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Citrus medica Mediated Ag Doped MgO Nanocomposites as Green Adsorbent and Its Catalytic Performance in the Rapid Treatment of Water Contaminants

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ABSTRACT

Among various physical and biological methods for the synthesis of the nanocomposite, the green synthesis method is one of the most sustainable approaches for the synthesis of the NCs. Nanomaterials are widely synthesized by using plant extract, which is considered a low cost and highly efficient reactant for the fabrication of nanomaterials. In this research article, *Citrus medica* peels extract acts as a capping and reducing agent for the synthesis of Ag-MgO NCs. Various characterization techniques were employed for the characterization of fabricated nanomaterial. Like UV-Visible spectroscopy, SEM, EDX, TEM, and TGA. Two different peaks were obtained at different wavelengths in the UV-Visible spectrum for fabricated nanocomposite. The first peak occurred at 346 nm, which corresponds to Ag-NPs, and the second peak was detected at 293 nm, which corresponds to MgO-NPs. X-ray diffraction pattern suggest that the synthesized nanomaterials are cubic in nature. It can be concluded from the TGA plot that the synthesized Ag-MgO nanocomposite is thermally stable up to 600°C. Nanomaterials are uniform and crystalline according to SEM analysis. Fabricated nanomaterial was used as adsorbent for the removal of MB dye which shows significant results about 100% of MB dye was removed when a 4g/L dose of Ag-MgO NCs was used further effect of dose, time and on adsorption was studied. The reduction of MB dye was used to evaluate the catalytic efficiency of the generated nano-catalyst. In this reaction, $NaBH_4$ was used as a reducing agent and nanomaterial as a catalyst. Synthesized NCs exhibit excellent catalytic activity as they degrade toxic dyes up to 90%, 8 min for MB. The rate of reaction was evaluated using a spectrophotometer, and it was reported that the reaction is pseudo-first order and rate constant; we found $8.69 \times 10^{-3} s^{-1}$. Synthesized NCs can be used as an excellent photo catalyst to degrade various hazardous dyes to improve water quality.

Keywords: Nanocomposite; Photo catalyst; Adsorption study; *Citrus medica*

Abbreviations: NCs: Nanocomposite; MB: Methylene Blue

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INTRODUCTION

Water is among the most crucial components for survival on this planet. Despite water covering around 71% of the earth's crust, human society continues to suffer an increasing water shortage. The production of wastewater is expanding exponentially due to the hasty growth in the human population and contamination levels. Wastewater management involves several methodologies, each of which depends on the contaminant in the wastewater. Industrial effluent contains inorganic and organic pollutants such as dyes, phenolic compounds, and toxic metals [1]. Toxic organic dyes are used significantly in textile, cotton, paints, and pathological and physiological industries for various applications [2–4]. Hazardous wastewater from such enterprises harms human and marine life, which is one of the scientific community's biggest concerns. One of the most successful and practical wastewater control approaches is using catalysts [5].

MgO-based metal oxide nanoparticles are a frequent topic among researchers, and they have been extensively investigated in the past due to their versatility. Enhanced morphology of MgO NPs, silver based MgO nanomaterials material, or Ag-MgO NCs, has been reported to have exceptional photocatalytic, antibacterial, anticancer, and anti-inflammatory properties [6–9]. Due to their distinctive optical and electrical properties and remarkable bioactivities, silver nanoparticles are one of the most extensively generated nanostructured materials among noble metals [10-12].

Citrus medica is a Rutaceae family evergreen aromatic tree with a 4 meter to 5 meter long stem and edible yellowish orange fruits [13]. The leaves are usually long, shaded, about 10 cm-12 cm long, with a transparent cell. *Citrus medica* is a grapefruit that evolved in China and India and has migrated to Western European countries [14]. *Citrus medica* is excellent in vital nutrients, and the fruit peel extract includes many essential oils. Fruit is a high quality source of vitamins [15]. The essential oil obtained from fruits has antifungal activity and antioxidant potential [16]. Several medicinal benefits of the plants have been reported as per literature [17-19]. Ag-MgO NCs is successfully synthesized in this research investigation using *Citrus medica* (**Figure 1**) peels extract. The reduction of methylene blue was used to evaluate the catalytic efficiency of the generated nano-catalyst. In this reaction, $NaBH_4$ was used as a reducing agent and nanomaterial as a catalyst. The significance of this investigation relates to the fact that Ag-MgO NCs from *Citrus medica* rind extract and their catalytic efficiency had been not determined as we had reviewed its literature.

Figure 1: Fruits of *Citrus medica.*

MATERIALS AND METHODS

Materials and Procedures

Citrus medica was collected from local gardens of Karokhi village of Rudraprayag district during mid–November from Ukhimath, Rudraprayag. Methylene blue chemical formula ($C_{16}H_{18}ClN_3S$) molecular weight 319.9 g/mol, λ_{max} 664 nm was secure from HiMedia Laboratories Pvt Ltd. $Mg(NO_3)_2$, $6H_2O$, $AgNO_3$, and NaOH which were utilized for the synthesis of NCs were obtained from Sigma-Aldrich. Chemicals were used directly without any purification. Double distilled water was utilized during the biosynthesis and dilution procedures.

Preparation of Peels Extract

For 15 days, the fresh peels of *Citrus medica* were shed dried, initially fresh peels was washed with double distil water to remove impurities, then dried peels were crushed into powdered form using hand grinder. About 10 g of powdered peels were added into 250 ml of distil water and resultant mixture was heated at 60 for 30 min. filtration was done with the help of Whattman no 01 filter paper and filtrate were kept for further experiments [20].

Role of Plant Extract

Alkaloids, flavonoids, steroids, phenols, and carbohydrates are secondary metabolites isolated from peels of *Citrus medica*. While major constituents isolated from peels are isolimonene 39.37%, citral 23.12%, limonene 21.78%, β-Mycene 2.70% neryl acetate 2.51% and neryl alcohol 2.25%. Different parts of plants have been extensively used in the green synthesis of nanomaterial due to the presence of various secondary metabolites like steroids, sapogenins, tannins, terpenoids, polyols, alkaloids, polysaccharides, flavonoids, phenolics, proteins, amino acids, enzymes, and vitamins. They act as chelating, reducing and stabilizing agents, which prevent agglomeration, uncontrol growth and provide stability to nanomaterial. Secondary metabolites Steroids, phenols, alkaloids and carbohydrates present in plant extract act as reducing and capping agents.

Preparation of Ag-Mgo Nanocomposite

Initially fresh 5 mM solution of $AgNO_3$ was prepared along with 0.1 M Mg $(NO_3)_2.6H_2O$ solution and 0.1 M NaOH solution were prepared to synthesize Ag-MgO NCs. Afterwards, prepared plant extract and $AgNO_3$ solutions were added in fixed ration (2:3 v/v %). 80 mL of this resultant solution (plant extract and $AgNO_3$) was added to 20 mL of 0.1M $Mg(NO_3)_2$. $6H_2O$ solution, which was stirred continuously for 2 hours. Furthermore, further 2 mL prepared NaOH solution was applied until complete precipitation was achieved. The reaction mixture was centrifuged for 10 minutes at 16000 rpm in a laboratory centrifuge.

Preparation of Stock Solution of Methylene Blue Dye

Methylene Blue dye (MB) of 1000 mg/L quantity stock solution was made ready by mixing precisely weighted 1 gm of MB in 1 L distilled water. The solution was further diluted as per the prerequisite.

Characterization Techniques

The synthesized Ag-MgO NCs was confirmed by utilizing various spectroscopic and microscopic techniques like TEM (Transmission Electron Microscopy), UV-Vis spectroscopy, and XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and TGA (Thermo Gravimetric Analysis). TEM was performed at JEM-1400 Transmission Electron Microscope (TEM) features high resolution/high contrast imaging. It has a maximum accelerating voltage of 120 KV, a ± 70 degrees tilted computer-controlled stage. UV-Visible spectra of the synthesized materials were recorded by Hitachi U-2900 double beam spectrophotometer, XRD was performed by Philips powder diffractometer type PW 1373 goniometer (Cu Ka=1.5406) at a scanning rate of 6/min in the 2Ɵ range of 10 to 80 and SEM-EDAX analysis of the prepared sample was performed on the model CRAL ZEISS, model No. MA15/EVO18, Oxford instruments x-act (EDAX).

Adsorption Study

Batch method was applied for the estimation of sorption trials in this process 10 mL of MB sample and fixed sorbent dose was mechanically agitating 100 mL Erlenmeyer flasks. The blend was agitated at 210 rpm for 0 to 120 min at pH 7 and ambient temperature conditions. UV-Visible spectroscopy was utilized to calculate the optimum supernatant quantity (sample) by measuring absorbance at 664 nm. The graph was plotted between absorbance and amount of MB solution gave initial quantity of MB solution, from initial and equilibrium concentration of dye % removal of dye can be easily calculated using the formula.

$Qe= (Co–Ce) V/m$

Where,

- Co=Initial dye quantity.
- Ce=Quantity at equilibrium.
- V(L)=Voluminous level of the liquid solvent.
- m(g)=Sorbent quantity.

All experiments were performed in triplet and the average value of Ce and Qe was taken for further experiments. The amount of sorbent pH, time, and were studied. Sorption quantity was calculated by the help of formula mentioned in the literature.

Catalytic Properties of Ag-Mgo NCs

The reduced hazardous dye was used to evaluate the catalytic efficiency of the generated nano-catalyst Methylene Blue (MB); UV-Visible spectroscopy was used to assess the reaction's progress. In summary, 1 mm dye solution was mixed with the newly prepared 0.5 M $NaBH_4$ solution and fabricated NCs. Furthermore, this reaction mixture was kept in a cuvette of 4 ml volume and 1 cm path length.

RESULTS AND DISCUSSION

UV-Visible Spectroscopy

A peak at 440 nm was obtained in the UV-Visible spectra of previously synthesized Ag-NPs. Two different peaks were obtained at different wavelengths in the UV-Visible spectra of the fabricated NCs. (**Figures 2 and 3**). The first peak occurs at 346 nm, which corresponds to Ag-NPs, and the second peak was noticed at 293 nm, which corresponds to MgO-NPs. Those two different peaks reveal the formation of belayed Ag-MgO NCs [21].

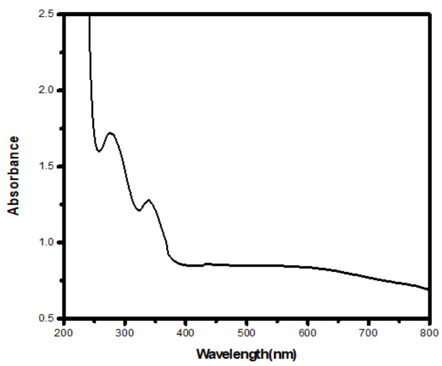

Figure 2: UV spectrum of Ag-NPs and Ag-MgO NCs.

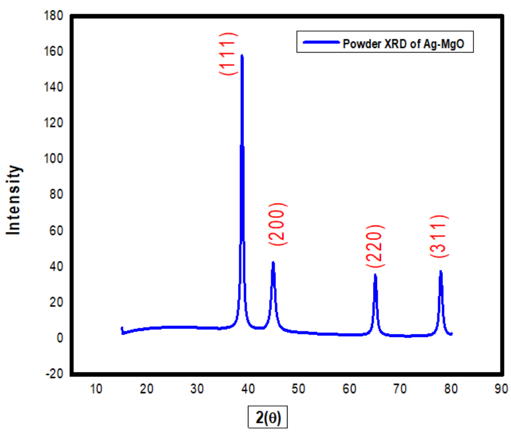

Figure 3: XRD of fabricated Ag-MgO NCs.

XRD Spectroscopy

Peaks obtained in the X-ray diffraction pattern of fabricated Ag-MgO NCs' are illustrated in Figure 3. Synthesized Ag-MgO NCs show a peak at (h,k,l) values indexed to (111), (200), (220), (311), and (312), respectively (222) and d spacing value are 2.38, 2.06, 1.45, 1.23 and 1.19 respectively, thus confirming the composite nature of the material with a cubical crystal lattice network. The Scherrer's equation was used to compute the average crystalline size of the synthesized Ag-MgO NCs, and the average crystalline size was found to be 16.43 nm [6].

SEM Analysis

In Figure 4, SEM photographs of synthesized nanomaterial are shown. This image depicts a multilayer assembled particle buildup. In nature, fabricated particles are non-uniform and crystalline. This aggregation could be due to heterocyclic chemicals in plant material.

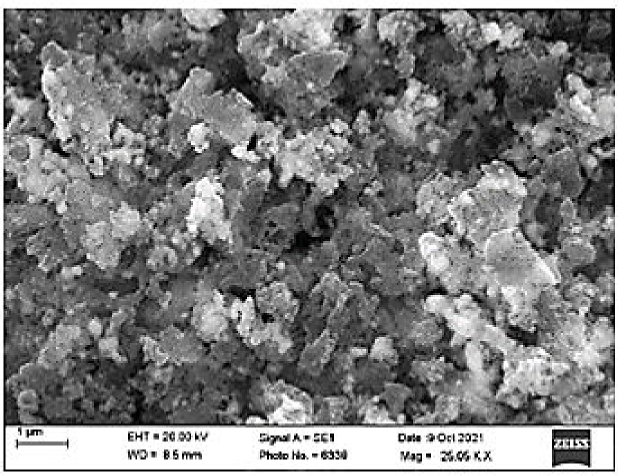

Figure 4: SEM micro images of fabricated Ag-MgO NCs.

SEM-EDX Analysis

The EDX study, illustrated in Figure 5, determines the basic structure of fabricated NCs. The occurrence of 58.19 percent oxygen, 35.91 percent silver, and 58.91 percent magnesium as major components is revealed by EDX results. SEM-EDX study discloses that the manufactured nano-material mainly comprises silver, oxygen, and magnesium.

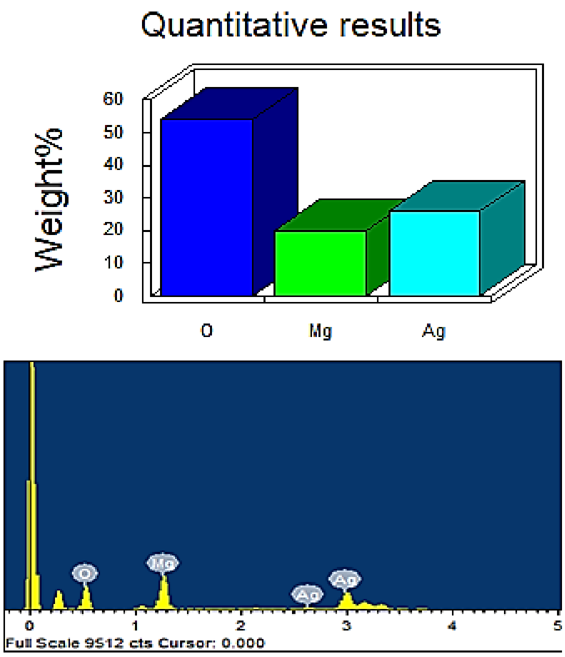

Figure 5: SEM-EDX data of synthesized Ag-MgO NCs.

TEM Study

TEM micro images suggest that most of the particles are spherical and very few particles are agglomerated (Figure 6). Since most of the particles are spherical then it can be concluded that synthesized nanomaterials are quite stable. The average grain size was estimated at around 24.93 nm.

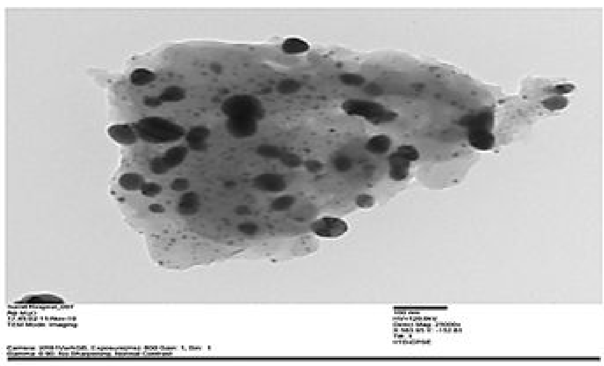

Figure 6: TEM images.

Thermal Gravity Analysis (TGA)

Thermal gravity analysis results are shown in Figure 7 results shows that Ag-MgO NCs remains almost stable until temperature reach 300°C around 10% of weight lose until 300°C this weight loss may be attributed due to lose of moisture in sample. Significant weight loss of 45% was observed when temperature reach up to 400°C and it may be due to decomposition of major chemical in the composition of Ag-MgO NCs. It can be concluded from TGA plot that the synthesized Ag-MgO NCs is thermally stable up to 600°C.

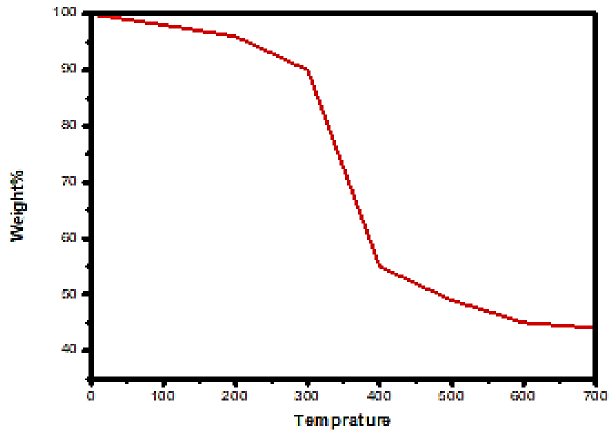

Figure 7: TGA plot of Ag-MgO NCs.

Band Gap Plot

Tauc equation was used to estimate the band gap of synthesized Ag-MgO NCs, in which UV-Visible data was exploited to plot the graph between (αhυ)2 and (αhυ)1/2 against hυ, where 'α' is the absorbance of photon energy, 'h' is Planck's constant, 'υ' is frequency, 'Eg' is optical energy band gap and 'n' is a constant represented the different types of electronic transitions. The obtained band gap is shown in **Figure 8** shown below. Band gap was estimated as 3.49 eV.

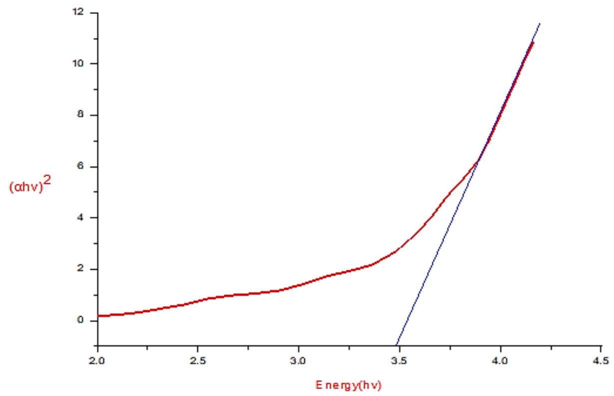

Figure 8: Band gap of synthesized Ag-MgO NCs.

Absorption Analysis

In luence of bio-sorbent dosage: Six doses of different amount ranging from 1 g/L-4 g/L were taken for the investigation of effect of Ag-MgO dose on adsorption efficiency. Results show that MB dye show greater adsorption with increase of Ag-MgO dose. At lowest dose of 1 g/L of Ag-MgO MB dye shows adsorption efficiency of 85% while maximum adsorption efficiency 100% was archived when highest dose of 4 g/L of Ag-MgO was used. It was observed that when medium adsorbent dose 2 g/L was used about 95% of MB was removed from the aqueous solution. That is why it was used for further studies.

In luence of time: The batch mode of analysis was performed to calculate equilibrium time for optimum treatment efficacy and to estimate the sorption kinetics, in which 10 mg/L of MB dye was studied at 20 min time duration ranging from 20 min-120 min with 2 g/L of Ag-MgO NCs dose. The graph was plotted between treatment efficiency and time of contact, and it was observed that the 70% of MB dye was removed in just 20 min and it reached state of equilibrium at 100 min, when removal efficiency was estimated 95%. Such observation may be due to fact that at initial period larger multitudes of empty active site was reachable over Ag-MgO NCs. Periphery for MB molecule, but after certain period surface get partially unavailable and reachable, so active site for Ag-MgO NCs. Decreases so MB molecules change their path to obtain reachable and unoccupied active site.

In luence of solution pH: The adsorption efficiency of MB sample is greatly affected by pH of the MB solution, because pH affects the sorbent periphery charge and the degree of ionization of MB molecule which also affect the adsorption efficacy of Ag-MgO NCs., which shows different result at various pHs. It was observed that Ag-MgO acquire positive charge on its surface due to protonation and negative charge on its surface due to deprotonation in basic medium. While MB exist in anionic form in aqueous medium at higher pH, less adsorption was observed when negatively energized Ag-MgO NCs. approaches toward negatively charged MB they get repulsion from each are. However, attraction was observed when positively charged Ag-MgO NCs approach toward negatively charged MB molecule at lower pH (**Figure 9**).

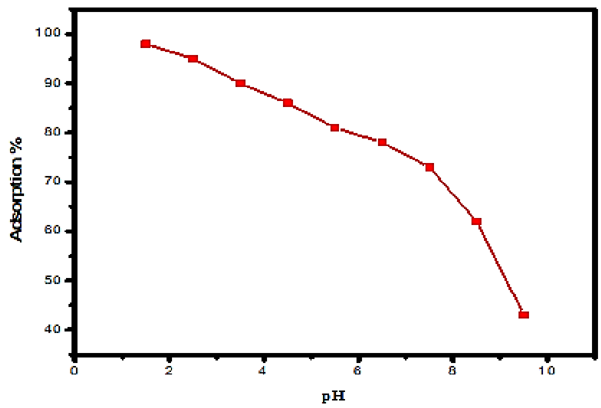

Figure 9: Effect of solution pH.

Catalytic Performance of Ag-MgO NCs for Deterioration MB

Methylene blue is a hazardous dye which displays λ_{max} at 664 nm in the UV spectra. When the dye is added to a mixture of NCs and $NaBH_4$, the absorbance value decreases rapidly with time, UV-Visible spectra results reveal that the MB degrade 91% in 8 min in the presence of the reaction mixture. The rate of reaction was evaluated using a spectrophotometer, and it was reported that the rate is independent of the concentration of Sodium borohydride. This implies that the reaction is pseudo first order (**Figure 10**). When we plotted the graph between ln (At/A0) and the radiation time rate constant was found $8.69 \times 10^{-3} s^{-1}$ for Ag-MgO NCs.

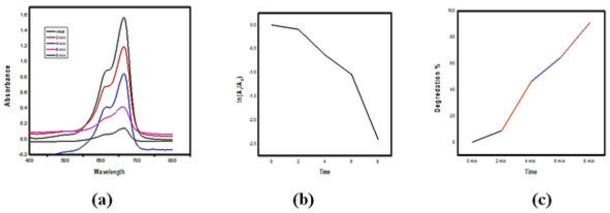

Figure 10: (a) Deterioration of MB by using $NaBH_4$ and nanocatalyst, (b) Deterioration performance, and (c) Rate of reaction.

CONCLUSION

In this research article, Ag-MgO NCs were effectively fabricated using *Citrus medica* rinds extract as capping and a reducing agent. Various characterization techniques were employed for the characterization of fabricated Ag-MgO nano-material. Two prominent peaks were obtained in the UV-Visible spectrum of the fabricated NCs, which is a clear indication of the synthesis of the NCs. X-ray diffraction pattern results indicate the cubic nature of synthesized NCs. The mean grain size was estimated to be 16.43 nm. It can be concluded from TGA plot that the synthesized Ag-MgO NCs is thermally stable up to 600°C. According to the SEM study, fabricated nano-materials were found to be poly dispersive and crystalline. Fabricated nanomaterial was used as adsorbent for removal of MB dye which shows significant results about 100% of MB dye was removed when 4g/L dose of Ag-MgO NCs was used further effect of dose, time and pH on adsorption was studied. The reduction of MB dye was used to evaluate the catalytic efficiency of the generated nano-catalyst. In this reaction, scream $NaBH_4$ was used as a reducing agent and nanomaterial as a catalyst. Synthesized NCs exhibit excellent catalytic activity as they degrade toxic dyes up to 90%, 8 min for MB. The rate of reaction was evaluated using a spectrophotometer, and it was reported that the reaction is pseudo first order and rate constant; we found $8.69 \times 10^{-3} s^{-1}$. Synthesized NCs can be used as an excellent photo catalyst to degrade various hazardous dyes to improve water quality.

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DECLARATION OF INTEREST STATEMENT

I, Dr. Sumit (research scholar department of chemistry), on the behalf of all entitle authors, declare that the submitted manuscript is original and has not been or is not being submitted to any other journal., and we have not received any grant from funding agency. Hope you will consider it as soon as possible. We are looking forward for your kind consideration.

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