

Silver recovery from laundry washwater: role of detergent chemistry

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.1c01111](#). It contains details on detergent composition (Table S1), resin removal and recovery performance under warm and hot thermal conditions (Table S2). Additional information on Ag⁺ speciation study (Figure S1 – S5); notes on Ag⁰ precipitation in presence of perborate/TAED (Figure S4); Ag₂S precipitate analysis (Figure S6), and reusability results & discussion of the resin and regenerant (Section S7).

Number of pages: 17

Number of tables: 2

Number of figures: 22

Table S1: Detergent components and their respective concentrations used in the study

Si. No.	Detergent components	Role in laundry	Concentration (g/l)
(1.)	Sodium Dodecylbenzene Sulfonate (SDBS)	Surfactant	0.6
(2.)	Sodium Dodecyl Sulfate(SDS)	Surfactant	0.2
(3.)	Berol 266	Surfactant	0.2
(4.)	Diethylenetriamine Pentaacetate (DTPA)	Builder	0.267
(5.)	Zeolite	Builder	0.267
(6.)	Sodium Metasilicate Pentahydrate	Builder	0.267
(7.)	Sodium Carbonate	Builder	0.1
(8.)	Sodium Carboxymethyl Cellulose (CMC)	Soil Anti-redeposition Agent	0.04
(9.)	Ethanol	Formulation Aid	0.24
(10.)	4,4' – diamino – 2,2' – stilbenedisulfonic acid	Optical Brightener	0.0023
(11.)	Sodium Perborate	Bleach	0.14; 0.52
(12.)	Tetraacetyleneethylenediamine (TAED)	Bleach Activator	0.021; 0.078

The concentration of detergent in laundry wash solutions is typically 1 g/l¹. In the present work, the detergent formulation we have used is ~2 g/l concentration. This is done to test the recovery scheme under conditions harsher than what is typically found in household laundry systems. The relative concentration and composition of each component is taken from^{2,3}.

Table S2: Ag-removal & recovery performance of the resin in presence of individual detergent components under warm (35°C) and hot (55°C) wash thermal conditions (Initial [Ag⁺]: 5 mg/l; resin mass: 0.05 g; solution volume: 0.5 l)

Si. No.	Detergent Component	Warm Wash		Hot Wash	
		% Removal	% Recovery	% Removal	% Recovery
(1.)	SDBS	95	84	96	92
(2.)	SDS	91	89	96	88
(3.)	Berol	94	94	99	92
(4.)	DTPA	92	89	98	96
(5.)	Carbonate	98	90	95	91
(6.)	CMC	97	86	98	83
(7.)	Metasilicate	94	91	98	97
(8.)	Ethanol	91	91	93	87
(9.)	Stilbene	99	87	98	93
(10.)	Perborate/TAED	-	68	-	57

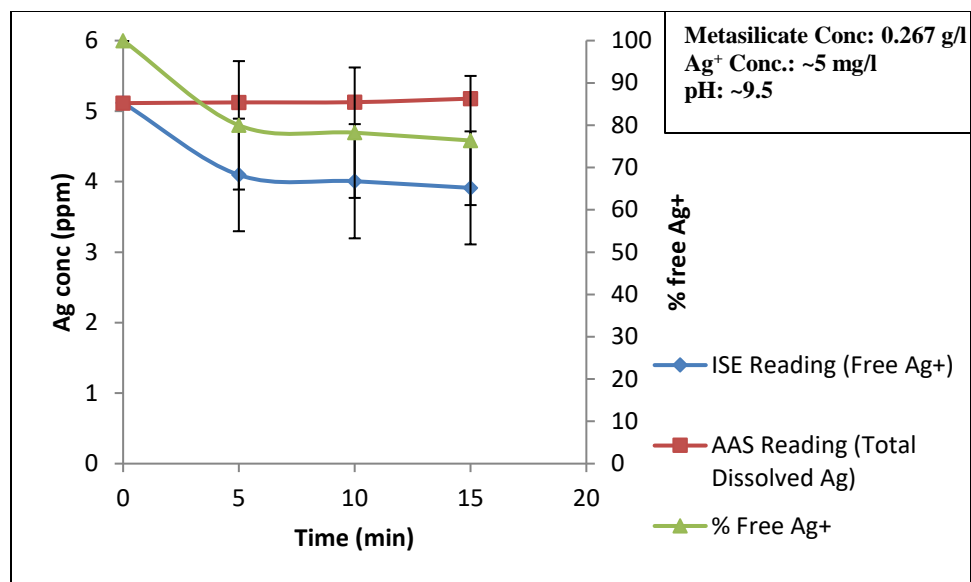


Figure S1(a.): Free Ag⁺ & total dissolved Ag concentration profile in presence of metasilicate at pH ~9.5

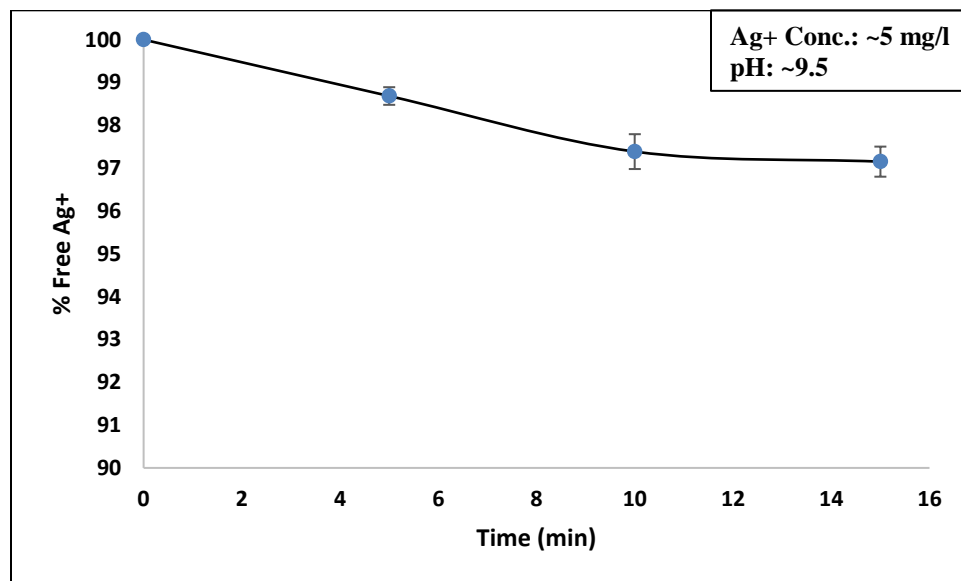


Figure S1 (b.): % Free Ag⁺ profile in the solution at pH ~9.5 (no metasilicate)

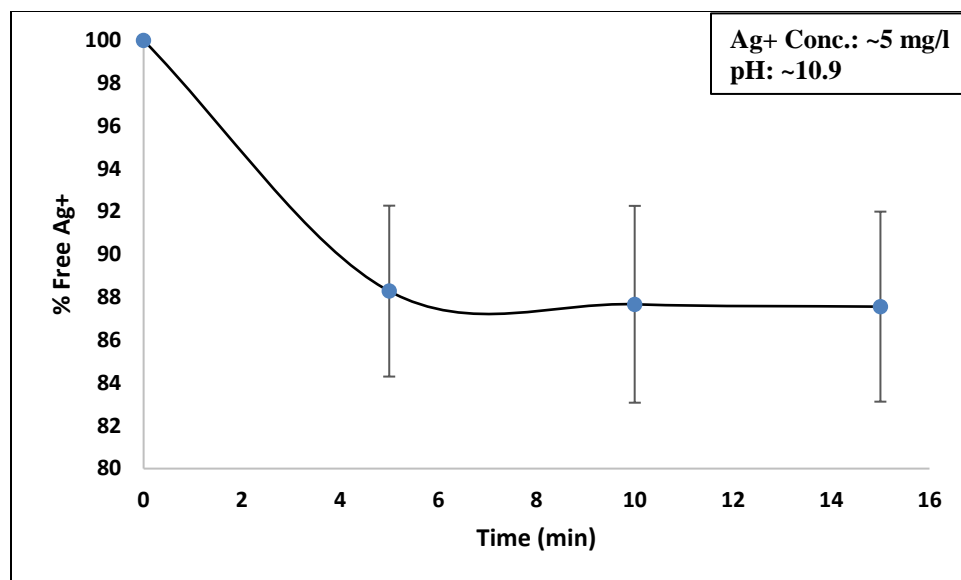


Figure S1 (c.): % Free Ag^+ profile in the solution at pH ~10.9 (no metasilicate)

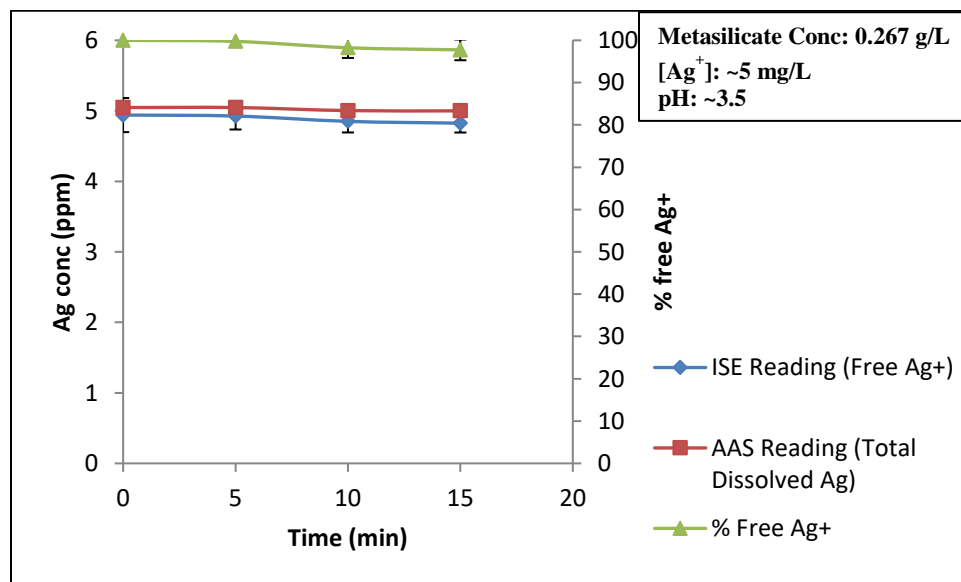


Figure S1 (d.): Free Ag^+ & total dissolved Ag concentration profile in presence of metasilicate at pH ~3.5

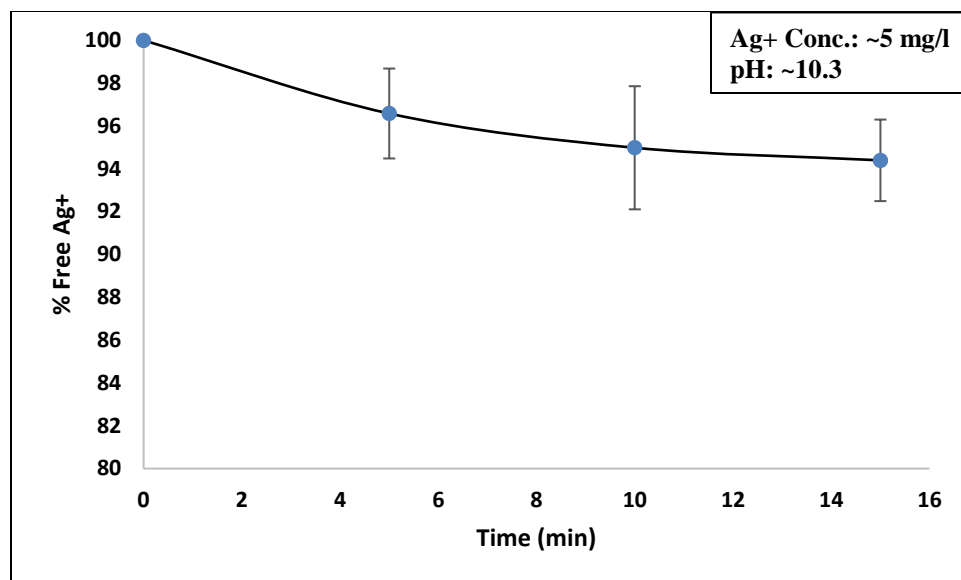


Figure S2: % Free Ag⁺ profile in the solution at pH ~10.3 (no detergent component present)

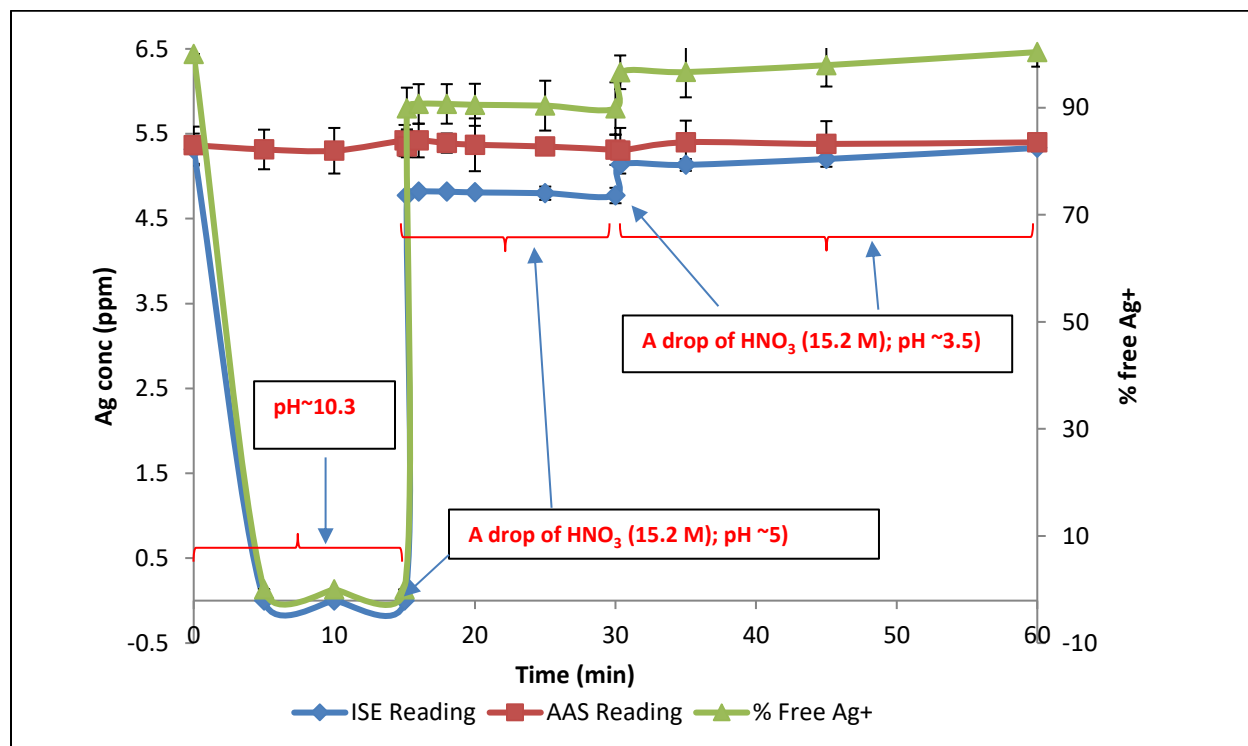


Figure S3(a): Free Ag⁺ concentration profile in the presence of DTPA under different pH values.

In alkaline pH ~10.3, free Ag⁺ signal is zero, at t=15 minutes, addition of a drop of 67-70% nitric acid reduces the pH to ~5, and free Ag⁺ signal rises instantaneously (~90% of its initial value),

indicating freeing up of Ag^+ from DTPA chelation, further addition of a drop the same acid, reduces the pH to ~ 3.5 , and free Ag^+ signal is fully restored, implying chelating groups in DTPA are protonated and not available to take up Ag^+ .

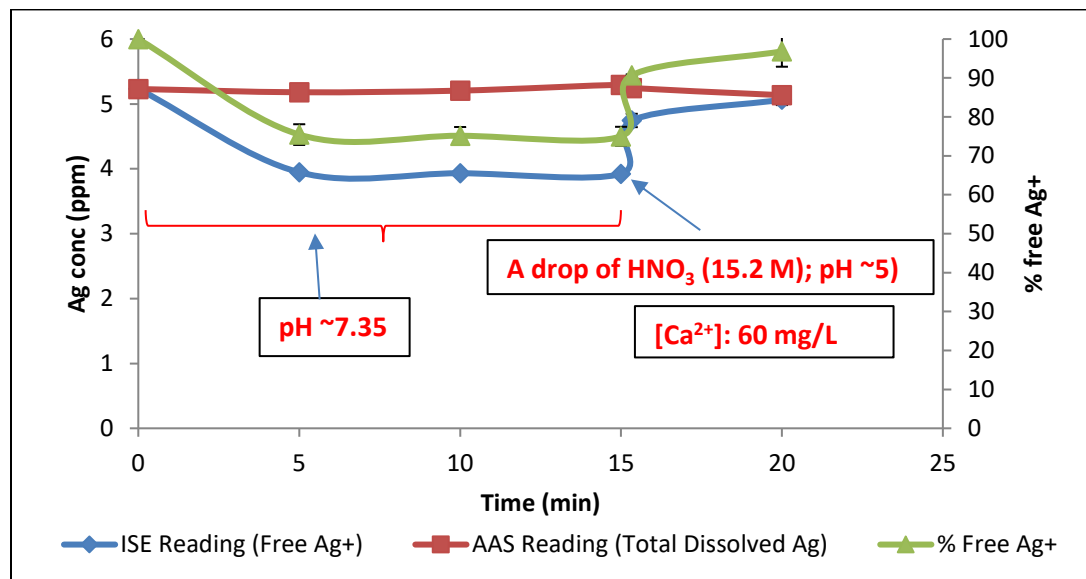


Figure S3(b.): Free Ag^+ concentration profile in the presence of DTPA, when 60 mg/l Ca^{2+} was present along with 5 mg/l Ag^+ from the beginning. The pH in this case rises to 7.35 from 5 on adding DTPA whereas in the previous case, when Ca^{2+} was not present, the pH rose to ~ 10.3 . Also free Ag^+ signal reduced only to $\sim 75\%$ of its initial value, unlike in the previous case where it completely vanished. This implies that DTPA is preferentially chelated with Ca^{2+} over Ag^+ ; however, it did take some Ag^+ (loss in signal) and H^+ (rise in pH). On adding a drop of 15.2M nitric acid, free Ag^+ signal was fully restored to its initial value.

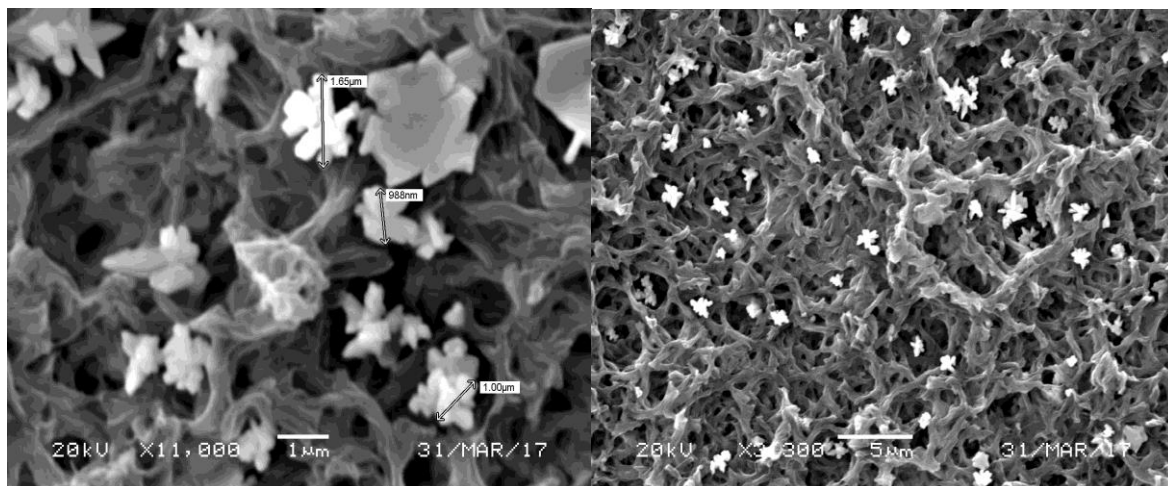


Figure S4(a): SEM image of the precipitate formed during Ag^+ speciation study with perborate/TAED at pH ~ 9.5 ; the background is of filter paper, and the flower like particles are Ag^0 . EDS spectra (Figure S4 (b.)) showed Ag, C & O peaks.

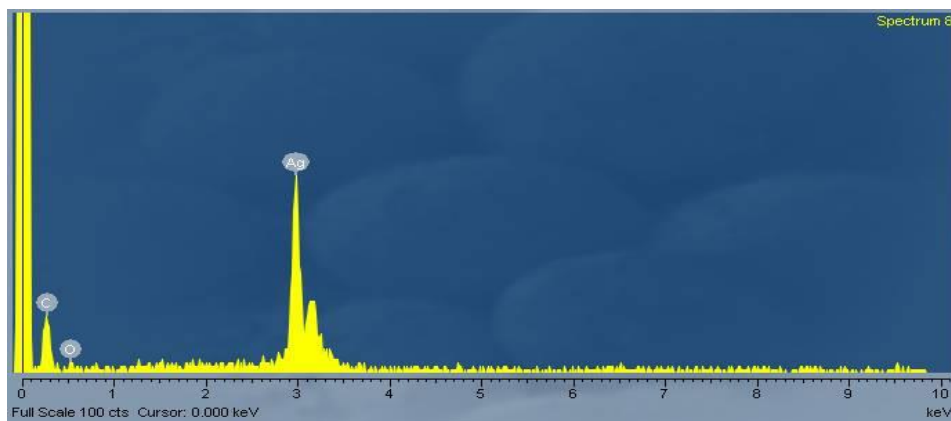


Figure S4(b): EDS spectra of the precipitate formed during Ag^+ speciation study with perborate/TAED at pH ~ 9.5 .

The spectra shows prominent Ag peak and small peaks of C & O due to the background filter paper. In order to eliminate the background signal, we conducted the experiment in a 5 liter solution. This produced 5 times more precipitate, which we collected and easily scraped as flakes from the filter paper, and put directly on the EDS stub, coating it completely. The EDS spectra

obtained thereby (Figure S4(c.)), revealed only Ag peaks, which indicated the precipitate to be pure Ag^0 .

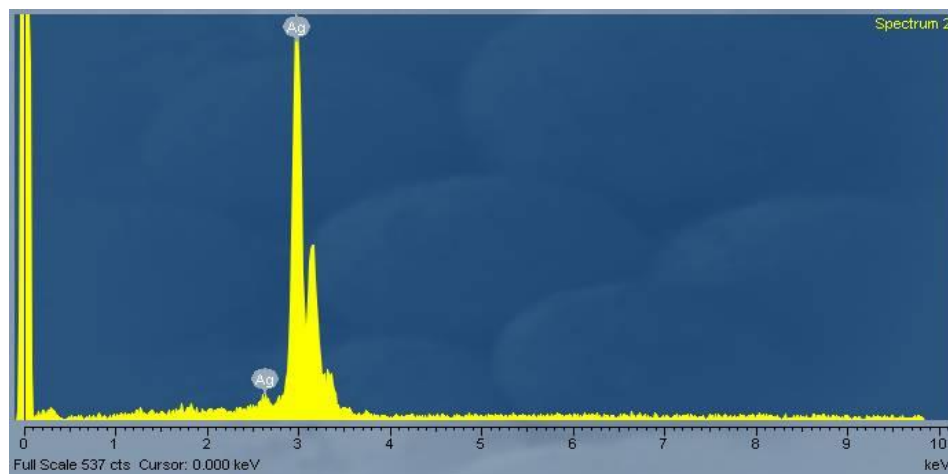


Figure S4(c.): EDS spectra of Ag^0 precipitate without filter paper background; this proves that precipitate formed during Ag^+ speciation study with perborate/TAED system is Ag^0 .

Elemental mapping done on the sample in EDS with filter background (Figure S4(d.) & (e.)) also conclusively proves that the precipitate was of pure Ag^0 .

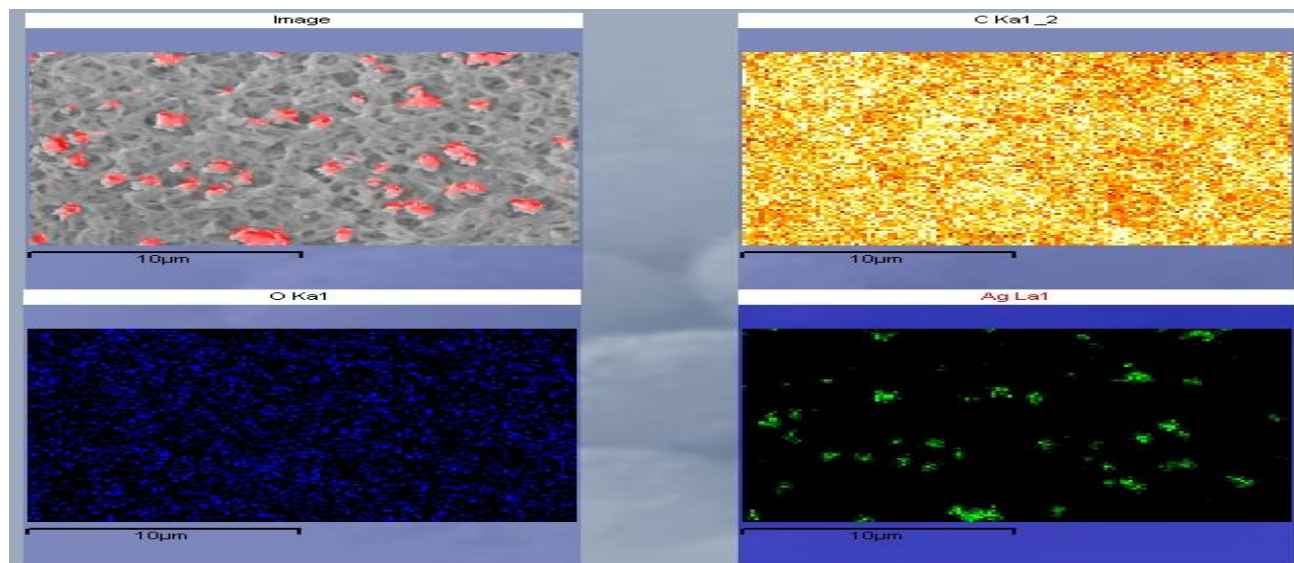


Figure S4(d.): Elemental mapping of the precipitate with filter paper background done on EDS.

In Figure S4(d.), it can be clearly seen that Ag signal exactly corresponds to the location of the particles in the sample, whereas C & O signals are everywhere, except at the particles' locations. This is indicative of the particle identity as Ag^0 . Figure S4(e.) also reveals similar elemental mapping results, where the particle location exactly corresponds to Ag signal; C & O signals due to the background are present throughout, but not at the particle location. Were the precipitate to be some salt of Ag, the elemental mapping would have shown the other elements' signals at the particles' location. In our case, we clearly see only Ag signals corresponding to the particles' locations.

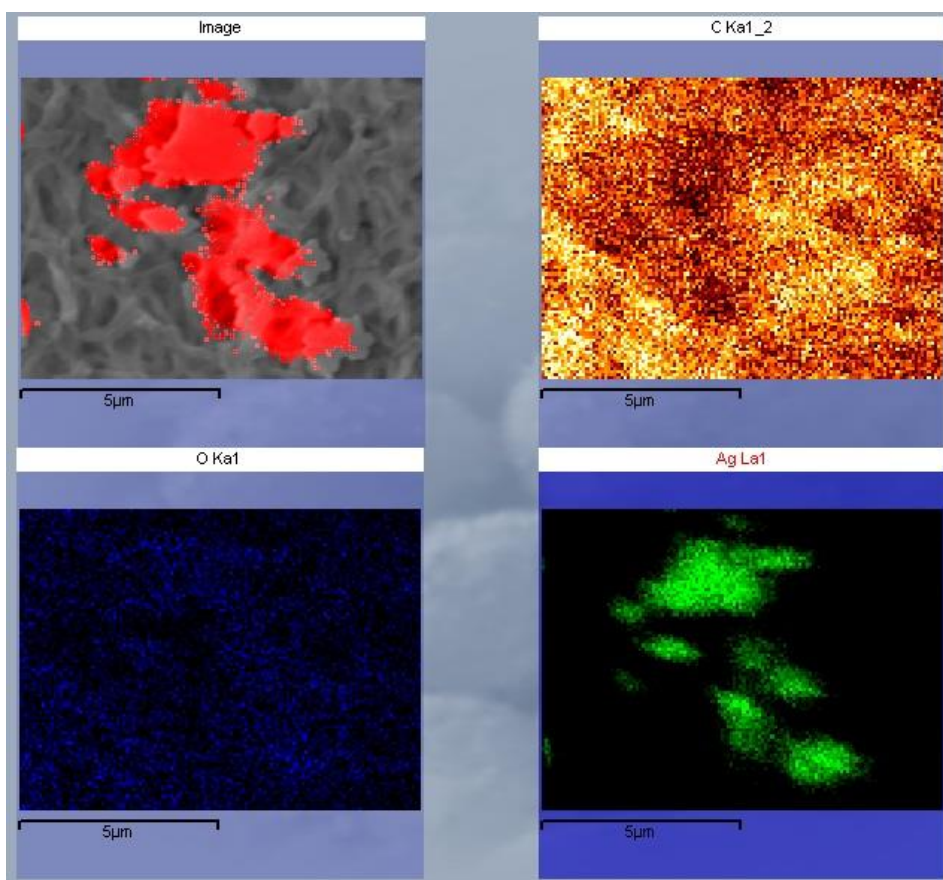


Figure S4(e.): Elemental mapping of the precipitate with filter paper background done on EDS.

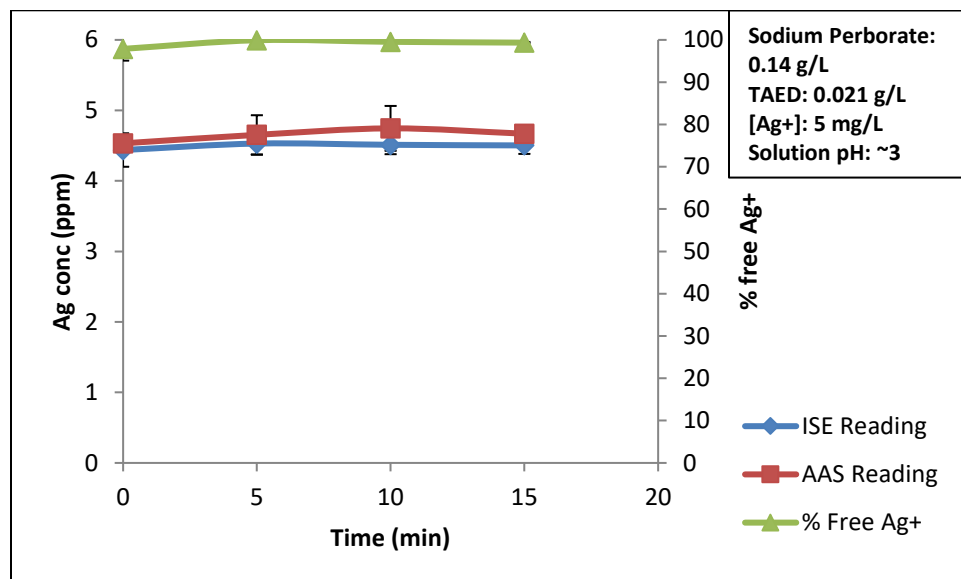


Figure S5(a.): Free Ag⁺ & total dissolved Ag concentration profile in presence of perborate/TAED at pH ~3

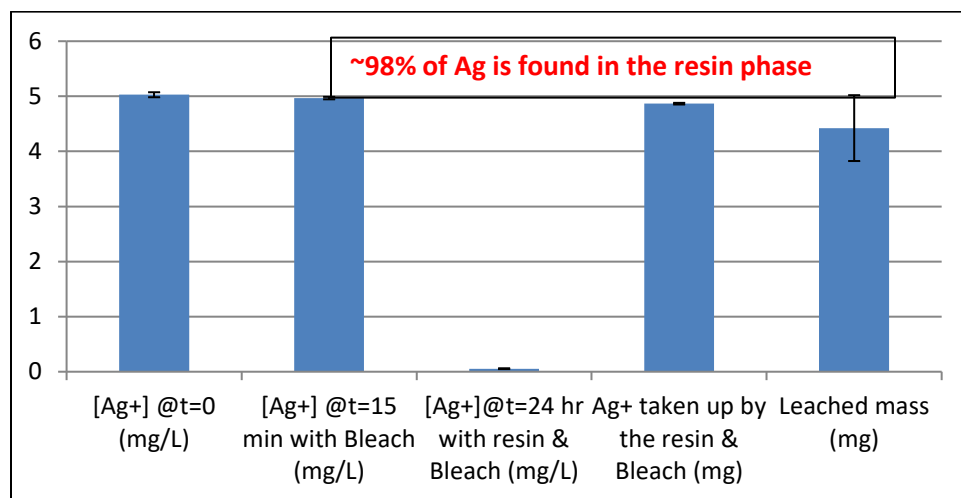


Figure S5(b.): Resin Ag-removal and recovery performance in presence of sodium perborate (0.14 g/l) and TAED (0.021 g/l) at pH ~3.

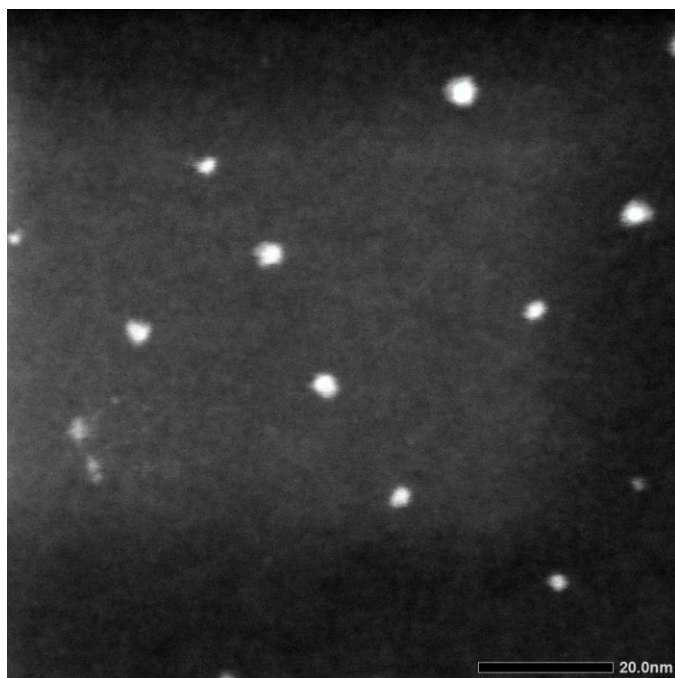
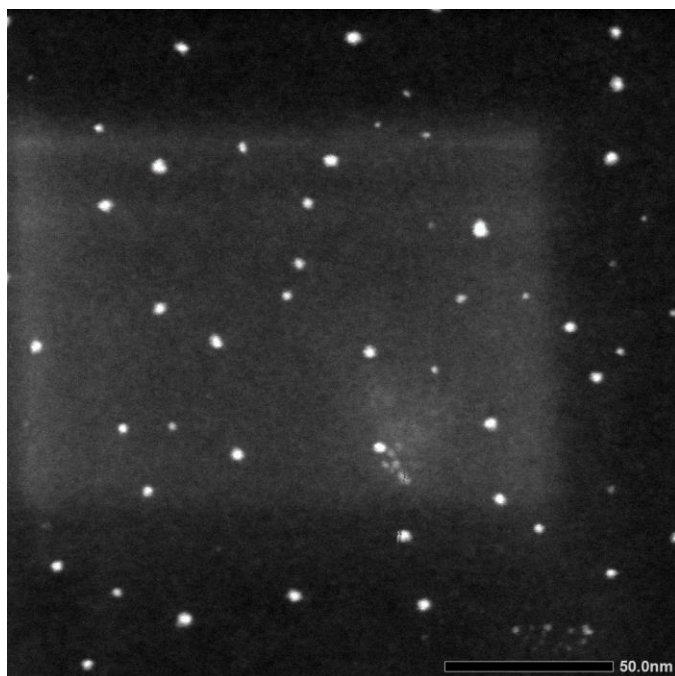


Figure S6 (a.): TEM images of the precipitate obtained during the onset of precipitation, when the solution turned light brown at a pH of ~ 7 -8; particles on size range ~ 3 -7 nm were prominently noticed

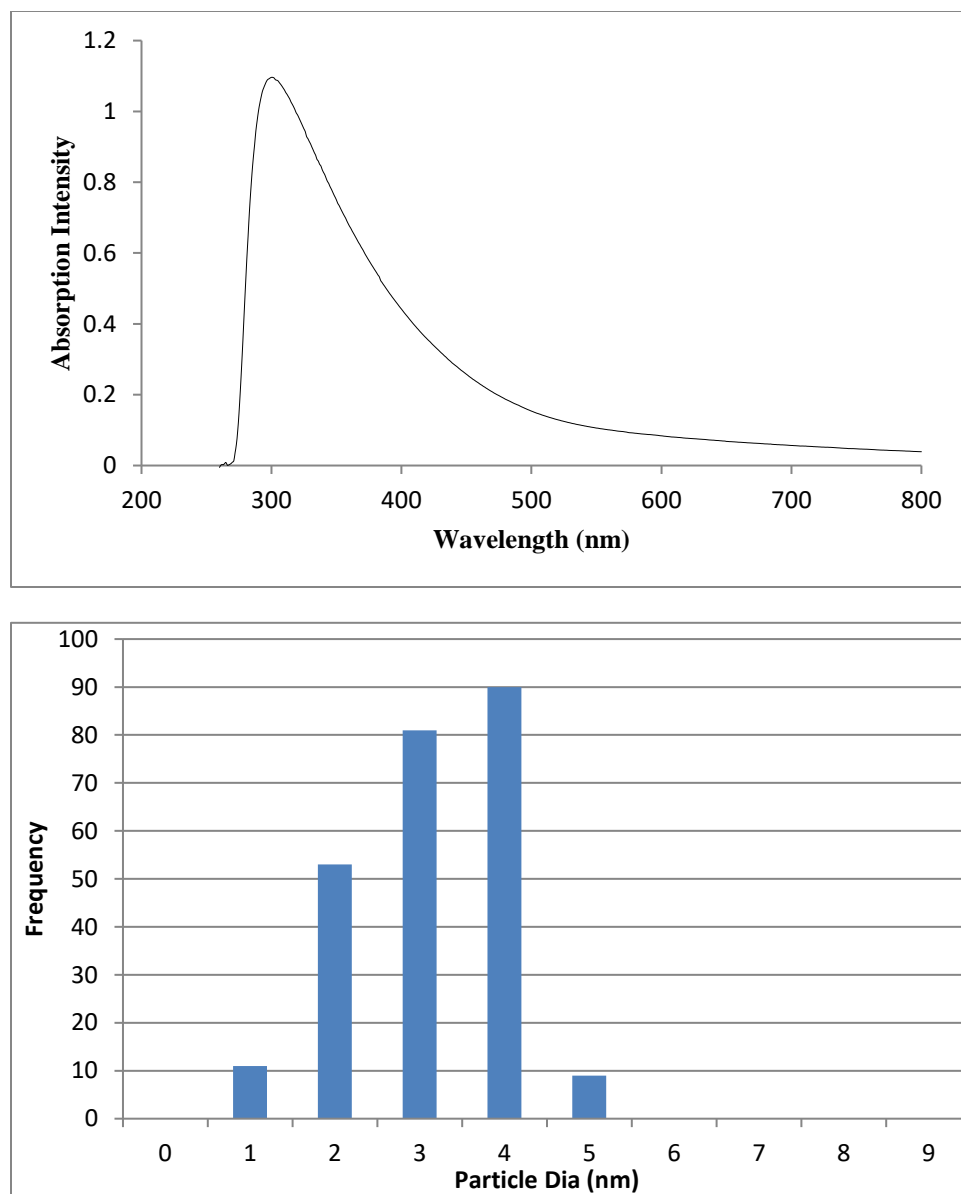


Figure S6 (b.): UV-Vis spectra of the solution during the onset of precipitation (pH ~7-8) and the particle size distribution analyzed Imagej (an image processing program developed at the National Institute of Health, USA). ~250 particles were analyzed from the TEM images; average particle size was calculated as ~3 nm.

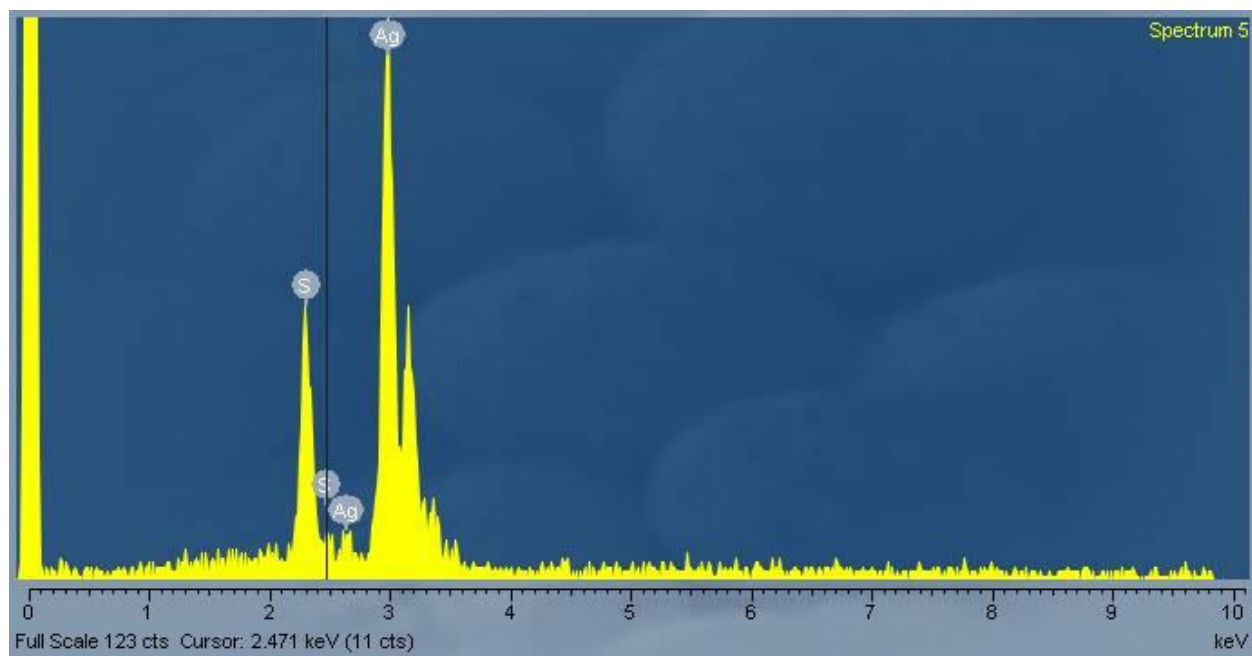


Figure S6 (c.): EDS spectra of black precipitate obtained by hydrolyzing the spent regenerant in 1N NaOH (elemental composition of the precipitate: Ag = 86.79%, S = 13.21%)

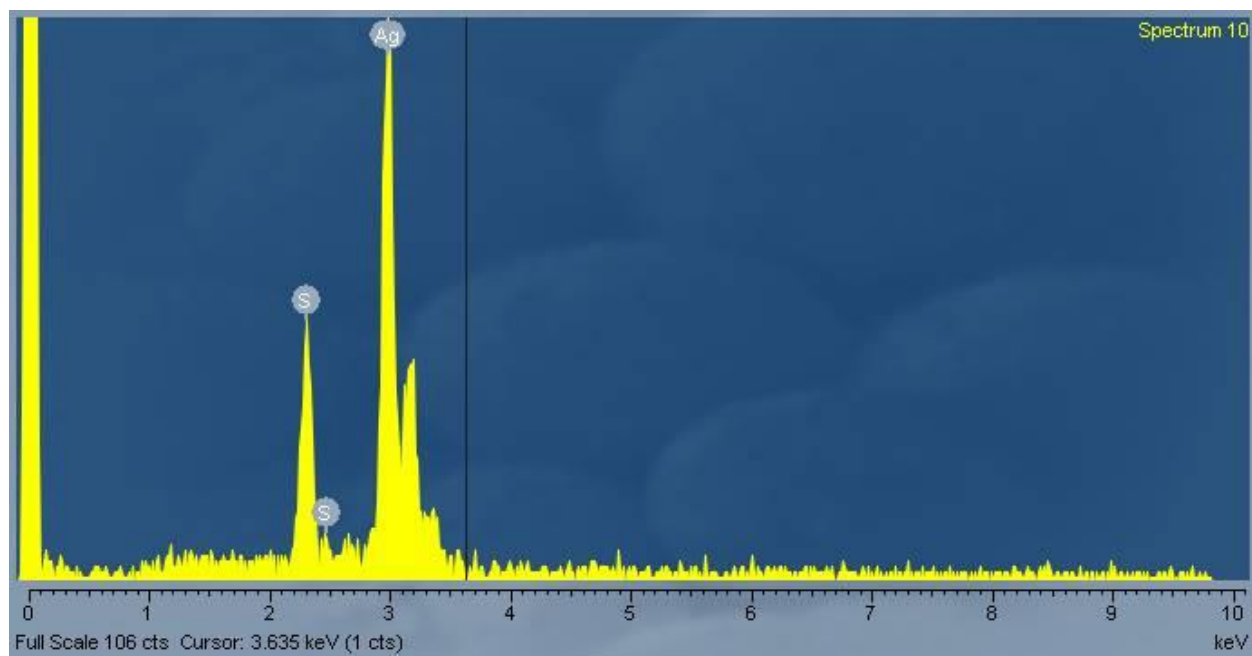


Figure S6 (d.): EDS spectra of 99.5% pure assay Ag_2S standard (Alfa Aesar) (elemental composition of the precipitate: Ag = 86.98%, S = 13.02%)

On comparing the spectra and elemental composition as shown by the EDS analysis of the precipitate and Ag_2S standard (Figure S6 (c.) & (d.)), it can be inferred that the precipitate obtained in the study is high purity (>99%) Ag_2S . The mechanism of the precipitation can be found in our previous work.

S7. Reuse & recycling of the resin & the regenerant.

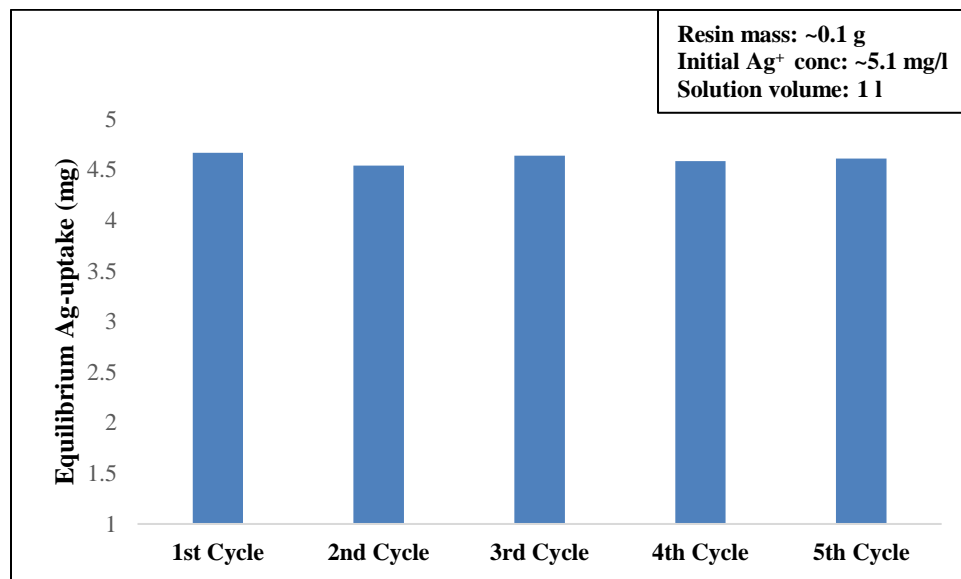


Figure S7 (a.): Reusability of the resin demonstrated over 5 cycles of Ag-uptake study in batch mode

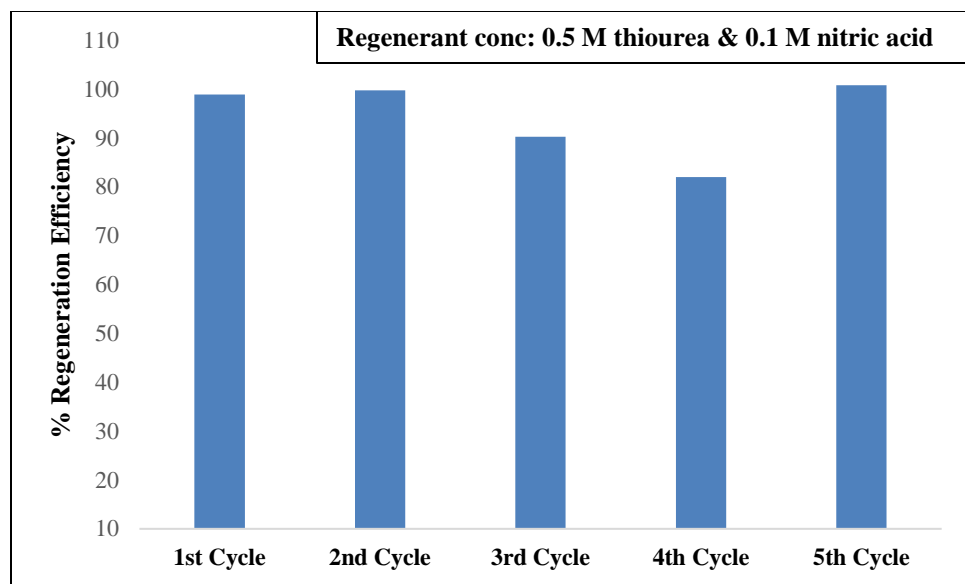


Figure S7 (b.): Reusability of the regenerant demonstrated over 5 cycles

To make the recovery scheme sustainable, the resin and the spent regenerant were reused over multiple cycles. The resin showed no compromise in its Ag-uptake capacity from the detergent solution (SI, Figure S7 (a)) over 5 cycles studied. The regenerant, after extraction of Ag, was reused for 5 cycles (SI, Figure S7 (b)). The regenerant in its first two cycles recovered ~100% of Ag in the resin phase. However, the regeneration efficiency declined in 3rd (~90%) and 4th (~82%) cycles. This is due to the loss of thiourea to Ag₂S precipitation after each reuse⁴. Also, during the pH adjustment (from ~11-12 to ~1-1.5) post-precipitation before each reuse, foul smell (most probably of H₂S gas) was noticed. This implied further loss of thiourea as H₂S. Additionally, volume loss was also observed at each successive stage, reducing to 86 ml (from 100 ml initially) at the end of 4th cycle. The volume loss was compensated by adding 14 ml of the fresh regenerant solution. This is reflected in the improvement in the regeneration efficiency (~100%) at the end of 5th cycle. The result provides a comparative idea about the performance of the resin and the spent regenerant over multiple cycles of reuse. It is concluded that the resin and the spent regenerant can be reused for at least 5 cycles without significant loss in their performance.

References:

- (1) Cameron, B. A. Family and Consumer Sciences. *Fam. and Consum. Sci. Res. Jour.* **2007**, 36(2), 151-162.
- (2) Sachdev, A.; et al. Heavy-duty liquid detergents. In *Liquid Detergents*; Lai, K.Y., Ed.; 2nd, ed.; Surfactant science series; V.129; CRC Press. **2006**
- (3) Smulders, E.; Von Rybinski, W.; Sung, E.; Rähse, W.; Steber, J.; Wiebel, F.; Nordskog, A. *Laundry detergents*. Wiley-VCH Verlag GmbH & Co. KGaA. **2007**
- (4) Nawaz, T.; Sengupta, S. Silver recovery from greywater: Role of competing cations and regeneration. *Sep. Pur. Technol.* **2017**, 176, 145-158.