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Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

SYNTHESIS OF NIO NANOPARTICLES BY THERMAL DECOMPOSITION AT LOW-TEMPERATURE OF NEW *AQUA* (2-AMINO-6-METHYL PYRIMIDINE-4-OL AND ISOLEUCINE)NI(II) COMPLEX AND ITS ANTIMICROBIAL STUDY

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ABSTRACT

Aqua (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex has been synthesized from nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and 2-amino-6-methyl pyrimidine-4-ol (HP) as primary ligand and Isoleucine as secondary ligand. Synthesized complex has been characterized by elemental analysis, infrared (IR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy and differential thermal/thermogravimetric analysis (TG/DTA). Prepared complex, subjected to thermal decomposition at low temperature of 400°C in an oven, revealed a novel and simplistic synthesis of pure NiO nanoparticles with regular spherical particle. The structure of the NiO NPs product was elucidated based on (FT-IR), UV, TG/DTA, XRD, SEM, TEM. Moreover, the synthesized nickel oxide nanoparticles demonstrated remarkable antimicrobial activity.

Keywords: Ni(II) complex, Thermal decomposition, NiO nanoparticle, Antimicrobial activity.

1. INTRODUCTION

In recent years, nanotechnology has been captured a marvellous impetus in this rapidly emerging technology area by creating an abundance of scientific aim to compete with the daily challenges of growing technology [1-2]. The nanomaterials have been exploring the numerous scientific and technological interests with their varied applications and specific properties [3-5]. These properties are conferred because of their characteristics size, shape and surface area [6-11]. Recently, metallic nanoparticles (NPs) have attracted attention specially because of their distinctive physical and chemical properties. Their properties can be controlled depends on the preparation method. One of the main effects, which are evolved by controlling particle size, is their antimicrobial action [12, 13]. The antimicrobial activity of NiO NPs is known to be a function of surface area in close contact with microorganisms. For this reason, high surface area of NPs insure a vast range of reactions on the surface of microorganisms, stops the normal function of cells or results cell death [14]. Based on the literature, there are several methods for the preparation of NiO NPs reported as thermal decomposition [15], combustion [16], sol-gel [17] co-precipitation [18], spray pyrolysis [19], anodic arc plasma method [20], etc. The present study reports the facile straight forward synthesis; it has an advantage over other methods, as it is simple, rapid and energy-saving [21]. Herein we communicate the synthesis, characterization, and applications of NiO nanoparticle and its antimicrobial study. The starting complex and final NiO nanoparticles product before and after thermal decomposition were characterized based on Fourier transform infrared (FT-IR), ultraviolet-visible (UV-vis) spectroscopy, differential thermal/thermogravimetric analysis (TG/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The present study also reports, the direct thermal decomposition process of the desired complex precursor. It is one of the most important and straight forward strategies to access structurally elaborated and pure NiO nanoparticles with regular spherical particle. Moreover, we have studied the antimicrobial activity of Ni(II) complex and NiO nanoparticles.

2. EXPERIMENTAL

All the chemicals used in the current work were of the analytical grade and were procured from Aldrich, E. Merck and S.D. Fine-Chem Ltd. Nickel chloride hexahydrate was procured from E. Merck and was used

as obtained. All solvents used were of analytical grade. L-isoleucine was obtained from S.D. Fine-Chem Ltd. Mumbai. In contrast, 2-amino-6-methyl pyrimidine-4-ol was purchased from Sigma Aldrich imported from United State. Solvents ethanol, methanol, DMF, DMSO and Chloroform whenever used were distilled and purified according to standard procedures [22].

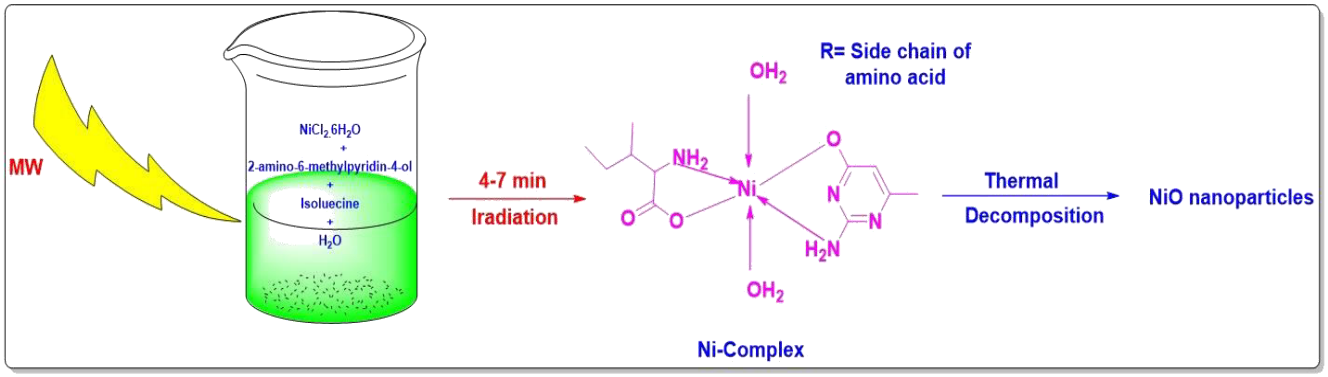

Fig. 1: Schematic Representation for the preparation of Ni(II) complex and NiO nanoparticles

2.1. Physical Measurements

Elemental analysis (C, H, N) was carried out on Thermo Finnigan Elemental Analyser model no FlASH EA 1113 series at IIT Bombay. Nickel content was estimated complexometrically by standard protocol [23-24]. Fourier transforms infrared spectra were recorded in the spectral range 4000-400 cm^{-1} on Perkin Elmer spectrum FT-IR model no 1500 at IIT Bombay. UV-vis spectra were recorded using a Perkin Elmer Lambda-950 UV-VIS spectrometer employing DMSO as a solvent in the range of 200-800 nm. Thermal Analysis were carried out in a controlled nitrogen atmosphere on a Perkin Elmer Diamond TG-DTA instrument. Microwave synthesis was performed in domestic microwave oven Model KENSTAR-OM20ACF, 2450MHz, 800W. The synthesized NiO NPs were characterized by scanning electron microscopy (SEM Hitachi S-4800) and X-ray diffraction (XRD- Bruker D 8 Advance X-ray diffractometer).

2.1.1. Synthesis of Ni(II) Complex by Microwave Method

An aqueous solution ($10cm^3$) of nickel chloride hexahydrate (237 mg, 1 mmol) was added in an aqueous solution (10 cm^3) of 2-amino-6-methyl pyrimidine-4-ol (HP) (124 mg, 1mmol). In the hot solution, an aqueous solution (10 cm^3) of an L-Isoleucine (HL) (131 mg, 1 mmol) was added with continuous stirring. The reaction mixture was kept in the microwave for about 4-7 min. The complex was obtained by raising the pH of the reaction mixture by adding an aqueous ammonia solution. The mixture was cooled. The solid complex obtained was filtered on suction pump and washed with ethanol and water [25].

2.1.2. Synthesis of NiO nanoparticles by thermal decomposition of Ni (II) complex

Approximately 0.5g of *Aqua* (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex was heated in an oven at 400°C for 30 min. During the reaction, the formation of brown color indicated the formation of NiO NPs. The resulting powder was cooled at room temperature and washed a few times with ethanol to eliminate residue; finally, the prepared NPs was dried in an oven.

2.1.3. Antibacterial Activity by Agar Cup Method

In agar cup method, single compound can be tested against many organisms or a given organism against various concentrations of same compound [26]. This method was found useful for liquid or semisolid samples and was used in the present work. In this technique, a plate of sterile nutrient agar was transferred with the chosen test strain to a height of about 5 mm and allowed to solidify and cut a particular cup of about 8 mm diameter from the centre of the plate with a sterile cork borer. Cup was filled with the test solution of well-known concentration, and the vessel was incubated at 38°C for 24 hour. The extent of growth inhibition from the verge of the cup was considered a measure of the given complex activity. Using some plates simultaneously, quantitatively examined the actions of some sample.

3. RESULTS AND DISCUSSION

3.1. Characterization of Metal Complex

The synthesis of Ni(II) complex may be represented as follows:

$NiCl_2.6H_2O + HP + HL \rightarrow [Ni(P)(L).2H_2O] + 2HCl + 4H_2O$

Where HP is 2-amino-6-methyl pyrimidine-4-ol and HL is –L-isoleucine. The prepared complex is light blue in colour, non-hygroscopic and thermally stable solids, indicating a solid metal-ligand bond. The complex is soluble to some extent in methanol, ethanol, chloroform, DMF and DMSO. The elemental analysis data of metal complex is consistent with their general formulation as 1:1:1, complex of the type [Ni(P)(L).$2H_2O$]. The molar conductance values of the complex in DMF at 10^{-3} M concentration are low (<1), indicating their non-electrolytic nature [27].

3.2. UV Spectra

The electronic spectra of the metal complex in methanol recorded in the U.V. region display intra ligand and charge transfer transitions. Spectra show three transitions in the range 203-263 nm, 337 nm and 384-386 nm, which can be assigned to $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ and the charge transfer transitions (LMCT) from ligands to the metal, respectively. Two transitions around 560-600 nm and 820-840 nm may be attributed to d-d transitions, which are characteristic of transition metal complexes [28-31]. It was clearly noticeable that the UV-vis spectrum of the NiO nanoparticles is quite different from that starting complex, confirming the strong band that appeared at 350 nm is due to NiO nanoparticle, not Ni(II) complex [32,33]. In addition, the UV-vis spectrum of a commercial bulk NiO powder does not show any observable absorption band [32].

3.3. FTIR Spectra

IR spectrum, in particular, shows five prominent bands of characteristic absorptions in the range 3400-3600, 2940, 1267-1212, 600-590 and 510 cm^{-1}, which can be assigned to, coordinated-H_2O, N-H, CO, N-O and M-N stretching vibrations, respectively. All bands of the *Aqua*(2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex disappeared after thermal decomposition at 400°C and a strong band at around 440 cm^{-1} is observed, which was assigned to the Ni-O stretching of the NiO NPs [33-37].

3.4. Thermal Studies

The synthesized complex thermal properties TG/DTA was investigated under an open atmosphere in the 0-800°C temperature range and heating rate of 10°C/min. Thermograms show the loss in wt. corresponds to two water molecules in the temperature range 104-185°C, followed by wt. loss in the range 286-522°C, which is about equal to the algebraic sum of wt. loss due HL and HP moieties [38-40]. The DTA of the complex show an endothermic peak in the range 104-185°C, indicating the presence of coordinated water molecules and a single exothermic peak in the range 286-522°C demonstrates that there may be the simultaneous decomposition of HL and HP moieties. The final main product (NiO) was confirmed by IR and then subjected to several available physical measurements [41-42].

3.5. Scanning Electron Microscopy (SEM)

The SEM micrographs of the *Aqua* (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex and its decomposition product at 400°C are presented in fig. 3. The powder form of the complex was made of giant block crystals in different sizes (Fig. 3a). The SEM image of the product in fig. 3b evidently shows that the shape and size of particles are quite different from the precursor complex. It can be seen that the product was formed from extremely fine semi-spherical particles that were loosely aggregated. No characteristic morphology of the complex is observed, indicating the complete decomposition into the very fine spherical particles.

3.6. Transmission Electron Microscopy (TEM)

The TEM images of the complex and its decomposition product at 400°C shown in fig. 4. It is observed that the TEM micrograph of the starting complex powder was made of very large block crystals in different sizes (Fig. 4a). Uniform NiO nanoparticles have sphere shapes with weak agglomeration (Fig. 4b) was collected after thermal decomposition of the complex. The particle sizes possess a narrow distribution range from 10 to 20 nm, and the mean particle diameter is about 15 nm. The mean particle size determined by TEM is very close to the average particle size calculated by the Debye-Scherer formula from the XRD pattern.

3.7. X-ray diffraction analysis (XRD)

Powder XRD patterns of the decomposition *Aqua* (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex product at 400°C reveals only the diffraction peaks attributable to NiO with face-centred cubic phase at 2θ = 37.40, 43.45, 62.95, 75.40 and 79.45 (Fig. 2), which can be perfectly correlated to (111), (200),

(220), (311) and (222) crystal planes, respectively (JCPDS card No. 73-1523). This finding confirms that at 400°C, the complex was decomposed completely to nickel oxide. No impurity peaks were found in the XRD pattern, indicating that the nanocrystal line NiO obtained via this synthesis method consists of an ultrapure phase [43]. The average size of the NiO nanoparticles estimated using the relative intensity peak (220) by the Debye-Scherrer equation, was found to be 16 nm and increase in sharpness of XRD peaks indicates that particles are in crystalline nature:

$$= (094\lambda)/(\beta\cos\theta) \quad (2)$$

Where λ is the wavelength (λ = 1.542 Å) (Cu-K_α), β is the full width at half maximum (FWHM) of the line, and θ is the diffraction angle.

3.8. Antimicrobial Study

The studies based on the agar cup method revealed that the complex is sensitive against *C. diphtheriae*, less sensitive against *C. Albicans, S. aureus* (Table 1). The Minimum inhibitory concentration (MIC) of complex ranges between 100-450 µg/mL. The biological study shows that complex is found to be more active against *C. diphtheriae* as compared to *C. Albicans* and *S. aureus* compared to the standard antibacterial compound, doxycycline. The NiO NPs show the highest activity against the selected strains of microorganisms compared to Ni(II) complex.

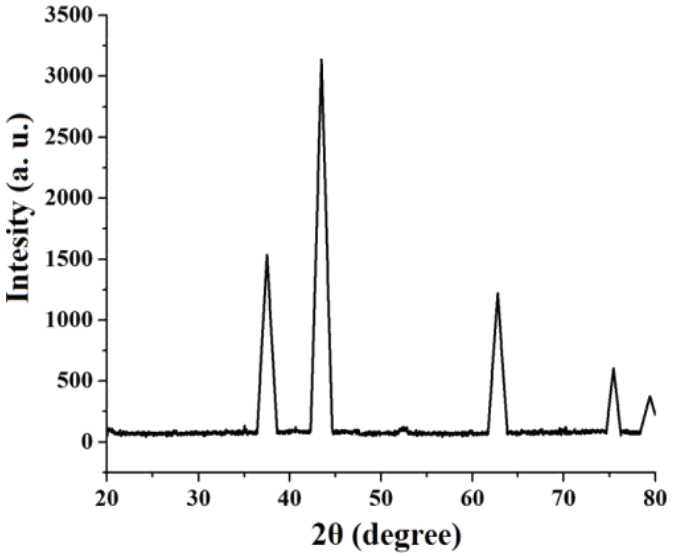

Fig. 2: XRD patterns of NiO nanoparticles

Table 1: Antibacterial activity of nickel (II) complex and NiO NPs by agar cup method (zone of inhibition in (mm) and MIC (ug/mL)

Sr. No.	Complex	*C. Albicans*		*S. diphtheriae*		*S. aureus*	
		MIC (µg/mL)	(mm)	MIC (µg/mL)	(mm)	MIC (µg/mL)	(mm)
1	[Ni(P)(Iso).2H_2O]	150	15	100	14	400	13
2	NiO nanoparticles	100	19	100	20	150	19
3	Doxycycline	2.0	24	1.5	22	1.5	24

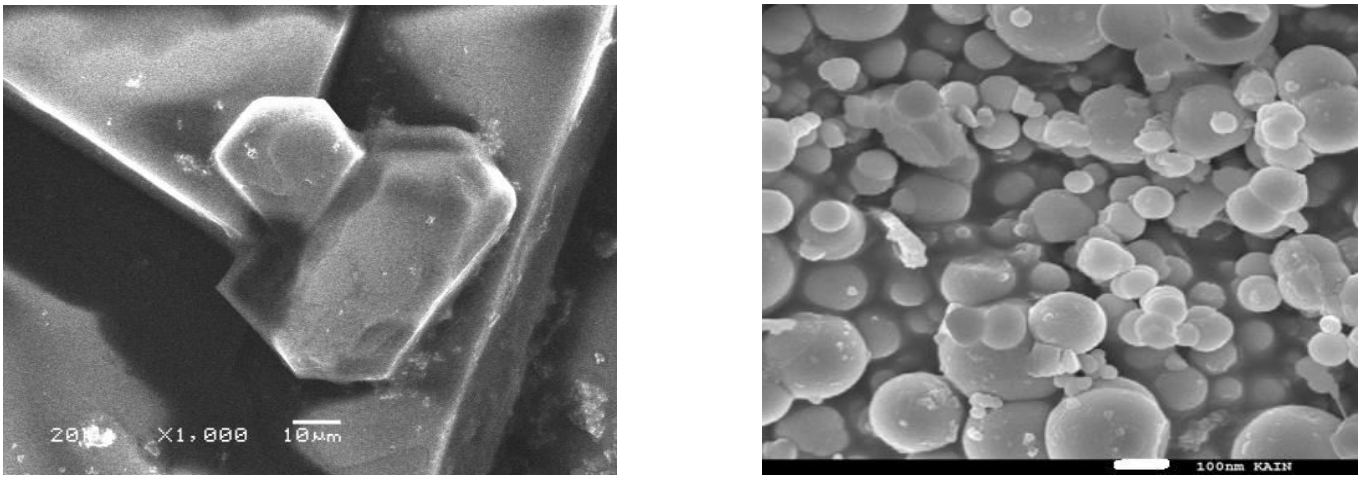

Fig. 3: SEM micrographs (a) *Aqua* (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex and (b) NiO nanoparticles

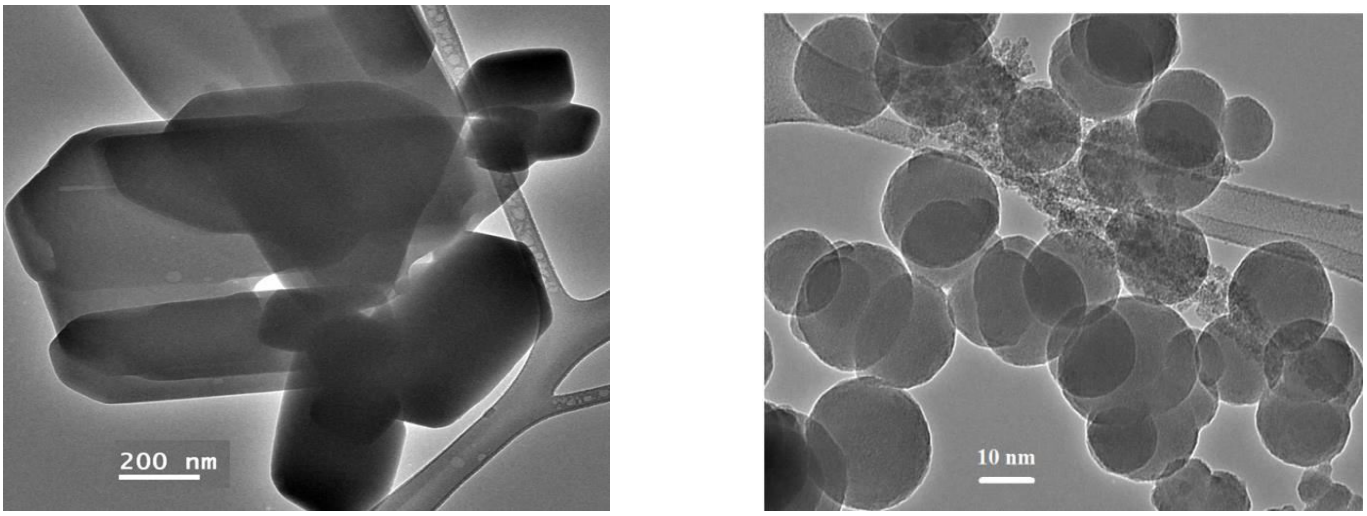

Fig. 4: TEM micrographs (a) *Aqua* (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex and (b) Ni Nanoparticles

4. CONCLUSION

The new *Aqua* (2-amino-6-methyl pyrimidine-4-ol and Isoleucine) Ni(II) complex was subjected to thermal decomposition at low temperature of 400°C to prepare uniformed spherical NiO nanoparticles in the range of 10-20 nm. The structure of the complex and the NiO nanoparticles product were elucidated based on FT-IR, UV-vis spectroscopy, TG/DTA, XRD, SEM, and TEM. NiO nanoparticles showed an inhibitory effect against *C. diphtheriae, C. Albicans, S. aureus* 100-150μg/mL, respectively. According to the finding, we can conclude that facile straight forward synthesis of NiO NPs; it has an benefit over other methods, as it is so simple, rapid and energy-saving and NiO NPs show considerable activity against the selected strains of microorganisms as compared to Ni(II) complex.

5. ACKNOWLEDGEMENT

The authors are grateful to Prof. V.D. Barhate, Principal, Changu Kana Thakur Arts, Commerce and Science College (Autonomous), New Panvel for continuous encouragement.

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