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ORIGINAL RESEARCH PAPER

A novel way to use metal nitrates for environmental remediation with the help of photocatalytic action of Titania Tenorite nanocomposite

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ABSTRACT

In this work, we are suggesting a method to reduce the number of metal nitrates used in industrial and agricultural applications with the help of the photocatalytic effect. Also, the work discusses how the residual amount of metal nitrates in the soil can be made useful through the same effect. Though metal nitrates like ferric nitrate and nickel nitrate show characteristic absorption in the UV region, what we observed is an enhancement in this UV absorption when we treated these metal nitrates with Titania Tenorite nanocomposite due to its photocatalytic action. This absorbance enhancement property is an indication of an increase in the concentration of the metal nitrates in the solution with light irradiation. The increase in M–OH bonds owing to the action of the nanocomposite in the presence of light is the reason by which metal nitrates absorption increases. In precise a tiny amount of metal nitrates is needed for any practical use as it can automatically increase its concentration in presence of the nanocomposite by the photocatalytic reaction. This will reduce the disposal of the unwanted amount of metal nitrates into the surrounding especially water bodies. Also, the residue amount in the soil can act as UV absorbers. Thus, the combination of the metal nitrates with the nanocomposite can be made used for environmental remediation where the metal nitrates are used in large quantities.

Keywords: *TiO_2/CuO nanocomposite; spectroscopic techniques; UV-Visible spectroscopy; absorbance enhancement; UV absorbers.*

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INTRODUCTION

Sunlight is the vital source of energy which sustains life on earth. Sunlight is composed of visible light (55%), infrared radiation (40%) and ultraviolet radiation (5%). The amount of radiation reaching the earth's surface has varied slightly from this due to the change in environmental conditions [1]. We can make use of sunlight as a light source for the photocatalytic effect. Even if sunlight can act as a light source for photocatalytic applications selection of a suitable photocatalyst that works with visible light is crucial in such cases. Titanium dioxide is a well-known photocatalyst, but its main drawback is that it responds to the light in the UV region and this inhibits its use as a good photocatalyst [2, 3]. The coupling of TiO_2 with suitable metal oxides is one way to overcome this drawback. TiO_2 has been coupled with different metal oxides such as Iron, Copper, Zinc, Cadmium, etc. to tune its bandgap and thereby extend the light response to the visible region [4–8].

The photocatalytic metal oxides and their composites were so far been used for the removal of heavy metals from sources like wastewater [9–12]. In our previous work, we have coupled TiO_2 (Titania) with CuO (Tenorite) to tune the bandgap of TiO_2 [13]. The resultant Titania

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Tenorite nanocomposites produced absorbance enhancement in Methylene Blue and Rhodamine B dyes in the presence of light. The nanocomposites thus acted as a photocatalytic color enhancer for both the dyes. Normally the color of a dye fades when it is exposed to light. But the treatment of dyes with the nanocomposites has resulted in the color enhancement of the dyes and the effect continued even after several months. By making use of this effect the nanocomposites can be used as a color additive with the dyes. Thus the amount of dye used can be reduced without reducing its color. So, in this work, our focus is to apply this photocatalytic absorbance enhancement property to heavy metals to reduce their negative impacts on the environment. Here our aim is not merely its removal from the wastewater instead preventing them from being waste by increasing its usage. For our study, we have chosen the nitrates of two heavy metals nickel and iron. The nitrates of these two heavy metals have been mostly used as precursors or for doping [14–17]. There are only a few reports about the optical properties of these nitrates [18–20]. The action of TiO_2/CuO nanocomposite on the optical properties of ferric nitrate and nickel nitrate were studied in this work.

The manuscript explains the absorbance enhancement of metal nitrates in water by the coupled Titania Tenorite (TiO_2/CuO) nanocomposite. The photocatalytic effect of the nanocomposite produces absorbance enhancement in the metal nitrates we selected (Ferric nitrate and nickel nitrate). This absorbance enhancement property is an indication of an increase in the concentration of the metal nitrates in the solution with light irradiation. In precise a tiny amount of metal nitrates is needed for any practical use as it can automatically increase its concentration in presence of the nanocomposite by the photocatalytic reaction. This will reduce the disposal of the unwanted amount of metal nitrates into the surrounding especially water bodies. Thus, the combination of the metal nitrates with the nanocomposites can be made useful for environmental remediation where the metal nitrates are used in large quantities. Here the photocatalytic property of the nanocomposites has led to an increase in the absorbance of metal nitrates in the UVA and UVB region and hence they can also be used as good absorbers in the UVA and UVB region.

MATERIALS AND METHODS

Preparation of nanocomposites

The initial step of the present study is the preparation of TiO_2/CuO nanocomposite (TC), the synthesis and complete characterizations of which are well described in our previous article. TiO_2 and CuO co-exist in the synthesized TiO_2/CuO nanocomposite, with band gaps E_g= 2.41eV and 1.34 eV respectively as reported by us [13].

Absorbance Enhancement Study

AR grade ferric nitrate and nickel nitrate purchased from Merck India Ltd. was used for the absorbance enhancement study. The experiment for the absorbance enhancement was done by agitating 0.04g of TC in a 100 ml solution of ferric nitrate (FeN-0.012g) on a rotary shaker at room temperature with and without visible light irradiation for three hours. The aliquots of the ferric nitrate solution treated with TiO_2/CuO nanocomposite (FeNTC) with and without irradiation were removed at different intervals of time. UV-visible absorption spectra and Fourier Transform Infra-Red (FTIR) spectra of the solutions were taken after completely removing the nanocomposite from the solution by centrifuging. The same procedure was repeated with 0.068g of nickel nitrate (NiN) instead of ferric nitrate. The light source used for irradiation was a 2.4W LED lamp. The absorption spectra were recorded with PG Instruments Ltd. T90+ UV/Vis Spectrometer. FTIR measurement was carried out with IRAffinity-1S of Shimadzu Laser Instruments in the wavenumber range from 400 to 4500 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per second. The method used was Attenuated Total Reflection (ATR) using NaCl crystal on which a single droplet of the treated metal nitrate solution is placed to collect the spectrum.

RESULTS AND DISCUSSION

Characterization of TiO_2/CuO nanocomposite

A brief description of the synthesis and characterization of the TiO_2/CuO nanocomposite is a prerequisite, as our present work is based on the nanocomposite. In our previous work, we synthesized TiO_2/CuO nanocomposite by co-precipitation method. The bandgap of TiO_2 was tuned to the visible region by changing the CuO content. The formation of the nanocomposite was confirmed by X-Ray Diffraction (XRD)

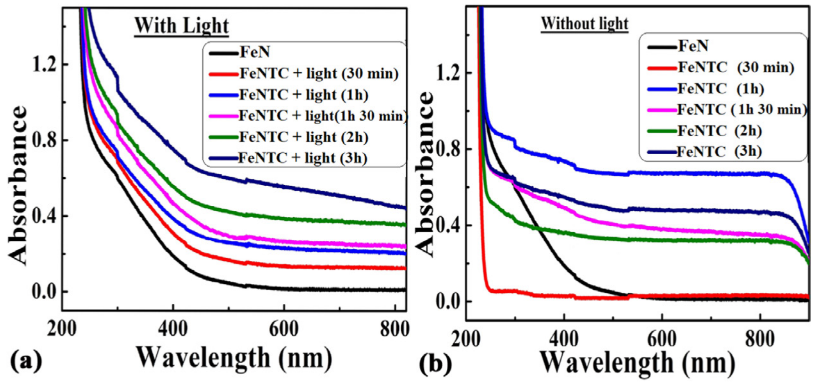

Fig. 1. Absorbance spectra of ferric nitrate treated with nanocomposite (a) under light irradiation; (b) without light irradiation.

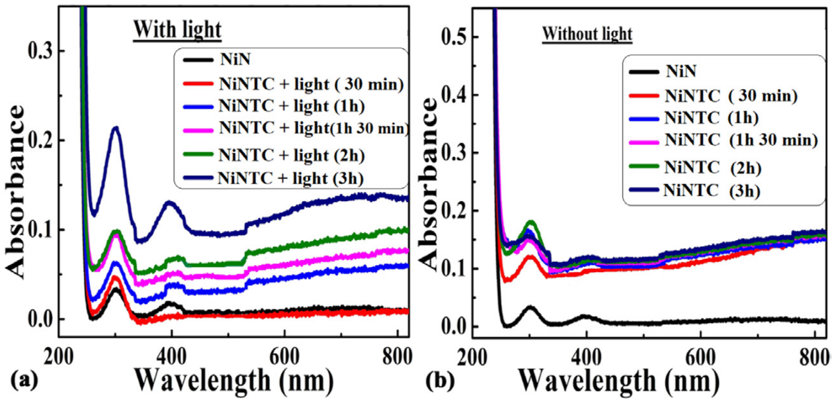

Fig. 2. Absorbance spectra of nickel nitrate treated with nanocomposite (a) under light irradiation; (b) without light irradiation.

analysis, Fourier Transform Infra-Red (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS). The characterization of the nanocomposite is described in detail in our previous work [13]. The nanocomposite exhibited a dual bandgap corresponding to TiO_2 and CuO. The nanocomposite produced a color enhancement property in Methylene Blue and Rhodamine B dyes in the presence of light [13].

Studying the effect of nanocomposite on the absorbance of metal nitrates in the presence and absence of light using spectroscopic techniques

The action of TiO_2/CuO nanocomposite on the absorption properties of ferric nitrate and nickel nitrate were examined in this work. As ferric nitrate and nickel nitrate are magnetic materials, very little data is available on their optical absorption behavior [18–20]. But in the case of nitrate ions in aqueous solutions, two bands are obtained at 200 nm and 300 nm [21–23]. The absorption spectra of ferric nitrate and nickel nitrate treated with TiO_2/CuO nanocomposite (FeNTC and NiNTC) were compared with that of the absorption spectra of the as-prepared ferric nitrate (FeN) and nickel nitrate (NiN) solutions. The result obtained in the case of ferric nitrate is presented in Fig.1. From Fig. 1(a) we can see that in presence of light the absorbance value increases with the increase in irradiation time. The variation of absorbance is entirely different in the absence of light. The absorbance spectra show a non-uniform variation without irradiation.

The results obtained for nickel nitrate closely resemble the nature of ferric nitrate (see Fig.2). From the close observation of the spectra we can see that for both FeNTC and NiNTC, the absorbance increases gradually with the duration of irradiation in the presence of light (Figs. 1(a) and 2 (a)), whereas the absorbance shows an irregular variation in absence of light irradiation (Figs. 1(b) and 2(b)). The absorbance spectra of FeN treated with TC show an increase in absorbance in the UV region, especially in the UVA and UVB regions. The comparison of absorbance in the UVA and UVB region is provided in Table 1. From the table,

Table 1. Comparison of absorbance of FeNTC and NiNTC under light irradiation

Irradiation Time	Absorbance of FeNTC		Absorbance of NiNTC	
	at 400 nm	at 300 nm	at 400 nm	at 300 nm
0	0.18	0.57	0.016	0.03
30 minutes	0.31	0.67	0.002	0.04
1 hour	0.38	0.71	0.036	0.06
1hour 30 min	0.47	0.81	0.051	0.093
2 hours	0.55	0.89	0.068	0.099
3 hours	0.75	1.04	0.128	0.214

we can see that the absorbance value of FeNTC at 400 nm (UVA region) increases from 0.18 to 0.75 which means the absorbance increases four times when irradiated with light for three hours and the absorbance at 300 nm (UVB region) shows a two-fold increase from 0.57 to 1.04. Thus by treating FeN with the nanocomposite, the absorbance value of the solution goes on increasing with the increase in irradiation time. A similar observation is detected in the absorbance of NiNTC. For NiNTC, the absorbance at 400 nm (UVA region) increases from 0.016 nm to 0.128 nm, an eight-fold increase is observed. The absorbance at 300 nm (UVB region) shows a seven-fold increase from 0.03 to 0.214. Hence it is clear that the absorbance enhancement can be attributed to two factors (i) the action of nanocomposite on metal nitrates (ii) the irradiation of light. The role of light irradiation is obvious from the absorbance spectra of FeNTC and NiNTC without irradiation (Figs. 1 (b) and 2 (b)) where there is an irregular variation in absorbance. In both these cases, even though the first factor that is the action of nanocomposite on metal nitrates is a common factor, the irregularity in absorbance variation arises because of the absence of light irradiation.

The absorbance and concentration are linearly related as given by Beer's law:

$$A = \log \frac{I}{I_0} = \varepsilon bc \quad (1)$$

where I_0 is the incident intensity, I denote the transmitted intensity, ε is the molar absorptivity, b is the path length of the sample, and c is the concentration of the absorber [24]. Hence, ε and b being constant, it is evident that the absorbance can increase only by the increase of concentration of FeN with irradiation. This implies that the absorbance of FeN gets enhanced because of the photocatalytic action of the TiO_2/CuO nanocomposite.

The increase in absorption can be attributed to the increase in the number of Fe(III)–OH bonds in the solution. This is because when ferric nitrate is added to water it is hydrolyzed to form Fe(III)–OH species, namely ferric hydroxide. We know that when a photocatalyst is excited with light it will produce charge carriers (electrons or holes) and they readily react with surrounding molecules [25]. Keeping this in mind, when we add a strong photocatalyst like TiO_2/CuO nanocomposite in the ferric nitrate solution and excite it with light, electrons and holes get generated in the solution. Thus generated electrons produce O^{2-} by reacting with O_2 and holes produce active OH radicals by reacting with water [26]. This can be represented by the following equations.

$$SC + h\nu \rightarrow e_{cb}^{-} + h_{vb}^{+} \quad (2)$$

$$O_2 + e_{cb}^{-} \rightarrow O_2^{\bullet -} \quad (3)$$

$$H_2O + h_{vb}^{+} \rightarrow OH^{\bullet} + H^{+} \quad (4)$$

These OH radicals formed may combine with Fe(III) ions to form Fe(III)–OH in addition to the already existing ones. More the time of light excitation, more OH radicals will be generated and more Fe(III)–OH species will be formed and this will cause an increased absorbance [27]. As the absorbance of NiNTC shows an identical behavior we can expect the same reason here. To be specific the increase in absorbance of NiNTC can be due to the increase in the number of Ni–OH bonds in the solution due to light irradiation. In the absence of light, the formation of Metal–OH bonds due to the photocatalytic action of the nanocomposites won't occur and so there will be a non-uniform variation in the absorbance.

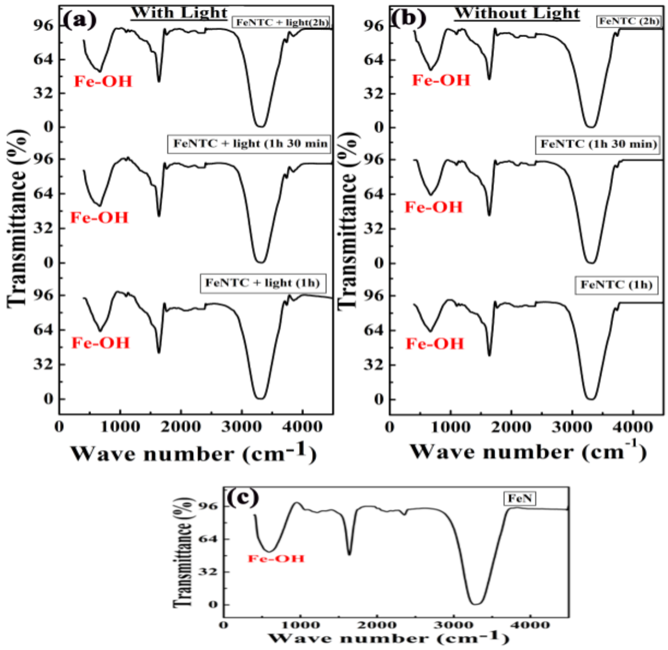

Fig. 3. FTIR spectra of ferric nitrate treated with TiO_2/CuO nanocomposite (a) with light irradiation; (b) without light irradiation; (c) FTIR spectra of untreated ferric nitrate.

Confirmation of the formation of M-OH bonds by Fourier Transform Infra-Red Spectroscopy

To check whether there is an increase in Fe–OH species with light illumination we compared the FTIR spectra of light irradiated and non-irradiated FeNTC.

Fig. 3(a) shows the FTIR spectra of FeNTC irradiated with light at different instants of time. Fig. 3(c) depicts the corresponding spectra for ferric nitrate solution without any treatments. Here, the three main peaks 670 cm^{-1}, 1624 cm^{-1} ,and 3280 cm^{-1} stand for Fe–OH and O–H vibrations respectively [19,28]. The peak corresponding to Fe–O (813 cm^{-1}) vibration appears to be merged with the Fe–OH vibration peak at 670 cm^{-1}. If we compare the percentage transmittance of Fe–OH vibration we can see that it decreases as the irradiation time increases.

According to Beer Lambert's law absorbance, A and transmittance T are related as,

$$A = -\log_{10} T \quad (5)$$

Hence we can say that absorbance and transmittance bear an inverse relationship. Thus as the transmittance decreases, corresponding absorbance increases. From eq. (1) we can say that as absorbance increases, the concentration also increases. As the percentage transmittance of Fe–OH vibration decreases, the corresponding absorbance increases and hence the concentration. Here, the increase in concentration means, increase in Fe-OH vibrations or Fe–OH species [24]. To be more specific, the number of Fe-OH species in FeNTC increases with an increase in irradiation time as we have observed from UV-visible analysis. But we cannot observe such an increase in absorption corresponding to Fe–OH vibration in FeNTC in the absence of light irradiation (Fig. 3(b)). The transmittance values corresponding to the Fe–OH bond vibration (at 670 cm^{-1}) in the presence and absence of light irradiation are given in Table 2. Thus it clearly shows that TiO_2/CuO nanocomposite here acted as a photocatalyst thereby increasing the production of OH species under light illumination which in turn produced more and more Fe–OH species as observed from both UV-visible and FTIR analyses. Here also the %T values without irradiation shows an irregular variation which proves the importance of light irradiation.

The FTIR spectra of NiNTC irradiated with light (Fig. 4(a)) also show a similar result. The transmittance value corresponding to Ni–OH bond, which can be identified in the range from 500 cm^{-1} to 700 cm^{-1}, is found to be decreasing

Table 2. %Transmittance values of Fe–OH and Ni–OH bond vibrations

Irradiation time	%T for Fe–OH at 680 cm^{-1}		%T for Ni–OH at 665 cm^{-1}	
	with irradiation	without irradiation	with irradiation	without irradiation
1 hour	64.44	62.74	55.77	51.79
1 hour 30 min	55.59	65.32	51.52	56.41
2 hour	52.09	54.05	42.58	49.98

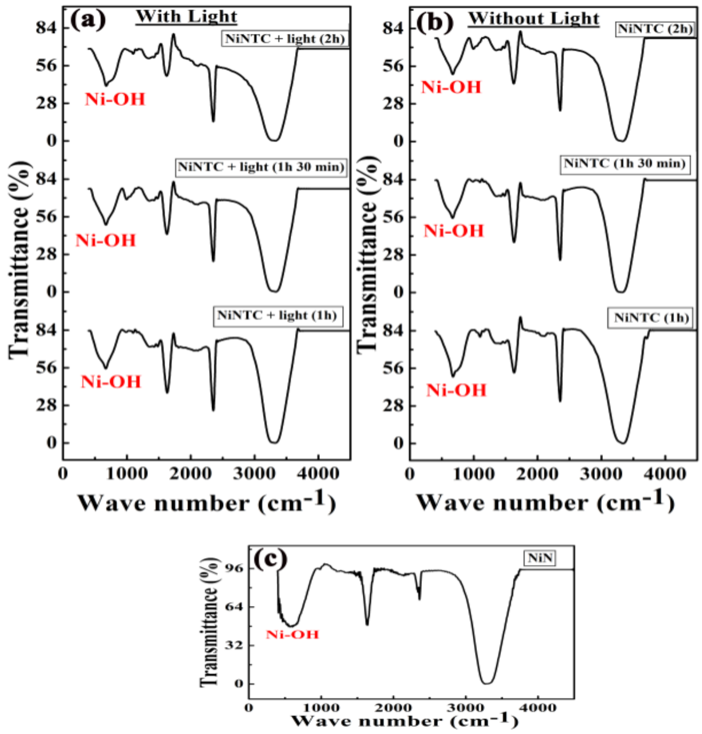

Fig. 4. FTIR spectra of nickel nitrate treated with TiO_2/CuO nanocomposite (a) with light irradiation; (b) without light irradiation; (c) FTIR spectra of untreated nickel nitrate.

with light irradiation [29–33]. But in the absence of irradiation (Fig.4 (b)), a non-uniform nature is observed in transmittance values. Thus it can be inferred that the treatment of nickel nitrate solution with the nanocomposite followed by light irradiation results in the increase of Ni–OH bonds. This result is in good agreement with the results obtained from UV-visible absorption analysis.

Metal nitrates treated with nanocomposite as UV absorbers

The treatment of TiO_2/CuO nanocomposite on ferric nitrate and nickel nitrate has resulted in an improvement in their optical absorption spectra. This clearly shows that TiO_2/CuO nanocomposite improves the optical properties of optically inert metal nitrates also. Here the photocatalytic property of the nanocomposite led to an absorbance increase in UVA and UVB region thereby increasing the concentration of the metal nitrates.

Thus, the combination of the metal nitrates with the nanocomposite can be made useful in industrial as well as agricultural applications of metal nitrates. We know that iron, nickel, and nitrogen are essential for the growth of plants [34–36]. Because of their role as essential plant nutrients they are mainly used as fertilizers in agriculture [37]. More precisely, Ferric nitrate solution is used to prevent and correct iron deficiencies in soils and plants [38]. From the above discussions what we observed is that with the photocatalytic effect of TiO_2/CuO nanocomposite we were able to achieve an increase in the concentration of the ferric nitrate solution which is indicated by the absorbance enhancement of nitrates in presence of light. A similar process can be expected in the case of nickel nitrate solution too. Now what we want to suggest is that as the combination of metal nitrate with Titania tenorite composite can help the metal nitrate to self-enhance their concentration, due to the photocatalytic effect of the composite, their combination can be utilized to reduce the number of nitrates that we directly introduced to the soil for plant intake. That is, we only need to introduce a tiny amount of metal nitrate to the plant or soil for intake if we use it with the combination of the Titania tenorite composite, and thereby, we can avoid wastage of the metal nitrate to the soil. Thus there will be a reduction in the chances of water being polluted by the residual amount of metal nitrates. Also, the solution left behind after the intake of these elements will be able to absorb more UVA and UVB radiation to reduce the harmful effects caused by UV radiation. This in turn also makes metal nitrates a useful material for the environment. In a nutshell, the absorbance enhancement property of the metal nitrates treated with TiO_2/CuO nanocomposite can be used for environmental remediation in two ways (i) reducing water pollution by reducing the number of unused elements being dissolved in water and (ii) for absorbing UV radiation. If we discuss other applications of metal nitrates (Ferric nitrate in particular) we can see that they are used for wastewater treatment [39, 40]. As a future application, we can think about extending this same photocatalytic concentration enhancement property of the metal nitrate with nanocomposite in this case too, and thus we can reduce the number of metal nitrates used in this case without reducing its effect.

CONCLUSIONS

The Titania Tenorite (TiO_2/CuO) nanocomposite prepared by the co-precipitation method was used to improve the optical properties of optically inert ferric nitrate and nickel nitrate. The metal nitrates were treated with the nanocomposite and then irradiated with light. The effect of nanocomposites on the metal nitrates in the presence of light was investigated by the spectroscopic techniques- UV- visible and FTIR spectroscopy. The UV-visible absorption spectra and FTIR spectra of the solutions were taken at different intervals of irradiation time. From the UV-visible absorbance spectra, it is seen that the absorbance of both the solutions increases with the irradiation time. The FTIR analysis confirmed that the increase in absorbance is due to the increase in M–OH bonds. As the absorbance increases the concentration also increases. So a small amount of metal nitrates is needed for any practical use as it can automatically increase its concentration in presence of the nanocomposite by the photocatalytic reaction. This will reduce the disposal of the unwanted amount of metal nitrates into the surrounding especially water bodies. Also, the residue amount in the soil can act as UV absorbers too. Thus, the combination of the metal nitrates with the nanocomposite can be made used for environmental remediation where the metal nitrates are used in large quantities.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

ABBREVIATIONS

TC	TiO_2/CuO nanocomposite
FeN	Ferric Nitrate
FeNTC	FeNTC- Ferric nitrate solution treated with TiO_2/CuO nanocomposite
NiN	Nickel Nitrate
NiNTC	Nickel nitrate solution treated with TiO_2/CuO nanocomposite

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