

Supplementary information:

Photocatalytic degradation kinetics of 0.45 μm ff HA and 100 kDa humic acid was also investigated by using ZnO as a baseline photocatalyst for Ce doping. Photocatalytic degradation experiments were performed using ZnO as prepared by Calza and co-workers (Calza et al., 2016).

The reported properties of the ZnO was as follows:

Band gap: 3.26 eV.

Atomic percentage of the elements obtained from EDS and XPS analyses : Zn 61.21 % and O 38.79 %.

Crystallite size: 121 nm. S_{BET} : < 10 m^2/g .

Photocatalytic degradation experiments were carried out according to the procedure outlined in Materials and Methods Section of the main text.

Photocatalytic degradation profiles of humic acid samples displayed a similar pattern to the case observed both for humic acids treated by using Ce doped ZnO as well as TiO_2 .

Degradation data were modelled by using first order kinetic model;

$$C=C_0e^{-kt}$$

Where:

C: humic parameters; UV-vis parameters (m^{-1}) as Color_{436} , UV_{365} , UV_{280} , UV_{254} and NPOC (mg/L).

C_0 : humic parameters; UV-vis parameters (m^{-1}) as Color_{436} , UV_{365} , UV_{280} , UV_{254} and NPOC (mg/L) under initial conditions.

k: pseudo first order kinetic rate constant, min^{-1} .

t: reaction time, min.

The kinetic model parameters were calculated as follows:

Photocatalyst ZnO	UV-vis spectroscopic parameters				NPOC	
	Rate constant k, min^{-1}				$\text{k} \times 10^{-2}, \text{min}^{-1}$	Rate, mg/L min
	Color_{436}	UV_{365}	UV_{280}	UV_{254}		
0.45 μm ff HA	0.154	0.189	0.121	9.94×10^{-2}	2.30	0.110
100 kDa HA	9.54×10^{-2}	8.79×10^{-2}	7.32×10^{-2}	6.44×10^{-2}	4.65	0.217

From a general perspective, 0.45 μm ff HA samples displayed higher degradation kinetic rate constants in comparison to 100 kDa HA. Following ZnO photocatalysis, UV-vis parameters of 0.45 μm ff HA displayed a decreasing sequence as $\text{UV}_{365} > \text{Color}_{436} > \text{UV}_{280} > \text{UV}_{254}$, whereas 100 kDa HA expressed an increasing trend as $\text{Color}_{436} < \text{UV}_{365} < \text{UV}_{280} < \text{UV}_{254}$. The removal kinetics as expressed by spectroscopic parameters indicated the diverse reactivity of UV-vis absorbing centers composed of various dense aromatic centers of conjugated double bond systems connected through aliphatic linkages. However, NPOC degradation data revealed higher removal of organic matter of 100 kDa HA in comparison to 0.45 μm ff HA. The reason could be attributed to the different interactions of the higher molecular size humic sub-fractions (> 100 kDa in 0.45 μm ff HA) with the ZnO particles. From a general perspective, the cause could be explained by the very low surface area of the ZnO specimen (<10 m^2/g) possibly leading to very weak surface attractions as explained by the very low initial adsorption of humic sub-fractions onto ZnO (< 10 %). In accordance with the successive removal of UV_{254} and NPOC, SUVA values displayed 0.61 and 2.17.

EEM fluorescence contour plots of the humic acid samples measured during photocatalytic treatment by using ZnO also revealed information on the reaction time dependent removal of humic-like and fulvic-like fluorophores (Fig. S1).

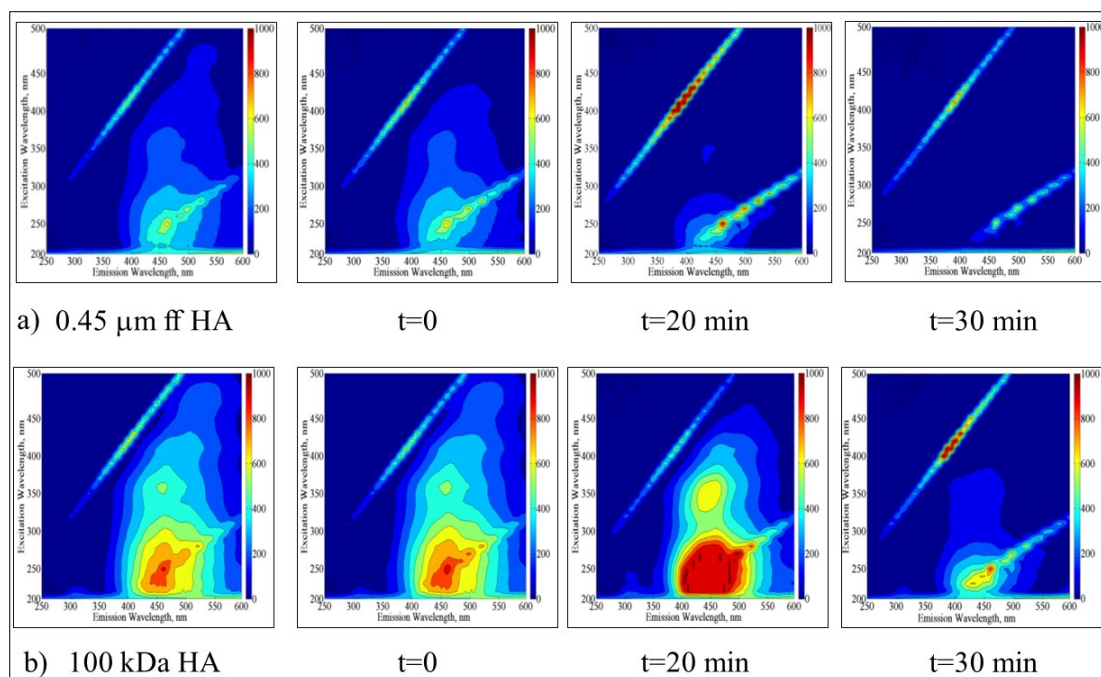


Fig. S1 Time dependent EEM fluorescence contour plots of 0.45 μm ff HA (a) and 100 kDa HA (b) upon photocatalytic treatment by using ZnO.

Following initial adsorption of 0.45 μm ff HA onto ZnO, the presence of humic-like and fulvic-like fluorophores was still evident up to irradiation period of 20 min. Upon further irradiation conditions, EEM contour plots were found to be devoid of any fluorescence signatures. However, following an initial adsorption of 100 kDa HA onto ZnO, the presence of humic-like and fulvic-like fluorophores were still evident and displayed considerably higher fluorescence intensities even up to irradiation period of 20 minutes in comparison to 0.45 μm ff HA. Upon further irradiation periods, humic-like and fulvic-like fluorophores were still present for 100 kDa HA.

Based on the above given information, it could be deduced that using humic acid and its sub molecular size fractions as representatives of NOM should be cautiously interpreted in elucidation of the photocatalytic activity of a novel photocatalyst.