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Green and Chemical Synthesis of Magnetite Nanoparticles for Corrosion Inhibition Applications

The contribution of this research is production, diagnosis, and characterization of iron oxide (Fe_3O_4) nanoparticles in new applications at the lowest possible cost and in straightforward methods. Pomegranate peel extract and reducing agent were utilized in the synthesis of iron oxide nanoparticles, and characterization was done. The results show that the compound in green synthesis had smaller particles than those in the chemical synthesis. The particle size of green synthesized nanoparticles is between 1 and 3 nm smaller than the chemically synthesized 1 to 4 nm, while an absorption peak was indicated in the range of 500 cm^{-1} for Fe_3O_4 appearing in both methods. Chemical nanoparticles were clustered while the green nanoparticles were uncertain because they formed with a biological material. The chemical and green nanoparticles were studied by the weight loss of carbon steel when immersed in the inhibitor solution at different temperature degrees, at low temperature degrees, the results show that green inhibitors have the ability to reduce the problem of corrosion. The numerous changes on the metal surface led to a decrease in the inhibitor efficiency as the temperature increased indicating that adsorption of inhibitor species on the C-steel surface is merely physical.

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1. Introduction

Science is a wide ocean, and its wheel is always turning, never stopping. As a result, we discover something new in a variety of scientific domains every day. Without a doubt, nanotechnology has emerged as the primary topic of contemporary research and the center of its attention. It is now at the forefront of several significant disciplines, including chemistry and biology. physics [1]. Recently, a novel, environmentally benign method based on natural materials was discovered for the plant-mediated synthesis of nanoparticles [2]. Previous research on the production and bio-diagnosis of nanomaterials has helped us to better understand what is happening in the field of chemistry with regard to nanotechnology as well as the advancements made in the production and diagnosis of these materials and the key applications of this cutting-edge technology. The fact that nanotechnology has significant future potential and objectives, such as the ability to treat diseases, is encouraging. Malware, creating environmentally friendly materials, cutting the size and cost of electronic equipment, increasing their performance, and solving the majority of modern issues that science is yet unable to resolve and understanding the role of nano-engineered materials is the main concern at the nanoscale [3].

Using chemical reduction and green technology, two different approach to synthesize nanoparticles [4]. Iron oxide is the fundamental component of the ultrastructure structure. Different shapes of nanoscale iron oxides, such as nanoscale porous spheres and deformable cubes, must be synthesized using an almost identical standard protocol by varying the simple precursor salts where the diversity of nanoparticles

depends surfactant as well as the choice of surfactant relies on the systems' chemical and physical characteristics, realizing the significance of nanoparticles. Among the nanoscale, nano-engineered materials are the main focus. The high surface-to-volume ratio of the iron oxide nanoparticles makes them interesting after nanoparticle manufacturing surface modification is crucial to prevent chemical corrosion that results from instability. Additionally, nanotechnology has been a major factor in enabling creative technological advancements in the opposition. Recent research on nanoparticles suggests that because of their surface ratio and crystal structure, they could play very promising and effective roles as antimicrobial agents [5]. Green nanotechnology is the term for the rapidly expanding field of recent agricultural advancements. It is focused on the creation of clean technologies that lessen possible threats to human and environmental health, which is researching matter at the nanoscale and how it varies in composition across plants and types.

Additionally, the practical, ecological, artistic, fiscal, and aesthetic aspects all heavily weigh on the protection of metals and alloys. Steel alloys are used as a substantial superior for the structure of manufacturing oil-well processing and pipeline apparatus in the petroleum sector apparatus due to their high strength and cost-effectiveness [6]. Acidic media are typically used in many industrial settings to remove undesirable scales and corrosion. The usage of both organic and inorganic chemicals as corrosion inhibitors has raised serious concerns over the past few decades due to their toxicity to the environment [7]. One technique to highlight new findings in the field of nanotechnology is to look at the rate at which metals corrode when

exposed to nanoparticles [8]. Nanomaterials exhibit enhanced corrosion prevention characteristics due to their larger surface-to-volume ratio. The preparation of nanoparticles has been accomplished through a variety of methods. Numerous investigators have effectively exhibited the suitability of nanoparticles as agents that reduce corrosion. Since corrosion results in yearly losses that are believed to be in the millions or even billions of dollars, it is seen as a contemporary problem. New buildings become crumbling structures due to corrosion, machinery becomes outdated, and piles of useless debris [9].

2. Methodology

The pomegranate peels were dried and ground using a pestle, and an extract of the pomegranate was then prepared by weighing 25 g of the pomegranate powder and placing it in a beaker. A 300 ml of distilled water is added and heated at 60°C for 20 minutes, then the residues are removed. The solid is filtered by filtration to obtain pomegranate extract. We put a mass of 1.39 g of ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and add 100 ml of distilled water to it, stirring until dissolved, to obtain a solution with a concentration of 5 M. When adding the pomegranate extract to it, we notice that the color of the solution changes from orange to brown, evidence of the beginning of the formation of iron oxide. It is placed in a reflux condenser device at a temperature of 85 degrees, stirring for two hours; its color changes to dark violet. Then we cool the reaction mixture and put it in a centrifuge for ten minutes to collect the precipitate. After that, the sample was placed in the oven at 500°C for three hours.

A 2 ml of HCl acid is mixed with 250 ml of distilled water. The molar ratio is prepared from 2:1 of the Fe^{3+} and the binary iron ions Fe^{2+} by mixing 6.5 g of FeCl_3 salt with 5.56 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salt and adding it to the solution prepared, then 500 ml of a (NaOH) solution with a concentration of 1.5 M is added to the previous solution in the form of drops with continuous stirring, and notice the appearance of a black precipitate, then wash it several times using distilled water until the washing water becomes neutral. The formed sediment was separated from the filtrate by using filter paper, the sediment was dried by placing it in an oven at 500°C. about 4 hours.

The corrosive medium used consists of an aqueous solution of hydrochloric acid (HCl) 1M, then preparing different concentrations of solutions of green and chemical inhibitors (Fe_3O_4 NPs). It is weighed from 0.016 g of (Fe_3O_4 NPs) extracted by chemical and green dissolved in 100 ml and placed in iron oxide solution extracted by green synthesis in a bottle and labelled stock solution at a concentration of 3×10^{-3} , then prepare the other concentrations by taking different sizes of the stock solution, which were 3×10^{-6} M, 5×10^{-6} M, 7×10^{-6} M, 9×10^{-6} M, and 11×10^{-6} M. After sanding the samples, different sizes of beakers are taken and placed

in 100 ml capacity beakers. Weigh the sample and place it inside the beaker containing the inhibited solution. The water bath is adjusted to different temperatures (25°C, 35°C, 45°C), and the six frosted samples are weighed and placed in the rollers. After half an hour of immersion, they are removed, washed with distilled water, dried with a tissue, weighed, and the weight is recorded. Then they are immersed again, and after another half hour, they are removed and weighed, and so on for up to three hours.

3. Results and Discussion

Some physical properties of green and chemical nanoparticles such as measurements of melting point, color of the material, solubility in water and alcohol ethanol are as shown in table (1).

The crystalline structure of iron oxide prepared by the chemical method and the green method using the x-ray diffraction (XRD) technique, the locations of the peaks shown in Fig. (2) show that the nanosized size of the iron oxide is small; it also shows that crystalline levels are clearer and have higher peaks for the chemical iron particles compared to the green method. However, the Debye-Scherrer equation can be applied to calculate the crystallite size (D):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is the dimensionless form factor (0.94), λ is the wavelength of the x-ray radiation, β is the full-width at half maximum (FWHM), and θ is the Bragg's angle of diffraction

From the result of XRD and by applying the Debye Scherer equation, the particle size of green nanoparticles is between 1 nm to 3 nm smaller than the chemically synthesized 1 nm to 4 nm.

Scanning electron microscopy (SEM) was used to see the nanostructures and examine the surfaces of iron nanoparticles produced by the chemical and green synthesis. The photos of the green-synthesized nanoparticles demonstrated that they are dense aggregates of particles that appear semi-regular because biological molecules have been applied to the green particles seen in pomegranate extract that have a smaller size than chemical, which suggests a higher surface area to volume ratio. These outcomes align with the findings of earlier research. Using a chemical technique and green chemistry, the morphology of iron nanoparticles was examined. shown in Fig. (1).

Because each particular chemical bond frequently has a distinct energy absorption band, Fourier-transform infrared (FTIR) spectroscopy is a helpful method for detecting functional groups in molecules. It may also be used to gain structural and bond information of a compound to examine bond strength and type.

Figure (2) shows the FTIR spectrum of the iron oxide nanoparticles prepared by the chemical method. A broad peak appears at 3402.43 cm^{-1} which is

attributed to the stretching vibration of O-H bond. The presence of absorption bands at 576-1011 cm^{-1} indicates different modes of bands of the bending vibration of Fe-O bond. The peak at 635.64 cm^{-1} indicates the Fe-O bond stretch vibration of the complete iron oxide nanoparticles.

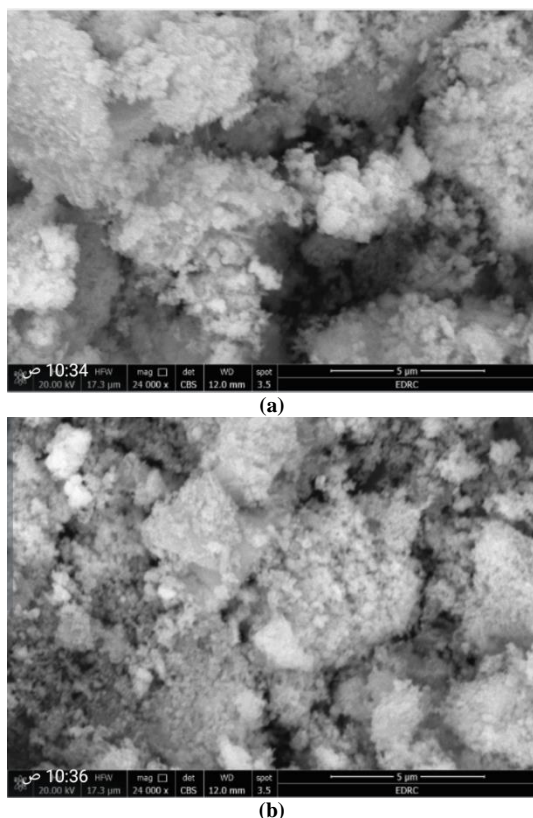


Fig (1) SEM images of Fe_3O_4 nanoparticles synthesized by (a) chemical method, (b) green synthesis

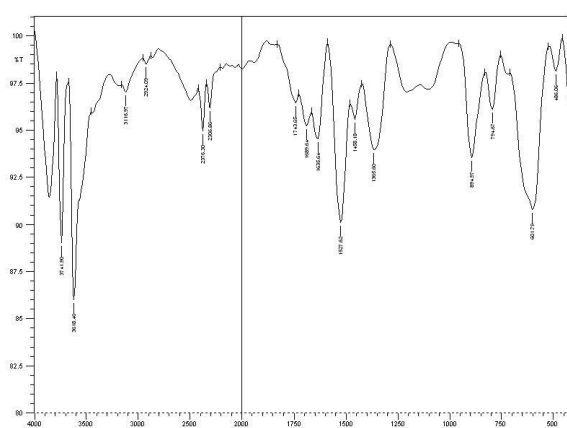


Fig (2) The FTIR spectrum of the Fe_3O_4 nanoparticles prepared by the chemical method

While in green nanoparticles as show in Fig. (3), the absorption band centered at 3368, 1635.64, 1458.18, 1230, 1055 cm^{-1} are respectively identified as stretching vibrations of O-H and C=O bonds, stretching

vibrations, C=C bond stretching vibrations, stretching vibrations of C-O bond, and bending vibration for C-OH peaks observed at 2842.00 and 2924.09 cm^{-1} represent respectively the asymmetric and symmetric C-H bond stretching vibrations of the methyl group. In addition, the peak that appeared at 1527.26 cm^{-1} can indicate the C-N stretching vibration band of amines. The peaks at 794.7 and 894.97 cm^{-1} indicate absorption of the bond C-C. The peaks located at 500 cm^{-1} are attributed to stretching vibrations of the Fe-O bond. The absorption of wavelength at 486.06 cm^{-1} is due to the bonding of the oxygen atom to the iron atom.

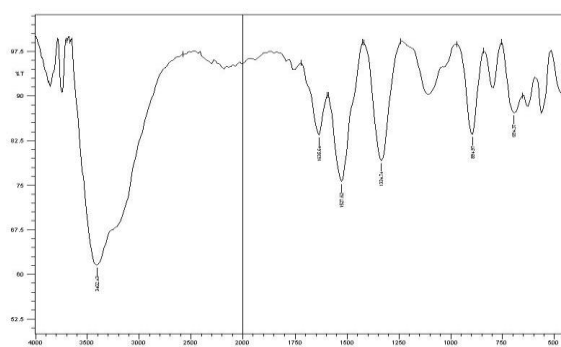


Fig (3) The FTIR spectrum of Fe_3O_4 nanoparticles prepared by the Green method

The process of corrosion on metal in a watery environment is characterized by its dissolution into the solution assessing the rate of corrosion is essential for gauging the corrosiveness of the environment being studied and for determining the average material loss due to corrosion. The common technique for calculating the corrosion rate is the weight loss. The method effectively assesses the inhibitor's quality and determines the maximum concentration at which the inhibitor remains effective under the specified condition.

The results of steel corrosion in 1M of hydrochloric acid were obtained within the temperature range of 25-45°C in the presence and absence of different concentrations of the chemically extracted inhibitor as shown in figures (4), (5), and (6).

The results of steel corrosion in 1M of hydrochloric acid were obtained within the temperature range of 25-45°C in the presence and absence of different concentrations of the plant-extracted inhibitor as shown in figures (7), (8), and (9).

These curves are distinguished by an abrupt increase in weight loss from the start. Curves for additives with a system full below that of the free acid showed that the concentration of these derivatives determines how much C-steel is lost in weight. Table (2) shows the metal solution with and without of various concentrations inhibitors at 35°C and 45°C.

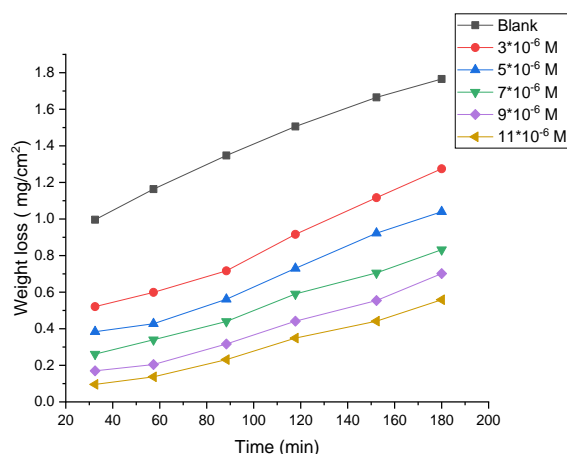


Fig (4) Weight loss vs. time of chemical inhibitor at 25°C

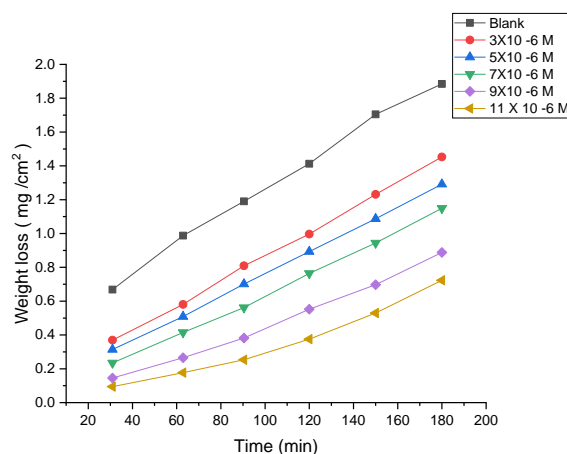


Fig (7) Weight loss vs. time of plant-extracted inhibitor at 25°C

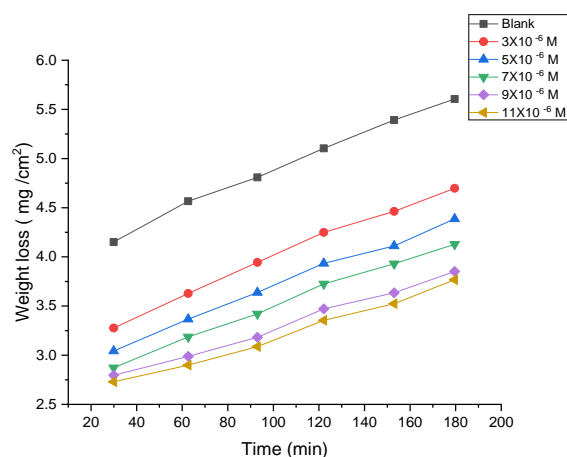


Fig (5) Weight loss vs. time of chemical inhibitor at 35°C

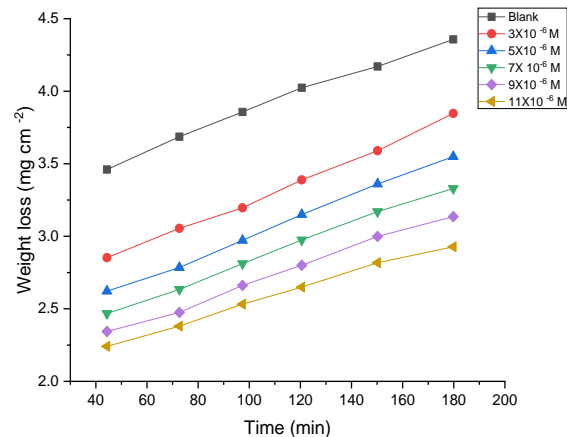


Fig (8) Weight loss vs. time of plant-extracted inhibitor at 35°C

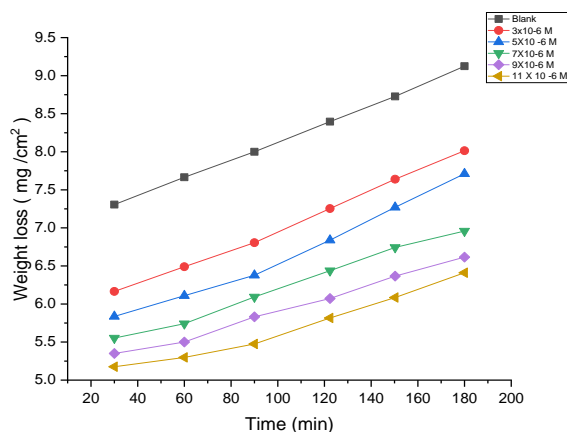


Fig (6) Weight loss vs. time of chemical inhibitor at 45°C

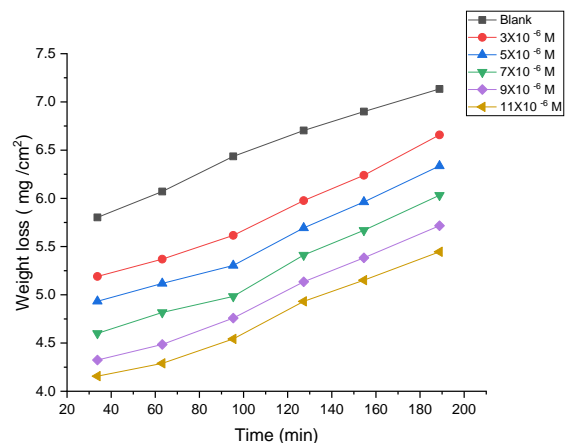


Fig (9) Weight loss vs. time of plant-extracted inhibitor at 45°C

In both inhibited and uninhibited solutions, the percentage IE values drop as the temperature rises within the investigated temperature range of 35°C to 45°C, as shown in table (3).

Table (2) Weight loss of metal solution

Compound	Concentration $\times 10^{-6}$ M	(CR)	θ	IE
1 M HCl		mg.cm ² /min	----	----
Chemical inhibitor	3	0.0125	0.392	39.2
	5	0.0076	0.512	51.2
	7	0.0061	0.608	60.8
	9	0.0049	0.704	70.4
	11	0.0037	0.768	76.8
Plant inhibitor	3	0.0029	0.336	33.6
	5	0.0083	0.408	40.8
	7	0.0074	0.488	48.8
	9	0.0064	0.632	63.2
	11	0.0046	0.752	75.2

Table (3) % IE values at 35°C to 45°C

Compound	Concentration $\times 10^{-6}$ M	35°C		45°C	
		θ	IE	θ	IE
Blank		----	----	----	----
Chemical inhibitor	3	0.332	33.2	0.313	31.3
	5	0.502	50.2	0.497	49.7
	7	0.588	58.8	0.521	52.1
	9	0.622	62.2	0.607	60.7
	11	0.704	70.4	0.693	69.3
Plant inhibitor	3	0.335	33.5	0.321	32.1
	5	0.398	39.8	0.389	38.9
	7	0.456	45.6	0.449	44.9
	9	0.602	60.2	0.587	58.7
	11	0.734	73.4	0.71	71

4. Conclusion

Iron oxide nanoparticles (Fe_3O_4 NPs) were produced in two different ways :the method of chemical precipitation of iron ions using iron (III) hydroxide, and the green method using pomegranate peel extract which is an easy, fast, inexpensive and environmentally, safe method compared to the chemical method. The measurements revealed that the particle size of green-synthesized nanoparticles is between 1 and 3nm, which is smaller than the chemically synthesized nanoparticles 1-4nm in size, according to SEM photographs of the particles, they are encased as opposed to the nanoparticles in pomegranate extract is uncertain because they formed with a biological material. Through the results obtained through the use of plant and chemical extracts as corrosion inhibitors, it was concluded that green inhibitors are better than chemical inhibitors. It was also concluded that green inhibitors have the ability to reduce the problem of corrosion more compared to other inhibitors. Chemicals because plants contain organic substances that are adsorbed on the surface of the metal to protect it from corrosion.

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Table (1) Physical properties of green and chemical synthesized Iron nanoparticles

Nanoparticle	Melting point (°C)	Solubility in water	Solubility in alcohol	Color and texture
Green Fe_3O_4 NPs	1539	soluble	Non soluble	Black hard powder
Chemical Fe_3O_4 NPs	1539	soluble	Non soluble	Brown powder