Ibn Al-Haitham Journal for Pure and Applied Sciences

Journal homepage: http://jih.uobaghdad.edu.iq/index.php/j/index

Green Synthesis of IONPs for Photocatalytic Activities

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Article history: Received 14 June 2022, Accepted 5 July 2022, Published in October 2022.

Doi: 10.30526/35.4.2886

Abstract

To make iron oxide nanoparticles (IONPs), a simple chemical approach was used to combine iron chloride ($FeCl_2$+$FeCl_3$) salt with onion peel extract. According to the study, iron salts can be converted into IONPs by the biomolecules in onion peel extract. From $FeCl_2$+$FeCl_3$ to γ -Fe_2O_3, the approach changes iron oxide NPs' size, shape, purity and phases. In water treatment, γ -Fe_2O_3 NPs are critical for the removal of the color methylene blue (MB). X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet (UV-Vis) and photoluminescence (PL) spectroscopy were used to identify IONPs. Results from the XRD experiment showed crystals having a tetragonal structure have average size of 13.4680 nm for γ- Fe_2O_3 NPs with a chemical method. Tetragonal diffraction peaks were observed in the data, and excellent crystal quality in a cubic shape. In the simple chemical process, the grain size was around (23.9 to 169.4) nm and average grain size 76.6 nm. UV-VIS measurements showed that the energy gap value had shifted to the blue from 1.94 to 2.96 eV in the simple chemical method.PL spectroscopy showed that the near band edge emission of γ-Fe_2O_3 NPs with a simple chemical approach was roughly 2.65 eV. NPs photocatalytic activity was as evidenced by the breakdown of MB dye when exposed to a moderate amount of light, as shown in this study. The results show that the synthesized material is of high quality γ-Fe_2O_3 NPs, with greater degrading efficiency when made using a simple chemical method, reaching 89.2% at 75 minutesfor 3 mg and 91.1% at 150 minutes for 5 mg, with a high level of photocatalytic efficacy the γ-Fe_2O_3.

Keywords: Onion Peel extract ;IONPs; Simple chemical way ; Photo catalytic Activity; MB dye.

1. Introduction

In the physical, chemical, and biological sciences, a new nanomaterial development has received considerable attention due to its performance in the fabrication of electronics such as microprocessors, lithium-ion batteries, transistors, emitting diodes, and sensors. Antimicrobial and antibacterial agents are also based on them, as are cancer treatments. Many essential applications rely on their use, including catalysts for pollution control and devices that detect the presence of gas. Nanomaterials will be able to get rid of heavy metals and organic and inorganic materials from polluted drinking water sources[1-6]. Structures of metallic oxides at the nanometer scale have been studied recently in an attempt to develop methods for monitoring them [7]. Copper oxide, titanium dioxide, bismuth oxide and iron oxide are just a few of the many metallic oxides (Fe2O3)[2, 8]. The crust of the earth (rocks, bedrock, and water) and biological beings both include common natural chemicals called iron oxides (animals and plants) [9]. It is common in nature to find Fe2O3 NPs that are stable under standard temperature and pressure conditions. They have a weak magnetic field [10] and do not react to hand magnets in most cases [11]. There is a new field in nanotechnology called ”green synthesis". Plants, algae and microorganisms are some species used in this process [12-16]. There are numerous ways to make efficient, environmentally-friendly metal NPs, such as those made from iron oxide nanoparticles (IONPs) and other metal oxide nanoparticles. Toxic chemicals can be reduced or eliminated by various green synthesis procedures for NPs employing plants [10]. An iron oxide (Fe2O3) NP's narrow band gap, chemical stability, magnetic properties and other features make it an excellent material for environmental or medicinal applications [11-14]. It is claimed that the environmentally friendly Fe NP green synthesis is long-term stable. Fe NPs have superior antimicrobial and cytotoxic properties and photocatalytic activity in the breakdown of MB dyes [15]. Shahana B. et al. [16] Cynometra ramiflora fruit extract was used to manufacture IONPs (chemical way). The synthesis of IONPs was confirmed by the appearance of a black solution. As the irradiation period rose, 663 nm is where the absorption peak is located (a hallmark of the MB dye) steadily diminished until it disappeared after 150 minutes. Chauhan et al. [17] prepared iron oxide NPs using a chemical way of Lawsonia inermis onion peel extract. In (2019), Sammy I. et al. [18], Preparation IONPs use Galinsoga parviflora, Conyza bonariensis, and Bidens pilosa extract as a catalyst to break down MB (chemical way). MB dye breakdown in normal light circumstances is a relatively novel concept tested using chemical methods. Using a simple chemical way, it is possible to produce higher-purity NPs with superior crystalline structures that are non-toxic, safe, and cost-effective for the environment. Because a green synthesis is more cost-effective and environmentally friendly than chemical and physical approaches, it can be easily scaled up for large-scale synthesis and does not take a lot of energy or dangerous chemicals. More control over crystal development can be achieved by green synthesis. Inexpensive and useful, green manufactured nanoparticles (green NPs) [10, 19, 20]. The simple chemical method was used to make IONPs from onion peel extract and iron (II+III) chloride (FeCl2+FeCl3) chloride. These films were formed on a glass substrate using the drop-casting process, and their structural and optical properties were measured. In order to determine the crystallinity and morphology of the samples produced, high-resolution X-ray diffraction and scanning electron microscopy (SEM) was used. These properties were studied using UV-VIS spectrophotometers and photoluminescence (PL) measurements. We also looked into the breakdown of MB dye in normal illumination conditions.

2. Experimental Details

2.1. Methods and Substances

From Iraq's local market, FeCl2+FeCl3 (iron (II+III) chloride) was Procured, and fresh onion peel from Baghdad, Iraq, was obtained. This plant contains abundant vitamins, amino acids, phenolic acid, glycosides, and minerals. Borosil was used to make all of the experimental glassware. Water was used to clean the glass and the substrates, and they were air-dried at room temperature to remove contamination or accidental imperfections.

2.2. Preparation of the Onion Peel Extract

Onion peels collected for this study were cleaned, diced, and dried for 8–10 days to remove contaminants. A professional stainless steel blender made a fine powder out of the dried. 10g of onion peel powder was mixed with 100 mL of deionized water to get the extract. Using a magnetic stirrer, the mixture was heated for two hours at 80 °C. Cooled to room temperature and filtered using Whatmn paper, the final product was ready to use. 1.

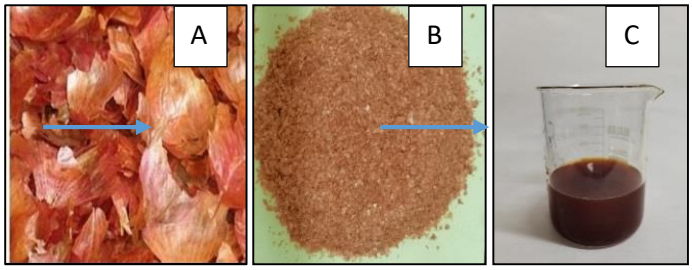

Figure 1. The procedure for converting the onion peelto extract for 2 hours at 80 °C, A) onion peel, , B) onion peelpowder, C) onion peel extract.

2.3. Preparation of iron oxide NPs by onion peel extract

In a simple chemical method, iron oxide NPs were synthesized by adding 100 ml of onion peel extract into (0.1 M (0.8 gm) + 0.2 M (2.7 gm), 100 mL) of $FeCl_2$+ $FeCl_3$.Then, the solution was agitated at 80 °C for 30 minutes using a magnetic stirrer. Translucent brown to black coloration changes occurred suddenly in the extract reaction during preparation; this indicated the creation of γ-Fe_2O_3 NPs. After this, the solution was slowly cooled to room temperature. A ceramic dish containing 25 mL of this mixture was heated to 200 °C for two hours in order to produce a fine powder from the solution.[2]. **Figure 2** shows how iron (II+III) chloride is used to prepare IONPs from onion peel extract.

Figure 2. Stages involved in the transformation of the mixture into IONPs with a simple chemical method include: A) $FeCl_2$ + $FeCl_3$ solution, B) onion peel extract, C) γ-Fe_2O_3 NPs solution, D) γ-Fe_2O_3 NPs powder.

2.5. Characterization of γ-Fe_2O_3 NPs.

Data from the Joint Committee on Powder Diffraction Standards (JCPDS) card helped XRD analysts identify the specimen.XRD measurements were taken across a temperature range of 20°–70°by using a step-by-step examination model (XRD-6000, Shimadzu) employment at 30 mA and 40 kv. A double-beam spectrophotometer was used to analyze the PL spectrum ((Jobin Yvon HR800UV)).

2.6. Photocatalytic Activity of Iron Oxide NPs by Onion Peel Extract under Normal light

In order to test the photocatalytic activity of the IONPs, a known amount of MB dye solution (1 mg, 3×10^{-5} M) was mixed with 100 mL of deionized water to make a final MB dye solution concentration of 10 mg/L. Then, for the first time, 3 mg of iron oxide NP powder was dispersed in a glass beaker; the IONP suspension was stirred for 5 minutes in the dark using a magnetic stirrer to maintain equilibrium. After 5 minutes, the combination was subjected to a direct normal (115 mW/mm2 intensity as measured by a solar power meter SM 206). The source of light is 0.15 meters away. Finally, 5 mL of the suspension were centrifuged at 4000 rpm for 20 minutes, and UV–vis spectrophotometers (Shimadzu, UV-1800) were used to test the supernatant's absorbance. At = 664 nm, the maximum absorption rate can be measured. Interactions between dye molecule particles (the adsorbent substance) and adsorbed substances are primarily affected by alterations to the dye molecule and the adsorbent material's surface [3]. The experiment was repeated at 5 mg every 10 minutes.

The degradation efficiency of MB dye was calculated using the following equation: according to this method, the MB dye degradation percentage was determined by Eq. (1): Degradation percentage (%)=$\left[\ 1-\frac{Cfin}{Cini}\ \right]\times\ 100\ \%$ (1)

Where: C_{ini} = the original (MB) dye concentration, C_{fin} = the dye concentration at the end. The constant kinetic rate (Kph) of the MB dye degradation was calculated using Eq. (2):

$\ln[\ Cini/Cfin] = Kph\ \times t$ (2)

Where: C_{ini} = the original (MB) dye concentration, C_{fin}=the dye concentration at the end, K_{ph}= constant rate of MB dye, t = radiation time.

The MB dye degradation efficiency can be calculated using the following equation: Efficacy of degradation:

(%)=$\left[\ Cini-\frac{Cfin}{Cini}\ \right]\times\ 100\ \%$ (3)

Where: C_{ini} = the original (MB) dye concentration, C_{fin} = the dye concentration at the end.

3. Results and Discussion

3.1. Synthesis and Characterization of Iron Oxide NPs by Onion Peel Extract

In a modern plant, onion peel extract is combined with iron salt at varied reaction conditions to produce IONPs. Iron oxide nanoparticle production, field, and stability can be regulated by the parameters of the onion peel extract. In a short time, the phytochemicals in onion peel extract can

reduce the amount used. In addition, the onion peel extract also plays a significant function in reducing and stabilizing many parameters in the synthesis of iron oxide NPs in a simple manner.

3.2. The XRD Analysis of Iron Oxide NPs (γ-Fe_2O_3) by Using Onion Peel Extract with Iron

XRD analysis is a suitable device used to determine the material, structure, and orientation of samples in this research. By mixing onion peel extract with $FeCl_2$+$FeCl_3$ for 2 hours at 200 ºC, IONPs were bio-synthesized using a simple chemical. In a simple chemical method, the peaks of the crystalline (γ-Fe_2O_3) phase (wustite, space group Fm-3m, JCPDS no. (00-025-1402))is (*102*) corresponding to (*112*),(116),(205), (109), (119),(209),(0012),(2112),(2115), and(*2018*) millers indices with the Tetragonal, as shown in figure 4[4]. The results of IONPs (γ- Fe_2O_3) phases and crystallite size appear in **Table (1).** The crystallite size (D) was determined by applying Scherrer's formula [5,6].

$$D\ (nm) = \frac{k.\lambda}{\beta\cos\theta} \qquad (4)$$

Where: λ is wave length (0.15418) nm (CuK_α), k is shape factor (0.9), β is full width at half maximum (FWHM), and θ is diffraction angle[6].

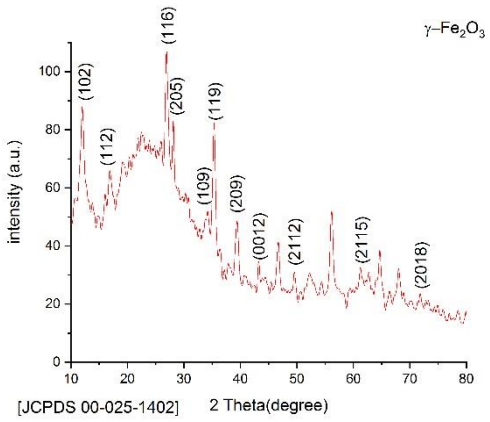

Figure 3. XRD pattern of IONPs extracted from onion peel using $FeCl_2$+ $FeCl_3$ salt for 2 hours at 200 °C by a simple chemical

Table 1. XRD results forγ-Fe_2O_3 NPs from onion peel extract using $FeCl_2$+$FeCl_3$ salt for 2h, 200 °C with simple chemical.

Method	Plant extract	Material	FWHM (deg.)	Plane (hkl)	Crystallite size D (nm)
Simple chemical	onion peel	γ-Fe_2O_3	0.5725	116	14.19491
			0.5583	119	14.85983
			0.7	102	11.34946

3.3. The FESEM Images of IONPs (γ-Fe_2O_3) Prepared from (Onion Peel) Extract

To see the distribution of size and surface morphology of environmentally friendly IONPs made from onion peel extract and iron (II+III) chloride, we used FESEM imaging at a temperature of 200 ^oC. In the chemical method, the grain size is from (23.9 to 169.4) nm, and the average grain size is 76.6 nm with the morphology is (nano-particles) structure for γ-Fe_2O_3 NPs (wustite), 200 ^oC, as appeared in figure 4 [29].

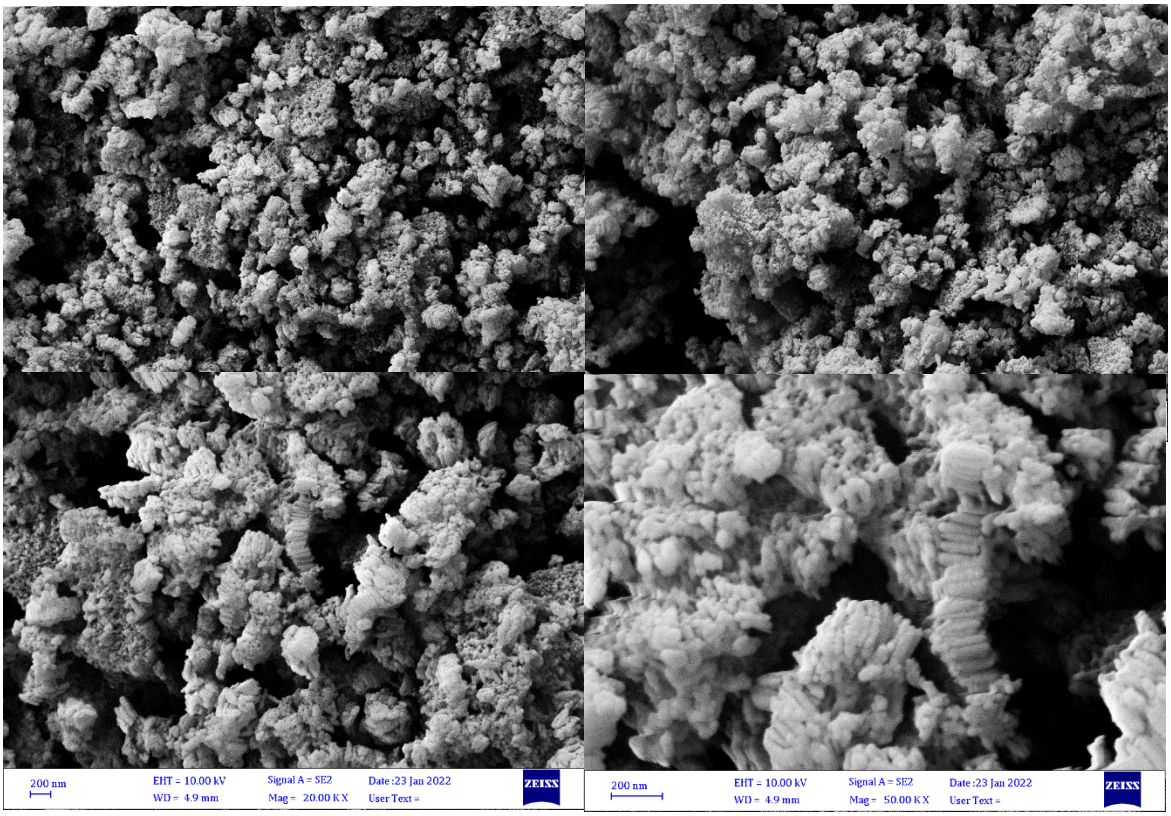

Figure 4. SEM images of iron oxide NPs made the simple chemical way by using onion peel extract.

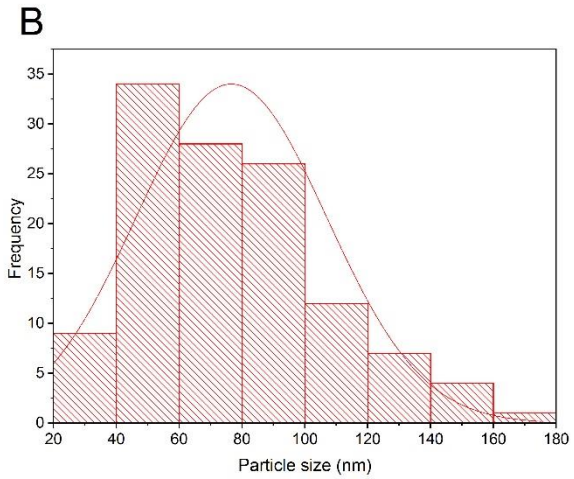

Figure 5. Particle size distribution by simple chemical way

3.4. UV–Vis Spectrophotometer of Iron Oxide NPs by Simple Chemical

Figure 6 (A-B-C) depicts that onion peel extract with FeCl2 and FeC3 salt was used to measure optical transmittance spectra for γ-Fe2O3 NPs[7]. Figure 7 (A-B-C) appears the energy band gap forγ-Fe_2O_3 NPs by a simple chemical way by onion peel extract, estimated by plotting the square of $(\alpha h\upsilon)^2$ vs. the photon energy ($h\upsilon$) in simple chemical methods. Using a straight line extrapolation to $(\alpha h\upsilon)^2$, Calculating the energy band gap is possible. According to the arrangement of atoms and distribution in a powder crystal's crystalline structure, the energy band gap can vary in various ways. The values of the optical band gap values of γ-Fe_2O_3 NPs ranged from 1.94 to 2.96 eV in the simple chemical method as in **Figure.9 (B-C)** [8]. The energy band gap can be calculated using the equation below [9,10].

$$(\alpha h\upsilon)^n = A\,(h\upsilon - Eg) \qquad (5)$$

Where :A is constant, $h\upsilon$ is the energy of light, α is the absorption coefficient, and n is a constant that depends on the electron transition's type[9]. For the iron oxide NPs prepared with a simple chemical method from onion peel extracted by $FeCl_2$ +$FeCl_3$ salt, the energy band gap showed a distinct blue shift, from 1.94 eVto 2.96eV for γ-Fe_2O_3 NPs.

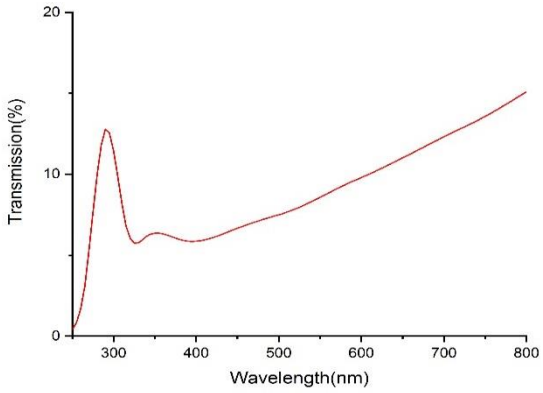

Figure 6. UV–VIS transmission spectra of iron oxide NPs prepared by using onion peel extract in $FeCl_2$+$FeCl_3$ salt for 2 hours at 200 °C using a simple chemical method.

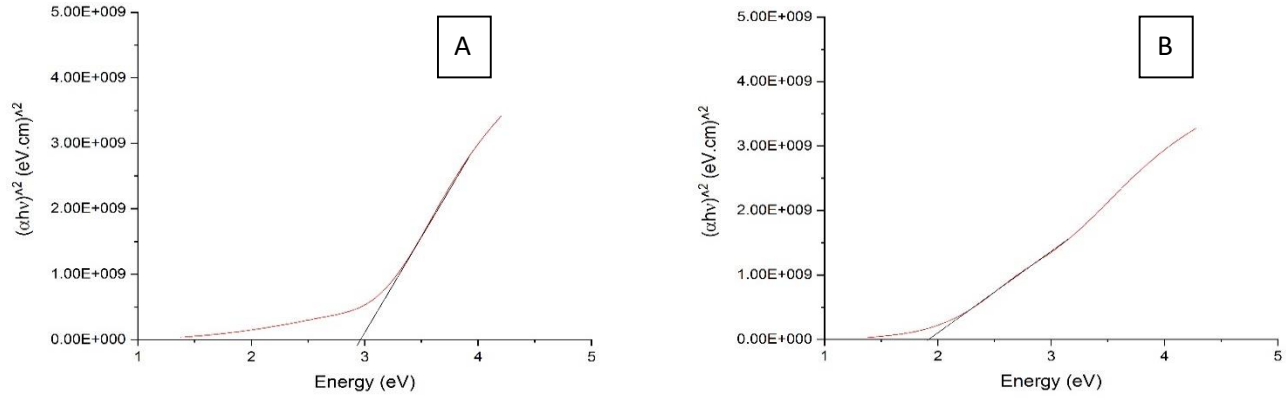

Figure 7. Energy band gap of iron oxide NPs prepared from onion peel extracted by $FeCl_2$+$FeCl_3$ salt A) simple chemical way, B) bulk$FeCl_2$+$FeCl_3$ material.

3.5_ The PL spectrum of iron oxide NPs (γ-Fe_2O_3) by using onion peel extract with $FeCl_2$+$FeCl_3$ extract.

Iron oxide NPs produced from onion peel extract with $FeCl_2$+$FeCl_3$ at (200°C) by a simple chemical procedure may be seen (2.65) eV in the PL spectrum at the near-band edge of the band[11]. In a simple chemical method, the near-band edge with 325 nm is the wavelength of the excitation band of γ-Fe_2O_3NPs (wustite, the near wavelength (469 nm)) at 200 °C, as appeares in **Figure 8**.

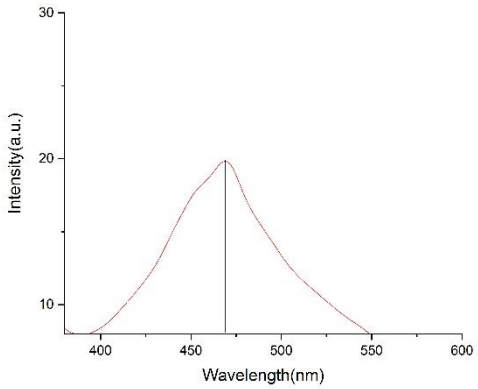

Figure 8. The PL spectra of iron oxide NPs by using onion peel extract with $FeCl_2$+$FeCl_3$ salt with a simple chemical method.

Table 2. Higher degradation efficiency (%),Weight (mg) and Time (min) Photocatalytic activity of iron oxide NPs from onion peel extract under normal light

Method	Weight (mg)	Time (min)	Percentage of Degradation (%)
Simple chemical	5	150	91.1
Simple chemical	3	75	89.2

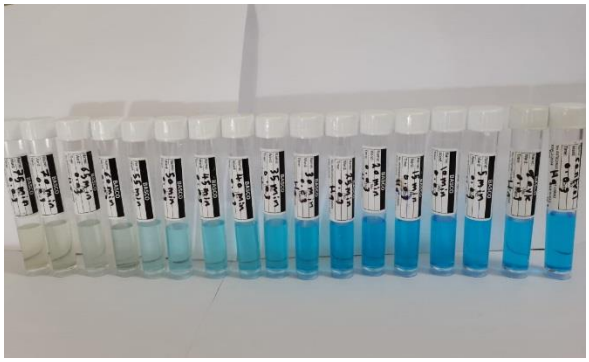

Figure 9. The images of the steps of the degradation of the MB dye in 1) original dye, 2) in darkness by γ-Fe_2O_3 (IONPs), 3) after 5 min, 4) after 10 min, and 5) after 15 min6) after 20 min, 7) after 25 min, until 75 min, by simple chemical technique.

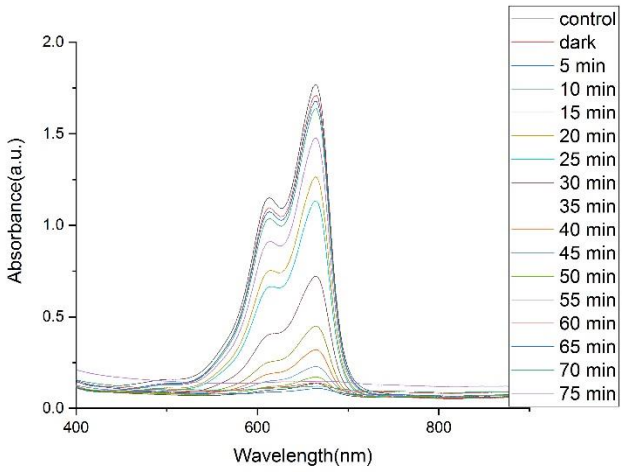

Figure 10. The degradation image for the MB dye with iron oxide NPs with normal light from onion peel extracted by $FeCl_2$ + $FeCl_3$ salt for 2 h,200 °C by simple chemical method**.**

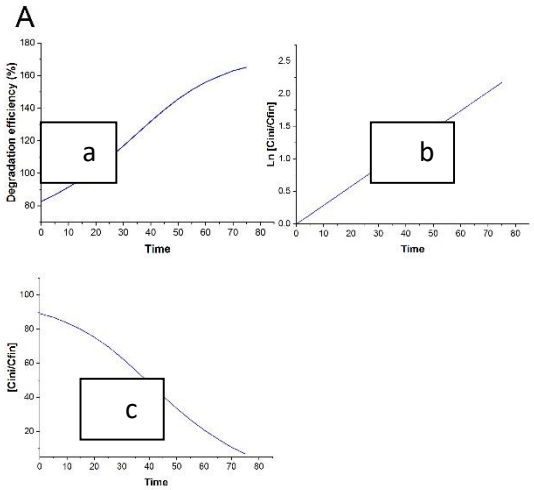

Figure 11. (a) The degradation efficiency (%) of MB dye at 10 mg/L by iron oxide NPs prepared from onion peel extract with $FeCl_{2+}$ $FeCl_3$ salt for 2h, 200 °C (b) In the presence of iron oxide NPs, the degradation of MB dye is plotted as a linear function of light intensity in the same conditions (c) The percentage of MB dye degradation by Simple chemical method,

Figure 12. The images of the steps of the degradation of the MB dye in 1) original dye, 2) in the dark byγ-Fe_2O_3 (IONPs), 3) after 10 min, 4) after 20 min, 5) after 30 min, 6) after 40 min, 7) after 50 min, until 150 min, by simple chemical technique.

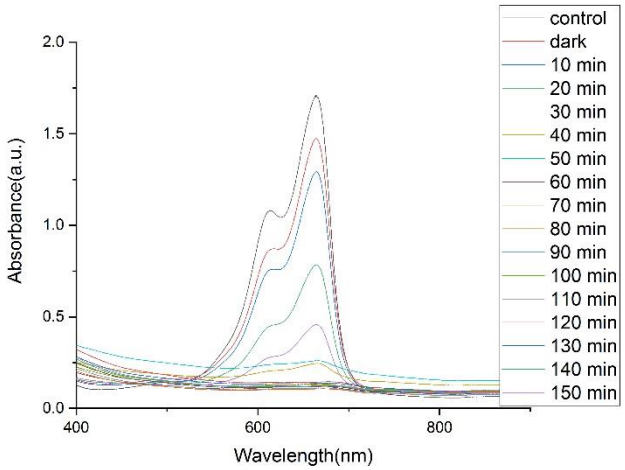

Figure 13. The degradation of MB dye with iron oxide NPs, in the chemical method with normal light by using onion peel extract with $FeCl_2$+ $FeCl_3$ salt for 2 h, 200 °C.

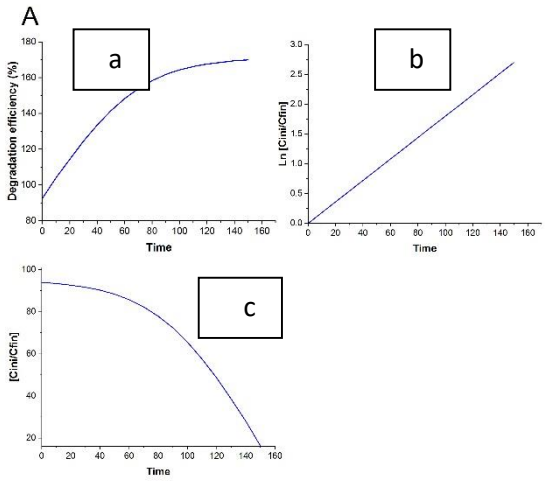

Figure 14. (a) Degradation efficiency (%) of MB dye at 10 mg/L by iron oxide NPs by using onion peel extract in $FeCl_2$+ $FeCl_3$ salt for 2 h, 200 °C.(b) Linear plot of degradation of MB dye under normal light irradiation in the presence of iron oxide NPs in the same conditions. (c) The percentage degradation of MB dye,A) Simple chemical method.

4. Conclusion

This work created IONPs (γ-Fe_2O_3) using modern plant onion peel extract and $FeCl_2$+$FeCl_3$ via chemical ways without using any catalytic chemical material. XRD measurements revealed the average crystalline size (13.4680 nm) with (tetragonal) structure (wustite) for (γ-Fe_2O_3) NPs, 200 ^oC using onion peel extract. FESEM appeared the grain size of (γ-Fe_2O_3) NPs, 200 ^oC using onion peel extract was in chemical from (23.9 to 169.4) nm, average grain size

76.6 nm. For γ -Fe_2O_3 NPs (wustite), 200 ^oC, the optical near band edge value was shifted to the blue by (2.65) eV in chemical using onion peel as a PL spectrum. The photocatalytic activity was achieved by using iron oxide NPs in environmental treatments. The results show that the

synthesized material is of high-quality γ-Fe_2O_3 NPs, with greater degrading efficiency when made using a simple chemical method, reaching 89.2% at 75 minutes for 3 mg and 91.1% at 150 minutes for 5 mg, with a high level of photocatalytic efficacy than the γ-Fe_2O_3.

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