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Chick-Watson kinetics of virus inactivation with granular activated carbon modified with silver nanoparticles and/or copper oxide

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ABSTRACT

This study aimed at analyzing the effect of silver nanoparticles (NP-Ag), copper oxide (NP-CuO) and silver and copper oxide (NP-Ag-CuO) concentrations, when impregnated with granular activated carbon (GAC), on viral inactivation. Bacteriophage T4 was used as virus indicator model and the experiments were carried out in batch mode under the controlled conditions of 25 °C and pH 7. Experimental data were represented by the kinetic equation of Chick-Watson. The results indicated a significant increase in virus inactivation and in the rate constant after the incorporation of nanoparticles on the GAC surface. Virus inactivation and rate constants were greater for the samples in which the synergistic effect of silver and copper oxide nanoparticles (NP-Ag-CuO) had occurred. From these results, it is possible to conclude that granular activated carbon, modified with NP-Ag-CuO (GAC/NP6), is a potential absorbent for application in virus inactivation over short contact times. The development of nanomaterials can be applied to water treatment processes as an alternative disinfection method.

1. Introduction

Viruses present in diameters ranging from 20 to 300 nm (nanometers) and they have threatened drinking water safety for decades (Zhang and Zhang, 2015). Both underground water and surface water may become contaminated with pathogenic viruses from various fecal sources (Yates et al., 1985). Viruses emerged into view as worrying contaminants in the United States, France, Canada, Brazil, Japan and other industrialized regions, partly due to the availability of disinfection processes (Page et al., 2009; Fumian et al., 2011; Kishida et al., 2012). A considerable amount of resistant bacteria have been detected in treated sewage (Huang et al., 2012a,b) and viruses and bacteriophages are known to persist longer than bacteria after disinfection procedures (Cantalupo et al., 2011; Allue-Guardia et al., 2012).

Inactivation of pathogenic viruses, such as Adenovirus, Norovirus, Rotavirus, Poliovirus, Hepatitis A, as well as virus indicators, has been employed in the evaluation of water purification processes (Gerba et al., 1975; Abad et al., 1994; Xagoraraki et al., 2004; Page et al., 2009; Kuo et al., 2010; Costa et al., 2012; Park et al., 2014). Bacteriophages were chosen as virus indicators of water supply microbiologic contamination due to their specificity and resistance when compared with bacterial indicators (Brehant et al., 2010). The bacteriophage is found in environments contaminated with *Escherichia coli*, such as residual waters and raw sewage, and it has been demonstrated that its presence is proportional to the level of fecal contamination (Monis and Blackbeard, 2010). When studying virus removal, bacteriophages are commonly used as substitutes for animal viruses because they are not infectious to human beings and are easier to manipulate (Schijven and Hassanizadeh, 2000; Grabow, 2001).

Bacteriophages have been used as infections model agents, serving as viral indicators in order to evaluate different inactivation/removal processes (Cookson and North, 1967; Schijven et al., 2002; Mamane et al., 2007; Sadeghi et al., 2013; Schijven et al., 2013). Bacteriophage T4, one of the greatest double-chain DNA bacterial viruses, has been used as a model virus in several research works (Lv et al., 2006; Mamane et al., 2007; Aronino et al., 2009; Timchak and Gitis, 2012). It is important to reassess conventional disinfection techniques and innovate with new approaches

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to obtain low cost drinking water (Biswas and Bandyopadhyaya, 2016).

Activated carbon adsorption is one of most efficient and reliable physicochemical methods (Babu and Gupta, 2008; Gentscheva et al., 2008). Activated carbon adsorption advantages reside in its simple and low cost operation, when compared with other separation methods (Bhattacharyya and Gupta, 2008; Sahmoune and Ouazene, 2012), due to its porosity, internal surface and high adsorption capacity (Pezoti et al., 2014). However, as long as the activated carbon filters do not remove microbial contaminants (such as bacteria and viruses) (Acevedo et al., 2014), a modification is needed. Activated carbon texture and chemical characteristics are related to the chosen precursor and high rates of adsorption are due to its surface functionalization, which enhance both adsorbent-adsorbate interactions and pore structure, allowing adsorption local access (Schijven et al., 2002).

Recently, nanoparticles have been used to modify activated carbon into promising and effective sorbents (Nekouei et al., 2016). Nanotechnology is one the fastest developing technologies, with products in various fields, due to its size (10^{-9} m) and great surface area (White et al., 2006). The literature lists several degrees of unfavorable biological effects induced by nanoparticles on cells, comprising subcellular and molecular scales alike (Fortner et al., 2005; Brunner et al., 2006; Lin et al., 2006).

There is a need to study the interactions between nanoparticles and viruses in water in order to improve current water treatments and develop new nanomaterials for water disinfection (Zhang and Zhang, 2015). Nanoparticles and silver and copper oxide components have been used in a variety of viral inactivation treatment processes (Zodrow et al., 2009; De Gusseme et al., 2011; Liga et al., 2011; Bryaskova et al., 2014; Kim et al., 2016; Minoshima et al., 2016; Shimabuku et al., 2016; Vincent et al., 2016).

The objective of this research is the kinetic study of bacteriophage T4 inactivation on these proposed materials (modified activated carbon with silver and copper oxide nanoparticles) with the aim of analyzing the effect of silver and copper oxide nanoparticles on viral inactivation.

2. Materials and methods

2.1. Materials

Analytical grade reagents, $AgNO_3$ (Nuclear Company) and $CuSO_4$ (II) (Vetec Quimica Fina Ltda), were used to modify the granular activated carbon surface for silver and copper oxide nanoparticles impregnation, respectively. Granular activated carbon (GAC) from palm coconut, made by Bahia Carbon Ltda (Bahia, Brazil), was utilized as the matrix (support) for modification by the presenting surface area of 575 $m^2\ g^{-1}$ and pore diameter of 1.19 nm.

Granular activated carbon surface was modified through silver and/or copper oxide nanoparticles impregnation according to Shimabuku et al. (2016), following a vacuum impregnation methodology by excess solvent and subsequent thermal decomposition. The metal concentrations (m/m (%)) relative to granular activated carbon appears in Table 1.

The material obtained, which has previously been characterized in Shimabuku et al. (2016), exhibited microporous characteristics (GAC/NP1-GAC/NP8), much like the GAC, with average pore diameters between 1.16 and 1.18 nm after impregnation (microporous characteristic). After the incorporation of silver and copper oxide nanoparticles on the GAC surface, the specific surface area (Brunauer-Emmet-Teller) decreased to values between 508 and 567 $m^2\ g^{-1}$ and silver and copper oxide nanoparticles with 22–40 nm in diameter were observed. Peaks of Ag^0 and CuO/Cu_2O were identified by X-ray diffraction (XRD) analysis.

Table 1
Silver and copper oxide nanoparticles (NP-Ag, NP-CuO and NP-Ag-CuO) nominal concentrations impregnated on the surface of granular activated carbon (GAC).

Sample	Nominal concentration w/w (%)		Nomenclature
	Ag	Cu	
GAC/NP-Ag0.5%	0.5	–	GAC/NP1
GAC/NP-Ag1.0%	1.0	–	GAC/NP2
GAC/NP-CuO0.5%	–	0.5	GAC/NP3
GAC/NP-CuO1.0%	–	1.0	GAC/NP4
GAC/NP-Ag0.5%CuO0.5%	0.5	0.5	GAC/NP5
GAC/NP-Ag0.5%CuO1.0%	0.5	1.0	GAC/NP6
GAC/NP-Ag1.0%Cu0.5%	1.0	0.5	GAC/NP7
GAC/NP-Ag1.0%Cu1.0%	1.0	1.0	GAC/NP8

2.2. Characterization of the obtained materials

In this study, several analyses were carried out: Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Absorption Spectroscopy. With the intent of analyzing the morphology by means of SEM, the samples were sputter-coated with gold and analyzed on a scanning electron microscope, model Shimadzu SS-550 SuperScan.

TEM images were obtained in the equipment JEOL JEM-1400 with 120 kV. The samples prepared in ethyl alcohol were left in ultrasonic treatment for 2 min and, shortly after that, were deposited on copper grids (200-mesh) (CF200-Cu, EMS), and dried at room temperature before being placed on the TEM sample support.

2.3. Analysis of metals in water

After the completion of the inactivation kinetics experiments, aliquots were collected for the analysis of silver and copper ion concentrations released in the water. The sample digestion methodology was adopted in agreement with the nitric acid digestion method for flame atomic absorption and high-level concentrations – 3030E – standard methods (Association, 1998). Silver and copper concentrations were analyzed by flame atomic absorption spectroscopy, using SpectraAA 50 B Varian Atomic Absorption Spectrometer equipment.

Tests were carried out with aqueous solutions of silver, copper and silver/copper at the maximum concentrations of the metals carried in water, to evaluate the effect of viral inactivation of the metals in solution.

2.4. Preparation and quantification of the Bacteriophage

Bacteriophage T4 was selected as a virus model due to its structural similarity to several enteric human viruses and also its usefulness (Templeton et al., 2007; Aronino et al., 2009; Timchak and Gitis, 2012). The water was sterilized in an autoclave at 121 °C for 15 min, contaminated with a bacteriophage T4 suspension ($\sim 10^9$ PFU mL^{-1}) and diluted in sterilized distilled water up to a concentration of $\sim 10^6$-10^7 PFU mL^{-1} (Zhang and Zhang, 2015).

Bacteriophage T4 was obtained according to Russel et al. (2004). *Escherichia coli* was used as a host cell, cultivated in tryptic soy broth (TSB) and, subsequently, inoculated with T4 and incubated at 37 °C for 24 h. The bacteriophage T4 suspension was obtained by centrifugation at 2000 rpm, for 10 min at −4 °C. The final stock of T4 was stored at the temperature of 4 °C. Bacteriophage T4 quantification was carried out by following the double-agar layer procedure (upper layer of 0.7% TSA, lower layer of 1.5% TSA) (Adams, 1959; Brady-Estévez et al., 2010; Bradley et al., 2011; Liga et al., 2011). After dilution of the viral suspension, *E. coli* suspension was added and the mixture was poured onto the solid agar plate and incubated