

*Full Paper*

## **Iron Oxide Nanoparticles-assisted Electrochemical Oxidation of Salicylaldehyde**

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**Abstract-** In this study, Fe-oxide-based NPs (Fe<sub>2</sub>O<sub>3</sub> NPs) were prepared via precipitation strategy, and characterized by transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD), X-ray photo-reduction spectroscopy (XPS), cyclic voltammetry (CV). The characterization data indicated that prepared Fe-based NPs possessed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase with 50-60 nm diameter. Next, the CV technique was employed to test the ability of the prepared Fe<sub>2</sub>O<sub>3</sub> NPs toward electrochemical oxidation of salicylaldehyde at a glassy carbon electrode (3 mm diameter) in an alkaline electrolyte. The results demonstrated that the electrochemical oxidation of salicylaldehyde followed first-order kinetics with a hydroxyl-radical aided process, requiring 18.4 kJ/mol activation energy at ambient temperature.

**Keywords-** Synthesis; Electrochemistry; Salicylaldehyde; Fe<sub>2</sub>O<sub>3</sub> nanoparticles; Oxidation

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### **1. INTRODUCTION**

Salicylaldehyde (o-hydroxybenzaldehyde), a typical example of a highly functionalized arene, finds use as an analytical reagent, a spice, and an additive for petrol. As a precursor in the organic synthesis of a wide variety of chemicals, including chelating agents, it is essential to the production of these compounds. Salicylaldehyde, a common organic contaminant in cosmetics, agricultural chemicals, and medicinal medications, finds its way into the water system [1]. A variety of foods and beverages, including cinnamon, grapes, tomatoes, milk,

beer, coffee, and tea, naturally contain salicylaldehyde. Some polycyclic aromatic hydrocarbons produce it as an intermediate during their aerobic metabolism [3]. The oxidation of salicylaldehyde can produce salicylic acid, one of several byproducts. Researchers have conducted extensive research on the electrochemical oxidation of salicylic acid [4,5] and acetylsalicylic acid [6]. The focus of these studies has been on electrochemical detection [7], electro-polymerization [8], electro-oxidation processes [9], and electrochemical elimination and degradation [10]. On the other hand, the electrochemical oxidation of salicylaldehyde has only been the topic of a small number of experiments [11]. Chen and others studied how salicylic acid and salicylaldehyde photoelectrochemically react on TiO<sub>2</sub> nanotube arrays [12] using in situ UV-vis spectroscopy. They also looked into how the same compounds changed when they were electrochemically oxidized in 0.5 M H<sub>2</sub>SO<sub>4</sub> at an electrode made of Ti, IrO<sub>2</sub>, SnO<sub>2</sub>, and Sb<sub>2</sub>O<sub>5</sub> [13]. A variety of parameters, including temperature, beginning concentration, current density, and supporting electrolyte, influenced the degradation kinetics, as demonstrated. It is necessary to conduct additional research in order to gain a better understanding of the salicylaldehyde electro-oxidation route. This will allow for a better understanding of its role and conversion in oxidative degradation, photosynthesis, and aerobic metabolism. On the other hand, the electrode's composition has a significant impact on the electrochemical oxidation process's efficiency and performance. For instance, using transition metal Ti/Sn-based electrodes (Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>) for the electrochemical oxidation process has recently shown great results, and this is a promising direction to go in the future [14,15]. While the low cost of Sn/Sb-based electrodes makes them an attractive option for commercial applications, their service life is limited. Within this agenda, Fe-based nanomaterials can efficiently assist the electrochemical processes of salicylaldehyde due to their high tendency to exchange electrons with the analyte and their high sensitivity towards interaction with the analyte oxygen atom under mild applied potential [16]. Therefore, to improve the efficiency of the electro-oxidation of salicylaldehyde, the purpose of this research is to develop an electrode material that is both affordable and efficient. In this study, we prepared Fe<sub>2</sub>O<sub>3</sub> nanoparticles and characterized them using various analytical methods. In addition, we experimented with the ability of a Fe<sub>2</sub>O<sub>3</sub> electrode to oxidize salicylaldehyde by modifying a glassy carbon electrode with Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The results demonstrated the constructed Fe<sub>2</sub>O<sub>3</sub> electrode's promising ability to oxidize salicylaldehyde.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and methods

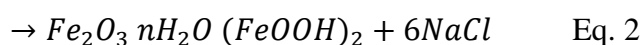
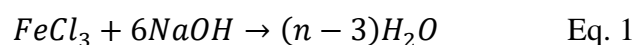
The chemicals salicylaldehyde (98%), FeCl<sub>3</sub>, NaOH pellets, and solvents were obtained from TCI Chemicals Ltd, India. All the chemicals used in this study were of analytical grade and were not subjected to any further purification procedures. We conducted transmission electron microscopic (TEM) and X-ray diffraction (XRD) investigations using FEI Tecnai G2

20 and Shimadzu XRD-6000, respectively. We used a Metrohm 663 VA Stand electrochemical workstation and a standard three-electrode cell (glassy carbon (GC) (having a diameter of 3.0 mm) as working electrode, Pt-wire as counter electrode, and Ag/AgCl as reference electrode) to conduct our electrochemical studies. Before every electrochemical experiment, there was a pre-treatment step. The electrode was made by subjecting a mixture of 5.0 mg of Fe<sub>2</sub>O<sub>3</sub>, 0.5 mL of ethanol, and 10 μL of a 5% Nafion solution to ultrasonic processing. Afterward, 11 μL of catalyst ink was delicately brushed onto the GC electrode's surface and left to dry at room temperature.

## 2.2. Preparation of Fe<sub>2</sub>O<sub>3</sub> Nanoparticles

Typically, in a 100 mL aq. solution of FeCl<sub>3</sub>, NaOH was progressively added while maintaining the pH at approximately 11.0, and the solution was constantly stirred. After 5 hours, the colloidal solution's pale red color changed to dark brown color as a result of the creation of hydrated Fe<sub>2</sub>O<sub>3</sub> NPs, which followed the mechanism depicted below [17,18].

**Step 1:** Fe<sub>2</sub>O<sub>3</sub> Nanoparticle's nucleation (Eq. 1 and 2)



In order to eliminate any clinging contaminants from the resultant colloidal solution, it was centrifuged numerous times at 5500 rpm for 10 minutes and rinsed with distilled water and ethyl alcohol repeatedly. In order to obtain deep red-colored Fe<sub>2</sub>O<sub>3</sub> nanoparticles, the liquid portion was dried using hot air at a temperature of 70 °C for an entire night. The resulting dark brown solid was then crushed and ground using a mortar and pestle. Subsequently, the material was subjected to calcination in a muffle furnace at a temperature of 650 °C for a duration of 5 hours, resulting in the production of deep red-colored Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

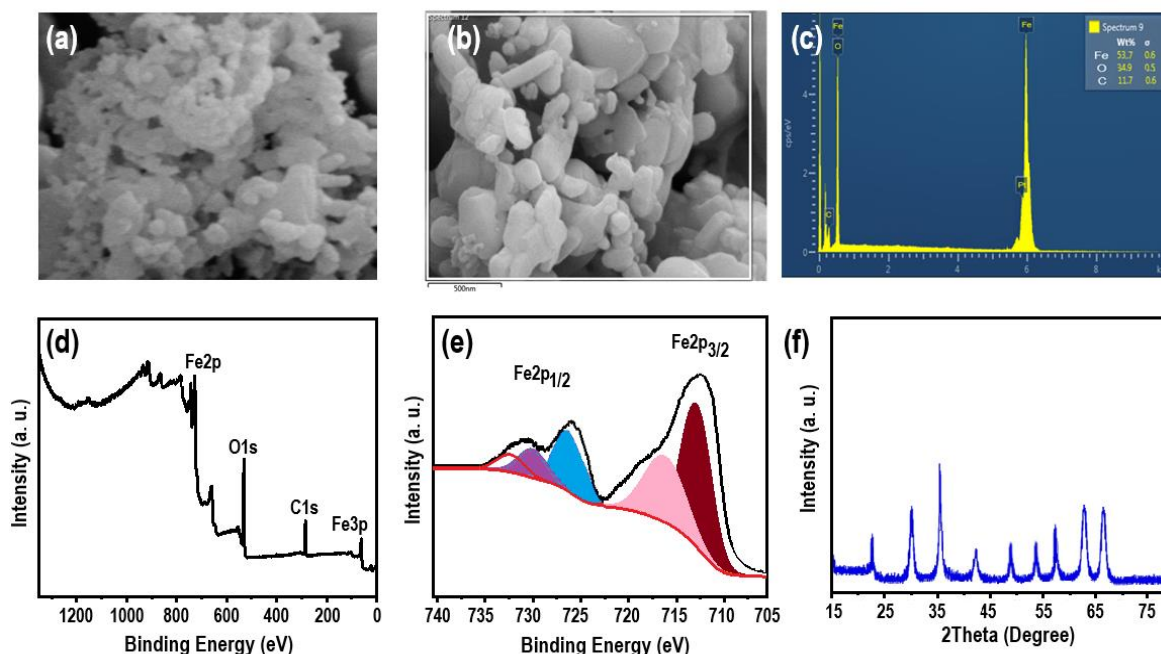
## 3. RESULTS AND DISCUSSION

### 3.1. Analysis of the synthesized Fe<sub>2</sub>O<sub>3</sub> nanoparticles

The morphology of freshly generated Fe<sub>2</sub>O<sub>3</sub> was studied using the transmission electron microscopy (TEM) technique. It can be seen in Figure 1(a-b) that the produced Fe<sub>2</sub>O<sub>3</sub> material has a spherical shape with a diameter of 80-90 nm [15]. The elemental mappings for the produced Fe<sub>2</sub>O<sub>3</sub> NPs, which include both Fe and O-components, are also in good accord with their chemical compositions (Figure 1c) [16,17].

XPS investigations were carried out on the synthesized Fe<sub>2</sub>O<sub>3</sub> NPs in order to better define the surface chemical configuration of the NPs. As shown in Figure 1d, the typical XPS survey spectrum for α-Fe<sub>2</sub>O<sub>3</sub> demonstrates the presence of the peaks of Fe2p, oxygen, and carbon in

hybrids, as well as the absence of other elemental peaks, which supports the conclusion that the manufactured  $\text{Fe}_2\text{O}_3$  NPs had mostly Fe and oxygen components.



**Figure 1.** (a-b) TEM picture, (c) EDX-elemental mapping, (d) XPS survey, (e) XPS Fe2p scan, and (f) XRD pattern, of the prepared  $\text{Fe}_2\text{O}_3$  NPs

The EDX spectra [18] also corroborated this conclusion. Furthermore, the Fe2p scan revealed two signals at 711.56 and 724.39 eV, which may be attributed to Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub>, respectively, on the basis of their eV values. The  $\text{Fe}^{3+}$  in  $\alpha\text{-Fe}_2\text{O}_3$  might be responsible for the satellite peak between Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> at 719.19 eV, which is consistent with previous results (Figure 1e) [19]. Investigations on the structural changes in the crystal structure of the produced  $\text{Fe}_2\text{O}_3$  NPs were carried out using X-ray diffraction (XRD). A representative XRD spectra of iron oxide nanoparticles is shown in Figure 1f, with the peak at  $32.88^\circ$  being considered strong evidence for the presence of the (104) plane of  $\alpha\text{-Fe}_2\text{O}_3$  phase. Furthermore, the other peaks are in good accord with the earlier observations [20] on  $\alpha\text{-Fe}_2\text{O}_3$  having a hexagonal structure, which was previously reported.

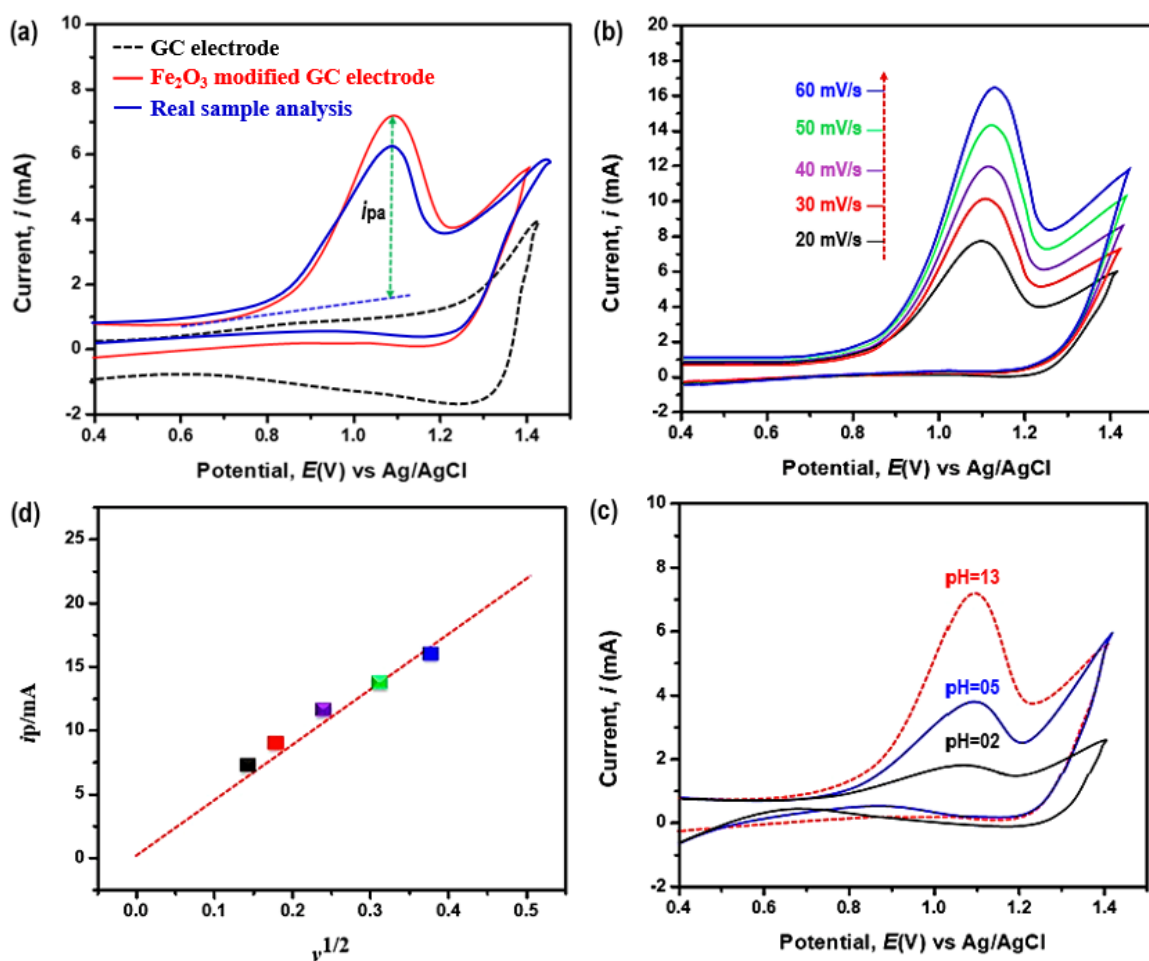
### 3.2. Electrochemical Oxidation of Salicylaldehyde on $\text{Fe}_2\text{O}_3$

In order to evaluate the oxidation of salicylaldehyde at a  $\text{Fe}_2\text{O}_3$  NPs modified glassy carbon electrode in 0.1 M NaOH medium (supporting electrolyte), cyclic voltammetry was performed. The cyclic voltammogram (CV) of the  $\text{Fe}_2\text{O}_3$  NPs modified glassy carbon electrode displayed one anodic peak close at  $E_p=1.04$  V when it was recorded in a solution of  $10^{-3}$  M salicylaldehyde at a scan rate of 20 mV (Figure 2a) and a pH of 13.0. When the experiment

was performed for a cathodic scan, the cathodic peak did not appear, indicating that the oxidation of salicylaldehyde is an irreversible process [21].

Additionally, the influence of scan rate on the electro-oxidation of salicylaldehyde under identical experimental conditions was investigated (Figure 2b). There was a linear relationship between the square root of the scan rate and the peak current, and this relationship ranged from 20 mV/s to 60 mV/s (Figure 2c). This behavior is characteristic of a diffusion-controlled reaction, and it may be represented by following the formula in Eq. 3.

$$I_{pa} \propto v^{1/2} \quad \text{Eq. 3}$$



**Figure 2.** (a) CV curves of GC electrode (Dotted black color), Fe<sub>2</sub>O<sub>3</sub> modified GC electrode (Red color), and Fe<sub>2</sub>O<sub>3</sub> modified GC electrode in a real sample (Blue color), (b) CVs for Fe<sub>2</sub>O<sub>3</sub> modified GC electrode, recorded at different scan rates, (c)  $v^{1/2}$  vs *i*<sub>p</sub> curve, and (d) CVs Fe<sub>2</sub>O<sub>3</sub> modified GC electrode recorded at various pH. All CVs were recorded in 0.1 M NaOH electrolyte containing 10<sup>-3</sup> concentration of salicylaldehyde.

In addition to this, there is a possibility that the pH of the medium might have an effect on the reaction that takes place at an electrode. The electro-oxidation of salicylaldehyde was investigated using CV across the pH range of 2.0 to 13.0 in an alkaline medium solution as depicted in Figure 2d. Based on the findings, it was clear that the pH solution had a significant effect on the peak current. At a higher pH, the electro-oxidation of salicylaldehyde is more facile, which may be due to a higher concentration of hydroxyl radicals for the action of Salicylaldehyde [22].

Further to evaluate the practical applicability of the Fe<sub>2</sub>O<sub>3</sub> NPs-modified glassy carbon electrode, the electrochemical investigation was performed against the real sample. Using a typical addition method, the concentration of salicylaldehyde in an industrial wastewater sample was monitored. Before being used, industrial wastewater was given a minimum of one day to stand. Due to the decreased salicylaldehyde concentration in the actual sample, the electrochemical results showed a comparable peak position to that of salicylaldehyde oxidation, but with a lower peak height (blue curve in Figure 2a). The results showed that the electrode made of Fe<sub>2</sub>O<sub>3</sub> NPs has good potential for oxidizing salicylaldehyde at a realistic level [23].

Overall, the GC electrode was found to be inactive towards the electrochemical oxidation of salicylaldehyde, whereas, Fe<sub>2</sub>O<sub>3</sub> NPs modified electrode was found to be promising towards the same electrochemical process. This can be attributed to the effect of Fe<sub>2</sub>O<sub>3</sub> NPs, these nanoparticles can assist the electrochemical electron transfer to the analyte initiating the electrochemical oxidation process of salicylaldehyde. Moreover, Fe-atoms show significant sensitivity towards oxygen-atoms of salicylaldehyde molecule, assisting the facile adsorption of salicylaldehyde molecules on Fe<sub>2</sub>O<sub>3</sub> NPs modified GC electrode, and thereby approaching the electrochemical oxidation of salicylaldehyde.

#### 4. CONCLUSION

In this study, Fe<sub>2</sub>O<sub>3</sub> nanoparticles were produced using a chemical approach and then analyzed using a variety of spectroscopic techniques. The XRD and XPS measurements indicated that the produced Fe<sub>2</sub>O<sub>3</sub> was in the  $\alpha$ -phase and that there were no impurities present. Further, the electrochemical behavior of Fe<sub>2</sub>O<sub>3</sub> NPs toward oxidation of salicylaldehyde was investigated at a glassy carbon electrode (3 mm diameter) in an alkaline electrolyte, and it was revealed that Fe<sub>2</sub>O<sub>3</sub> NFs could be used as a possible material for the degradation of salicylaldehyde in the potential window of 0.4 to 1.4 V vs. Ag/AgCl. The high sensitivity of Fe<sub>2</sub>O<sub>3</sub> NPs modified GC electrode as compared to bare GC electrode can be attributed to the effect of Fe<sub>2</sub>O<sub>3</sub> NPs. These nanoparticles can assist the electron transfer to salicylaldehyde molecules, offering facile adsorption of salicylaldehyde molecules on Fe-atom via Fe (of Fe<sub>2</sub>O<sub>3</sub>) and O-atom (of salicylaldehyde) bonding. This interaction can initiate the oxidation of salicylaldehyde, displaying an anodic response in the electrochemical study. This study

demonstrated the ability of low-cost transition metal-based nanoparticles towards electrochemical salicylaldehyde oxidation, and open the venue for these nanoparticles to be used to activate various organic and inorganic molecule oxidation and reduction reactions.

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### Declarations of interest

The authors declare no conflict of interest in this reported work.

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