



Chemical and economic optimization of the coagulation-flocculation process for silver removal and recovery from industrial wastewater



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ABSTRACT

Silver is a crucial element in several fields of industry. Its removal from aqueous waste streams before discharging is essential for environmental protection. Due to the environmental toxicity of Ag, stringent discharge limits are imposed by governments. Several removal techniques exist of which coagulation-flocculation is a favourable option for reasons of robustness and limited investment costs. The objective of the present work is to optimize the coagulation-flocculation process to remove silver from industrial wastewater by a profound screening and Central Composite Design. More specifically, this study focuses on maximizing the removal of silver on the one hand, and reducing the cost of operation on the other hand. Use of Poly Aluminium Chloride (PAC) coagulant in combination with a pH-correction and an anionic polyelectrolyte as flocculant led to decreasing the wastewater's Ag concentration from 2.50 mg L⁻¹ to a residual Ag concentration of 0.027 mg L⁻¹. Application of sodium poly-acrylated aluminium chloride (Magnasol 5155) as coagulant could even reduce the Ag concentration further to 0.004 mg L⁻¹. Both coagulants are able to achieve the stringent Ag discharge standard in Flanders, Belgium (0.08 mg L⁻¹), however the latter one corresponds to a higher price sensitivity, meaning that a larger removal of Ag was achieved against the same cost of chemicals used in the recovery process. Moreover, it facilitated the formation of a sludge that is 42.4 ± 3.4 m% rich in Ag, which is extremely beneficial when recovery of the precious metal is targeted.

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1. Introduction

1.1. Background

Silver (Ag) has many applications, both as precious metal and as a more common commodity. The high value of Ag, ca. 550 EUR kg⁻¹ for the raw material [1], is associated to investment goods, use in jewellery and – as from ancient times – in coins. Additionally, the single electron s-orbital occupancy of Ag's configuration, similar to Cu and Au, results in an exceptional good electrical conductivity of 6.30 × 10⁸ S m⁻¹ [2]. It is the indispensable element in traditional and X-ray photography. Its physicochemical properties make it furthermore remarkably interesting in the fields of catalysis [3] and nano-synthesis [4].

In the mirror industry, it is used to form the essential reflective back side layer. After polishing the glass surface with CeO₂ particles, spraying of SnCl₂ and PdCl₂ solutions facilitates the final reduction of AgNO₃ to metallic Ag. The majority of the dosed Ag is however discarded in the drained spray solution. As such, the mirror industry is responsible for around 1.2% of all Ag emissions in Flanders, Belgium [5].

On the one hand, Ag discharge puts an ecological pressure and is subjected to standards imposed by governments. The current discharge limit is set by the Flemish Government at 0.08 mg L⁻¹ in accordance with the Vlare II legislation [6]. Although exceptions for specific industrial sectors exist, there is a general tendency towards decreasing discharge limits for an increasing number of companies. This is especially the case for direct discharge to surface waters, which accounts for 42% of the total emitted Ag in Flanders (Belgium). Meanwhile, the majority of Ag (57%) is discharged to sewage systems and only 1% is treated on site in the first place [7]. High metal prices and depletion of high grade ores, on the other hand, drive innovations to recuperate Ag from wastewaters [8].

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1.2. Speciation of silver

The information of how Ag appears in wastewater promotes an efficient removal. In the water phase, Ag can principally occur in three species: silver nanoparticles Ag^0 , silver complexes and free Ag^+ -ions. These different species can be transformed into each other depending on the medium. Silver nanoparticles can release free Ag^+ -ions and subsequently react with either organic or inorganic ligands to form silver complexes. The stability is influenced by the silver concentration, type and concentration of ligands present and the pH of the solution [9]. Firstly, higher Ag concentrations ($>20 \text{ mg L}^{-1}$) favour cationic Ag^+ species, rather than Ag complexes, which are dominantly present below that Ag concentration [10]. This latter includes complexes of sulphide and chloride anions also prevalent in industrial wastewaters. Given the solubility product constants of $8 \times 10^{-51} \text{ mol}^2 \text{ L}^{-2}$ and $1.8 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$ for respectively Ag_2S and AgCl [11], the sulphide precipitate is thermodynamically favoured over chloride precipitates. The presence of free sulphide is however strongly influenced by the redox potential and pH of the solution. Chloride meanwhile, can form several complexes of formula $\text{AgCl}_n^{(n-1)-}$, with n varying between 0 and 4 [12]. It can be concluded that the speciation of Ag depends on many factors and the source of wastewater. A full characterisation of the Ag and matrix conditions is therefore indispensable for a successful removal strategy.

1.3. Removal and recovery approach

A handful techniques can be considered for Ag removal from wastewaters. In the mirror industry, the silver removal is currently conducted using different approaches, but none of them lead to optimal results [13]. The metal ion is often reduced by sodium borohydride [14] and precipitated by $\text{Ca}(\text{OH})_2$, NaOH or Na_2CO_3 . Specific to precious metals, electrolytic precipitation [15] or reduction [16] and ion-exchange are also applied [17].

The use of coagulation-flocculation for treatment of the Ag containing stream is the subject of optimisation in this research. This robust technique has a low investment cost and was previously proven to be effective for both silver [18,19] and other base metals [20]. The process first neutralises small particulates or colloids by addition of cationic species, such as Fe^{3+} or Al^{3+} . In the following step, colloids further aggregate to larger particles that settle under the influence of slow water agitation. This yields a metal rich sludge, which is further refined after drying. Achieving low remaining concentrations of Ag in the treated waste water thereby goes hand in hand with a larger immobilised Ag fraction.

To the current understanding, the coagulation-flocculation process was never optimized so far upstream. In literature, the removal of silver from artificially spiked water [19], effluent of waste water treatment plants (WWTPs) [18] and simulated WWTP [21] was described. In this work however, real wastewater collected at the production line is subject of the recovery process. This approach is economically beneficial for the company since it maximizes the silver recovery and more economical in lowering the discharged concentration.

2. Materials and methods

2.1. Industrial wastewater sampling and characterisation

A silver containing wastewater stream was sampled at the mirror producing site of Deknudt Mirrors (Deerlijk, Belgium). Right after plating of the glass surface with a AgNO_3 solution [22], 10 L was collected from the production line drain and stored at 4°C as soon as possible. The wastewater was characterised for pH

(Thermo Scientific Orion Star A211, Waltham, MA), electrical conductivity (EC), particle size (Malvern Mastersizer, Worcestershire, UK), TOC (Shimadzu, Kyoto, Japan) and anions by Ion Chromatography (Metrohm, Herisau, Switzerland). The metal content in the solutions was determined using atomic spectroscopy. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, Varian MPX, Palo-Alto, CA) was the primary choice, unless concentrations did not exceed the limit of detection. In that case, Inductively Coupled Plasma – Mass Spectrometry (ICP-MS, Elan DRCE, Perkin-Elmer SCIEX, Waltham, MA) was used as analytical technique. Prior to analysis, the solutions were digested using microwave-assisted digestion in open-vessels (Mars 5, CEM, Matthews, NY) after addition of 3 mL 65% HNO_3 (Chem-Lab, Zedelgem, Belgium) to 5 mL of sample. The soluble metal content was determined in the filtrate after $0.45 \mu\text{m}$ pore size filtration (Chromafil RC-45/25, Machery-Nagel, Düren, Germany) of the solutions, followed by digestion of the filtrate and analysis using the same procedure.

The determined parameters were used as input to model the chemical speciation of Ag in the wastewater at 25°C with Visual MINTEQ 3.0 [23]. The effect of pH was studied in the range between 0 and 14 with a 0.5-unit interval.

2.2. Setup of coagulation-flocculation experiment

The coagulation-flocculation jar experiments were carried out on the collected wastewater at room temperature in 500 mL beakers according [24]. Two common coagulants were added in separate experiments, namely poly aluminium chloride (PAC, Brenntag, Deerlijk, Belgium) and Magnasol 5155 (H&V Chemicals, Vilvoorde, Belgium), the latter being a mixture of PAC and sodium polyacrylate. After the addition of coagulant, diluted H_2SO_4 was used to correct the solution pH towards near neutral. H_2SO_4 was chosen instead of HCl since chloride interferes with the Ag speciation, by easily forming complexes with silver. The mixture was consequently stirred at 100 rpm during the first 2 min and 40 rpm during the subsequent 8 min. Then, four different flocculants, two anionic and two cationic polyelectrolytes, were tested separately. Respectively Praestol 2640 and 810 (Brenntag, Belgium) and Praestol 1502 and 1504H (Caldic, Belgium) were added prior to the additional stirring for 10 min. Lastly, the treated wastewater underwent sedimentation for 30 min. The performance of each coagulant and flocculant was evaluated by measuring the remaining Ag concentration in the supernatant. As such, the optimal coagulant dosage range, pH, flocculant choice and dosage could be derived and served as input for further optimisation of the Ag removal.

2.3. Chemical analysis

After sedimentation, 5 mL of the supernatant was taken and analysed for its remaining Ag concentration, along with the original solution for reference. The samples were digested according to the method described above. Ag was measured after digestion using ICP-OES or ICP-MS as previously described.

The sludge fraction was also retained as the residue of filtration over $0.45 \mu\text{m}$ pore size. The solid was dried for 48 h at 105°C . After cooling down, 0.5 g was weighted and digested in 7.5 mL HCl and 2.5 mL HNO_3 at 100°C for 2 h. The solution was diluted to 100 mL with demineralised water and analysed for its Ag concentration.

2.4. Modelling of the coagulation-flocculation process and optimisation

Considering independent performance of the coagulant and flocculant used, Praestol 2640 was selected as best product and used in the optimisation of both PAC and sodium-poly acrylated-

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