Summary

This thesis focused on studying the preparation, characterization, and spectroscopic studies of noble metals (gold and silver) and some magnetic nanoparticles (iron and cobalt) with different particles size. Besides, examine the effect of our prepared nanoparticle samples on decreasing the concentration of nickel elements in water. To be informed, this thesis is containing four chapters, where the first one displays a general introduction of nanomaterials with some literature reviews related to our studies. The second one is explaining the mathematical expression of characterizing our samples, while the third chapter exposes the experimental methods of nanoparticle preparation, including used instrumentation devices. Eventually, chapter four discusses the outlined results in the whole thesis.

Chapter 1

This chapter is divided into two main parts, which is a general introduction of nanomaterials and literature review. The first part is subdivided into several sections beginning with a historical overview of nano and some definitions of nanomaterial terminologies. Follow that, classification of nanomaterials according to their dimensions. Besides, the main factor which affects on nanoparticle properties as surface energy and quantum size effect was explained including the mechanical, magnetic, and optical properties. In addition, the general methods of nanomaterials preparation were presented in this chapter with both types, which is either top-down method or bottom-up method involving physical and chemical fabrication techniques as ball milling, chemical vapor deposition, sol-gel, and laser ablation. The fabrication also illustrates metal and magnetic nanoparticle preparation. At the end of this part, the application of nanomaterials in agriculture, food, medicine, energy, and water remediation was demonstrated.

The second part of this chapter outline a number of previous researches regarding of synthesized method for gold, silver, iron, and cobalt nanoparticles and their application in environments. Furthermore, an objective plan was evident at the end of the chapter.

Chapter 2

This chapter clarifies the theoretical background and mathematical basics for measurement device that utilized in characterization purpose in our prepared samples. Starting with introduction of light radiation passing through theoretical electromagnetic radiation. Follow that, an explanation of ultraviolet-visible spectroscopy concept and discussion of theoretical absorbance light by Beer-Lambert's law. Then the theory of UV electronic transition spectroscopy was demonstrated. In addition, The principle of transmission electron microscope technique was discussed with details information about electron beam generating and transferring through specimen as well as the theoretical consideration of x-ray diffraction was mentioned with details configuration of Bragg's law. Last of all, the basics of infrared spectroscopy was represented with a mathematical proof of absorbing spectra and stretching vibrations. The normal vibration modes of infrared were also illustrated in this chapter.

Chapter 3

This chapter was opened with chemical materials used in our preparation samples. Afterward, the methodology of nanoparticles synthesized was demonstrated. In the last of this chapter, the utilized characterization techniques were illustrated.

It begins with gold nanoparticles methodology, AuNPs were prepared by using a constant concentration of gold chloride hydrate $HAuCl_4.H_2O$ and different

concentrations of lemon extract. In contrast, silver nanoparticles AgNPs were synthesized with a various ratio of silver nitrate $AgNO_3$ and constant quantity of lemon extract. On the other hand, the iron nanoparticles FeNPs coated with chitosan was prepared with a different molar ratio of iron salt ($Fe^{3+}: Fe^{2+}$) and fixed concentration for both chitosan and sodium hydroxide $NaOH$. While the cobalt nanoparticles CoNPs were synthesized by adding equivalent ratio of cobalt salt $CoCl_2.6H_2O$ and various concentrations of sodium hydroxide $NaOH$. Follow that, four characterization techniques of prepared nanoparticles covering explanation of devices parts; these devices involve ultraviolet-visible spectroscopy, transmission electron microscope, x-ray diffraction, and Fourier transform infrared spectroscopy.

Chapter 4

In this chapter, the obtained results from prepared samples were discussed and interpreted. The results of UV-Vis spectroscopy for gold nanoparticles AuNPs were demonstrated in range (300 nm – 900 nm) with surface plasmonic resonance SPR band position appeared at wavelength 564 nm, 556 nm, and 548 nm. There is an inverse relation between lemon extract and band position SPR it is shifted to lower wavelength (blue shift); This shift indicates decreasing particle size with increasing lemon extract. While the UV-Vis measurement of silver nanoparticle AgNPs illustrated in a range of (320 nm – 890 nm) representing surface plasmon resonance SPR appeared at wavelength 432 nm, 452 nm, and 448 nm. The recorded notes is wavelength increasing with adding more concentration of $AgNO_3$ and then decrease again. The increasing of AgNPs wavelength is interpreted as the silver nanoparticles aggregate Ag atoms by reducing Ag^{+} ions into nanoscale so its particle size increase with increasing $AgNO_3$ then shifted to red-shift, and the extra amount of precursor cause what named blue shift due to new nucleation centers, which would appear as really small metal NPs. On the contrary, the UV-Vis of iron nanoparticles FeNPs

were characterized in the wavelength range (205 nm – 800 nm) with absorption peak appeared at 336 nm, 340 nm, and 344 nm. There was a direct relationship between increasing iron salt ratio and wavelength shifted (redshift) as traditionally known, the particle size and wavelength position have a direct relation. Hence of that, we interpreted increasing in wavelength has no doubt increasing in particle size due to increasing ions in solution, which allows for more nucleation. Furthermore, the results of UV-Vis spectra of prepared cobalt nanoparticles CoNPs were measured using spectral wavelength in a range of (250 nm – 800 nm) has an absorption band appeared at 520 nm, 548 nm, and 528 nm. The increasing and then decreasing again in wavelength of cobalt samples is interpreted as, the increasing in wavelength lead to increase in particle size due to the increasing sodium hydroxide in solution, which acts in nanoparticle formation, and the decreasing again is maybe due to some nanoparticles transfers to nanorod and nanofiber, the difference in band position indicating of forming CoNPs in different sizes.

The whole prepared nanoparticles were characterized via high-resolution transmission electron microscope HR-TEM, and their average particle size was estimated. The HR-TEM of AuNPs is shown spherical shapes with other different geometrical shapes as trigonal, hexagonal, trapezoidal, pentagonal, rectangular, small rod, and oval. The average particle size of AuNPs for spherical shapes was calculated according to Gaussian distribution, and it found to be 54 nm, 22 nm, and 28 nm. These results notified that some results agree with UV-vis while others not, which may be owing to nonuniform shapes beside spherical shapes that appeared in visualized images in the same sample. In contrast, the HR-TEM of AgNPs shows a random distribution with almost spherical shapes and smooth edges it also has other geometrical shapes such ellipsoidal and hexagonal. The average particle size of AgNPs according to Gaussian distribution for spherical particles in image and it

found to be 31 nm, 15 nm, and 28 nm. This result is incompatible with surface plasmon band position of UV data it could attribute to the obtained aggregation during visualize TEM. On the other hand, the HR-TEM of FeNPs were characterized after and before drying. The results demonstrate a random distribution of non-uniform and homogenous particles besides other spherical shapes. The average particle size of spherical shape was 22 nm, 17 nm, and 32 nm for iron after drying, as well as it has 10 nm, 9 nm, and 18 nm for iron before drying. The result clarifies that the FeNPs after drying were larger particle sizes than FeNPs before drying; this probably due to the aggregation of FeNPs after heating has happened. Moreover, the visualization image of HR-TEM for CoNPs show a various geometrical shape in the first sample with spherical, ellipsoidal, pentagonal, and hexagonal in addition to some aggregation particles. This sample has average particle size 27 nm from Gaussian distribution. The morphology of the last two samples appeared as nanorod and nanofiber with an aspect ratio between 5.2 ~ 8.5 nm and 5.6 ~ 8.33 nm. It also has ambiguous particles in some regions; it almost does not have spherical shapes that why the average particle size was ignored in both samples.

The x-ray diffraction result of prepared iron nanoparticles samples was characterized in $2\theta°$ with a range between $(25° \sim 60°)$. Its shown that the diffraction pattern of FeNPs has a direct relationship between iron salt ratio and peaks intensity, as the iron salt increase the diffraction pattern peaks be clear and sharp with high intensity. Moreover, the average crystalline size of FeNPs was calculated using Scherrer's equation, and it found to be 38.2 nm, 34.1 nm, and 49.5 nm. Equally important, the XRD pattern of prepared cobalt nanoparticles were measured in $2\theta°$ with a range between $(30° \sim 60°)$. The result shows that there is a direct relationship between concentration of sodium hydroxide and peak intensity, as the concentration of sodium hydroxide increase the diffraction pattern intensity increase. In addition,

the crystalline size of CoNPs was estimated via Scherrer's equation, and it found to be 32.9 nm, 31.3 nm, and 41.5 nm.

The results of Fourier transform infrared spectroscopy of gold nanoparticles capped by lemon extract have observed peak at 621 cm^{-1}, 609 cm^{-1}, and 602 cm^{-1} assigned for Au – O stretching vibration. While the FTIR of silver nanoparticles capped by lemon extract have peaks at 567 cm^{-1}, 592 cm^{-1}, and 587 cm^{-1}, which assigned for Ag – O stretching vibration. In addition, the observed peak in iron nanoparticles sample capped by chitosan has appeared at 642 cm^{-1}, 647 cm^{-1}, and 650 cm^{-1} was assigned for Fe – O stretching vibration while the cobalt nanoparticles have peaks at 512 cm^{-1}, 528 cm^{-1}, and 532 cm^{-1} assigned for Co – O stretching vibration. As a matter of fact, the oxygen here comes from capping materials. The theoretical results of prepared nanoparticles samples were calculated, and it found to be 757.04 cm^{-1}, 778.76 cm^{-1}, 824.33 cm^{-1}, and 819.43 cm$^{-1,}$ which assigned to Au – O, Ag – O, Fe – O, and Co – O respectively. It noted that there are differences between theoretical and practical results, which interpreted as a consequence of presence nanoparticles to be coordinated with other functional groups. Every sample had different peaks which is relating to the functional groups existing in capping of our samples as C – H, N – H, C – C, C = O, and C – C as well as it has similar peaks at around 3400 cm^{-1} assigned to O – H functional group, which relates to presented water in samples.

The effect of prepared nanoparticles samples in decreasing nickel concentration was studied by applying them into WILKERSON filter element then pass different concentrations of nickel solution through the filter. It noted that there is a relationship between absorbance intensity and concentration, as the concentration of nickel increase the absorbance increase according to Beer-Lambert law. Besides, the absorbance intensity of nickel solution decrease after using

nanoparticles as impregnated onto membrane filter. Important to note, at low concentration of nickel element, the AgNPs and CoNPs are not active as much as AuNPs and FeNPs, which is owing to electronegativity of elements. In contrast, at high concentration, the CoNPs is more efficient than AuNPs, FeNPs, and AgNPs, respectively. This means it could be utilized prepared nanoparticles in water purification from heavy metals.