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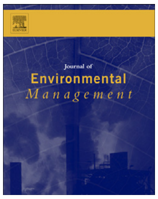

Research article

Oxidation of municipal wastewater by free radicals mechanism. A UV/Vis spectroscopy study

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ABSTRACT

This study investigates the oxidation of municipal wastewater (WW) by complexation with natural polyphenols having radical scavenging activity, such as (3,4,5 tri-hydroxy-benzoic acid) gallic acid (GA) in alkaline pH (>7), under ambient O_2 and temperature. Physicochemical and structural characteristics of GA-WW complex-forming are evaluated by UV/Vis spectroscopy. The comparative analysis among UV/Vis spectra of GA monomer, GA-GA polymer, WW compounds, and GA-WW complex reveals significant differences within 350–450 and 500–900 nm. According to attenuated total reflectance (ATR) spectroscopy and thermogravimetric analysis (TGA), these spectra differences correspond to distinct complexes formed. This study suggests a novel role of natural polyphenols on the degradation and humification of wastes.

1. Introduction

Nowadays, the reclamation of municipal wastewater (WW) has been widely recognized as a promising solution to overcome the growing pressure on water resources (Wintgens et al., 2005). This could release clean water for use in other sectors that need fresh water and provide water to sectors that can use WW e.g., especially in agriculture, which is the major user of water, withdrawing about 70% of all water (WMO, 1997). WW irrigation of crops, with raw or reclaimed WW, is already a widespread practice (Smit and Nasr, 1992). Many countries such as Australia, USA, Hashemite Kingdom of Jordan, the Kingdom of Saudi Arabia, Iran, Turkey and in some Mediterranean countries have included WW reuse as an important dimension of water resources planning (Pescod, 1992; Kalavrouziotis and Alaton, 2008; Pedrero et al., 2009; Kalavrouziotis et al., 2013, 2015; Kellis et al., 2013). Risks arise from a great variety of microbial pathogens, organic pollutants and heavy metals found in WW (Kalavrouziotis, 2015; Fatta-Kassinos et al., 2011; Muñoz et al., 2009). The conventional WW treatment consists of a combination of physical, chemical, and biological processes that remove solids, organic matter, and sometimes, nutrients from wastewater. The literature reports a multitude of conventional and alternative processes for the decontamination of contaminated water and WW such as coagulation, precipitation, extraction, evaporation, adsorption on activated carbon, ion-exchange, oxidation and advanced oxidation, incineration, electro-floatation, electrochemical treatment, biodegradation, and membrane filtration (Mondal, 2008; Moo-Young, 2007; Lefebvre and Moletta, 2006; Swami and Buddhi, 2006; Dabrowski et al., 2005; Matsumoto et al., 1996; Cotillas et al., 2014, 2015; Llanos et al., 2014). Coagulation/flocculation is a frequently applied process in the primary purification of WW (Manu, 2007; Moreno et al., 2007; Grenoble et al., 2007; Stechemesser and Dobiαš, 2005; Kulkarni et al., 2006; Aboulhassan et al., 2006; Dovletoglou et al., 2002; Jiang and Graham, 1998). The use of coagulants may have several environmental consequences: (i) an increase in metal concentration in water (which may have human health implications) (ii) production of large volumes of (toxic) sludge (iii) dispersion of acrylamide oligomers which may also be a health

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hazard (Bolto and Gregory, 2007; Bratby, 2006; Mukherjee et al., 2004; Bolto et al., 1998; Bolto, 1995; Levine, 1981; Türkman and Uslu, 1991). Recent developments in flocculation technology use natural organic polymers (biopolymers) (Kalavrouziotis et al., 2014) polyelectrolytes as flocculants and/or flocculation aids in river water and WW treatment (Al-samawi and Hama, 2012; Aygun and Yilmaz, 2010; Miller et al., 2008; Theodoro et al., 2013) taking precedence over inorganic and synthetic polymers.

Biopolymers are natural low-cost products, characterized by their environmentally friendly behavior (Bratby, 2006). The advantages of these polymeric flocculants are as follows: easy to handle, high solubility in water, reduction of sludge volume, readily available and biodegradable and they produce large, dense, and compact flocs with good settling characteristics (Renault et al., 2009).

A number of natural polymers and polyelectrolytes have been explored and established to be effective in WW decontamination either through adsorption or coagulation/flocculation processes. These include Alginate (*brown algae*) (Olad and Azhar, 2013; Zambrano et al., 2013), cellulosic materials (*green plants and algae*) (Ahmad and Kumar, 2011; Gupta et al., 2015), starch (*green plants*) (Chukwudi and Uche, 2008; Tripathy and De, 2006), chitosan (*fungi*) (Renault et al., 2009; Srinivasan and Viraraghavan, 2010), *xanthan gum* (Mukherjee et al., 2014; Verma et al., 2012), *moringa oleifera* (Ali et al., 2010; Beltran-Heredia and Sánchez-Martín, 2009; Bichi, 2013; Debora et al., 2013; Kazi and Virupakshi, 2013), *okra* (Al-samawi and Hama, 2012), *guar gum* and *cassia tora gum* (Sharma et al., 2006; Tripathy and De, 2006) and tannins (*polyphenol plants*) (Sánchez-Martín et al., 2010; Thakur and Choubey, 2014) just to mention a few.

Studies regarding plant products as potential WW treatment agents have a long history. In particular, wood derivatives are considered to be highly effective adsorbents (Geay et al., 2000) as are tannins (Sánchez-Martín et al., 2010; Thakur and Choubey, 2014). Natural polyphenolic compounds, such as tannins, bind and precipitate proteins and various other organic compounds including aminoacids (e.g. peptides) and alkaloids (Siebert et al., 2006; Hagerman et al., 1998a,b; Baxter et al., 1997; Riedl and Hagerman, 2001; Riedl et al., 2001; Charlton et al., 2002; Chen and Hagerman, 2004). A new tannin-based coagulant-flocculant was tested for water treatment at a pilot plant level for four water types: surface (collected from a river) and municipal water, textile industry, and laundry WW. The pilot plant trials gave a significant improvement in contaminant, turbidity, and BOD_5 removal. In spite of the continuous flow, an increase in color reduction (up to 50%), surfactant removal (up to 75%), and organic matter (COD and BOD_5) removal (40% and 60%, respectively), total turbidity removal in the municipal WW, about 95% dye removal in the case of the textile industry WW, and about 80% surfactant removal in the laundry WW were observed (Sánchez-Martín et al., 2010). A natural indigenous coagulant such as tannin, obtained from Acacia catechu, is examined as a primary coagulant. At the optimal dosage of 3.0 mgL^{-1}, acacia catechu powder can remove turbidity up to 91% (Thakur and Choubey, 2014). Natural tannins are found in the leaves, fruits, barks, roots, and wood of trees. The term “tannins” covers many families of plant chemical compounds. However, the term “tannin” by extension is widely applied to any large polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls) to form strong complexes with various macromolecules. The base unit of the tannin structure is the gallic acid (GA) monomer (Fig. 1) (Pengelly, 2004) GA is a natural product of tannin hydrolysis and is present in food of plant origin (Strlič et al., 2002). Among natural polyphenols, GA exhibits the most considerable antioxidant capacity in plants and possesses a higher radical scavenging activity than alkylgallate derivatives (Gunckel et al., 1998) as well as protocatechuic acid and 4-hydroxybenzoic acid (Fukumoto and Mazza, 2000; Rice-Evans et al., 1996). Theoretical calculations for GA (Saiz-Jimenez et al., 1975; Giannakopoulos et al., 2005), and other phenolic compounds provided a theoretical foundation for their vibrational spectroscopic characteristics (Mohammed-Ziegler and Billes, 2002) as well as the mechanism of their antioxidant activity (Leopoldini et al., 2004). Based on the electron paramagnetic resonance spectroscopy, GA is a good model for the radicals of humic acids (Giannakopoulos et al., 2005, 2006). In a spectrophotometric study at pH > 7, GA and its analogues are rapidly oxidized by atmospheric oxygen (Friedman and Jurgens, 2000). In an electrochemical study of GA and alkyl-gallate derivatives at pH 2–7, it was observed that oxidation was irreversible and a two electron oxidation scheme leading to the production of quinone structures in acidic media was postulated (Gunckel et al., 1998). Given the importance of polyhydroxybenzoic acids, the adsorption of the GA onto hanging mercury drop electrode (HMDE) depending on the pH and temperature was investigated (Giannakopoulos and Deligiannakis, 2011, 2012). In this context, the HMDE offers an ideal hydrophobic surface where adsorption and redox events can be monitored under controlled conditions. The interaction of GA with the HMDE is a complex thermodynamic process which involves chemisorption of radical-species as weak interactions of H-bonding and hydrophobic adsorption (Giannakopoulos and Deligiannakis, 2011). Additionally, with the increase of OH-groups at the benzoic ring, the molecules orientate from a parallel position of the benzoic ring to a perpendicular position towards the electrode surface. This position aids the adsorption of more molecules at the HMDE surface (Giannakopoulos et al., 2012). The possibility of polymer production, with no use of a catalytic material, of several polyphenolic molecules mono- di- and tri-hydrobenzoic acids under ambient O_2 by oxidative complexation has been investigated (Giannakopoulos et al., 2009). The oxidative copolymerization between GA and protocatehuic acid (PA) (3,4-dihydroxybenzoic acid), gave a water soluble humic-acid-like polycondensate which mimics fundamental physicochemical and spectroscopic properties of natural humic acids. Solid state ^{13}C NMR and EPR spectroscopy for polymer (GA-PA) showed that (i) ring-opening reactions of GA, PA monomers are involved in (GA-PA) formation and (ii) contains stable phenol-based radicals, with pH-dependent concentration respectively (Giannakopoulos et al., 2009).

The purpose of the present work is to study spectroscopically the complexation mechanism among GA and municipal WW compounds in the presence of atmospheric O_2 at pH > 7.

2. Materials and methods

2.1. Materials

All solutions were prepared with analytical-grade chemicals and purified water (Milli-Q Academic) with a conductivity of 18.2 $\mu S\ cm^{-1}$. NaOH was used for the adjustment of the pH of samples at pH 10.5.

2.1.1. GA stock solution

GA (3,4,5 tri-hydroxy-benzoic) was obtained from Sigma–Aldrich (Lot. G7384, Aldrich, assay >99%), and used without further purification. Stock solution of GA was prepared at concentrations of 2 mM.

2.1.2. Municipal WW samples

Municipal WW samples were taken from the sewage treatment plant of Nafpaktos, a small town in western Greece. This wastewater treatment plant receives municipal WW from approximately 20,000 people per day. The sources of WW are household effluent,

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