A COMPARATIVE APPROACH TO SURFACE INTERACTIONS BETWEEN MOLECULAR SIZE FRACTIONS OF HUMIC ACID AND ANION DOPED TITANIA BINARY SYSTEM

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ABSTRACT

In this study, surface interactions between different molecular size fractions of humic acid (0.45 µm filtered fraction, 100 kDa fraction and 30 kDa fraction) and two commercially available bare and anion doped titanium dioxide (TiO_2) suspensions (Degussa P-25 and Hombikat UV-100) in the range of 0.1-1.0 mg mL^{-1} were comparatively evaluated.

Adsorption properties of humic acid (HA) and its molecular size fractions onto bare TiO_2 and anion doped TiO_2 specimens were evaluated and compared in terms of UV-vis spectroscopic parameters *i.e.* color forming moieties ($Color_{436}$) and UV absorbing centers (UV_{365}, UV_{280} and UV_{254}) and respective specific UV-vis parameters (SCoA, $SUVA_{365}$, $SUVA_{280}$, and $SUVA_{254}$) and also fluorescence spectroscopy in emission and synchronous scan modes as well as dissolved organic carbon (DOC, mgL^{-1}). In equilibrium studies, the data obtained by adsorption experiments were evaluated by Freundlich, Langmuir and Dubinin-Radushkevich isotherm models.

Freundlich, Langmuir and Dubinin-Radushkevich isotherm model parameters of DOC for all of molecular size fractions of HA following adsorption onto bare and anion doped TiO_2 P-25 and UV-100 specimens displayed significantly differences. The reason could be attributed to the role of the functional groups (fluorophoric and chromophoric groups) existing in the diverse molecular size fractions of HA. Assessment of the consequences obtained from different molecular size fractions of HA pointed out remarkable diversities both with respect to the type of dopant and also to the morphological character of TiO_2 specimens.

Keywords: humic acids, anion-doped TiO_2, natural organic matter, photocatalysis, adsorption

1. Introduction

The most spread natural organic matter (NOM) existed in the water supplies is humic substances (HS), which are anionic hydrophobic macromolecules having surface functional groups containing carboxylic and phenolic groups (Moussavi *et al*., 2011). HA that is widespread in the soil and water sources especially in the ground water brings about some major issues such as developing colour in water source and occurring disinfection by products (DBPs) during chlorination process in the treatment systems. Because of these problems, the removal of HA from water sources has gained much attention (Suffet and MacCarthy, 1989). Extensive studies have been performed concerning the removal methods of NOM in natural waters by using the application of photocatalysis by Bekbolet and co-workers (Uyguner and Bekbolet, 2009).

TiO_2, which is employed as a standard photocatalyst, is a wide band gap semiconductor that has been extensively investigated and applied to a wide spectrum of chemical disciplines. Aside from its excellent pigmentary properties, titanium dioxide, as a chemical has dielectric features, high ultraviolet absorption, high stability, relative chemical and biological inertness, non-toxicity, high photocatalytic efficiency, relatively inexpensive and commercially available in various crystalline forms as well as strong oxidation activity which allow it to be used in special applications, such as electroceramics, glass, deodorization, sterilization, air purification, anti-fouling and mist removal as well as wastewater treatment (Balzani and Scandola, 1991; Sayle *et al*., 1995; Zaleska, 2008, Sato *et al*., 2005; Yu *et al*., 2006; Xekoukoulokatis *et al*., 2010). The most outstanding obstacle as to TiO_2 photocatalyst is that it can only benefit from UV light in its photoactivation because of its wide band gap. However, solar light attaining the surface of the earth includes approximately 3 to 5 % UV light (Xekoukoulokatis *et al*., 2010; Rashed and El-Amin, 2007; Tryba *et al*., 2009). The ultraviolet region can be identified as zone in which is small from 5 % of the overall solar intensity (Anandan *et al*., 2008). One of the remarkable solutions to decrease the band gap energy of TiO_2 is doping with non-metallic elements such as carbon, nitrogen, and sulfur either as mono- or co-doped states (Yalcin *et al*., 2010). Because of the surface oriented nature of photocatalysis, adsorption of the substrate onto TiO_2 plays an important role in degradation process. Hence, adsorption of HA onto bare TiO_2 and anion doped TiO_2 powders needs to be explored provided that the adsorbent dose should resemble the photocatalytically active range of TiO_2 (Akan *et al*., 2015). Consequently, the fundamental objective of this study was to comparatively evaluate adsorption properties between HA subfractions and two commercially available bare and anion doped TiO_2 suspensions (Degussa P-25 and Hombikat UV-100).

2. Materials and methods

HA was purchased from Aldrich. Detailed information relating to materials and methods used in this study was presented by Akan and co-workers (Akan *et al*., 2015). Briefly, HA (20 mgL^{-1} for 0.45 µm filtered fraction as well as 50 mgL^{-1} for 100 kDa and 30 kDa fraction) and TiO_2 (0.1 – 1.0 mg mL^{-1}) concentrations were kept constant throughout the experimental study. TiO_2 Degussa P-25 provided from Evonik Corp. (Germany) (crystal structure: 80% anatase and 20% rutile, nonporous, BET surface area (SA): 55 ± 15 m^2 g^{-1}, average particle size: 30 nm, density: 3.8 g mL^{-1}) and TiO_2 Hombikat UV-100 (Sachtleben Chemie) (crystal structure: 100% anatase, porous, BET surface area: > 250 m^2g^{-1}, average particle size: <10 nm, density: 3.9 gmL^{-1}) were used as the adsorbent. Batch adsorption experiments were implemented in accordance with a previously outlined procedure (Akan *et al*., 2015). After each run, the absorption of supernatant was determined using Perkin Elmer Lambda 35 UV-vis double beam spectrophotometer with Hellma quartz cuvettes of 1.0 cm optical path length at 436 nm ($Color_{436}$, m^{-1}), 365 nm (UV_{365}, m^{-1}) and 280 nm (UV_{280}, m^{-1}) as well as 254 nm (UV_{254}, m^{-1}). Specified UV-vis parameters measured at 254 nm (UV_{254}), 365 nm (UV_{365}) and 280 nm (UV_{280}) were used to display aromaticity removal, while 436 nm ($Color_{436}$) was employed to explain the removal of color forming groups. Non-Purgeable Organic Carbon (NPOC) measurements of HA solutions were carried out with a Shimadzu TOC Vwp Total Organic Carbon Analyzer. NPOC was expressed simply as DOC, mg OrgC L^{-1}. Properties of bare and anion doped TiO_2 specimens were given in Table 1.

Table 1: Properties of bare and anion-doped TiO_2 specimens

TiO_2 specimens	pH_{zpc}	Crystallite size, nm
Bare Degussa P-25	6.25	22.3
Bare Hombikat UV-100	6.30	16.6
C-doped Degussa P-25	6.01	20.8
N-doped Degussa P-25	5.15	18.8
N-doped Hombikat UV-100	5.23	13.7
S-doped Degussa P-25	5.38	18.5
S-doped Hombikat UV-100	5.23	14.1
N-S co-doped Degussa P-25	5.61	16.9
N-S co-doped Hombikat UV-100	5.42	13.8

Specified and specific parameters of 0.45 µm filtered fraction, 100 kDa fraction and 30 kDa fraction of HA were previously reported by Akan and co-workers (Akan *et al*., 2015).

3. Results

The effect of the doping on two TiO_2 specimens (Degussa P-25 and Hombikat UV-100) could be evaluated through the role of decreasing molecular size of humic acid. The most significant effect could be attributed to the surface properties of TiO_2 specimens present in aqueous solutions of humic acid.

3.1. Spectroscopic Properties of Diverse Molecular Size Fractions of Humic Acid Following Adsorption onto TiO_2 Specimens

Humic acid and its molecular size fractions were characterized with spectroscopic analyses including UV-vis spectroscopy and fluorescence spectroscopy. The aim of the application of UV-vis and fluorescence spectroscopy was to elucidate the composition organic matter (Knapik *et al.*, 2011). UV-vis spectrum of HA is generally broad, does not demonstrate any peak properties and monotonously diminish with increasing wavelength (Uyguner and Bekbolet, 2005).

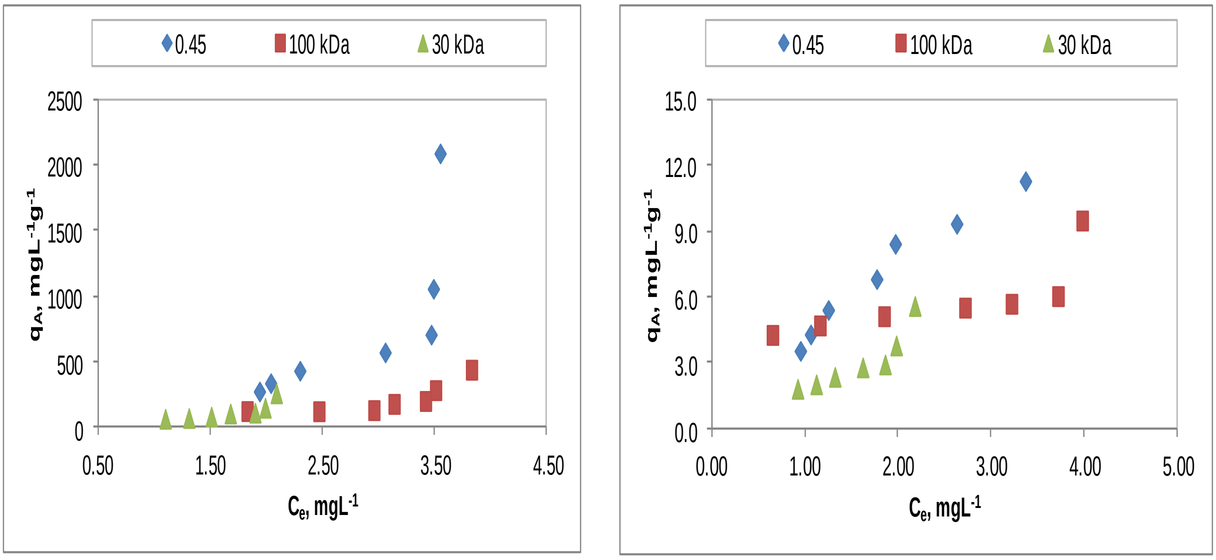
UV-vis absorbance values of all of molecular size fractions of HA were analyzed between 200-600 nm wavelength region. UV-vis absorbance values of HA with diverse molecular size fractions decreased with increasing wavelength and they levelled off after 450 nm. UV-vis absorbance values recorded at wavelengths longer than 400 nm expressed the presence of conjugated systems and chromophoric groups displaying color, it could be seen that the humic acid molecular size fractions displayed lower color properties. Through ultrafiltration process, UV-vis absorbance values of HA exhibited a decreasing trend due to decreasing molecular size (Uyguner and Bekbolet, 2005). A decreasing trend was observed among UV-vis absorbance values of distinct molecular size fractions of HA as 0.45 μm filtered fraction > 100 kDa fraction > 30 kDa fraction. Emission scan fluorescence spectra and synchronous scan fluorescence spectra of all of molecular size fractions of HA displayed that fluorescence intensity decreased as a result of decreasing molecular size fractions of HA. Comparison of UV-vis spectral features of 0.45 μm filtration fraction of humic acid with lower molecular size fractions of humic acid recorded following adsorption onto two bare TiO_2 specimens (Degussa P-25 and Hombikat UV-100) indicated that the influence of pure anatase form (Hombikat UV-100) was more pronounced with respect to the presence of mixed crystal phases (Degussa P-25) in the UV region. On the other hand, no remarkable differences could be visualized in the visible region. Chromophoric as well as fluorophoric groups of humic acid could be stated by the UV-vis and fluorescence spectral features. Fluorescence spectral features attained either upon emission scan mode or synchronous scan mode displayed an inconsistent trend with respect to the molecular size of humic acid. These results indicated that fluorescence intensities should be regarded as specific for characterization of humic acid but non-specific in terms of quantification of humic acid. It should also be indicated that UV-vis parameters could well serve as indicative parameters of humic chromophores that played significant effects in adsorptive interactions.

3.2. Adsorption Isotherm Modelling

Adsorption isotherms with different molecular size fractions such as 0.45 μm filtered fraction, 100 kDa fraction and 30 kDa fraction of HA onto bare TiO_2 and anion doped TiO_2 (N-doped TiO_2, S-doped TiO_2, C-doped TiO_2 and N-S co-doped TiO_2) specimens were presented. Adsorption isotherms were modelled to Freundlich, Langmuir and Dubinin- Radushkevich adsorption isotherm models by using DOC parameter.

From a general perspective with one exception, adsorption isotherms of all of molecular size fractions of HA onto N-S co-doped TiO_2 Hombikat UV-100 and adsorption isotherms of 100 kDa and 30 kDa fractions of HA onto N-S co-doped TiO_2 Degussa P-25 displayed C-type isotherm. The exception was 0.45 μm filtered fraction of HA onto N-S co-doped TiO_2 Degussa P-25 displaying S-type isotherm (Figure 1).

All of the adsorption isotherms were fitted to Freundlich (K_f and 1/n), Langmuir (K_L and q_{max}) and also Dubinin-Radushkevich (q_{max}, β and E) adsorption isotherm models ($R^2 > 0.84$). Adsorption isotherm model parameters in terms of DOC are presented in Table 2.



(A) (B)

Figure 1: Adsorption isotherms of different molecular size fractions of HA onto (A): N-S co-doped TiO_2 Degussa P-25, (B): N-S co-doped TiO_2 Hombikat UV-100.

Freundlich, Langmuir and Dubinin- Radushkevich adsorption isotherm model parameters for all of molecular size fractions of HA following adsorption onto bare and anion doped TiO_2 specimens exhibited outstanding diversities owing to functional groups particularly chromophoric groups existing in subfractions of HA and also the morphological features of TiO_2 specimens.

Comparison of Freundlich adsorption isotherm model parameters with respect to the results obtained from 30 kDa fraction of HA following adsorption onto C-doped TiO_2 P-25 and C-doped TiO_2 UV-100 indicated similar adsorption intensity factors (1/n) representing strong concentration dependency of molecular size fractions of HA. The highest K_F (4.55) and the lowest intensity factor (1/n=0.204) was attained for 100 kDa molecular size fraction of HA onto N-S co-doped TiO_2 Hombikat UV-100. Similarly, the highest K_L (2.06) was also attained for 100 kDa molecular size fraction of HA onto N-S co-doped TiO_2 Hombikat UV-100. The lowest K_L (0.0240) was also attained for 100 kDa molecular size fraction of HA following adsorption onto S doped TiO_2 Hombikat UV-100. These results could be attributed to the role of anion doping onto surface features of TiO_2 specimens. Comparative presentation of attained results using Langmuir and Dubinin Radushkevich model for q_{max} value indicated that 30 kDa fraction of HA following adsorption onto N-doped TiO_2 Hombikat UV-100 displayed the lowest q_{max} value in Langmuir model contrary to Dubinin Radushkevich. According to Dubinin Radushkevich adsorption isotherm parameters, out of the four values, the value of E (E = 4.25-7.81 kJ mol^{-1}) signified that the fundamental mechanism of the adsorption of different molecular size fraction of HA onto bare and anion-doped TiO_2 specimens could be attributed to physical forces. The exceptions were adsorption of 30 kDa fraction of HA onto S-doped TiO_2 UV-100 (E =12.3 kJ mol^{-1}) and adsorption of 100 kDa fraction of HA onto N-doped TiO_2 P-25 and onto N-S co-doped TiO_2 UV-100 (E = 11.3 kJ mol^{-1} and 17.1 kJ mol^{-1}, respectively) as well as adsorption of 0.45 µm filtered fraction of HA onto C-doped TiO_2 UV-100 (E = 8.51 kJ mol^{-1}) exhibiting that chemical forces could be accounted for the surface interactions. All E values being less than 8 kJ mol^{-1} expressing the role of physical forces could be related to the pH_{zpc} condition of the bare as well as doped TiO_2 specimens. Since the working pH of the solutions was pH 6.7 ± 0.2 being greater than pH_{zpc} of all TiO_2 specimens, the surface of all of the TiO_2 specimens would attain more positively charged centers. Furthermore, under these conditions carboxylic groups existing in humic subfractions would be deprotonated acquiring negative charge leading to electrostatic interactions (Akan *et al*., 2015).

Table 2: Adsorption isotherm model parameters expressed in terms of DOC (R^2>0.84)

System	Adsorption isotherm model parameters						
	Freundlich model		Langmuir model		Dubinin Radushkevich		
	K_F	1/n	K_L	q_{max}	q_{max}	β	E
0.45 µm filtered fraction							
Bare TiO_2 P-25	2.71	1.49	0.150	17.1	5.154	1.40x10^{-8}	5.98
Bare TiO_2 UV-100	1.64	1.31	0.0754	23.1	1469	1.27x10^{-8}	6.27
C-doped TiO_2 P-25	1.40	2.37	0.208	10.4	369.165	2.34x10^{-8}	4.62
C-doped TiO_2 UV-100	4.07	0.746	0.167	27.8	171	6.90x10^{-8}	8.51
N-doped TiO_2 P-25	1.22	0.797	0.0469	22.5	109	8.65x10^{-8}	7.60
N-doped TiO_2 UV-100	0.520	2.36	0.201	4.29	122838	2.31x10^{-8}	4.65
S-doped TiO_2 P-25	1.15	1.78	0.122	13.1	11.992	1.73x10^{-8}	5.38
S-doped TiO_2 UV-100	3.10	1.37	0.158	16.9	2892	1.27x10^{-8}	6.27
N-S co-doped TiO_2 P-25	1.50	2.31	0.191	12.5	232.815	2.23x10^{-8}	4.74
N-S co-doped TiO_2 UV-100	4.11	0.883	0.0851	48.0	495	8.20x10^{-8}	7.81
100 kDa fraction							
Bare TiO_2 P-25	1.70	1.70	0.172	10.2	10.027	1.61x10^{-8}	5.57
Bare TiO_2 UV-100	2.81	1.32	0.0428	70.9	1978	1.21x10^{-8}	6.43
C-doped TiO_2 P-25	0.531	1.67	0.146	3.47	186	9.70x10^{-8}	7.18
C-doped TiO_2 UV-100	0.894	2.15	0.191	6.46	52628	2.04x10^{-8}	4.95
N-doped TiO_2 P-25	3.53	0.406	0.651	8.45	28	3.90x10^{-8}	11.3
N-doped TiO_2 UV-100	1.36	1.32	0.0798	18.0	1276	1.28x10^{-8}	6.25
S-doped TiO_2 P-25	1.39	1.24	0.128	8.17	6.438	1.68x10^{-8}	5.46
S-doped TiO_2 UV-100	2.07	1.05	0.0240	95.2	453	1.00x10^{-8}	7.07
N-S co-doped TiO_2 P-25	0.873	1.63	0.187	3.25	527.023	2.77x10^{-8}	4.25
N-S co-doped TiO_2 UV-100	4.55	0.204	2.06	6.61	12	1.70x10^{-8}	17.1
30 kDa fraction							
Bare TiO_2 P-25	0.894	0.962	0.0269	34.1	112	0.90x10^{-8}	7.45
Bare TiO_2 UV-100	0.326	1.96	0.240	1.35	4832	1.77x10^{-8}	5.31
C-doped TiO_2 P-25	0.926	1.01	0.0447	22.6	145	9.40x10^{-8}	7.29
C-doped TiO_2 UV-100	0.663	1.12	0.211	3.09	5151	1.66x10^{-8}	5.49
N-doped TiO_2 P-25	1.20	1.90	0.284	3.35	13.561	1.73x10^{-8}	5.38
N-doped TiO_2 UV-100	0.773	2.44	0.334	2.03	133252	2.23x10^{-8}	4.74
S-doped TiO_2 P-25	2.09	0.611	1.37	3.67	13	3.30x10^{-8}	12.3
S-doped TiO_2 UV-100	1.12	1.86	0.270	3.41	10840	1.70x10^{-8}	5.42
N-S co-doped TiO_2 P-25	1.15	1.79	0.216	4.81	777	1.18x10^{-8}	6.51
N-S co-doped TiO_2 UV-100	1.80	1.11	0.132	14.0	408	1.00x10^{-8}	7.07

4. Conclusions

In this study, spectroscopic properties and adsorption properties of different molecular size fractions of HA (0.45 µm filtered fraction, 100 kDa fraction and 30 kDa fraction) onto commercially diverse type of TiO_2, namely Degussa P-25 and Hombikat UV-100 were elucidated in order to evaluate surface interactions between diverse molecular size fractions of HA and TiO_2 specimens, namely bare TiO_2 and anion-doped TiO_2 specimens. In other words, the effect of doping on two TiO_2 specimens (Degussa P-25 and Hombikat UV-100) could be evaluated through the role of decreasing molecular size of HA. The most significant effect could be attributed to the surface properties of TiO_2 specimens present in aqueous solutions of humic acid. It should also be indicated that depending on the pH_{zpc} condition, positively and negatively charged surface sites developed and played significant roles on the adsorptive properties of the deprotonated humic functional groups.

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