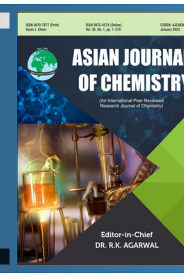
Asian Journal of Chemistry; *Vol. 35, No. 3 (2023), 578-584*

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2023.26896



Green Synthesis of Bimetallic ZnO-CuO Nanocatalyst for the Hydro-dechlorination of 1,2-Dichlorobenzene and 3-Chlorophenol

PAVANI PEDDI[1,*], P.T.S.R.K. PRASADA RAO[2], CHEBOLU NAGA SESHA SAI PAVAN KUMAR[3], SATWINDER SINGH MAROK[4], NANNAPANENI USHA RANI[1] and S. LAKSHMI TULASI[1]

[1]Department of Chemistry, Freshman Engineering Department, Prasad V. Potluri Siddhartha Institute of Technology, Kanuru, Vijayawada-520007, India
[2]Department of Chemistry, P.B. Siddhartha College of Arts and Science, Vijayawada-520010, India
[3]Division of Chemistry, Department of Sciences and Humanities, Vignan's Foundation for Science, Technology and Research, Vadlamudi, Guntur-522213, India
[4]Apotex Inc, 150 Signet Drive, Toronto, ON, M9L 1T9, Canada

*Corresponding author: E-mail: pavanipeddi7@gmail.com

Received: 9 October 2022; *Accepted*: 7 January 2023; *Published online*: 27 February 2023; AJC-21148

Bimetallic nanoparticles exhibit advantageous catalytic, optical and electrical properties and among the various methods of synthesis of nanoparticles, green synthesis gained great attention due to its simplicity, cost effective, ecofriendly and versatility. In view of this, the present work intended to synthesize the ZnO-CuO bimetallic nanoparticles using aqueous root extract of *Suaeda maritima* (L.) *Dumort.* The bimetallic nanoparticles synthesized were observed to be spherical in shape with particle size in the range of 20-45 nm and the particles were distributed with less aggregation. The synthesized nanoparticles have 41% of zinc element and 33% copper with hexagonal phase crystalline structure of zinc oxide and monoclinic copper oxide phase. The synthesized ZnO-CuO bimetallic nanoparticles were used for the hydro-dechlorination of 1,2-dichlorobenzene and 3-chlorophenol. The results indicated that rapid dechlorination was observed during the initial time of study. The percentage dechlorination of 19.37 ± 0.243 and 15.52 ± 0.193% was observed within 5 min of the study for 1,2-dichlorobenzene and 3-chlorophenol, respectively. The high % dechlorination was achieved within 25 min wherein the % dechlorination was observed to be 93.35 ± 0.103 and 89.75 ± 0.091 for 1,2-dichlorobenzene and 3-chlorophenol, respectively. This study reports the cost-effective and eco-friendly method for synthesizing ZnO-CuO bimetallic nanoparticles that can utilize for the dechlorination of various polychlorinated aromatic compounds in natural samples.

Keywords: Bimetallic ZnO-CuO nanoparticles, Green synthesis, Hydro-dechlorination, 1,2-Dichlorobenzene, 3-Chlorophenol.

INTRODUCTION

Nanomaterials not only have a high surface-volume ratio when compared to bulk materials, but they also have unique physico-chemical and biological properties [1]. Due to the numerous drawbacks, including the formation of toxic byproducts, high energy usage, usage of corrosive chemicals, high production costs, *etc*., researchers have taken a strong interest in the green synthesis of nanomaterials [2]. The green synthesis methods also referenced as the biological methods that are environmental friendly and cost-effective [3]. The biological materials such as algae, fungi, bacteria and plant extracts were used as reduction and capping agent in the green synthesis of nanomaterials [4].

The nanoparticle that consists of two different metals in its composition was known as the bimetallic nanoparticles. The bimetallic nanoparticles have gained remarkable attention due to its distinctive properties than the monometallic nanoparticles that shows significant applications in optical, magnetic, catalytic and other applications [5]. These bimetallic nanoparticles have more reactive sites, enhanced efficiency with high stability [6]. The simple and convenient methodology for the synthesis of bimetallic nanoparticles involves the addition of two different metal aqueous solutions with a eco-friendly reducing agent such as plant extract. The nanoparticles formed as a consequence of the reduction of metal ions by the bioactive chemicals in the plant extract [7,8].

Metal oxide nanoparticles such as copper oxide (CuO), zinc oxide (ZnO), *etc*. have been shown to have a wide range of applications. The CuO nanoparticles were utilized as antimicrobial agents, photocatalytic agent for degradation of the pollutants, anticancer agent and also used in the formation of biofilms [9-11]. The ZnO nanoparticles have various activities such as anti-inflammatory, wound healing, optic, UV filtering and high catalytic activity [12]. They have significant UV filtering activity and hence are widely used in preparing various cosmetics such as sunscreen lotions for protecting skin from UV light [13]. The studies presented proved that these nanoparticles having various applications as potential antibacterial agents, manufacturing rubber, paints, removal of sulfur and arsenic from water, adsorption of protein and dental applications, *etc*. [14].

The bimetallic nanoparticle made of two distinct metals that exhibits the properties of both metals as well as the synergy between the metals. The ZnO-CuO nanocomposite shows significantly enhanced activities than the individual nanoparticles due to its synergistic effects [15]. The ZnO-CuO bimetallic nanoparticles were proved to be having various activities such as photocatalytic degradation, gas sensor, solar cell, hydrogen generation, humidity sensor, optoelectronic, pharmacological and agricultural applications [16].

Suaeda maritima (L.) *Dumort* is the mangrove herb locally called as Elakura that belongs to Amaranthaceae family. It was widely distributed and grown in tidal wetlands and coastal salt flats near the sea. Previous findings proved that the aqueous leaf extract of *S. maritima* shows the efficient activity for the formation of nanoparticles using copper [17] and nickel [18] metals and nanoparticles shows enhanced pharmacological as well as photocatalytic activity. In view of this, the present work was aimed to synthesize and characterization of ZnO-CuO bimetallic nanoparticles using aqueous root extract of *S. maritima*. Further, the synthesized nanoparticles studied for its efficiency on hydro-dechlorination of 3-chlorophenol and 1,2-dichlorobenzene.

EXPERIMENTAL

The chemicals such as sodium hypochlorite, zinc acetate and copper sulphate, sodium hydroxide, 3-chlorophenol and 1,2-dichlorobenzene were purchased from Sigma-Aldrich and Merck, India. The gas chromatography analysis of 3-chlorophenol and 1,2-dichlorobenzene was carried using Shimadzu (QP 2010, Japan) GC instrument equipped with AOC-20i autosampler, DB-5 fused silica capillary column (30 m × 0.25 mm; 0.25 μm id) and flame ionized detector.

Plant material: The fresh roots of *S. maritime* (L.) *Dumort* were collected from the mangrove forest located at Gilakaladindi, Machilipatnam, India. The root sample was collected in accordance with the institutional rules and necessary permissions have taken from local legislation. It was verified and authenticated by Dr. Ch. Srinivasa Reddy, Department of Botany, SRR & CVR Government Degree College (A) Vijayawada, India whose voucher specimen number SRR-CVR/2022/PI/05 was deposited at Department of Botany. The collected roots were surface cleaned to remove the sand and dirt on it using sterile cotton followed by distilled water. The water droplets on the cleaned material were then removed with tissue paper and the root material was cut into small pieces before being dried under shade and stored in an Amber coloured bottle [19].

Preparation of aqueous root extract: An accurately weighed about 10 g of root powder was taken in 500 mL conical flask containing 100 mL of sterile distilled water and boiled for 10 min at 80 ºC. Then the solution was cooled and filtered through Whatman's no. 42 filter paper and the filtrate was used for the synthesis of nanoparticles [20].

Synthesis of ZnO-CuO nanoparticles: The zinc acetate and copper sulphate were selected as metal precursors in the synthesis of ZnO-CuO bimetallic nanoparticles. An accurately weighed 1.6 g of zinc acetate was added to 250 mL beaker containing 100 mL of aqueous root extract. The content was heater at 80 ºC to dissolve zinc acetate completely in aqueous extract. Then 0.8 g of copper sulphate was added and the pH of the solution was adjusted to 8 using 1 M NaOH solution. The reaction mixture was sterilized for 3 h at 70 ºC. The ZnO-CuO bimetallic nanoparticles formed in the reaction mixture was separated by centrifugation and purified by washing the nanoparticles multiple times with distilled water. The obtained nanoparticles were dried in an air oven for 3 h at 70 ºC and then calcined for 6 h at 400 ºC.

Characterization: The functional groups present in the plant extract involved in the formation of nanoparticles were evaluated by FT-IR-Bruker, USA in the range of 4000 to 500 cm^{-1}. The field emission scanning electron microscope (FE-SEM Nova, Nanosem-450, USA) coupled with energy-dispersive X-ray spectroscopy (EDX-RONTEC's, QuanTax 200, Germany) analysis was performed to evaluate the surface morphology, size and the elemental composition of the synthesized bimetallic nanoparticles. The expected crystal structure of the bimetallic nanoparticles was confirmed by performing X-ray diffractometer (XRD Rigaku Corporation, Japan) and the analysis was conducted in the diffraction angle (2θ) scan range of 20 to 80º with scan speed of 2º/min. Dynamic light scattering (DLS Malvern Zetasizer Nano ZS90, UK) analysis was performed to evaluate the zeta potential and the particle size distribution of the synthesized nanoparticles.

Catalytic applications: The synthesized bimetallic ZnO-CuO nanoparticles were applied for its ability to hydrodechlorinate two organic pollutants *viz.* 1,2-dichlorobenzene (1,2-DCP) and 3-chlorophenol (3-CP). The dechlorination study was conducted using synthesized ZnO-CuO nanoparticles as catalyst and 3-CP and 1,2-DCP in methanol as substrate separately. In 25 mL multi reactor, 0.5 mg of catalysts, 20 mL of 3-CP and 1,2-DCP in 3 mM in methanol were taken separately. In both the multi-reactor flasks, 5 mL of methanol and 3 mL of 5% NaOH solution was added and then the reaction mixture was kept at room temperature in an orbital shaker at 100 rpm [21]. The dechlorination ability was assessed by analyzing the reaction mixture for every 5 min time interval using gas chromatography.

RESULTS AND DISCUSSION

The significance of trace elements in various applications made the metal and metal oxide nanomaterials promising candidates for exploring its novel applications. Hence in present study, the bimetallic ZnO-CuO nanoparticles were successfully synthesized in one-step using aqueous root extract of *S. maritima*. Therefore, we showed the promising potentials of this plant extract for the cost-effective, green and eco-friendly fabrication of bimetallic ZnO-CuO nanoparticles. The preliminary confirmation of the reduction of metal ions was confirmed by observing the colour change in the reaction mixture. The colour of the reaction mixture was changed from light green colour to the dark brownish-green colour confirms the formation of nanoparticles. The formed nanoparticles were centrifuged, purified and calcinated. The obtained bimetallic ZnO-CuO nanoparticles were characterized and further applications was studied. The synthesized bimetallic nanoparticles were characterized using different characterization techniques such as XRD, SEM, EDX, TEM and FT-IR.

XRD studies: The obtained XRD spectrum (Fig. 1) clearly shows the prominent peak at 2θ of 32.6º, 34.9º, 37.1º, 47.2º, 56.8º, 6.70º and 69.1º proved that hexagonal phase crystalline structure of ZnO nanoparticles and the crystal structure was in correlation with the standard JCPDS card no. 01-080-0075. The CuO nanoparticles crystal structure was confirmed by identifying intense peaks at 2θ of 35.8º, 39.6º, 49.2º, 66.1º and 68.9º corresponds to monoclinic copper oxide phase which is in correlation with the standard JCPDS card no. 01-080-1917 [22].

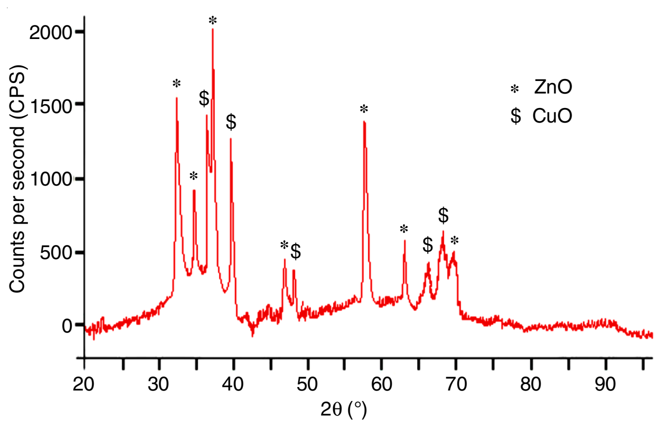


Fig. 1. XRD spectrum of the bimetallic ZnO-CuO nanoparticles

The XRD spectrum also confirms that the diffraction peak intensity of ZnO nanoparticles was observed to be very high than the diffraction peaks identified for CuO nanoparticles. This proved that the CuO nanoparticles were observed to be less percentage in the zinc-copper bimetallic nanoparticles mixture and hence have low crystallinity. The low crystallinity of CuO nanopartilces may be due to the coating of CuO nanoparticles with the ZnO nanoparticles. The findings observed in the study were in good argument with the findings reported in literature [23]. In the XRD patterns, no additional peaks were identified, which proved that the bimetallic nanoparticles obtained in the study having high degree of purity.

Morphological studies: The SEM image and EDX results of the synthesized bimetallic ZnO-CuO nanoparticles are shown in Fig. 2. The SEM image (Fig. 2a) clearly indicate that the bimetallic nanoparticles were spherical in shape and the particles were isometric in nature with size range of 20-45 nm with a average particle size of 31 nm. The SEM analysis also confirms that the bimetallic nanoparticles were clearly separated and very less aggregation was identified. The quantitative elemental analysis of the synthesized bimetallic nanoparticles was also evaluated using EDX analysis. The EDX spectrum (Fig. 2b) shows the characteristic signal corresponds to zinc and copper was detected at 8.63 ($K\alpha$) and 1.07 ($L\alpha$) for zinc and 8.02 ($K\alpha$) and 0.95 ($L\alpha$) for copper. The characteristic signal corresponding to oxygen was also detected in the EDX spectra confirmed the oxide form of synthesized bimetallic nanoparticles. The % composition was observed to be 41%, 33% and 12% for zinc, copper and oxygen, respectively. Based on the EDX results, it was confirmed that the composition of zinc was observed to be higher than copper. There is no additional elements detected in the EDX spectra proves the high purity of bimetallic nanoparticles and the results were in good agreement with the results observed in the XRD analysis.

The crystalline structure and surface morphology of the synthesized nanoparticles was further confirmed by TEM analysis and the TEM bright-feld image observed in the study is shown in Fig. 3a. Based on the results, it was confirmed that the nanoparticles were isometric in size and shape with less tended to form agglomerates and exhibited narrow particle size distribution. The nanoparticles obtained in the study were

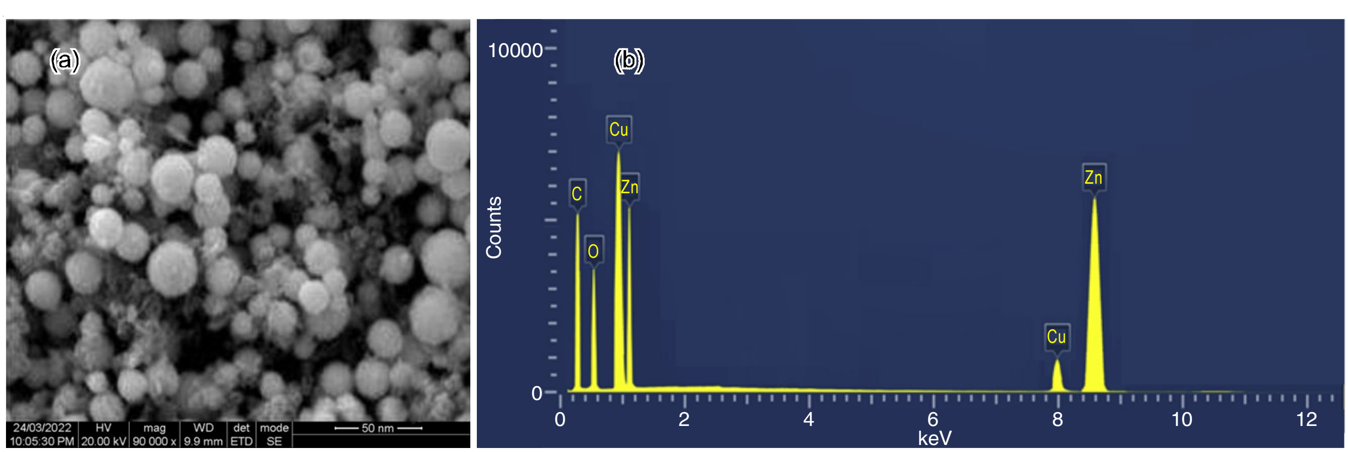


Fig. 2. SEM (a) and EDX spectra (b) of the ZnO-CuO nanoparticles

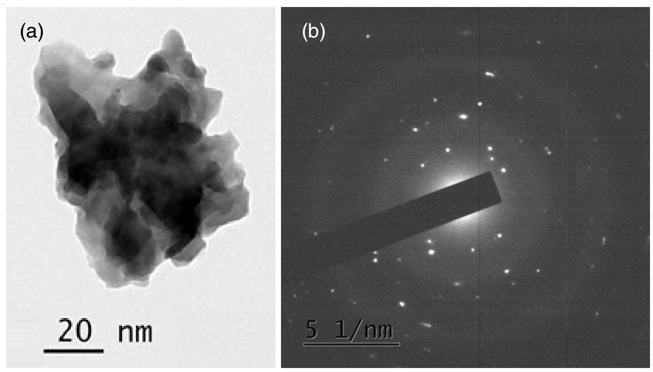


Fig. 3. TEM analysis (a) Bright-feld image and (b) SAED difraction pattern

observed to circular in shape with irregular/rough surfaces. The average particles size was confirmed as 31 nm. The TEM selected area electron diffraction (SAED) diffractogram as shown in Fig. 3b exhibited the quite low diffraction intensities. This is due to the deposition of small particles on carbon film and the nanoparticle diffractions were hidden in amorphous carbon background.

FT-IR studies: The FT-IR analysis of the synthesized bimetallic nanoparticles was carried for the evaluation of possible biomolecules responsible for capping and efficient stabilization of the nanoparticles synthesized by aqueous root extract of *S. maritima*. The FT-IR spectrum (Fig. 4) shows a strong bond at 3353 cm^{-1} corresponds to the N-H stretching in aliphatic primary amines. The band at 2987 cm^{-1} represents O-H stretch-ing and at 2948 cm^{-1} is due to C-H stretching in alkanes. Weak bonds were identified at 2833 cm^{-1} and 2177 cm^{-1}, which were due to the O-H stretching and C-C stretching in alkynes, respec-tively. The FT-IR spectra also shows the peaks at 1721 cm^{-1} corresponds to C=O stretching in aliphatic ketone, 1640 and 1284 cm^{-1} was due to the C-H bending and C-O stretching in aromatic compounds. The FT-IR spectra of the synthesized bimetallic nanoparticles doesn't shows any peak corresponds to the H-C-H asymmetric and symmetric bands, S=O and N–H bends may be due to the utilization of these functional groups in the process of reduction of zinc and copper metals [24]. From these studies, the phytochemical constituents present in the aqueous root extract of *S. maritima* were actively involved in the reduction of metals and formation of bimetallic nanoparticles.

Catalytic studies: The synthesized bimetallic nanoparticles was studied for its dechlorination ability towards the

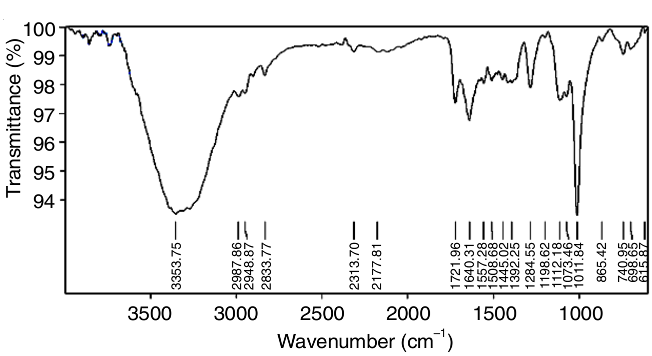


Fig. 4. FTIR spectrum of nanoparticles

environmental pollutant of soil and water sources such as 3-chlorophenol and 1,2-dichlorobenzene.

Catalytic dechlorination of 1,2-dichlorobenzene: The dechlorination efficiency of the synthesized ZnO-CuO bimetallic nanoparticles was evaluated on 1,2-dichlorobenzene. The % degradation was studied in every 5 min time intervals and the experiment was completed within less time of 40 min. The % degradation was calculated using gas chromatography analysis using the pure compound as standard. The peak response and peak area values of 1,2-dichlorobenzene (1,2-DCP) were decreased during the dechlorination research, while the peak response and peak area values of benzene were increased, confirming that the dechlorination of 1,2-DCP resulted in benzene as the final product. The chromatograms observed in the GC analysis of 1,2-DCP dechlorination study using the synthesized ZnO-CuO nanoparticles is shown in Fig. 5.

The dechlorination efficiency of bimetallic nanoparticles was observed to be very high in the initial time of dechlorination study. At a very less time of 5 min, the 19.37 ± 0.243% of dechlorination was observed. The % dechlorination of 1,2-DCP was increased to 41.58 ± 0.304%, 73.60 ± 0.355% and 86.26 ± 0.051% for 10 min, 15 min and 20 min of dechlorination process, respectively. This confirms that maximum 86% dechlorination was completed with in less time of 20 min, whereas the studied high time of 40 min, the dechlorination was observed to be 96.37 ± 0.429%. The dechlorination study results obtained in the study was shown in Fig. 6a.

To determine quantitatively, the dechlorination efficiency of ZnO-CuO bimetallic nanoparticles, the kinetic rate constants in dechlorination reaction were calculated by adopting pseudo-first-order correlation *i.e.* $K_t = -\ln (C_t/C_0)$, where K is the rate constant, C_0 and C_t are 1,2-DCP strength at initial and at time t respectively. The plot of $\ln (C_t/C_0)$ as a function of reaction time for the dechlorination reaction of 1,2-dichlorobenzene by synthesized nanoparticles shows a linear correlation (Fig. 6b). The rate constants were calculated as 0.095 and hence it can be confirmed that the nanoparticles shows highest catalytic efficiency.

Catalytic dechlorination of 3-chlorophenol (3-CP): The synthesized ZnO-CuO bimetallic nanoparticles were further evaluated for its dechlorination efficiency of 3-chlorophenol. The study was conducted within less time of 40 min and the efficiency was assessed in every 5 min of time interval. The gas chromatography analysis was carried for the evaluation of the degradation of 3-chlorophenol by ZnO-CuO bimetallic nanoparticles. In the process of dechlorination study, the peak response and the peak area values of 3-chlorophenol was decreased and the peak response and the peak area values phenol was increased confirms that the dechlorination of CP results in the formation of phenol as final product (Fig. 7).

The dechlorination efficiency of synthesized bimetallic nanoparticles was observed as 15.52 ± 0.193% within the time of 5 min of the study. The % dechlorination of 3-chlorophenol was increased to 36.79 ± 0.191%, 59.38 ± 0.260%, 76.72 ± 0.231% and 89.75 ± 0.091% for 10 min, 15 min, 20 min and 25 min of dechlorination process, respectively. This confirms that maximum 89% dechlorination was completed with in less

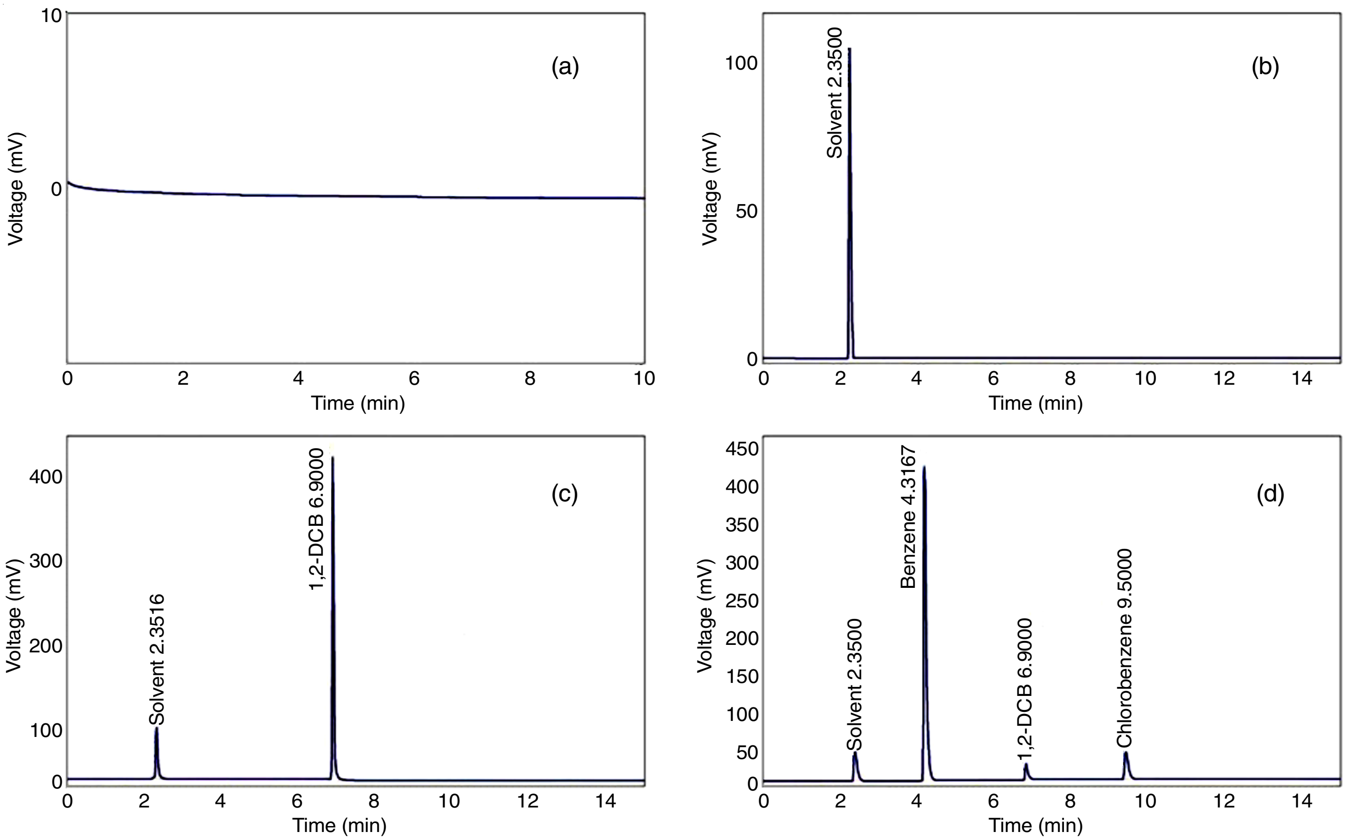


Fig. 5. GC chromatograms observed during the dechlorination study of synthesized nanoparticles on 1,2-dichlorobenzene; (a) Blank run chromatogram, (b) Solvent chromatogram, (c) dechlorination chromatogram at time 0 min, (d) dechlorination chromatogram at time 30 h

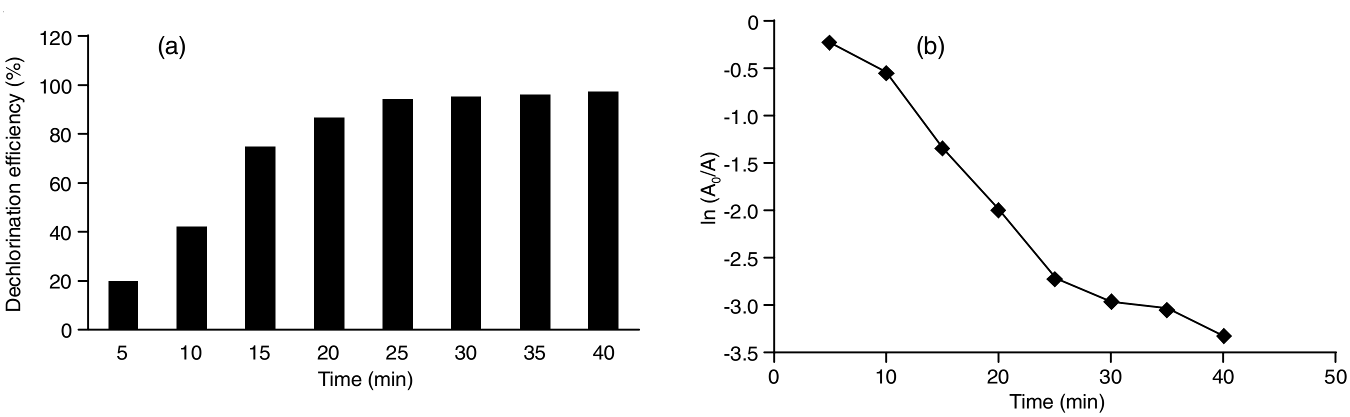


Fig. 6. 1,2-Dichlorobenzene dechlorination efficiency results of ZnO-CuO nanoparticles; (a) 1,2-Dichlorobenzene dechlorination efficiency of ZnO-CuO nanoparticles; (b) $\ln(A_0/A)$ graph obtained in the study

time of 25 min, whereas the studied high time of 40 min, the dechlorination was observed to be 94.05 ± 0.059%. The dechlorination results obtained in the study is shown in Fig. 8a. The pseudo-first-order correlation was utilized for the calculation of the rate constant and the rate constant was calculated as 0.084 and linear relation was followed in the dechlorination study (Fig. 8b).

Conclusion

In summary, a simple and inexpensive method is established for the green and eco-friendly synthesis of nanoscale bimetallic ZnO-CuO particles using aqueous root extract of *S. maritime* as a reducing and stabilizing agent. The high purity of these bimetallic nanoparticles with spherical shape having an average particle size of 31 nm with monoclinic and hexagonal crystalline structures of ZnO-CuO nanoparticles were confirmed by SEM, TEM/SAED and XRD studies. The synthesized bimetallic ZnO-CuO nanoparticles were investigated for the degradation of 3-chlorophenol and 1,2-dichlorobenzene. The synthesized bimetallic nanoparticles can effectively degrade 3-chlorophenol and 1,2-dichlorobenzene by dechlorination mechanism and the degradation completed within very less time. Hence, it

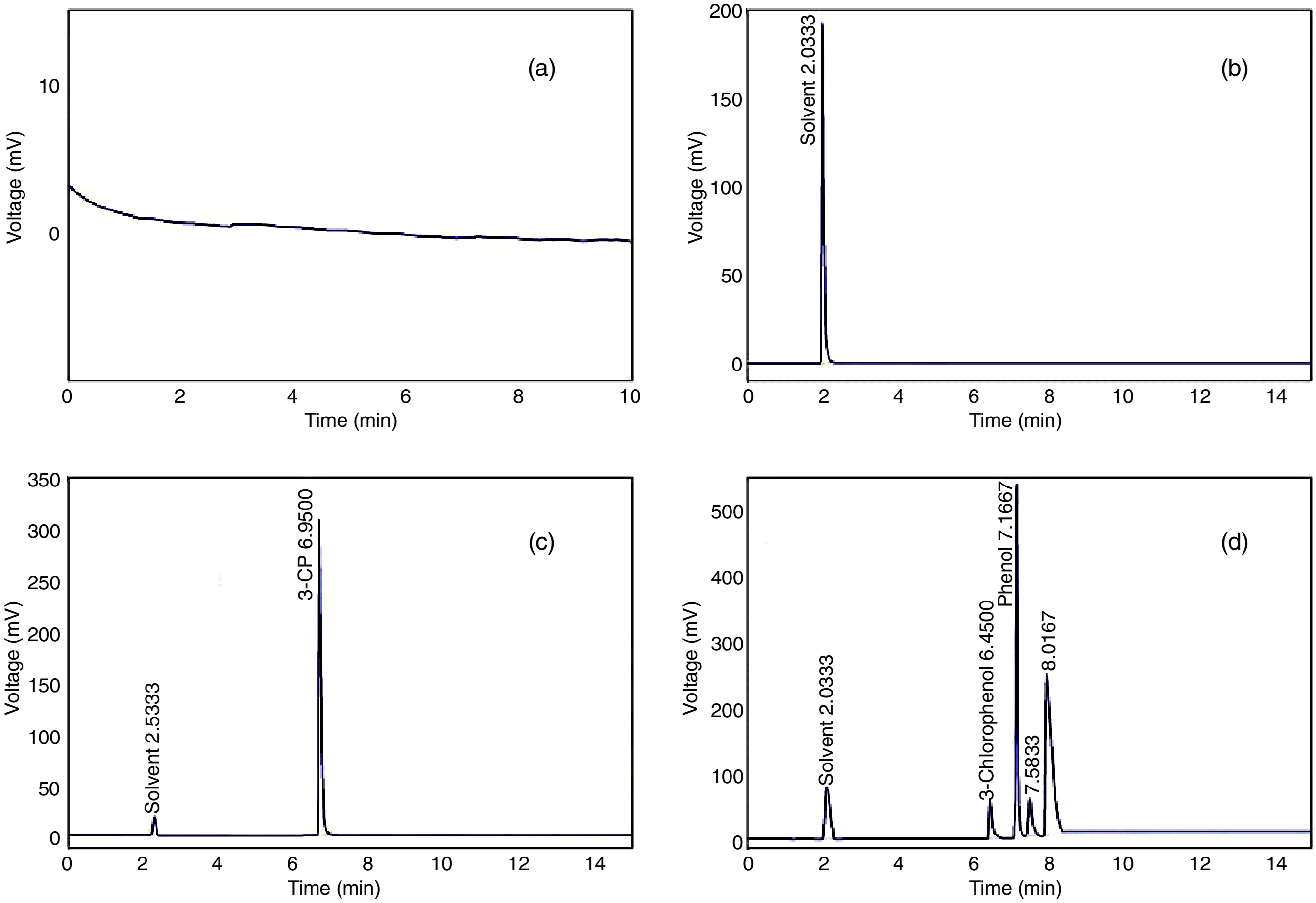


Fig. 7. GC chromatograms observed during the dechlorination study of synthesized nanoparticles on 3-chlorophenol; (a) Blank run chromatogram, (b) Solvent chromatogram, (c) dechlorination chromatogram at time 0 min, (d) dechlorination chromatogram at time 30 h

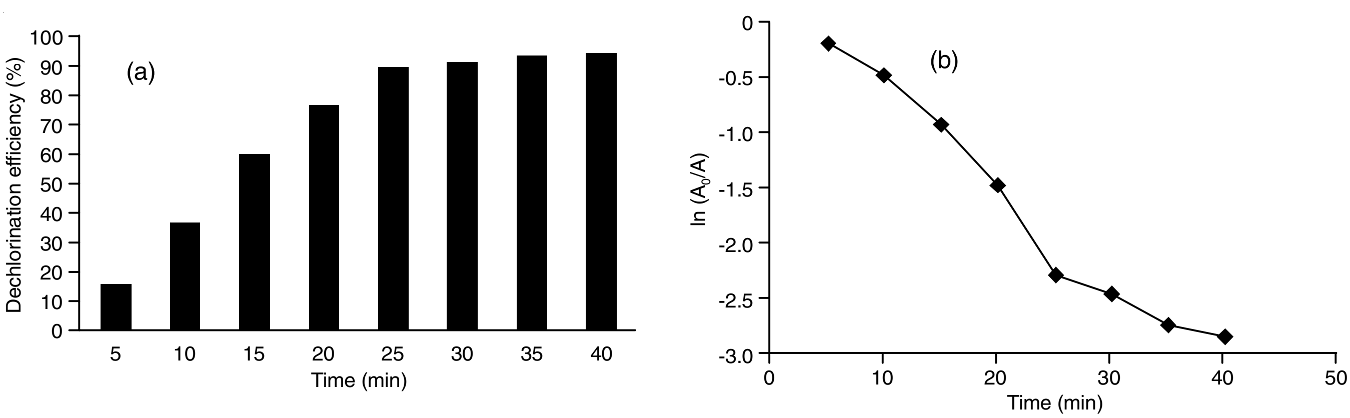


Fig. 8. 3-Chlorophenol dechlorination efficiency results of ZnO-CuO nanoparticles; (a) 3-Chlorophenol dechlorination efficiency of ZnO-CuO nanoparticles; (b) ln(A_0/A) graph obtained in the study

can be concluded that the rapid dechlorination of 3-chlorophenol and 1,2-dichlorobenzene suggests that the ZnO-CuO bimetallic nanoparticles can be used in the purification treatment of polychlorinated aromatic compounds present in the environment.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C.M. Magdalane, K. Kaviyarasu, G.M.A. Priyadharsini, A.K.H. Bashir, N. Mayedwa, N. Matinise, A.B. Isaev, N. Abdullah Al-Dhabi, M.V. Arasu, S. Arokiyaraj, J. Kennedy and M. Maaza, *J. Mater. Res. Technol.*, **8**, 2898 (2019); https://doi.org/10.1016/j.jmrt.2018.11.019
2. S. Ying, Z. Guan, P.C. Ofoegbu, P. Clubb, C. Rico, F. He and J. Hong, *Environ. Technol. Innov.*, **26**, 102336 (2022); https://doi.org/10.1016/j.eti.2022.102336

3. S. Pirtarighat, M. Ghannadnia and S. Baghshahi, *J. Nanostruct. Chem.*, **9**, 1 (2019); https://doi.org/10.1007/s40097-018-0291-4
4. D. Chugh, V.S. Viswamalya and B. Das, *J. Genet. Eng. Biotechnol.*, **19**, 126 (2021); https://doi.org/10.1186/s43141-021-00228-w
5. A. Dsouza, M.P. Shilpa, S.C. Gurumurthy, B.S. Nagaraja, K. Ramam, S. Mundinamani, M. Gedda and M.S. Murari, *Clean Technol. Environ. Policy*, **23**, 2145 (2021); https://doi.org/10.1007/s10098-021-02120-0
6. H.Q. Alijani, S. Iravani, S. Pourseyedi, M. Torkzadeh-Mahani, M. Barani and M. Khatami, *Sci. Rep.*, **11**, 17431 (2021); https://doi.org/10.1038/s41598-021-96918-z
7. P. Kuppusamy, M.M. Yusoff, G.P. Maniam and N. Govindan, *Saudi Pharm. J.*, **24**, 473 (2016); https://doi.org/10.1016/j.jsps.2014.11.013
8. G. Sharma, A. Kumar, S. Sharma, M. Naushad, R. Prakash Dwivedi, Z.A. ALOthman and G.T. Mola, *J. King Saud Univ. Sci.*, **31**, 257 (2019); https://doi.org/10.1016/j.jksus.2017.06.012
9. A. Waris, M. Din, A. Ali, M. Ali, S. Afridi, A. Baset and A.U. Khan, *Inorg. Chem. Commun*., **123**, 108369 (2021); https://doi.org/10.1016/j.inoche.2020.108369
10. B.D. Harishchandra, M. Pappuswamy, P.U. Antony, G. Shama, A. Pragatheesh, V.A. Arumugam, T. Periyaswamy and R. Sundaram, *Asian Pac. J. Cancer Biol.*, **5**, 201 (2020); https://doi.org/10.31557/APJCB.2020.5.4.201
11. S. Kandasamy, S. Anbazhagan, V.A.M. Arokia, X. Hu, H.W. Myeong, *Int. J. Biol. Macromol*., **153**, 207 (2020); https://doi.org/10.1016/j.ijbiomac.2020.02.250
12. A.R. Prasad, L. Williams, J. Garvasis, K.O. Shamsheera, S.M. Basheer, M. Kuruvilla and A. Joseph, *J. Mol. Liq.*, **331**, 115805 (2021); https://doi.org/10.1016/j.molliq.2021.115805
13. J. Jiang, J. Pi and J. Cai, *Bioinorg. Chem. Appl.*, **2018**, 1062562 (2018); https://doi.org/10.1155/2018/1062562
14. H. Agarwal, S. Venkat Kumar, S. Rajeshkumar, *Resour.-Effic. Technol.*, **3**, 406 (2017); https://doi.org/10.1016/j.reffit.2017.03.002
15. S. Das and V.C. Srivastava, *Nanotechnol. Rev.*, **7**, 267 (2018); https://doi.org/10.1515/ntrev-2017-0144
16. K.-H. Tseng, C.-J. Chou, T.-C. Liu, D.-C. Tien, C.Y. Chang and L. Stobinski, *Nanotechnol. Rev.*, **7**, 1 (2018); https://doi.org/10.1515/ntrev-2017-0167
17. P. Peddi, P.R. Ptsrk, N.U. Rani and S.L. Tulasi, *J. Genet. Eng. Biotechnol.*, **19**, 131 (2021); https://doi.org/10.1186/s43141-021-00229-9
18. T. Krishnasree and P. Peddi, *J. Exp. Biol. Agric. Sci.*, **9**, 823 (2021); https://doi.org/10.18006/2021.9(6).823.830
19. P. Thatoi, R.G. Kerry, S. Gouda, G. Das, K. Pramanik, H. Thatoi and J.K. Patra, *J. Photochem. Photobiol. B*, **163**, 311 (2016); https://doi.org/10.1016/j.jphotobiol.2016.07.029
20. Y. Cao, H.A. Dhahad, M.A. El-Shorbagy, H.Q. Alijani, M. Zakeri, A. Heydari, E. Bahonar, M. Slouf, M. Khatami, M. Naderifar, S. Iravani, S. Khatami and F.F. Dehkordi, *Sci. Rep.*, **11**, 23479 (2021); https://doi.org/10.1038/s41598-021-02937-1
21. H. Jung, S. Lee, R. Koutavarapu, S. Kim, H. Choi and M. Choi, *Catalysts*, **8**, 390 (2018); https://doi.org/10.3390/catal8090390
22. J. Fang and Y. Xuan, *RSC Adv.*, **7**, 56023 (2017); https://doi.org/10.1039/C7RA12022B
23. M. Wasim, M.R. Khan, M. Mushtaq, A. Naeem, M. Han and Q. Wei, *Coatings*, **10**, 364 (2020); https://doi.org/10.3390/coatings10040364
24. A.N. Awwad, N.M. Salem and A.O. Abdeen, *Int. J. Ind. Chem.*, **4**, 29 (2013); https://doi.org/10.1186/2228-5547-4-29