Adsorption of molecular size fractions of humic acid onto anion-doped TiO₂ specimens

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ABSTRACT

Humic acids (HA) constitute the major fraction of natural organic matter that should be removed during water treatment. Besides conventional treatment methods, application of advanced oxidation processes more specifically photocatalysis has gained much attention in recent decades. Titanium dioxide (TiO₂) is universally recognized as a standard photocatalyst. Since photocatalysis occurs through a surface-oriented mechanism, adsorptive properties of TiO₂ specimens deserve special attention. Moreover, nowadays visible light activated TiO₂ developed by modifications through the use of various dopants has been the subject of numerous investigations. Understanding of the surface interactions prevailing between the anion-doped oxide surface and humic subfractions is important for the determination of the role of humic substances during photocatalysis. The aim of this study was to investigate surface interactions between different molecular size fractions of HA and TiO₂, namely bare TiO₂ and anion-doped TiO₂ (C-doped, N-doped, S-doped and N–S co-doped) specimens. Therefore, adsorption properties of HA and its molecular size fractions onto bare TiO₂ and anion-doped TiO₂ specimens were evaluated by dissolved organic carbon, UV–vis spectral properties, and respective specific UV–vis parameters (SCoA, SUVA365, SUVA280, and SUVA254). Furthermore, the data achieved by adsorption experiments were assessed by Freundlich, Langmuir as well as Dubinin–Radushkevich isotherm models. The results based on varying molecular size fractions of HA displayed remarkable differences with respect to the type of the dopant in comparison to the bare TiO₂ specimen. Consequently, when different molecular size fractions of HA were compared, Freundlich model displayed lower KF and higher 1/n values as well as Langmuir model exhibited maximum quality adsorbable in the presence of lower molecular size fraction. The reason could be also attributed to the compositional properties of HA subfraction along with the alterations in TiO₂ specimens due to doping. From a general perspective, E values in Dubinin–Radushkevich model indicated that the main mechanism for the adsorption of diverse molecular size of HA onto
bare and anion-doped TiO₂ specimens could be mainly attributes to physical forces. Referring to the fundamental aim of the study indicating that the studied dose range of TiO₂ (0.1–1.0 mg mL⁻¹) was selected with respect to the photocatalytically active concentration range, the attained results should be carefully interpreted.

*Keywords:* Humic acids; Photocatalysis; Natural organic matter; Water treatment