Cureus Journal of Engineering

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Letter

Removal of Heavy Metal Co(II) Using Trioctylphosphine Oxide as an Extractant

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Review began 11/18/2024
Review ended 01/22/2025
Published 01/24/2025

DOI: https://doi.org/10.7759/s44388-024-02512-0

Abstract

Environmental degradation, driven by human activities, is worsened by persistent metal contamination and industrial waste pollution. The rising demand for cobalt in various industries poses major environmental and health risks, underscoring the importance of recycling and proper waste treatment to reduce its negative impacts. In the present investigation, the extraction of cobalt from a nitrate solution using a solvating extractant Trioctylphosphine oxide (TOPO) dissolved in toluene, by the technique of liquid-liquid extraction, has been explored. The effects of equilibration time, nitric acid concentration, concentration of organic solution, metal ion concentration and effect of salting-out agent were systematically investigated. The extraction equilibrium for Co(II) was achieved within 15 minutes. Using 0.005M TOPO, the extraction efficiency decreased with increasing HNO_3 concentration, from 96.7% at 0.005M HNO_3 to 86.7% at higher acid levels. In contrast, at a lower TOPO concentration (0.0025M), the extraction efficiency improved with rising HNO_3 concentration, reaching a maximum of 70.4% at 0.1M HNO_3. Increasing Co(II) concentrations in the aqueous phase adversely affected extraction efficiency, which decreased from 70.4% at 0.0005M Co(II) to 40.7% at 0.01M Co(II). Increases in TOPO concentration enhanced extraction efficiency, with a maximum of 90% at 0.005M TOPO before saturation was observed. The use of KNO_3 as a salting-out agent significantly enhanced the extraction efficiency, reaching a maximum of 98.7% with 0.2M KNO_3. This improvement is likely attributed to increased ionic strength or the formation of complexes.

Categories: Chemical Process Optimization, Sustainable Technologies, Environmental and Sustainable Engineering
Keywords: topo, cobalt (ii), liquid-liquid extraction, potassium nitrate, nitric acid

Introduction

Environmental degradation refers to the unfavorable changes in the natural environment, often caused by human activities. This degradation affects biodiversity, ecosystems, and human well-being by polluting essential resources such as air, water, and soil [1]. One significant contributor to environmental degradation is the contamination caused by metals, which do not decompose easily and can persist in the environment [2]. The industrial revolution introduced widespread environmental pollution, particularly through the release of untreated chemicals and waste into land and water systems [3-6]. Cobalt, a critical metal, is widely used in several key industries, including rechargeable batteries, catalysts, inks, pigments, alloys, and magnets [7-10]. Due to its extensive applications, global demand for cobalt has surged, nearly doubling from 71,000 tons in 2010 to 136,000 tons in 2017. This demand is projected to increase by another 60%, reaching approximately 222,000 tons by 2025 [11,12]. However, cobalt mining and production release harmful particles, including radioactive materials and carcinogens, which can cause severe health effects such as vision issues, nausea, heart problems, thyroid damage, asthma, and pneumonia [13]. The recycling of cobalt plays a crucial role in minimizing environmental contamination. To prevent further environmental damage, the treatment of metal-containing hazardous industrial waste is essential before discharge. Liquid-liquid extraction is an effective method for the removal of toxic metals from waste streams. This process is favored for its high efficiency and precision, even when dealing with trace amounts of toxic heavy metals. The technique is well-established for the separation and purification of metal ions after leaching, and it can produce pure metal solutions suitable for electrowinning processes. Additionally, this method is cost-effective, fast, and innovative. Among the extractants, organophosphorus compounds have shown remarkable success in Co(II) extraction due to their strong coordination with cobalt ions. Reagents such as di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid (PC88A), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA) have demonstrated high efficiency, making them integral to optimizing cobalt recovery processes [14-18].

In the present investigation, extraction of cobalt (II) from aqueous solution has been carried out using Trioctylphosphine oxide (TOPO) as the extractant. The impact of various extraction parameters, including the impact of phase contact time, the effect of nitric acid concentration, the effect of aqueous phase concentration, the effect of extractant concentration, and the effect of adding salting-out agents have been extensively studied to optimize the efficiency of metal extraction processes. Through systematic variation of these parameters, the study aimed to develop an optimized process for the efficient extraction of cobalt (II), contributing to sustainable metal recovery practices.

How to cite this article
Mohanty A, Das P, Devi N (January 24, 2025) Removal of Heavy Metal Co(II) Using Trioctylphosphine Oxide as an Extractant. Cureus J Eng 2 : es44388-024-02512-0. DOI https://doi.org/10.7759/s44388-024-02512-0

Materials And Methods

Materials and reagents

TOPO, supplied by Heavy Water plant Talcher, was used without further purification. Toluene was employed as the diluent. Cobalt(II) nitrate hexahydrate, Potassium nitrate (KNO_3) and nitric acid (HNO_3) were purchased from Merck, and all other chemicals were used in analytical grade. A 0.01M stock solution of Co(II) was made by dissolving cobalt nitrate hexahydrate ($Co(NO3)_2 .6 H_2O$) with Millipore water.

Solvent extraction

Solvent extraction experiments were conducted by mixing equal volumes (10 mL each) of the organic and aqueous phases in a 60 mL Teflon stopcock separating funnel at room temperature (25 ± 2°C). To ensure complete phase separation, the solution was left to settle for a few minutes after equilibration. Once the phases had separated, the raffinate (aqueous phase) was collected in a sample tube. Samples were taken from the aqueous phase both before and after the extraction process. The metal concentration in the aqueous phase was analyzed using a Systronics Atomic Absorption Spectrophotometer instrument. The metal concentration in the organic phase was determined by calculating the difference in metal ion concentrations in the aqueous phase before and after extraction.

$$[A^{2+}]_{(org)} = [A^{2+}]_i - [A^{2+}]_f (1)$$

Here, $[A^{2+}]_{(org)}$, $[A^{2+}]_i$ and $[A^{2+}]_f$ represent the concentration of metals in the organic phase and the metal ion concentrations before and after extraction, respectively. The distribution coefficient (D) and percentage extraction efficiency (%E) were calculated using the following equations.

$$D = \frac{[A^{2+}]_{(org)}}{[A^{2+}_f]} \times \frac{V_{aq}}{V_{org}} (2)$$

$$\%E = \frac{D}{D + \frac{V_{aq}}{V_{org}}} \times 100 (3)$$

Where, V_{aq} and V_{org} represents volumes of aqueous and organic phases, respectively.

Results

Effect of shaking time

Experiments were carried out at room temperature to study the effect of shaking time on the extraction of 0.0005M Co(II) solution using 0.0025M TOPO dissolved in toluene. The shaking time was varied between 1 and 20 minutes, with the results displayed in Figure *1*. The data show a significant increase in cobalt extraction efficiency, starting at 20% after 1 minute of shaking and reaching 70.4% after 15 minutes. Beyond 15 minutes, further increases in shaking time did not significantly impact extraction efficiency, suggesting that equilibrium had been reached. At this point, the transfer of Co(II) ions from the aqueous to the organic phase became saturated, indicating that no additional cobalt could be extracted. Based on these observations, 15 minutes was identified as the optimal shaking time for the effective extraction of Co(II) from the aqueous phase.

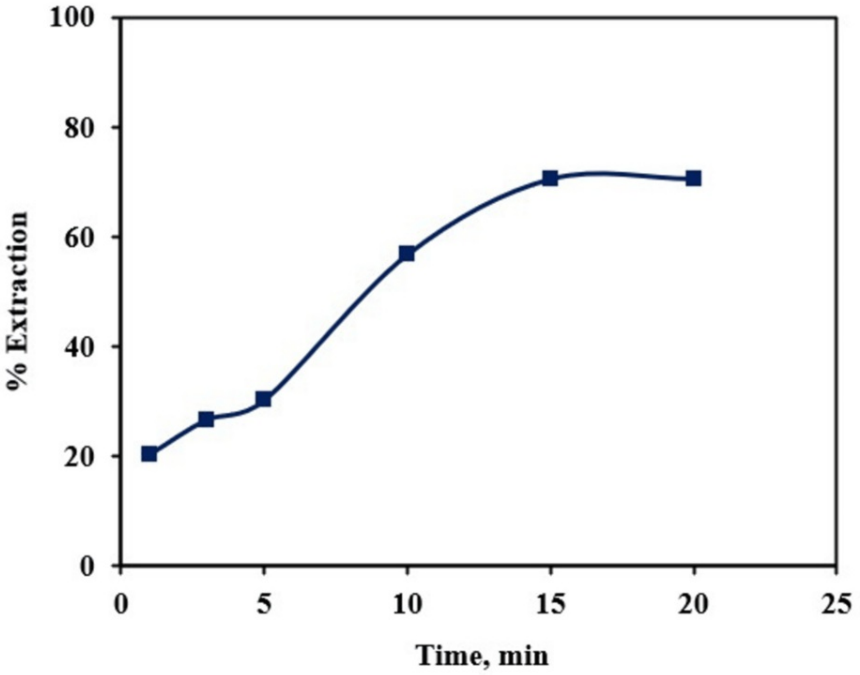

FIGURE 1: Plot of percentage extraction vs. shaking time for the extraction of 0.0005M Co(II) using 0.0025M TOPO in Toluene

TOPO, Trioctylphosphine oxide

Effect of nitric acid concentration

The extraction of 0.0005M Co(II) from a nitrate solution was investigated using two different concentrations of TOPO dissolved in toluene: 0.005M and 0.0025M. The study focused on assessing the effect of varying nitric acid (HNO_3) concentrations, ranging from 0.005M to 1M, on the efficiency of cobalt extraction. When 0.005M TOPO was used, the extraction efficiency of Co(II) decreased as the concentration of HNO_3 increased (Figure 2). This trend is likely due to the common ion effect, as nitrate ions (NO_3^-) are present in both the Co(II) salt and nitric acid. With the addition of HNO_3, which is more soluble than Co(II) nitrate, the common ion effect promotes the reassociation of Co(II) with nitrate ions to form a non-extractable salt. This reduces the availability of Co(II) ions to bind with TOPO. Initially, at a low nitric acid concentration of 0.005M, the extraction efficiency was high, at 96.7%. However, as the HNO_3 concentration increased, the efficiency declined, reaching 86.7% at 1M HNO_3. This indicates a negative correlation between nitric acid concentration and extraction efficiency at higher TOPO concentrations. In contrast, when 0.0025M TOPO was used as the extractant, the cobalt extraction efficiency followed a different pattern. As the concentration of HNO_3 increased from 0.005M, the efficiency improved, peaking at 70.4% at 0.1M HNO_3 (Figure 2). This initial improvement can be attributed to the ability of the strong acid to enhance the solubility of the metal salts, facilitating extraction. However, beyond 0.1M HNO_3, the efficiency began to decline, dropping to 56.7% at 1M HNO_3. This decrease can again be explained by the common ion effect, which reduces the availability of Co(II) ions for binding with TOPO. The findings of this study highlight the critical role of both TOPO concentration and nitric acid levels in optimizing cobalt extraction. At higher TOPO concentrations (0.005M), extraction efficiency decreases with increasing nitric acid due to the common ion effect. In contrast, at lower TOPO concentrations (0.0025M), moderate levels of nitric acid (around 0.1M) enhance extraction efficiency, but further increases in acid concentration lead to a decline. Thus, achieving a balance between TOPO concentration and nitric acid levels is essential for maximizing cobalt extraction efficiency.

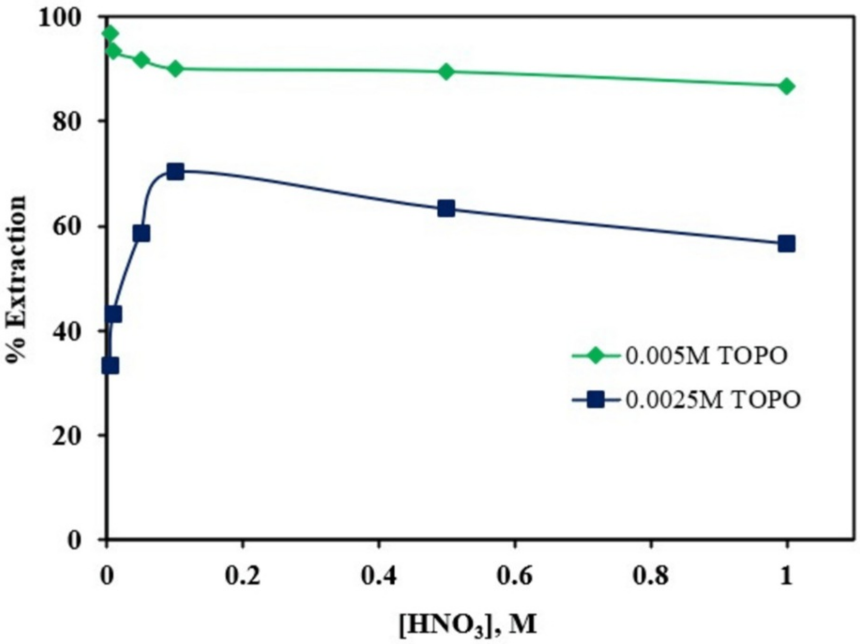

FIGURE 2: Plot of percentage extraction vs. [HNO3] for the extraction of 0.0005M Co(II) using 0.0025M and 0.005M TOPO in Toluene

TOPO, Trioctylphosphine oxide

Effect of concentration of aqueous phase

The effect of varying Co(II) concentrations in the aqueous phase, ranging from 0.0005 M to 0.01M in 0.1M HNO_3 using 0.0025M TOPO in toluene, was investigated. As shown in Figure *3*, the percentage of cobalt extraction decreases as the concentration of Co(II) in the aqueous phase increases. At a lower concentration of 0.0005M Co(II), the percentage extraction is 70.4%. However, as the concentration increases to 0.01M, the percentage extraction drops to 40.7%. This indicates a decline in extraction efficiency with higher aqueous Co(II) concentrations.

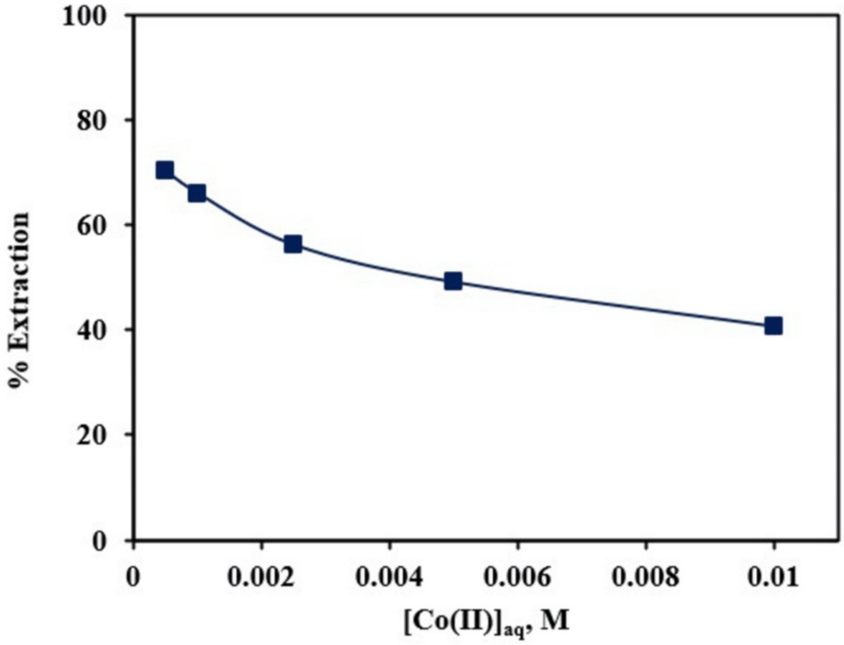

FIGURE 3: Plot of percentage extraction vs. [aqueous phase] using 0.0025M TOPO in Toluene

TOPO, Trioctylphosphine oxide

Discussion

Effect of extractant concentration

The influence of extractant concentration on the extraction process is critical for elucidating the underlying extraction mechanism. In this study, the effect of varying TOPO concentrations, ranging from 0.0025M to 0.1M, was investigated while keeping the aqueous phase composition constant at 0.0005M Co(II) and 0.1M HNO3. As illustrated in Figure *4*, the percentage extraction of Co(II) increases steadily with the rise in TOPO concentration. At lower TOPO levels, such as 0.0025M, the extraction efficiency was 70.4%. This indicates that a relatively low concentration of TOPO is sufficient to extract a substantial portion of cobalt ions from the solution. However, as the TOPO concentration increases, the percentage extraction significantly, reaching approximately 90% at a TOPO concentration of 0.005M, suggesting that a higher concentration of the extractant enhances the interaction between TOPO and cobalt ions, thus improving extraction efficiency. However, beyond 0.005M, further increases in TOPO concentration resulted in minimal improvement, suggesting that saturation occurs and most available Co(II) ions have already formed complexes with TOPO. Cobalt ions (Co^{2+}) in the aqueous phase coordinate with the lone pair of electrons on the phosphorus atom of TOPO, forming a complex, typically $[Co(TOPO)_2]^{2+}$. The complex is hydrophobic and more soluble in the organic phase (toluene), enabling Co(II) to transfer from the aqueous phase to the organic phase. Nitrate ions (NO_3^-) from nitric acid assist in balancing the charge of the complex, stabilizing it and improving extraction efficiency. The Co(II)-TOPO complex then moves into the organic phase due to the hydrophobic nature of TOPO.

$$Co(aq)^{2+} + 2TOPO(org) \Leftrightarrow [Co(TOPO)_2](org)^{2+}(4)$$

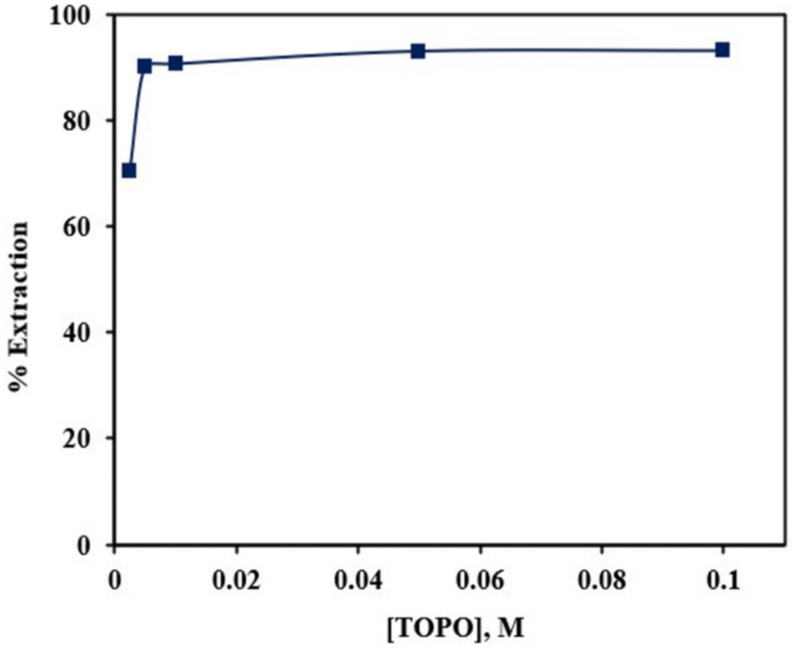

FIGURE 4: Plot of percentage extraction vs. [Extractant] for the extraction of 0.0005M Co(II) with 0.1M HNO3 using TOPO in Toluene

TOPO, Trioctylphosphine oxide

Effect of salting-out agent

The effect of a salting-out agent on cobalt extraction was investigated by adding varying concentrations of KNO_3 to the aqueous phase. Concentrations of KNO_3 ranging from 0.01M to 0.2M were evaluated to determine the role of salting-out agent in enhancing cobalt extraction from a solution containing 0.0005M Co(II) with 0.1M HNO_3, using 0.005M TOPO in toluene as the organic phase. The results indicate that cobalt extraction efficiency increased with rising KNO_3 concentration, reaching a maximum at 0.2M. This suggests that the presence of nitrate ions enhances the extraction process, likely by increasing the ionic strength of the solution or by facilitating the formation of extractable complexes. A plot of the percentage of extraction versus KNO_3 concentration is presented in Figure *5*, illustrating the positive correlation between salt concentration and extraction efficiency. The maximum Co(II) extraction was found to be 98.7% using 0.2M KNO_3.

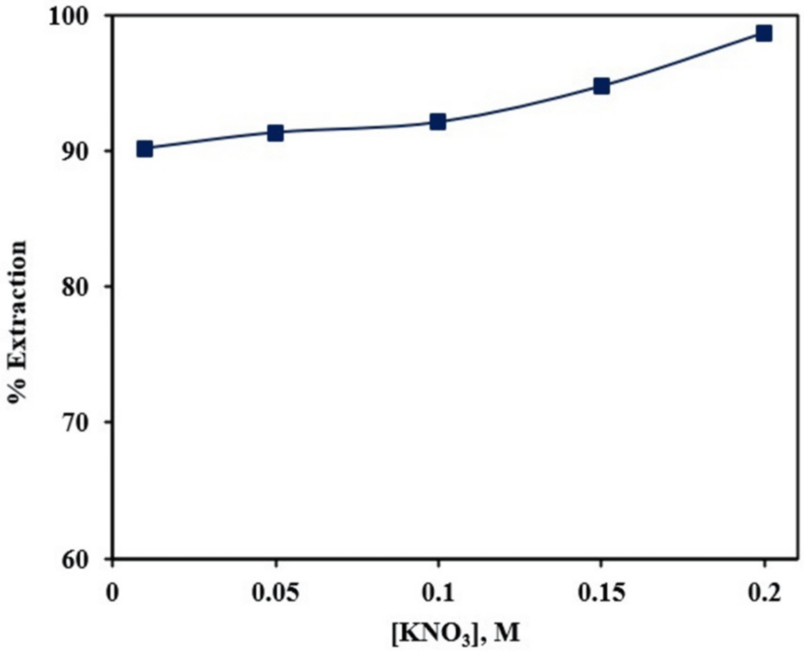

FIGURE 5: Plot of percentage extraction vs. [Extractant] for the extraction of 0.0005M Co(II) with 0.1M HNO3 using 0.005M TOPO in toluene

TOPO, Trioctylphosphine oxide

Conclusions

This study successfully demonstrated the efficient extraction of Co(II) from aqueous solutions using TOPO dissolved in toluene as the organic phase at room temperature. The findings underscore the importance of optimizing key parameters, including effect of shaking time, TOPO concentration, HNO_3 concentration, variation of Co(II) concentration, and the use of a salting-out agent (KNO_3), to achieve maximum extraction efficiency. At a TOPO concentration of 0.005M, extraction efficiency decreased with increasing HNO_3 concentration due to the common ion effect, with a high initial efficiency of 96.7% at 0.005M HNO_3 dropping to 86.7% at higher acid concentrations. In contrast, at a lower TOPO concentration of 0.0025M, the extraction efficiency peaked at 70.4% at 0.1M HNO_3 before declining, indicating that 0.1M HNO_3 is optimal under these conditions. Furthermore, increasing the initial Co(II) concentration in the aqueous phase led to a decrease in extraction efficiency, highlighting the reduced extraction capacity at higher metal ion concentrations. Higher TOPO concentrations significantly improved extraction efficiency, reaching 90% at 0.005M, though further increases showed minimal benefit, suggesting saturation of the Co(II)-TOPO complexes. The addition of KNO_3 as a salting-out agent further enhanced extraction, with a maximum efficiency of 98.7% observed at 0.2M KNO_3. Overall, the study provides valuable insights into the critical factors influencing Co(II) extraction and offers practical guidance for optimizing the process. These findings pave the way for further research and industrial applications aimed at efficient cobalt recovery from aqueous solutions.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

Concept and design: Niharbala Devi, Prasanjit Das

Acquisition, analysis, or interpretation of data: Niharbala Devi, Archita Mohanty, Prasanjit Das

Critical review of the manuscript for important intellectual content: Niharbala Devi, Prasanjit Das

Supervision: Niharbala Devi

Drafting of the manuscript: Archita Mohanty, Prasanjit Das

Disclosures

Human subjects: All authors have confirmed that this study did not involve human participants or tissue. **Animal subjects:** All authors have confirmed that this study did not involve animal subjects or tissue. **Conflicts of interest:** In compliance with the ICMJE uniform disclosure form, all authors declare the following: **Payment/services info:** All authors have declared that no financial support was received from any organization for the submitted work. **Financial relationships:** All authors have declared that they have no financial relationships at present or within the previous three years with any organizations that might have an interest in the submitted work. **Other relationships:** All authors have declared that there are no other relationships or activities that could appear to have influenced the submitted work.

Acknowledgements

The authors express their gratitude to Siksha 'O' Anusandhan (Deemed to be University) for providing the research facilities.

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