Removal of silver from aqueous solutions by complexation–ultrafiltration using anionic polyacrylamide

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ABSTRACT

Wastewaters containing silver ions are produced by several sources like metal finishing, electroplating, electronics, hazardous waste disposal sites, galvanic industries, etc. Complexation–ultrafiltration (CUF) is a developing hybrid process for the removal and recovery of heavy metals, even at trace level concentrations, which uses the selectivity of complexing agent and filtration ability of ultrafiltration (UF) membrane. In the present work, separation of silver ions from aqueous solutions by CUF using a novel complexation agent, namely anionic polyacrylamide (average molecular weight >50 kDa) and a polyethersulfone UF membrane (molecular weight cut-off: 10 kDa) was studied along with the effects of operating parameters on metal ions rejection including fouling behavior of the UF membrane used and decomplexation of silver ions for recovery. The UF experiments were performed on Perma®-pilot plant using synthetic aqueous solutions of metal salt at different applied pressures (4, 5, 6 atm), initial metal ions concentration in feed (5, 10, 15, 20, 50 ppm), feed pH (4, 5, 6, 7, 8, 9) and polymer-to-metal ions ratio (0.5, 1, 1.5) at a constant feed flow rate of 15 L/min. Maximum rejection, close to 100%, of silver ions has been obtained at optimum operating parameters. Kinetics of complexation reaction of metal ions with anionic polyacrylamide (aPAM) was studied in a separate experiment which suggested that about 24 min is required for silver ions to reach complexation equilibrium.

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1. Introduction

As the worldwide legislative trends are leading toward lowest discharge levels of naturally occurring metal ions in effluents, continuous increase of the world's need for most of the metals and also the decrease in grade of the available ores make it essential to find effective and efficient methods for processing wastewaters containing metal ions, even at very low concentrations. Conventional treatment processes like chemical precipitation, ion exchange, adsorption, coagulation and flocculation, electrodialysis, flotation and electrochemical removal have significant disadvantages like incomplete removal, high-energy requirements, and production of toxic sludge [1]. Recently, membrane separation processes, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been increasingly used for metal removal from effluents. The main problem with membrane processes in the treatment of effluents containing metals is ionic size of dissolved metallic salts. RO and NF methods are capable of separating the metal ions but have high operating cost; hence to have more selective process with high permeate fluxes, low energy costs and high rejection the complexation–ultrafiltration (CUF) can be practiced for the removal of metal ions from wastewaters [2,3]. CUF process uses the selectivity of a complexation agent (a water soluble macromolecular polymer) along with filtration ability of UF membrane to retain metal–polymer complexes of macromolecular size greater than its molecular weight cut-off (MWCO). Though CUF process has not been adopted on industrial scale but it has been reported as a useful method for the treatment of wastewaters, ground waters, seawaters for trace metal removal and recovery [3–9].

Wastewaters containing silver ions are produced by several sources like metal finishing, electroplating, electronics, hazardous waste disposal sites and galvanic industries, etc. Silver is a naturally occurring transition metal and also a noble metal. It is known to be discharged to the environment from its industrial applications, especially in its ionic form (Ag^+), which is detrimental to aquatic and terrestrial organisms and also is known to convert into the more innocuous forms as it reacts rapidly with natural chemical ligands in sewer systems, sewage treatment and the environment [10].

Metal rejection depends on complexation of metal ions by polymer and the complexation depends on some parameters like applied pressure (P), initial metal ion concentration in feed solution (C_o), pH of feed and polymer-to-metal (P/M) ratio. Some authors

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Nomenclature

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pH	H$^+$ ions concentration in solution
P/M	polymer-to-metal ion ratio (w/w basis)
C_o	Initial metal ion concentration in feed solution, ppm
P	applied pressure across the membrane, atm
L	constant feed flow rate, L/min
R_o	observed rejection of solute, %
J_v	permeate volume flux, L/m^2 h
C_p	metal ion concentration in permeate, ppm
M	metal ion concentration, ppm
t	time, min
k	rate constants
C_x	concentration of complexation agent, ppm
a, b	reaction orders
k'	observed rate constant
k_1	pseudo first-order rate constant
$[M]_0$	initial metal ion concentration in feed, ppm
$[M]_t$	metal ion concentration at any time t, ppm
R_2	correlation coefficient
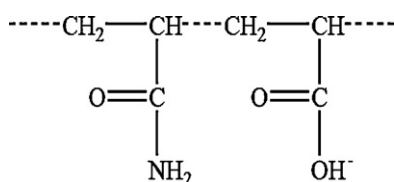
Fig. 1. Molecular structure of anionic polyacrylamide (aPAM).

have studied the separation of silver ions from aqueous solutions using complexation–ultrafiltration [9,11,12].

The main objective of present work is to study the suitability of a novel complexation agent, anionic polyacrylamide (aPAM), for silver ions removal and to study the effects of operating parameters such as applied pressure, initial metal ions concentration in feed, pH of feed and polymer-to-metal ions ratio on metal ions rejection using CUF process on pilot scale. The aPAM is widely used as a flocculation agent in wastewater treatment, soil stabilization, oil recovery, metal processing, metal recovery, nano particles preparation and construction, etc. The aPAM offers no systemic toxicity to aquatic organisms and also has no potential for bioaccumulation. The sensitivity of polyacrylamide to ultraviolet light is well known and leads to degradation of the polymer chain due to photolysis. Molecular structure of aPAM is given in Fig. 1 and some of its characteristics are listed in Table 1 [3,13–15].

2. Experimental

2.1. Chemicals and materials

Commercially available anionic polyacrylamide with an average molecular weight >50 kDa and silver nitrate (AgNO$_3$) of reagent grade were used to prepare the macro-molecular metal complexes. A commercial thin film flat sheet polyethersulfone membrane (Perma-PES-10) from M/S. Permionics, Vadodara, India, was used,

Table 1
Specifications of anionic polyacrylamide (aPAM).

Material	Average molecular weight (kDa)	Charge density	
		(mol%)	(meq/g)
aPAM	>50	30.0	4.0

Table 2
Specifications of membrane.

Membrane type	Molecular weight cut-off (kDa)	Surface area, m^2	Nature
Polyethersulfone	10	0.0164	Hydrophilic

which is an asymmetric membrane. It is a modified hydrophilic membrane and carries negative charge which helps in reducing gel layer formation due to polymer. The specifications of ultrafiltration membrane are given in Table 2. Perma-PES-10 membrane is capable of withstanding pH in the range of 2 to 10, pressure up to 10 atm and temperatures up to 50 °C. The pH of the feed was adjusted using required amount of 0.1 M NaOH and 0.1 M HNO$_3$ solutions. The deionized water from Millipore-Q apparatus was used throughout the experimental runs.

2.2. Experimental setup and procedure

The Perma-PES-10 membrane was employed in a Perma®-pilot scale membrane system supplied by Permionics, Vadodara, India. The system consists of a rectangular flat membrane housing cell and a 40 L feed tank. The pilot scale experimental setup is shown in Fig. 2. The membrane housing cell is made of stainless steel with two halves fastened together with high tensile bolts. The top half of cell contained the flow distribution chamber and the bottom half is used as the membrane support system. A perforated 1 mm thick stainless steel plate is laid over with a stainless steel gauge of 300 mesh size, which is topped by the actual membrane with its active layer exposed to the high pressure fluid. The upper half of the test cell contains a groove for the arrangement of HDPR 'O' ring to avoid leakage at high pressures. The 1 mm thin channel passage in the membrane test cell and the high cross-flow feed rates used in the experiments will enable the system in controlling gel polarization.

Prior to the experiments the membrane was compacted at 8 atm pressure for 2 h using distilled water to avoid any intermittent compaction of membrane during the experiment. A 40 L synthetic aqueous solution of AgNO$_3$ of desired concentration as a precursor to metal ions was fed to the feed tank after thorough cleaning of pilot plant using distilled water. Prior to the ultrafiltration experiments, the required amount of metal salts and aPAM were dissolved separately in water and then metal ion solution was mixed with aPAM solution to make total 40 L feed solution. Feed solution containing metal ions and complexation agent was allowed to stand for 30 min with continuous mixing to reach the complexation equilibrium for each run. The pH of the mixture was adjusted as per requirement during the mixing period. The experiments were performed using synthetic aqueous solution of metal salt at a constant feed flow rate (L) of 15 L/min (LPM) to minimize the gel polarization by varying the operating parameters as applied pressure (3, 4 and 5 atm), initial metal ions concentration (5, 10, 15, 20 and 50 ppm), pH (4, 5, 6, 7, 8 and 9), polymer-to-metal ion ratio on w/w basis (0.5, 1.0 and 1.5). Samples of permeate and retentate were collected at a given time interval, to measure the observed solute rejection (R_o) and permeate volume flux (J_v). Both the streams of permeate and retentate were recycled to the feed tank except for the samples drawn for analysis purpose.

An experiment to study the kinetics of complexation reaction between silver ions and complexation agent (aPAM) was performed separately. Feed tank was fed with 40 L of feed solutions containing silver ions (C_o = 5, 10 and 15 ppm) and ultrafiltered continuously for 30 min to saturate the membrane with metal ions at P = 5 atm, pH 7 and L = 15 LPM. When the setup is in operation the complexation agent (aPAM) is introduced while maintaining P/M = 50 and continuous mixing. The permeate and retentate samples were collected at