

Fabrication of Conifer Gum Based Metal Nano Particles for Pollution Control Applications

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Abstract

In recent decades, the analysis of nanoparticles is of greater importance for their applications in various fields. This present work also focuses the novel biological green material to synthesize the copper and cobalt oxide nanoparticles. The copper oxide (CuO) and cobalt oxide (Co₃O₄) nanoparticles (nps) have been synthesized by biological strategy utilizing AH (*Araucaria heterophylla*) gum extract. The characterization techniques, i.e. UV, GC-MS, FT-IR, XRD, SEM, HR-TEM provide concrete information about the morphology, crystalline nature and structure of the synthesized nanoparticles. The high resolution TEM and SAED images confirm the formation of spherical shaped (Co₃O₄) and oval shaped (CuO) isolated nanoparticles. The catalytic adequacy of the developed catalyst, copper oxide (CuO) and cobalt oxide (Co₃O₄) nanoparticles was analyzed for the degradation of dyes: Methylene Blue (MB), Congo Red (CR), Acid Violet (AV). The kinetic investigations for the reduction of synthetic dyes by the nanoparticles were assessed and the reduction contemplates are very much fitted with the pseudo second order kinetic model with less time. The antibacterial and antifungal activity of the prepared nanoparticles have been evaluated against *Escherichiacoli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Aspergillusniger* and *Candida albicans*.

Highlights

- Novel biological green material *Araucaria heterophylla* to synthesize the copper and cobalt oxide nanoparticles
- The synthesized CuO and Co₃O₄ nanoparticles are characterized by FT- IR, XRD, SEM, TEM and EDS procedures.
- The incorporated CuO and Co₃O₄ nanoparticles were utilized as proficient catalysts in the catalytic degradation of MB, AV and CR
- The antifungal activities of the synthesized copper oxide (CuO) and cobalt oxide (Co₃O₄) nanoparticles are tried against the organisms, such as, *Aspergillusniger* and *Candida albicans*.

1. Introduction

As of late, there is an extensive enthusiasm on metal nanoparticles as a result of their trademark property, which are totally not quite the same as the mass. Nanoparticles are exceptionally encouraging in light of the fact that they utilize imaginative materials with new electronic, attractive and warm properties. They have expansive surface to volume proportion and it display expanded surface reactivity contrasted with mass materials, which gives them to go about as a decent impetus [A. Muthu Kumara Pandian et al. 2021]. Recent research recommended that when metal particles turned out to be little in size, their redox properties vary from mass metal. In this manner, nano particles have pulled in consideration from both essential and mechanical perspectives in view of their quantum measure impact which is from the decrease of free electrons [Jinming Liu et al. 2020]. Synthesis of nanoparticles is of extraordinary significance, as particles developed from a couple of hundred molecules have properties unique in relation to the mass. Various techniques i.e., physical, compound, natural strategies have been utilized for the readiness of metal nanoparticles [Zhongliang Ma et al. 2018]. There is a need to create eco-accommodating procedures to maintain a strategic distance from the utilization of hazardous/cancer-causing synthetic substances in the process are termed as the "green synthesis". Green combination of metal nanoparticles have points of interest over the existing different strategies and methods as a result of its modest, eco-accommodating, effectively utilized for huge scale blend and it needn't bother with high weight, temperature and poisonous synthetic concoctions for the union [Reza Mohammad inejad et al. 2016]. The different bio molecules found in the plant extricates, incorporate polysaccharides, polyphenols, aldehydes, ketones, proteins, catalysts, amino acids, peptides that can decrease the metal particle and balance out the nanoparticles with required shapes and sizes [Ahmed Barhoum et al. 2020].

Among the different metal nanoparticles, copper nanoparticles are conceivably appealing, on the grounds that they are powerful in different properties like optical, electrical, thermal properties [Xiulin Shu et al. 2020]. Because of their prevalent quality, they are utilized as sensors, energy storage devices and it is mostly utilized as an antimicrobial operators and antifungal specialists [S. Pavithradevi et al. 2017]. Furthermore, besides, copper nanoparticles have high thermal and electrical conductivity. Copper nanoparticles have additionally been utilized as an option for gold, silver and platinum nanoparticles in numerous different fields, for example, thermal and microelectronics [Xiang-nan Zhua et al. 2021]. Among the different inorganic specialists, copper nano particles are generally utilized as fungicide, pesticide, algacide and herbicide [Mostafa Khajehzadeh et al. 2021].

Copper nanoparticles have unique qualities including reactant and antifungal/antibacterial exercises that are not typically seen in commercial copper [Prashansa Sharma et al. 2021]. It produces solid reactant movement; this can be accomplished in light of their expansive synergist surface territory, smaller in size and extraordinary porosity [Mandalparthi Phanindrudu et al. 2020]. It is very well may have the capacity to accomplish a higher response yield when it is used as officials in natural and organometallic combination [Huaqiao Tang et al. 2018]. Copper nanoparticles that are smaller in size and have a high surface to volume proportion that can be a source of antimicrobial movement. It is extremely successful in controlling a scope of pathogens [A.A. Menazea and M.K. Ahmed 2020]. The utilization of the less economic part of *Myristicafragrans* fruit's pericarp was carried out for the preparation of antimicrobial copper oxide nano particles [Drishya Sasidharan et al. 2020].

As of late, metal oxides have made substantially more significance because of their attractive properties and applications in numerous fields. Metal oxides can embrace a huge assortment of auxiliary geometries with an electronic structure that may show a few different attributes with the physical, synthetic properties [K. Yazhini and S.K. Suja 2019]. Among the various metal gatherings, cobalt oxide (Co₃O₄) is a standout amongst the most essential nano materials in view of its attractive properties and thermal strength. Co₃O₄ is an imperative antiferro magnetic p-type semiconducting materials with synthetic solidness at high temperature, high mechanical quality and band hole of 2.19V [M.Mayakannan et al. 2020]. The Co₃O₄ nanoparticles demonstrate great conductivity because of the Co³⁺ particles. The Co₃O₄ is a spinel structure which is more complicated than CoO with the stone salt structure. Dissimilar to CoO, there are two sorts of Coparticlesin Co₃O₄, tetrahedrally organized Co²⁺(II) and octahedrally planned Co³⁺(III). The unit cell of Co₃O₄ has 8 Co²⁺, 16 Co³⁺ and 32 Oxygen particles, which gives an expansive unit cell [Shikha DubeyJay Kumar et al 2018], [SwarupRoy and Jong-WhanRhim 2021]. In green amalgamation, the concentrates of different parts of plants, for example, root, stem, bark, leaf, natural product, bud, and latex are utilized as diminishing operators [Erica Rodríguez-León et al. 2019], [Kunle Okaiyeto et al. 2021]. The different biomolecules found in the plant removes, incorporate polysaccharides, polyphenols, aldehydes, ketones, proteins, chemicals, amino acids, peptides that can diminish the metal particle and settle the nanoparticles to suitable shapes and sizes [Akhil Rautela et al. 2019]. In this present work, the green synthesis of copper and cobalt oxide nanoparticles was carried out by utilizing *Araucaria heterophylla* plant gum concentrate and it go about as a bio-diminishing and bio-balancing out specialist.

Microorganisms are primarily delegated as Gram positive and Gram negative, where the fundamental distinction lies in their cell divider composition [Saba Pirtarighat et al. 2019]. The cell mass of both gram positive and gram negative microorganisms comprises of a solid peptidoglycan layer, yet this layer is thicker in Gram positive and marginally more thinner in Gram negative bacteria [Roonak Golabiazar et al. 2019]. The Gram negative microscopic organisms contain a lipopolysaccharide layer in their external film, which makes their cell divider arrangement more startling than Gram positive microbes [Liheng Chen et al. 2020], [Mahruha Sultana Niloy et al. 2020]. Some antimicrobial operators affect Gram positive microscopic organisms than Gram negative microbes, on account of

their less intricate cell divider structure. Microscopic organisms have a few distinct intends to acquire and share obstruction [Jixing Cui et al. 2020]. Among these are transformation and even quality exchange, the last of these can occur by plasmids, transposons and lysogenic bacteriophage [Subhajit Chakraborty et al. 2021], [Vivek Ahluwalia et al. 2018].

In the present work the antibacterial and antifungal activities of the synthesized copper oxide (CuO) and cobalt oxide (Co₃O₄) nanoparticles were tried. The microbes utilized in the antibacterial movement were *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Salmonellaparatphi*. *Staphylococcus aureus* and *Bacillus subtilis* are gram positive microorganisms. *Escherichia coli* and *Salamonellaparatyphi* are the gram negative bacteria. *S.aureus* and *E.coli* are known to develop a few of the bacterial diseases in the network. The organisms utilized for the antifungal activity are *Aspergillusniger* and *Candida albicans*. Metal nanoparticles are fabricated based green approach using AH gum and will tested for antimicrobial, antifungal apart from dye adsorption phenomena described in the article.

2. Materials And Methods

2.1. Preparation of gum extract and metal nanoparticles

The collected plant gum was washed in distilled water to remove residues and powdered to get the dark brown powder and stored in humid free atmosphere. 0.1 wt. % gum in double distilled water was used for the preparation of copper and cobalt oxide nanoparticles. 0.1M cobalt nitrate (Co (NO₃)₂.6H₂O) was dissolved in distilled water and mixed with gum extract and kept under constant magnetic stirrer for around 30 min. After that 0.2M NaOH solution were added drop wise to the above blended solution and while the addition of NaOH solution the pink colored solution was changed to olive green and to light brown. After the entire addition of NaOH solution, stirring was proceeded for around 2 hr at room temperature. The dark brown color cobalt hydroxide precipitate settles down and the excess solution found on the top disposed off very carefully and the brown color precipitate which was separated, washed with distilled water for a few times. Also, it was warmed in a muffle furnace at 400°C for 3 hr. Finally, the black color cobalt oxide (Co₃O₄) precipitate was obtained. Similarly, the copper oxide (CuO) nanoparticles were set up by the above strategy utilizing copper nitrate (Cu(NO₃)₂.3H₂O) and NaOH solution (1:2M proportion). The brown colored precipitate was separated and washed with distilled water for few times and heated in a muffle furnace at 400°C for 3 hr. At last, the brownish black color copper oxide (CuO) precipitate was obtained for further investigations.

2.2. Characterization of nanoparticles

Synthesized metal (Co₃O₄, CuO) nanoparticles were characterized by conventional analytical techniques. Dimensions, morphological features and chemical compositions of samples were examined by GC-MS using Shimadzu make GCMS-QP2010 SE instrument, Scanning Electron Microscopy (SEM), using a Scanning Electron Microscope with an Energy dispersive X-ray spectrometer (JSM 6390 LV) at magnification of 30,000. The films of the samples were set up on a carbon covered copper network by setting a little measure of the sample and after that allowed to dry earlier estimations. Qualitative confirmation of the metal nanoparticles composition was measured by various techniques. Fourier-transform infrared spectroscopy (FTIR) were recorded with a FT/IR-4600typeA, JASCO to detect functional groups of Co₃O₄, CuO nanoparticles. X-ray diffraction (XRD) recorded for Co₃O₄, CuO to understand crystal indices, structure and size of the nanoparticles using X-ray diffractometer (Shimadzu, XRD 6000) with Cu k α radiation ($\lambda = 0.1548$ nm) at 40 kV and 80 mA in the region of 2θ from 10 ° to 90 °. Size, morphology and crystalline nature of Co₃O₄, CuO nanoparticles were investigated by high resolution through transmission electron

microscope (TEM) and selected area electron diffraction (SAED) were also recorded on a Technai G20-stwin using an accelerating voltage of 200 kV and different magnified images have been displayed.

2.3. Degradation of Organic Dyes

Degradation of Methylene Blue (MB), Acid Violet-49 (AV) and Congo red (CR) dyes utilizing the green-integrated copper and cobalt oxide nanoparticles as catalyst in the presence of sodium borohydride (NaBH_4). The 20mg of synthesized nanoparticles was added to different concentrations (10, 20, 25, 30, 40, 50ppm) of aqueous dye solution with freshly prepared NaBH_4 and the response analyzed by UVVIS spectrophotometer. Color change observed once the reaction completes, i.e. colored solution changes in to colorless. In the present examination, degradation of above dyes by Co_3O_4 , CuO in the presence of NaBH_4 and impact of gum extract (20mg, 50mg concentrations) incorporated nanoparticles was examined for the degradation of dyes. Catalyst (NaBH_4) used in the reaction is centrifuged, washed with distilled water and dried for further experiments.

2.4. Antimicrobial investigation

2.4.1. Antibacterial activity

Standardized inoculums were vaccinated in the plates and leave it to dry at room temperature with closed lids. Each petri dish was partitioned into 3 sections for each sample, such as Co_3O_4 , CuO(100 μg) plate (plates are absorbed overnight in sample solution) and standard *Ciprofloxacin* 10 μg , was placed in the plate with the assistance of sterile forceps and placed in the fridge at 4 $^\circ\text{C}$ for 24 hr. Zone of inhibition developed by various samples measured using scale and recorded the average of two diameters of each zone.

2.4.2. Anti fungal activity

Inoculums for the test were set up from fresh sabouraud \bar{x} s broth and standardized by altering the culture turbidity to that of McFarland standards. Each petri dish was separated into 3 sections, i.e. Co_3O_4 , CuO (100 μg) plate (discs are soaked overnight in sample solution) and standard *Fluccanazole* 10 μg , are set in the plate with the assistance of sterile forceps and placed at 28 $^\circ\text{C}$ for 48 hr. Zone of inhibition measured for various samples.

3. Results And Discussions

3.1. Characterization of metal nanoparticles

3.1.1. GC-MS Analysis

Fig.1 shows the GC-MS spectrum of AHG. Interpretation of GC-MS spectrum was done using the database of National Institute Standard and Technology (NIST) having more than 62,000 patterns and NIST library. Thirty peaks were identified from the GC-MS analysis and Table 1 presents the data associated with each of the lines in the spectrum.

Table 1 Phytochemical constituents identified in the acetone extract of AHG

using GC-MS

S.No.	Retention time	Compounds
1	10.861	ALPHA-CUBEBENE
2	12.263	GAMMA-ELEMENE
3	12.378	CYCLOHEXANE
4	13.487	NAPHTHALENE
5	13.627	1,6-CYCLODECADIENE
6	14.014	BICYCLO[8,1,0]UNDECA-2,6-DIENE
7	14.486	ISOLEDENE
8	14.665	BETA-CADINENE
9	15.149	BETA-PANASINSENE
10	15.559	GERMACRENE B
11	15.631	1,6,10-DODECATRIEN-3-OL
12	16.047	10,12-TRICOSADIYNOIC ACID
13	24.703	PHENANTHRENE
14	26.825	BUTANOIC ACID
15	29.152	RETINOL
16	29.68	DIHYDROTACHYSTEROL
17	30.451	THUNBERGOL
18	30.587	CHOLEST-14-ENE
19	30.65	BETA-GUAIENE
20	30.85	BICYCLO[5,3,0]DECANE
21	30.958	ACETIC ACID
22	32.002	9,19-CYCLOERGOST-24(28)-EN-3-OL
23	32.151	BETULIN
24	32.217	CARYOPHYLLENE
25	32.512	ABEIETIC ACID
26	32.617	1,3,6,10-CYCLOTETRADECATETRAENE
27	33.513	2-PROPENAL
28	34.451	BETA-PIMARIC ACID
29	35.311	BETA-SITOSTEROL
30	36.705	2-PENTENOIC ACID

3.1.2 X-Ray Diffraction Analysis

Figure 2 (a) displays the X-diffraction pattern of the copper oxide (CuO) nanoparticles, which shows 0 sharp peaks at $2\theta = 32.4761^\circ, 35.5294^\circ, 38.7619^\circ, 48.7658^\circ, 58.348^\circ, 61.5522^\circ, 66.2714^\circ, 68.0937^\circ, 74.9736^\circ, 75.2964^\circ, 83.6025^\circ$ corresponds to the crystal indices of (110), (110), (111), (020), (211), (211), (202), (220), (221), (212), (310) and coordinated with their *JCPDS card number 01-089-5899*. These confirms the formation of copper oxide nanoparticles with the *monoclinic* structure using Debye- Scherrer's formula, average crystalline size (20.11 nm) of the copper oxide calculated. Whereas, Co_3O_4 (Fig. 2b) shows nine sharp peaks at $2\theta = 10.2931^\circ, 19.1325^\circ, 31.3816^\circ, 36.9141^\circ, 44.8747^\circ, 59.7425^\circ, 60.0062^\circ, 65.3978^\circ$ and 77.6806° correspond to the crystal indices of (010), (100), (110), (101), (111), (210), (211), (211) and (221). And these are well coordinated with their *JCPDS card number 01-080-1539*. From the outcomes acquired, it affirms the development of cobalt oxide nanoparticles with the *cubic* structure. From the PXRD reports and by utilizing the Debye-Scherrer's formula, the normal crystalline size of the cobalt oxide (13.06 nm) was figured. The diffraction pattern affirms that the incorporated cobalt oxide nanoparticles quality and its crystalline nature [M. Mayakannan et al. 2020]. Fig. 1. (a) XRD pattern of copper oxide (CuO), cobalt oxide (Co_3O_4) nanoparticles.

3.1.3. FT-IR Studies

FT-IR spectra of cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles displayed as figure (3a,b) which exhibits the quality and nature of the metal oxides. Cobalt oxide (Co_3O_4) nanoparticles shows significant absorption peaks at 555.50, 582.50 (Co-O stretching vibration) and 659.66cm^{-1} (bridging vibration of O-Co-O bond), which confirms the formation of Co_3O_4 nanoparticles. Spectral absorption bands observed for CuO at 605.65, 482.20, 412.77cm^{-1} confirms pure monoclinic phase. There is sharp peak seen at 605.65cm^{-1} highlights the qualities of Cu-O band formation and broad absorption bands affirms development of copper oxide (CuO) nanoparticles production [AliBashiri Rezaie et al. 2018].

3.1.4. SEM and EDAX Analysis

SEM visual images of cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles with different magnifications shown in figure (4). SEM images reveal the presence of porous (various sizes) morphology with entrenched smoothness on the nanoparticle surface. It was observed that the cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles are in agglomerated condition and the blended cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles were almost spherical and oval in shape individually. The SEM pictures of the nanoparticles of different magnifications like little grains with about round shape(Co_3O_4) and oval shape (CuO) [Subhajyoti Samanta and Rajendra Srivastava et al. 2016].The EDAX spectrum confirms the qualitative presence of surface level atomic distribution and arrangement of chemical components present in the cobalt and copper oxide nanoparticles. The strong signal of the Co and Cu atoms demonstrates the crystalline property and other major peaks are Cu, Co and O atoms. Apart from these major peaks, no other peaks are noted in figure, which confirms the qualitative nature of Co_3O_4 , CuO [M.A.Abdo and A.A.El-Daly et al. 2021].

3.1.5. TEM Analysis

The size, morphology and crystalline nature of the integrated cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles were evaluated by TEM. High resolution TEM pictures, SAED sample of the integrated cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles are shown in the Fig. 5 (a) and (b). The TEM pictures provides reasonable recommendations about size, shape and size distribution of the nanoparticles. In the Fig. 5 (a)demonstrate that particles are very much isolated and almost spherical in shape with the slight agglomeration.

Whereas, Fig. 5(b) shows particles are isolated with substantial grains and almost oval in shape and with uniform size [A.Klegova A.Inayat et al. 2019].

3.2. Catalytic activity of synthesized CuO and Co₃O₄ nanoparticles

Organic dyes (non-degradable) are broadly utilized as a shading agent for various matrices, material, paper, plastic and nourishment enterprises. Numerous reports are recommended that metal and metal oxide nanoparticles are utilized as catalyst to reduce hazardous dyes from water through photo degradation process. Here, catalytic reduction ability of green synthesized CuO and Co₃O₄ nanoparticles (as catalyst 20mg) was explored for degradation of MB, AV, CR dyes (20ppm) within the sight of NaBH₄ (10mMol) as a hydrogen generator. Dyes MB, AV-49, and CR demonstrates the respective absorption peaks at 664, 545, 614 nm individually. After adding NaBH₄, the reduction of MB, AV-49 and CR without CuO and Co₃O₄ nano catalyst demonstrates the small decreases in the absorption maximum. In the presence of nano catalyst (20mg), the reduction procedure was observed to be quick decline in the absorption intensity. The intensity of the characteristic blue, violet and red shade of MB, AV-49 and CR systematically diminishes and wind up rapid. Reduction reaction of MB, AV-49 and CR affirmed by the electronic spectra and the respective solid absorption peak has been vanished in double beam uv-vis spectrophotometer. Cobalt oxide nanoparticles performs better degradation, with quicker timing of 25 min, 30min, 35min to degrade completely the AV-49, MB and CR dye solution respectively.

3.2.1. Effect of dye concentration

The impact of an initial dye concentration is a vital parameter for degradation process. Degradation limits of the catalyst relies upon the impact of time with dye concentration at consistent temperature and measurement of catalyst. Rate of degradation gets diminished with the increase in dye concentration of methylene blue with time for both CuO and Co₃O₄ nanoparticles. The most notable degradation rate of cobalt oxide nanoparticle is less for MB compared to CuO nanoparticles. Similarly, AV dye concentration investigated from 20ppm- 50ppm solution with both CuO and Co₃O₄ nanoparticles. Degradation rate diminished with expanding the underlying grouping of reduction process, Co₃O₄ nanoparticles set aside lesser time for the entire degradation of AV dye solution contrasted to CuO nanoparticles. Subsequently the cobalt oxide nanoparticle has most notable degradation rate which sets aside less time for degradation of dye solution. Cobalt oxide (Co₃O₄) nanoparticles set aside lesser time for the entire exploitation of CR solution than CuO nanoparticles. Degradation rate of all the above dyes (MB, AV-49, and CR) emphatically relies upon the underlying dye concentration. The proficiency of synergistic degradation of the colors diminished with increment of the underlying dye concentration. The cobalt oxide (Co₃O₄) nanoparticles are exceptionally compelling and it has the higher productivity for the degradation of the (MB, AV-49 and CR) dyes analysed the outcomes acquired for the CuO nanoparticles [Revathi Kottappara et al. 2021].

3.2.2. Kinetics studies of catalytic reduction

Catalytic degradation is a quickly growing innovation for waste water treatment, including an extensive variety of organic poisons. In this way, understanding the kinetics and mechanisms of catalytic degradation of synthetic dyes is a fundamental part of evaluation. The degradation phenomena was inspected by two active models, pseudo first order and pseudo second order.

The pseudo first order equation can be communicated by,

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$$

Where k_1 is the pseudo first order rate constant (min^{-1}), q_e and q_t are the amount of colors (MB, AV-49 and CR) reduced (mg/g) at equilibrium and at time t (min) required for the reduction procedure. The plot of $\log(q_e - q_t)$ against time t should give the direct relationship from which k_1 and q_e can be ascertained by the slope and intercept acquired from the chart individually.

The pseudo second order equation is given beneath:

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

Where k_2 is the pseudo second order rate constant (g/mg/min), q_e and q_t are the measures of dyes (MB, AV-49 and CR) diminished (mg/g) at equilibrium and at time t (min) required for the reduction procedure. The plot of t/q_t against time gives the slope of $1/q_e$ and an intercept of $1/k_2 q_e^2$.

The kinetic examinations are completed by different concentrated solutions of MB, AV-49, CR solution blended with cobalt and copper oxide nanoparticles. The estimations of k_1 , q_e and correlation coefficient (R^2) are given in the Table 2. The observed results for both cobalt and copper oxide nanoparticles demonstrates that R^2 values for pseudo first order kinetic model are generally lesser and figured q_e values are suggestively not the same as the exploratory qualities. Along these lines, further the investigational outcomes were fitted with the pseudo second order active model. The slope of $1/q_e$ and an intercept of $1/k_2 q_e^2$ and the values of k_2 , q_e , are displayed in the Table 2. The plots were observed to be in great concurrence with the correlation coefficients. The figured q_e (hypothetical) values are very much coordinated with the trial q_e qualities and R^2 are additionally high, which speaks to the relevance of pseudo second order to clarify the reduction procedure. The outcomes got affirm that the second order kinetic equation is the best fitting model for both the cobalt and copper oxide nanoparticles.

Table 2
Kinetic data of pseudo first order and second order reaction of catalytic reduction

Dye	Catalyst	Conc (ppm)	Pseudo first order			Pseudo second order		
			qe(cal) (mg/g)	k1(min ⁻¹)	R2	qe(cal) (mg/g)	k2(g/mg/min)	R2
Methylene blue	Co3O4	10	9.3003	0.0755	0.9473	22.54429	0.00084357	0.9901
		20	12.2360	0.0586	0.9511	37.78351	0.00057015	0.9824
		25	19.5169	0.01220	0.9741	43.850732	0.00032846	0.9903
		30	35.6736	0.01267	0.9667	58.25975	0.00015251	0.9838
	CuO	10	15.48418	0.09769	0.8492	20.46857	0.0007885	0.9954
		20	18.96602	0.06860	0.8699	41.91065	0.00055251	0.9841
		25	11.83288	0.02194	0.9048	58.78351	0.00023857	0.9918
		30	24.68606	0.012505	0.9678	38.09906	0.00017011	0.9912
Acid violet 49	Co3O4	20	10.541441	0.06248	0.9697	31.56069	0.0007865	0.9904
		30	15.63147	0.04890	0.9503	48.78067	0.0002383	0.9923
		40	20.706413	0.020972	0.9282	55.51035	0.0001998	0.9907
		50	37.98336	0.022622	0.9503	37.93249	0.00012693	0.9928
	CuO	20	9.162485	0.07856	0.9539	22.075055	0.0008879	0.993
		30	14.41452	0.038946	0.9634	44.68063	0.00055252	0.9898
		40	23.28627	0.014025	0.9392	52.86792	0.00028019	0.9877
		50	29.48936	0.015197	0.9468	39.79245	0.00011195	0.9903
Congo red	Co3O4	10	8.61164	0.08944	0.8646	23.746400	0.0005189	0.9901
		20	17.7648	0.49657	0.8804	49.962931	0.0002784	0.9967
		30	25.150795	0.19843	0.9011	78.113377	0.0001680	0.9809
		40	33.545683	0.14242	0.871	46.155076	0.0001034	0.9973
	CuO	10	7.852356	0.072079	0.8947	28.271433	0.000573720	0.9906
		20	13.91573	0.049155	0.9356	63.598952	0.000353713	0.9915
		30	28.19786	0.022448	0.9050	48.7265980	0.000227960	0.9935
		40	39.97567	0.013808	0.8710	53.8672625	0.000157235	0.9899

3.2.3. Effect of NaBH₄ in the presence and absence of the cobalt and copper oxide nanoparticles

Reduction of MB, AV-49, CR dye by NaBH₄ without cobalt and copper oxide nanoparticles for a time period of 120 min shown in Fig. 6. The little diminishing pattern in the ingestion shows reduction of previously mentioned dyes

however in the moderate way. Furthermore, the level of decline using NaBH_4 is less and it took extensive stretch of time to degrade the dyes [Changshun Chu et al. 2019]. The reductions of MB, AV-49 and CR by NaBH_4 in the presence of chemically dynamic copper and cobalt oxide nanoparticles are shown in the Fig. 6. Furthermore, rates of evacuation of colors are likewise highly contrasted with the reduction done by NaBH_4 without catalyst.

3.2.4. Mechanism of dye degradation process

The catalytic activity of synthesized copper and cobalt oxide nanoparticles was measured through the reduction of MB, AV-49 and CR. The MB, AV-49 and CR solutions treated with the NaBH_4 and blended catalysts. The dye molecules were rapidly degraded due to the electron exchange between the dye molecules (MB, AV-49 and CR - acceptor) and NaBH_4 (donor). Nucleophile BH_4 ions give electrons to electrophilic organic atoms [Komal N. Patil et al. 2021] present in MB, AV-49 and CR dyes, through copper and cobalt oxide nanoparticles. Rate of reduction of MB, AV-49 and CR dyes by NaBH_4 was expanded within the sight of both of the catalyst and moderate reduction observed without copper and cobalt oxide nanoparticles.

3.2.5. Effect of the mixture of the two organic dyes

The effluents from the industries contain few synthetic organic dyes, which are discharged directly into the water source. Here an attempt was made to study the effect of mixture of (MB and AV) were examined. Catalytic degradation of the mixture of two synthetic dyes (MB and AV) was exceptionally good, i.e mixed dyes were degraded 96% and 98% with 20mg of the copper and cobalt oxide nanoparticles separately. Similar in line, catalytic degradation of the blend of two synthetic dyes (MB and CR) provides 85% and 88 % degradation with the 20mg of the copper and cobalt oxide nanoparticles separately. The outcomes acquired when these dyes are treated alone in similar parameters and concurrent presence of two organic dyes in solution did not decline catalytic reduction process. Degradation rates acquired for both mono and bi-component framework were similar. It is recommended that both copper and cobalt oxide nanoparticles can be capable to form complex frameworks with excess of one organic atom or molecule [Mohammed Hachemaoui et al. 2021].

3.2.6. Effect of the gum extract

Reduction of organic dyes (MB, AV-49 and CR- (20ppm), by the regular green fluid concentrate of *Araucaria heterophylla* gum extract (1% solution) with the presence of copper and cobalt oxide nanoparticles. The absorbance data demonstrate the concentrate to degrade dyes (MB, AV-49 and CR) solution and 120 mins time date shows appreciable decline in dyes absorbance. Therefore, copper and cobalt oxide nanoparticles may act as an electron exchange mediator between the extract and the dyes molecule solutions by executing as a redox catalyst, which is assigned as an electron transfer impact (Fig. 9). Copper and cobalt oxide nanoparticles act as an electron exchange mediator between the extract and the methylene blue dye solution. Fig. 9 reveals the dye removal of methylene blue by the gum extract within the sight of various quantity (20mg and 50mg) of copper and cobalt oxide nanoparticles. Fig. 10 indicates the level of the reduction of acid violet-49 dye solution by the gum extricate within the sight of various quantities (20mg and 50mg) of copper and cobalt oxide nanoparticles. The reduction of absorbance demonstrates the concentrate to degrade the color solution. This technique towards the finish of 120 min time interim demonstrated a detectable reduction in the absorbance of dye solution. Fig. 11 speaks the reduction of Congo Red dye solution by the gum extract within the sight of various amounts (20mg and 50mg) of copper and cobalt oxide nanoparticles. Reduction of mixture of dyes (MB and AV-49) solutions by the characteristic green fluid extract of *Araucaria heterophylla* gum and within the sight of copper and cobalt oxide nanoparticles also investigated in detail. Blended dyes were degraded 80%, 90%, 77% and 85% with the 20mg and 50mg of the cobalt

and copper oxide nanoparticles individually, after 120 min of light and same outcomes have been gotten when these dyes are dealt with alone in similar parameters. Presence of the two organic dyes in the solution did not interfere with the catalytic degradation of every one of them and degradation rates got for both mono and bi-component framework were same [Arnaud Viola et al. 2019]. In any case, it is less compelling when contrasted with the catalytic reduction of both mono and bi-component solutions of dyes by NaBH_4 within the sight of both cobalt and copper oxide nanoparticles. Fig. 12 speaks the level of the reduction of mixed of dyes (MB and AV-49) solutions by the gum extract within the sight of various amounts (20mg and 50mg) of copper and cobalt oxide nanoparticles. Reduction of mixture of dyes (MB and CR) solutions by the normal green aqueous extract of *Araucaria heterophylla* gum and were degraded 86%, 90%, 79% and 85% with the 20mg and 50mg of the cobalt and copper oxide nanoparticles individually. Presence of the two organic dyes in the solutions did not intrude on the catalytic degradation and degradation rates follows both mono and bi-component framework (Fig. 13). The outcomes acquired for the reduction of MB, AV-49 and CR dyes solutions by utilizing gum extract in the presence of various measure of catalyst are less viable and it required long investment to degrade the dye solutions.

3.2.6. Recycling of cobalt and copper oxide nanoparticles

The wide utilization of new recyclable catalyst has been the crucial point in the field of catalysis. After completion of the reaction, the nano catalyst powder was centrifuged and separated off from the reaction mixture pursued by washing with ethanol, $(\text{CH}_3)_2\text{CO}$ and water for several times. The recuperated catalyst then reused under similar conditions for numerous cycles to check its catalytic adequacy. Fig. 14 shows the effect of incorporated cobalt and copper oxide nanoparticles which remains relatively steady, where there is a little debilitating in the action of the recouped catalyst with each synergist run [Palash Kumar Dhar et al. 2021]. After the fourth and fifth cycles, the productivity of exploitation essentially diminished. However, rate of degradation is overwhelming after multiple times of copper and cobalt oxide NPs reuse. Accordingly the cobalt and copper oxide nanoparticles were promising in destroying the synthetic organic dyes in the water sanitization framework as a potential catalyst [Serpil Kılıç Depren et al. 2020].

3.3. Antibacterial and antifungal activity

The antibacterial and antifungal activities of the synthesized cobalt oxide (Co_3O_4) and copper oxide (CuO) nanoparticles shown in Fig. 15 were studied and the results obtained are compared with the standard ciprofloxacin. In this present work, the antibacterial activity was tested in the *Escherichiacoli*, *Salmonella paratphibacteria* (gram negative) and *Staphylococcus aureus*, *Bacillus subtilis* (gram positive). The antibacterial activities of Co_3O_4 and CuO nanoparticles against the above mentioned bacteria were studied by determining the inhibition zone which was shown in the Table 3. From the tabulated results, the copper oxide nanoparticles shows the good inhibition zone against the bacteria. The antibacterial activity of both cobalt and copper oxide nanoparticles are shown in the below diagram.

The antifungal exercises of the incorporated Co_3O_4 and CuO nanoparticles were contemplated and the results are contrasted with the standard *Fluccanazole* [Suresh ChandMali et al. 2020]. In this present work, the organisms utilized for the antifungal movement are *Aspergillusniger* and *Candida albicans* and the inhibition zone are shown in the Table 3. From the results, it was observed that the cobalt oxide nanoparticles demonstrates the great hindrance zone against the parasites [M.Elango et al. 2018].

Table 3
Antibacterial and Antifungal activity of the copper oxide and cobalt oxide nanoparticles.

S.No.	Organisms	Zone of Inhibition(mm)		
		STD (Ciprofloxacin) (100µg/disc)	Samples (100µg/disc)	
Copper oxide (CuO)	Cobalt oxide (Co3O4)			
1.	<i>Staphylococcus aureus</i>	45	26	16
2.	<i>Bacillus subtilis</i>	48	20	33
3.	<i>Escherichia coli</i>	41	20	11
4.	<i>Salmonella paratyphi</i>	45	30	14
5	<i>Aspergillusniger</i>	13	15	20
6	<i>Candida albicans</i>	16	16	18

4. Conclusion

In this present work, the effective copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles are blended by utilizing the green synthesis technique. The synthesized copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles are characterized by Infrared spectroscopy (FT- IR), X-beam diffraction (XRD), Scanning electron microscope (SEM), Transmission electron microscope (TEM) and EDS procedures. The catalytic action of the blended copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles in the reduction of organic dyes, such as, Methylene blue (MB), Acid violet-49 (AV) and Congo red (CR) colors have been examined. The synthesis of copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles through the green blend approach utilizing the gum extract from the *Araucaria heterophylla*. The synthesized nanoparticles are exceptionally steady at room temperature and it demonstrates the brilliant catalytic property. So it tends to be utilized for the commercial applications. The normal crystalline size of the copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles was ascertained from the XRD results and the size of the copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles was observed to be 20.11nm and 13.06 nm respectively. The kinetic investigations for the reduction of synthetic dyes by utilizing the integrated nanoparticles are likewise assessed and the reduction contemplates are very much fitted with the pseudo second order kinetic model and in the lesser time, it totally reduces the organic dyes. This outcome covers the incorporated copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles as a proficient catalyst in the catalytic degradation process. The Antibacterial activity of the synthesized copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles are tried for both gram positive and gram negative microorganisms. The copper oxide (CuO) nanoparticles demonstrated the preferred movement over the cobalt oxide (Co3O4) nanoparticles. The copper oxide (CuO) nanoparticles are most dynamic against the *Salmonella paratyphi* microscopic organisms contrasted with the other microbes, such as, *Escherichiacoli*, *Staphylococcus aureus*, *Bacillus subtilis*. The antifungal activities of the synthesized copper oxide (CuO) and cobalt oxide (Co3O4) nanoparticles are tried against the organisms, such as, *Aspergillusniger* and *Candida albicans*. The cobalt oxide (Co3O4) nanoparticles demonstrated the preferable action over the standard (*Fluccanazole*) and the copper oxide (CuO) nanoparticles. Hence, the copper and cobalt oxide nanoparticles are as superb antimicrobial materials.

Declarations

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Author contribution

Rathika Govindasamy contributed to the conception and design, acquisition, analysis, and interpretation, drafted the manuscript, and gave final approval. **Suba Velu** contributed to statistic preparation and acquisition and gave final approval. **Shanthana Lakshmi Duraikkannu** contributed to draft preparation and gave final approval. RoopalaRani Sekar contributed to experimental analysis and statistic preparation.

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Data availability

The datasets analysed during the current work are available from the corresponding author on reasonable request.

Declarations

This material is the authors' own original work, which has not been previously published elsewhere.

The paper is not currently being considered for publication elsewhere.

The paper reflects the authors' own research and analysis in a truthful and complete manner.

The paper properly credits the meaningful contributions of co-authors and co-researchers.

All sources used are properly disclosed (correct citation).

All authors have been personally and actively involved in substantial work leading to the paper, and will take public responsibility for its content.

Ethics approval

This article does not contain any studies involving animals performed by any of the author

Consent to participate

Informed consent was obtained from all individual participants included in the study.

Consent for publication

All authors have approved this version of the work.

Competing interests

The authors declare no competing interests

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Figures

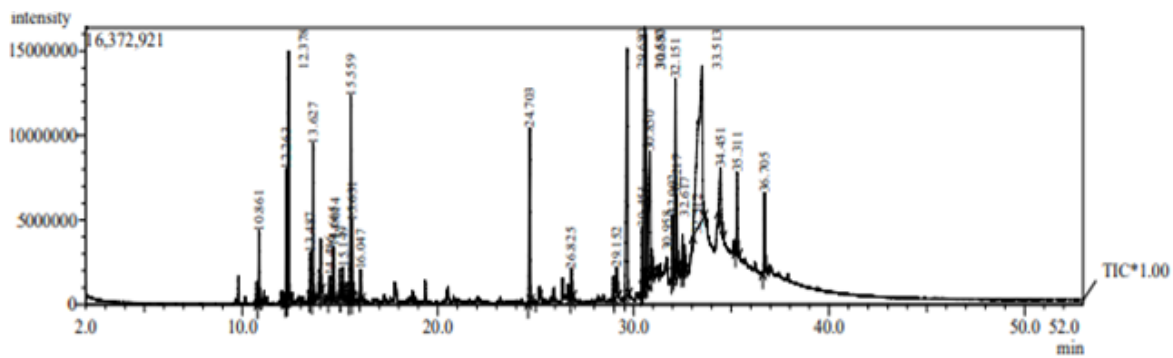


Figure 1

GC-MS spectrum of *Araucaria heterophylla* gum (AHG)

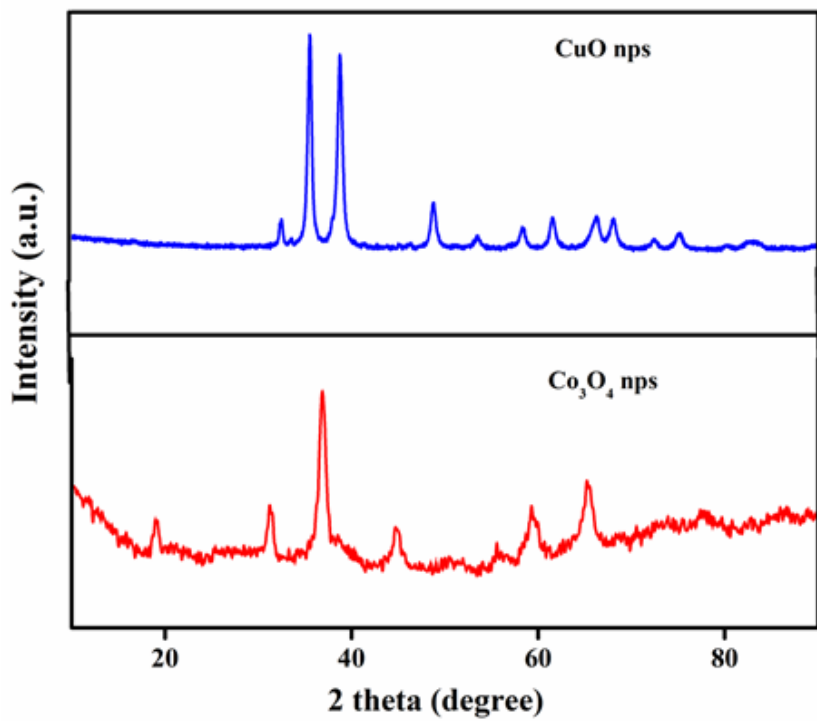


Figure 2

XRD pattern of (a) copper oxide (CuO); (b) cobalt oxide (Co₃O₄) nanoparticles.

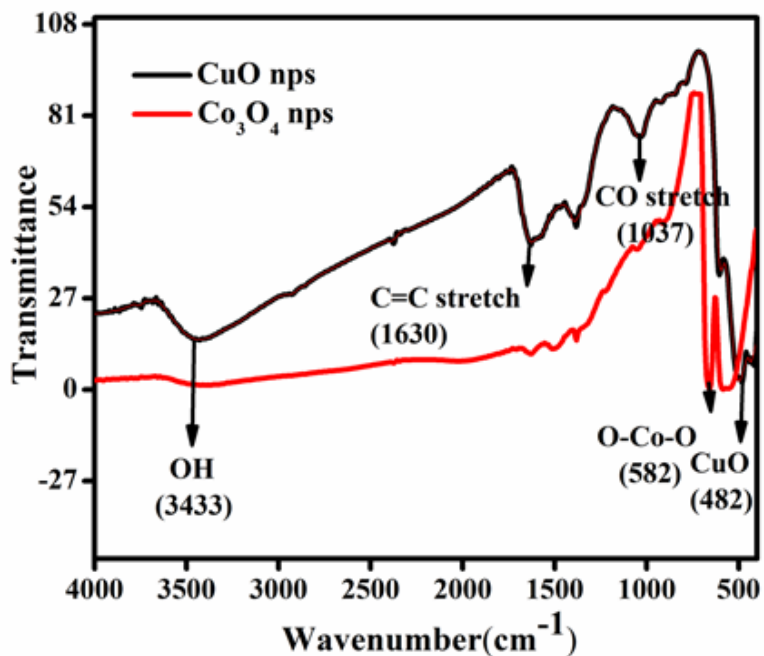


Figure 3

FT-IR spectra of cobalt oxide and copper oxide nanoparticles.

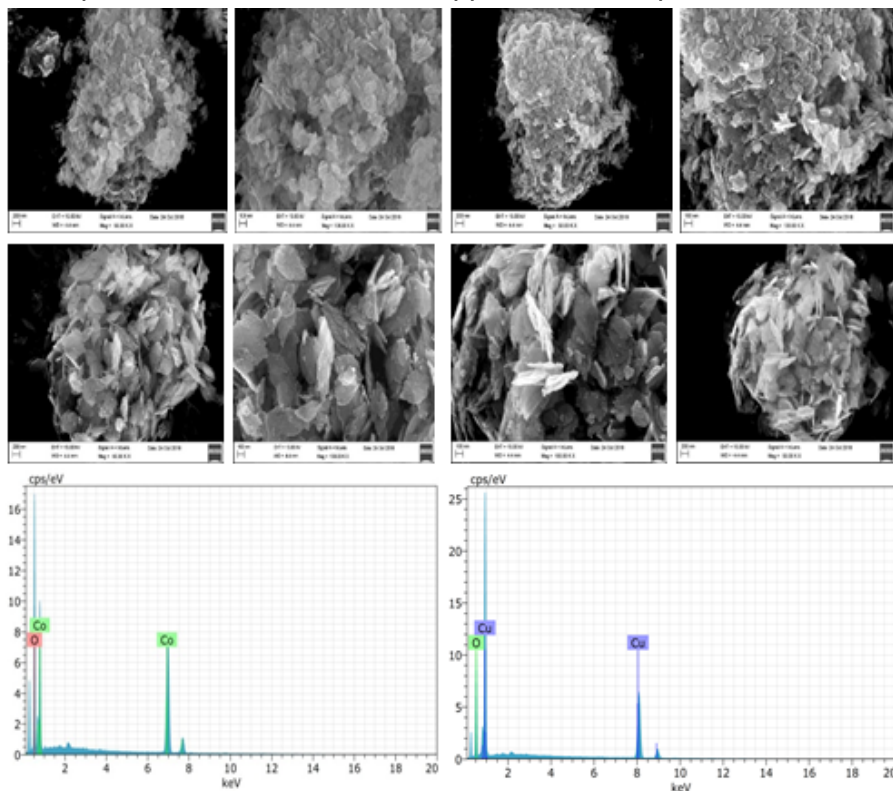


Figure 4

SEM morphology images of (a).Cobalt oxide (Co₃O₄) ; (b). Copper oxide (CuO) nanoparticles and EDAX spectrum of synthesized (a) cobalt oxide (Co₃O₄); (b) copper oxide (CuO)nanoparticles.

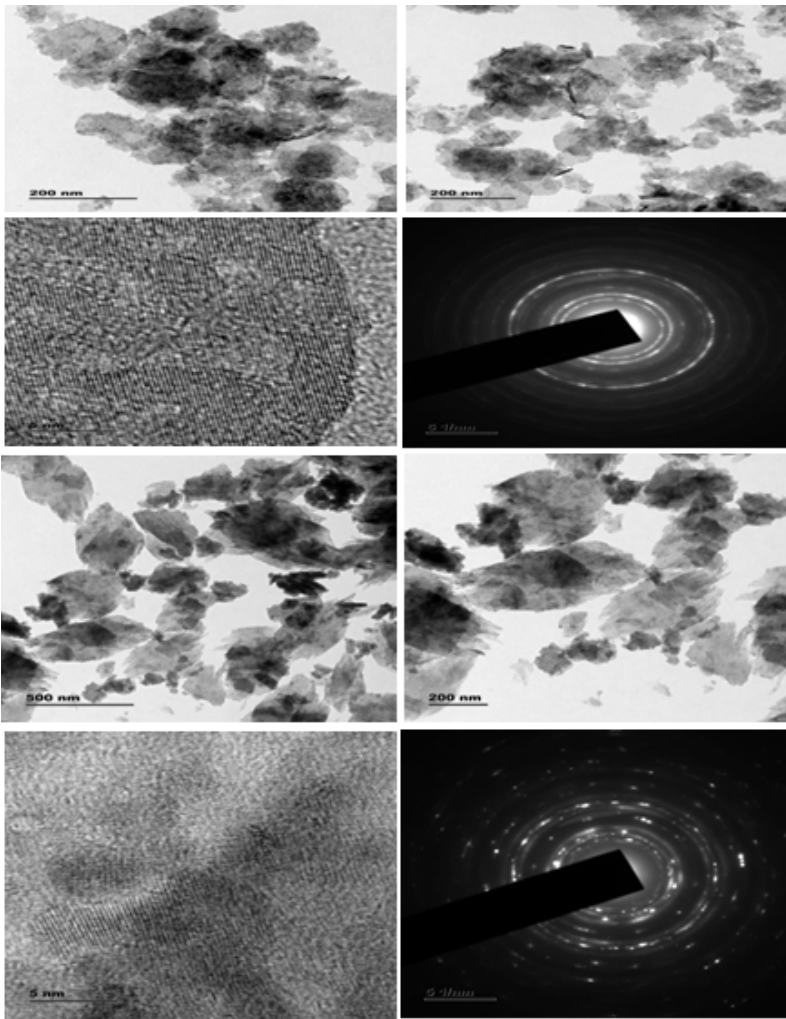


Figure 5

(a) HR-TEM and SAED images of synthesized cobalt oxide (Co₃O₄) nanoparticles under different magnifications.

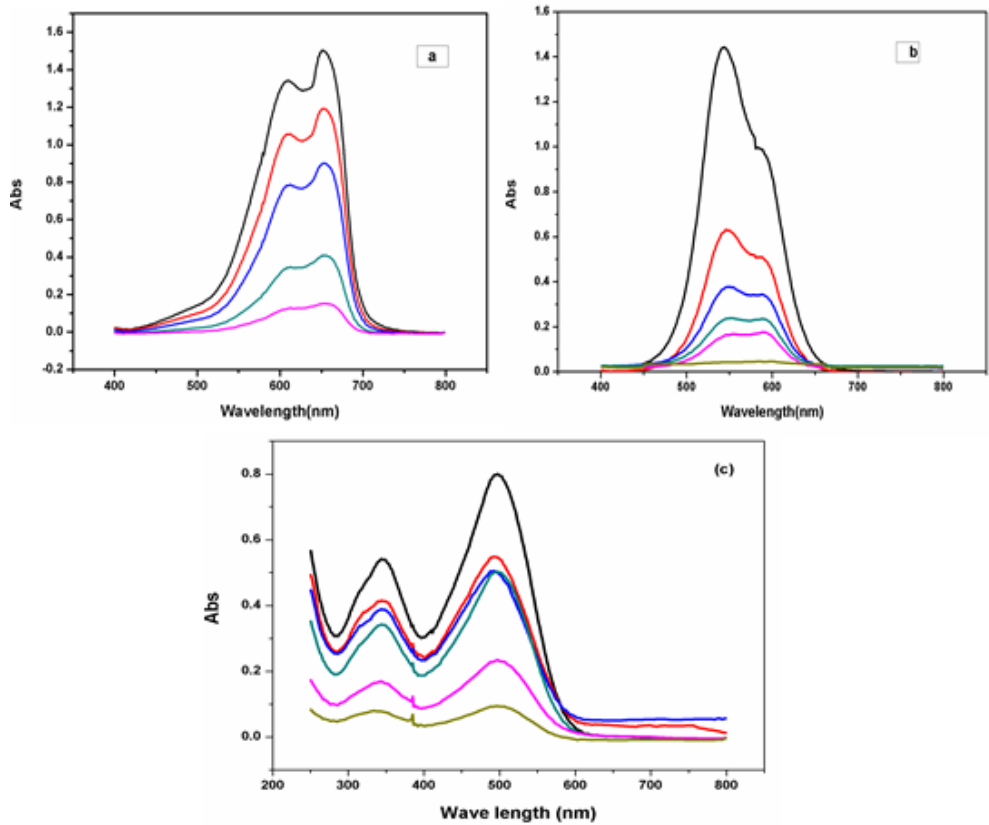


Figure 6

UV-Vis spectra of Methylene blue (a), Acid Violet-49 (b) and Congo red (c) reduction by NaBH₄ in presence of nano catalyst.

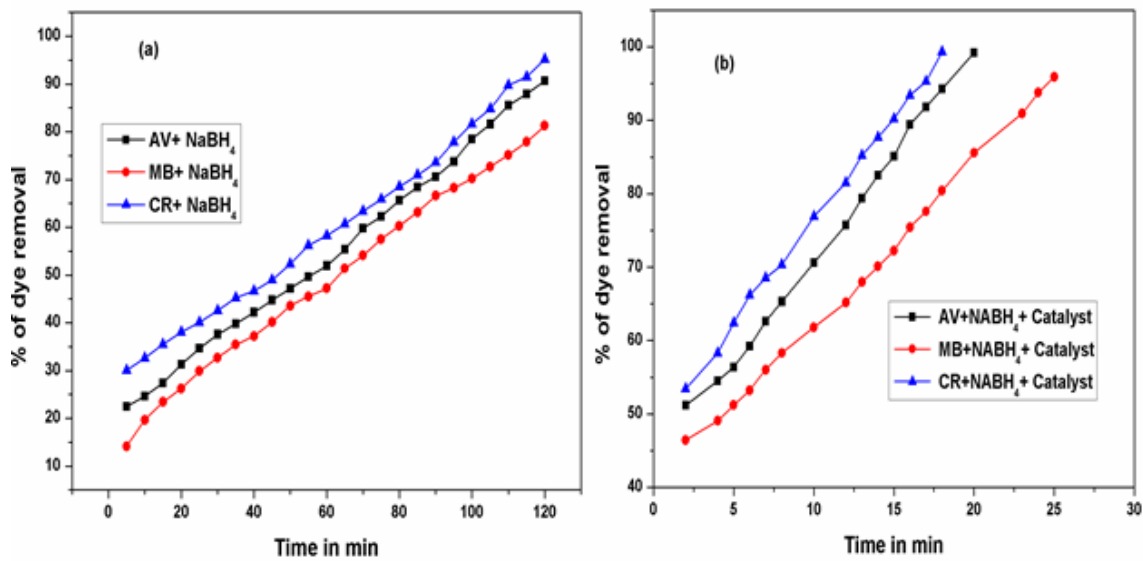


Figure 7

Reduction of MB, AV-49 and CR dyes by NaBH₄ a) in the absence of catalyst and b) in the presence of catalyst.

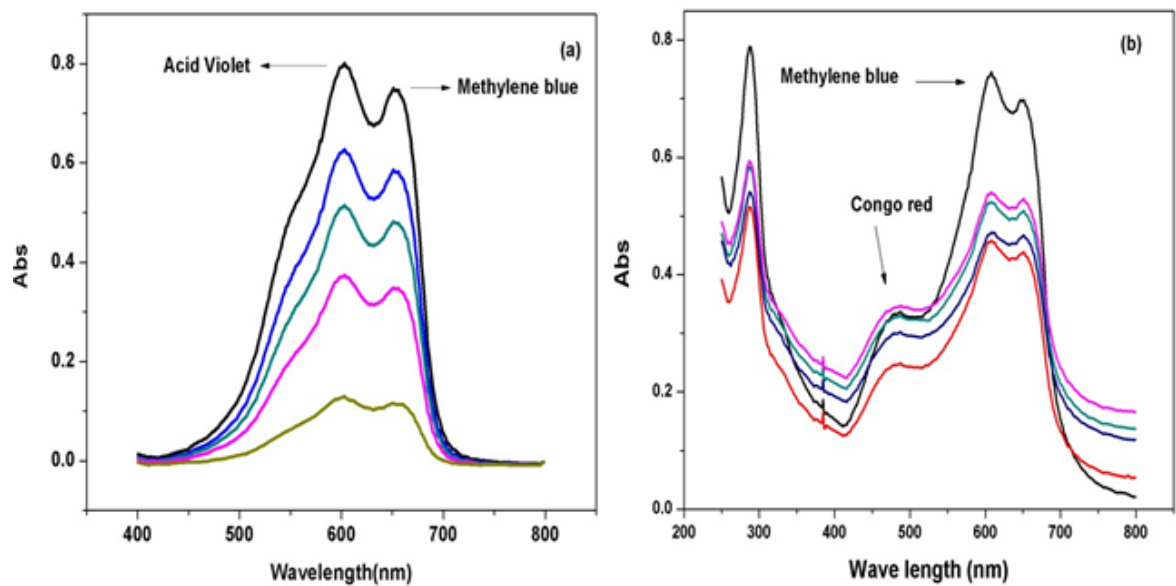


Figure 8

UV-Vis spectra for the catalytic reduction of mixture of two dyes (MB and AV) and (MB and CR)

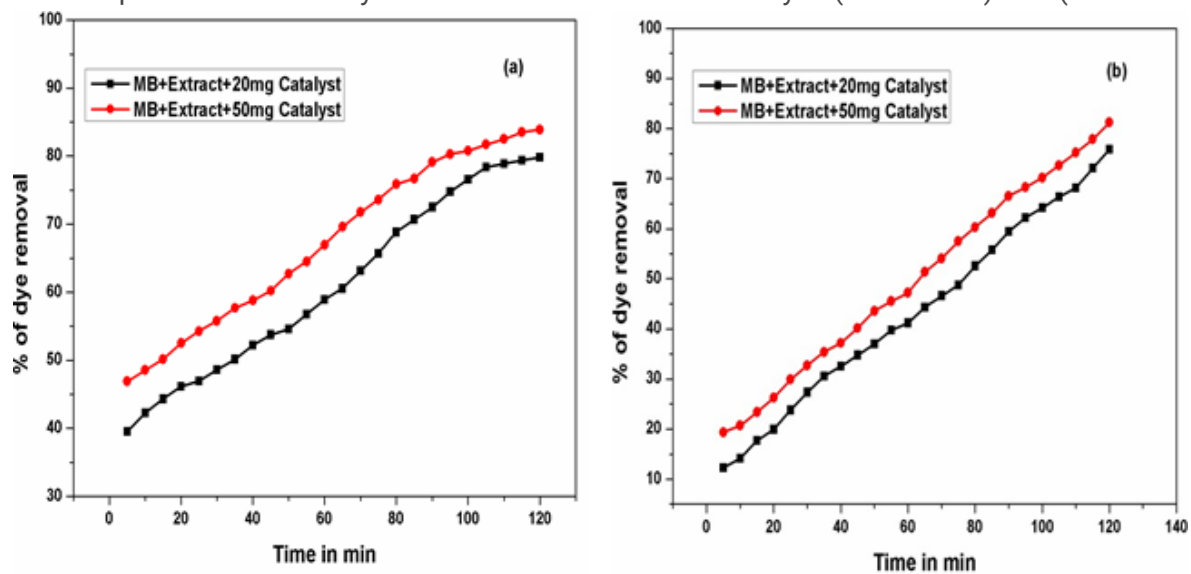


Figure 9

The percentage of the dye removal obtained on the reduction of methylene blue dye solution by the gum extract in the presence of different amounts (20mg and 50mg) of cobalt oxide (a) and copper oxide (b) nanoparticles.

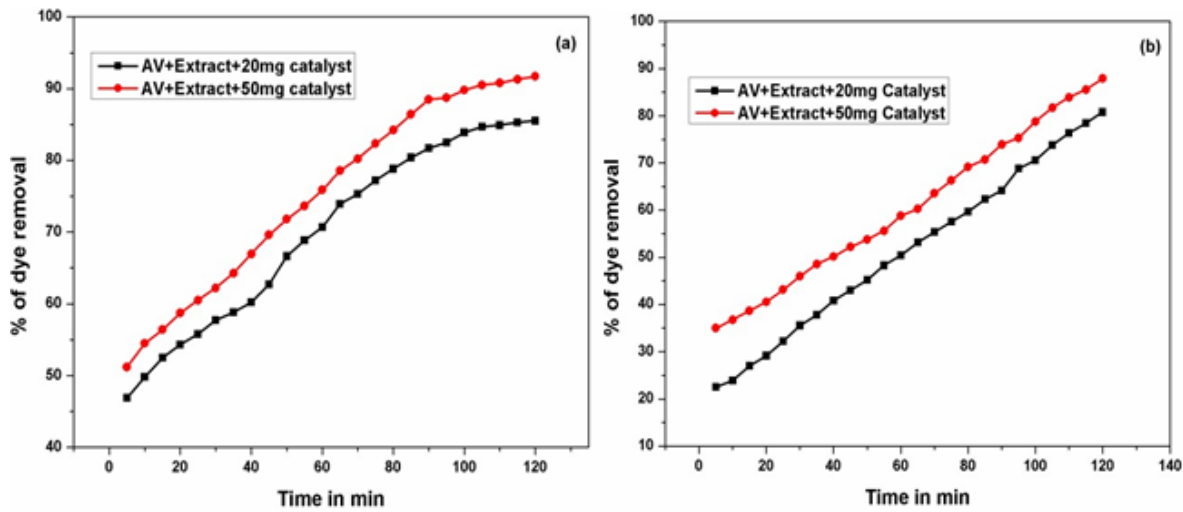


Figure 10

Percentage of the dye removal obtained on the reduction of AV-49 dye solution by the gum extract in the presence of different amounts (20mg and 50mg) of cobalt oxide (a) and copper oxide (b) nanoparticles.

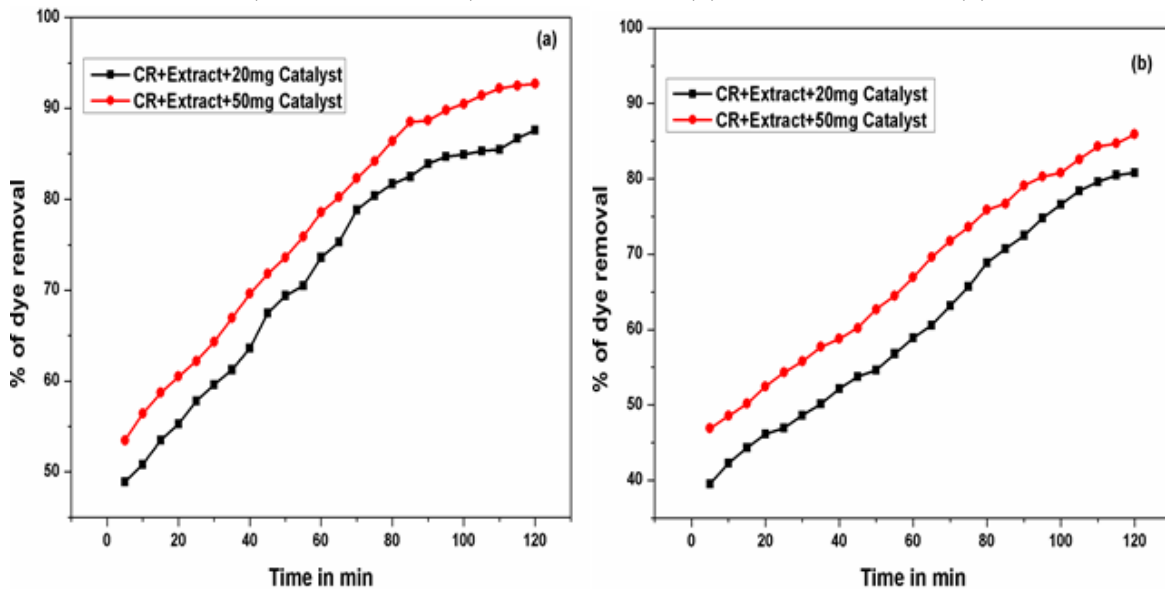


Figure 11

The percentage of dye removal obtained on the reduction of Congo Red dye solution by the gum extract in the presence of different amounts (20mg and 50mg) of cobalt oxide (a) and copper oxide (b) nanoparticles.

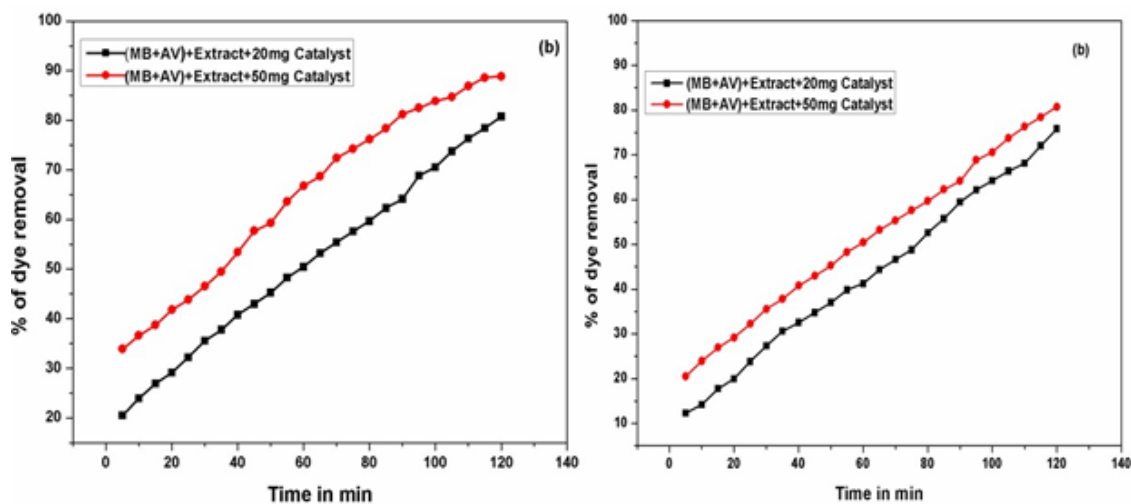


Figure 12

The percentage of dye removal obtained on the reduction of mixture of two dyes (MB and AV-49) solution by the gum extract in the presence of different amounts (20mg and 50mg) of cobalt oxide (a) and copper oxide (b) nanoparticles.

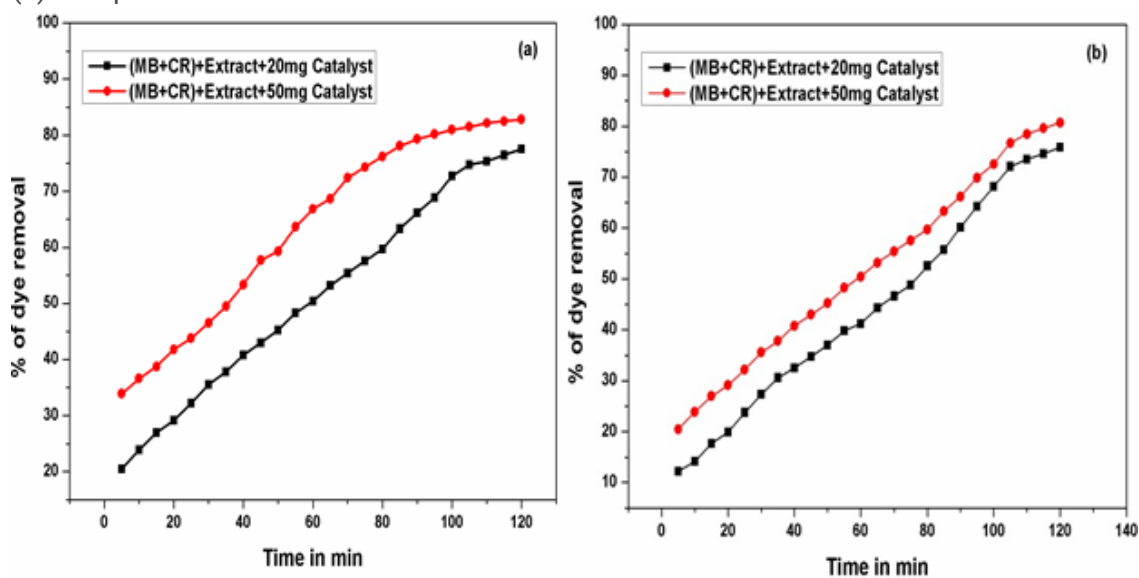


Figure 13

The percentage of dye removal obtained on the reduction of mixture of two dyes (MB and CR) solution by gum extract in the presence of different amounts (20mg and 50mg) of cobalt oxide (a) and copper oxide (b) nanoparticles.

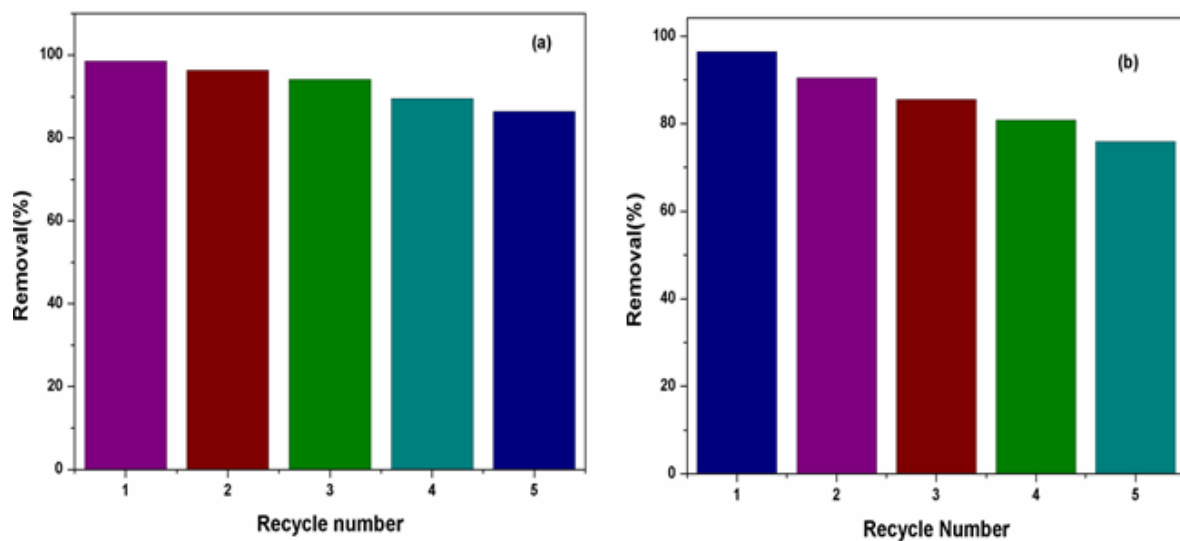


Figure 14

The catalytic performance and reusability of (a) cobalt and (b) copper oxide

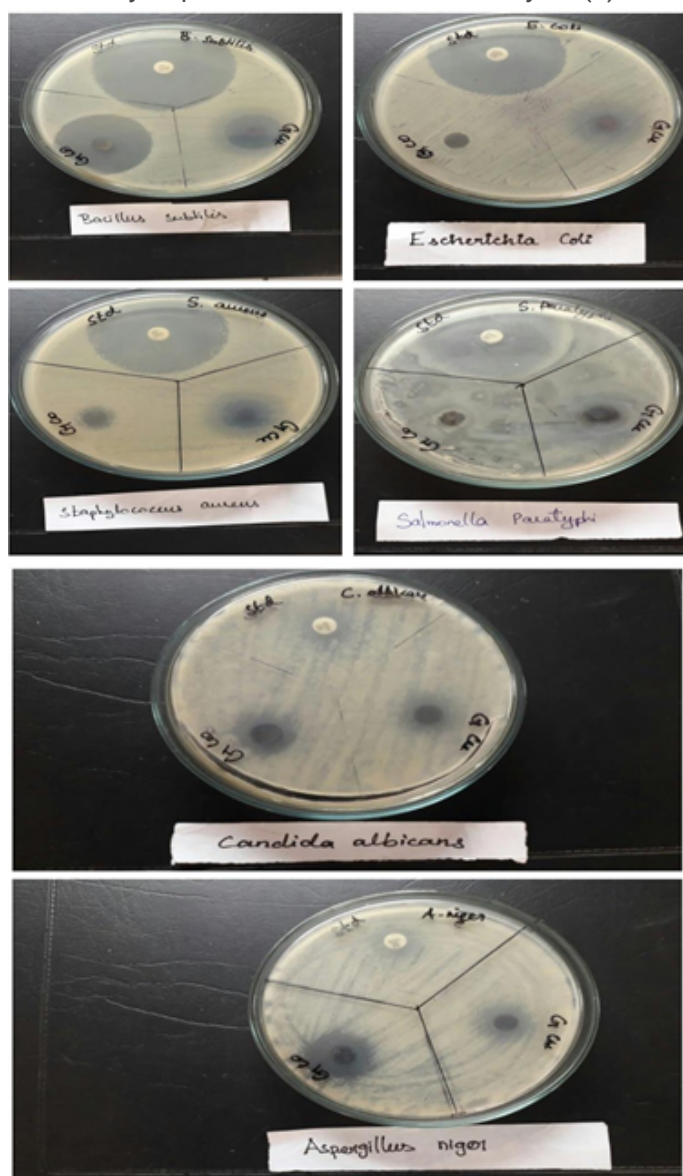


Figure 15

Images of antibacterial and antifungal activities obtained for the copper oxide (Cu) and cobalt oxide (Co) nanoparticles.

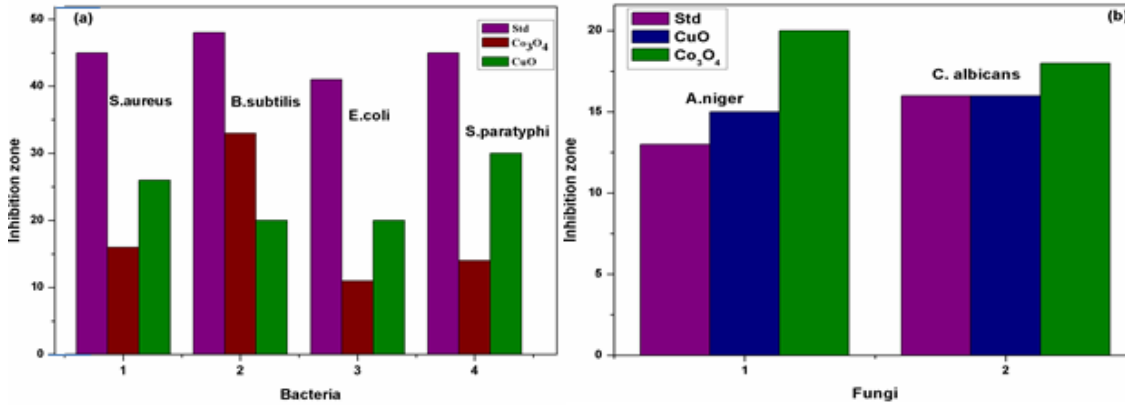


Figure 16

Bar diagram of antibacterial (a) and antifungal (b) activities of CuO and Co₃O₄ nanoparticles

Supplementary Files

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