

ENHANCING THE DEGRADATION POTENTIAL OF INDIGO CARMINE BY A MEDIATED ELECTROCHEMICAL OXIDATION USING Ce^{4+} MEDIATOR AND Ag^+ CATALYST IONS

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ABSTRACT

Wastewater runoff containing hazardous dyes must be treated properly before being discharged into the environment. Indigo carmine (IC), a kind of dye, has been recognized to be potentially toxic. In this work, mediated electrochemical oxidation (MEO) using cerium (Ce^{4+}) mediator ions incorporated with an Ag^+ catalyst ion was tested to treat IC solution in a reactor as a simulation. The experimental results demonstrated that the IC molecules can be degraded quickly in a relatively short time by MEO. It was clearly shown that the degradation performance of IC by MEO was affected by the $\text{Ce}_2(\text{SO}_4)_3$ concentration, working potential, time, and catalyst ion concentration as well. In addition, the high percentage recovery of Ce^{4+} proves the reusability of Ce^{4+} as a mediator ion. As an outstanding result, the percentage degradation of IC using $\text{Ce}^{4+}/\text{Ag}^+$ ions was remarkably higher than that without Ce^{4+} mediator ions (100% vs 2%). In summary, our work suggests that MEO using a combination of Ce^{4+} mediator and Ag^+ catalyst ion has great potential to improve the wastewater quality.

Keywords: Mediated Electrochemical-Oxidation, Cerium, Silver, Mediator, and Catalyst.

RASAYAN J. Chem., Vol. 15, No.3, 2022

INTRODUCTION

Indigo carmine (IC) (5,5'-indigodisulfonic acid sodium salt) is a synthetic dye belonging to the indigoid family with a strong blue characteristic. It is the most used dye in the jeans and denim industry.¹ In wastewater, IC is potentially toxic and carcinogenic to nature. Thus, it is important to remove IC from industrial effluents to maintain the environmental sustainability.² Various chemical and physical treatments have been studied to remove IC from wastewater, including coagulation,³ absorptions, adsorption, as well as biodegradation.⁴⁻⁶ However, those methods were found to bear with inconvenience and are expensive. More importantly, the presence of IC is only displaced, then additional treatment is needed, thereby triggering secondary disposal problems. Electrochemical have shown an important role in a wide distinct field, including photo-electrocatalytic devices, anaerobic reactions, sensors and biosensors, and organic pollutant degradation.⁷⁻¹² In terms of organic pollutant degradation, mediated electrochemical oxidation (MEO) has received great attention.¹³⁻¹⁵ Recently, MEO-based degradation has been successfully applied for the mineralization of several organic pollutants. The mediators used for MEO reactions include Ce^{4+} , Ag^{2+} , Co^{3+} , etc. Those mediators showed a satisfying result in the mineralization of liquid organic pollutants, including dyes.¹⁴⁻¹⁹ More importantly, by using MEO the dye effluents were efficiently decolorized in only a short duration time.²⁰ In our laboratory, we have successfully evaluated the MEO potency for the degradation of several organic pollutants, including methylene blue and nonylphenol ethoxylate.⁹⁻¹⁰ The mediator used in our work is the Ce^{4+} ion. This mediator is favoured because of its

advantages that are easily recovered and re-usable.^{9,21-22} Previous studies have shown that IC can be degraded into smaller molecules, including isatin.^{20,23,24} Further, the increment of IC degradation activity by MEO was reported in the presence of a mediator that was chlorine species (Cl^{2-}) electrogenerated on the anode surface.²³ As far as we know, the utilization of Ce^{4+} as a mediator for IC degradation is rarely studied, therefore we focused on exploring this. The presence of metal catalysts has been shown to improve degradation performance.^{9,25-26} However, some of them (Pt, Au, and Pd) are expensive. Considering the inexpensive of Ag-based catalyst, this metal has received more attention. In our previous work, the presence of Ag^+ ions has shown a satisfying result in improving the degradation of dyes.^{9,10} This was also emphasized by the catalytic potential of the Ag^+ ion. Therefore, we are interested to test the IC degradation performance by incorporating the Ce^{4+} mediator with the Ag^+ catalyst ion in a reactor system. Herein, this paper exemplified the developed cell setup as outlined in Fig.-1, with the simultaneous generation of Ce^{4+} mediator ion from $\text{Ce}_2(\text{SO}_4)_3$ in the presence of Ag^+ ion to mineralize IC. The concentration of $\text{Ce}_2(\text{SO}_4)_3$ to generate Ce^{4+} mediator ion, working potential, and time were also observed to optimize the degradation performance. Then, to confirm that the degradation occurred as well as the formation of carbon dioxide (CO_2) after mineralization, the solutions were then evaluated by UV-Vis spectrophotometry, high-performance liquid chromatography (HPLC), and back titration analysis.

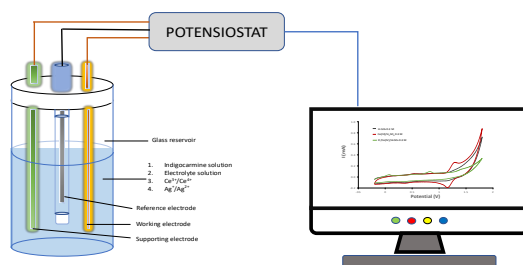


Fig.-1: Schematic Representation of Cell Set up for IC Degradation and Analysis

EXPERIMENTAL

Materials

Indigo carmine, sulphuric acid (H_2SO_4) (98%), silver nitrate (AgNO_3), potassium chloride (KCl), sodium carbonate (Na_2CO_3), barium hydroxide ($\text{Ba}(\text{OH})_2$), acetonitrile, and chloride acid (HCl) were from Merck. Cerium sulfate ($\text{Ce}_2(\text{SO}_4)_3$) octahydrate (> 99.0%) was from Sigma Aldrich.

The Electrochemical Reactor set up

A single-pot-container reactor was operated for the electro-degradation of IC. The reactor consisted of a 100 ml glass bottle sealed by rubber caps with three open slots for the electrodes assembled. A Pt electrode was used as the anode. A DC potentiostat with a cell potential (difference) range of 0–36 V or a current of 0–3 A was used as a power supply for the system. The analysis was performed in a potential range of 200 mV to 1800 mV with a scan rate of 100 mV/s.

Optimization of $\text{Ce}_2(\text{SO}_4)_3$ Concentration, Working Potential, Time, and Ag^+ Catalyst ion Concentration

To optimize the degradation potential of IC, we observed the degradation percentage based on various $\text{Ce}_2(\text{SO}_4)_3$ concentrations (0.02, 0.025, 0.03, 0.035, and 0.04 M), different working potentials (1.5, 3, 4.5, 6, 7.5, and 9 V), and time (10 to 50 mins with 10 mins interval). While for the effect of Ag^+ catalyst ion, the test was evaluated at Ag^+ concentrations of 0.5, 1, 2.5, and 3 mM. The percentage degradation of IC was calculated according to Eq. (1):

$$\% \text{ Degradation} = [(I_o - I_t)/I_o] \times 100\% \quad (1)$$

Where, I_o is the initial current of the IC oxidation peak, and I_t is the current of the IC oxidation peak after processing by MEO.

UV-Vis Spectrometry and High-Performance Liquid Chromatography (HPLC) Analysis

The absorbances of IC solution (before and after degradation) were recorded at λ 200 to 800 nm using a UV-Vis Spectrophotometer (Hitachi U2800, Japan). The HPLC analysis was conducted using an HPLC Agilent Technology – 1260 instrument with a BEH C-18 column to confirm the IC degradation. About 20 μ L of IC solution was injected into the HPLC instrument. The mobile phase was a mixture of acetonitrile (A) and distilled water (B) at 90:10. The flow rate was set at 1 mL/min.

Back Titration Analysis

The back titration analysis was used to confirm the possible complete degradation of IC and calculate the formation of CO_2 . The test was carried out according to our previous work published.¹²

RESULTS AND DISCUSSION

The electrochemical behavior of the Ce^{4+} mediator ion and IC/ Ce^{4+} was first studied by cyclic voltammetry (CV). As depicted in Fig.-2a, the CV voltammogram of Ce^{4+} mediator from $\text{Ce}_2(\text{SO}_4)_3$ in an acidic solution (0.3 M H_2SO_4) (red line) presented a couple of reductions and oxidation peak potential (E_{pa} and E_{pc}) at 1.28 V and 1.20 V, respectively. While in the CV voltammogram of 0.3 M H_2SO_4 (black line), no peak was recorded. The voltammogram of Ce^{4+} presented a reversible reaction and confirmed the generation of Ce^{4+} from $\text{Ce}_2(\text{SO}_4)_3$, in line with the investigation previously reported.²⁷

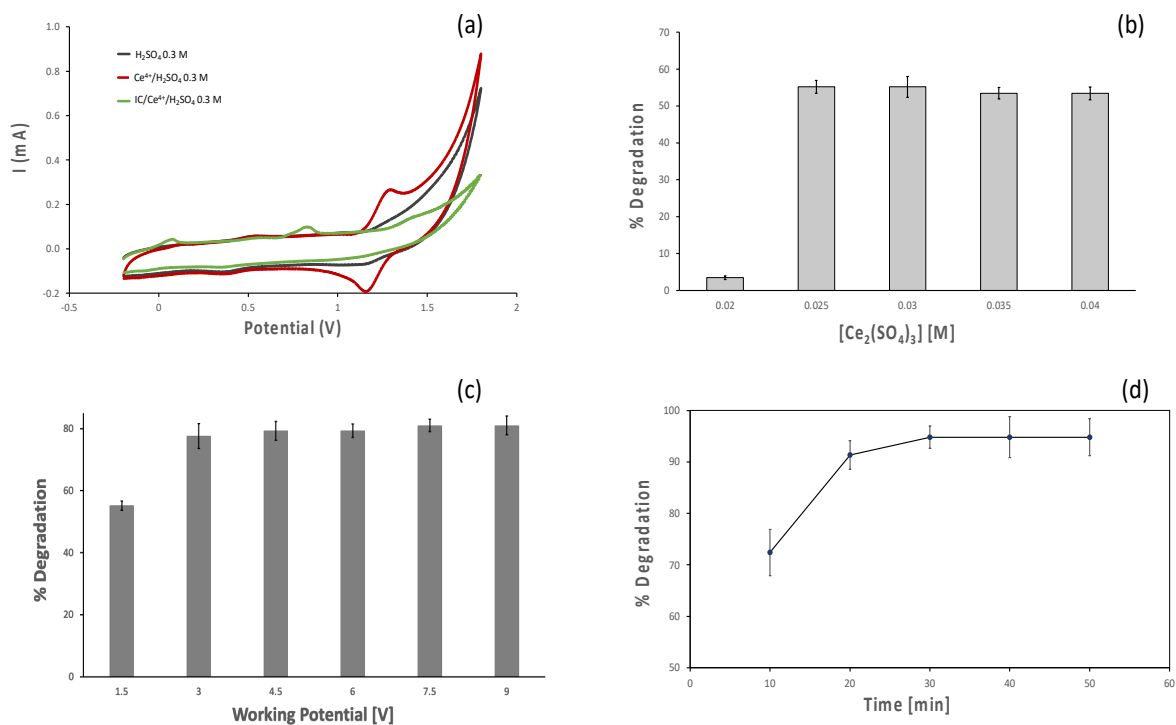
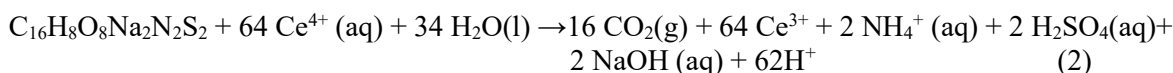


Fig.-2: (a) The Electrochemical Profile of 0.3 M H_2SO_4 , Ce^{4+} in 0.3 M H_2SO_4 , and IC/ Ce^{4+} in 0.3 M H_2SO_4 . The Effect of (b) $\text{Ce}_2(\text{SO}_4)_3$ Concentration, (c) Working Potential and (d) Time for Degradation of 300 ppm IC in 0.3 M H_2SO_4 .

While the CV voltammogram of IC, was presented with a green line, it shows two oxidation peak potential/ E_{pa} values at 0.08 V and 0.70 V in the absence of E_{pc} value. Suggesting an irreversible oxidation process. As also depicted in Fig.-2a, the signature peak oxidation potential of Ce^{4+} mediator and IC are significantly different, allowing the evaluation of IC in one pot reaction container. Next, the effect of $\text{Ce}_2(\text{SO}_4)_3$ concentrations was tested on five different concentrations (0.02, 0.025, 0.03, 0.035, and 0.04 M) with an initial IC concentration of 300 ppm and working potential of 1.5 V. The result are given in Fig.-2b. Using $\text{Ce}_2(\text{SO}_4)_3$ at 0.02 M to generate Ce^{4+} mediator ion, the degradation percentage was less than 10%. A significant increment was observed when $\text{Ce}_2(\text{SO}_4)_3$ at 0.025 M was applied. The degradation percentage

increased up to 5 times. However, at concentrations in the range of 0.025-0.04 M, the degradation percentage tends to be flat. The low degradation that occurred when 0.02 M $\text{Ce}_2(\text{SO}_4)_3$ was applied is probably because there are not enough electrons to be transferred for oxidizing IC. It was also recorded that the maximum destruction in the liquid phase was achieved at a ratio of Ce^{4+} : IC of 42:1, as against the theoretical ratio of 64:1 as given in Eq. (2). It seems the formation of some smaller organic compounds accounted for this phenomenon.²²



Further, we evaluate the effect of working potential value on the electro-degradation of IC. As depicted in Fig.-2c, the degradation percentage increases when the working potential value is elevated. In the electro-degradation process, working potential serves as the driving force and the power of repolarization for the particle electrode. Therefore, when the working potential is elevated, the degree of repolarization is enhanced, and the electron transfer becomes faster.²⁹ Then, increase the electro-degradation percentage up to above 90%.

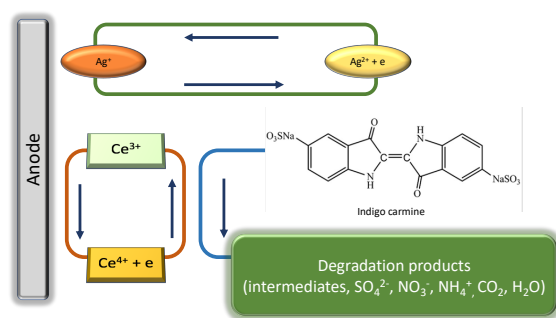


Fig.-3: The Schematic Proposed Mechanism of IC Degradation by MEO using Ce^{4+} Mediator ion and Ag^+ Catalyst ion

We also observed the effect of degradation time for a time ranging from 10 to 50 min in solutions containing 0.3 M H_2SO_4 and 0.025 M $\text{Ce}_2(\text{SO}_4)_3$ at a working potential of 3 V. This observation is important to evaluate the degradation efficiency. As depicted in Fig.-2d, it shows that in the first 20 min, the degradation percentage increased rapidly. A small enhancement was observed at min 20 to 30, indicating the optimum degradation time has been reached. In the indirect degradation of organic pollutant, the reaction mainly occurs in a bulk solution with an electrogenerated active species. Therefore, the oxidation rate depends on the concentration of mediator oxidized to activate species on the anode surface, as suggested by the proposed mechanism in Fig.-3. We observed the potential of Ag^+ catalyst ion, to enhance the degradation potential of IC by MEO, in a range of concentration of 0.5, 1, 2.5, and 3 mM (Fig.-4a). As shown, the presence of Ag^+ ions enhance the degradation potential as suggested by an increment in degradation percentage. The degradation percentages of IC containing Ag^+ ions at 2.5 and 3 mM were up to 100%. This is because the standard reduction value of $\text{Ag}^{2+}/\text{Ag}^+$ is higher than $\text{Ce}^{4+}/\text{Ce}^{3+}$.^{14,29} Therefore, the earlier Ag^{2+} will be reduced to Ag^+ , providing more electrons and augmenting the efficiency of Ce^{3+} conversion. Hence, undoubtedly, the IC degradation was improved. However, it should be noted, that the presence of Ag^+ at 0.5 mM resulted in a lower degradation percentage. This is most likely due to the reaction Ag^+ with supporting electrolytes (H_2SO_4) to form Ag_2SO_4 . Here, we also observed the electrochemical profile of IC before and after electro-degradation. As presented in Fig.-4b., the couple reduction-oxidation peaks at 1.16 and 1.42 V after degradation refers to the peaks of $\text{Ce}^{3+}/\text{Ce}^{4+}$. Additionally, as recorded, the oxidation peaks of IC disappeared after degradation, while a new peak arise at 0.48 V. This is because during the degradation process, the IC molecules are destructed, forming intermediates including isatin and its derivatives. At the same time, a reduction-oxidation reaction of $\text{Ag}^+/\text{Ag}^{2+}$ occurred. Theoretically, the Ag ions may possibly react with isatin or other intermediate molecules, forming Ag-isatin or Ag-intermediate complex molecules. We also calculated the % recovery of Ce^{4+} mediator in the 3-batch degradation process. By comparing the peak current response of Ce^{4+} without IC and after degradation under optimal conditions, the percentage recovery of Ce^{4+} mediator ion was found in the range of 95 - 102%, suggesting the high reusability of Ce^{4+}

mediator. However, since our work applies a one-pot reactor container, we therefore further propose to use a membrane for trapping the Ce^{4+} mediator ion in a two-compartment reactor system. The UV spectra of the IC before and after degradation are given in Fig.-4c. As presented, a maximum peak at λ of 618 nm with an absorbance value of 1.056 (blue line), showing the presence of IC in keto form. The absorbance value at λ of 618 nm was decreased to 0.001, indicating a successful degradation of IC. Further, the HPLC chromatograms in Fig.-4d showed that about 95% of IC was degraded, as suggested by a reduction in the AUC value from 3249.32 mAU to 156.31 mAU after electro-degradation. Then, to ensure the formation of CO_2 , as given in the theoretical reaction Eq. (2), we performed the back-titration analysis of the solutions after degradation. In this work, the calculated CO_2 formation was 61.79%. Studies have shown that the oxidation of IC in aqueous and aqueous acidic medium results in cleavage of the C=C bond, thereby forming indigo, isatin-5-sulfonic acid, and isatin as the main aromatic products. Later, the presence of OH radicals continuously oxidized those compounds into SO_4^{2-} , NH_4^+ , and NO_3^- .³⁰ Therefore, although the degradation percentage of IC was high, above 90%, this could not lead to complete conversion to CO_2 due to the formation of intermediate molecules. Finally, we compared the results of IC degradation in the presence and absence of Ce^{4+} mediator. As presented in Fig.-4e, it clearly shows that in the presence of Ce^{4+} mediator and Ag^+ catalyst ions, the degradation percentage significantly improved, corroborating the potency of MEO for degradation of organic pollutants.

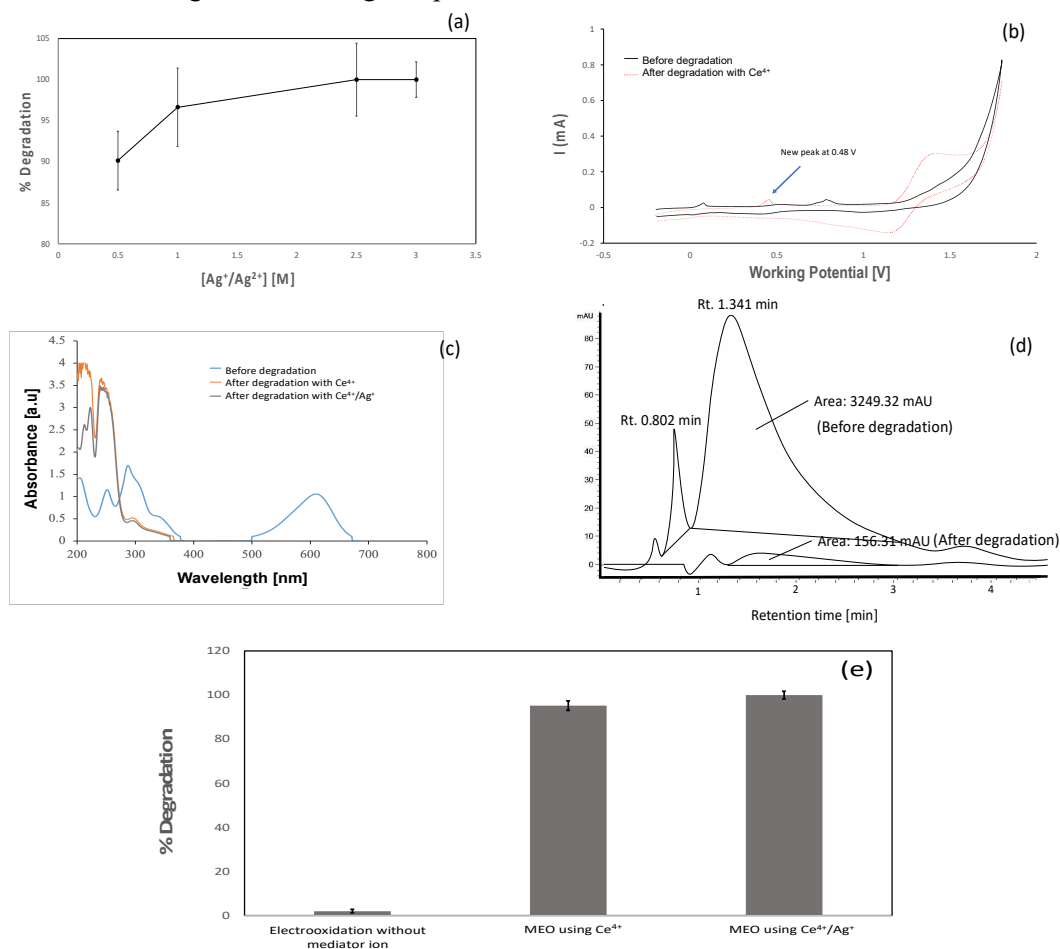


Fig.-4: (a) The Effect of Ag^+ Catalyst ion on the Degradation of IC. (b) The Squarewave Voltammogram, (c) UV-Vis Spectra, and (d) the HPLC Chromatograms of IC before and after Degradation. (e) The Percentage Degradation of IC in the Absence, Presence of Mediator ion, and Combination Ce^{4+}/Ag^+

CONCLUSION

In summary, MEO is a promising green technology for environmental remediation, particularly for improving the quality of wastewater runs-off from dyes.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Research and Higher Education of Indonesia through Riset Inovasi KK (ITB) for Analytical Chemistry Research Group ITB fiscal year of 2018 under HS.

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