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Review

Significance of analytical parameters for the understanding of natural organic matter in relation to photocatalytic oxidation

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ABSTRACT

In this review, special interest was devoted to provide information on the surrogate parameters expressing both quality and quantity of organic matter for the understanding of the photocatalytic oxidation of humic substances. Detailed investigation was directed to the application of photocatalysis with reference to source, origin and modeling of organic matter. Evaluation of the literature findings emphasizes that organic matter taken from natural waters are site specific and should be characterized in detail to be comparable to other studies. Taking into account the photocatalytic degradation studies of natural organic matter, humic substances, humic acids and fulvic acids in slurry systems, a procedure could be deduced that depends on the selection of a standard model sample with a representative concentration, selection of a standard photocatalyst and dose (*e.g.*, TiO_2 Degussa P-25, 0.25 mg mL^{-1}), application of standardized reaction conditions such as light intensity, pH, and temperature. Furthermore, standardized filtration step avoiding organic leaching and selection of the most suitable analytical parameter are the crucial points to be considered. The use of such a protocol could form a basis for the determination of "relative degradation efficiency" of any sample containing natural organic matter, humic substances, humic acids and fulvic acids regardless of dependency on source and origin.

Contents

1. Introduction

Natural organic matter (NOM) is a collective term assigned to the realm of all of the broken down organic material that comes from plants and animals in the environment. A great diversity of organic molecules of both humic and non humic nature constitutes NOM in soils, sediments and natural waters (Aiken et al., 1985). The chemical characteristics of NOM are influenced both by material source and biogeochemical processes involved in the carbon cycle in terrestrial and aquatic systems. The main component of NOM is referred to as humic substances (HS) that are classified as humic acid (HA), fulvic acid (FA) and humin. Hu-

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mic substances play an important role in transport, binding, analysis and remediation of pollutants in natural environments due to their ubiquitous occurrence and chemical reactivity. They mainly act as precursors for the formation of carcinogenic disinfection by-products (DBPs) during the chlorination process in water treatment systems (Rook, 1976; Bond et al., 2009). It is estimated that they constitute 50–90% of dissolved organic carbon (DOC) in freshwater systems.

Despite the fact that humic substances contain a variety of building blocks and various functional groups, their structure and behavior in the environment remain unclear. A comprehensive overview of the research for the application of conventional treatment of natural organic matter has been presented by Matilainen et al. (2010). Additionally, adsorption and removal of humic acids by various adsorbents such as granular activated carbon, minerals, and kaolinite has been studied (McCreary and Snoeyink, 1980; Jiang and Cooper, 2003; Chang and Juang, 2004). Recently, removal of natural organic matter from drinking water by advanced oxidation processes (AOPs) via homogeneous and heterogeneous systems has been reviewed by Espinoza and Frimmel (2009) and Matilainen and Sillanpää (2010). During the last decade, extensive research has been devoted to the removal of humic substances by the application of physico-chemical treatment and advanced oxidation techniques mainly ozonation and photocatalysis (Bekbolet et al., 2002, 2005; Uyguner and Bekbolet, 2005a,b). Besides the application of photocatalysis, the oxidative degradation of aqueous humic acid with ozonation, catalytic ozonation, photocatalytic ozonation and sequential oxidation composed of ozonation followed by photocatalysis was investigated and the results were evaluated in terms of removal kinetics. Up to date presented data only focused on the UV–vis properties of humic acid in relation to color ($Color_{436}$ and $Color_{400}$) and aromaticity (UV_{280} and UV_{254}) parameters (Bekbolet, 1996; Bekbolet et al., 2002; Kerc et al., 2003a,b). However, due to the complex nature of DOC *i.e.*, mainly humic acids, comprising a high number and a wide variety of chromophores that do not possess a unique and easily distinguishable absorption spectrum, the precise understanding of the UV spectra is a complicated process. The internal vibration and rotation of the molecules and inter-molecular interactions broaden the absorption peaks in the UV spectrum of humic substances eliminating any conspicuous and sharp features from the UV spectra of natural waters (Ghosh and Schnitzer, 1979; Stevenson, 1982; Korshin et al., 1997b).

The main idea of this paper comes from the experience of using humic acids as model compounds for the photocatalytic degradation of natural organic matter as reported by Bekbolet and coworkers since 1996. More than five different types of humic substances, natural water and algae derived NOM have been investigated. The retardation and competition effects on the TiO_2/UV system in the presence of different types of humic and fulvic acids, different TiO_2 brands, various metal ions (Zn, Cu, Cr, Mn, and Fe), common cations and anions (Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}), oxyanions (OCl^-, ClO_2^- and ClO_3^-), oxidizing species (H_2O_2) and inhibitory effects due to alkalinity (*i.e.*, HCO_3^- and CO_3^{2-}) have also been revealed to understand the limitations of the photocatalytic system (Bekbolet, 1996; Bekbolet and Balcioglu, 1996; Bekbolet et al., 1998; Gonenc and Bekbolet, 2001; Uyguner and Bekbolet, 2007a, 2009). Some of our recent efforts have focused on fractionating humic acids by ultrafiltration before and after photocatalytic oxidation to elucidate the changes in molecular size of humic acids (Uyguner and Bekbolet, 2005a,b, 2010). In a similar approach size exclusion chromatography to fractionate NOM at different stages of the photocatalytic degradation process was used to gain insight to the time evolution of its molecular size distribution (Espinoza and Frimmel, 2008; Liu et al., 2008a).

In the light of these studies, it could be possible to evaluate humic acid removal by photocatalytic oxidation, performed under intra-laboratory self calibrated conditions, in terms of organic carbon measurements, UV–vis and fluorescence spectroscopy. Due to the presence of a large number of studies related to the photocatalytic removal of humic acids and natural organic matter, different data available in literature could only be compared on a standardized basis of the experimental conditions. Although the reported parameters are sufficient to give a general assessment, they do not elucidate the chemistry of the process in any detail. Moreover, the final filtration step applied for the effective removal of TiO_2 particles constitutes the most important common point of slurry systems and definition of dissolved organic carbon. The majority of the researchers use filters of 0.45 μm pore size that represent the discriminating size of total organic carbon (TOC) and DOC. Furthermore, the universal question of the determination of "humic acid concentration" requires to be solved by the use of appropriate surrogate parameters.

The scientific community has so far experienced difficulties in proving a unified understanding of humic materials. The chemistry is not only highly complex, but it is also a function of the different general properties of the ecosystem in which it is formed, such as vegetation, climate, and topography (Piccolo, 2001). Despite the efforts of many scientists in the distant and recent past there is still much to be done to achieve an appropriate awareness of humic matter (Kördel et al., 1997; Esteves et al., 2009). Studies on this subject are of long-standing and continued interest can only be justified on theoretical and practical grounds with the development of new analytical methods and approaches.

The amazing chemistry of "humic substances" invokes interest for proper understanding of the substrate. Besides evaluation of the reaction kinetics or removal efficiencies, what is subjected to oxidative degradation should also be clearly visualized. In order to provide a comprehensive basis for the elucidation of this question, the prepared paper was specifically based on the relevant literature survey and constructed as follows:

(i) Review of literature on the photocatalytic degradation of natural organic matter and humic substances namely humic and fulvic acids.
(ii) Evaluation of operational parameters as indicated in the respective publications.
(iii) Evaluation of kinetics and removal efficiency data achieved upon application of photocatalysis.
(iv) Understanding of the properties of NOM and humic substances.

In relation to the qualitative and quantitative properties surveyed in literature for the characterization of natural organic matter, humic substances and humic/fulvic acids, special interest was devoted to the explanation of surrogate parameters of these substances. Hence, prior to the presentation of the critical review, a background section was prepared to provide basic information on the chemical nature and properties of NOM and its related fractions. The operative descriptors expressing both quantity and quality of organic matter were also examined. It should be stated that any literature survey performed on the keywords "photocatalysis" and "humics", reveals a significant number of publications examining the effects of humic substances on the photocatalytic oxidation of organic or inorganic compounds (*e.g.* Bems et al., 1999; Minero et al., 1999; Selli et al., 1999; Enriquez and Pichat, 2001; Marinas et al., 2001; Doll and Frimmel, 2005). However, in this review emphasis was particularly focused on papers reporting on the photocatalytic oxidation of natural organic matter and model humic substances mainly humic and fulvic acids.