



Halide removal from waters by silver nanoparticles and hydrogen peroxide



A.M.S. Polo^a, J.J. Lopez-Peñalver^a, J. Rivera-Utrilla^a, U. Von Gunten^{b,c}, M. Sánchez-Polo^{a,c,*}

^a Department of Inorganic Chemistry, Faculty of Science, University of Granada, Campus Fuentenueva s/n, ES18071 Granada, Spain

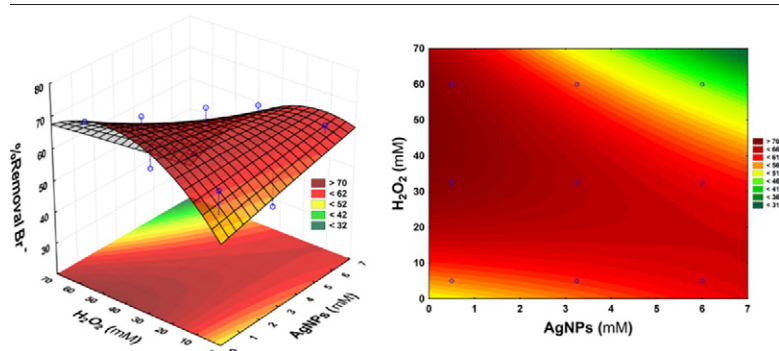
^b Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland

^c EPFL, École Polytechnique Fédérale de Lausanne, Route Cantonale, 1015 Lausanne, Switzerland

HIGHLIGHTS

- AgNP/H₂O₂ system is effective to remove bromide and chloride from waters.
- The formation of OH•, O₂•⁻ radicals was detected during the oxidation of Ag(0) into Ag(I).
- The presence of NaCl and tannic acid during AgBr precipitation slightly reduced the efficacy of bromide.
- The optimal H₂O₂ and AgNP concentrations depend on the halide considered.
- The reaction mechanism by which the AgNPs act on halide ion removal from waters was determined.

GRAPHICAL ABSTRACT



Effect of operational parameters (H₂O₂ and Ag-nanoparticles dose) on bromide removal by Ag-nanoparticles/H₂O₂ process. [Br⁻]₀ = 50.0 mM; [AgNPs]₀ = 0.5–6.0 mM; [H₂O₂]₀ = 5.0–60.0 mM.

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ABSTRACT

The objective of this study was to remove halides from waters by silver nanoparticles (AgNPs) and hydrogen peroxide (H₂O₂). The experimental parameters were optimized and the mechanism involved was also determined. The AgNP/H₂O₂ process proved efficacious for bromide and chloride removal from water through the selective precipitation of AgCl and AgBr on the AgNP surface. The optimal AgNP and H₂O₂ concentrations to be added to the solution were determined for the halide concentrations under study. The removal of Cl⁻ and Br⁻ anions was more effective at basic pH, reaching values of up to 100% for both ions. The formation of OH•, O₂•⁻ radicals was detected during the oxidation of Ag(0) into Ag(I), determining the reaction mechanism as a function of solution pH. Moreover, the results obtained show that: i) the efficacy of the oxidation of Ag(0) into Ag(I) is higher at pH 11, ii) AgNPs can be generated by the O₂•⁻ radical formation, and iii) the presence of NaCl and dissolved organic matter (tannic acid [TAN]) on the solution matrix reduces the efficacy of bromide removal from the medium due to: i) precipitation of AgCl on the AgNP surface, and ii) the radical scavenger capacity of TAN. AgNPs exhausted can be regenerated by using UV or solar light, and toxicity test results show that AgNPs inhibit luminescence of *Vibrio fischeri* bacteria.

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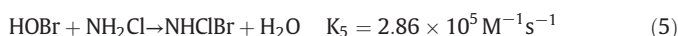
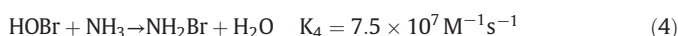
* Corresponding author at: Department of Inorganic Chemistry, Faculty of Science, University of Granada, Campus Fuentenueva s/n, ES18071 Granada, Spain.
E-mail address: mansach@ugr.es (M. Sánchez-Polo).

1. Introduction

The disinfection of drinking waters has been one of the major advances achieved over the past century, allowing the reduction and/or elimination of numerous diseases transmitted by bacteria, viruses, and parasites, including gastroenteritis, typhoid fever, and typhus, among many others (Bitton, 2014; Szabo and Minamyer, 2014; Arnold and Colford, 2007; Payment et al., 1997). The removal of pathogenic agents requires the use of disinfectants (Bitton, 2014), mainly free chloride, chlorine dioxide, chloramine, or ozone. However, the utilization of these chemicals can react with natural organic matter dissolved gives rise to the formation of disinfection by-products (DBPs) (Richardson et al., 2000) with potentially genotoxic and carcinogenic effects (Richardson et al., 2007; Glaze et al., 1993; Villanueva et al., 2014). In an *in vivo* study, 20 DBPs were found to exert carcinogenic effects while an *in vitro* study found that most of a further 100 DBPs tested were positive for genotoxicity and mutagenicity (Richardson et al., 2007).

The first investigations into DBPs formation were conducted in the 1970s, when Rook established a relationship among chlorination, natural organic matter (NOM), and trihalomethane (THM) formation (Rook, 1974). Since then, >600 DBPs have been identified (Bond et al., 2014; Richardson, 2012). They are formed by the reaction of chemical oxidants with the organic and inorganic compounds present in natural waters. NOM, and in particular humic compounds, are the most abundant group of organic compounds that react with disinfectants and give rise to DBPs. DBP formation depends on: the nature and concentration of the ions Br^- , I^- and Cl^- , the organic matter present in natural waters (Kim and Yu, 2005), the pH of the water, the type of disinfectant, and the contact time (Sadiq and Rodriguez, 2004; Li et al., 2014; Rocco et al., 2014; Xiangru et al., 2000). Therefore, in natural waters where it has been detected the presence of bromides ([65 mg/L]) and/or iodides ([50 $\mu\text{g/L}$]), after the disinfection process has been measured bromine-derived and/or iodine-derived organic compounds (Br-DBP and/or I-DBP). Bromide is naturally present in waters intended for consumption. Bromide concentrations range of 0.024–1.2 mg/L has been reported in the USA (Richardson et al., 2008), in the range of 0.139–4.13 mg/L in Australian surface waters (Magazinovic et al., 2004), and in the range of 0.9–1.2 mg/L in Spanish surface waters (Valero and Arbós, 2010; Garcia-Villanova et al., 2010). In all of these studies, the highest values were detected in coastal supplies, attributable to seawater intrusions (Kampioti and Stephanou, 2002). The presence of bromides in water modifies the type and distribution of the THMs and haloacetic acids (HAAs) formed, because the bromine derivatives are generated (Cowman and Singer, 1995; Hua et al., 2006). Bromide is rapidly oxidized during chlorination, forming hypobromous acid (HOBr)

(Reaction (1)) (Heeb et al., 2014), the predominant species at neutral pH (Reaction (2)), which reacts with the NOM to form the corresponding Br-DBPs (Reaction (3)). HOBr can also react with the ammonia and chloramines present in water to form NH_2Br , NHClBr , and NH_2Br (Reactions (4)–(6)), which in turn would react with NOM and generate the respective Br-DBPs (Sharma et al., 2014).



Toxicity studies have shown that DBPs are genotoxic, mutagenic and carcinogenic. The toxicity of DBPs increases in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ because of their increased genotoxicity and cytotoxicity compared to their chlorinated analogues (Richardson et al., 2007; Richardson et al., 2008; Jeong et al., 2012; Zong et al., 2013). Maximum reference levels have therefore been established for the sum of four THMs; chloroform (CHCl_3), bromoform (CHBr_3), bromodichloromethane (CHBrCl_2), and dibromochloromethane (CHBr_2Cl). This “total THMs” value was established at 100 $\mu\text{g/L}$ by the European Union (E. Communities, 1998).

The development of new procedures to reduce the exposure of populations to DBPs is therefore of prime importance. The present study describes the utilization of silver nanoparticles (AgNPs) to remove bromide and chloride from drinking waters before their disinfection, thereby reducing the generation of Cl-DBPs and Br-DBPs. The objectives of the study were i) to remove halides (chloride and bromide) from waters using AgNPs and hydrogen peroxide (H_2O_2) as oxidant agent; ii) to optimize the experimental conditions, and to determine the mechanism underlying selective chemical precipitation of the halides. The regeneration of AgNPs and its toxicity will be also evaluated.

2. Materials and methods

2.1. Materials and reagents

All chemicals used (sodium chloride, potassium bromide, sodium nitrite, H_2O_2 , para-chlorobenzoic acid (PCBA), 3-(*N*-Morpholino)propanesulfonic acid (MOPS), *tert*-butanol, thiourea, formic acid,

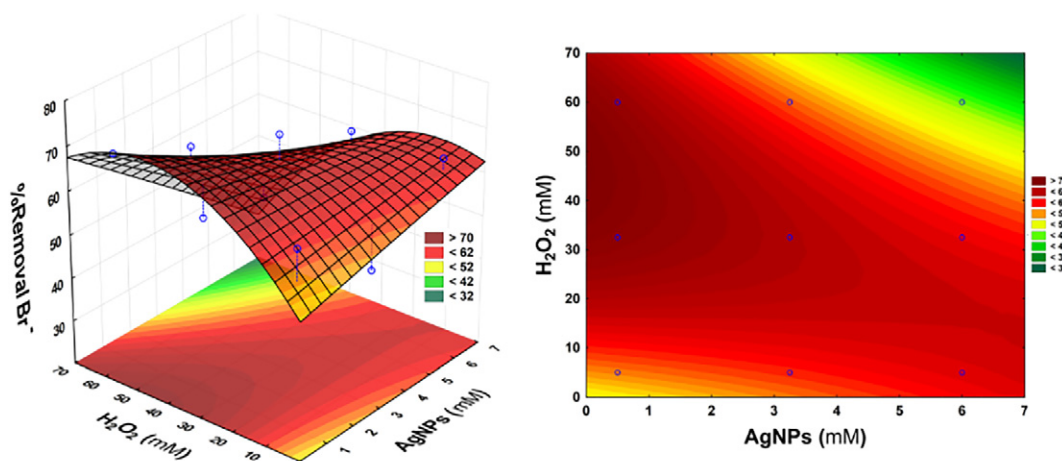


Fig. 1. Response surface obtained by CCD. $[\text{Br}^-]_0 = 50.0 \text{ mM}$; $[\text{AgNPs}]_0 = 0.5\text{--}6.0 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 5.0\text{--}60.0 \text{ mM}$.

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