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Green Synthesis of Quinoline Metal Nanostructures Using Saffron and Lemon Extracts Applied in Organic Light Emitting

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Abstract

The control over size, shape, and morphology, combined with mild conditions of processing parameters (mainly in terms of temperature and pressure), are important conditions to be fulfilled for sustainable and cost-efficient production of functional inorganic materials. Environmentally friendly methodologies for the controlled synthesis of inorganic nanostructures are a noticeably stimulating research field since this encompasses not only the control of the final composition but also, and more importantly, a fine tuning of the obtained materials in terms of crystallinity (crystalline phase, crystallite size), shape, morphology. In this research, we investigated the green synthesis of organic-metal complex nanoparticles to be used in organic light-emitting diodes using saffron and lemon extracts. Saffron and lemon extracts were used as surfactants for bio-production of Zinc and Cadmium complex nanoparticles. The crystalline structures of Zinc and Cadmium complex nanoparticles were confirmed by X-ray powder diffraction (XRD). The morphology and the presence of Zinc and Cadmium complex nanoparticles were also analyzed and confirmed by SEM and EDAX. Then, the functional groups of these nanoparticles were studied using FTIR analysis. The optical properties of Zinc and Cadmium complex nanoparticles were confirmed by UV-Vis spectrometry, as well as the luminescence behavior of synthesized Zinc and Cadmium complex nanoparticles were confirmed by photoluminescence spectra (PL) in order to apply OLED as light-emitting and electron transporting layers.

1. Introduction

Nanotechnology is an integral part of our reality. It is hard to imagine modern life without materials, especially nanomaterials. They can be found in a variety of human activities, including food production and preservation, medicine and biotechnology, computers, telecommunications, transportation, and space exploration. Unfortunately, the production of materials, including nanomaterials, as a chemical process, inevitably results in environmental pollution. Due to the growing trend of materials (nanomaterials) production, problems associated with the environment are becoming more and more apparent, and therefore finding radical solutions to meet the requirements is a priority. Hence, we increasingly need a low-cost method without the production of toxic substances as well as without environmental damages. One method to produce nanoparticles is bio-production (green-production). Nowadays, this method is of great interest to produce nanoparticles. For example, one effort made to biosynthesize nanoparticles, is the production of nanoparticles by microorganisms. Microorganisms can solve problems related to the synthesis, and simultaneously, stabilization of nanoparticles in mild conditions. For example, the chemical synthesis of gold nanoparticles may lead to the presence of some toxic species being adsorbed on the surface of nanoparticles that may have adverse effects in medical applications. Synthesis using microorganisms can potentially solve this problem. Various green methods have been developed to synthesize nanoparticles. One reason is that synthesis of metallic nanoparticles using green agents has attracted much attention due to different optical, chemical, photo electrochemical and electronic properties. Green synthesis of nanoparticles is also a clean, non-toxic, and environmentally friendly method involving various organisms such as bacteria, fungi, yeast, and plants [1-12].

In this study, we chose organic-metal complexes to be used in organic light-emitting diodes for green synthesis using saffron and lemon extracts, because the use of organic-metal complexes in the fabrication of organic light-emitting diodes is increasing dramatically. We use these complexes as the electron transferring layer or light emitting layer. Therefore, we investigated the green synthesis of organic-metal nanoparticles to be used in organic light-emitting diodes using saffron and lemon extract. Extracts of saffron and lemon were used as surfactants for bio-production of Zinc and Cadmium complex nanoparticles. Finally, structural properties, morphology, the presence of complexes and functional groups were studied using XRD, SEM, EDAX and FTIR analysis. Their optical properties were also investigated by UV-Vis and PL in order to utilize organic light emitting diodes as electron transferring as well as light emitting layers.

2. Experimental

2-1. Materials

Zinc nitrate, Cadmium and trace Quinoline were purchased from Sigma Aldridge Company and the solvents were purchased from Merck Company.

2-2. Synthesis

Materials extracted from plant cells, using solvents such as water or organic solvents, are called extracts. In general, extraction is applicable in two ways of using heat as well as without using heat. If the materials inside the plants are sensitive to heat, then it is better to apply the second method. Extraction using heat is performed with a device called Soxhelt, and extraction without using heat is performed with a device called Percolate. In this study, we done the extraction using a Soxhelt apparatus, in such a way that the sample was poured into its tank, and a desired solvent was poured into its balloon, which was evaporated by the heat of the solvent and poured onto the sample. When the Soxhelt tank was full, it returned to the balloon through a thin glass siphon, thus completing the cycle.

For the green synthesis of the Zinc and Cadmium complexes, we first dissolved each of Zinc and Cadmium nitrates and Hydroxyquinoline in 100 ml of water, separately. Then stirred each one individually for 1 hour using a magnetic stirrer in order to be well dissolved and to obtain a uniform solvent. Then, we mixed Zinc complex and Hydroxyquinoline solutions (Cadmium complex and Hydroxyquinoline solutions) in one container and placed the mix in a water bath at 50 °C and stirred with a magnetic stirrer for 1 hour in order to allow it to produce a uniform solution. In continue, we needed to add the saffron extract to the solution. To do this, we used a decanter and add the extract to the solution drop by drop. Then we autoclaved them at 180 °C for 15 hours to evaporate the solvent and obtain crystal complexes. To synthesize the complexes using lemon extract, we repeat the process except that we added 0.5 ml of lemon extract instead of the saffron extract. In this way, the divalent complexes were synthesized using Hydroxyquinoline ligand and lemon and saffron extracts (Fig. 1 shows a schematic of how to synthesize Zinc and Cadmium complexes by saffron and lemon extracts).

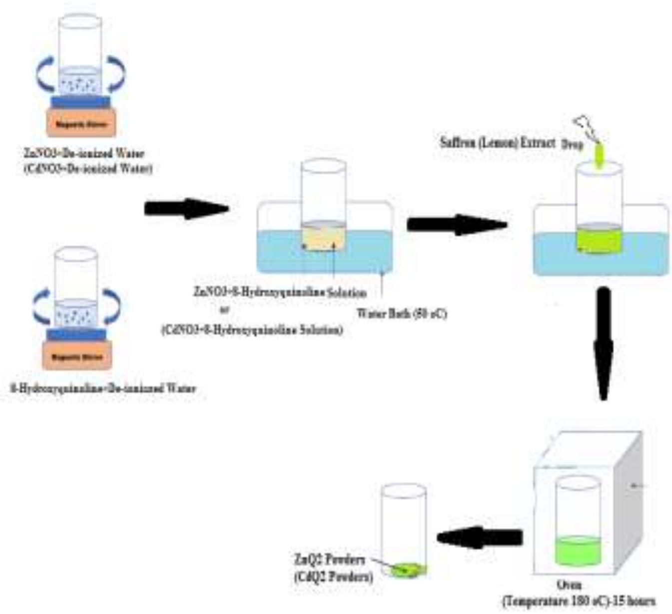

Fig. 1. Schematic of how to synthesize Zinc and Cadmium complexes by saffron and lemon extracts

3. Result and discussion

3-1. Structural characterization

Crystal structure of complexes synthesized by lemon and saffron extracts, shown in Figs. 2 and 3, were measured using Philip X'pert X-ray diffractometer having $\lambda = 1.5418$ Å, Cu Kα radiation at room temperature and at angles of 2θ between 5 and 100 degrees. It can be seen from the diffraction patterns of the complexes that, the diffraction patterns of Znq_2, Cdq_2 complexes synthesized by saffron extract (Fig. 2) have almost the same crystalline structure. The main diffraction peaks of Znq_2 complex (JCPDS 48-2116) at 2θ are correspond to (102), (112), (311), (100), (610), and (802) plates, and for the Cdq_2 complex, they are corresponding to (301), (402), (203), (413), (311), (324), (100), (405), (610), and (802) main plates [13-14]. All the sharp peaks of the diffraction patterns of the synthesized complexes are in a good agreement with the literature [15-18] that synthesized these materials using methanol and without any extract. This diffraction pattern also shows a very good crystallinity for these complexes.

It is also obvious from the diffraction patterns of Znq_2 and Cdq_2 complexes synthesized by lemon extract (Fig. 3) that, the crystal structure of Znq_2 complex using lemon extract at 2θ angles corresponds to (302), (203), (112), (311), (404), (405), and (802) plates and for Cdq_2 complex using lemon extract, it corresponds to (200), (202), (301), (401), (303), (015), and (802) main plates. By comparing the groups of plates at different angles for the lemon and saffron extracts, we can see that the structures of Zinc and Cadmium complexes have grown in different phases when using lemon and saffron extracts. It can also be found from literature that for Zinc and Cadmium complexes using lemon extract, mostly the quinoline-related plates are formed [19-22].

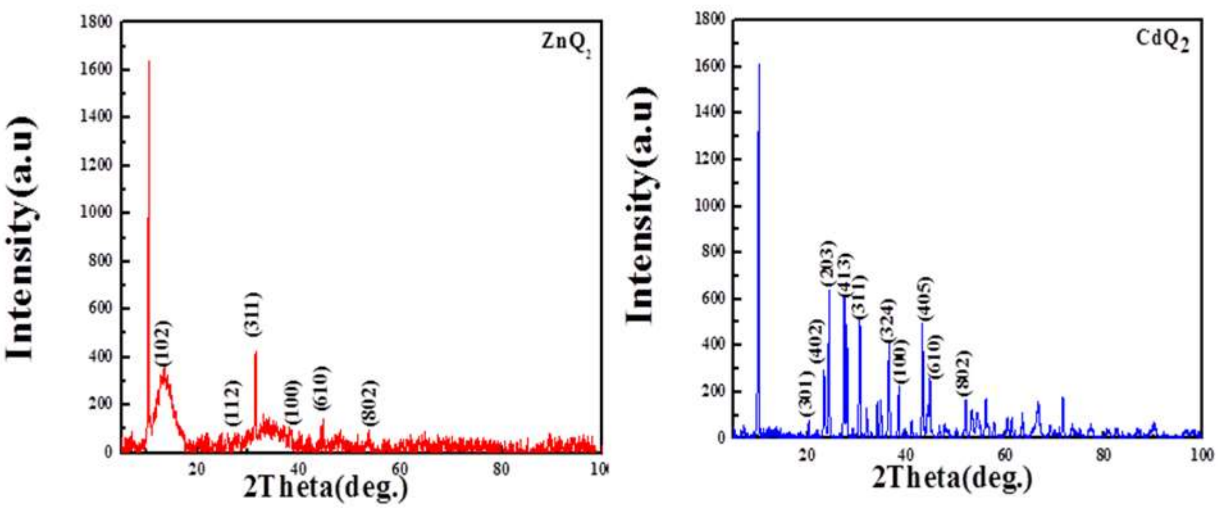

Fig. 2. X-ray diffraction patterns of Cadmium and Zinc complexes synthesized by saffron extract

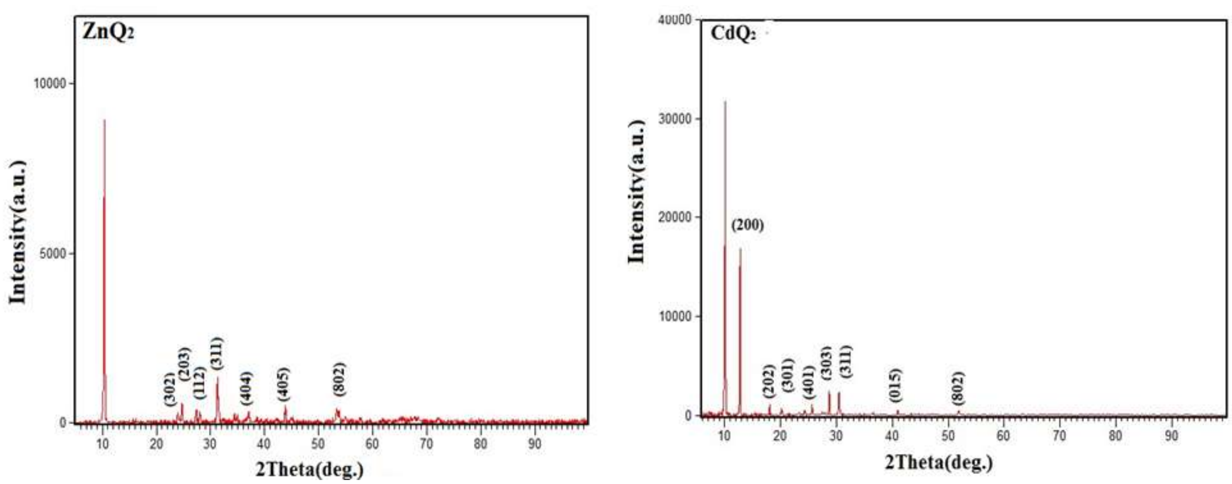

Fig. 3. X-ray diffraction patterns of Cadmium and Zinc complexes synthesized by lemon extract

3-2. Morphology

To obtain the morphology of Znq_2 and CdQ_2 bivalent complexes using saffron and lemon extracts, the final product was analyzed by SEM. Figures 4 and 5 show the SEM images of bivalent Zinc and Cadmium complexes using lemon juice and saffron extracts, which are consist of nanostructures (Nano sheets) at different magnifications. These Figs. Also show the nanostructure images of bivalent Zinc and Cadmium complexes using saffron extract having a plate thickness of about 30 to 60 nm and a diameter in the range of 800 nm to 1500 µm. They also show plates of Zinc complex using lemon extract as well as Nano spheres with a diameter of 500 nm. Figures 6 and 7 show the EDX elemental analysis spectra of the bivalent Zinc and Cadmium complexes using lemon juice and saffron extracts. As can be seen, the samples have acceptable purity and only the peaks of Oxygen, Cadmium, Zinc, Carbon and Nitrogen are appeared.

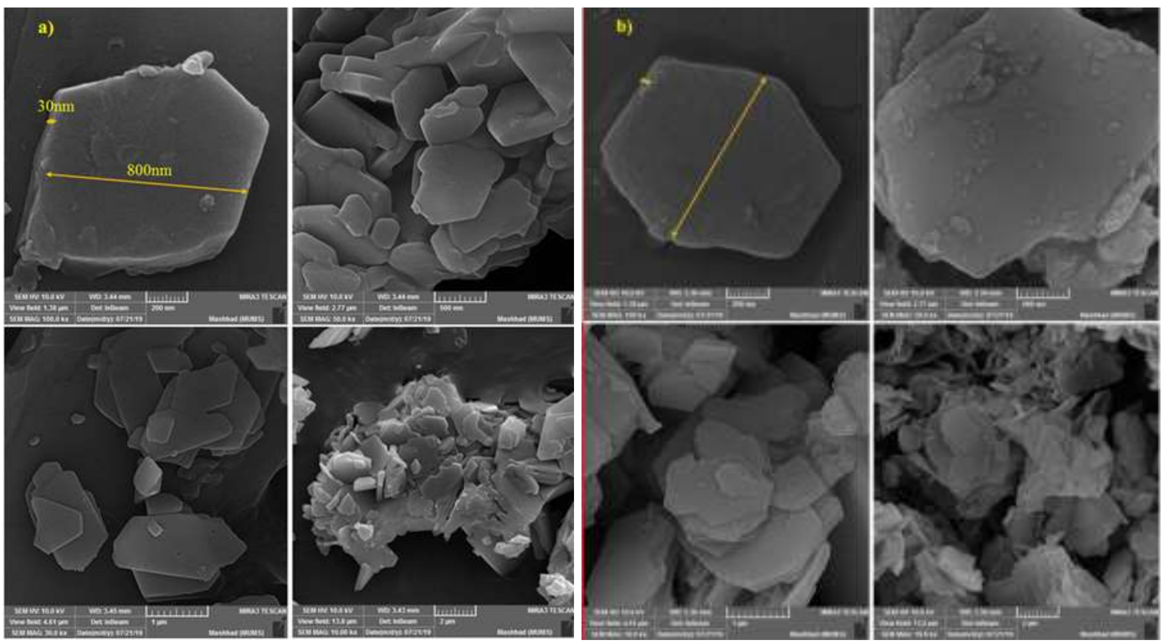

Fig. 4. SEM images of (a) ZnQ_2 and (b) CdQ_2 complexes using saffron extract

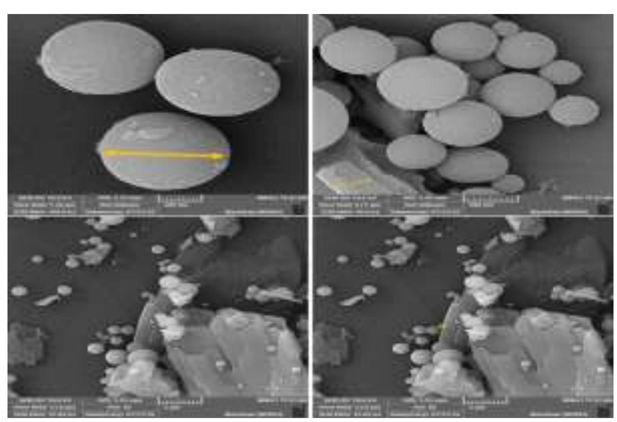

Fig. 5. SEM images of ZnQ_2 complexes using lemon extract

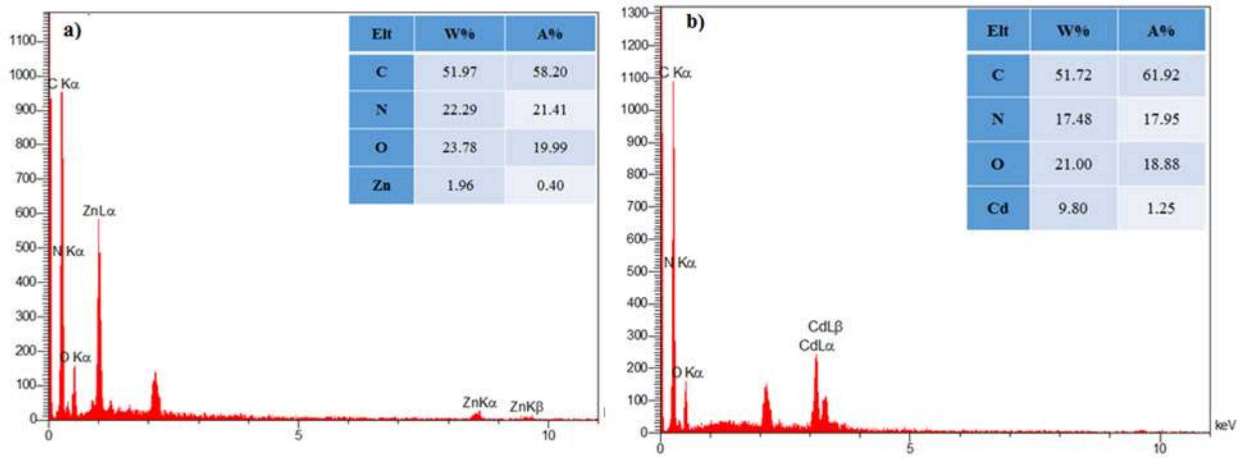

Fig. 6. EDAX spectra of (a) Zinc and (b) bivalent Cadmium complexes using saffron extract

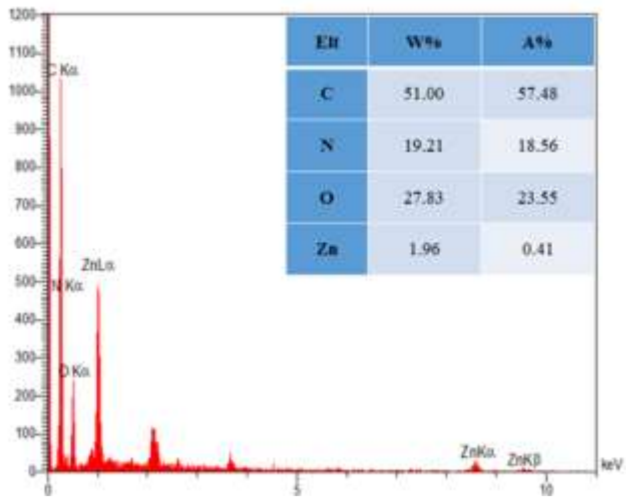

Fig. 7. EDAX spectrum of Zinc complex using lemon extract

3-3. Functional groups

In order to obtain bonds and functional groups formed in the synthesis of complexes using lemon and saffron extracts, FT-IR spectra were measured using KBr plate technique. As can be seen from Figures 8 and 9, the spectrum ranges from 200 to 4000 cm^{-1}. The tensile vibrations of the central metal ions for the M-N and M-O bonds, herein Zinc and Cadmium are referred to as M, are concentrated in the range of 400 to 600 cm^{-1}. Also the band vibrations belong to the quinoline group ranges from 700 to 1200 cm^{-1}, the band vibrations in the range of 600 to 700 cm^{-1} are related to the modified interplanetary ring. We also see band vibrations of C = N, tensile band vibrations of C-O, aromatic tensile band vibrations of C = C, C-C, C-N and C-C-H in the range of 1200 to 2300 cm^{-1}. The above results are in a very good agreement with the literature. Peaks in the range of 2500 to 3700 cm^{-1} represent the vibrational bands associated with the O-H bond.

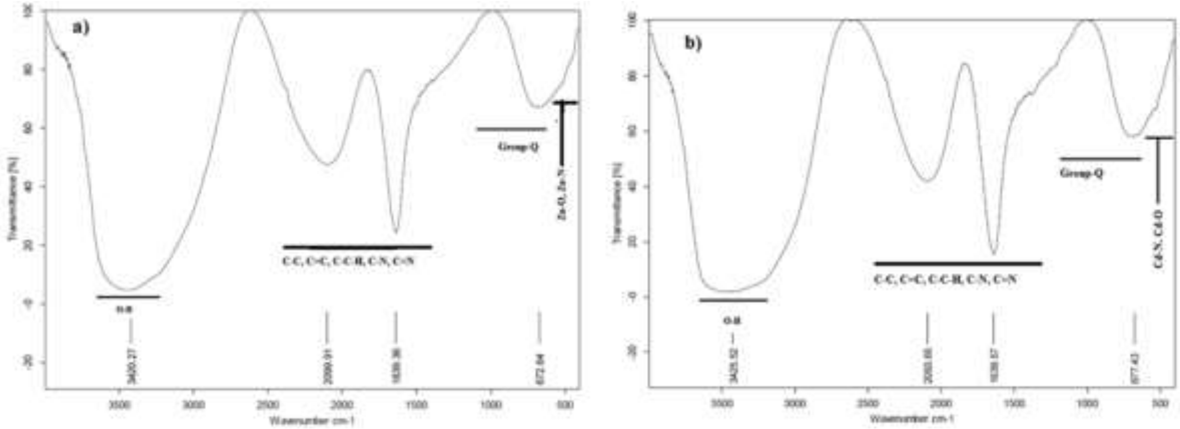

Fig. 8. FT-IR spectra diagrams of (a) Zinc and (b) Cadmium complexes synthesized by saffron extract

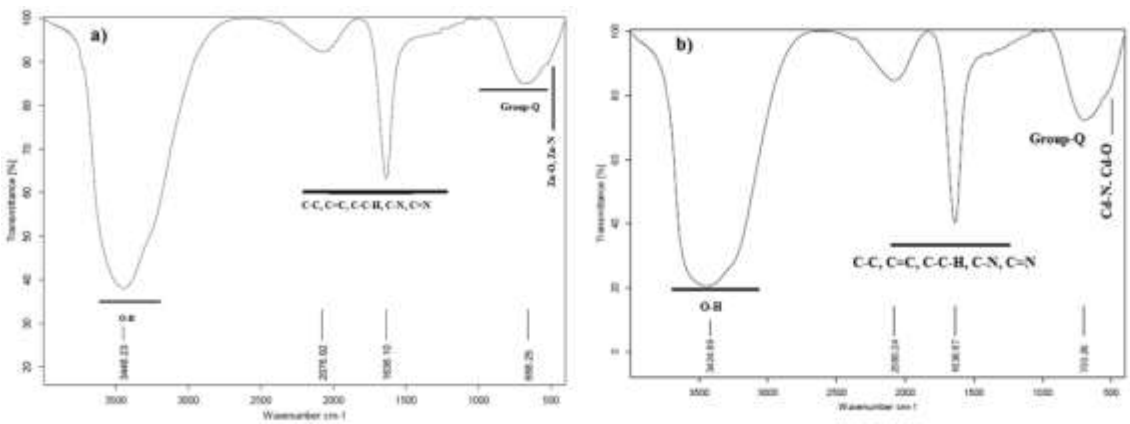

Fig. 9. FT-IR spectra diagrams of (a) Zinc and (b) Cadmium complexes synthesized by lemon extract

3-4. Optical properties

In order to find the internal vibrations of the synthesized complexes, we take an absorption spectrum. Also, we take a 360 nm excitation wavelength photoluminescence spectrum, to confirm their luminescence.

3-4-1. Absorption

Figures 10 and 11 show the UV-Vis absorption spectra of the divalent complexes synthesized by hydroxy quinoline ligand together with saffron and lemon extracts. As we can see from figures, the absorption peaks for the divalent complexes synthesized by the hydroxy quinoline ligand (Znq_2, Cdq_2) are in the range of 250 to 700 nm. The maximum absorption peaks for Znq_2 and Cdq_2 complexes were 306.87, 320.34 and 312.88 for saffron extract and 306.87 and 306 nm for lemon extract, respectively. The bands having these wavelengths are related to electron transferring from the HOMO orbital of the Phenoxide ring to the LUMO orbital of the peridine ring due to the π-π* bands from the hydroxy quinoline unit of the Cadmium and Zinc complexes. The results from a comparison between the absorption spectra of Zinc complex and Cadmium complex for both lemon and saffron extracts show that the π-π* band peak of Zinc complex is significantly stronger than that of Cadmium complex sample. The stronger π-π* band of Zinc complex provides a more efficient electron transferring path than that of other samples. Also, other band peaks were observed at 358.36 and 359.49 nm for the Znq_2 and Cdq_2 complexes using saffron extract and at 359.611 and 364.36 nm using lemon extract for the n-π* band, respectively.

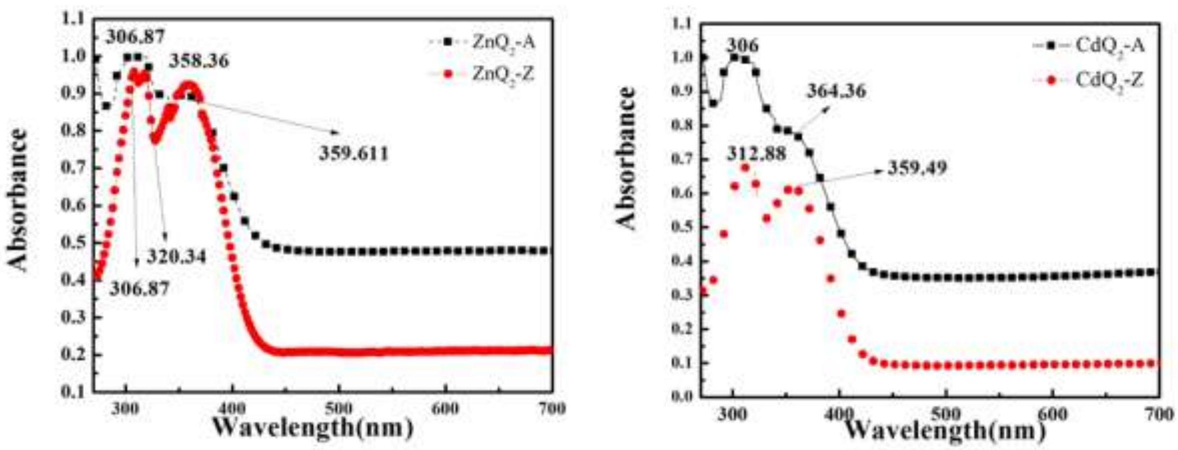

Fig. 10. Comparative absorption spectra (UV-Vis) of (a) Zinc and (b) Cadmium complexes synthesized by saffron and lemon extracts

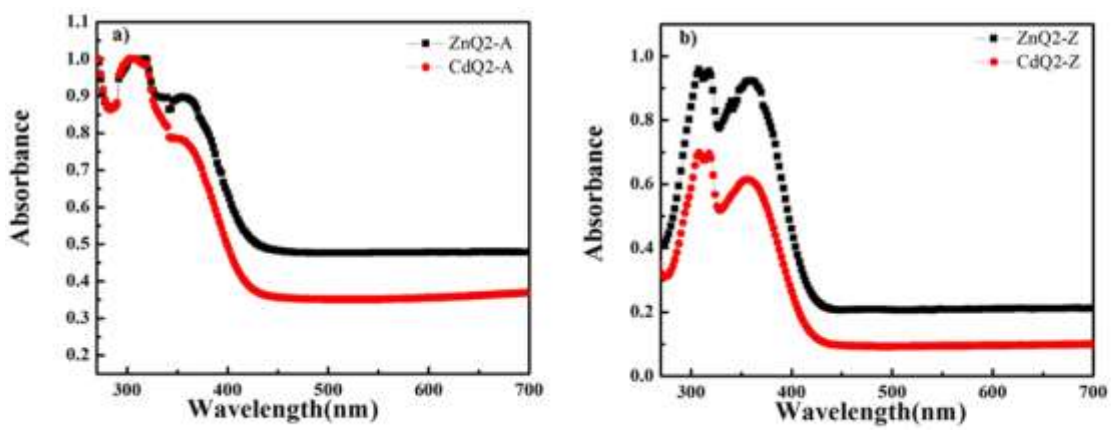

Fig. 11. Comparative absorption spectra (UV-Vis) of Zinc and Cadmium complexes synthesized by (a) lemon extract and (b) saffron extract

3-4-2. Photoluminescence

Figures 11 and 12 show the photoluminescence (PL) spectra of the divalent complexes synthesized by hydroxy quinoline ligand together with saffron and lemon extracts. As we can see from photoluminescence (PL) spectrum, the maximum intensity of photoluminescence spectra for Znq_2 and Cdq_2 are 515.41, 489. 493, and 513 nm for saffron extract as well as 507.57 and 510.48 for lemon extract, respectively, in the range of green light, which are suitable for the manufacture of organic green light-emitting diodes (OLED), liquid crystal fluorescent displays (PLLCD), and solid-state lighting applications. It was also observed that the fluorescence intensity of Znq_2 complexes is significantly lower than that of Cdq_2 complexes. This is because of increasing the atomic number of central metal ion, which is known as the effect of the heavy atom, so that as the atomic number of the central metal ion increases, the fluorescence intensity of the material will decrease and we will see a shift toward red wavelengths [23]. Here, complexes synthesized using saffron extract have significantly higher fluorescence intensity than complexes synthesized using lemon extract, which may be due to impurities or poor formation of the complex [24-26].

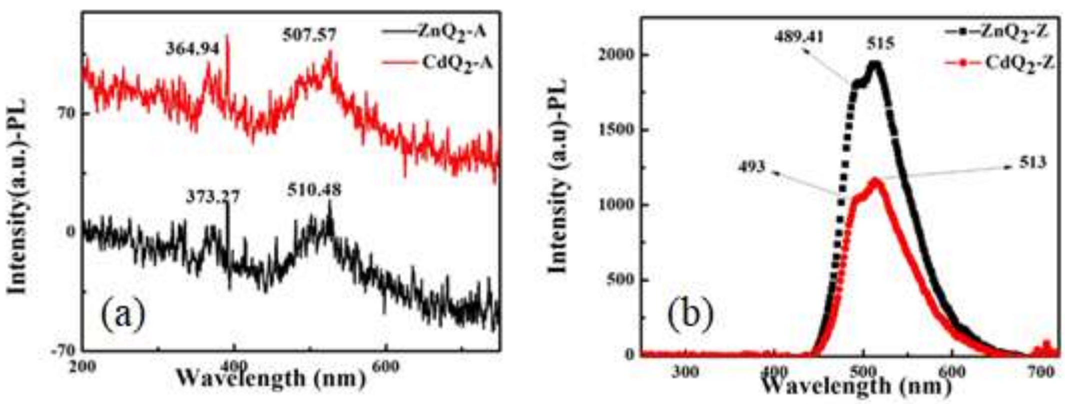

Fig. 12. Comparative photoluminescence (PL) spectra of Zinc and Cadmium complexes synthesized by (a) lemon and (b) saffron extracts

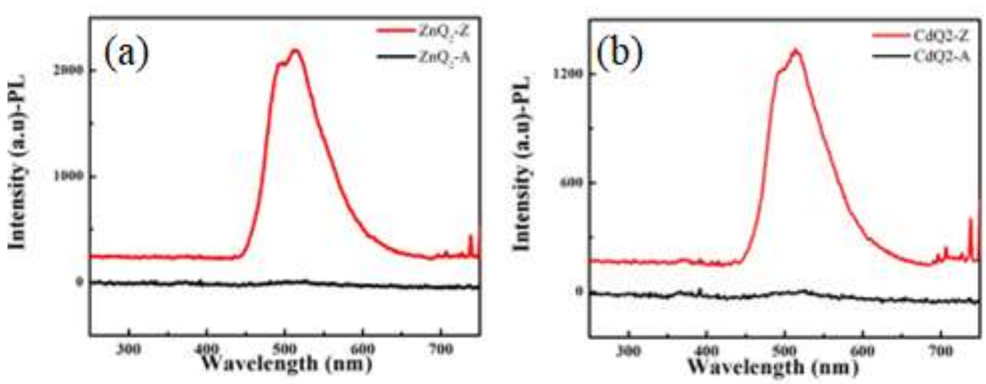

Fig. 13. Comparative photoluminescence (PL) spectra of (a) Zn complex and (b) Cadmium complex, synthesized by saffron and lemon extracts

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