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Green Synthesis Zinc Nanoparticles in the Treatment of Heavy Metals in the form of Complexes

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Abstract

Myrtle plant was washed, dried, and powdered after harvesting to produce a fine powder that was used in water treatment. created an alcoholic extract from the myrtle plant using ethanol, which was then analyzed using GC-Mass, Fourier Transform Infrared spectroscopy, and ultraviolet-visible spectroscopy to identify the active components. Zinc nanoparticles were created using alcoholic extract. We used FTIR, UV-Vis, SEM, EDX, and TEM to characterize zinc nanoparticles. Using a continuous processing procedure, zinc nanoparticles with myrtle extract and powder were employed to clean polluted water containing heavy metals.

Firstly used 2g with 20ml polluted water and the result was (Fe 96.20%, Cr 84%, Pb 100%, Sb 93.70, Cd 100%, andCu 90.60%) Secondly, weused Zinc nanoparticles to treat water the result was (Fe 96.20%, Cr 84%, Sb 54%, 64.50%, Cu 64.80). When Comparing between results myrtle powder and zinc nanoparticle we found myrtle plant was prefer in treatment water.

Keywords: Myrtle plant, Zinc nanoparticle, pollutant water treatment, Heavy metals.

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1. Introduction

There was a pressing need to reuse water, particularly in the fields of industry or irrigation, as the sources of clean water over time started to diminish as the demand for it grew[1]. It was crucial creating scientific, practical, and effective ways to treat water because of the growing demand for pure and industrial water, which simultaneously increases water pollution and affects water sources with chemical pollution (both organic and inorganic)[2]. A qualitative and quantitative analysis of the pollutants in the water must come before choosing a treatment procedure, and only then can the optimal course of action be decided. There are therapies that use physical techniques, and there are others that use chemical or biological techniques. However, cost and efficiency[3,4]. are the key factors to consider when comparing various systems. Therefore, researchers looked for affordable and effective therapy options that wouldn't disturb the delicate balance of the environment. Due to their propensity to absorb chemical contaminants, plant residues are used in water treatment, according to many studies. Wastewater has been treated using water hyacinth, water lettuce, duckweed, and vetiver grass. Due to its unchecked development in water bodies, Eichhornia crassipes have been labeled a problematic aquatic free-floating weed. It is also challenging to manage and eradicate this plant from water bodies[5,6]. However, it has been regarded as a bioindicator because of its capacity to absorb heavy metals from aquatic habitats. Only a little amount of study has been done on the phytoremediation method of employing Eichhornia crassipes to clean kitchen wastewater. Chemists have been concentrating on nanotechnology in recent years, particularly nanotechnology connected to plants, or "Green Nano"[7]. In this work, we will investigate the treatment of heavy metals polluted water using zinc nanoparticles in combination with alcoholic myrtle extract using customized columns processing. In order to cleanse water tainted with phenols and aromatic chemicals, silver nanoparticles have already won the use of extracts utilizing specialized capsules[8]. To purify water of inorganic pollutants, another study combined zinc nanoparticles with cumin leaf extract [9].

2. Materials and method

2.1. Materials and instrumentation

The following chemical substances were employed, and a Shimadzu-3800 Spectro-meter equipped with a (FTIR) in the range (4000-400) cm-1 was used as a detector: methanol, ethanol, zinc sulphate, sodium hydroxide, ascorbic acid, and polyvinyl alcohol. Shimadzu 160 Spectro-photometer was used to find the electronic spectrum data. Compounds were subjected to mass indication analysis using a GC Mass100P Shimadzu. This study used scanning electron microscopy (SEM) to manage the analysis and describe the size and morphology of nanoparticles. The best technique for determining the NPs' morphology is (TEM). A sample is passed through an intense electron beam during this technique for microscopy, and the outcome of the electrons' interactions with the material is the creation of a picture.A little drop of nanoparticles was applied on a copper grid that had carbon coating, and it was left to dry under a mercury lamp for five minutes. Finally, readings were taken under stable voltage conditions at magnifications of 5000x, 10000x, 20000, and 50000x. To validate the presence of the zinc nanoparticle, EDX measurements were performed using a high-resolution spectrophotometer in a transmission electron microscope.

2.2 Plant harvest and preparation for grinding and extraction

Used myrtle plants for this study came from the Kadhimiya District in Iraq's Baghdad Governorate. It was thoroughly cleaned with deionized water many times to get rid of any impurities, dried at room temperature, and then ground into a very fine powder using a special laboratory grinder for 15 seconds. Alcoholic myrtle extract was produced by mixing a solution of 65% methanol, 20% ethanol, and 15% free ionized water, allowing it to sit for a while, and then heating it to 50C. It was condensed simultaneously for eight hours using a laboratory condenser. At 50°C, the extraction procedure is carried out, then evaporation and condensation are used to boost enrichment. Show **Figure 1.**

Figure1.A. myrtle plant after wash B. myrtle plant after dryed C. myrtle plant after grinded

2.3 Preparation of zinc nanoparticles

The following steps were used to manufacture zinc nanoparticles with myrtle extract, using a modified version of Elumalai's method: placing 10 ml:20% of myrtle extract and 1000 ml of pure water in a round flask. The flask was left to be heated and stirred at different temperatures. After one minute, 17.5 g of zinc sulfate was added gradually while being continuously stirred [10] the mixture's acidity was then equalized by adding pure sodium hydroxide. The mixture was then put into a glass container and heated to 200°C for two hours. The filtered solution separates from the precipitate to complete the separation, and the precipitate is then collected and dried from the remaining water in A furnace set to 70°C will be used to do the drying; after it has been crashed, 17.5g of zinc sulfate will be gradually added to finish the mixing of the components. green powder that was produced is kept in an airtight container for characterization.[11]. Show **Figure 2.**

Figure 2: A. zinc nano-particles during prepare B. zinc nano-particles after dry

2.4 Determining the activated compounds of myrtle plant extract

The gas chromatography-mass spectroscopy technique (GC-Mass), which is cleaner, quicker, and less expensive than conventional extraction methods, was used to identify the activated compounds in the alcoholic myrtle plant extract. GC-Mass is an analytical technique for a qualitative and quantitative group of a broad domain of compounds[12]. Substances found in the myrtle extract by GC-Mass are shown in **Figure 3**, **Table 1.**

Table 1. Compounds characterized in the myrtle extract by GC-Mass

Peak No.	R.T	Area %	Comp. Name	Classification	
1	25.145	6.60	Benzoic acid	Organic acid	Soapy compounds
2	25.817	2.14	Benzoic acid	Organic acid	
3	33.075	0.92	Cyclopentane-1-thione, 2,3,4,4-2-tetramethyl	Thiophen compounds	
4	34.898	1.22	Tetradecane	Aliphatic compounds	
5	39.871	1.53	Durohydroquinone	Glycol	Soapy compounds
6	43.116	4.28	Hexadecane	Aliphatic compounds	
7	50.336	1.89	Furazan 2-(dimethyl amino methylene amino)-4-(1,2,4-trizol-2-yl)	Triazol	
8	50.518	2.62	Hexa decanal, 2-methyl	Aliphatic compounds	
9	51.770	13.37	Oxirane undecanoic acid, 3-pentyl methyl ester, trans	Alcohol	
10	53.999	3.30	n-hexadecanoic acid	Alcohol	
11	54.759	1.13	Epoxy-1-vinylcyclododecene-1,2	Fatty acid methyl esters	Soapy compounds
12	56.062	16.52	Methyl (furan-2-yl)-6-hydroxy x-2-ynoate	Fatty acid	Soapy compounds
13	57.171	5.23	4-(4-chlorophenyl)-2-diethyl amino-2-cyclo buten-1,2-dione	Epoxyd compounds	Soapy compounds
14	57.451	3.41	Oleic Acid	Methyl esters	
15	57.654	2.50	1-cyclo hexylnonene	Amino acid mrthyl esters	Soapy compounds
16	58.731	1.67	(Octadecanoic acid (Z-1)	Fatty acid	

17	59.709	5.16	Iron, tricarbonyl (2,3,4,5-tetrahydroxy-2,4-cyclopentadien-1-one)	Aliphatic compounds	
18	60.332	1.48	1,3-cyclopentadiene, 5-(1-methylpropylidene)	Fatty acid	Soapy compounds
19	60.526	1.26	Octadic-9-enoic acid		
20	61.183	1.49	1,3-cyclopentadiene,5-(1-methylpropyldene)-	Cyclic compounds	Soapy compounds
21	61.606	17.77	Octadic-9-enoic acid	Fatty acid methyl esters	
22	62.326	6.41	Thiosulfunic acid ($H_2S_2O_2$), S- (minoethyl) ester		
23	62.778	1.83	9-octadecenoic acid, (E)-	Fatty acid methyl esters	Soapy compounds

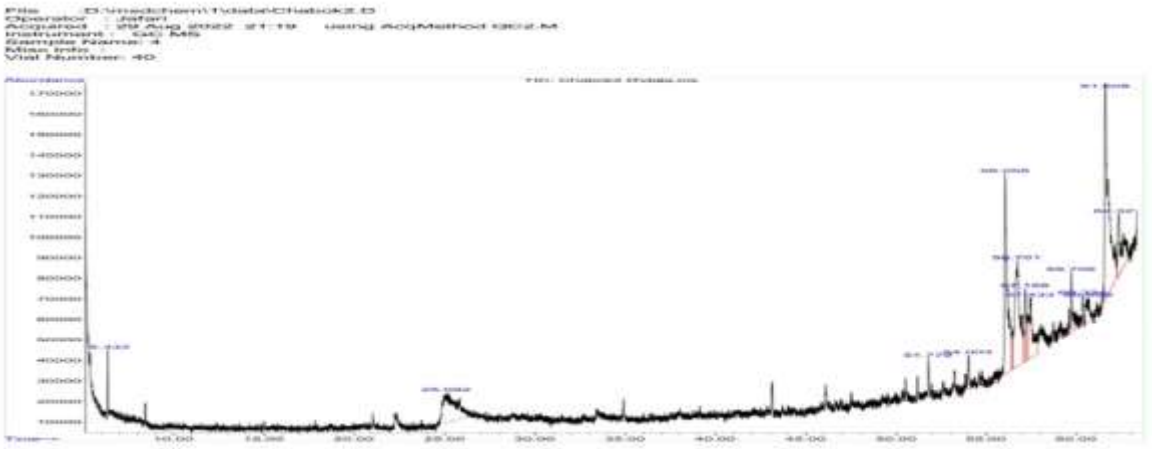


Figure 3. GC-Mass for the myrtle extract

3. Results and discussion

This section describes the results of treating water that has been contaminated with inorganic elements including Cd, Sb, Fe, Cr, and Cu either using myrtle plants or with zinc nanoparticles and evaluates the effectiveness of the treatment. The water treatment technique that was used was the m. processing research. contrasting the standards for standard water adopted by the WHO and treated water.

3.1 Ultraviolet visible (UV-Vis)

Ultraviolet-visible spectroscopy is the main part to distinguish active compounds in the myrtle plant by studying the absorptions that are visible in spectra due to the colors of the myrtle plant, which has been screened as an alcoholic extract and zinc nanoparticle with myrtle extract then absorbed peaks inthe first one appear at 307,676nm and in nano292nm this peakrefers to the ultraviolet area belong (n→ σ*), (π→π*) [13]. 307 and 676nm these peaks belong to (n→π*) and (π→π*) in the UV area, 676 nm refers to myrtle plant plus organic and inorganic compounds. When comparing the alcoholic extract to the green myrtle plant and the zinc nanoparticle with the alcoholic extract, alcoholic extract peak shifted towards a shorter longer wavelength 10 nm red shift, and another peak in visible area refers to zinc nanoparticle [14,15], as shown **Figure4.**

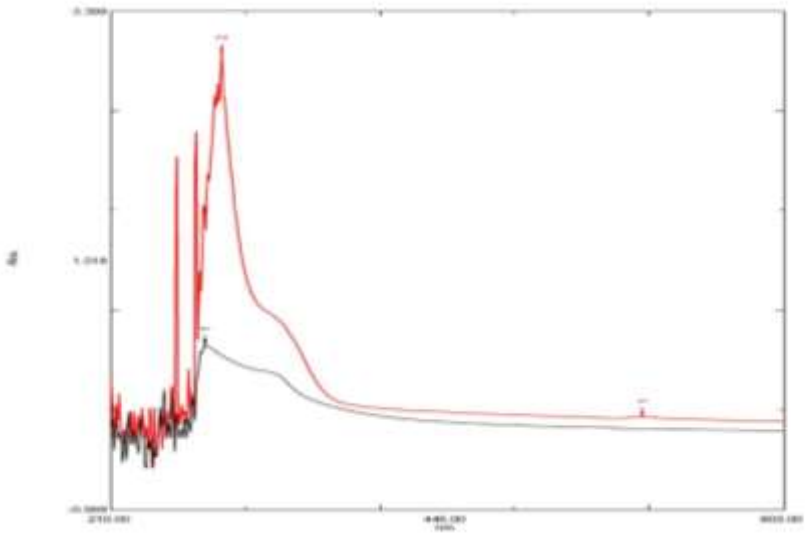
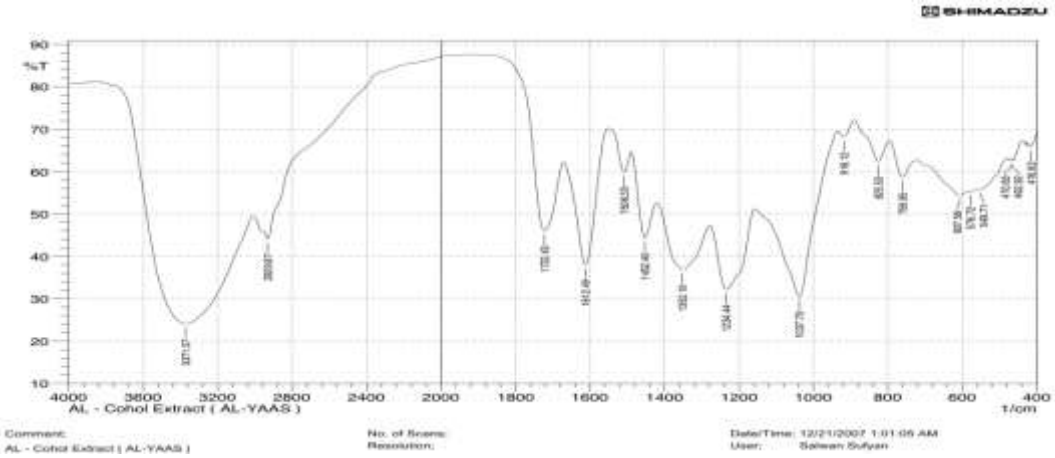


Figure 4. Ultraviolet-Visible for two samples

3.2 Fourier Transform-Infrared (FTIR)

Infrared Fourier transform is a key method. When comparing alcoholic extract with myrtle plant and alcoholic extract with nanocomposite, the method for defining organic components in alcoholic extract refers to the creation of nanoparticles. It is employed to identify active chemicals and test whether they can be joined with another element to create new complexes. A peak may be seen at 3371 cm^{-1}, and at 3417 cm^{-1} zinc nanoparticles can be seen. The (O-H) group has altered in two compounds at around 46 cm-1 in these peaks, which are then followed by further peaks on 2929 cm^{-1} in alcoholic extract and 2926 cm-1 in zinc nanoparticle. These peaks correspond to the (CH) aliphatic group (1612 cm^{-1}), the carbonyl group (1552 cm^{-1}), the (CH) group (1037 cm^{-1} in the myrtle alcohol extract), and the (CH) group (1116 cm^{-1} in nanoparticle) [16,17]show **Figure 5,6.**



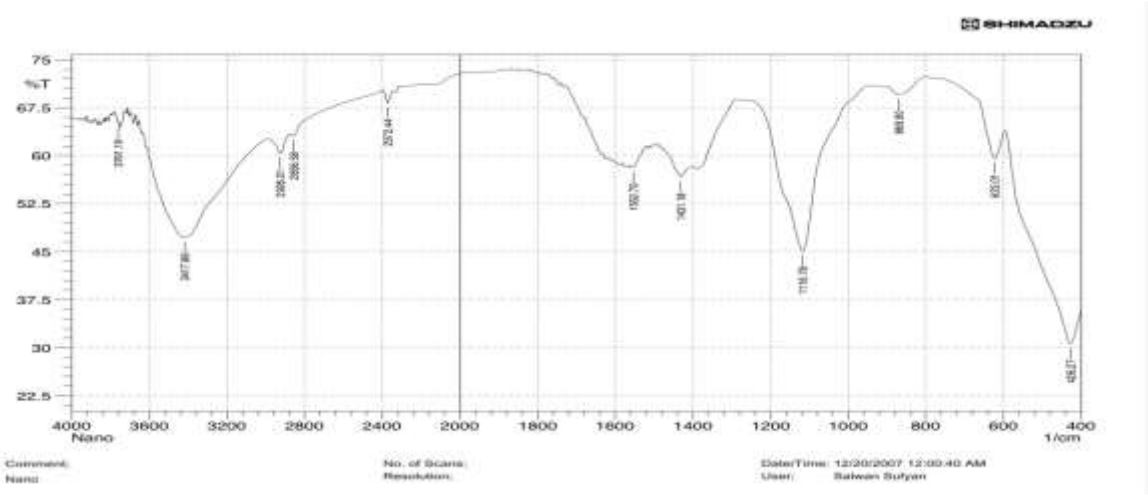


Figure 6. FT-IR Spectrum of zinc nanoparticle with alcoholic myrtle

3.3.Scanning Electron Microscope (SEM)

Scanning Electron Microscope for zinc nanoparticles shows spherical crystal shape in average particles (122.8 nm), which refers to zinc element, this indicates that it has granules size includes a range of nano, this result is consisted [18] Other nanoparticles appear on (55.96, 63.93, 60.66, 85.32,97.20, 100.1, 122.8) nm, which refer to hydrocarbon group range of nano except for hydrogen because the small size of it[19].

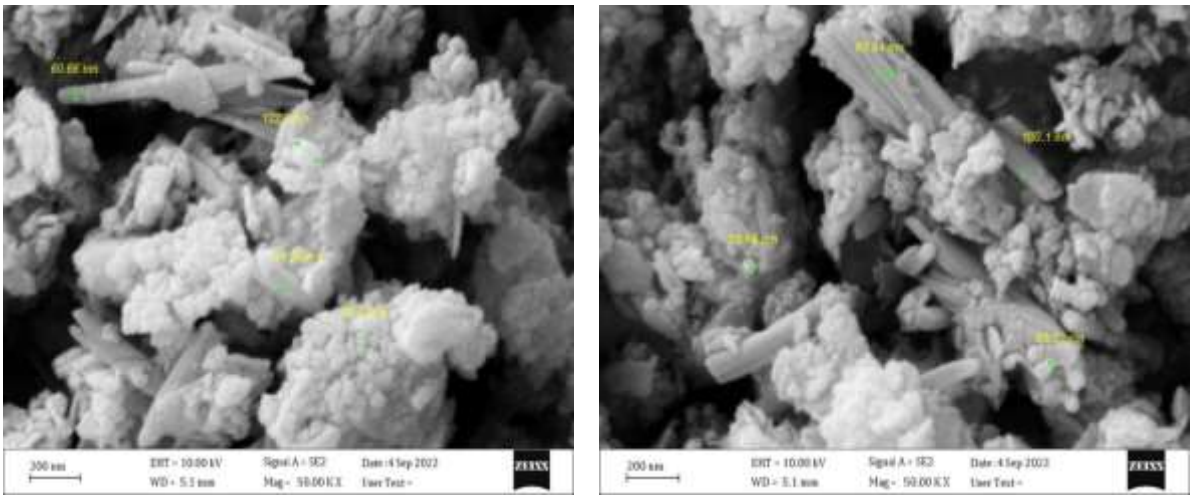


Figure7. Show SEM for zinc nanoparticle with alcoholic extract of myrtle

3.4. X-Ray diffraction spectroscopy

X-Ray technique was used to identify the arrangement of the crystal atoms, where the X-RAY hit the crystal to show certain directions according to the angles and strength of reflected rays, where 3D images are formed for the Electrondensity inside the crystal. This technique measure the diffraction of X-RAY, the nano-crystals are inserted into the angle meter and transformed while targeting the X-RAY on it, which shall result in random diffraction called measurements. All directions image of angles is taken for 2D dimensions in order to be transformed to 3D images representing the electronic density inside the crystal. In the study of X-RAY diffraction used for identifying the crystal molecular weight,the result of X-ray testing, where

the three readings between were 30-40 due to Zinc elements presence in more readings due to the size of nano-molecule with Zinc elements, while the remaining values show the presence of Hydrocarbon compounds except for the Hydrogen which does not appear because of its small size[20]. show **Figure 8.**

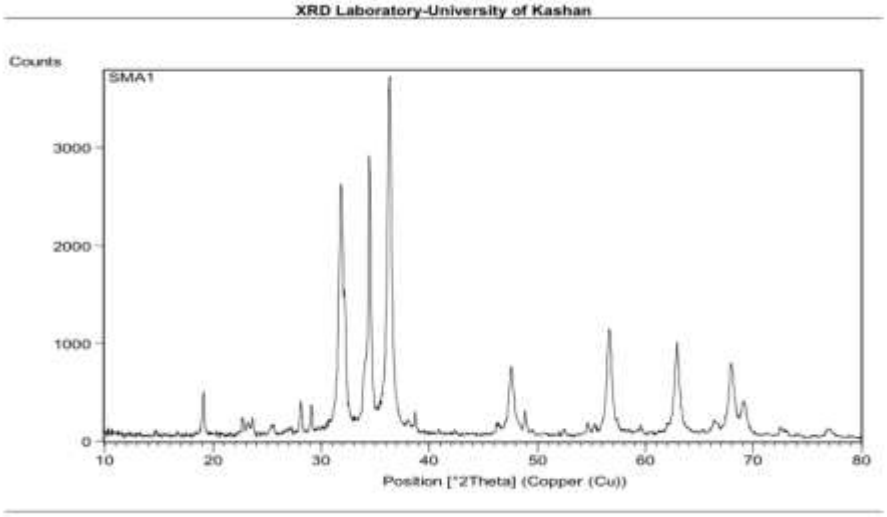


Figure 8. XRD-diffraction of Zinc nanoparticles

3.5 Energy dispersive X-Ray spectroscopy

X-ray spectroscopy uses EDX, a form of X-ray emission, to determine the chemical compounds of the samples; on the other hand, each element has a unique atomic structure and set of values. Three peaks in a zinc nanoparticle examined verified it. (1,8.6, 9.8) keV and they were crystal spherical structures[21]. Show **Figure 9.**

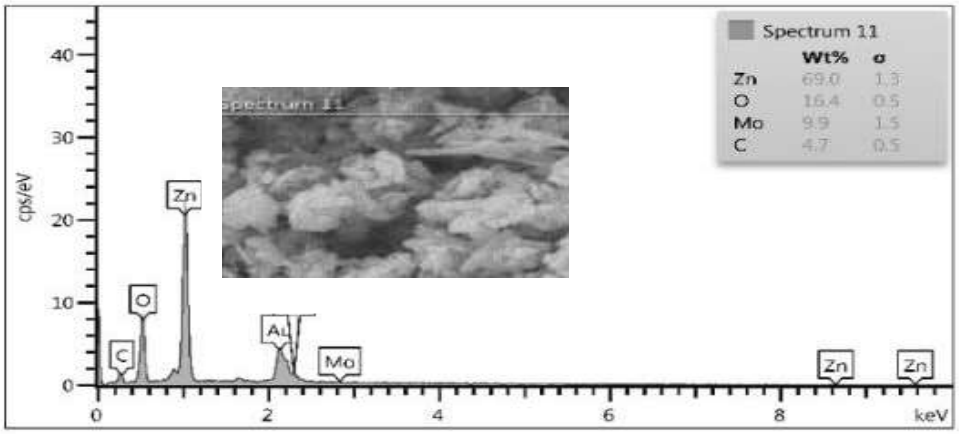


Figure 9. Energy-dispersive X-ray spectroscopy for zinc nanoparticle (EDX)

3.6 Transmission electron microscopy (TEM)

is the greatest method for figuring out how nanoparticles are shaped. A sample is run through a powerful electron beam in this sort of microscopy, and the outcome of the electrons' interactions with the material is the creation of an image. After that, the image is magnified and focused onto

an imaging medium, such as a charge-coupled device, a fluorescent screen, or a sheet of photographic film[22]. a smaller magnification Because of differences in the material's composition or thickness, contrast can be seen in TEM pictures of that substance, When using a sample of zinc nanoparticles with myrtle extract, high-resolution transmission electron microscopy (HRTEM) revealed that the sample was smooth and spherical on the outside[23]. show **Figure 10**.

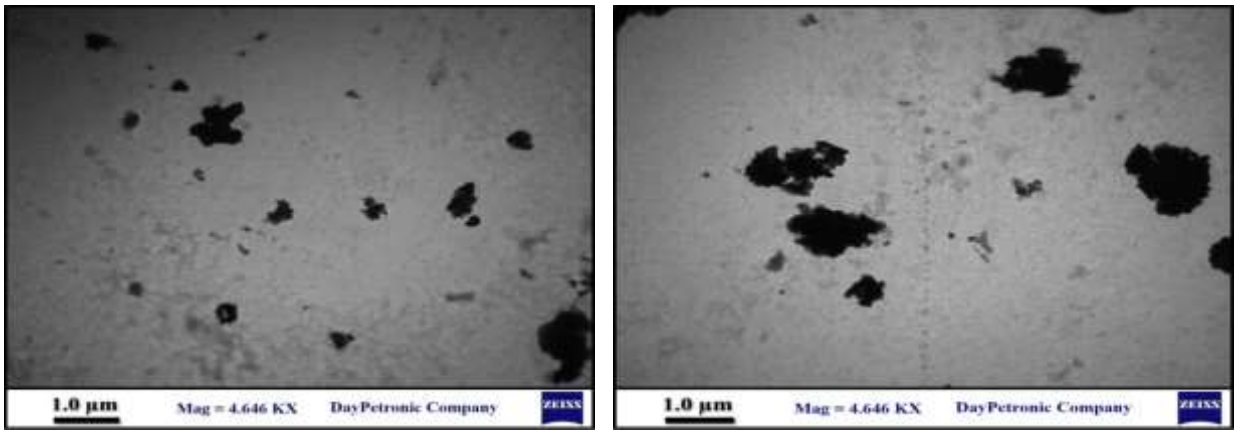


Figure 10. Transmission Electron Microscope of zinc nanoparticles (TEM)

4. Treatment of heavy metals

The polluted water was identified using a specific ratio of (Ag, Cd, Cr, Sb, Fe, and Pb) 2g to each element. Thereafter, a continuous technique of treatment was used. Ten milliliters of polluted water were added along with two grams of myrtle powder and the same method with zinc nanoparticles. After that, the shaking and mixing process was completed by placing the ingredients onto a magnetic stirrer. A portion of the sample was pulled out after the end flowrate, and the treatment % was calculated. The subsequent myrtle powder percentages are 62%. Comparatively, 72%, 82%, 54%, 64.50%, and 64.80% of the components were found. [24,25]. Show schemes 1,2.Show **tables 2,3,4,5**.

Table (2). Treatment percentages by continuous process by use zinc nanoparticle with extract myrtle plant

		Metal (ppm)		
	2gm	**Before**	**After**	**Percentage**
1.	Fe	10	3.8	62%
2.	Cr	10	2.8	72%
3.	Pb	10	1.8	82%
4.	Sb	10	4.6	54%
5.	Cd	10	3.55	64.50%
6.	Cu	10	3.52	64.80%

Table (3). Treatment percentages by continuous process by use zinc nanoparticle with extract myrtle plant

	4gm	Before	After	Percentage
1.	Fe	10	B.D.L	100%
2.	Cr	10	B.D.L	100%
3.	Pb	10	B.D.L	100%
4.	Sb	10	B.D.L	100%
5.	Cd	10	B.D.L	100%
6.	Cu	10	B.D.L	100%

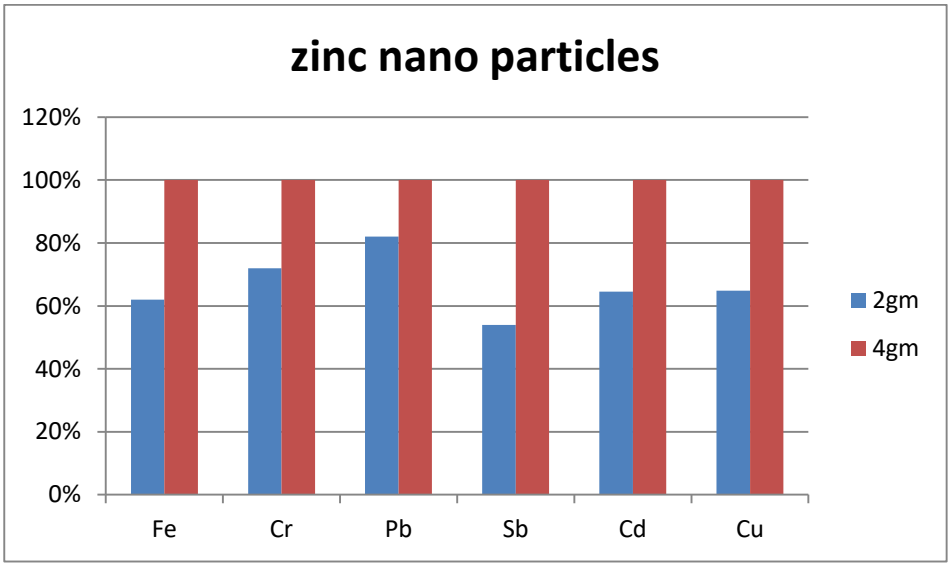


Figure 11. Using zinc nanoparticle to treatment water from some heavy metals

Table 4. Treatment percentages by continuous process by use myrtle powder

	Metal (ppm)		
2 gm	Before	After	Percentage
Fe	10	0.38	96.20%
Cr	10	1.6	84%
Pb	10	B.D.L	100%
Sb	10	0.63	93.70%
Cd	10	B.D.L	100%
Cu	10	0.94	90.60%

Table 5. Treatment percentages by continuous process by use myrtle powder

		Metal (ppm)		
	4 gm	Before	After	Percentage
1.	Fe	10	0.3	97%
2.	Cr	10	0.18	98%
3.	Pb	10	B.D.L	100%
4.	Sb	10	B.D.L	100%
5.	Cd	10	0.18	98%
6.	Cu	10	0.26	97%

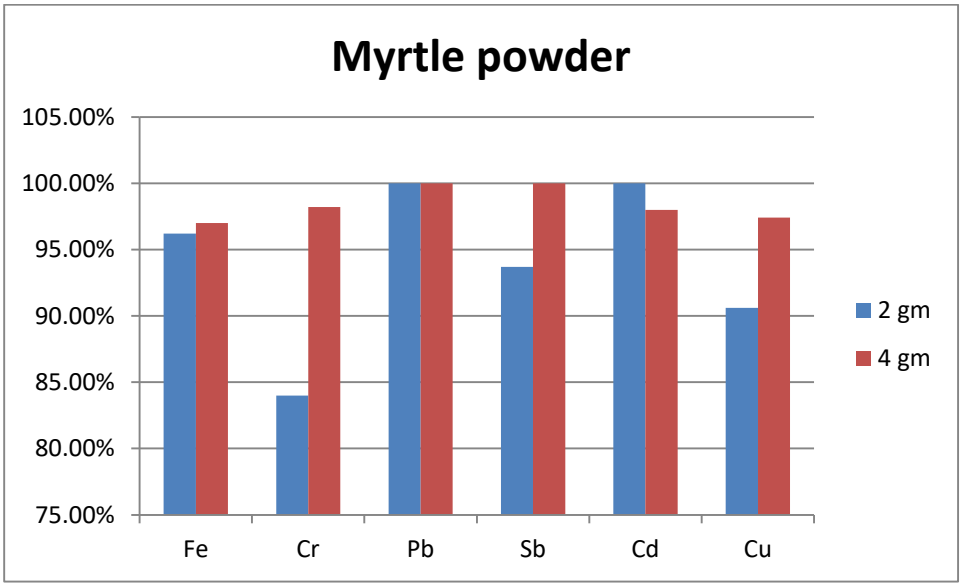


Figure 12. myrtle plant to treatment water from some heavy metals

5. Conclusion

By utilizing zinc nanoparticles, which were in turn manufactured using zinc sulfate as a starting material and whose creation was proven by the following methodology, we were able to successfully treat water in this study using ecologically acceptable techniques: SEM, TEM, EDX, FTIR, UV -Visible. Then, we treated the contaminated water due to heavy metals using continuous process by flowrate polluted water with myrtle powder and zinc nanoparticle with extract myrtle plant, We found that myrtle powder waspreferred to zinc nanoparticle.

6. Acknowledgments

Department of Chemistry, College of Science for Women, University of Baghdad, Prof. Dr. Abbas Ali Salih Al-Hamdani, and Ministry of Higher Education & Scientific Research & Science and Technology/ Directorate of Environment & Water.

7. Conflicts of Interest

- I hereby confirm that all the Figures and Tables in the manuscript are mine. Besides, the Figures and images, which are not mine, have been given the permission for re-publication attached with the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

8. Author's declaration:

Abbas Al- Hamdani presented the idea, analysis, discussion of the results and writing of the manuscript. Suzan Muslim abdullah contributed to the design and implementation of the research, laboratory work, Farqad Abdullah Rashid, Labeeb Ahmed Al-Zbaidi, Suha Mohamed Ibrahim verified the analytical methods and discussed the results and contributed to the final manuscript.

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