



Silver recovery from greywater: Role of competing cations and regeneration



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ABSTRACT

The use of silver in consumer products and its subsequent leaching in greywater show an increasing trend. Silver recovery is not only commercially lucrative but also an environmental necessity. Trace concentration of Ag^+ and high concentration of other competing cations (Na^+ , Ca^{2+} , Mg^{2+}) in a typical laundry wash water makes the separation process challenging. The use of ion-exchange resin with thiol group in its chain offers a potential solution due to its high selectivity for silver. This work successfully recovers silver (>90%) as high purity grade Ag_2S powder (>99%) from synthetic greywater solution using a commercially available resin, Ambersep GT74, in a fixed-bed column mode. The regeneration process in the work has been optimized with respect to the solution pH and thiourea concentration (0.5 M thiourea concentration at pH 1). The resin and the regenerant have been used in multiple cycles (4 times) without compromising on their performance. The study successfully demonstrates a closed-loop sustainable scheme by reusing and recycling all the raw materials to the point of exhaustion with no chemicals/toxic released into the environment.

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1. Introduction

Due to its anti-microbial properties, nano-particulate silver has been increasingly used in consumer goods, particularly clothing and textiles [1]. Starting with surgical and medical clothing about two decades ago [2], now use of silver-coated textiles - primarily socks and undergarments [3,4] - and wound dressings [5] is commonplace with worldwide production exceeding 100,000 tonnes in 2000 and growing 15% annually [6].

Silver loading on textiles has been variedly estimated by different studies from 0.9 mg/kg to 21,600 mg/kg [7–9]. Lorenz et al. [10] opine that silver loading ranging from 1 mg/kg to >1000 mg/kg can be considered normal for silver-containing textiles in market today. Silver leaching during laundry has been recently reported by many investigators [8–14]. It is a complex phenomenon and results in terms of the form and amount of silver show a wide range [12,13]. Both the parameters depend on method, form and amount of silver loaded on textiles, wash solution chemistry and washing procedure [9,10]. Benn & Westerhoff [8] reported up to 1.3 mg/L (68 μg Ag/g of fabric) of silver leaching with >86% as Ag^+ in distilled water. Geranio et al. [9] studied nine different silver-loaded textiles in a variety of real-life laundry conditions

and reported that TAED (Tetraacetylenediamine)/perborate bleach system commonly found in detergents greatly accelerates the dissolution of Ag-nano-particles to Ag^+ . The textiles released silver (1.3–377 μg Ag/g of textile) in both particulate and ionic form with some of the textiles releasing entirely in Ag^+ form. Reed et al. [11] observed that the quantity of Ag released in detergent solution is only slightly lower than distilled water but the speciation varied widely (80–92% in Ag^+ form in distilled water; 22–31% as Ag^+ in detergent solution). Chlorine bleach detergent can convert >50% Ag nano-particles to AgCl [13,15], however chlorine bleach wash hampers anti-bacterial efficacy of the textiles [16]. Benn & Westerhoff [17] established that 470 μg Ag per person per day can potentially be released in the USA. In this study, Ag released from a shirt washed with tap water passed 20 nm filter, suggesting that the released Ag is in ionic and/or nano forms. Lorenz et al. [10] studied eight different textiles in a standardized protocol of washing and rinsing condition and observed particulate (~80%) [Both coarse and fine AgCl , Ag_2S and metallic Ag] and ionic (~19%) forms leaching in the washing solution (0.32–38.5 mg/L; 4.5–575 mg/kg) and rinsing solution (0.36–22.7 mg/L; 1.8–113 mg/kg). Modeling results also indicate textiles to be a major source of silver in the environment [18,19]. These studies confirm release of silver in aqueous solution; however the speciation of released silver widely varies among particulate and dissolved ionic forms. The silver released to the environment can cause potential

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ecotoxicological risks [20,21] and has been reported to harm the bacterial treatment processes in wastewater treatment plants (WWTPs) [22]. Westerhoff et al. [23] suggests recovering silver from waste streams as potentially most lucrative. Therefore, recovery of leached silver from laundry wash water at the source is favorable from environmental and economic points of view.

Separating precious metals from their concentrated solution is relatively easy, e.g., by reduction, precipitation or electrolysis; however, metals in dilute solutions are challenging separation problems. Ion exchange technology provides a promising approach as it harnesses the high affinity for silver by elements that can donate a pair of electrons, e.g., sulfur and nitrogen. Ion exchange resins having particularly sulfur in their chain are most often utilized to selectively recover silver, as silver ion is a soft Lewis acid and it has smaller effective ionic radii (2.5 Å) in aqueous solution and sulfur, a soft Lewis base, easily donates its lone pair of electrons [24]. Jacobson et al. [25] used a commercial resin Duolite 73 containing thiol group to recover silver from organic and sandy soil. El - Ghaffar et al. [26] prepared resin derived from condensation of 3-amino-1,2,4, triazole-5-thiol and glutaraldehyde which recovered 3.6 mmoles of silver per gram of its dry weight. A thiourea-modified adsorbent having styrene backbone selectively removed silver in the presence of platinum with an uptake capacity of 101.58 mg/g and a high separation factor of 1155 [27]. Quang et al. [28] prepared silica beads by grafting thiol functional group on silica gel which recovered as well as reduced silver with an uptake capacity of 75.8 mg/g. Ladhe et al. [29], using a thiol functionalized silica – mixed matrix membrane, studied silver uptake in the presence of significant concentration of other co-contaminants like Ca^{2+} . Li et al. [30], using Amberlite IRN-78, a thiol group based resin recovered silver nanoparticles completely from real environmental water. Roy et al. [31] incorporated a thiosemicarbazide group onto a weakly acidic resin Amberlite IRC-50 to entrap silver with an exchange capacity of 0.49 meq/gm. Most of these studies focused only on silver removal, and did not elaborate on selective recovery and regeneration process. This work selectively recovers silver (>90%) as high purity grade Ag_2S powder (>99%) against a host of competing cations (Na^+ , Ca^{2+} & Mg^{2+}) in a concentration range that is typically found in domestic waste streams and reuses and recycles the resin and regenerant solution. Unlike previous works, this is a detailed study on the regeneration process using thiourea and elaborates on the role of different species of silver-thiourea complex ($\text{Ag}(\text{Tu})_n^+$; $n = 1-4$; $\text{Tu} = \text{Thiourea}$) in regeneration. The regeneration process in the work has been optimized with respect to the solution pH and thiourea concentration (0.5 M thiourea concentration at pH 1). For the first time the role of different species of silver-thiourea complex in affecting the regeneration efficiency in a fixed-bed column mode is reported here. Precipitation of $\text{Ag}(\text{Tu})_3^+$ complex and re-adsorption of $\text{Ag}(\text{Tu})_2^+$ complex on the resin have been noticed depending on the thiourea concentration in the regenerant solution. Therefore, thiourea concentration in the study has been estimated from speciation analysis of silver-thiourea complexes at different thiourea and silver concentrations such that $\text{Ag}(\text{Tu})_4^+$ species remains dominant in the solution so as to avoid precipitation and re-adsorption of the above mentioned other two species.

2. Materials and experimental methods

2.1. Materials

The commercial resin Ambersep™ GT74 was obtained from Supelco Analytical (Bellefonte, PA); refer to Table 1 for the resin's salient properties.

High purity grade chemicals (>99% assay) sodium chloride (NaCl), sodium nitrate (NaNO_3), calcium nitrate tetrahydrate (Ca

Table 1

Salient properties of polymeric ion-exchanger (Ambersep™ GT74) used in the study.

Characteristics	Description
Matrix	Macroporous styrene copolymer
Functional groups	Thiol
Physical form	Beads
Ionic form as shipped	H
Total exchange capacity	≥ 1.3 eq/L (SH form)
Moisture holding capacity	48–55% (H form)
Harmonic mean size	0.450–0.700 mm
Uniformity coefficient	≤ 1.8
Fines content	<0.425 mm: 12% max
Coarse beads	>0.850 mm: 15% max

(NO_3)₂·4H₂O), thiourea ($\text{CH}_4\text{N}_2\text{S}$) and sodium hydroxide (10 N NaOH) were purchased from Fisher Scientific; Silver nitrate (AgNO_3), nitric acid (HNO_3 67–70% strength) and silver sulfide standard (Ag_2S) were purchased from Alfa Aesar; magnesium sulfate (MgSO_4) was obtained from Allied Chemical; and silver nitrate standard (AgNO_3 , 1000 mg/L as Ag^+) was obtained from Perkin Elmer.

2.2. Analytical procedure

Standard Methods of Water and Wastewater Treatment [32] was used for the analysis of all the chemicals. The cations Na^+ , Ca^{2+} and Mg^{2+} were analyzed using a DIONEX Ion Chromatograph (Model – ICS 900) coupled with an AS40 auto-sampler. Silver was analyzed using a Perkin Elmer Atomic Absorption Spectrometer (AAS) (AAnalyst 300) fitted with hollow silver cathode lamp and absorption wavelength set at 328 nm and spectral slit of 0.7 nm with air-acetylene flame. Elemental analysis of precipitate was done on an energy dispersive X-ray (EDS) obtained from Oxford Instruments, Inc. (High Wycombe, United Kingdom) INCA Energy EDX system in conjunction with a Scanning Electron Microscope (SEM) (JSM 5610 from JEOL, Inc. Peabody, MA) with an accelerating voltage of 18 kV. Structural analysis of the silver-thiourea precipitate was done using Bruker D8 Venture CMOS single crystal X-ray diffractometer at 200 K with a Cu μF source and HELIOS MX optics. All non-hydrogen atoms were refined anisotropically (XL) by full matrix least squares in F2. Hydrogen atoms were placed in calculated positions and then refined with a riding model with N–H lengths of 0.88 Å and O–H lengths of 0.87 Å with isotropic displacement parameters set to 1.20 times U_{eq} of the parent N atom and 1.50 U_{eq} of the parent O atom. The sulfate anion is disordered over two sets of sites with a refined occupancy ratio of 0.785 (4):0.2359 (5).

2.3. Experimental methods

2.3.1. Ion exchanger preparation

10 g of dried virgin resin was added to 1.0 L of 2% solution of NaCl to convert from the H^+ form of the resin to Na^+ form. The mixture was gently stirred for 24 h, after which it was filtered and rinsed in deionized (DI) water to ensure removal of excess ions sticking on the resin's surface. The resin was oven dried at 45 ± 2 °C for 24 h, and subsequently used in experiments.

2.3.2. Synthetic greywater preparation

The synthetic greywater used in the study was prepared by mixing NaNO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, MgSO_4 and AgNO_3 salts in DI water with typical greywater concentrations of Na^+ as 120 mg/L; Ca^{2+} as 60 mg/L; Mg^{2+} as 10 mg/L [33] and Ag^+ as 5 mg/L. Silver concentration had been chosen on the basis of 4.25 mg/L concentration limit set by the USEPA (United States Environmental Protection Agency) for influent streams to WWTPs such that silver concentration

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