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Phytosynthetic Nanoparticles for Dye Degradation of Contaminated Water

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KEYWORDS
Nanoparticles (NPs), Andrographis Paniculata, Phytochemicals, Alizarine red (AR), photo degradation.

ABSTRACT:
Green synthesis of nanomaterials is rapidly growing in the field of nanotechnology which replaces the use of toxic chemicals and much time consumption. An environmentally benign cost effective method is here with reported for green synthesis of copper oxide (CuO) nanoparticles by using *Andrographis Paniculata* leaf extract. The phyto molecules present in the extract are acting as reducing agents, stabilizing and capping agents for the biosynthesized nanoparticles instead of harmful chemicals. The characterization studies are done by UV-VISIBLE, FTIR, XRD, SEM-EDX and TEM analysis. These nanoparticles are further applied as photocatalysts for degradation of Alizarine red dye which is water contaminant. The photodegradation of the dye is carried out with these green synthesized CuO nanoparticles by irradiation under sunlight. The degradation study reveals that the 40 ppm dye solution could be degraded by 60 mg of copper oxide nanoparticles with in a time period of three hours producing degradation of 73.23%. The kinetics studies on the other hand, shows degradation process following pseudo first order reaction kinetics with rate constant 3.1474×10^{-4} sec^{-1}.

1. INTRODUCTION

1.1 Nanotechnology

Nanotechnology is the intervention of new techniques to manipulate atoms and tiny particles. The most significant products of nanotechnology are particles with sizes ranging from 1 to 100 nm, known as nanoparticles [1].The properties of NPs show immense variations to those of bulk materials due to their extremely small size [2]. The development of nanotechnology has made it possible to synthesise nanoparticles with size control and provide NPs with specific qualities. There are two main causes for the features of NPs: higher surface to volume ratio and unique quantum impact [3]. As compared to their bulk counterparts, the greatest surface to volume proportions in NPs exhibit enhanced catalytic reactivity [4].

Various physical, chemical and biological methods have been employed for the synthesis of metallic nanoparticles [5], [6]. Several advantages of biological methods over physical and chemical methods are the biological process is environmentally benign, less time consuming, cost effective with almost negligible industrial waste without use of toxic chemicals [7]. Biosynthesized nanoparticles are used in several contemporary fields viz. imaging, luminescence tagging, drug delivery and biomedical field because of their superior properties.

1.2 Alizarine red dye

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Dyes are used widely in various fields such as cosmetics, leather, food and textile industries. The release of these industrial dye effluents into water shows adverse effect on quality of water [9]. One of such dyes is Alizarine red (AR). So the degradation of AR contaminated water has much attention for the safety of the mankind.

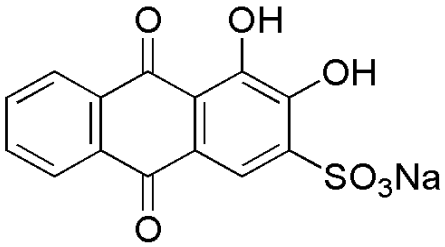

Figure 1: Chemical Structure of Alizarine red [10]

1.3. *Andrographis Paniculata*

Andrographis Paniculata is a herbal plant belonging to the family Acanthaceae (**Figure 2**) which is usually found in agricultural lands of India. In native language it is called as Nelavemu. Literature reveals that the parts of this plant are used to treat inflammation and pain in the human body and also used as a potent antiviral and antidiabatic agent [11-13]. It is found to be a good source of phytochemicals such as terpenoids, flavonoids, alkaloids, phenolic compounds, glycosides, gums, tannins, terpenes, carbohydrates and amino acids [14].

.

Figure 2: *Andrographis Paniculata* plant

2. Experimental work

2.1. Collection of *Andrographis Paniculata* leaves

Fresh leaves of *Andrographis Paniculata* plant are collected from botanical garden of Dr.V.S. Krishna Government Degree College, Visakhapatnam (**Figure 3**). 100 g of leaves are weighed and thoroughly cleaned with running tap water to eliminate debris on surface of leaves followed by deionized water to remove other contaminants from leaves and dried up under shade for six days i.e., until the weight of the dried leaves remains constant. These leaves are sliced into tiny pieces and made homogenized powder by using home blender. The obtained powder is stored in an air tight container for further usage.

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Figure 3: Map showing plant collection site in India

2.2. Preparation of leaf Extract

250 mL deionized water is taken in 500 mL beaker to this 10 g stored powder weighed and added. The contents in the beaker boiled for 20 minutes with occasional stirring with glass rod and then cooled to attain room temperature. The cooled leaf broth is filtered 2 times with Whatmann No.1 filter paper and reserved in refrigerator at 4ºC. This is taken as leaf extract throughout the experiment (**Figure 4**).

Figure 4: Image of *Andrographis Paniculata* leaf extract

2.3. Preparation of copper sulphate solution

Accurate amount of 1mM copper sulphate solution is prepared by dissolving 0.0622 g of $CuSO_4$ in 250 mL of double distilled water and stored in clean and dried reagent bottle.

2.4. Preparation of copper oxide nanoparticles

10 mL of leaf extract is added to a 90 mL of 1 mM copper sulphate solution and stirred magnetically at room temperature. The colour of the solution changes from blue to light green colour. This colour change is attributed to the interaction of the functional groups of the phytochemicals, thereby forming capped-metal complexes. Then the mixture is heated at 80^0 C for 20 minutes followed by addition of 5 mL of 0.1M sodium hydroxide drop by drop to maintain alkaline pH at 11. A green colour precipitate is formed immediately (**Figure 5**). This could be probably due to the formation of capped copper hydroxide complex in the presence of sodium hydroxide which acts as a stabilizing agent. The green precipitate is then taken out and washed repeatedly for three times with deionized water followed by ethanol to remove the impurities. In the next step the precipitate is collected in to a clean crucible and calcinated at 180 ^{0} C for three hours. Finally we get copper oxide nanoparticles.

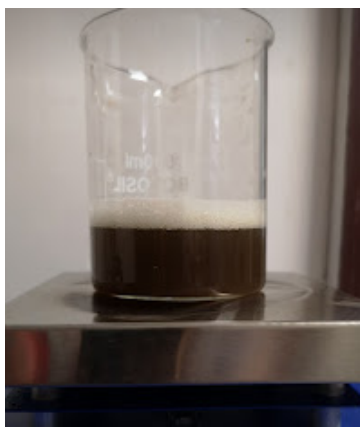

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Figure 5: copper oxide nanoparticles in the leaf extract

2.5. Characterization techniques

The formed copper oxide nanoparticles are characterized by using UV-Visible (Systronics-2201), FT-IR (IR-prestige-21 Shimadzu), XRD (X-pro petro,), FESEM-EDX (Philips-XL-30), TEM (JEM-1230 JEOL).

2.6. Photo degradation

The photocatalytic activity of green synthesized copper oxide nanoparticles is tested against aqueous solution of methylene blue dye. 40 ppm stock solution is prepared by dissolving 40 mg of Alizarin red dye in one litre double distilled water.

25 mL of 40 ppm solution is taken into 50 mL clean glass beaker and 60 mg of green synthesized CuO nano catalyst is added. This solution mixture is exposed to sun radiation under continuous stirring for three hours.

In every 30 minutes of time intervals, 5 mL of reaction mixture was taken out into centrifuging tubes and centrifuged. The filtrate is examined using UV-visible spectrophotometer to monitor the absorption maximum values. Before exposure to the sun radiation, the aqueous Alizarin red dye solution gives UV-visible absorption maximum value (λ_{max}) at 424 nm, which in subsequent experiments under sunlight absorbance has been reduced. The pink colour of the solution is found to be slowly decolourised within an exposure time of three hours.

3. Results and discussions

3.1. UV-Visible spectral study

The green synthesized copper oxide nanoparticles are dispersed in demineralised water and subjected to UV-Visible absorption study. CuO nanoparticles represent the two absorption bands at 292 and 355 nm, conveying to the inter band transitions of core electrons of Cu metal and CuO nanocrystals. The oscillating nature of free electrons in conduction band are excited by the electromagnetic radiation is the reason for surface Plasmon absorption of metal oxide.surface Plasmon resonance is the resonate oscillation of conduction electrons at the interface between negative and positive permittivity material stimulated by incident light.

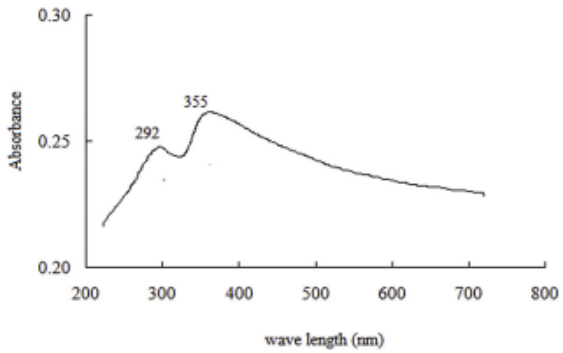

Figure 6: UV-Visible spectrum of copper oxide nanoparticles.

3.2. FTIR spectral study

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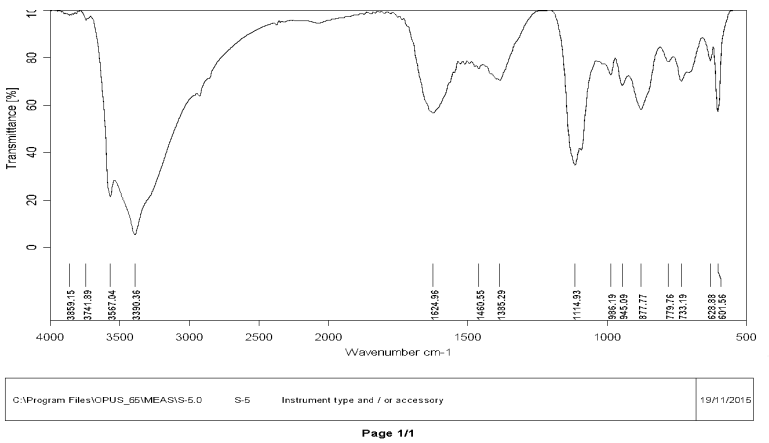

Figure 7: FTIR spectrum of copper oxide nanoparticles.

The FTIR spectrum obtained for copper oxide nanoparticles by leaf extract of *Andrographis Paniculata* is shown in **Figure 7**.The band at 3391 cm^{-1}corresponds to strong O-H stretching of H-bonded alcohols and phenols. The peak at 1626 cm^{-1} corresponds to the carbonyl stretching frequency in amide functional group. The bands appeared at 1461 cm^{-1} and 1387 cm^{-1} due to C=C stretching frequency of aromatic functional groups. The band at 1112 cm^{-1} corresponds to C-O stretching frequency of alcohols and amides. The peak at 778 cm^{-1} corresponds to C-H stretching. The peaks corresponding to 601 cm^{-1} and 627 cm^{-1} are assigned to M-O stretching of copper oxide.

3.3 XRD spectral analysis

The XRD spectrum of synthesiszied copper oxide nano particles from *Abutilon indicum*is shown in Figure (5.5).The peaks appearing at 2θ values of 32.57, 35.06, 49.05, 52.10, 58.14, 61.63, 67.67, 72.22, 74.68 (degrees) correponds to theBragg's reflections of (110), (111), (202), (020), (202), (113), (311), (311) and (004) planes respectevely.The above diffraction peaks indicate crystalline monoclinic structure of copper oxide nanoparticles. The data is in good agreement with JCPDS card no-45-0937. The average size of copper oxide nanoparticles is calculated by using Debye-Scherrer equation given below.

$D = K\lambda / \beta \cos \theta$

D = the crystallite size of copper nanoparticles

λ = the wavelength of x-ray source (0.1541 nm) used in XRD

β = the full width at half maximum of the diffraction peak.

K = the Scherrer constant with value from 0.9 to 1.

θ = the Bragg angle

The maximum peak appears at 2 theta value of 32.49 ° which corresponds to an average size of 49.21 nm for the copper oxide nanoparticles.

3.4 FESEM analysis

The FESEM image obtained for the green synthesized copper oxide nanoparticles is shown in **Figure 8.** The images of copper oxide nanoparticles indicate spherical morphology with a size in the range of 47-70 nm.

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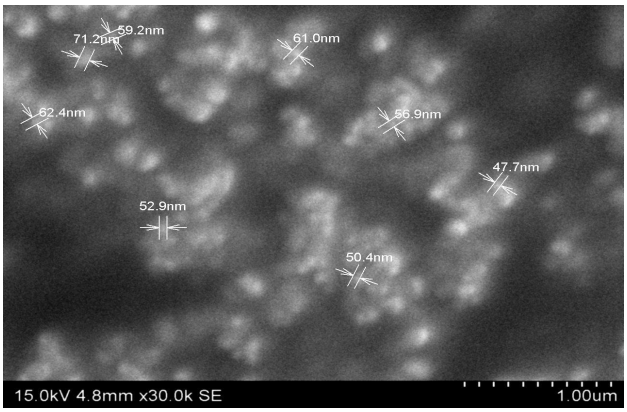

Figure 8: FESEM images of synthesized copper oxide nanoparticles.

3.5 EDX analysis

The EDX spectrum of green synthesized Copper oxide nanoparticles formed from *Andrographis Paniculata* leaf extract is shown in **Figure 9**. From EDX spectrumthe composition of copper and oxygen is 59.59% and 40.41%.

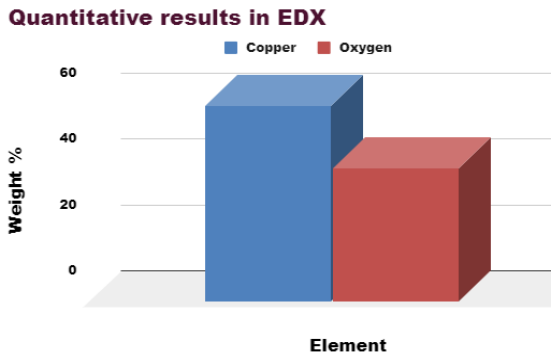

Figure 9: EDX analysis of copper oxide nanoparticles

3.6 TEM analysis

The TEM image of synthesized copper oxide nanoparticles from leaf extract of *Andrographis Paniculata* is shown in **Figure 10**. It is obvious from the image that the copper oxide nanoparticles are spherical with 100 nm size.

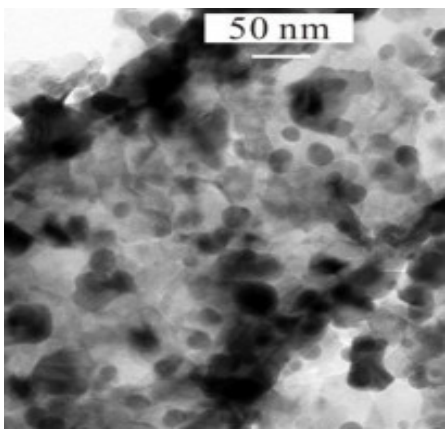

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Figure 10: TEM image of copper oxide nanoparticles.

3.7 Photodegradation

The green synthesized copper oxide nanoparticles are used as a photo catalyst in in the degradation of organic dye Alizarin red dye. The dark pink colour of 40 ppm Alizarin red dye is slowly decolourised on the addition of copper oxide nanoparticles.The time duration for the degradation reaction is 3 hours.The degradation experiment is pictorially shown in **Figure 11**.

Figure 11: Dye solution after three hours

3.8 Time vs absorption graph

The degradation study is evaluatedby using time vs light absorption graph by collecting absorption data using UV-Visible spectrum at various time intervals. The results are given in Table-1 and shown graphically in **Figure 12**. 40 ppm solution gives absorption maximum value of 0.681. This value decreases slowly on the addition of copper oxide nanoparticles along with time.

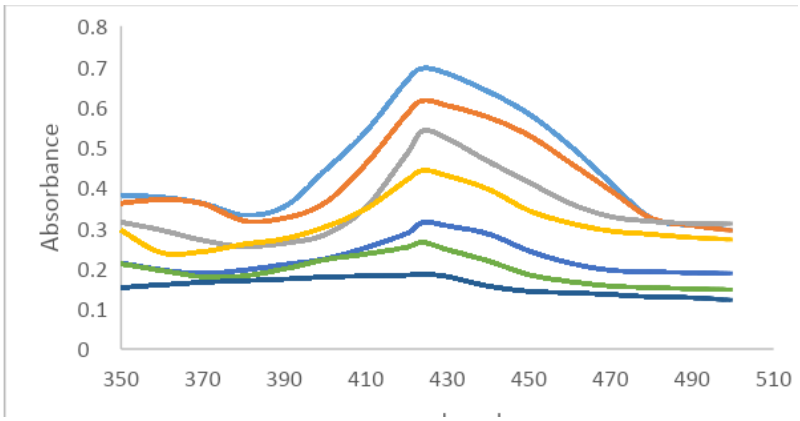

Figure 12: Photodegradation of Alizarin red

3.9 Time vs % of degradation

The photo catalytic efficiency of copper oxide nanoparticles is evaluated by calculating the percent degradation at various intervals of time. The corresponding graph is shown in **Figure 13**. After 3 hours of the reaction time the degradation is 73.23% and the graph indicates that % degradation increases with time.

$$\% \text{ of degradation} = [(A_0-A)/A_0] \times 100$$

Table 1: percentage degradation values of Alizarin red

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TIME (minutes)	ABSORBANCE	% OF DEGRADATION
0	0.681	----------
30	0.608	10.7195
60	0.538	20.9985
90	0.441	35.2423
120	0.311	54.3319
150	0.254	62.7019
180	0.181	73.4214

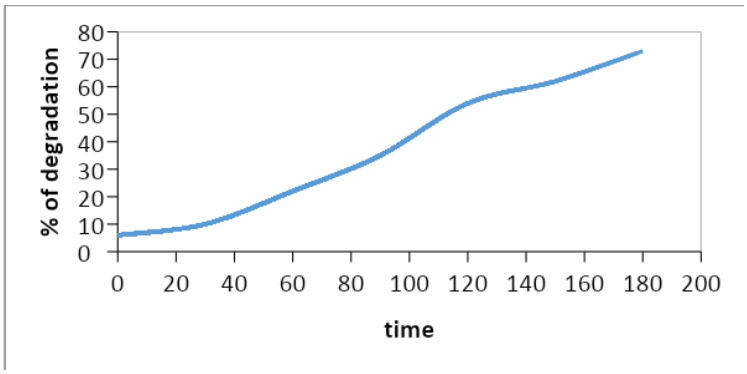

Figure 13: Time vs % degradation graph

3.10. Time vs 2+log(A) graph

The kinetic study of the photodegradation reaction is evaluated by plotting a graph between time and 2+ log(A) values given in Table 2 is shown in **Figure 14**. It gives a straight line with a negative slope. The slope is found to be 0.0128.the plot indicates that photo degradation of Alizarin red aqueous solution carried out by green synthesized copper nanoparticles follows pseudo first order reaction [16].

Time (minutes)	Absorbance(A)	log(A)	2+log(A)
0	0.681	-0.384192972832	1.615807027167
30	0.608	-0.497580397015	1.502419602984
60	0.538	-0.619896718820	1.3801032811796
90	0.441	-0.818710403535	1.182895964647
120	0.311	-1.167962366802	0.8302376331970
150	0.254	-1.370421011963	0.6295789880363
180	0.181	-1.709258247716	0.2907417522836

Table 2: 2+log values of absorption of copper oxide nanoparticles

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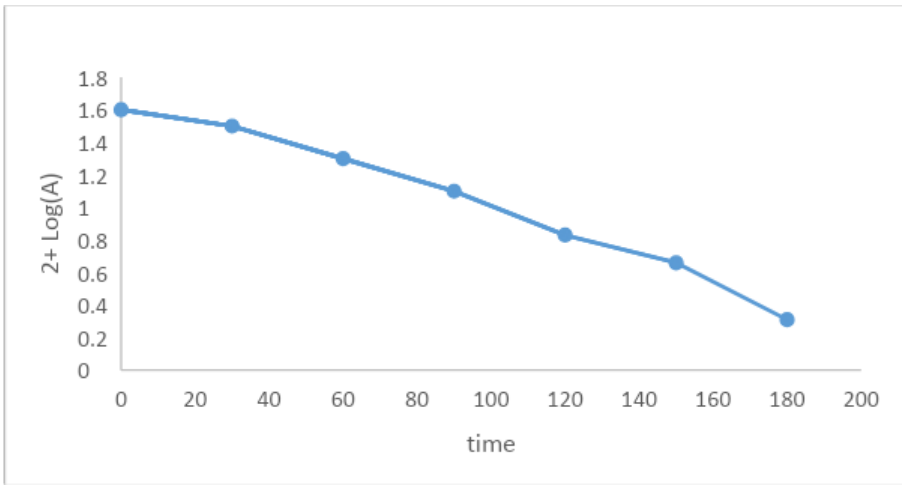

Figure 14: time vs 2+log(A) graph of copper oxide nanoparticles

3.11 Time vs log(A_0/A) :

The kinetics of photodegradation can also be studied by plotting the time vs log(A_0/A) values. A plot (**Figure 15**) gives a straight line with a positive slope. The slope is 0.0082.

Table 3: time vs log(A_0/A) of copper oxide nanoparticles

Time (minutes)	absorbance	A_O/A	log(A_O/A)
0	0.681	---------	--------
30	0.608	1.1200657894	0.1133874242
60	0.538	1.2657992565	0.2357037459
90	0.441	1.5442176871	0.4345174307
120	0.311	2.1897106109	0.7837693939
150	0.254	2.6811023622	0.9862280391
180	0.181	3.7624309392	1.3250652749

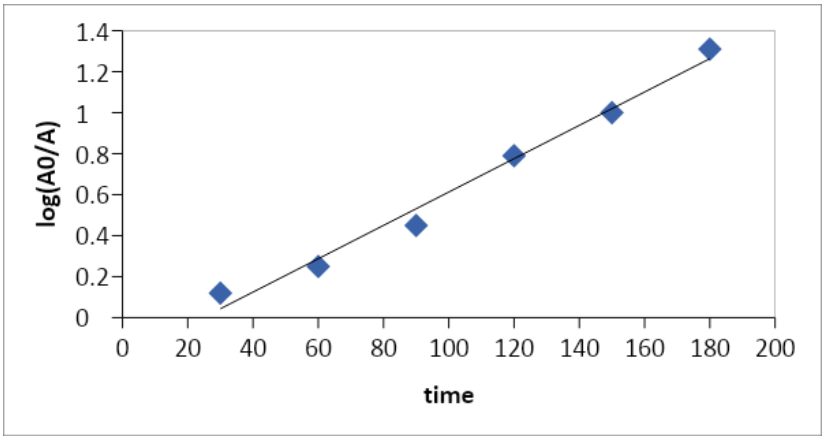

Figure 15: time vs log (A_0/A) graph of copper oxide nanoparticles

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The rate constant of the degradation reaction of Alizarin red using green synthesized copper oxide nanoparticles is calculated by following equation.

$$K = (2.303 \times M) / 60$$

$$K = (2.303 \times 0.0082) / 60$$

$$K = 3.1474 \times 10^{-4}\ Sec^{-1}$$

The rate constant obtained from above equation is 3.1474×10^{-4} sec^{-1}.

4. Conclusions

Copper oxide nanoparticles are synthesised from leaf extract of Andrographis paniculata. The nano particles are characterized by UV-Visible (292 nm, 355 nm), FT-IR, XRD (49 nm), SEM-EDX and TEM. The SEM and TEM images reveal spherical morphology for the nanoparticles.

The nanoparticles are applied to the photo degradation study of dilute solutions of Alizarin red dye. The degradation study reveals that the 40 ppm dye solution could be degraded by 60 mg of copper oxide nanoparticles with in a time period of 3 hours producing degradation of 73.23%. The kinetics studies on the other hand, shows degradation process following pseudo first order reaction. The rate constant of the photodegradation reaction is found to be 3.1474×10^{-4} sec^{-1}.

5.Conflict of Interest

The authors of this paper have no conflict of interest.

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