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Size separation of silver nanoparticles by dead-end ultrafiltration: Description of fouling mechanism by pore blocking model

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ABSTRACT

The aim of this study was to evaluate the application of dead-end ultrafiltration for the preparation of silver nanoparticles (AgNPs) with narrow size polydispersity. Aspects as the reaction yield, purification, size-based fractionation, and fouling mechanisms were analyzed. AgNPs were synthesized by chemical reduction, and diafiltration experiments were performed by the washing method. Our results suggest that the cut-off size of the membrane can be used as a primary criterion to define the particle size in the permeate, and eliminate Ag^+ from a colloidal dispersion of AgNPs by removing NPs with a size less than the exclusion limit of the membrane. In addition, it was evidenced that ultrafiltration is not an effective method for elimination of AgNPs from aqueous effluents or for exact determination of reaction yield. In the prediction of J_0, the lowest error was obtained for the cake formation (7.6% and $J_0 = 1.36 \times 10^{-2}$ m/s) followed by internal and intermediate pore blocking models with 32.5 ($J_0 = 9.91 \times 10^{-3}$ m/s) and 29.1% ($J_0 = 1.04 \times 10^{-2}$ m/s), respectively. Cake formation was identified to be the main fouling mechanism associated with the filtration of the AgNP colloidal dispersion.

1. Introduction

Silver nanoparticles (AgNPs) have received much attention due to their diverse properties and varied applications [1–5]. However, it has been demonstrated that the spectral, thermal, antimicrobial, and electrical properties of AgNPs are strongly dependent on their size, shape, interparticle spacing and chemical environment [6–10]. Recently, it was established that the shape of AgNPs plays an essential role in determining important properties of nanoparticles (NPs) and colloidal systems that they are part of [10–12]. Currently, many synthesis methods for AgNPs have been reported, including thermal decomposition in organic solvents, electrochemical methods, reversed micelle processes, ultrasonic and microwave irradiation, photoreduction, and chemical reduction synthesis (CRS) [13–17]. Compared to other methods, CRS is simple, relatively easy, not time consuming and can easily be scaled up. However, a wide size distribution is obtained with this synthesis route because the nucleation kinetic is very sensitive to many experimental parameters, such as temperature and time of heating, stirring rate, concentration of reagents, adding rate of reducing agent, purity of reagents, ionic strength, and nature of dispersant [13,18–23].

For colloidal particles, on the micrometer scale, narrow size distributions can be easily achieved by post-synthesis techniques. For AgNPs, due to their nanometer scale, separation methods have been limited to low-volume and time-intensive techniques (i.e., cloud-point extraction, field-flow fractionation, fractional crystallization, chromatographic methods, gel electrophoresis, and filtration-based methods) [24–26]. These exhibit some advantages, e.g., low cost, easy handling, and applicability to a wide range of sizes; however, some methods require ideal conditions to carry out a good separation of NPs, including different pH, ionic strength or time consuming [25]. In this context, ultrafiltration appears to be a simple method without adding other separating agents and, in addition, membrane properties can be controlled in order to improve the separation features [25].

Accordingly, a membrane-based filtration process could provide a solution for the size and shape heterogeneity problem in the CRS of AgNPs. However, studies focused on the separation of NPs via diafiltration techniques have been limited to cross-flow ultrafiltration without considering the effect of the membrane features, system functionality (i.e., permeability changes, fouling or chemical stability) or nature of the NPs [24–26].

The aim of this study was to analyze the application of dead-end UF to obtain AgNPs with a narrow size polydispersity by the washing method. Therefore, purification, size-based fractionation, and membrane fouling were investigated.

1.1. Dead-end ultrafiltration

Operation of ultrafiltration membrane can be performed in two different modes: dead-end flow and cross-flow. The dead-end ultrafiltration mode consists only of a feed and a permeate flow.

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On the other hand, in the cross-flow ultrafiltration there is an additional flow associated with the concentrate [27]. For cross-flow and dead-end mode, fouling represents a real limitation. Indeed, this phenomenon, attributed as much to adsorption as to gel formation or particle deposition, leads to an unavoidable rise in production costs by increasing both the energy consumption (to maintain a constant flux) and the cleaning frequencies (back-washes or chemical cleaning) [27,28].

1.2. Washing method

Washing method (or dilution method) is a diafiltration method based in the dilution at constant volume of a dissolved sample; in this method, species with size lower than the pore diameter of the membrane are continuously eliminated as a result of continuous addition of solvent [28,29]. A retention profile can be obtained by quantifying the concentration in permeate as a function of the time, permeate volume or filtration factor; this profile describes the changes that occur throughout the experiment associated with the retention [29]. A schematic illustration is shown in Fig. 1.

1.3. Fouling mechanism by pore blocking

Depending on the pore blocking mechanism, the permeate flow decline can be described by

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV_p}\right)^n \tag{1}$$

where t and V_p are the filtration time and permeate volume, respectively, and k and n are two experimental parameters where n is a dimensionless number that is related to the fouling mechanism [30–32]. Commonly, four pore blocking mechanisms are considered:

Complete pore blocking ($n=2$):

$$J_{n=2} = J_0(k_b A_m)/t \tag{2}$$

where A_m is the membrane area, k_b is a phenomenological coefficient "fouling constant by complete pore blocking", $J_{n=2}$ is the flux and J_0 is the initial flux (or flux reference).

Internal pore blocking ($n=1.5$):

$$J_{n=1.5} = \frac{4J_0}{[2+k_s(A_m J_0)^{1/2}t]^2} \tag{3}$$

where k_s is a phenomenological coefficient "fouling constant by internal pore blocking" and $J_{n=1.5}$ is the flux.

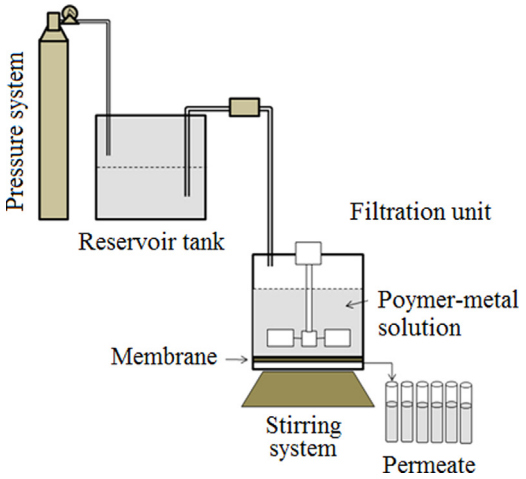

Fig. 1. Ultrafiltration system operated by dead-end ultrafiltration.

Intermediate pore blocking ($n=1$):

$$J_{n=1} = \frac{J_0}{1+k_i(A_m J_0)t} \tag{4}$$

where k_i is a phenomenological coefficient "fouling constant by intermediate pore blocking" and $J_{n=1}$ is the flux.

Cake formation ($n=0$):

$$J_{n=0} = \frac{J_0}{[1+2k_c(A_m J_0)^2 t]^{1/2}} \tag{5}$$

where k_c is a phenomenological coefficient "fouling constant by cake filtration" and $J_{n=0}$ is the flux.

2. Materials and methods

2.1. Reagent and filtration equipment

AgNPs were prepared from silver nitrate ($AgNO_3$, Aldrich). Sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$, 99%, Aldrich) was used as reducing and stabilizing agent (Turkevich's method) [33,34]. Regenerated cellulose membranes were used in all of the cases (Amicon Bioseparations-Millipore Co., cut-off sizes of 1, 5, 10, 50, and 100 kDa). The filtration experiments were performed using a stirred-cell filtration unit (Millipore 8050 model) with four main components including a pressure system (N_2 in our case), magnetic stirrer, reservoir, and membrane unit [35] (see Fig. 1).

2.2. Synthesis of colloidal AgNPs

AgNPs were prepared by refluxing 100 mL of 1.04 mmol/L $AgNO_3$ solution. Heating was performed in a batch of ethylene glycol previously heated to 94 °C. When the $AgNO_3$ solution reached the boiling temperature, 2.0 mL of a 1.0% w/v sodium citrate solution was added dropwise. This procedure was performed at 20 s intervals using a 100 μL micropipette. The heating was performed for 45 min [36,37]. The synthesis of the AgNPs was verified by transmission electronic microscopy (TEM, microscope JEM 1200 EXII). The size distribution and shape of AgNPs were determined by image analysis using a Digital Micrograph (TM) 3.7.0 for GMS 1.2 (Gatan Inc.). FT-IR spectra of the AgNPs were obtained using an OMNIC 5.2a (Nicolet Instrument Corp.).

2.3. Diafiltration experiments

2.3.1. Reaction yield (E_r)

10 mL fractions of the colloidal dispersion were ultrafiltered using ultrafiltration membranes (1 kDa). The experiments were performed in triplicate, with varying volume, an applied pressure of 300 kPa and a stirring rate of 400 rpm. The total silver concentration in the permeate was quantified by atomic absorption spectroscopy (AAS, Unicam Solaar M5). With this procedure, E_f can be defined with respect to the NP size (i.e., fraction of Ag^+ that is converted to Ag^0 with a size larger than the cut-off of the membrane). Therefore, E_f can be determined by the following equation:

$$E_r = R_m = 1 - \frac{C_p}{C_{in}} \tag{6}$$

where R_m is the retention coefficient, C_p is the total concentration of Ag in the permeate and C_{in} is the total concentration of Ag placed in the cell.

In addition, E_r was also determined by the quantification of residual Ag^+ using a silver ion-selective electrode. In this case, 0.2 mL of a $NaNO_3$ solution (5.0 mol/L) was added to 10.0 mL of the AgNP dispersion. The electric potential of the sample was correlated with