SIMULTANEOUS REMOVAL AND CONVERSION OF SILVER IONS FROM WASTEWATER INTO ANTIBACTERIAL MATERIAL THROUGH SELECTIVE CHEMICAL PRECIPITATION

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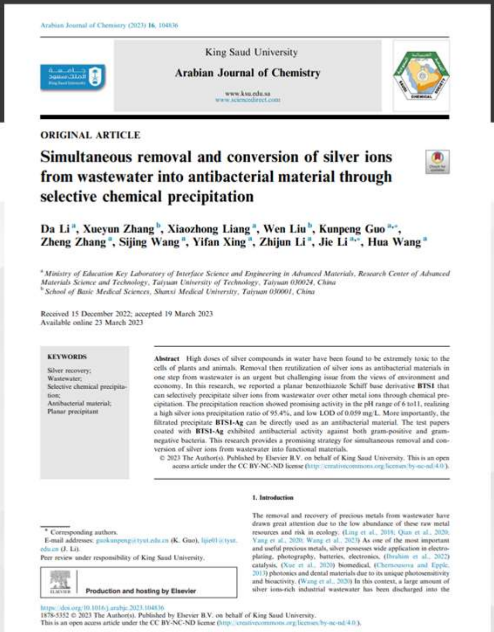

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ORIGINAL ARTICLE

Simultaneous removal and conversion of silver ions from wastewater into antibacterial material through selective chemical precipitation

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KEYWORDS
Silver recovery;
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Planar precipitant

Abstract High doses of silver compounds in water have been found to be extremely toxic to the cells of plants and animals. Removal then reutilization of silver ions as antibacterial materials in one step from wastewater is an urgent but challenging issue from the views of environment and economy. In this research, we reported a planar benzothiazole Schiff base derivative **BTS1** that can selectively precipitate silver ions from wastewater over other metal ions through chemical precipitation. The precipitation reaction showed promising activity in the pH range of 6 to11, realizing a high silver ions precipitation ratio of 95.4%, and low LOD of 0.059 mg/L. More importantly, the filtrated precipitate **BTS1-Ag** can be directly used as an antibacterial material. The test papers coated with **BTS1-Ag** exhibited antibacterial activity against both gram-positive and gram-negative bacteria. This research provides a promising strategy for simultaneous removal and conversion of silver ions from wastewater into functional materials.

1. Introduction

The removal and recovery of precious metals from wastewater have drawn great attention due to the low abundance of these raw metal resources and risk in ecology. (Ling et al., 2018; Qian et al., 2020; Yang et al., 2020; Wang et al., 2023) As one of the most important and useful precious metals, silver possesses wide application in electroplating, photography, batteries, electronics, (Ibrahim et al., 2022) catalysis, (Xue et al., 2020) biomedical, (Chernousova and Epple, 2013) photonics and dental materials due to its unique photosensitivity and bioactivity. (Wang et al., 2020) In this context, a large amount of silver ions-rich industrial wastewater has been discharged into the

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INTRODUCTION

- Limited availability of precious metals in wastewater.
- Significance of silver in various industries
- Environmental and resource concerns with silver ion discharge
- Overview of recovery methods with a focus on chemical precipitation
- Overview of recovery methods with a focus on chemical precipitation

BACKGROUND

➢When

- The concern for precious metal recovery from wastewater has been steadily growing over the past few decades.
- The significance of this issue has been particularly emphasized in recent years due to increasing environmental awareness and resource scarcity concerns.

➢Why

- The limited abundance of precious metal resources and their critical role in various industries have prompted the need for efficient recovery methods
- The unchecked discharge of silver ions-rich wastewater poses ecological risks and represents a wasteful loss of valuable resources

BACKGROUND

➢ Where

- The challenge of precious metal recovery from wastewater is a global concern, with applications and implications spanning across industries and geographical regions
- Our research focuses on addressing this challenge by introducing a novel approach to selectively recover silver ions and convert them into valuable antibacterial materials

MATERIALS AND METHODS

➢Benzothiazole Schiff Base Synthesis:

To create the planar benzothiazole Schiff base (BTS1), a one-pot condensation reaction was employed. This involved the combination of 4-(thiophen-2-yl)benzaldehyde (1-CHO) and 2-hydrazinobenzothiazole (HBT) in a reaction that yielded BTS1 with an impressive 82% yield.

➢Comparison with Control Derivatives:

- To assess the impact of planarity on precipitation efficiency, we synthesized two control derivatives, BTS2 and BTS3. BTS2 replaced 1-CHO with [2,20-bithiophene]-5-carbaldehyde (2-CHO), while BTS3 replaced it with 4-(diphenylamino)benzaldehyde (3-CHO).
- The precipitating efficiency was observed to decrease from BTS1 to BTS2, and BTS3 exhibited no precipitation, highlighting the importance of planar molecular structure

MATERIALS AND METHODS

- **Antimicrobial Testing:**
  - We conducted rigorous antimicrobial testing on the precipitate BTS1-Ag to evaluate its antibacterial properties.
  - The testing included assessments against both gram-positive bacteria, such as Staphylococcus aureus (S. aureus), and gram-negative bacteria, including Escherichia coli (E. coli) and Pseudomonas aeruginosa (P. aeruginosa).
- **Significance of Schiff Bases:**
  - Schiff bases are known for their effectiveness in complexing with metal ions through ligand–metal coordination. This property was leveraged in our study to facilitate the selective complexation of Ag^+ ions.
  - This unique feature of Schiff bases makes them ideal for converting Ag^+ ions directly from wastewater into antibacterial materials, opening up new possibilities for sustainable resource management and material innovation.

MATERIALS AND METHODS

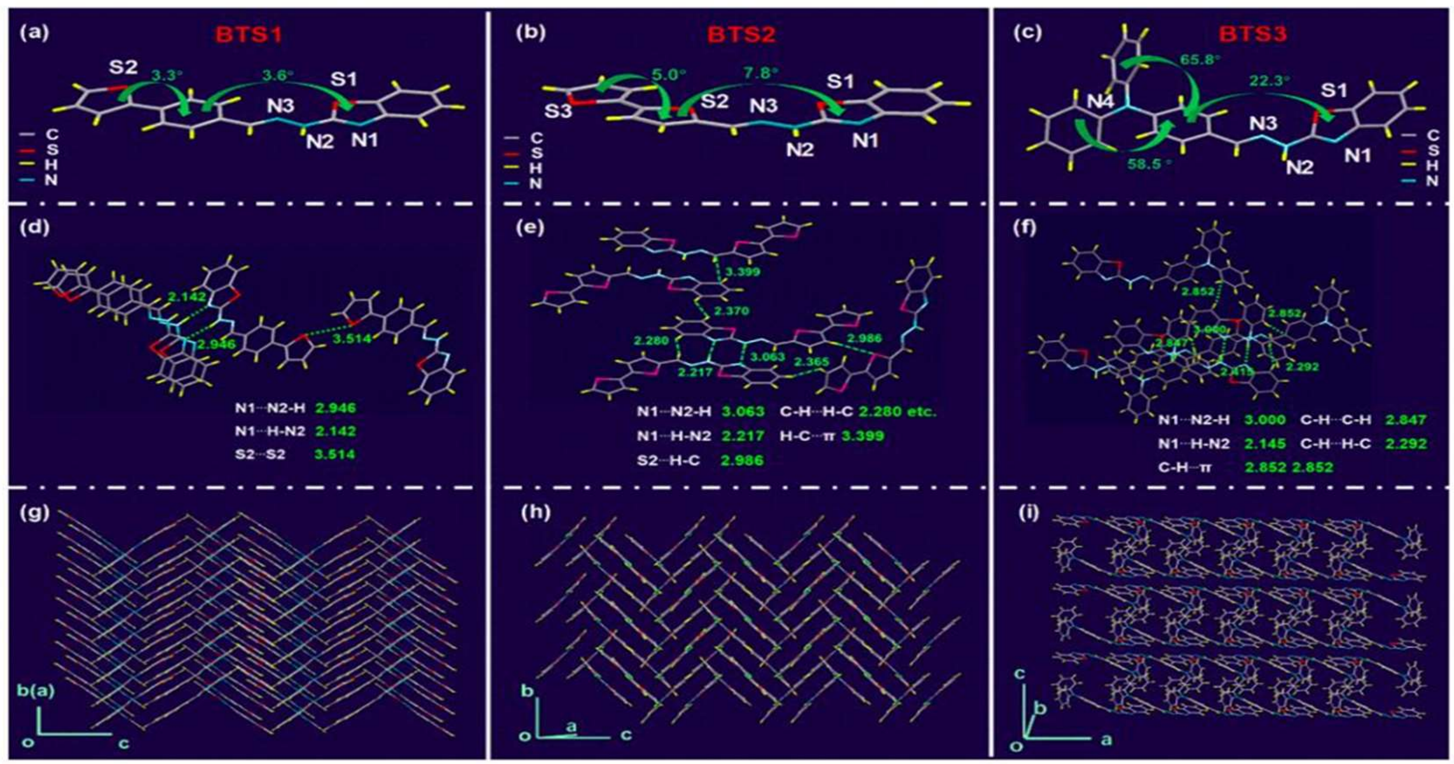

Fig. 2 Molecular structures of (a) **BTS1**, (b) **BTS2**, and (c) **BTS3**. Non-covalent interactions of (d) **BTS1**, (e) **BTS2**, and (f) **BTS3**. Molecular packing of (g) **BTS1**, (h) **BTS2**, and (i) **BTS3**.

RESULT AND DISCUSSION

➢Schiff Base configuration:

- Single crystals of BTS1–3 were grown from a THF/methanol mixture at 25°C.BTS1 exhibited a nearly planar configuration.
- In contrast, BTS2 and BTS3 showed progressively more twisted structures.The planar configuration of BTS1 was favored for precipitate formation due to its molecular structure.

➢Selective Precipitation of Ag+ Ions:

- BTS1, with a concentration of 25 µM, underwent testing to evaluate its effectiveness in precipitating Ag+ ions within an aqueous solution.
- The confirmation of selective Ag+ ion precipitation was established through the observation of a substantial reduction in absorption intensity at 363 nm.Additionally, a yellow flocculent precipitate formed rapidly in the solution, further validating the successful removal of Ag+ ions.
- BTS2 and BTS3, characterized by their nonplanar configurations, demonstrated lower efficiency in precipitating Ag+ ions during the process.

RESULT AND DISCUSSION

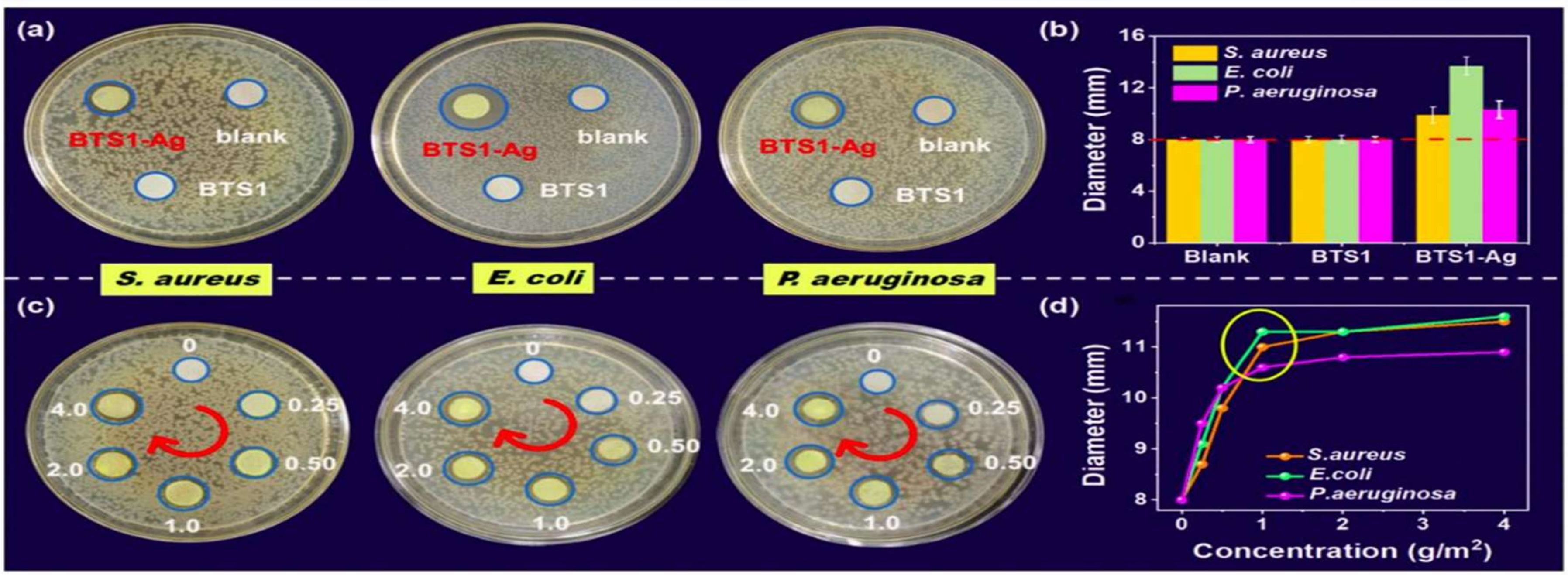

Fig. 7 (a) Antibacterial activity and (b) corresponding DIZ (mm) of blank, **BTS1** (1.0 g/m^2), and **BTS1-Ag** (1.0 g/m^2) against *S. aureus*, *E. coli* and *P. aeruginosa* in culture at 37 °C. (c) Antibacterial activity and (d) corresponding DIZ (mm) of **BTS1-Ag** with different concentrations against *S. aureus*, *E. coli* and *P. aeruginosa*.

RESULT AND DISCUSSION

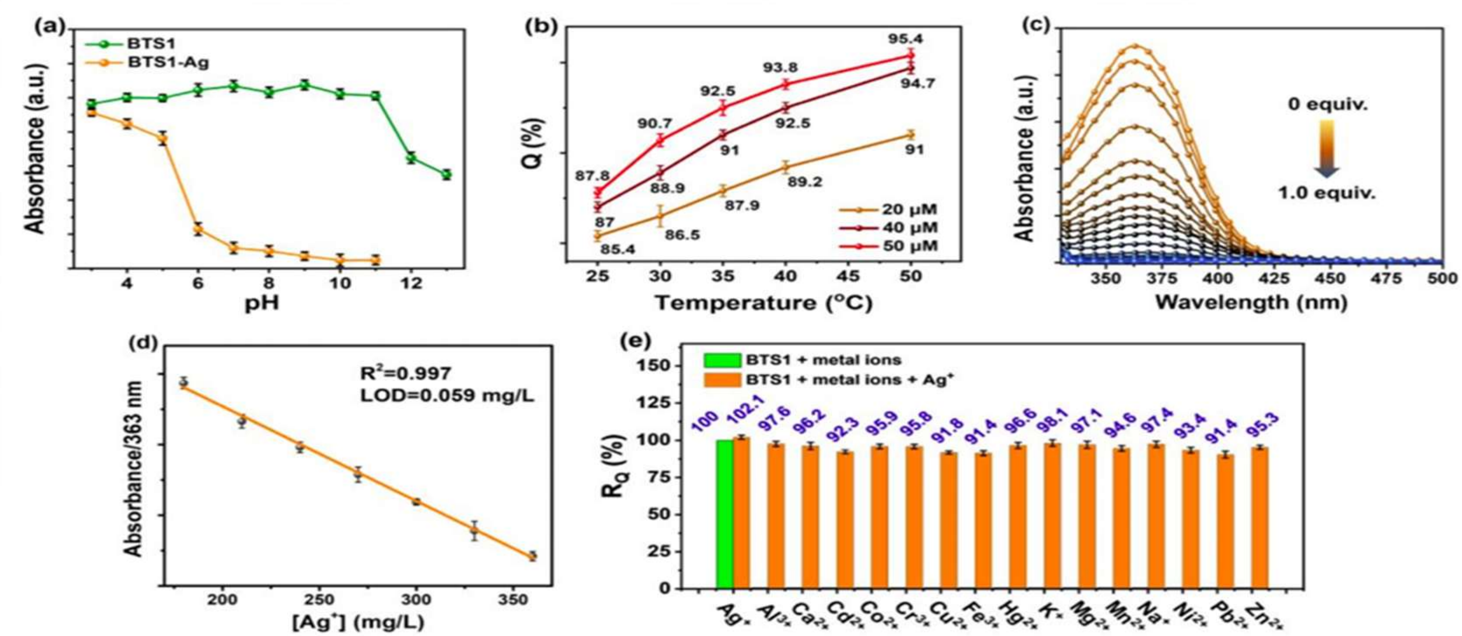

Fig. 6 (a) The absorbance changes of absorption peak at 363 nm for **BTS1** (25 μM) and **BTS1-Ag** (adding 10 mM of Ag^+ ions) under different pH conditions. (b) Q variations at different temperatures (25–50 °C) with predetermined **BTS1** concentrations (20 μM, 40 μM, 50 μM). (c) UV–vis absorption spectra of **BTS1** (25 μM) with various Ag^+ concentrations (0–1.0 equiv.). (d) The linear relationship at the concentrations of 180–360 mg/L. (e) R_Q variations in the simulated wastewater with different competing ions. Except (a), the rest were all conducted in acetone/H_2O (v/v, 1/99) HEPES buffer (10 mM, pH 7.4).

RESULT AND DISCUSSION

➢ **Characterization of BTS1-Ag Precipitate:**

- Scanning electron microscopy (SEM) examination showed that BTS1-Ag formed aggregated nanosheets.
- Elemental mapping and X-ray Photoelectron Spectroscopy (XPS) analysis provided confirmation of the presence of Ag within the BTS1-Ag precipitate.
- XPS analysis further revealed the coordination of imine and thiazole nitrogen atoms with Ag+ ions in BTS1-Ag.

➢ **Complexation and Stoichiometry:**

- The confirmation of a 2:1 complex stoichiometry between BTS1 and Ag+ ions was obtained.
- A linear correlation was established between the absorption intensity at 363 nm and Ag+ ion concentration in the range of 180-360 mg/L, indicating high sensitivity to Ag+ ions.
- BTS1 exhibited exceptional selectivity for Ag+ ions, even in the presence of competing metal ions.

RESULT AND DISCUSSION

➢Optimization for Precipitation:

- The optimal pH range for precipitation was determined to be between 6 and 11, with the highest efficiency observed at pH 7.4.
- Precipitation efficiency was found to increase with higher concentrations of BTS1 and elevated temperatures.
- BTS1 exhibited a low limit of detection (LOD) for Ag^+ ions, measuring at 0.059 mg/L, which complies with wastewater discharge standards.

➢Antimicrobial Properties:

- BTS1-Ag demonstrated antimicrobial activity against three bacterial strains: S. aureus, E. coli, and P. aeruginosa.
- The size of inhibition zones observed correlated with the concentration of BTS1-Ag coating, and even at low concentrations (0.25 g/m^2), it exhibited significant antimicrobial effects.
- The cost-effective antimicrobial properties of BTS1-Ag support its potential utilization as a valuable by-product within the recovery process.

CONCLUSION

- In this study, we successfully synthesized BTS1, a planar benzothiazole Schiff base derivative, with an impressive yield of up to 82%. To provide a meaningful context for our research, we also prepared two control derivatives, BTS2 and BTS3, characterized by progressively non-planar structures.

- Our investigation primarily focused on assessing the efficiency of BTS1 in selectively precipitating Ag^{+} ions from wastewater. Additionally, we conducted antibacterial testing on the resultant precipitate, BTS1-Ag, targeting both gram-positive (S. aureus) and gram-negative bacteria (E. coli and P. aeruginosa). The outcomes revealed the remarkable antimicrobial properties of BTS1-Ag.

- These experiments underscore the potential of BTS1 as an efficient agent for Ag^{+} ion recovery from wastewater, emphasizing the significance of molecular configuration in this process. Our findings present a sustainable and innovative solution for metal recovery while concurrently generating valuable antibacterial materials.

Thank you

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