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Review

Elucidation of background organic matter matrix effect on photocatalytic treatment of contaminants using TiO_2: A review

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ABSTRACT

A web-based survey has been performed in order to visualize the never ending interest on the topic “photocatalysis” since 1990. Studies related to photocatalysis have been continuously increasing throughout the literature for two decades. In this review, special emphasis is directed to photocatalytic degradation of pollutants in the presence of natural organic matter (NOM) using TiO_2 as the photocatalyst. Considering the diversity in surface waters, major concern will be on critical evaluation of the “NOM effect” on the photocatalytic degradation of organic compounds. To provide a broader perspective of NOM properties for the assessment of its role in photocatalytic degradation process of priority pollutants (PPs) and organic emerging contaminants (ECs), recent literature findings are surveyed. Current limitations and future research needs are discussed.

Contents

Abbreviations: AI, acridine; AO, acridone; AO7, acid orange 7; AOP, advanced oxidation processes; ATL, atenolol; BET, Brunauer, Emmett and Teller; BOD, biochemical oxygen demand; BPA, bisphenol A; CB, conduction band; CBZ, carbamazepine; CBZ-E, carbamazepine epoxide; CFA, clofibric acid; CMT, cimetidine; COD, chemical oxygen demand; CP, chlorophenol; CYN, cylindro spermopsin; DEET, *N,N*-diethyl-meta-toluamide; DLS, dynamic light scattering; DOC, dissolved organic carbon; DOM, dissolved organic matter; DPs, degradation products; E1, estrone; E2, 17β-estradiol; ECs, emerging contaminants; EDCs, endocrin disrupting compounds; EE2, 17α-ethinyestradiol (EE2), [93]; EE2, 17α-ethinyestradiol (EE2), [95]; EEM, excitation emission matrix; EP, ethyl paraben; FA, fulvic acid; FFA, furfuryl alcohol; FTIR, fourier transform infrared; GC–MS, gas chromatography mass spectroscopy; HA, humic acid; HALP, humic acid like polycondensate; HOMU, hydroxy methyl uracil; HPLC, high-performance liquid chromatography; HPLC-DAD, high-performance liquid chromatography diode array detector; HPLC–MS, high-performance liquid chromatography mass spectroscopy; HPLC-PDA, high-performance liquid chromatography photodiode array detector; HPLC-UV, high-performance liquid chromatography ultraviolet detector; HS, humic substances; IHSS, International Humic Substances Society; LC, liquid chromatography; LC-UV, liquid chromatography UV; LC-OCD, liquid chromatography organic carbon detection; LC–MS, liquid chromatography mass spectroscopy; LHA, lignite humic acid; MB, methylene blue; MC-LR, microcystin-LR; MOX, moxifloxacin; MS, mass spectroscopy; MW, molecular weight; NF, nanofiber; NMR, nuclear magnetic resonance spectroscopy; NOM, natural organic matter; NPs, nanoparticles; NTB, Ti-doped β-Bi_2O_3; OP, octylphenol; PbTx-2 and PbTx-3, brevetoxins; PLFA, Pony lake fulvic acid; PLHA, Pony lake humic acid; POM, particulate organic matter; PPs, priority pollutants; PRP, propranolol; PPCPs, pharmaceuticals and personal care products; RR195, reactive red 195; ROS, reactive oxygen species; SEC-OCD, size exclusion chromatography with organic carbon detector; SEC-DOC, size exclusion chromatography dissolved organic carbon; SEM, scanning electron microscope; SRFA, Suwannee river fulvic acid; SRHA, Suwannee river humic acid; SRNOM, Suwannee river natural organic matter; SSL, simulated sunlight; SMX, sulfamethoxazole; SUVA, specific UV absorbance; TA, tannic acid; TEM, transmission electron microscope; TiHAP, Ti-substituted hydroxyapatite; TOC, total organic carbon; UPLC-EI-HRMS, ultra-performance liquid chromatography-electrospray ionization-high resolution mass spectrometry analysis; VB, valence band; VL, visible light; XRD, X-ray diffraction.

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1. Introduction

A web-based survey has been performed in order to visualize the never ending interest on the topic “photocatalysis”. Using bibliographic records from Web of Science since 2010, keyword (selected as topic) search for “photocatalysis” has revealed approximately 17,500 papers among which 64% is TiO_2 photocatalysis. Natural organic matter (NOM) photocatalysis (137) constitutes 0.8% in which 82% is TiO_2 photocatalysis. With respect to the aim of the study “NOM effect” topic was searched within the above given results revealing a significant percentage as 44%. This findings show that studies related to “NOM effect” holds prime importance in TiO_2 photocatalytic treatment of contaminants.

The presence of priority pollutants (PPs) and organic emerging contaminants (ECs) including pharmaceuticals, personal care products (PPCPs), pesticides, hormones, surfactants and various endocrine disrupting compounds (EDCs) in surface waters have become an environmental concern due to their potential adverse effects on humans and ecosystems [1,2,3]. The trend in identifying unknown contaminants especially environmental transformation products continues, with increasing number of studies related with products generated during photolysis and advanced oxidation processes [4,5].

Treatment of PPs and ECs by advanced oxidation processes (AOPs) has been considered as a necessity for the removal of these compounds from water sources [6,7]. Presence of $OH^•$ scavengers in aqueous medium reflected as the main shortcomings of the application of AOPs. The major scavenger was reported as organic matter *e.g.* humic acids (HAs) and fulvic acids (FAs). Since NOM is omnipresent in water, optimization of AOPs should be performed taking into account these conditions. Heterogeneous photocatalysis has been extensively studied and considered as the second most used treatment process after ozone-based AOPs. From a general perspective, TiO_2 photocatalysis holds prime importance [8]. Therefore, the role of NOM, dissolved organic matter (DOM), humic substances (HSs), HAs and FAs on the TiO_2 photocatalytic degradation of PPs and ECs deserves special attention.

Semiconductor photocatalytic process has shown a great potential as a low cost, environment friendly treatment technology and demonstrated its efficiency in degrading a wide range of pollutants. The field of photocatalysis dates back to early 1980s, which has grown uniformly at an overall rate of about 15% annually for new articles and reviews [9–13]. The readers are directed to two pioneering books and specific chapters therein for detailed information on fundamentals and applications of photocatalysis [14,15]. Recently, a special issue was devoted to the advances and developments in photocatalysis for the treatment of contaminants of emerging concern [16].

Basic principles of photocatalysis depends on the formation of reactive oxygygen species (ROS) upon excitation of a semiconductor particle with light energy greater than the respective band gap energy of the photocatalyst. The most widely studied photocatalyst is TiO_2 holding the significance of superiority over others [17]. An important drawback of TiO_2 photocatalysis is its wide band gap energy which requires the use of UV light which is 3–5% of natural solar light. For the correct use of terminology on photocatalysis, the readers are strongly advised to refer to specific references [18,19]. Modification of TiO_2 surface is one of the promising routes to enable TiO_2 sensitive to visible light for its use in water purification [20]. A variety of strategies have been employed to improve the photocatalytic efficiencies of photocatalysts [21]. Transition from first generation photocatalysts (pristine dispersed solids) to second-generation photocatalysts (chemically doped and/or physically modified dispersed solids) has extended the knowledge to achieve better spectral sensitivity and photoactivity [22]. Recent advances in composite based photocatalytic systems were presented by various researchers [23,24,25].

Application of photocatalysis for NOM removal in natural waters dates back two decades [26]. TiO_2 photocatalytic removal of NOM, namely HAs and FAs has been studied using a bench scale UV initiated system by Bekbolet and coworkers [27–32]. The retardation and competition effects on the TiO_2/UV system in the presence of different types of HAs and FAs, TiO_2 brands, various metal ions, common cations, anions, and inhibitory effects due to alkalinity have also been revealed to understand the limitations of the photocatalytic system [31]. Recently, photocatalytic performance of various anion doped second generation TiO_2 specimens (*i.e.* Fe-doped, N-doped, S-doped, and S-N co-doped) for the degradation of HAs was also assessed [33,34]. Although a vast number of non-TiO_2 third generation photocatalysts have been developed, applicability to the treatment of NOM or PPs and ECs is still under investigation [35,36]. Current advances on application of emerging pollutants bring together about the necessity to evaluate the basic water component as NOM. Recent papers report on inhibition or enhancement of the photocatalytic removal of PPs and ECs in the presence of NOM/HAs/FAs with primary focus on substrate removal. However, studies with photocatalytic degradation investigating humic matter removal and characterization in the presence of organic pollutants of concern are limited.

In this review special emphasis is directed to photocatalytic degradation of pollutants using TiO_2 photocatalysts. Taking into account the diversity in surface waters, major concern will be on critical evaluation of the effect of NOM/HAs on the photocatalytic degradation of organic compounds. Main restrictions can be outlined as follows:

i TiO_2 was selected, since most of NOM (and analog compounds) degradation studies were performed using TiO_2 and its modified forms,
ii Disinfection was excluded due to the mode of action of photocatalysis,
iii Inorganic species including metals were also excluded.

Photocatalytic degradation of selected contaminants in aqueous matrices using different types of TiO_2 such as doped TiO_2, modified TiO_2, immobilized TiO_2 were reviewed, evaluated and compared.

2. Background information

Based on the purpose of the paper, to provide a broader perspective on the evaluation of the current status relevant background information was compiled and presented.

2.1. Background information on NOM and its analogs

Dissolved organic matter represents an important part of NOM. Conte and Berns showed that HSs, HAs and FAs considered as representatives of NOM/DOM consisting of condensed aromatic hydrophobic cores surrounded by more hydrophilic molecules [37,38]. The chemical and structural nature of organic matrix could be explained either by classical view as macromolecular pattern or by a different model as supramolecular pattern upon examination of various HSs covering International Humic Substance Society (IHSS) HA, Suwannee River humic acid (SRHA), Suwannee River fulvic acid (SRFA) and HA (Aldrich) [39]. A critical review on molecular characterization of DOM described it as a complex mixture of low molecular weight (MW) substances and larger MW biomolecules *e.g.* proteins, polysaccharides and exocellular macromolecules [40]. A major comment could be derived as that “DOM cannot be correctly regarded as a chemical solution; it is rather a very fine col-

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