



Electrosynthesis of Polythiophene/Cr₂O₃ Nanocomposite as a Model of Health Topics (Water Treatment)

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Abstract

A Nanocomposite film consisting of Cr₂O₃ and polythiophene (PT), has been successfully fabricated on a stainless steel substrate (SS) by a simply electrochemical deposition method. The fabrication mechanisms are based on electrolytic deposition ELD method of Cr₂O₃ thin film and electropolymerization deposition of PT. The papered Cr₂O₃ and PT/Cr₂O₃ were characterized by FT-IR, FESEM, TEM, XRD, and Raman spectra. Electrochemical degradation of Reactive Blue 4 (RB4) was studied by Cr₂O₃ and PT/Cr₂O₃ coated anodes in the existence of sodium chloride as a supporting electrolyte to investigate the effect of polythiophene /Cr₂O₃ Nano composite coating. The color removal efficiencies were 51.7% and 92 % respectively for above anodes, after 25 minutes of electrolysis at applied potential 3V.

Keywords: *Nanocomposite, Electrolytic deposition, Electrodegradation.*

Introduction

The combination of polymer science and nanotechnology is emerging field of research. Nanocomposites of conducting polymer are unique because of rise in electrical disruption down power of conductive polymers, melting point temperature, color, and magnetization charge volume is extra and relating region is rising such that we be able to acquire our believed property [1]. The features of nanocomposites are affected by the singular constituents, the systems morphology, capacity, and form segment of the filling in addition to the type of the interface of the constituents' interphase [2].

Amongst these nanocomposites, the polymer based has been known as the best attractive in numerous research parts, such as engineering, optoelectronics, medicine, and water remediation because their characteristic possessions developing from the specific modules [3]. The incorporation of metal oxide and polymers have been an effective area of study; in actual, the industrial of variable nanocomposites has obtained widely consideration owing to the considerable electrical, mechanical, thermal, and magnetic possessions contrasted to the polymers structure and metal oxide [4]. In this type of nanocomposites, the polymer substantial offers useful processing,

structural elasticity, photo conductivity, metallic performance, tunable electrical possessions, and effective luminescence [5], however the metal oxide proposes important carrier flexibility's, thermal, band gap tenability, and mechanical strength in addition to magnetic and dielectric properties [6]. As well as the individual characteristics, novel or enhanced phenomena can too happen when the interface between the metal oxide and polymer [7]. Owing to the significant surface area, nanocomposites show several differences in their properties paralleled to the single constituent of the metal oxide.

The features of the nanocomposites are affected by the interface among the polymer and the metal oxide, where a broad kind of covalent and hydrogen links might inhibit phase split [8]. Currently, several electrochemical treatments are processes applied for elimination of organic and inorganic contaminations from renewed, consumption and waste waters. Anodic oxidation of organic contaminants can be performed in several different ways, including both direct and indirect oxidation [9]. The process contains of functioning the oxidation reaction at the anode where contaminants are conveyed into non-toxic

materials, through breakdown into simple materials or transporting into oxidation formula. It is utilized generally for organic substances. In this present work focusing on preparation of Cr₂O₃ and Nanocomposite PT/Cr₂O₃ thin films. The PT/Cr₂O₃ Nanocomposite substantial were synthesis by electro polymerization of thiophene on the SS -plate coated by Cr₂O₃ thin film process. After the synthesized PT/Cr₂O₃ Nanocomposite thin films were distinguished by FTIR, XRD, Raman, TEM and FESEM. PT/Cr₂O₃ and Cr₂O₃ thin films were used as anode for electrodegradation of reactive blue 4 dyes.

Experimental

Chemicals

Chromium chloride hydrate (CrCl₃.6H₂O), Sodium acetate (CH₃COONa), thiophene (Th), Perchloric acid (HClO₄) and sodium perchlorate (NaClO₄) were purchased from Sigma Aldrich, Acetic acid from G.C.C. (ITO) glass substrate and stainless steel substrate were used as working electrodes.

Electrochemical Deposition of Cr₂O₃ thin film

Thin films of Cr₂O₃ nanostructure were synthesis by utilizing potentiostatic method on SS and ITO glass substrates. The ITO glass substrate (2 cm²) was polished by acetone, alcohol and DI water consecutively at 10minutes; 1037-stainless steel (2cm²) substrates were cleaned with a sequence of emery papers, after that immersion in acetone and DW, and dry in air. 6mM CrCl₃.6H₂O dissolved in 0.1 M acetate buffer at pH 4 were worked as the precursor solution. For electrodeposition method used electrochemical cell contain a three electrode ITO glass and/or SS substrate were used as

working electrode, coiled gold (Au) wire as counter electrode and SCE as reference electrode. The prepared Cr₂O₃ thin film afterward washed with DI water and dried. The electrodeposition potential was 0.65 V, electrochemical cell temperature was saved at 45°C and electro deposition time was 100 seconds.

Electropolymerization of PT/ Cr₂O₃ thin film

PT deposited electrochemically on the earlier prepared Cr₂O₃ thin film by deposition potential (1.75 V). The potential (1.75) was predetermined from the cyclic voltammetry (CV) in 70mM HClO₄/acetonitrile solution including 60mM Th and 0.1M NaClO₄.

Potentiostatic method was operated on synthesis of PT/ Cr₂O₃ in the same cell at lab temperature at 100 seconds. SS and ITO glass electrodes coated by the synthesized Cr₂O₃ utilized as working electrodes, coiled Au wire was utilized counter electrodes and SCE reference electrode. The thin films of nanocomposite were lastly washed with DI water.

Results and Discussion

Fig.(1) Shows a characteristic form of i-t curve associated to the creation of Cr₂O₃ on SS electrode through used deposition potentials 0.65V for 100 seconds. In the acetate buffer pH 4 solutions as supporting electrolyte, In Figure 1, initially, the current rises owing to the creation and growing of Cr₂O₃ nanoparticles. At following steps of the nucleation method the singular diffusion regions grow and the current reach a highest peak and then declines. This behavior indicates that the reaction kinetics was diffusion controlled of electroactive ions to the electrode surface [10].

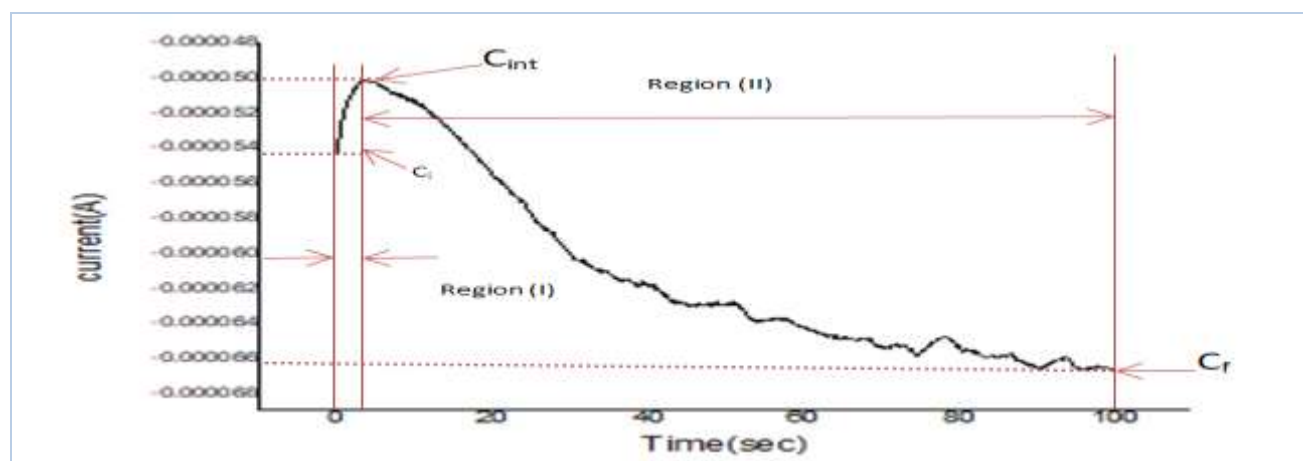
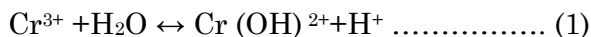


Figure 1: i-t curve related to the formation of Cr₂O₃ on SS plate

In acidic solutions of pH 4, Cr (III) occurs as Cr (III) ions and in the form of Cr (OH) ²⁺, which then oxidize to Cr₂O₃ film.

In the previous studies, the electrochemical reaction involved in protons transfer process was verified and the mechanism was proposed as:



The cyclic voltammetry Fig. 2 is utilized to detect the electropolymerization voltages that will be operated on synthesized of PT on

the earlier synthesis Cr₂O₃ thin film by potentiostatic method. Fig. 2 illustrates the CV throughout the electropolymerization of PT on the Cr₂O₃ coated SS plate. Nearly at 1.4 V, the immediate rise of the forward scan can be allocated to the oxidation of the Th monomer at the working electrode surface [11]. Oxidation of the Thiophene monomer is began directly once the Th monomer reach the SS surface creating cationic radical [12]. Dimers are shaped from the cation radical's reaction on the area of the electrode surface. Deprotonation will happen to permit the polymerization to repeat for n stages.

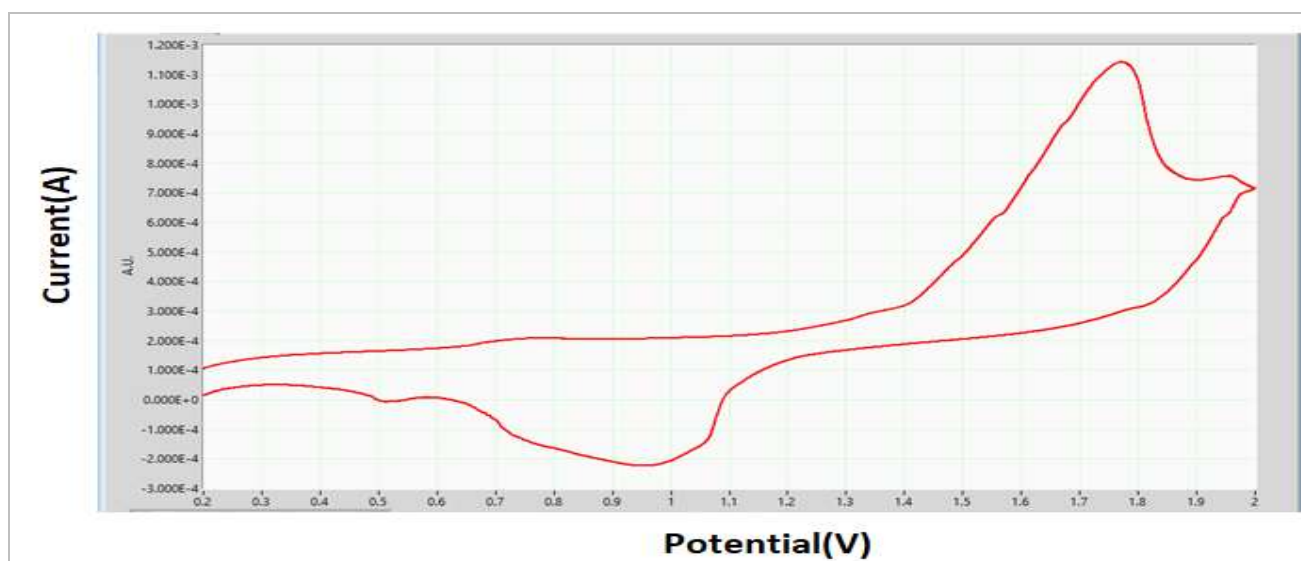


Figure 2: Cyclic voltammogram of 6mM Th and 70mM HClO₄ on the prepared Cr₂O₃ at 50mV scan rate

Characterization of Cr₂O₃ and PT/ Cr₂O₃ Thin Films

X-ray Diffraction (XRD) Analysis

XRD patterns of the Cr₂O₃ thin film, is shown in Figs. (3a). For Cr₂O₃ thin film, all the detected reflection peaks are reliable with preceding study [13, 15]. The peaks show a rhombohedral structure, which were in good concords with those viewed in previously reports [16, 17]. The particle size of the Cr₂O₃ extended from 23 to 51nm with an mean of 39.6nm from XRD data.

The characteristic XRD form of PT/ Cr₂O₃ nanocomposite thin film as presented in Fig. (3b). The spectrum obviously showed that amorphous nature of polymer structure giving in this film and adding to that film having some diffracted crystalline peaks also. The diffracted peaks characterized by crystalline inorganic Cr₂O₃ nanostructure integrating to the polymer constituents. The crystalline sizes were computing to usage

Scherer's method, the peaks location at around 2θ = 24.60, 36.30, 50.20 and 63.60 correspond to the crystal plane of (012), (110), (024) and (214) of crystalline Cr₂O₃. It is seen from Figure (3b), that the rhombohedral peak of Cr₂O₃ indicates the crystalline nature of the composite. By comparing the XRD pattern of the composite and Cr₂O₃, it is confirmed that Cr₂O₃ has retained its structure even though it is dispersed in PT during polymerization reaction.

It is evident from this Figure (3b), that the relative intensity of this peak decreases after the embedding of Cr₂O₃ nanoparticles in PT matrix, with small shift in 2θ position about 0.3° and new peaks at 2θ values of 25.8, 26.7, 37.9, 38.8, 42.3 and 46.6 start emerging in nanocomposite of polythiophene with chromium oxide. The average crystallite size of sharp peaks is estimated by using scherrer's formula leads to the crystallite size of about 32.0 nm for PT/Cr₂O₃ nanocomposite thin film.

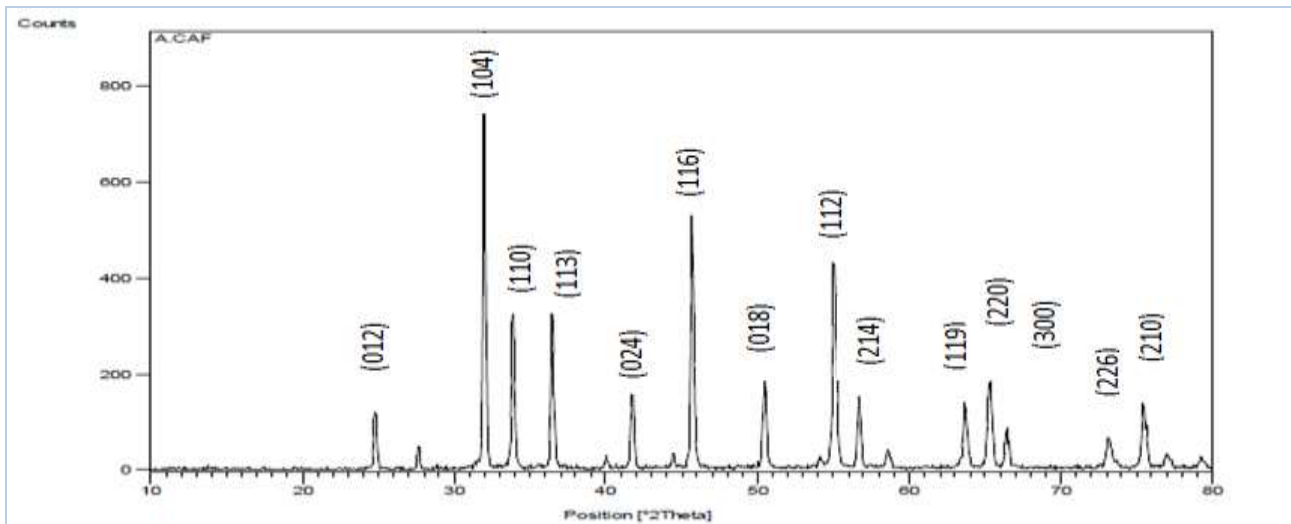


Fig. 3a: XRD pattern of Cr₂O₃ film

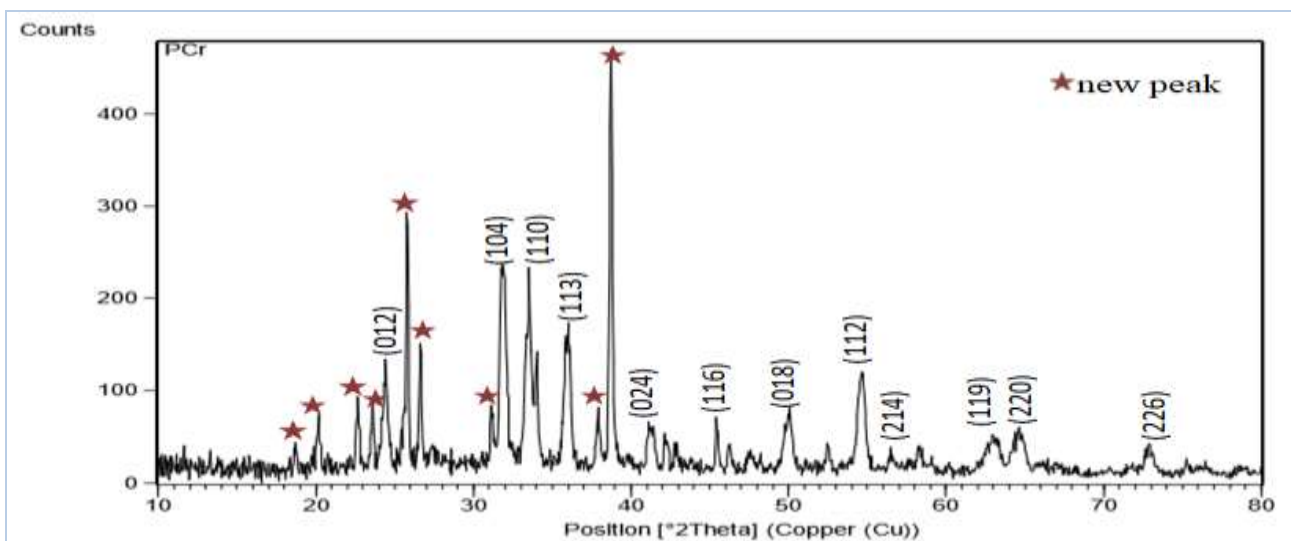


Fig.3b: XRD pattern of PT/ Cr₂O₃ nanocomposite film

Force Emission Scanning Electron Microscopy (FESEM) and ED's Analysis

FESEM utilized to examine the surface morphology such as rectangle, triangle, radial hexagonal, rod and spherical shapes of the Nanocomposites (Fig. 4). The surface morphology of synthesized pure Cr₂O₃ and PT/ Cr₂O₃ was analyzed from FE-SEM

micrographs. The surface morphology of neat Cr₂O₃ exhibits no uniform irregularities with smooth surfaces. However doping of polythiophene developed a strong interaction between PT and Cr₂O₃ which forms a secondary phases, and was expected to have greater influence on the absorption, emission and electrochemical characterization.

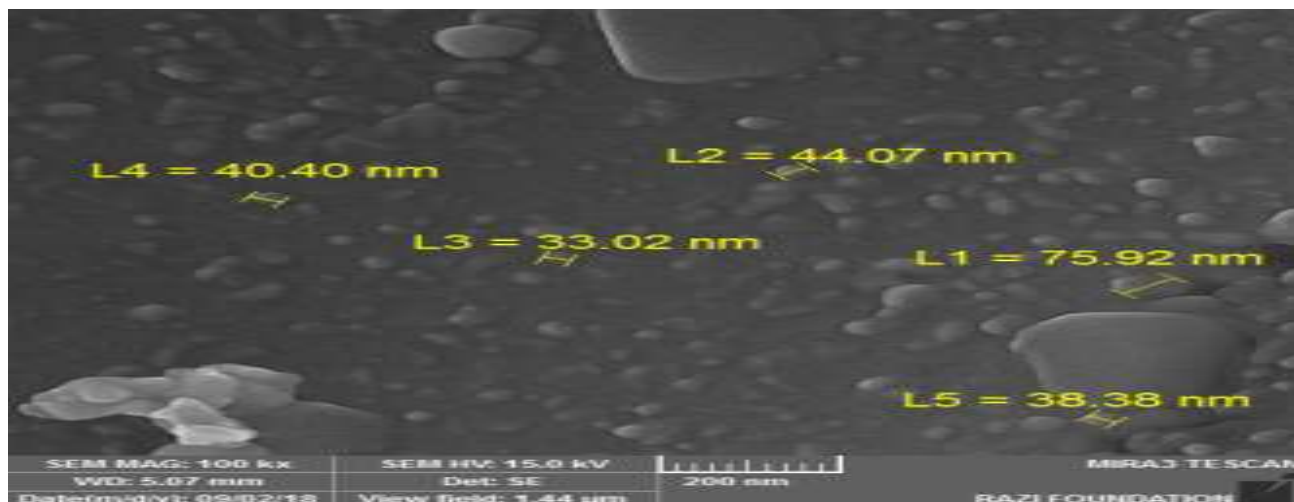


Fig 4a: FESEM image of Cr₂O₃ thin film

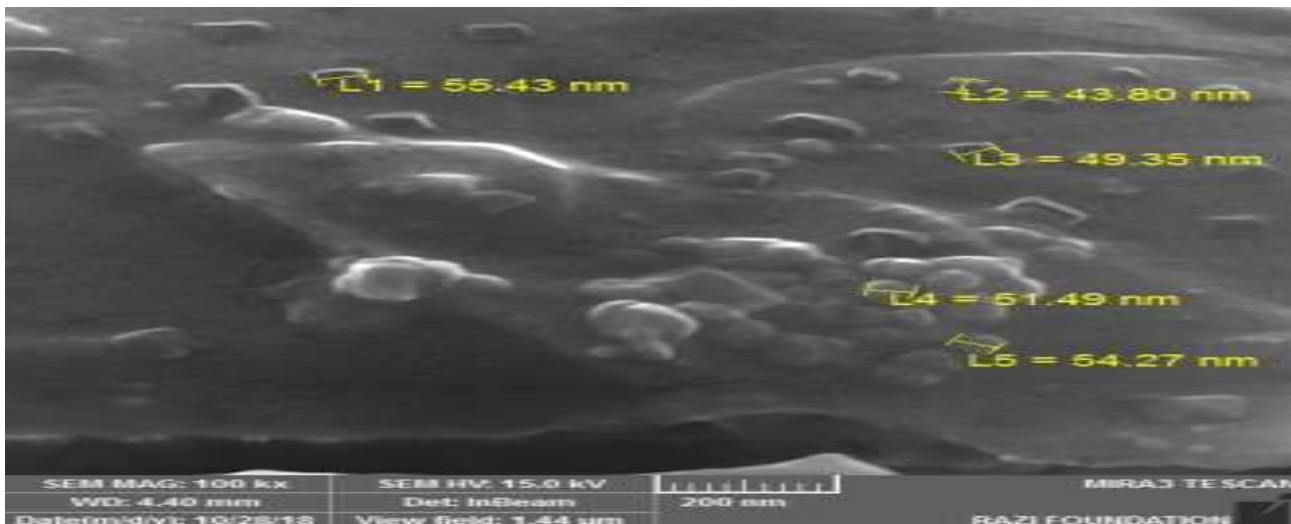


Fig.4b: FESEM image of PT/ Cr₂O₃ nanocomposite thin film

Fourier Transform Infrared (FTIR)

From Fig.(5a), the vibrational peaks found in the range 576.14 and 636.15 cm⁻¹ are attributed to Cr-O and 1112.93 cm⁻¹ [18], which indicates Electrodeposition of Cr₂O₃ nanocrystalin t. A wide absorption band in the wave numbers 3400-2500 cm⁻¹ is owing to the asymmetric -OH stretching form. Note through a spectrum (5b) new absorption bands and slight changes in the intensities of some absorption bands for PT/Cr₂O₃ at 1111.00 cm⁻¹ and new bands appear at 511.14

cm⁻¹ whereas these bands are not observed in pure polythiophene. It has been reported by D. Pavia et al. that the bands with 510–780 cm⁻¹ are associated to M-O. The peaks absorbed at 626.87 it is ascribed C-S bending style vibration, and C=C distinguishing band at 1625.99 cm⁻¹ of polymer .In its contrast of performances study like bands are detected between 400-3500 cm⁻¹ signifying that the major components of polymer and its nanocomposite at extant in this band ranges.

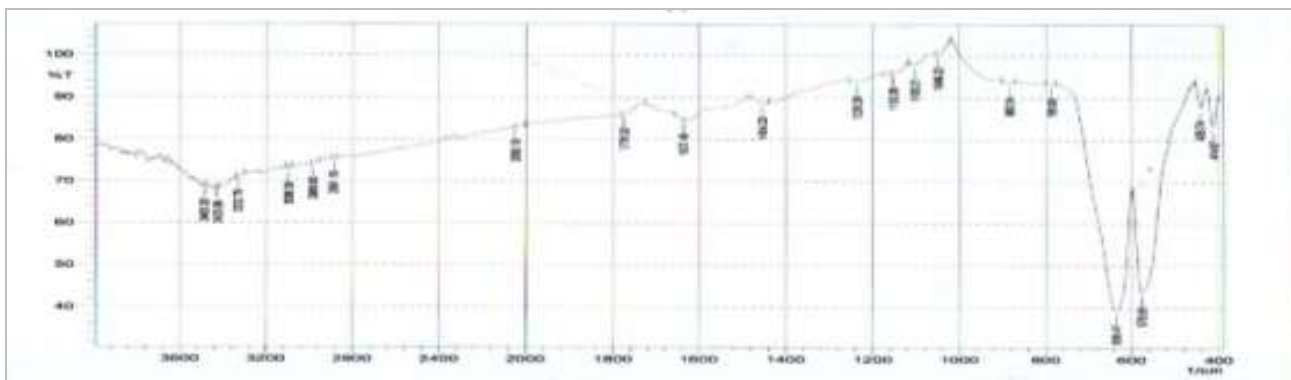


Figure 5a: FT-IR spectrum of Cr₂O₃

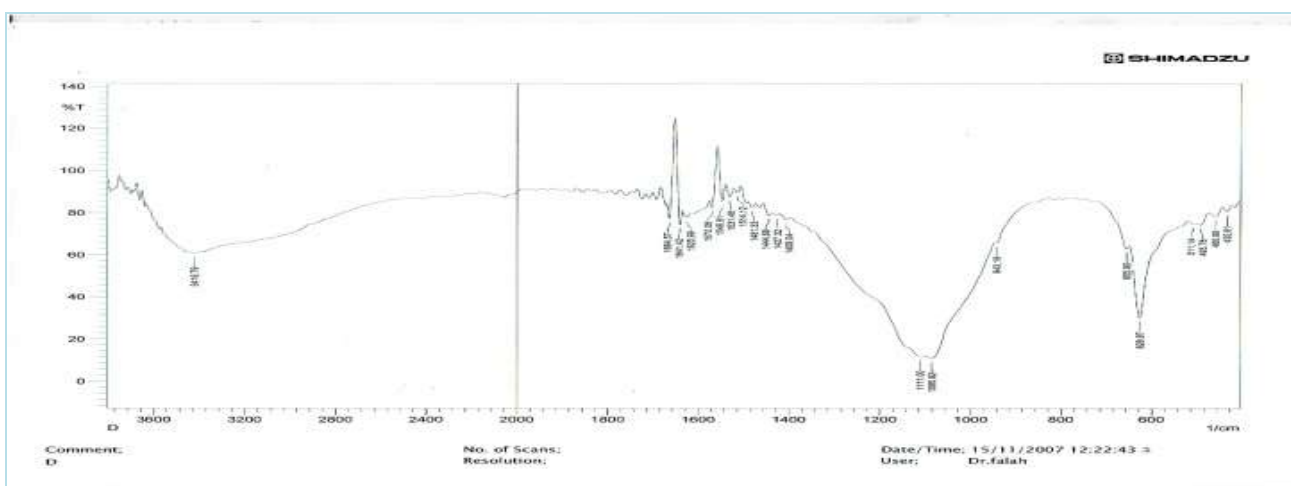


Figure 6b: FT-IR spectrum of PT/Cr₂O₃

Raman Spectroscopy Measurements

Raman spectrums were achieved as a for complete FTIR results so as to ensure a well depiction on the chemical bending structure of the constituents. The Raman spectrum observed for the Cr_2O_3 nanostructure in Figure 6a show two main bands at 983 - 1111 cm^{-1} .

These bands must be allocated to $\text{Cr}=\text{O}$ vibrations. This Raman band are moreover escorted by a low band at 573 cm^{-1} that is distinctive of $\text{Cr}-\text{O}-\text{Cr}$ vibrations. The related $\text{O}-\text{Cr}-\text{O}$ bending vibration between 300-400 cm^{-1} range. This area, however, might be retrieved with 309 nm excitation that discloses a raman band to 390 cm^{-1} from the $\text{O}-\text{Cr}-\text{O}$ bending styles [19]. Raman spectroscopy was carried out to ensure the interaction between PT and Cr_2O_3 . After modification by the polymer, the intensity of

specific peaks decreased, which resulted from the polymer suppressing the production. The typical Raman spectra of Cr_2O_3 -PT composite shown in Fig. 6b. The Raman spectra of pure PT show two main peaks, where the first prominent peak appeared within 1400-1600 cm^{-1} corresponds to $\text{C}=\text{C}$ stretching region, which is symmetric in phase vibration of thiophene ring.

The second small peak observed in the range 1033-1094 cm^{-1} corresponds to $\text{C}-\text{C}$ stretching lengthways with $\text{C}-\text{H}$ wagging component. This vibrational feature confirmed that the π electrons in PTH are confined within each thiophene ring. The peaks at 628 cm^{-1} was credited to the ring $\text{C}-\text{S}-\text{C}$ deformation which has blue shift about 3 cm^{-1} than pure PTh. The peaks located at about 483 cm^{-1} are detected in composite, which can be attributed to $\text{Cr}-\text{O}$ lattice vibrations [20].

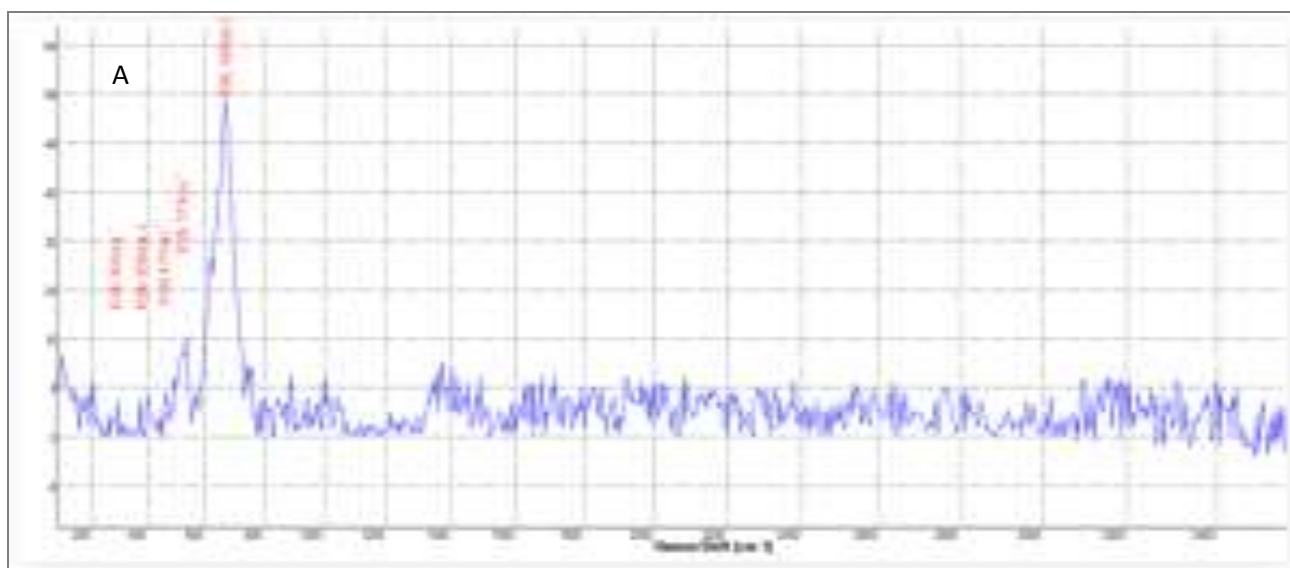


Fig. 6a: Raman spectroscopy of pure Cr_2O_3 nanostructure

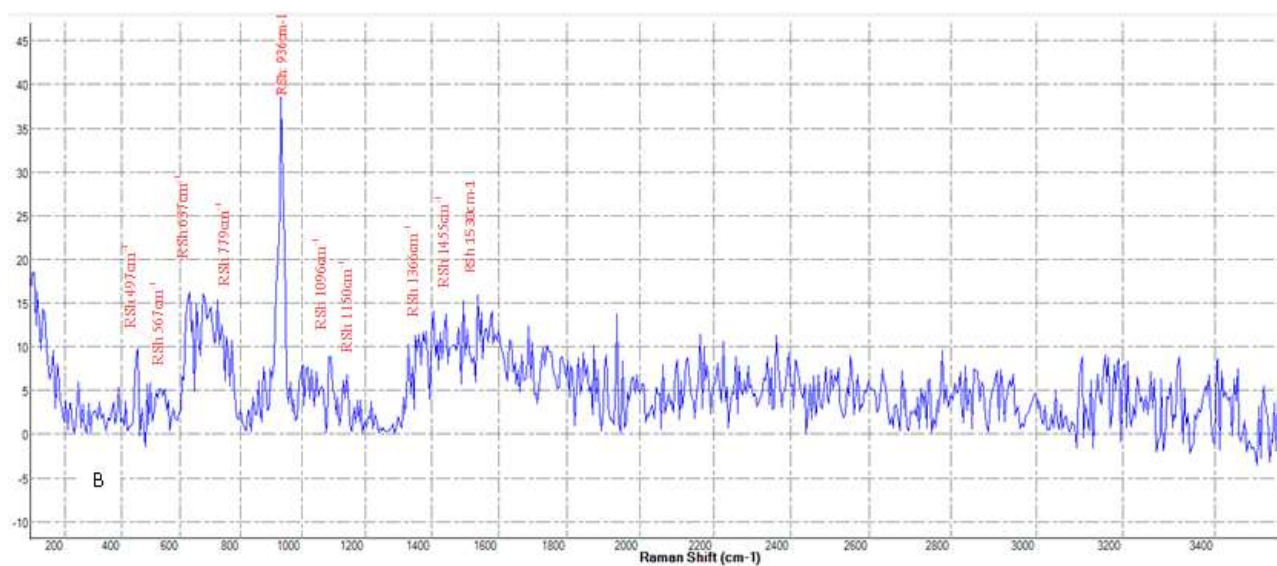


Fig. 6b: Raman spectroscopy of PTH/ Cr_2O_3 nanocomposite

Applications

Electrocatalytic Degradation of Reactive Blue 4 dye (RB4)

Investigation of electrocatalytic activity of Cr_2O_3 and $\text{PT}/\text{Cr}_2\text{O}_3$ nanocomposite deposition on SS substrate. The electrocatalytic experiments have been achieved to define the electrolytic efficiency of Cr_2O_3 and $\text{PT}/\text{Cr}_2\text{O}_3$ nanocomposite. From the physicochemical properties of RB4 utilized as a reference in the arena of degradation dye, which selected because it's great solubility in water and its simple study by UV / Vis.

UV-Vis Analysis of Degradation Dye

Fig.7 displayed the UV-Vis absorption spectrum of RB4 aqueous solution having NaCl through 15 min. electrocatalytic times. As presented in the figure, the RB4 concentration reduces after 15 min reaction durations suggesting the devastation of the chromophores groups and conjugated. Above (37 and 54) % of RB4 was destroyed at 15 minutes by using Cr_2O_3 and $\text{PT}/\text{Cr}_2\text{O}_3$ respectively suggesting a good catalytic property of the prepare nanocomposite film than oxides.

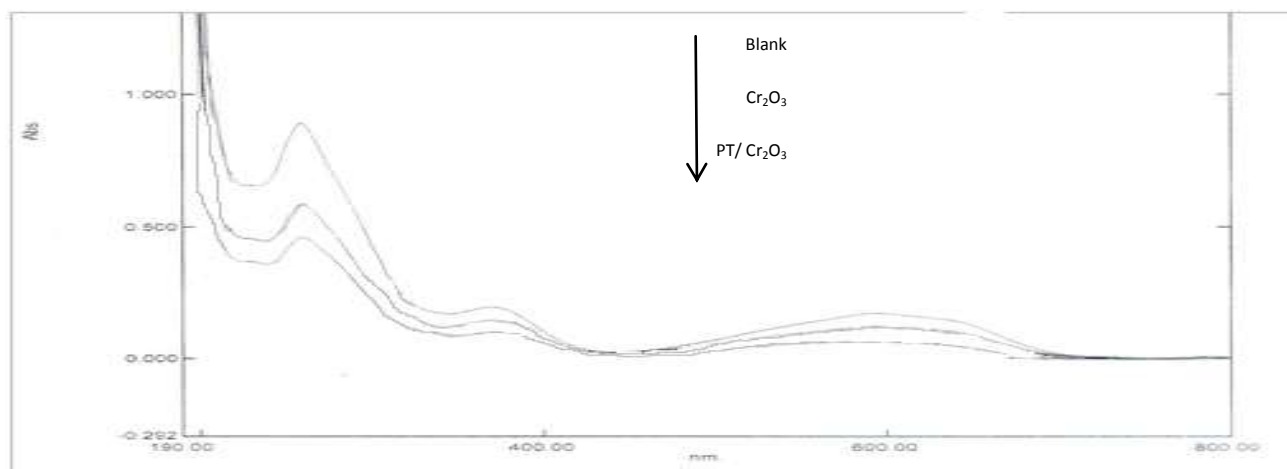


Fig.7: Absorption spectra of RB4 solution after 15min electrodegradation by different coated anode

FTIR Analysis of Degradation Dye

The electrodegradation RB4 dye was characterized by FTIR. Altered spectra were equaled through the 500-3500 cm^{-1} area. Every dry remainder was mix by KBr previous to analysis. The dye, in addition to their degradation yields were studied by FTIR and the results are obtainable in Figs. 8a, 8b. Figures 8a, 8b were correspondingly FTIR spectra of control RB4 and the degraded RB4 sample by $\text{PT}/\text{Cr}_2\text{O}_3$. Figure 13a of RB4 before treatment obtainable a large peak to 3450.41 cm^{-1} characterizing -NH- and hydroxyl groups' extensions. The peaks at 1614.31 cm^{-1} , 1541.02 cm^{-1} and

1409.87 cm^{-1} are individuals of the C=C aromatic ring. The peaks positioned among 1234.36 cm^{-1} and 1134.07 cm^{-1} represented C-N extensions. Peaks to 1039.56 cm^{-1} , 684.68 cm^{-1} and 617.18 cm^{-1} correspondingly of the s S=O and -C-S- vibration. Lastly, the peaks among 74.62 cm^{-1} and 729.04 cm^{-1} for the C-Cl vibration mode. The spectrum of yields degradation RB4 (Fig. 8b) presented the vanishing of many peaks for example at 617.18 cm^{-1} for sulfonic groups in addition to peaks of the aromatic rings at 1541.02 cm^{-1} and 1409.87 cm^{-1} . Together, there were the emergence of peaks at 1604.66 cm^{-1} for aldehydes and acids C=O distortions [21].

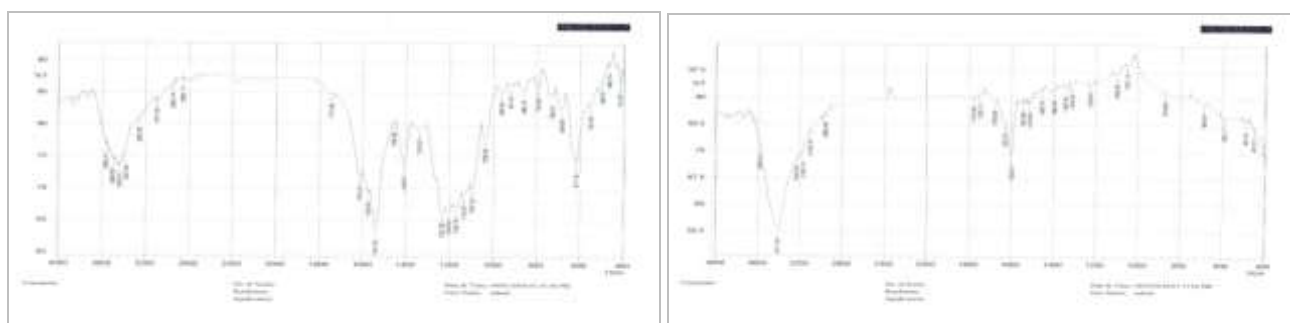


Figure 8: FTIR spectra of RB4 control (a), RB4 sample degraded by $\text{PT}/\text{Cr}_2\text{O}_3$ (b)

Conclusions

Cr₂O₃ and PT/ Cr₂O₃ nanocomposite thin films has been successfully synthesis by serial electrochemical deposition method at electrolytic deposition 0.65V for Cr₂O₃ thin film and electropolymerization potentials

(1.75 V). XRD, FESEM, FTIR, raman spectroscopy analyses have been utilized for characteristic both compounds. The PT/ Cr₂O₃ nanocomposite film showed efficient electrocatalytic activity for degrading an RB4 dye in aqueous solution under different conditions.

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