1 **Silver recovery from greywater: role of competing cations and regeneration**

2 Tabish Nawaz^a, Sukalyan Sengupta^{a,*}

3 ^a Civil and Environmental Engineering Department

4

5 University of Massachusetts Dartmouth, 285 Old Westport Road

6 Dartmouth, MA, 02747

7 ^{*} Corresponding author

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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.

Keywords: Silver recovery, Ion-exchange resins, Greywater treatment, Sustainability, Thiourea regeneration

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 21600 mg/kg [7-9]. Lorenz et al. (2012)[10] opine that silver loading ranging from 1 mg/kg to more than 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 (2008) [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. (2009) [9] studied nine different silver-loaded textiles under laundry condition and reported that TAED/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. (2016) [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 more than 50% Ag nano-particles to AgCl [13, 15], however chlorine bleach wash hampers anti-bacterial efficacy of the textiles [16]. Benn & Westerhoff (2010) [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. (2012) [10] studied eight different textiles under washing and rinsing condition and observed particulate (~80%) [Both coarse and fine AgCl, Ag₂S 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 (1.8 – 113 mg/L; 0.36 – 22.7 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 ecotoxicological risks [20, 21] and has been reported to harm the bacterial treatment processes in wastewater treatment plants (WWTPs) [22]. Westerhoff et al. (2015) [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. (2004) [25] used a commercial resin Duolite 73 containing thiol group to recover silver from organic and sandy soil. El - Ghaffar et al. (2009) [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. (2013) [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. (2009) [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. (2012) [30], using Amberlite IRN-78, a thiol group based resin recovered silver nanoparticles completely from real environmental water. Roy et al. (2005) [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 ($\text{Ag}(\text{Tu})_n^+$; $n = 1 - 4$; Tu = 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 AmbersepTM GT74 was obtained from Supelco Analytical (Bellefonte, PA); refer to Table 1 for the resin's salient properties.

Table 1: Salient properties of polymeric ion- exchanger (AmbersepTM 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

High purity grade chemicals (>99% assay) sodium chloride (NaCl), sodium nitrate (NaNO_3), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$) and sodium hydroxide (10N 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 200K 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 hours, 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 $45 \pm 2^\circ\text{C}$ for 24 hours, 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 120mg/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 remains within limit for fresh water supply [8], and so as to study the equilibrium condition of the fixed-bed column in reasonable time period. The effect of dissolved organic matter, typically found in laundry wash water, was not addressed in this research. The study aimed at determining the role of competing cations found in laundry wash on uptake and selective removal by the ion-exchanger. Dissolved organic matter being anionic, it is not expected to affect this aspect of the study. It is acknowledged that dissolved organic matter may compete with the ion-exchanger for Ag^+ uptake [34], this is being studied but will form part of a separate article.

2.3.3 Batch equilibrium tests: Isotherm, uptake and regeneration

Batch equilibrium tests were performed according to the constant normality bottle-point method [35]. The constant Ag^+ concentration was fixed at 100 mg/L in 1 L solution. The resin mass varied from 0.04 g to 0.4 g. The tests were performed in a tightly sealed glass jars. Mixing was achieved in a rotary mixer for 24 hours at temperature of $20 \pm 2^\circ\text{C}$. The chosen time period of 24 hours ensured attainment of equilibrium as sample analyzed at 48 hours showed no change in equilibrium Ag^+ concentration.

Aliquots of 10 ml were withdrawn at the beginning and end of the tests from each sample for analysis. 5-6 drops of concentrated HNO_3 (67-70% strength) were added to each aliquot

withdrawn to prevent the precipitation of Ag^+ . Next, the exchanger was filtered out and rinsed in DI water before regeneration. The uptake of the resin at equilibrium was calculated as:

$$\text{Equilibrium uptake (mg of Ag}^+/\text{g dry resin)} = \frac{(C_{\text{initial}} - C_{\text{final}})V}{\text{Mass of dry resin}}$$

Where C_{initial} = initial Ag^+ concentration; C_{final} = final Ag^+ concentration; V = volume of solution 100 ml of 0.5M thiourea & 0.1M HNO_3 solution was used as the regenerant. Batch regeneration was accomplished by stirring the fully loaded resin in the regenerant solution for 2 hours in a rotary mixer. The regeneration efficiency was determined as follows:

$$\% \text{ regeneration efficiency} = \frac{\text{Mass leached from the resin}}{\text{Mass loaded on the resin}} \times 100\%$$

The regenerated resin was rinsed in DI water, stirred for 2 hours in 100 ml of 1N NaOH solution and again rinsed in DI water before using it in the next uptake cycle.

Non-linear least square (NLLS) method was used to curve-fit the equilibrium data with Langmuir and Freundlich isotherm models [36] in MATLAB r2011b. Error calculations for both the fits were performed by following non-linear error functions – Sum of the squares of errors (SSE), Composite fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), Average relative error (ARE) and Sum of the absolute errors (EABS) [35]. Akaike's Information Criterion (AIC) [35] was also determined to establish which of the two models describes the isotherms more accurately.

2.3.4 Fixed-bed column runs: uptake and regeneration

Fixed-bed column runs were carried out in Adjusta Chrome[®] #11(Ace Glass Inc., Vineland NJ) glass columns 300 mm long with 10 mm inner diameter. 2 g of the dry resin was used to prepare the fixed-bed. The resin was introduced into the column as a wet slurry. The synthetic greywater

influent was passed downward into the column using a synchronous FMI lab pump, Model QSY (Fluid Metering Inc., Syosset, NY). The flow rate provided an Empty Bed Contact Time (EBCT) of ~3 minutes. Effluent from the column was collected by a Spectra/Chrome[®] CF-1 Fraction Collector (Spectrum Chromatography). The break-through of the column was set at an effluent concentration equal to 10% of the influent concentration. An inline pH meter (AB15 pH meter, Fisher Scientific) was also present in the system to monitor the effluent pH. After break-through, the bed was regenerated by passing 0.5 M thiourea & 0.1M HNO₃ solution. The spent regenerant effluent was collected similarly in the fraction collector. The regenerated bed was first rinsed with DI water, and then by 30 ml 1N NaOH solution, and then by 0.1 M HNO₃ till the effluent pH was about ~7, and subsequently used for another exhaustion run.

2.3.5 Precipitation of silver sulfide

6-8 mL of 1N NaOH spent wash solution was added drop-wise to the spent regenerant solution. The pH rose to 11-11.5 and a dark black precipitate started to form. The precipitate was allowed to settle for 30 minutes. The supernatant was filtered through 0.2µm filter and analyzed for silver using an AAS. The precipitate was dried in the oven at $45 \pm 2^{\circ}\text{C}$ for 2 days, and elemental analysis of it was conducted using EDS. Silver sulfide standard was also analyzed using EDS and compared with the precipitate obtained in the study.

2.3.6 Reuse of spent regenerant

After the precipitation and subsequent filtration, 67-70% strength HNO₃ was added drop-wise to the spent regenerant till the pH dropped to ~1.5-1.6. The spent regenerant was reused 4 times in this study to regenerate an exhausted resin.

3. Results

3.1 Fixed-bed column run: exhaustion

Figure 1: Breakthrough profile of the cationic contaminants in the synthetic greywater from the fixed-bed column run

Figure 1 shows the break-through profiles of Na^+ , Ca^{2+} , Mg^{2+} and Ag^+ ions from the fixed-bed column run. It is seen that Na^+ , Ca^{2+} and Mg^{2+} broke-through within 10 bed volumes whereas for Ag^+ it took ~20,000 bed volumes. This shows preferential selectivity for Ag^+ by the thiol group in the resin against a host of other co-contaminants. This is particularly useful for the process application as the resin exclusively recovered Ag^+ when present at a trace concentration against a background of competing cations at a concentration that is at least one order of magnitude higher. The selectivity sequence follows the typical sequence mentioned in the literature, $\text{Ag}^+ \gg \text{Ca}^{2+} > \text{Na}^+$ [37]. The resin column showed an uptake capacity of ~300 mg of Ag^+ per g of the dry resin.

3.2 Fixed-bed column run: regeneration

Figure 2: Regeneration profile of the fixed-bed column

Figure 2 shows the regeneration profile of the exchanger in the fixed-bed column run for a regenerant solution containing 0.5M thiourea and 0.1M HNO₃. Recovery of more than 96% of the sorbed silver was attained in 90 bed volumes.

3.3 Precipitation of silver sulfide

Table 2 and figure 3 and show the results of EDS study of the precipitate, and it can be inferred that the precipitate was Ag₂S, and it does not contain any impurity. AAS analysis for Ag on the spent regenerant both pre and post-precipitation showed ~99% silver recovery as Ag₂S.

Table 2 – EDS analysis of the silver precipitate recovered in the study: Elemental Composition

Element	Precipitate obtained in the study		Standard Silver Sulfide	
	Weight %	Atomic %	Weight %	Atomic %
Sulfur	13.21	33.87	13.02	33.5
Silver	86.79	66.13	86.98	66.5

Figure 3 – a: EDS analysis of solid-phase amorphous precipitate (Ag_2S) obtained from regenerant by adding spent NaOH wash solution; see Table 2 for elemental weight % of the constituents. b: EDS analysis of Ag_2S standard from Alfa Aesar; see Table 2 for elemental weight % of the constituents.

3.4 Batch equilibrium tests: Uptake, isotherm, reuse & recycling of the regenerant and the resin

Constant normality bottle-point batch tests uptake data were described more accurately by NLSS Freundlich isotherm model than NLSS Langmuir isotherm model (Figure 4 & Table 3).

Figure 4: Non-linear least square (NLLS) model fits (a) Langmuir Isotherm fit (b) Freundlich Isotherm fit for silver uptake; Refer to Table 3 for error analysis and fit quality

Table 3: Non-linear error functions values for fitting of Langmuir and Freundlich isotherm data

Non-linear Error Functions	Langmuir Isotherm Model	Freundlich Isotherm Model
HYBRID	47.507	13.118
SSE	1023.794	301.72
MPSD	4.23	2.137
ARE	4.087	1.785
EABS	86.38	40.3
AIC	56.572	44.35
R ²	0.841	0.953

Langmuir isotherm model predicted a maximum uptake capacity of 289 mg Ag⁺/g of dry resin and Freundlich isotherm model predicted a maximum uptake capacity of 297 mg Ag⁺/g of dry resin, which is closer to the value obtained during column run (300 mg Ag⁺/g of dry resin).

Figure 5: Reusability of Ambersep GT74 with the repeated uptake and regeneration cycle in batch mode (Initial Ag⁺ conc. = 100 mg/L; Resin mass = 0.1 g; Volume of solution = 1 L)

Figure 5 shows the resin's uptake performance for 4 cycles of use. The consistent uptake capacity of ~300 mg silver per g of dry resin demonstrates that the resin performance is not compromised over at least four cycles of its use.

Figure 6: Comparison of the regeneration efficiency of the fresh and recycled regenerant (0.5M Thiourea and 0.1 M HNO₃) in batch mode

Figure 6 shows multiple reuses of the spent regenerant. It is seen that the fully loaded resin was ~100% regenerated by the fresh regenerant in batch mode. In its 1st reuse post-precipitation and after pH adjustment, the regenerant was as effective as the fresh regenerant in achieving ~100% regeneration of fully loaded resin. In its 2nd and 3rd reuse percent regeneration achieved was ~98%. The result provides a comparative idea about the performance of spent regenerant over multiple cycles of reuse, and it is concluded that the spent regenerant is as effective as the fresh regenerant over atleast 4 cycles of use.

4. Discussion

4.1 Uptake mechanism: Cation exchange capacity(CEC) & selectivity

4.1.1 Fixed-bed column run

High uptake capacity (~300 mg Ag⁺/gram of dry resin) and high selectivity (Ag⁺ break-through BV# ~20,000; others within 10 BVs) for silver even when it is in trace concentration (5 ppm) compared to other cations, suggest silver-sulfur complexation as the dominant mechanism of

sorption. Sulfur, a soft Lewis base, and silver, a soft Lewis acid, have high mutual affinity [24] and form stable complexes (stability constants in $\sim 10^{3.7} - 10^{13}$ [38]). The other cations Na^+ , Ca^{2+} and Mg^{2+} are hard acids [24], and therefore, are easily rejected within 10 BVs by the ion-exchanger. Early rejection of divalent cations – Ca^{2+} & Mg^{2+} - present at much higher concentration than monovalent Ag^+ shows silver-sulfur complexation, and not merely electrostatic interaction, to be the governing mechanism.

4.1.2 Batch equilibrium runs

In a batch mode study, conducted at the pH values of 6, 7.5 and 8.5 with 0.1 g of resin stirred in 1 L solution containing 100 mg/L as Ag^+ , uptake capacities were noted as 300 mg, 328 mg and 267 mg Ag^+ /g of dry resin respectively. The trend is in agreement with earlier reported works on thiol-group based silver separation where it is concluded that complexation is due to the free lone pair on sulfur atom [26, 39]. Higher pH value deprotonates sulfur and creates more active sites for sulfur-silver complexation as compared to a lower pH value, thus leading to an increased uptake. Lower uptake at pH = 8.5 is attributed to possible AgOH precipitation ($K_{\text{sp}} \sim 10^{-8}$ [40]). The study was not conducted for pH > 8.5, as typical greywater pH is $\sim 7-8$ [41]. The increase in uptake capacity with pH shows that complete modification of the resin from hydrogen to sodium form was not achieved, suggesting that both $-\text{SNa}$ and $-\text{SH}$ sites were involved in the ion-exchange. Selectivity studies in batch mode (data not reported) demonstrated that exchange process is ternary; however, it does not affect the column operation as the resin is found to be far more selective for Ag^+ than any other cations found in greywater [33]. Additionally, it is concluded that modification of the hydrogen form of resin to sodium form is not necessary and can be avoided for silver removal and subsequent recovery.

Based on error functions (Table 3) it is inferred that Freundlich model describes the ion-exchange process more accurately than Langmuir model. Lower value of AIC obtained for Freundlich curve-fitting [35] affirms to the suitability of the Freundlich model over Langmuir model. This result shows that the ion-exchange was heterogeneous and not restricted to monolayer exchange; heat of sorption was not a constant [35]. The curve-fitting yielded the following equations for Freundlich and Langmuir models respectively:

$$q_e = 184.3676C_e^{0.103482} \quad \text{Equation (1)}$$

$$q_e = \frac{149.7766C_e}{1 + 0.5176C_e} \quad \text{Equation (2)}$$

Maximum uptake capacity obtained from Freundlich model (297 mg of Ag⁺/g of dry resin) matches more closely to the value observed during fixed-bed run (300 mg of Ag⁺/g of dry resin) than the value predicted by Langmuir model (289 mg of Ag⁺/g of dry resin). This further proves the suitability of Freundlich model in describing the ion-exchange process.

4.2 Regeneration

4.2.1 Role of thiourea

Thiol group in the resin strongly holds silver by forming stable complexes. In order to recover silver from the resin, a complex forming ligand with stronger affinity for silver is needed. Thiourea is a soft ligand that forms stable complexes with silver (stability constant: $\sim 10^{13}$ [42]). Thiourea contains N & S in its chain, thus it is potentially capable of co-ordinating with silver from both N & S. However, S, a softer Lewis base than N, predominantly complexes with silver, a soft acid.

The regeneration is governed by following equation:

n = 1 – 4; Tu = Thiourea; over bar represents the solid phase

In the regenerant solution thiourea is in much higher concentration than what is required stoichiometrically, and by law of mass action this dominantly shifts the reaction (equation 3) in the forward direction. Moreover, sulfur in thiourea is more electron-rich than the sulfur in the thiol group in the polystyrene chain of the resin. This phenomenon is attributed to the electron donating resonance effect of N atoms in thiourea [43]. No such electron donating group is available to sulfur in the polystyrene chain of the resin. Therefore, sulfur in thiourea is a softer base and makes stronger complex with silver than the sulfur present in the thiol group on the resin.

4.2.2 Role of H^+

The presence of both acidic and basic groups in thiourea makes regeneration efficiency strongly dependent on regenerant pH. H^+ serves two roles in the scheme – replacing Ag^+ on the resin (according to equation 3) and providing stability to the silver-thiourea complexes formed, as thiourea makes more stable silver-thiourea complex in pH range of 0 – 1 [44]. At a fixed thiourea concentration of 0.1M, regeneration efficiency was observed to decline with decreasing H^+ concentration (Figure 7).

Figure 7: % regeneration efficiency of 0.1M thiourea regenerant solution with different H^+ concentrations

This confirmed the direct role of H^+ in affecting the regeneration. However, $pH < 1$ was not studied in order to avoid acid shock to the resin and corrosion to the column fixtures. Therefore, $pH = 1$ was selected for all subsequent regenerations.

4.2.3 Optimum thiourea concentration: Role of different silver-thiourea complex species

In order to make the recovery scheme sustainable, thiourea concentration in the regenerant solution was minimized without compromising regeneration efficiency. The batch mode study noted that at $pH = 1$, regeneration efficiency increases with increasing thiourea concentration before saturating at ~100% regeneration for 0.2M thiourea concentration (Figure 8).

Figure 8: % regeneration efficiency as a function of thiourea concentration in regenerant solution (at $pH = 1$).

This trend is in agreement with the mechanism of regeneration (Equation 3) and reported literature [45]. From figure 8, 0.2M thiourea at $pH = 1$ was considered optimum for regeneration. However, in fixed-bed column regeneration, the considered regenerant concentration resulted in

heavy in-line precipitation within 10 BVs. XRD study on the precipitate (Figure 9) determined the crystals as $\text{Ag}_2(\text{Tu})_6\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

Figure 9: The asymmetric unit of polymeric silver-thiourea complex as determined by X-ray diffraction study

Figure 9 shows the asymmetric unit of the precipitate and its sulfur-bridged silver chains which propagate along the A-axis of the crystal (refer to Appendix A). There is hydrogen bonding between the thiourea, water and sulfate ion as shown with the dashed lines. Similar silver-thiourea precipitate has been noticed in earlier works [46]. Figure 10 shows the SEM image and EDS elemental peaks.

Figure 10 – a: EDS analysis of needle-like precipitate of silver-thiourea complex formed during column regeneration; b: SEM image of the needle-like precipitate of silver-thiourea complex

It was suspected that high thiourea concentration (0.2M) rapidly desorbed silver from the resin.

Therefore, subsequently 0.1M thiourea was considered for the regeneration schemes.

374 With 0.1M thiourea, no in-line precipitation was observed. However, when the spent regenerant
 375 was stored over-night, similar silver-thiourea complex precipitate (Figure 9 & Figure 10) was
 376 seen for bed volume concentrations greater than ~1000 mg/L (Refer to Appendix C, Figure C.1).
 377 The precipitation prevented calculations to conduct an overall mass balance in the regeneration.
 378 Therefore, to account for an overall mass of silver leached, another fully loaded column was
 379 regenerated with 0.1M thiourea and 0.1M HNO₃ with the protocol of diluting the spent
 380 regenerant 10 times before storing them at room temperature. No precipitate was thus
 381 subsequently seen and mass of silver leached was properly accounted (Refer to Appendix C,
 382 Figure C.2). 95% of the resin bed was regenerated in 210 BVs, with 75% of it taking place in
 383 first 50 BVs and 20% in subsequent 160 BVs. This observation is possibly due to re-sorption of
 384 silver as silver-thiourea complex. Pleysier & Cremer (1973) [47] first reported preferential
 385 sorption of silver-thiourea complex over Ag⁺ ions, particularly as Ag(Tu)₂⁺ due to its higher
 386 polarizability and softer acidity than Ag⁺ ions. Ag(Tu)₂⁺, and not Ag(Tu)₃⁺ or Ag(Tu)₄⁺ was
 387 preferentially sorbed due to its higher fraction in the concentration range studied and lower co-
 388 ordination number [47]. It was also reported that the thermodynamic constant of formation for
 389 Ag(Tu)₂⁺ was three orders of magnitude higher in the solid phase than in the solution phase.
 390 Dohrmann (2006) [48] attributed hydrophobic interaction and higher ionic strength of the
 391 complex in the solution for enhanced and preferential sorption. This was confirmed in this study
 392 when the resin bed was used for its next cycle of uptake without following the step of washing it
 393 with NaOH. A black coating emerged on the bed top within passage of ~20 BVs of the fresh
 394 synthetic greywater as influent. The black coating was suspected to be Ag₂S and thiourea was the
 395 source of S²⁻ ions necessary for the coating as noticed in previous works [44, 49]. thiourea is
 396 unstable at a pH > 4.3, and hydrolyzes to release S²⁻ ions [50]. The influent greywater at pH~6

hydrolyzed sorbed silver-thiourea complex and released S^{2-} ions which formed a black coating of Ag_2S with the influent Ag^+ . Therefore, NaOH wash of the resin post-regeneration was incorporated as an essential step to hydrolyze the sorbed thiourea before the next cycle of uptake. No black coating was observed after adopting this protocol. Iodometric titration [32] on spent NaOH wash solution confirmed the presence of S^{2-} ions, indicating thiourea and its subsequent hydrolysis in alkaline medium. The resin post-NaOH wash acquired darker hue than its initial green color which is due to the formation of Ag_2S patina on the ion-exchanger. This is confirmed by its dissolution, and the release of foul smelling H_2S gas in the regenerant solution according to the following equation [51, 52]:

Presence of S^{2-} and patina formation during NaOH wash confirmed thiourea and Ag on the resin. The % speciation of different silver-thiourea complexes in the spent regenerant shows $Ag(Tu)_2^+$ remained a dominant species (Refer to Appendix B), reaching a fraction as high as 90% at silver concentration ~ 5000 mg/L (peak concentration at 25th BV). High ionic strength of $Ag(Tu)_2^+$ in the spent regenerant during the first 50 BVs also suggests probable simultaneous re-sorption of $Ag(Tu)_2^+$ on the resin [47 – 49]. And, since it is more favorable energetically for $Ag(Tu)_2^+$ to complex on ion-exchanger surface than in solution [47], achieving regeneration after 50 BVs was evidently difficult (only 20% regeneration was accomplished in the next 160 BVs (Refer to Appendix C, Figure C.2)).

210 BVs for regeneration was considered too high for the process to be termed efficient. Therefore, another fully loaded fixed-bed column was regenerated (96.2%) using 0.5 M thiourea and 0.1 M HNO_3 solution as regenerant in 90 BVs (Figure 2). The rationale of increasing thiourea concentration was derived from the speciation analysis (Appendix B) of the spent

420 regenerant at different thiourea concentration and total silver concentration. It was observed that
 421 re-adsorption of $\text{Ag}(\text{Tu})_2^+$ and precipitation of $\text{Ag}(\text{Tu})_3^+$ were co-related to their respective %
 422 fractions in the effluent regenerant and total silver concentration. With 0.1 M thiourea as
 423 regenerant, speciation analysis showed that $\text{Ag}(\text{Tu})_2^+$ reached a fraction as high as 90%. The
 424 calculation also revealed that at 0.1M thiourea concentration, $\text{Ag}(\text{Tu})_3^+$ dominated at higher total
 425 silver concentration (500-2000 mg/L) ranging from 35-40%. At 0.2 M thiourea, $\text{Ag}(\text{Tu})_3^+$
 426 consistently remained in the fraction of 40% for the typical range of effluent total silver
 427 concentration. Due to lack of literature on the solubility product of $\text{Ag}_2(\text{Tu})_6\text{SO}_4 \cdot 4\text{H}_2\text{O}$, exact
 428 concentration of $\text{Ag}(\text{Tu})_3^+$ necessary for precipitation could not be determined but a strong co-
 429 relation was observed between precipitation of $\text{Ag}_2(\text{Tu})_6\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and % fraction of the
 430 species, $\text{Ag}(\text{Tu})_3^+$, resulting in precipitation for fraction >35% and total silver concentration >
 431 ~1000 mg/L. This also explains precipitation of $\text{Ag}(\text{Tu})_3^+$ observed in figure C.1 (Refer to
 432 Appendix C), as $\text{Ag}(\text{Tu})_3^+$ remained around 35-40% at higher concentration (500-2000 mg/L). In
 433 order to address the possible precipitation and re-adsorption, the % fractions of $\text{Ag}(\text{Tu})_2^+$ and
 434 $\text{Ag}(\text{Tu})_3^+$ were suppressed by increasing the thiourea concentration, as it encourages formation
 435 of the most stable $\text{Ag}(\text{Tu})_4^+$ species. At 0.5 M thiourea concentration $\text{Ag}(\text{Tu})_4^+$ % fraction ranged
 436 from 60-70%, $\text{Ag}(\text{Tu})_2^+$ 3-7% and $\text{Ag}(\text{Tu})_3^+$ 24-30% (Refer to Appendix B). However, at BV#8,
 437 9 and 10 for regeneration with 0.5M thiourea, a precipitate was noticed in the test tubes collected
 438 from the auto-sampler. Addition of 6 ml (equal to 1 BV) of 0.7M thiourea solution to each bed
 439 volume containing precipitate dissolved all the precipitate confirming the hypothesis that
 440 precipitation was caused by the dominance of $\text{Ag}(\text{Tu})_3^+$ species at high silver concentration and
 441 lower thiourea concentrations (0.1M and 0.2 M); and increasing of thiourea concentration (0.5M)
 442 shifted the equilibrium to the right leading to the dominance of most stable $\text{Ag}(\text{Tu})_4^+$ species

according to the equilibrium relations (Refer to Appendix B). Therefore, in order to prevent in-line precipitation of $\text{Ag}_2(\text{Tu})_6\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and re-adsorption of $\text{Ag}(\text{Tu})_2^+$ species on the resin, 0.5 M thiourea concentration was considered optimum for the regeneration as it led to an efficient regeneration (96.2%) in fewer number of bed volumes (90). 0.3 M & 0.4 M thiourea concentration was not chosen as speciation analysis showed that $\text{Ag}(\text{Tu})_3^+$ remained at fraction 30-40% for the typical concentration range of total silver observed in effluent regenerant bed volumes (Refer to Appendix B).

4.3 Silver recovery, reuse and recycling of the resin and the regenerant

The spent regenerant solution contains free thiourea, free silver ions, H^+ and $\text{Ag}(\text{Tu})_n^+$ complex (where $n = 1 - 4$) governed by equilibrium equations [42]. Addition of the spent NaOH wash solution to the spent regenerant hydrolyzed thiourea and released S^{2-} ions [53, 54] according to the following equation:

Since K_{sp} of Ag_2S is $\sim 10^{-51}$ and its solubility in aqueous medium is 10^{-15} g/L [40], even a fractional conversion in equation (5) precipitated Ag^+ as Ag_2S (as shown in equation 6), until all silver from the solution precipitated as Ag_2S . This was also confirmed by AAS analysis which detected no silver in the spent regenerant solution post precipitation. This showed ~99% silver recovery from the spent regenerant. The elemental constitution and characteristics elemental peaks (Table 2, Figure 3) matched closely with that of 99.5% pure assay of Ag_2S standard. This validated the identity and high purity of the silver-sulfide precipitate obtained in the study. Ag_2S obtained in the study can be used as an anti-microbial agent [55], in cancer treatment [56],

fabrication of electric bistable devices [57], in semi-conducting devices [58], photo-sensitizer in photography and as a lab reagent.

To align this process scheme with principles of sustainability, the resin and the spent regenerant were reused in multiple cycles. The resin showed no compromise in its uptake capacity (~ 300 mg Ag^+ / gm dry resin) over 4 cycles studied (Figure 5).

The regenerant after extraction of silver was reused for multiple cycles (Figure 6). The regenerant at the first reuse was as effective as its fresh counterpart. In the third and fourth use the regeneration efficiency reduced to $\sim 98\%$. This is due to the loss of thiourea from the regenerant due to Ag_2S precipitation and oxidation by air, as sulfur particles were seen in the regenerant (Refer to Appendix C, Figure C.3). The regenerant must be tightly sealed after each reuse, so as to minimize the thiourea loss to atmospheric oxidation. The reuse of thiourea was an intended goal of the study. Thiourea reuse makes the process sustainable and environmental friendly, as thiourea is toxic [59] and its disposal is a concern.

5. Conclusion

Selective recovery of trace silver from typical greywater against a high background concentration of other competing cations is challenging. However, potential cost benefits and environmental harm are too formidable to ignore the persistently rising silver use and its subsequent leaching in household wastewater. Ion exchange technology provides a promising approach as it utilizes the high affinity of atoms like sulfur for silver. More importantly, it can be reused multiple times without compromising its performance. The objective of this work was to demonstrate a closed-loop sustainable scheme to recover and recycle silver from synthetic greywater, with strong emphasis on reuse and recycle of the raw materials (the resin, the regenerant and NaOH wash solution) used, such that the scheme is implemented multiple times

at no additional cost, without compromising on performance and environmental safety.

Following conclusions can be made from the study:

1. Ambersep GT74, a thiol based resin showed high selectivity and high uptake capacity (300 mg of Ag^+ /g of resin) of silver while treating ~20,000 BVs of synthetic greywater containing trace silver (5 mg/L) against high background concentrations of other co-contaminants.
2. The ion-exchange is ternary with silver-sulfur complexation as the mechanism of uptake, however it has no implication on the fixed-bed column performance.
3. Non-linear Freundlich isotherm model describes the ion-exchange process more accurately than non-linear Langmuir isotherm model.
4. 0.5M thiourea at pH 1 is considered optimum regenerant specification for the fixed-bed regeneration achieving 96.2% regeneration in 90 BVs.
5. Re-sorption of silver-thiourea complex ($\text{Ag}(\text{Tu})_2^+$) is noted on the ion-exchanger during regeneration step. Precipitation of $\text{Ag}(\text{Tu})_3^+$ is noted at 0.1M and 0.2 M thiourea concentration and high silver concentration (500-2000 mg/L). The problems of re-adsorption and precipitation have been addressed by using 0.5M thiourea concentration in the regenerant solution.
6. More than 90% of silver was recovered as silver sulfide precipitate from the spent regenerant solution.
7. The resin showed no compromise in performance for upto 4 cycles of its use.
8. The regenerant remained as effective as fresh regenerant (~100% in batch mode) in its second reuse post-precipitation. However, its effectiveness dropped slightly in its 3rd and 4th reuse (~98%).

9. The work successfully demonstrated the recovery of silver as Ag₂S and reuse of the raw materials – resin, acidified thiourea, NaOH wash solution – in a close loop scheme, and ensured no toxics were disposed or released.

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Appendix A

The single crystal XRD study on the precipitate determined the crystal as $\text{Ag}_2(\text{Tu})_6\text{SO}_4 \cdot 4\text{H}_2\text{O}$. Figure 8 in the main text shows crystal's asymmetric unit. Figure A.1 shows the silver thiourea chain in the precipitate. Figure A.2 packing of the precipitate along the C face of the crystal. There is hydrogen bonding between the thiourea, water and sulfate ion. Figure A.3 shows the A face of the crystal. The complete modeling study can be made available on request in a separate crystallographic information file (.cif).

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705 Figure A.1: Silver thiourea chain observed in the precipitate.

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714 Figure A.2: Crystal lattice along the C-axis of the crystal.

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716 Figure A.3: The lattice propagation along the A-axis of the crystal.

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Appendix B

The species in the spent regenerant solution at equilibrium is represented by the following equations:

The solution contains free thiourea, free silver ions, H^+ and four silver-thiourea complexes governed by following equilibrium equations:

Applying Ag mass balance:

Applying thiourea mass balance:

Using $[\text{TU}]_{\text{total}}$ as 0.1M, 0.2M, 0.3M, 0.4M & 0.5M equations B.5 to B.11 were simultaneously solved for different $[\text{Ag}]_{\text{total}}$ concentrations of the effluent spent regenerant. The result of the

calculation (Figure B.1 to B. 5) shows silver-thiourea complex speciation of the effluent spent
regenerant solution.

Figure B.1: Equilibrium distribution of four silver-thiourea complexes in the spent regenerant
solution at 0.1M thiourea & different total silver concentrations

Figure B.2: Equilibrium distribution of four silver-thiourea complexes in the spent regenerant
solution at 0.2M thiourea & different total silver concentrations

Figure B.3: Equilibrium distribution of four silver-thiourea complexes in the spent regenerant solution at 0.3M thiourea & different total silver concentrations

Figure B.4: Equilibrium distribution of four silver-thiourea complexes in the spent regenerant solution at 0.4M thiourea & different total silver concentrations

Figure B.5: Equilibrium distribution of four silver-thiourea complexes in the spent regenerant solution at 0.5M thiourea & different total silver concentrations

Figure C.1: The column regeneration profile where silver-thiourea complex precipitate was seen for effluent Ag^+ concentrations $> 1000 \text{ mg/L}$ while storing under refrigerated condition; The mass balance could not be performed

Figure C.2: Fixed-bed column regeneration without in-line precipitation

Figure C.3: EDS analysis showing elemental peak and composition of the yellowish particles found in the regenerant solution