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Nanofiltration ability to remove copper oxide and silver nanoparticles: The role of surface charge and size

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Abstract

This work pretends to study the performance of nanofiltration (NF) membranes in the removal of copper oxide and silver nanoparticles (NPs) and evaluate the role of surface charge and size of the NPs on this performance. Results demonstrate that positive charged CuO NPs are adsorbed onto negatively charged NF membrane, whereas for the negatively charged Ag NPs the adsorption on the membrane surface is much lower. For CuO NPs, NF270 is very efficient and the main mechanism of removal seems to be adsorption. For Ag NPs, removals are low due to the hydrodynamic diameter of the NPs at this pH compared to the membrane cut-off (~170 Da).

INTRODUCTION

Engineered nanoparticles (NPs) are synthesized to achieve unique physicochemical properties, such as size, composition, structure and surface area [1, 2]. Due to these properties, NPs are used in numerous industrial and commercial applications (e.g. electronics, ceramics, polymers, medicine, and cosmetics) and although nanomaterials have been used in materials research for at least two decades, the production of NPs has increased in recent years [2]. The high demand for, and use of, such materials has led to their release into the environment, which increase the exposure of humans and other organisms to NPs [2, 3], and adverse effects due to its toxicity[1]. Since NPs will, eventually, be deposited in aquatic environment, effective solutions must be found in order to remove NPs from water. According to Leppard *et al*. [4], conventional water and wastewater treatment plants have not sufficient capacity to cope with this problem. Therefore, it is necessary to ensure their removal in water treatment plants by innovative and effective treatments. In recent years, nanofiltration (NF) has become an attractive alternative technology to conventional water treatment due to the capacity to remove inorganic and organic compounds with low molecular weight cut-offs and low operating pressures [5]. Since separation process in nanofiltration primarily occurs due to steric hindrance and membrane solute interactions [6], this work pretends to study the performance of NF membranes in the removal of copper oxide and silver NP and evaluate the role of surface charge and size of the NP on this performance.

METHODS

Laboratory NF experiments were performed in a bench-scale plate and frame unit, using four NF270 hydrophilic membranes (0.0720 m^2, kindly supplied by DOW, Filmtec). The membrane pure water permeability varied between 95.7 and 102.8 kg/(h.m^2.bar) at 21ºC, and the membrane molecular weight cut-off was approximately 170 Da. The isoelectric point of NF270 membrane is at pH 3.5 [7] and at pH 7 the membrane is negatively charged with a zeta potential about -21.6 mV (KCl solution of 30 μS/cm) [8]. Experiments were performed at a constant pressure and temperature of 10 bar and 21ºC, respectively, for seven hours in recirculation mode.

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Commercial available copper oxide (CuO) and silver (Ag) nanopowder (Sigma-Aldrich) were used in this study. Two different NPs solutions were prepared, one with CuO NP and other with Ag, by dispersing 100 mg/L of nanopowder in deionized water and then sonicated for 15 minutes. At the beginning of the experiments the solutions were given time to equilibrate, after which a flux measurement and samples from both the feed and permeate were taken. Permeate flux was continuously measured during the experiments and samples from both the feed and permeate were taken periodically, and conductivity, pH, turbidity and UV adsorption at 400 nm for CuO and 208 nm for Ag were measured. UV adsorption was used as an indirect determination of NPs removal. Hydrodynamic diameter and zeta potential of the nanoparticles were determined by dynamic light scattering and electrophoretic scattering, respectively.

RESULTS AND DISCUSSION

Table 1 presents the superficial charge (zeta potential) and hydrodynamic diameter of the CuO and Ag NPs in deionized water at pH 6.2 and 5.4, respectively. At these pH values, CuO NPs are positively charged and Ag NPs are negatively charged, both highly charged and stable. Under these conditions, aggregation is avoided due to the high repulsion forces, so small aggregates are formed. The isoelectric point, where particles have little or no charge, is at pH~10 for CuO NPs (unpublished data yet) and pH~1.5 for Ag NPs [9]. At this pH, repulsive forces are weakened so aggregation is higher than at other pH values.

Table 1. Zeta potential and hydrodynamic diameter of CuO and Ag NPs, at pH 6.2 and 5.4, respectively.

	Zeta Potential (mV)	Hydrodynamic Diameter (nm)
CuO NPs	29.0	276.2
Ag NPs	-32.9	178.8

Figure 1 shows the flux decline monitored by the ratio of flux at specific time (*J*) to initial flux (J_0), over the test period (7h). Results show a slightly decrease in flux, higher for CuO than for Ag. These results are related with the greatest adsorption of CuO NPs to NF270 membranes comparatively to Ag NPs. The adsorption of CuO and Ag NPs to membrane is visible in Figure 2. In this figure, UV absorbance of CuO NPs in feed dramatically decreases over operation time and after 4 h of operation the feed practically has not CuO NPs. This indicates that NPs are adsorbed onto NF membrane, since they disappear from the feed and did not appear in the permeate (permeate remains with very low quantities of CuO NPs). For Ag NPs (Figure 3) this tendency was not observed and UV absorbance did not vary significantly in the feed water. Therefore, results demonstrate that positive charged CuO NPs are adsorbed onto negatively charged NF membrane, whereas for the negatively charged Ag NPs the adsorption on the membrane surface is much lower. For CuO NPs, NF270 is very efficient and the main mechanism of removal seems to be adsorption. For Ag NPs, removals are low due to the hydrodynamic diameter of the NPs at this pH compared to the membrane cut-off (~170 Da).

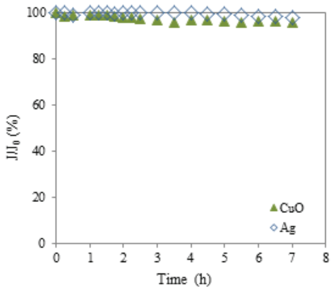

Figure 1. Relative flux with experimental time.

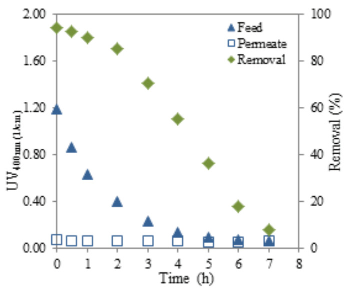

Figure 2. UV absorbance and removal for CuO with experimental time.

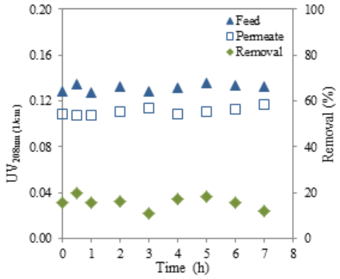

Figure 3. UV absorbance and removal for Ag with experimental time.

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