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Spectroscopic evaluation of humic acid adsorption onto TiO_2 in the presence of clay minerals

Sibel Sen-Kavurmaci*, Miray Bekbolet

Institute of Environmental Sciences, Bogazici University, Bebek, Istanbul 34342, Turkey, Tel. +90 212 359 7145; Fax: +90 212 257 5033; emails: sibel.sen@boun.edu.tr (S. Sen-Kavurmaci), bekbolet@boun.edu.tr (M. Bekbolet)

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ABSTRACT

Adsorption of humic acid (HA) onto TiO_2 in the presence of clay minerals should be investigated to provide information for understanding of photocatalytic behavior of HA. In accordance with previous studies, adsorption of HA onto TiO_2 in the presence of clay minerals, i.e. kaolinite (Kt) or montmorillonite (Mt) was further elucidated by using UV–vis and fluorescence spectroscopic parameters. Moreover, in the presence of clay particles, effect of Ca^{2+} ions was also assessed in comparison with the conditions attained in the presence of sole TiO_2. Adsorption of HA onto TiO_2 could well be explained by the changes in the UV–vis spectral features in relation to the successful elimination of the dissolved organic carbon. Specific UV–vis parameters (m^{-1} $mg^{-1}L$) as SCoA, $SUVA_{365}$, $SUVA_{280}$, and $SUVA_{254}$ displayed variations depending on TiO_2. Although no definite discrimination was attained with respect to the individual effect of each clay type, a distinct influence was observed in the presence of Ca^{2+} ions. Fractional UV–vis parameters (E_{254}/E_{365}, E_{254}/E_{436}, E_{280}/E_{365}, E_{280}/E_{436}, and E_{365}/E_{436}) indicating the removal of color-forming groups in relation to the removal of UV-absorbing centers showed variations with respect to the TiO_2 dose. Regarding the changes in the specific UV–vis parameters, it could be indicated that the HA adsorption mechanism was significantly different in the presence of either Kt or Mt. Furthermore, as a correlative approach, fluorescence-derived index defined as fluorescence intensity (FI) was successfully employed. FI values were correlated to the specified UV–vis parameters revealing an inverse relationship.

Keywords: Adsorption; Humic acid; Kaolinite; Montmorillonite; UV–vis and fluorescence spectroscopic properties

1. Introduction

It is very well documented that dissolved organic matter (DOM) represents the largest pool of reduced organic carbon in aquatic ecosystems [1]. Humic substances, mainly acid-insoluble fraction as humic acids (HA) constitute the major part of DOM. Clay minerals which are responsible for the transport of both inorganic and organic contaminants are defined as the main part of the suspended solid material in natural waters. Humic substances could form strong complexes with clay minerals [2]. HA in drinking

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*Corresponding author.

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water has been associated with several adverse properties including imparting undesirable esthetic problems, i.e. color, taste, and odor, increasing treatment chemical demands and forming disinfection by-products [3]. In order to eliminate many health-related contaminants, removal of both suspended colloidal particles and organic matter constitute the major concern of drinking water authorities. Due to the refractory nature of the natural organic matter, besides the conventional treatment methods, application of advanced oxidation processes has also been considered as effective for removal of organic matter [4–11]. Among various semiconductor materials, TiO_2 has been proven to be the most powerful photocatalyst so far [12]. Degradation of HA by TiO_2 photocatalysis in the presence of clay particles representing phyllosilicates displaying different layer types, i.e. kaolinite (Kt, 1:1 type) and montmorillonite (Mt, 2:1 type) has also been investigated by the authors [13,14].

Spectral properties of humic substances have been studied extensively due to the presence various chromophoric groups of the complex organic matrix [15]. HAs express characteristics in the ultraviolet–visible (UV–vis) region as decreasing absorption with increasing wavelength in an approximately near-exponential trend in the range of UVA–UVC [16,17]. The spectral shape could be explained by either charge transfer interactions within aromatic moieties or superposition of independent chromophores. The presence of unsaturated carbon centers with delocalized lone pair of electrons usually imparts a distinct yellowish color to the water, and UV–vis light spectroscopy could therefore be used to estimate the absorbing compound properties as well as removals by treatment [18,19]. Under non-oxidative conditions, UV–vis spectroscopic profiles of model HAs could express featureless trend with respect to increasing wavelength irrespective of the source and origin of the substrates [5,18,19]. Changes in UV–vis properties of HA could also be characterized by the ratio of the absorbances [19,20]. Fractional UV–vis absorbance parameters (i.e. E_{254}/E_{365}; E_{254}/E_{436}; E_{280}/E_{365}; E_{280}/E_{436}; and E_{365}/E_{436}) were also investigated in relation to the previously reported results attained under oxidative conditions [13]. UV–vis properties of DOM as well as HA have been extensively used for the understanding of the changes in organic matter under various treatment conditions [9,21].

Besides UV–vis spectroscopic features, DOM exhibits fluorescence properties via absorption of high-energy photons and re-emission of lower energy photons at longer wavelengths [22]. Fluorescence spectroscopic properties could also display further information on the humic structural changes upon various treatment conditions as well as by adsorption [18,23]. With reference to the natural water colloidal systems, effect of clay particles on the adsorption of HAs deserves to be investigated. Isotherm modeling of the natural colloidal system composed of HA and either Kt or Mt adsorption onto TiO_2 has been previously studied by Sen Kavurmaci and Bekbolet [24]. Furthermore, adsorption of HA onto TiO_2 is a crucial step in photocatalysis since the initiation of photocatalytic degradation process strongly depends on the adsorption of HA on the surface of TiO_2. For this reason, adsorption of HA onto TiO_2 should be considered as an important issue for the elucidation of the efficiency of photocatalytic degradation. In this study, a complementary approach is presented indicating the use of the specific UV–vis as well as fluorescence spectroscopic properties to provide a further insight to the adsorption properties of HA onto TiO_2 in the presence of either Kt or Mt. Considering the ionic strength effect on the clay–humic–TiO_2 system, the role of calcium ions was also investigated.

2. Experimental

2.1. Materials

HA (supplied from Aldrich) solution ($50\,\mathrm{mg\,L^{-1}}$) was prepared by dilution of the stock solution ($1{,}000\,\mathrm{mg\,L^{-1}}$) using ultra pure water (Millipore Milli-Q system resistivity of $18.2\,\mathrm{M\Omega\,cm}$ at 25˚C). Titanium dioxide (P-25, Evonik) was used as the adsorbent. Kt and Mt were supplied from the Clay Minerals Society, Source Clays Repository (West Lafayette, IN). Montmorillonite (Mt, cation exchange capacity (CEC): 120 meq $100\,\mathrm{g^{-1}}$, and N_2-BET surface area: 97.42 $\mathrm{m^2\,g^{-1}}$) and kaolinite (Kt, CEC: 2.0 meq $100\,\mathrm{g^{-1}}$, and N_2-BET surface area: $10.02\,\mathrm{m^2\,g^{-1}}$) were used. Aqueous Ca^{2+} solution was prepared in the concentration range varying from 5×10^{-4} to 5×10^{-3} M by using $Ca(NO_3)_2$.

2.2. Methods

Batch adsorption experiments: TiO_2 concentration was selected in the range from 0.1 to 1.0 $\mathrm{mgmL^{-1}}$ for a fixed HA concentration ($50\,\mathrm{mg\,L^{-1}}$). Kt or Mt concentration was selected as 0.2 $\mathrm{mgmL^{-1}}$. TiO_2, Kt, and Mt concentrations were chosen in accordance with the formerly reported studies [14]. Equilibration time was found to be 16 h; however, for practical reasons, all of the adsorption experiments were run for 24 h. Centrifugation, followed by filtration through 0.45 μm membrane filters, was applied for the removal of the suspended material (TiO_2, Kt, or Mt) from the aqueous medium. Experiments were carried out for the following cases: (i) HA adsorption onto sole TiO_2, (ii) HA adsorption onto TiO_2 in the presence of Kt, and (iii) HA adsorption onto TiO_2 in the presence of Mt. All of these experiments were also performed in the presence of Ca^{2+} ions. All of the adsorption experiments were run in duplicate, and the average results (±5%) were further evaluated. Under all conditions, pH was 6.5 ± 0.5.

2.3. HA measurements

UV–vis absorbance spectra were recorded in the wavelength range of 200–600 nm by using Perkin–Elmer Lambda 35 UV–vis spectrophotometer. Fluorescence spectroscopic measurements were conducted using a Perkin–Elmer LS55 Luminescence spectrometer. Samples were analyzed using a 1-cm quartz cell, which was rinsed with deionized water prior to each analysis. Dissolved organic carbon (DOC) (mgL^{-1}) was measured using Total organic carbon analyzer (Shimadzu TOC-VWP). DOC contents were reported as a mean value of three valid measurements with an error of ≤5%.

2.4. Specified and specific humic parameters

Parameters used for the elucidation of the adsorption properties of HA onto TiO_2 both in the absence and presence of clay minerals, i.e. Kt or Mt as well as Ca^{2+} ions were selected by UV–vis spectral properties. Specified UV–vis parameters were absorbance measurements recorded at the following wavelengths as 436 nm ($Color_{436}$), 365 nm (UV_{365}), 280 nm (UV_{280}), and 254 nm (UV_{254}) [18]. Correspondingly, specific UV–vis parameters (m^{-1} $mg^{-1}L$) were defined as follows: SCoA as $Color_{436}/DOC$, $SUVA_{365}$ as UV_{365}/DOC, $SUVA_{280}$ as UV_{280}/DOC, and $SUVA_{254}$ as UV_{254}/DOC. Fractional UV–vis parameters were displayed by the following ratios where for practical reasons, E term designated either UV or Color, i.e. E_{254}/E_{365}; E_{254}/E_{436}; E_{280}/E_{365}; E_{280}/E_{436}; and E_{365}/E_{436}. HA solution was prepared in concentration of 50 mg L^{-1} with a DOC content of 17.00 mg L^{-1} expressed $Color_{436}$: 23.9 m^{-1}; UV_{365}: 46.5 m^{-1}; UV_{280}: 46.5 m^{-1}; and UV_{254}: 119.9 m^{-1}.

3. Results and discussion

HA DOC adsorption onto TiO_2 in the presence of clay minerals either Kt or Mt revealed completely different trends as further evaluated by the spectroscopic parameters.

3.1. Evaluation of HA adsorption by specific UV–vis absorbance parameters

HA adsorption onto sole TiO_2 and TiO_2 in the presence of either Kt or Mt were evaluated by using specific UV–vis parameters. Adsorbent dose-dependent variations attained in the absence and presence of Ca^{2+} ions were presented Fig. 1(A–C) and Fig. 2(A–C), respectively. All of the specific UV–vis parameters displayed slight variations irrespective of the dose of TiO_2 and clay type resulting from adsorptive interactions (Fig. 1(A–C)). However, all of the specific UV–vis parameters exhibited significant variations with clay type resulting from adsorptive interactions of HA in the presence of Ca^{2+} ions (Fig. 2(A–C)).

Based on the significance of $SUVA_{254}$ expressing the aromaticity of the humic fraction, specific UV–vis parameters were investigated [25]. Edzwald and colleagues reported that $SUVA_{254} > 4$ indicated the presence of mainly hydrophobic and aromatic humic moieties whereas for $SUVA_{254}$ ratios in the range of 2–4, humic matrix was normally dominated with a mixture of hydrophobic and hydrophilic fractions. $SUVA_{254} < 2$ significantly represented hydrophilic properties [26]. It could be visualized from Fig. 1(A–C) that under all conditions in the absence of Ca^{2+} ions, $SUVA_{254}$ values were higher than four, whereas in the presence of Ca^{2+} ions, were well less than four for HA

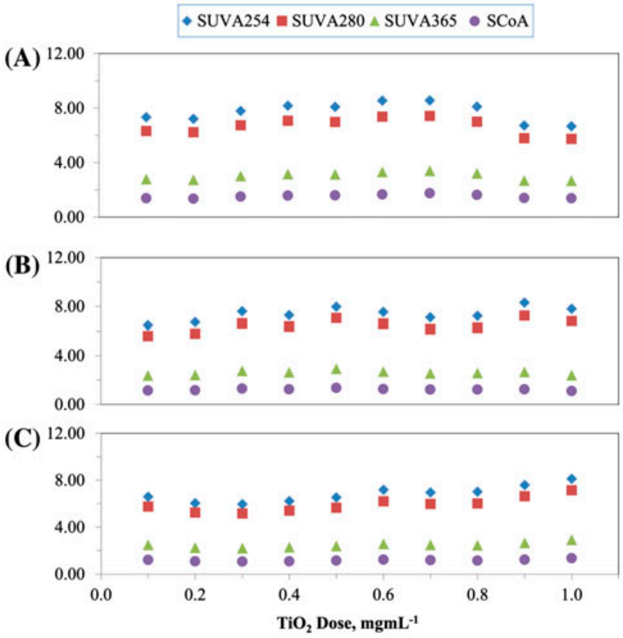

Fig. 1. Specific UV–vis parameters of HA following adsorption onto sole TiO_2 (A), TiO_2 and Kt (B), and TiO_2 and Mt (C).

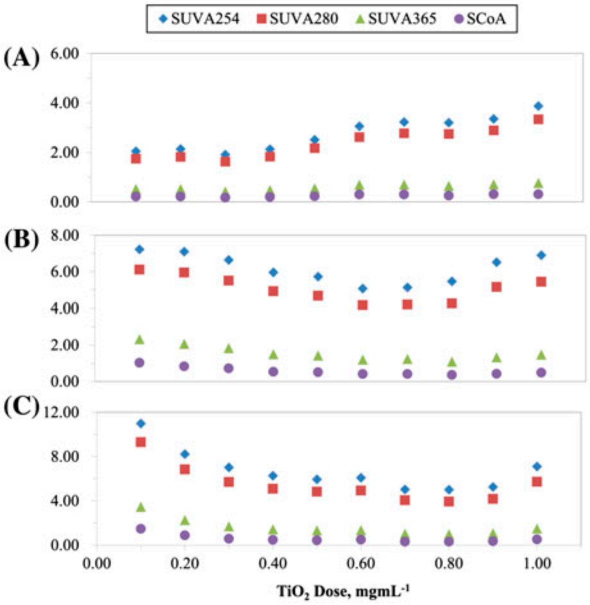

Fig. 2. Specific UV–vis parameters of HA following adsorption onto sole TiO_2 (A), TiO_2 and Kt (B), and TiO_2 and Mt (C) in the presence Ca^{2+} ions.

adsorption onto sole TiO_2 (Fig. 2(A)). It should be indicated that the presented specific UV–vis parameters expressed the properties of HA remaining in aqueous solution following adsorption.

The lowest $SUVA_{254}$ was determined in the presence of 0.3 $mgmL^{-1}$ of sole TiO_2 that represented the applicable dose to be used for photocatalytic treatment [18] (Fig. 2(A)). However, the continuously increasing trend of specific parameters with respect to increasing sole TiO_2 dose could not be observed in the presence of clay particles. The lowest $SUVA_{254}$ was recorded for TiO_2 dose of 0.7 $mgmL^{-1}$ for both of the clay types (Fig. 2(B–C)). Considering the applied dose of TiO_2 as 0.5 $mgmL^{-1}$ in photocatalytic degradation experiments, the removal of the UV-absorbing centers could be related to the surface humic properties attained by adsorption prior to photocatalysis [13,14].

The effect of Ca^{2+} ions through electrostatic interactions was more pronounced in the presence of Kt in comparison with Mt. Considerably higher $SUVA_{280}$ and $SUVA_{254}$ indicated the dominating aromatic character of the residual HA fractions. Surface interactions of HA with sole TiO_2 resulted in successive removal of color-forming moieties rather than the counterpart's inner structural core aromatic domains with respect to the removals of DOC, under the specified adsorbent dose range. A plausible reason could be attributed to the prevailing electrostatic attractions between the charged humic functional groups and exposed surfaces of TiO_2, Mt, and Kt. Concurrently, by the removal of the color-forming moieties, the resultant effect could well be visualized by the changes attained in SCoA as well as $SUVA_{365}$. A plausible explanation could also be related to the conformational changes of humic sub-fractions resulting from adsorptive interactions. The adsorbed humic fractions might undergo reformations through "train loop and tails" style prior to the successive removal by filtration [27]. Moreover, it should also be considered that HAs did not express monolayer coverage due the complexicity of their 3D structure [28]. Therefore, removal of humic UV–vis parameters should be interpreted as elimination of UV–vis absorbing centers in accordance with DOC.

From the molecular size diversity point of view, since HAs are composed of various molecular size fractions, further fractionation might simultaneously be taking place upon interaction with oxide surfaces as well as colloidal particles, e.g. clay [29,30]. Through electrostatic interactions co-precipitation of lower molecular size fractions by Ca bridging would also affect the removal of the UV–vis parameters.

Absorption of UV light by HA is caused by π-electrons and expresses conjugated aromatic systems, whereas functional groups with quinoide structures and keto-enol systems are more responsible for the visible light absorption [19]. Various absorption wavelengths at 254, 280, 365, 436, and 465 nm as well as ratios like E2/E3 (e.g. UV_{254}/UV_{365}), E3/E4 (e.g. UV_{365}/UV_{436}) have been reported as suitable parameters the spectral differentiation of humic substances [18,19]. In a similar manner, E_{254}/E_{365}; E_{254}/E_{436}; E_{280}/E_{365}; E_{280}/E_{436}; and E_{365}/E_{436} parameters have been selected for the possible differentiation of the prevailing systems under various conditions (Fig. 3(A–C)).

Fig. 3A demonstrated the changes attained in the fractional UV–vis parameters of HA following adsorption onto TiO_2 in the presence of Kt or Mt. E_{254}/E_{436} and E_{280}/E_{436} ratios displayed the most significant variations for HA in the presence of Kt. The reason could be attributed to the predominant role of the aromatic domains represented by UV_{254} and UV_{280} parameters with respect to the color-forming moieties ($Color_{436}$). Slight variations were observed for higher doses of TiO_2 (>0.7 $mgmL^{-1}$) in the presence of clay particles being more pronounced in the presence of Kt in comparison with Mt (Fig. 3(B–C)). From a general perspective, a plausible explanation would be attributed to the concurrent removal of the UV–vis parameters via adsorptive interactions.

Fig. 4(A–C) presented the alterations in the fractional UV–vis parameters of HA upon adsorption onto TiO_2 and either Kt or Mt in the presence of Ca^{2+} ions.

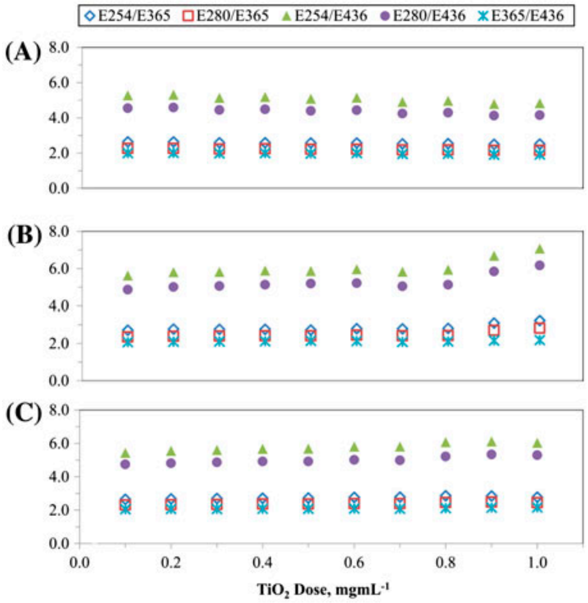

Fig. 3. Fractional UV–vis parameters of HA following adsorption onto sole TiO_2 (A), TiO_2 and Kt (B), TiO_2 and Mt (C).

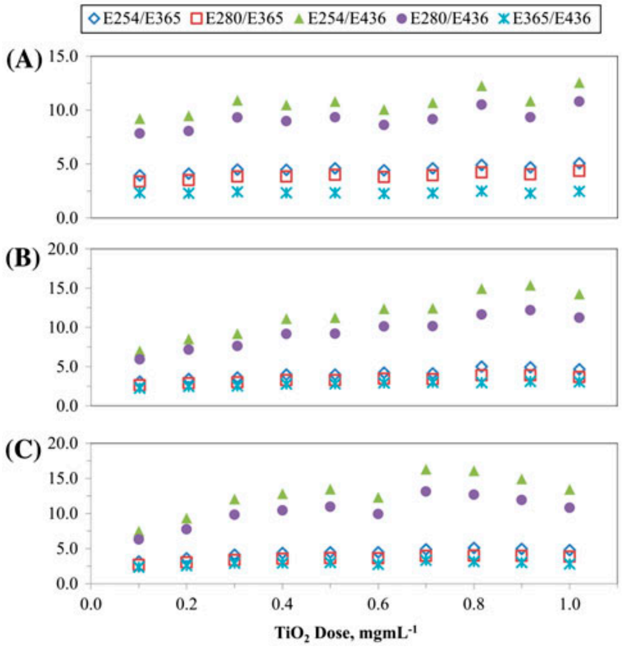

Fig. 4. Fractional UV–vis parameters of HA following adsorption onto sole TiO_2 (A), TiO_2 and Kt (B), and TiO_2 and Mt (C) in the presence Ca^{2+} ions.

The most remarkable differences were attained for E_{254}/E_{436} and E_{280}/E_{436} revealing a differentiation between sole TiO_2 and TiO_2–clay systems in the presence of Ca^{2+} ions. The reason could be related to the competitive interaction mechanism prevailing between humic functional groups, TiO_2, Mt, Kt, and Ca^{2+} ions. UV-absorbing centers (UV_{254}) in accordance with the color-forming moieties ($Color_{436}$) of humic sub-fractions displayed the major effect on the adsorption mechanism. Considering the neutral pH conditions, due to the deprotonation of the functional domains mainly composed of carboxylic groups, Ca-humate complexation would result in lower $Color_{436}$ in comparison with the UV-absorbing centers composed of dense aromatic regions as expressed by both UV_{254} and UV_{280}.

3.2. *Correlation between fluorescence intensity and humic parameters*

Fluorescence Index is defined as the ratio of the emission intensity at λ_{emis} 450 nm to that of λ_{emis} 500 nm following excitation at λ_{exic} 370 nm [31]. Adsorption of HA onto sole TiO_2 and TiO_2 in the presence of either Kt or Mt was evaluated by UV–vis parameters as $Color_{436}$ and UV_{254} in relation to the fluorescence intensities (FI) ($r^2 > 0.80$) (Figs. 5(A–B) and 6(A–B)).

It could be visualized that no discrimination could be attained with respect to clay type in the absence of Ca^{2+} ions (Fig. 4(A)). However, in the presence of Ca^{2+} ions, an inverse relationship could be shown between FI and UV_{254} for HA adsorption onto sole TiO_2 ($r^2 = 0.825$). Upon addition of Kt or Mt to the solution matrix, a linear relationship was obtained displaying an indifferent trend in comparison with the case observed in the absence of Ca^{2+} ions. Therefore, UV_{254} and FI variations observed via adsorption could not be accepted as indicative parameters for the evaluation of the individual effects of the clay types (Eqs. (1) and (2)).

In the absence of Ca^{2+} ions;

$$FI = -0.230\ UV_{254} + 1.20 \quad r^2 = 0.760 \tag{1}$$

In the presence of Ca^{2+} ions;

$$FI = -1.10\ UV_{254} + 1.49 \quad r^2 = 0.780 \tag{2}$$

A similar relationship was also reported previously for the photocatalytic degradation of HA in the presence of clay particles [32].

It could also be deduced that no discrimination could be attained for $Color_{436}$ with respect to clay type in the absence of Ca^{2+} ions (Fig. 6(A)) (Eq. (3)).

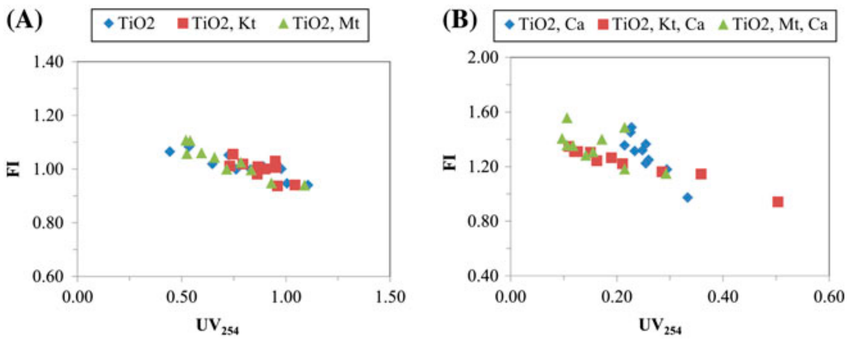

Fig. 5. Correlation of UV_{254} with FI in the absence (A) and presence (B) of Ca^{2+} ions.

$$FI = -1.21\ Color_{436} + 1.20 \quad r^2 = 0.760 \tag{3}$$

However, in the presence of Ca^{2+} ions, no significant correlation ($r^2 = 0.494$) could be shown displaying the role of Ca^{2+} ions on the removal of color-forming moieties with respect to the removal of fluorophores upon adsorption (Fig. 6(B)). It could also be mentioned that a regional cluster-type distribution was evident for HA adsorption onto sole TiO_2. Therefore, $Color_{436}$ and FI variations observed via adsorption could be carefully interpreted as indicative parameters (Fig. 7).

Moreover, DOC variations and respective FI changes were visualized as non-discriminative with respect to the clay type in the absence of Ca^{2+} ions (Eq. (4)).

$$FI = -0.0133\ DOC + 1.17 \quad r^2 = 0.673 \tag{4}$$

In the presence of Ca^{2+} ions, a regional separation excluding sole TiO_2 was observed the reason of which could be attributed to the role of Ca^{2+} ions on the humic fractions upon adsorption of sole TiO_2 rather than the effect of Kt or Mt. The linear relationships were expressed by the following equations (Eqs. (5) and (6)):

In the presence of sole TiO_2;

$$FI = -0.0358\ DOC + 0.785 \quad r^2 = 0.785 \tag{5}$$

In the presence of both Kt and Mt excluding sole TiO_2 through a very rough estimation;

$$FI = -0.0595\ DOC + 1.49 \quad r^2 = 0.567 \tag{6}$$

Since by definition the specific UV–vis parameters incorporated the removal of DOC, following adsorption spectroscopic properties of HA as $SUVA_{254}$ and SCoA were also correlated with FI (Figs. 8 and 9). It could be visualized that the effect observed due to the presence of Ca^{2+} ions were more pronounced as expressed by both $SUVA_{254}$ and SCoA parameters.

The effect due to the presence of either Kt or Mt could be differentiated by $SUVA_{254}$ rather than SCoA in comparison with HA and sole TiO_2 adsorption system in the presence of Ca^{2+} ions. However, SCoA variations with respect to FI attained in the presence of Ca^{2+} ions did not reveal any difference with respect to clay type even for sole TiO_2.

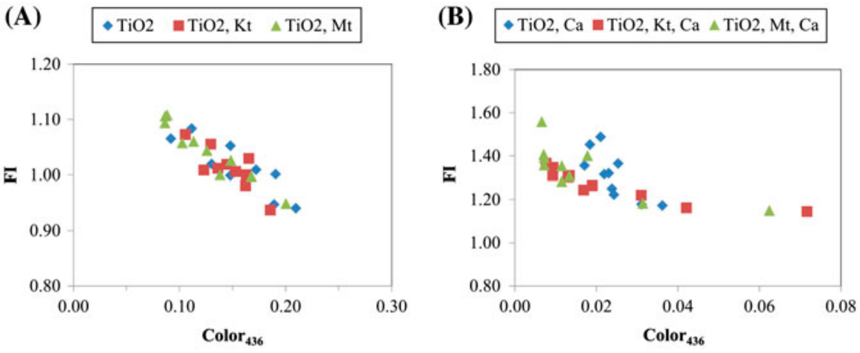

Fig. 6. Correlation of $Color_{436}$ with FI in the absence (A) and presence (B) of Ca^{2+} ions.

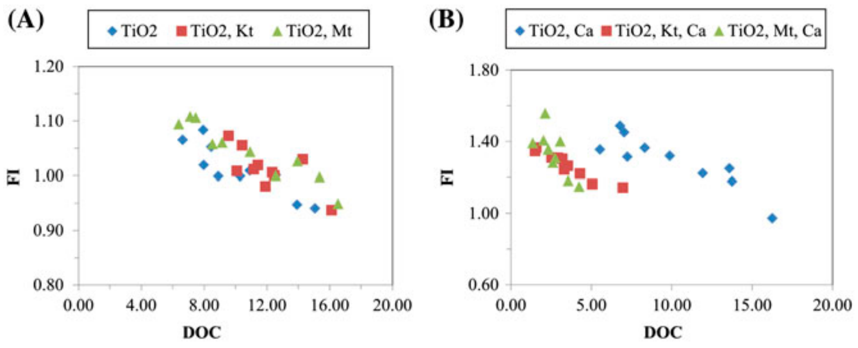

Fig. 7. Correlation of DOC with FI in the absence (A) and presence (B) of Ca^{2+} ions.

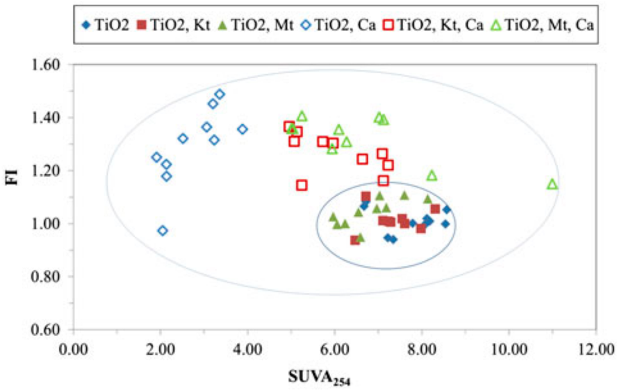

Fig. 8. Correlation of $SUVA_{254}$ with FI in the absence and presence of Ca^{2+} ions.

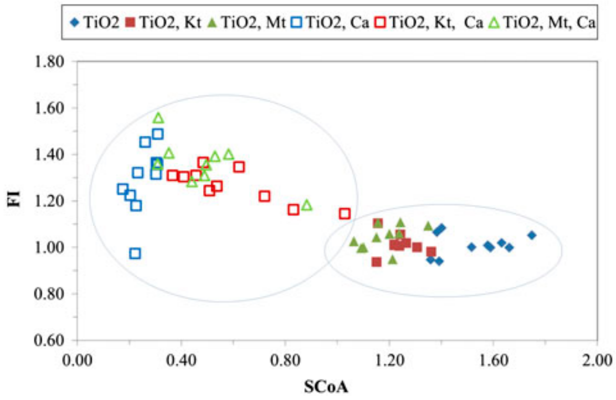

Fig. 9. Correlation of SCoA with FI in the absence and presence of Ca^{2+} ions.

4. Conclusion

Calcium ion and clay mineral effect on TiO_2 adsorption process of HA were investigated. UV–vis and fluorescence spectral features of HA upon adsorption onto TiO_2 in the presence of Kt or Mt were elucidated. The study demonstrated the helpful use of specific UV–vis (i.e. SCoA, $SUVA_{365}$, $SUVA_{280}$, and $SUVA_{254}$) and fractional UV–vis parameters (i.e. E_{254}/E_{365}; E_{254}/E_{436}; E_{280}/E_{365}; E_{280}/E_{436}; and E_{365}/E_{436}) of HA for the visualization of the adsorption process. Moreover, the effect of Ca^{2+} ions on the adsorption of HA onto TiO_2 in the presence of clay particles was evaluated by the UV–vis parameters. As a correlative approach, fluorescence-derived index defined as FI was successfully employed. FI values were correlated to specified UV–vis parameters revealing an inverse relationship. As a conclusive remark, it could be indicated that spectroscopic investigation as a non-destructive simple technique could still hold importance for the understanding of the adsorption of HA onto TiO_2 in the presence of clay minerals as well as Ca^{2+} ions.

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