster. The COD measurements show ~77% decrease in 5 hr. and complete mineralization in 10 hr. of electrolysis. In the case of NaCl electrolyte under identical conditions, the COD decreases by ~23% only in 10 hr. (figure 11).

The possibility of exploiting the superior decolorization efficiency of NaCl and mineralization efficiency of Na₂SO₄ by using their combination (1:1) as electrolyte is examined experimentally. The COD values at two different time periods of electrolysis, i.e. 5 and 10 hr. are determined and compared with those in electrolytic systems with different electrolyte-electrode combinations. The results are presented in Table 4. The mineralization efficiency in SO₄²⁻ electrolyte (cathode: graphite) is reduced in the presence of Cl⁻ and the efficiency of the combination is in between that in presence of SO₄²⁻ and Cl⁻ as electrolyte individually (~23% COD decrease in the case of NaCl, ~100% COD removal in the case of Na₂SO₄ and ~76% COD decrease in the case of NaCl+Na₂SO₄ combination in 10 hr. electrolysis). The degradation of IC and its mineralization are facilitated by insitu formed (during the electrolysis in Na₂SO₄ electrolyte) SO₄⁻ radical anions which are very strong oxidants (oxidation potential: 2.5-3.1V) and can facilitate the breakdown

Table 3: Intermediates formed during electrolytic degradation of IC in SO₄²⁻ electrolyte

| Mol. weight | Molecular formula | Molecular structure |
|-------------|--|---------------------|
| 90 | C ₂ H ₂ O ₄ | |

| | | |
|-----|--|--|
| 172 | C ₆ H ₆ SO ₃ N | |
| 202 | C ₆ O ₅ H ₄ SN | |
| 153 | C ₇ H ₇ O ₃ N | |
| 428 | C ₁₅ H ₁₂ N ₂ S ₂ O ₉ | |
| 420 | C ₁₆ H ₈ N ₂ S ₂ O ₈ | |
| 422 | C ₁₆ H ₁₀ N ₂ S ₂ O ₈ | |
| 188 | C ₆ H ₆ SNO ₄ | |
| 116 | C ₄ H ₄ O ₄ | |

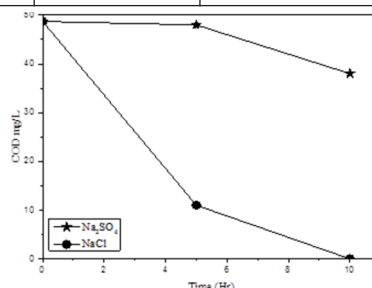


Fig.11: Comparison of NaCl and Na₂SO₄ as electrolytes for the mineralization of IC

[IC] = 1x10⁻⁴M, [Electrolyte] = 5x10⁻³M, Anode: BiO_x/TiO₂/Ti, Cathode: Graphite

Table 4. Mineralization efficiency of various systems in Cl⁻ and SO₄²⁻ electrolytes

[IC] = 1x10⁻⁴M, [NaCl] = 0.05M. [Na₂SO₄] = 0.05M, Anode: BiO_x/TiO₂/Ti

| Cathode | Electrolyte | Initial COD before electrolysis (mg/L) | COD after 5 hr. electrolysis (mg/L) | COD after 10 hr. electrolysis (mg/L) |
|----------|--|--|-------------------------------------|--------------------------------------|
| SS | NaCl | 48.7 | 48.3 | 37.1 |
| Graphite | NaCl | 48.7 | 48.0 | 37.3 |
| Graphite | Na ₂ SO ₄ | 48.7 | 11.5 | 0.5 (~0) |
| Graphite | NaCl/Na ₂ SO ₄ (1:1) | 48.7 | 32.5 | 11.8 |

of organics by attacking the C-C bond [36]. Unlike in the case of Cl⁻, the SO₄⁻ does not give rise to any recalcitrant 'difficult to mineralize' intermediates such as chloro-compounds and this is favorable for the mineralization. The study clearly shows that [BiO_x/TiO₂/Ti, Na₂SO₄, graphite] is a promising electrochemical system for the decontamination of water from IC pollutant.

4.CONCLUSION

Electrochemical Advanced Oxidation Processes (EAOP) with suitably

designed and optimized electrode/electrolyte systems is successfully used for the decontamination of water from the dye pollutant Indigo Carmine. The method is based on the electrochemical generation of highly reactive OH and other radicals in solution which interact with the pollutants and oxidize them irreversibly. Of the different combinations of electrodes and electrolytes tested, the most efficient system consists of BiO₂/TiO₂/Ti anode, Graphite cathode and Na₂SO₄ electrolyte. NaCl as the electrolyte makes the system extremely efficient for the decolorization of the dye, due to the faster formation of various Cl⁻ based oxidants. However, these oxidants transform the pollutants into more recalcitrant chloro-compounds thereby making the mineralization difficult and slower. Various intermediates formed during the process are identified by LC-MS. The effect of various reaction parameters on the efficiency of the decolorization/mineralization process is evaluated experimentally and relevant parameters are optimized.

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