

## **Characterization of Humic Acid and its Size Fractions Following Adsorption onto Anion-Doped TiO<sub>2</sub> Specimens by Fluorescence Spectroscopic Studies**

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### **Extended Abstract**

Humic acids (HA<sub>s</sub>) which are environmental decomposition products of plant, fungal and bacterial biopolymers, are significant in the binding mechanism of toxic chemicals in soil and water, in the formation and maintenance of good soil structure [1]. Titanium dioxide (TiO<sub>2</sub>) is universally recognized as a standard photocatalyst. Due to the fact that photocatalysis occurs through a surface-oriented mechanism, adsorptive interactions between TiO<sub>2</sub> specimens and organic compounds need further attention [2]. Recent interest has been devoted to the application of three dimensional excitation-emission matrix (3D-EEM) spectrofluorometry for the characterization of humic acid under oxidative and non-oxidative conditions [3]. Humic substances state fluorescence in the excitation wavelength range of  $\lambda_{exc} \sim 300\text{-}400$  nm and the emission wavelength range of  $\lambda_{emis} \sim 400\text{-}500$  nm. Fluorophoric regions could be described as humic-like fluorescence (fluorescence excited between  $\lambda_{exc}= 220$  and 250 nm, and emitted between  $\lambda_{emis}= 400$  and 460 nm), fulvic-like fluorescence (fluorescence excited between  $\lambda_{exc}= 300$  and 340 nm, and emitted between  $\lambda_{emis}= 400$  and 460 nm), and protein-like (tryptophan and tyrosine) fluorescence (fluorescence excited between  $\lambda_{exc}= 270$  and 280 nm and emitted between  $\lambda_{emis}= 330$  and 370 nm) [4]. The objective of this study was to investigate surface interactions between different molecular size fractions of humic acid and anion-doped TiO<sub>2</sub> specimens through excitation-emission matrix fluorescence features.

In this study, commercial humic acid (HA) in the concentration of 20 mgL<sup>-1</sup> was purchased from Aldrich (Aldrich Company, USA). HA solutions were fractionated using a 50 mL Amicon Model 8050 ultrafiltration stirred cells into two different molecular size fractions (100 and 30 kDa) in order to attain different humic matrices. An incipient wet impregnation method was used to prepare anion doped TiO<sub>2</sub> specimens (C-doped, N-doped, S-doped and N-S co-doped) as the adsorbents. TiO<sub>2</sub> Hombikat UV-100 (Sachtleben Chemie) was used as the adsorbent (crystal structure: 100% anatase, porous, BET surface area: >250 m<sup>2</sup>g<sup>-1</sup>, average particle size: <10 nm, density: 3.9 gmL<sup>-1</sup>). Concentrations of bare and anion doped TiO<sub>2</sub> specimens used in batch adsorption experiments were selected in the range of 0.1-1.0 mgmL<sup>-1</sup> and kept constant throughout the experimental studies. Fluorescence spectroscopic measurements were conducted employing a Perkin Elmer luminescence spectrometer. To attain fluorescence EEMs, excitation wavelengths ( $\lambda_{exc}$ ) were incrementally increased from 200 to 500 nm at 10 nm steps, the emission at longer wavelengths ( $\lambda_{emis}$ ) was detected at 0.5 nm steps. Excitation and emission slit widths were set to 12 nm. Matlab R2012a was used to plot the EEM data[2;5].

Fluorescence intensity strength was indicated by a symbol (+) with reference to the presented color intensity. Besides the aforementioned fulvic-like (Region III) and humic-like fluorophores (Region V), Region I (tyrosine-like) and Region II (tryptophan-like) signified the fluorophores arising from aromatic proteins either free or as protein constituents. Region IV represented fluorophores attributed to the components of the dissolved organic carbon derived from microbial byproducts. Following adsorptive interactions between HA and TiO<sub>2</sub> specimens, EEM contour-plots exhibited the presence of both humic-like and fulvic-like fluorophores under all conditions. However, in the presence of anion doped TiO<sub>2</sub> specimens, presence of humic-like fluorophores were found to be more prominent than fulvic-like fluorophores. It could be deduced that HA fluorophores illustrated the presence of regions III and V expressing fulvic-like and humic-like fluorophores and absence of regions I, II and IV.

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## References

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