



Electrochemical synthesis, characterization and evaluation of antioxidant activity of Co₃O₄ nanoparticles and Co₃O₄/TiO₂ nanocomposite

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Abstract

Cobalt oxide and Co₃O₄ / TiO₂ hybrid nanoparticle were prepared utilizing the one step electrolytic deposition method. The new nanoparticle antioxidant has been diagnosed according to the infrared spectroscopy by the emergence of new groups in the Co₃O₄ / TiO₂ spectrum, which indicates the formation of a new antioxidant. X-ray diffraction technology has shown the emergence of new diffraction levels in the anti-Co₃O₄ / TiO₂ spectrum compared to the cobalt oxide diffraction spectrum. The morphology of synthesized compounds were examined by Field Emission Scanning Electron Microscopy (FESEM), pure Co₃O₄ which have sphere-shaped aggregations forms have 30.27 nm size, while TiO₂/ Co₃O₄ nanocomposite shows Hexagonal sheets structure and clearly indicates that the Co₃O₄ is diffusion on surface of TiO₂ with 33.9 nm size. The EDS of the elemental is indicating uniform formation of TiO₂ / Co₃O₄ composite by presented of titanium, cobalt and oxygen. Antioxidant activity of pure Co₃O₄ and Co₃O₄- TiO₂ samples were compared using H₂O₂ scavenging activities. Considerable in vitro antioxidant activities in a concentration-dependent manner were recorded. Interestingly, Co₃O₄ / TiO₂ showed more elevate scavenging in H₂O₂ antioxidant assays in low concentrations but this activity decrease with increase the nanocomposite concentration.

Keywords: nanocomposite, electrolytic deposition, scavenging in H₂O₂ antioxidant

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INTRODUCTION

During the metabolic processes free radicals are formed as by products. These highly reactive species have harmful interactions with various biomolecules. This leads to many noxious diseases in human beings like growth, cardiovascular diseases, CNS diseases, arthritis, etc. Body has its own protection mechanism against these free radicals, still there is demand for supplementary antioxidants. Synthetic antitoxin combination with dietetic ones can help to prevent these diseases. There are several in vitro methods for impost of antioxidant property like hydrogen peroxide, nitric oxide, hydroxyl radical, proxy nitrite, superoxide scavenging activity, DPPH assay, etc. (Saikia et al., 2010), Among these methods, hydrogen peroxide method is moreover rapid, simple and cheap in comparison to other methods. Nanoparticles have been studied for their various applications including catalytic, photoelectric, antimicrobial, anticancer and antioxidant Works survey shows that metal oxides alike Fe₂O₃, NiO, CuO nanoparticles exhibit near 48-85% antioxidant activity in DPPH assay (Das et al., 2013). Some

nanoparticles show important role in the breakdown of these free radicals, so destroying the oxidative loss of the human body (Purkayastha et al., 2014).

Today it is a growing interest in the development of nanotechnology, the science which treaties with the creation, production, characterization and manipulation of materials at the nanoscale (Thakkar et al., 2010) and (Thakkar et al., 2010). Nano-sized materials, celebrated as nanoparticles, possess unique and improved properties because of their larger surface area to volume ratio and are measured building hunks of nanotechnology to design materials with exciting properties (Bunghez et al., 2012; Ali, AL-Noor, et al, 2015). Lactic Acid as Spacer between Poly Acrylic Acid and 4-Aminoantipyrine. The International Journal of Biotechnology, 4(6), 36-45).

Metal oxide nanoparticles has been normally synthesized and tried in a wide range of applications (Khan et al., 2015). Quick developments on the nano-

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biotechnological interface has caused in a wide array of biomedical applications including remedy delivery and preparation administration (Wang et al., 2005). Cobalt oxide have interesting properties and so has involved numerous researchers for studying their possible biomedical applications. Beside their physiological role as a cofactor of vitamin B12, cobalt can be used in a wide range of productions (Raman et al., 2016). Cobalt oxide is a multifunctional, antiferromagnetic p-type semiconductor (with a direct optical bandgap of 1.48 and 2.19 eV has been used in electrochromic devices, energy storage, heterogeneous catalysis, pigments, dyes, and in lithium ion rechargeable batteries as an contact material (Diallo et al., 2015).

Several methods have been invented in order to prepare metals oxide nanoparticles, including powder immobilization (Jiang & Tseung, 1990), chemical vapor deposition (Cushing & Kolesnichenko, 2004), sonication (Zhu et al., 2002), thermal salt decomposition (Dasilva et al., 2001), sol gel (Svegl et al., 2000), and electrodeposition (Nakaoka et al., 2002).

Just, titanium dioxide nano powder has received much interest (Kobayashi et al., 2008). This is due to its use in various applications for example cosmetics, paper and medical devices coating and gas sensors (Qiong et al., 2008) Some papermaking trends necessitate more use of TiO₂ including reduction in basis weight and the increasing use of cheap, discolored fibers. Too, because TiO₂ is used in a large variety of products, its global demand growth is increasing rapidly along with its unusually high price. It has variety of advantages such as high surface tension, specific surface area, magnetic property, lower melting point, good thermal conductivity and environmentally friendly (Debanjan et al., 2016).

Especially cobalt oxide dispersed in titanium dioxide delivers interesting applications. The Antioxidant activity of Co₃O₄ may be improved with incorporation of Co₃O₄ into TiO₂ as nanocomposite.

In the present investigation we have reported an competent and simple synthesis of Co₃O₄/TiO₂ and Co₃O₄ NPs by electrolytic deposition process. The antioxidant activity of Co₃O₄/TiO₂ and Co₃O₄ NPs was assessed using H₂O₂ scavenging tests.

MATERIAL AND METHODS

Materials: hydrate Cobalt nitrate Co(NO₃)₂·6H₂O, sodium hydroxide NaOH, sodium dodecyl sulfate (SDS) were used as precursor. Stainless steel (1 x 1 cm), Titanium sheet (1 x 1 cm) and (1 x 1 cm) platinum sheet) used as electrodes hydrogen peroxide.

Electrosynthesis of Co₃O₄ nanoparticles

Electrodeposition of cobalt oxide is done using two electrode system, where cleaned Stainless steel is used as the working electrode and platinum wire as counter electrode. The Co₃O₄ is deposited under basic (pH=11) solution containing 0.1M Co(NO₃)₂·3H₂O and by

applied 1.5V potential for one hour. The solution decant in witch glass and dried at 200 °C for 24 h. Finally, the product were calcined at 500 °C for 2 h.

Electrosynthesis of TiO₂/ Co₃O₄ nanocomposite

In the preparation of TiO₂/ Co₃O₄ nanocomposite, electrolysis cell vessel of volume capacity 50 ml and two electrode systems consisting of the bulk titanium sheet (1 x 1 cm) and the same inert cathode (1 x 1 cm platinum sheet). Both electrodes were immersed in aqueous solution (pH=12) of 0.1 M Co(NO₃)₂·6H₂O and SDS. The SDS serves not only as the supporting electrolyte but also as the stabilizer for nanoparticles to prevent their further growth. During the synthesis, the bulk titanium metal is oxidized into titanium ion which reduced at inert cathode to form titanium oxide nanoparticles most probably at the interfacial region of the cathodic surface and within the electrolytic solution. A controlled voltage (10V) electrolysis was carried out for 1h. During the course of electrolysis, the solution became dark precipitate. After one hours electrolysis was stopped. The solid particles were separated from solution by simple decantation process and washed for 3 to 4 times with water to remove unreacted SDS. Theparticipate dried at 200 °C for 24 h. Finally, the product were calcined at 500 °C for 2 h.

Hydrogen Peroxide Scavenging Activity

A solution of H₂O₂ (40mM) was freshly prepared in 0.05 M KH₂PO₄-K₂HPO₄ phosphate buffer (1 M pH 7.4). Co₃O₄/TiO₂ and Co₃O₄ at different concentrations of (0.1-0.6)mg/ml were added to H₂O₂ solution (0.6ml) and the total volume was made up to 3ml. After 10 min the concentration of the H₂O₂ was determined the absorbance at 230nm in a spectrophotometer. A blank solution containing phosphate buffer, without H₂O₂ was prepared. Accordingly, the calculation of the ability of compounds having hydrogen peroxide scavenging activity was calculated using following formula 1:

$$\% \text{H}_2\text{O}_2 \text{ scavenging activity} = 1 - \frac{A_{\text{test}}}{A_{\text{blank}}} \times 100 \dots 1$$

where A_{blank} is the absorbance of solution containing H₂O₂ and A_{test} is the absorbance of the solution containing Co₃O₄/TiO₂ and Co₃O₄ and H₂O₂. (Hadjiev et al., 1988).

RESULTS AND DISCUSSIONS

FTIR Study

FTIR study was plain for the structural confirmation of Co₃O₄ and Co₃O₄/TiO₂ nanomaterial. **Fig. 1** shows the FTIR spectrum of Co₃O₄ in the choice of 400-4000 cm⁻¹ The broad peaks at the absorption bands at around 658 and 560 cm⁻¹ are owing to the IR absorption of Co₃O₄ with extending vibration of the metal -oxygen bond (Tang et al., 2008) and (Zhou et al., 2005). The presence of this band shows that cobalt is situated in an oxygen octahedral environment in the hexagonal structure so Co₃O₄ is shaped (Hadjiev et al., 1988). While, in the spectrum of Co₃O₄/TiO₂, it was observed that it gather

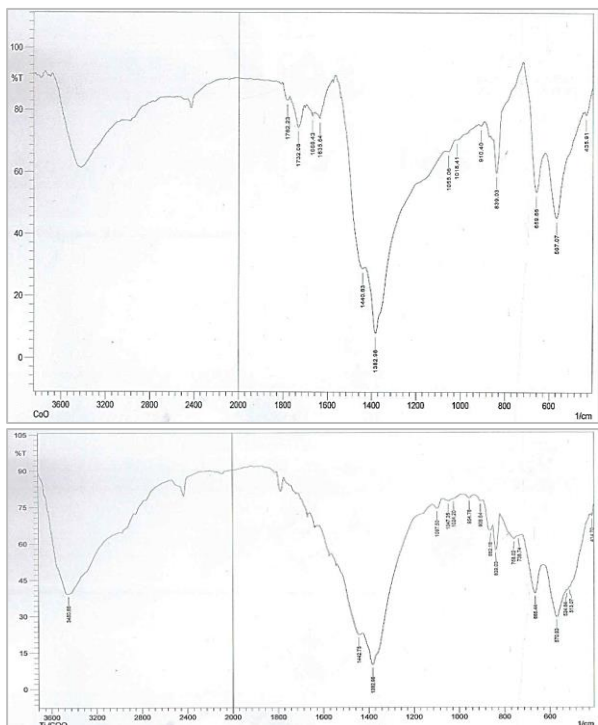


Fig. 1. FTIR spectrum of Co₃O₄ and Co₃O₄/TiO₂ nanocomposite

between bands of Co₃O₄ and TiO₂, that settles no bond formed between the two nanoparticles.

XRD Study

For the structural elucidation of the Co₃O₄ and Co₃O₄/TiO₂, XRD was exploited in the 2θ range of 20–80°. Fig. 2 shows the XRD pattern of Co₃O₄ and Co₃O₄/TiO₂. The XRD pattern revealed the formation of Co₃O₄ with cubic crystal structure [JCPDS card no. 42-1467]. The diffraction peaks at angles (2θ) of 32.1°, 37.1°, 39.2°, 45.2°, 59.7 and 65° are assigned to the (220), (311), (222), (400), (511) and (440) planes of the Co₃O₄ crystal lattice, respectively (Kelpsaite et al., 2011). Additionally, from the XRD result the crystallite size was estimated on the basis of full width at half maxima intensity of XRD peak for (311) plane by using Scherrer's formula 2: (Karthick et al., 2013).

$$D = \frac{0.9\lambda}{\beta \cos\theta} \dots\dots\dots(2)$$

where 'D' is crystallite size, 'β' is full width at half maxima, 'λ' is wavelength of X-ray used and 'θ' is diffraction angle. the crystalline size of Co₃O₄, calculated from the strongest peak, locating at (311) plane, are estimated to be 51.64 nm.

According to the XRD pattern of Co₃O₄/TiO₂, all of the diffraction peaks were observed at angles (2θ) of 31.46°, 37.21°, 59.57° and 65.42° which are assigned to the (220), (311), (511) and (440) planes of the Co₃O₄

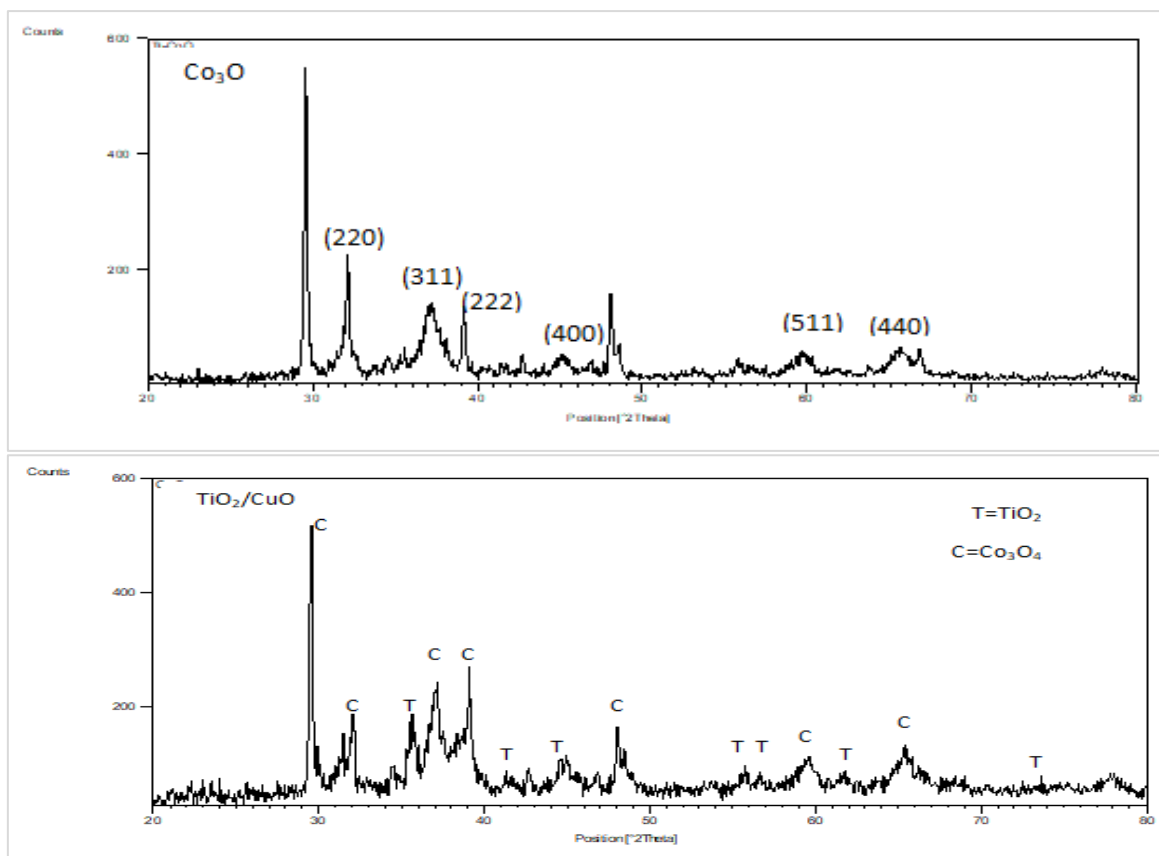


Fig. 2. XRD spectrum of Co₃O₄ and Co₃O₄/TiO₂ nanocomposite

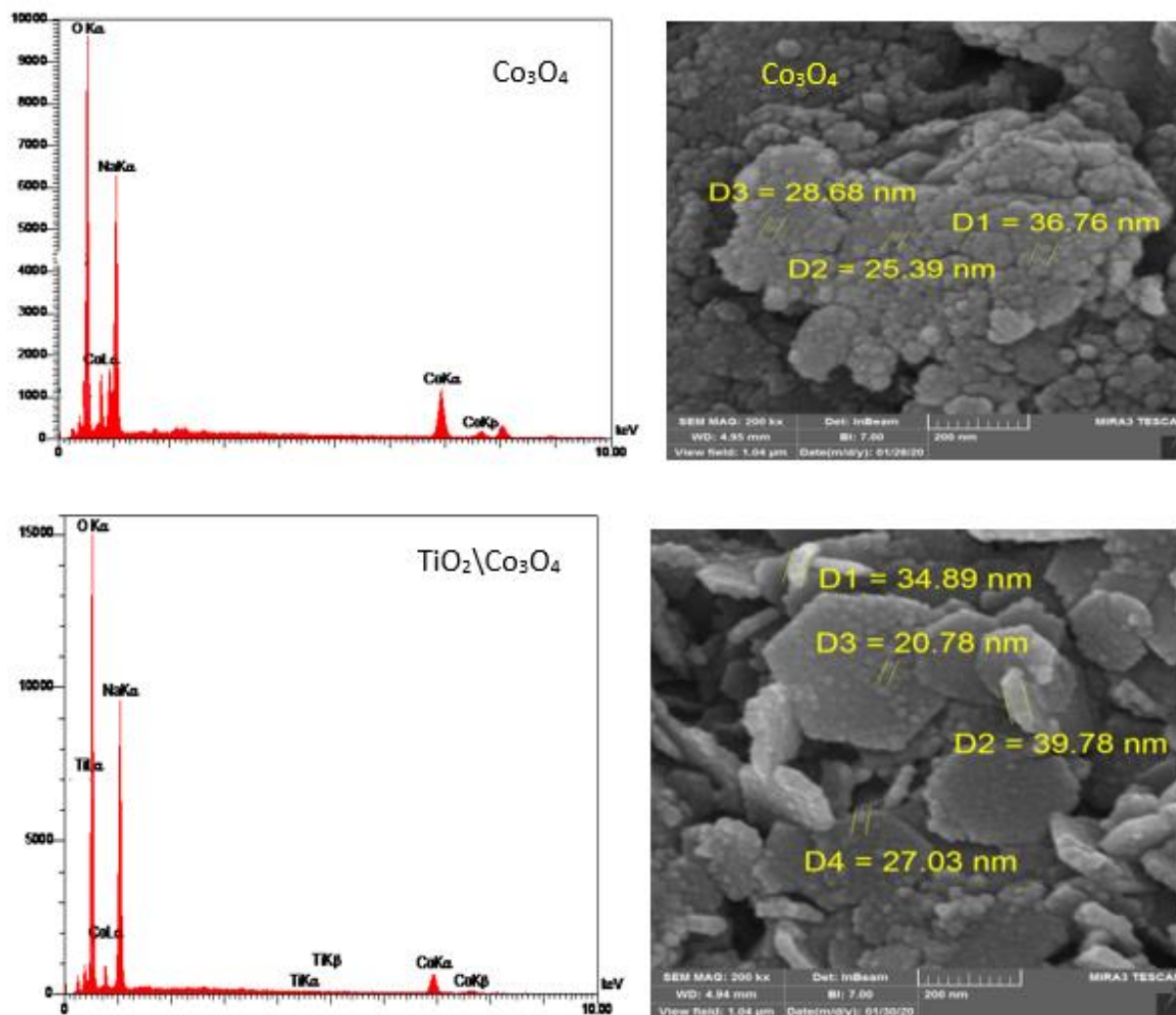


Fig. 3. FESEM and EDS image of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{TiO}_2$ nanocomposite

Table 1. Values of H_2O_2 absorbance and inhibition % with Co_3O_4 and $\text{Co}_3\text{O}_4/\text{TiO}_2$ concentrations

Concentration of nanoparticle Co_3O_4 and $\text{Co}_3\text{O}_4/\text{TiO}_2$ (g/l)	Co_3O_4 nanoparticles		$\text{Co}_3\text{O}_4/\text{TiO}_2$ nanocomposite	
	H_2O_2 absorption	Inhibition %	H_2O_2 absorption	Inhibition %
0.000	0.177	0.177
0.001	0.160	6.21	0.118	33.3
0.002	0.139	21.46	0.088	50.28
0.003	0.126	28.81	0.086	51.4
0.004	0.103	41.80	0.078	55.93
0.005	0.039	77.96	0.088	50.28
0.006	0.060	66.10	0.091	48.58

crystal lattice, respectively (Binitha et al., 2010), While the peaks located at $2\theta = 35.67^\circ, 41.35^\circ, 44.58^\circ, 55.75^\circ, 56.72^\circ, 61.87^\circ$ and 73.69° are indexed to (101), (111), (210), (211), (200), (002) and (112) diffraction peaks of rutile TiO_2 (Du et al., 2016).

FESEM study

FESEM were utilized to observe the morphology and microstructure of pure Co_3O_4 and $\text{TiO}_2/\text{Co}_3\text{O}_4$ powders, as exposed in Fig. 3. Pure Co_3O_4 and $\text{TiO}_2/\text{Co}_3\text{O}_4$ nanocomposite samples show different morphology and crystallite size. The pure Co_3O_4 which have forms sphere-shaped aggregations have size

about 30.27 nm. While $\text{TiO}_2/\text{Co}_3\text{O}_4$ nanocomposite powders shows Hexagonal sheets structure and clearly indicates that the Co_3O_4 is diffusion on surface of TiO_2 . These effects thus justify the successful formation of composite with 33.9 nm size. The composition of Co_3O_4 and $\text{TiO}_2/\text{Co}_3\text{O}_4$ composite is similarly confirmed by EDS mapping. EDS of the elemental mappings is performed on the sample of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{TiO}_2$ composite and the results are shown in Fig. 3. The cobalt, titanium, and oxygen signals overlap uniformly across the entire example, indicating uniform formation of $\text{TiO}_2/\text{Co}_3\text{O}_4$ composite. The

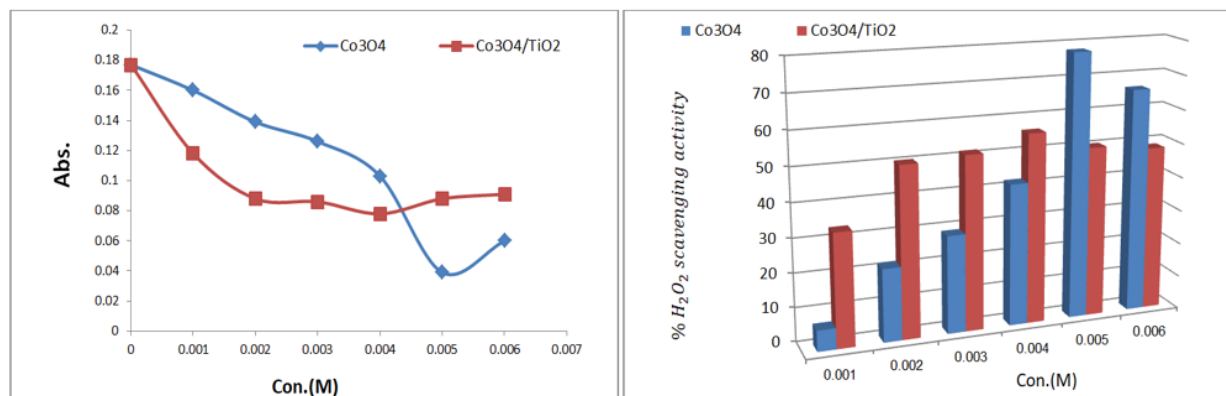


Fig. 4. Comparing between H₂O₂ absorbance at 230 nm at different concentration of Co₃O₄ and Co₃O₄/TiO₂ (A) and scavenging of free radical as a function of Co₃O₄ and Co₃O₄/TiO₂ concentration

corresponding FESEM image, EDS, and XRD pattern obviously demonstrate the morphology and structure of TiO₂/Co₃O₄ compound.

Antioxidant Activity Result

Fig. 4 represent a comparison amongst the susceptibility of TiO₂/Co₃O₄ nanocomposite and Co₃O₄ nanoparticles to the scavenging of hydrogen peroxide at concentrations ranging since (1-6) mg/ml. As the results showed that the nanocomposite have other efficiently as antioxidant than Co₃O₄ in low concentrations but this efficiently reduction with concentration increase this may be owed to that nanocomposite have big molecular size than Co₃O₄ and this mean that surface area of TiO₂/Co₃O₄ nanocomposite smaller than Co₃O₄. Hydrogen peroxide is a weak and inactive oxidizing cause, but it is a source of effective free radicals for example the hydroxyl radical, and the peroxide danger lies through the accumulation of the hydroxyl radical through an interaction with some metal ions such as iron and copper. It is possible to inhibit the action of specific enzymes by oxidizing sulfa groups (SH). Therefore, the scavenging of hydrogen peroxide is an significant factor

in getting eliminate of free radicals (Kumaran & Karunakaran, 2007). The aim for the peroxide capture can be due to adsorption on the surface of the composites.

Fig. 4 shows a steady decrease in absorbance at 230 nm in H₂O₂ with Co₃O₄ and TiO₂/Co₃O₄ NPs. As seen in **Fig. 4** the H₂O₂ scavenging percentage of TiO₂/Co₃O₄ and Co₃O₄ NPs was 65.07 and 77.96 at 4mg/ml concentration. The observed antioxidant activity strength be due to neutralization of free radical charm of H₂O₂ by the transfer of an electron.

CONCLUSION

In this paper, we have synthesis cobalt oxide nanostructure and titanium dioxide cobalt oxide nanocomposite by Electrosynthesis and studied their antioxidant activity. The synthesized compounds were characterized by FTIR, XRD and FESEM analysis. In 4mg/ml of Co₃O₄ NPs show 77.96% free radical scavenging activity which is relatively higher in comparison to Co₃O₄/TiO₂ nanocomposite.

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