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A new silver based composite material for SPA water disinfection

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ABSTRACT

A new composite material based on alumina (Al_2O_3) modified by two surface nanocoatings – titanium dioxide (TiO_2) and silver (Ag) – was studied for spa water disinfection. Regarding the most common microorganisms in bathing waters, two non-pathogenic bacteria *Escherichia coli* (Gram-negative) and *Staphylococcus epidermidis* (Gram positive) were selected as surrogates for bacterial contamination. The bactericidal properties of the Al_2O_3–TiO_2–Ag material were demonstrated under various operating conditions encountered in spa water (temperature: 22–37 °C, presence of salt: $CaCO_3$ or $CaCl_2$, high oxygen content, etc.). Total removal of 10^8 CFU mL^{-1} of bacteria was obtained in less than 10 min with 16 g L^{-1} of material. Best results were observed for both conditions: a temperature of 37 °C and under aerobic condition; this latest favouring Reactive Oxygen Species (ROS) generation. The $CaCO_3$ salt had no impact on the bactericidal activity of the composite material and $CaCl_2$ considerably stabilized the silver desorption from the material surface thanks to the formation of AgCl precipitate. Preliminary tests of the Al_2O_3–TiO_2–Ag bactericidal behaviour in a continuous water flow confirmed that 2 g L^{-1} of material eliminated more than 90% of a 2.0×10^8 CFU mL^{-1} bacterial mixture after one water treatment recycle and reached the disinfection standard recommended by EPA (coliform removal = 6 log) within 22 h.

1. Introduction

Since 1968, when Roy Jacuzzi integrated a mobile hydrotherapy pump in a home bath, hot tubs or spas have transformed bathing into a genuine moment of rest and relaxation. However, the operating conditions of a hot tub (constant temperature of water at 37 °C, aeration, intense agitation during bathing, the presence of organic matter from the body, etc.) are the most favourable for the development of microorganisms (bacteria, viruses, micro-algae, etc.). To protect human health and reduce the risk of infection, all spas, without exception, for public or private use, must be equipped with a water treatment system. Although there are no legislative restrictions for private users, the water quality for public spas has to obey the Statutory Instruments of the Bathing Water Quality Regulations 2008 (Gormley, 2008).

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The majority of hot tubs (over 98%) are traditionally disinfected by adding chemicals with high oxidation potential, such as chlorine (Cl), bromine (Br), etc., into the water. It should be borne in mind that for the same efficiency, it is necessary to add 5 times more Cl or Br to spa water at 37 °C that to pool water at 21 °C. The temperature and the intense aeration of water by bubbling considerably increase the evaporation of the active chemicals. Moreover, the doses are often poorly quantified by users, so these "classic" chemicals generally have a very irregular efficiencies in hot spa waters. When misused, the added chemicals can be hazardous to health and cause very unpleasant effects (irritation of the eyes, respiratory tract, skin, etc. (Kim et al., 2002)). Attempts have been made to use modern electronic devices, such as ozonators or UV-light reactors, in order to reduce the amount of chemicals in water but ozonators are often associated with unwanted effects (exposure to odourless toxic O_3) and UV-light is systematically blocked by the air bubbles. In reality, apart from large doses of chemicals (Cl, Br or O_3) there is no real soft treatment for spa waters. An ideal system has to overcome three main conditions that traditional water treatment methods to date have failed to conquer: highly intense bacterial development, high water temperature and high oxygen content.

Silver (Ag) is an element with very specific bactericidal properties that have attracted scientists for decades. Despite their efforts, the mechanisms by which Ag destroys microorganisms are not completely understood, although several have been discussed. They include interactions between silver ions and thiol groups (-SH) of cytoplasmic proteins (Feng et al., 2000; Brook, 1989), Reactive Oxygen Species (ROS) generation (for example $OH^{\bullet}$, H_2O_2, or $O_2^{\bullet-}$) (Inoue et al., 2002; Matsumura et al., 2003) and the creation of cavities on the external membranes of microorganisms (Li et al., 2008; Sondi and Salopek-Sondi, 2004). On the other hand, silver is successfully applied today as a disinfectant in the medical (Peng et al., 2012), textile (Windler et al., 2013), water treatment (Davies and Etris, 1997) and many other fields. It has been reported that silver ions (Ag^+) are more active that the classical metal silver (Ag^0) (Feng et al., 2000) and, in recent years, the high anti-bactericidal performance of silver nanoparticles has been highlighted (Kheybari et al., 2010). However, as for all disinfectants, we believed that silver concentrations were clearly limited by safety regulations. After a thorough search of European and US legislation (Health Protection Agency, 2006; American National Standards Institute, 2009; World Health Organisation, 2006), we conclude that there is no restriction on the silver concentration in bathing waters. Because of this lack of regulations for bathing waters, the limit recommended by the United States Environmental Protection Agency (US EPA) for Drinking Waters (EPA, 2012), i.e. a silver concentration lower than 0.1 mg L^{-1}, was chosen in this study to ensure that the treated water would be safe for health.

In order to take advantage of the bactericidal capacities silver while keeping it out of the solution, research has focused on silver based composite materials in recent years. Several works (De la Rosa-Gomez et al., 2008; Matsumura et al., 2003) using silver supported on zeolites showed a total inactivation of 2×10^7 CFU mL^{-1} *Escherichia coli* with only 0.1 mg L^{-1} of Ag released in solution. Other studies indicated that the combination of silver with alumina supports allowed an inactivation of about 2×10^8 CFU mL^{-1} *E. coli* along with a desorption of silver ions leading to a concentration of about 0.9 mg L^{-1} (Chang et al., 2008). Even better, silver nanolayers strongly covalently bonded to activated carbon didn't release any traces of silver in solution (Gallion et al., 1998). However, even if this sophisticated material was intended for bactericidal treatment, no bactericidal study has been reported until now to the best of our knowledge. Moreover, silver composite materials can, in some cases, limit silver desorption while maintaining a high bactericidal activity due to the synergistic action of the supported silver and silver ions. For example, a zeolite-Ag material decreased the desorption concentration to 0.1 mg L^{-1} of silver ions while keeping a high bactericidal activity comparable to that achieved with 2 mg L^{-1} of a silver nitrate solution (Matsumura et al., 2003). In spite of their bactericidal performance and chemical stability, these silver based composite materials remain difficult to manufacture and handle (due to their powder form). Expensive and sophisticated methods (such as Cold Plasma, Plasma Assisted Ion-exchange, etc.) are often required and, once made, these particles are very difficult to control in applications such as water treatment. These drawbacks have condemned silver based products to remain at laboratory scale for now. Furthermore, among the silver supported materials cited, there are few studies on alumina supports (Chang et al., 2008; Chen et al., 2007) – the most common porous material – compared with those on zeolites, silica or activated carbon. This lack of interest in alumina-Ag materials is mainly due to the difficulty of binding silver to the alumina supports. These composite materials are often very unstable and, even if they show good bactericidal efficiencies, the concentration of Ag desorbed in solution may, in some cases, exceed the limit concentration required by the regulations, as in the case studied by Chen et al. (2007) with a silver desorption of 11 mg L^{-1} from an Al_2O_3–Ag material.

In this context, the CARDPool Company (France) developed an innovative composite material based on Al_2O_3–TiO_2–Ag as a disinfectant for spa waters. It consists of an alumina support (macro-granular form) treated by two successive nanocoatings, of titanium dioxide (TiO_2) and of silver (Ag) (Chis, 2013). The TiO_2 layer was designed to strongly bind the silver to the alumina in order to stabilize the material and control its desorption. Up to now, a few studies have been performed on Al_2O_3–TiO_2–Ag materials for other applications, related more to their high specific area or photocatalytic properties, such as sorption processes for the desulfurization of jet and diesel fuels (Hussain and Tatarchuk, 2013), reduction of nitrogen monoxide with propene found in automobile emissions (Caplan et al., 2009) and industrial waste (Li et al., 2008), separation of bacteria in groundwater and their inactivation by UV-photocatalysis for drinking water production (Ma et al., 2009), etc.

To the best of our knowledge, the present paper reports the first use of an Al_2O_3–TiO_2–Ag material for the disinfection of spa waters. The main aim of this study is to evaluate the bactericidal capacities of this new material under the influence of key operating parameters specific to spa waters: high bacteria concentration, high temperature, presence of salts and high oxygen content.