

# The role of visible light active TiO<sub>2</sub> specimens on the solar photocatalytic disinfection of *E. coli*

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**Abstract** Solar photocatalytic disinfection efficiency of novel visible light activated (VLA) photocatalysts was evaluated with the aim of assessing inactivation of *Escherichia coli* as the pathogen indicator organism present in drinking water. Influence of humic acid (HA) on the photocatalytic disinfection efficiency of the specified VLA TiO<sub>2</sub> specimens i.e., N-doped, Se-doped, and Se-N co-doped TiO<sub>2</sub> was also investigated. Photocatalytic disinfection efficiency was assessed by the enumeration of bacteria following selected irradiation periods. Degradation and compositional changes in organic matter (OM) was also tracked by means of UV-vis and advanced fluorescence spectroscopic (EEM features) parameters. Photocatalytic mineralization of the organic matter was followed by dissolved organic carbon contents. Presence of HA as a model organic compound of natural organic matter (NOM) displayed a retardation effect on solar photocatalytic abatement of *E. coli*. However, no distinctly different effect was observed under solar photolytic conditions due to the presence of HA. Regrowth of *E. coli* could not be assessed under the specified experimental conditions. A comparison was introduced with respect to the use of undoped TiO<sub>2</sub> P-25 as the photocatalyst.

**Keywords** Disinfection · EEM · Photocatalysis · TiO<sub>2</sub> · Visible light active photocatalysts

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## Introduction

As a novel approach, advanced oxidation methods utilizing reactive oxygen species (ROS) has been successfully applied for water and wastewater treatment as well as disinfection purposes (Malato et al. 2009). Photocatalytic inactivation of *Escherichia coli* as the representative of pathogenic microorganisms present in water has been studied extensively since Matsunaga and co-workers (Matsunaga et al. 1985). Application of photocatalysis for disinfection purposes received widespread attention since three decades.

TiO<sub>2</sub> has generally been demonstrated to be the most active photocatalyst exhibiting strong resistance to chemical breakdown and photocorrosion. Although there are many different sources of TiO<sub>2</sub>, Evonik (Degussa) P25 TiO<sub>2</sub> has effectively become a standard because it has (i) a reasonably well defined nature (i.e., typically a 70:30 anatase/rutile mixture, non-porous, Brunauer–Emmett–Teller (BET) surface area  $55 \pm 15 \text{ m}^2/\text{g}$ , average particle size 30 nm), (ii) a substantially higher photocatalytic activity than most other readily available (commercial) TiO<sub>2</sub>, (iii) thermal stability. Since only ca. 5 % of the solar radiation at sea level is in the UV domain, various approaches have been utilized to improve the solar efficiency for TiO<sub>2</sub> including metal doping (or metal loading of the surface) and non-metal doping. Successful utilization of solar light could only be achieved by the use of visible light active (VLA) photocatalysts. A critical evaluation of the literature findings was presented by Bekbolet in a book chapter, and recent developments were also reviewed by various working groups (Bekbolet 2006; Chong et al. 2010; Markowska-Szczupak et al. 2011; Helali et al. 2014). A detailed comparative study was performed on assessment of TiO<sub>2</sub> photocatalytic removal efficiency using chemical compounds (e.g., methylene blue) and microorganisms (e.g., *E. coli*) (Marugán et al. 2010).

Solar photocatalytic disinfection studies were mainly carried out at Plataforma Solar de Almeria in Spain (McLoughlin et al. 2004). The technical feasibility and performance of photocatalytic TiO<sub>2</sub> coatings in batch-process solar disinfection (SODIS) reactors have been studied under simulated sunlight conditions (100 mWcm<sup>-2</sup>) by Duffy and colleagues (Duffy et al. 2004). The efficiency of solar disinfection was shown to be improved by the use of TiO<sub>2</sub> either as a suspended powder or in an immobilized form. The concentration of TiO<sub>2</sub> greatly affected the efficiency, with a maximum effect at 1 mgmL<sup>-1</sup> (Rincón and Pulgarin 2003). The use of BLF lamps was also found to be efficient in bacterial inactivation studies by Bekbolet and Araz (1996), as well as by Armon et al. (1998). TiO<sub>2</sub> photocatalytic disinfection efficiency under simulated light conditions was studied in detail by Pulgarin and co-workers (Rincón and Pulgarin 2003, 2004a, b, c).

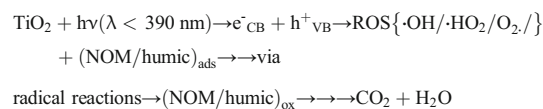
Robertson et al. (2005) reported a comparative study on the effectiveness of TiO<sub>2</sub> photocatalysis and UVA photolysis for the destruction of three pathogenic microorganisms; *E. coli*, *Salmonella enterica serovar Enteritidis*, and *Pseudomonas aeruginosa*. A relatively high rate of bacterial inactivation was observed for all three bacterial samples upon irradiation using a xenon UVA lamp (480 W, spectral output 330–450 nm, and light intensity of 3.42 × 10<sup>-5</sup> Es<sup>-1</sup>). The findings of Robertson et al. (2005) corroborated well with the previous research (Matsunaga et al. 1985; Ireland et al. 1993; Bekbolet 1997, and Rincón and Pulgarin 2003).

Development of VLA photocatalysts for the successful utilization of solar light leads to numerous studies on the photocatalytic degradation of organics as well as microorganisms. Although no significant enhancement on disinfection efficiency was reported for the VLA photocatalysts as N-, S-, and N-S co-doped TiO<sub>2</sub> specimens, research on the application of VLA TiO<sub>2</sub> still continues (Rengifo-Herrera and Pulgarin 2010). Rockafellow and colleagues reported that Se-doped TiO<sub>2</sub> could be successfully used as VLA following which Gurkan and co-workers also demonstrated the expected photocatalytic activity using cefazolin as the model compound of emerging pollutants (Gurkan et al. 2012; Rockafellow et al. 2010).

Photocatalytic disinfection mechanism using *E. coli* and a model compound (phenol) was explained in detail by Rengifo-Herrera and Pulgarin (2010). Photocatalytic disinfection mechanism was explained by dimerization of DNA (Matsunaga et al. 1985). Photocatalytic destruction of *E. coli* cell-wall bilayers at the TiO<sub>2</sub> porous film was followed by FTIR focusing on the main functional groups in the bilayers (Pulgarin et al. 2012). The decrease of these functional groups occurred with the simultaneous appearance of aldehydes, ketones, and carboxylic acids.

Considering the natural water conditions, in the presence of natural organic matter (NOM), simultaneous reactions could also be visualized leading to possible retardation in

disinfection efficiency. The following reaction scheme could also display the photocatalytic degradation of humic material.



Kinetics photocatalytic disinfection of bacteria has been reported by application of various models by Bekbolet and Araz in 1996 (Bekbolet and Araz 1996). Recent studies also presented prevailing mechanisms and disinfection kinetics (Castillo-Ledezma et al. 2014; Dalrymple et al. 2010; García-Fernández et al. 2015). Consequently, photocatalytic inactivation kinetics is mostly expressed in terms of simple pseudo first order kinetic model i.e., Chick’s Law.

Most of the above given studies were carried out in the presence of various microorganisms excluding the major role of NOM as the most significant component of drinking waters. Therefore, recent interest is directed to the elucidation of the inhibition of organic matter due to its high reactivity towards ROS during photocatalytic treatment. Moreover, characterization of the organic matrix released during photocatalytic treatment of *E. coli* has not been investigated in detail so far. The major aim of this research is to investigate the solar photocatalytic removal of *E. coli* in the absence and presence of organic matter by using VLAs. Since Se-doped TiO<sub>2</sub> has not been investigated so far for disinfection purposes, in accordance with the performance observed for N-doped TiO<sub>2</sub>, Se-N co-doped TiO<sub>2</sub> also holds importance to be investigated. Sole photocatalytic performance of mono- and co-doped TiO<sub>2</sub> specimens was investigated using *E. coli* as the indicator organism. More specifically, the characterization of the released organic material was elucidated both in the absence and presence of humic acid (HA) as a representative of NOM. For comparison purposes, TiO<sub>2</sub> P-25 was used as a photocatalyst under similar experimental conditions.

## Materials and methods

*E. coli* (strain O157) stock suspension was prepared in Luria Bertani (LB) medium. Working *E. coli* suspensions (10<sup>6</sup> CFU/mL) were prepared in deionized/distilled water (Rincón and Pulgarin, 2004c). HA was purchased from Aldrich. Working HA solution was prepared by dilution of the stock solution (1.0 g/L) and used following filtration through 0.45 μm membrane filters with an initial non-purgeable organic carbon (NPOC<sub>i</sub>) 4.87 mg/L.

## Visible light active photocatalysts

N-, Se-, and Se-N co-doped TiO<sub>2</sub> specimens were prepared according to the procedures details of which were presented

by Gurkan et al. 2012. TiO<sub>2</sub> was selected as Degussa P-25, and doping was carried out by using urea and SeCl<sub>3</sub> as sources of N and Se, respectively. Characterization of the photocatalysts was performed (Gurkan et al. 2012, 2013; Birben et al., Solar photocatalytic degradation of humic acid using mono- and co-doped TiO<sub>2</sub> specimens, Under Review). Photocatalyst loading was 0.25 mg/mL. TiO<sub>2</sub> P-25 was supplied from Evonik (Degussa). All chemicals were of analytical grade. Millipore Milli-Q water (with a resistivity of 18.2 MΩ cm at 25 °C) was used as reagent water in preparation of the solutions.

## Experimental methodology

Solar photocatalytic experiments were carried out using an ATLAS Suntest CPS+ simulator with a cutoff irradiation at λ 290 nm. Light source was air cooled Xenon lamp, and light intensity was measured as 250 W/m<sup>2</sup> with radiometer.

## Analytical methodology

*E. coli* (CFU/mL) enumeration was performed according to the methods given in the Standard Methods as 9010 Membrane filter method (Standard Methods for the Examination of Water and Wastewater 2012). NPOC was measured by Total Organic Carbon Analyzer Shimadzu TOC-VWP calibrated by using potassium phthalate. UV-vis and fluorescence spectroscopic parameters were measured by Perkin Elmer lambda 35 UV-vis Spectrometer and Perkin Elmer LS 55 Luminescence Spectrometer respectively. Se and NO<sub>3</sub><sup>-</sup> leaching was followed by inductively coupled plasma optical emission spectrometer (ICP-OES), Perkin-Elmer Optima 2100DV, and by ion chromatography (DIONEX ICS-3000), respectively.

Evolution and subsequent degradation of organic matter (OM) was followed by NPOC and by spectroscopic parameters based on absorbance values measured at specified wavelengths of 245, 280, 365, and 436 nm (UV<sub>254</sub>, UV<sub>280</sub>, UV<sub>365</sub>, and color<sub>436</sub>, cm<sup>-1</sup>). Specific UV absorbance as SUVA: UV<sub>254</sub>/NPOC, L/m mg and fluorescence index as FI: ratio of the emission intensity at λ<sub>emis</sub> 450 nm to that at λ<sub>emis</sub> 500 nm, following the excitation at λ<sub>exc</sub> 370 nm were calculated. Fluorescence techniques were employed for the elucidation of excitation emission matrix (EEM) features and fluorescence index FI (Bekbolet and Sen Kavurmaci 2015).

## Results and discussion

### Solar photolytic removal of *E. coli*

Preliminary experiments were carried out to elucidate the solar photolytic removal of *E. coli* either in the absence or presence

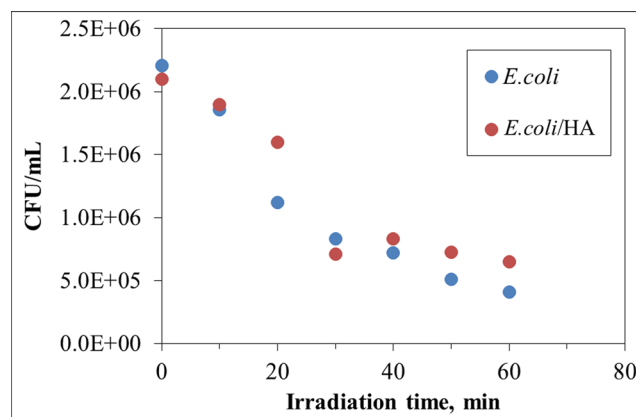


Fig. 1 Solar photolytic removal of *E. coli*

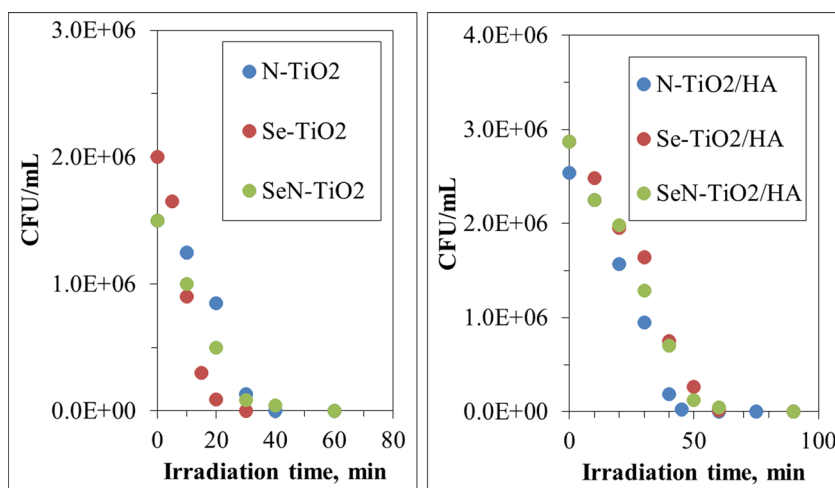
of HA and in the absence of photocatalyst specimens (Fig. 1). Solar photolytic removal of *E. coli* expressed a decreasing profile with respect to irradiation time reaching almost one log removal in 60 min. Presence of HA possibly acting as natural sensitizer did not significantly alter the photolytic removal of *E. coli* upon irradiation period of  $t_{irr}$  30 min, and removal of *E. coli* did not significantly change even under prolonged irradiation conditions ( $t_{irr}$  60 min). Similar findings were also presented by Maraccini and colleagues (Maraccini et al. 2016).

### Solar photocatalytic removal of *E. coli* in the presence of doped TiO<sub>2</sub> specimens

Alrousan and colleagues reported that the photocatalytic removal of bacteria was unaffected by the initial pH of the aqueous medium (pH 5.5–8.5); all experiments were performed under natural pH conditions (Alrousan et al. 2009).

Solar photocatalytic removal of *E. coli* using doped TiO<sub>2</sub> specimens was followed both in the absence (Fig. 2a) and presence of HA (Fig. 2b). Based on the decay profiles, pseudo first-order kinetic model was applied to the solar photocatalytic removal data of *E. coli*. The following rate constants ( $k$ ) were achieved in the absence of HA as 0.153 min<sup>-1</sup> for N-doped TiO<sub>2</sub>, 0.317 min<sup>-1</sup> for Se-doped TiO<sub>2</sub>, and 0.155 min<sup>-1</sup> for Se-N co-doped TiO<sub>2</sub>. Moreover, in the presence of HA, solar photocatalytic removal of *E. coli* using N-doped TiO<sub>2</sub> expressed slightly higher removal rate constants as  $k = 0.163$  min<sup>-1</sup>. On the other hand, rate constants were 0.110 and 0.096 min<sup>-1</sup> for Se-doped TiO<sub>2</sub> and Se-N co-doped TiO<sub>2</sub>, respectively. In the presence of HA, a retardation effect was observed for Se-doped and Se-N co-doped TiO<sub>2</sub> specimens, and an enhancement was attained for N-doped TiO<sub>2</sub>. The reason could be attributed the dual role of HA acting either as a photosensitizer, ROS scavenger, and surface blocker or exerting a stabilizing effect on photocatalyst particles (Planchon et al. 2013). Marugán and colleagues reported that the presence of humic acids affected the removal of *E. coli*

**Fig. 2** Solar photocatalytic removal of *E. coli* in the absence of HA (a) and in the presence of HA (b)



upon photocatalytic treatment using undoped TiO<sub>2</sub> P-25 (Marugán et al. 2008, 2010). It should also be indicated that both the surface properties of TiO<sub>2</sub> and the deprotonation capacity of humic functional groups are strongly pH dependent (Uyguner-Demirel and Bekbolet, 2011; Hossain et al. 2014).

**Regrowth experiments**

Prolonged irradiation conditions (t<sub>irr</sub> 120 min) were applied prior to the assessment of the regrowth of *E. coli*. As was reported previously that no regrowth of *E. coli* was observed under dark conditions, samples were tested directly following photocatalytic treatment (Rincón and Pulgarin 2004c). Regrowth test of *E. coli* was performed with respect to the procedure using Luria-Bertani medium and appropriate conditions. No regrowth of *E. coli* was observed both in the presence and absence of HA. Triplicate analysis was carried out for elucidation of regrowth. The results indicated bactericidal property of the doped TiO<sub>2</sub> and undoped TiO<sub>2</sub> excluding the possibility of bacteriostatic effect.

**Characterization of organic matter released by solar photolytic treatment of *E. coli***

UV-vis absorbance spectra and EEM fluorescence contour plots of the released OM was scanned with respect to irradiation time. UV-vis absorption spectra of OM released by solar photolytic treatment of *E. coli* resembled humic-like logarithmic decaying profile with decreasing absorbance with respect to increasing wavelength (Fig. 3a, b). Organic matter released following 60 min of irradiation period in the absence of HA expressed the following UV-vis parameters (cm<sup>-1</sup>), color<sub>436</sub> 0.057, UV<sub>365</sub> 0.081, UV<sub>280</sub> 0.167 and UV<sub>254</sub> 0.197, and NPOC as 3.56 mg/L. On the other hand, in the presence of HA comparatively higher values were attained for UV-vis parameters (cm<sup>-1</sup>) as color<sub>436</sub> 0.103, UV<sub>365</sub> 0.205, UV<sub>280</sub> 0.482 and UV<sub>254</sub> 0.575, and NPOC 6.08 mg/L. Based on

the data attained upon solar photolytic treatment for the irradiation period of 60 min, SUVA values as 5.53 L/m mg (in the absence of HA) and 9.46 L/m mg (in the presence of HA) represented the evolution of complex organic matrix of which aromatic character predominated (Edzwald et al. 1985; Roccaro and Vagliasindi 2010; Roccaro et al. 2015).

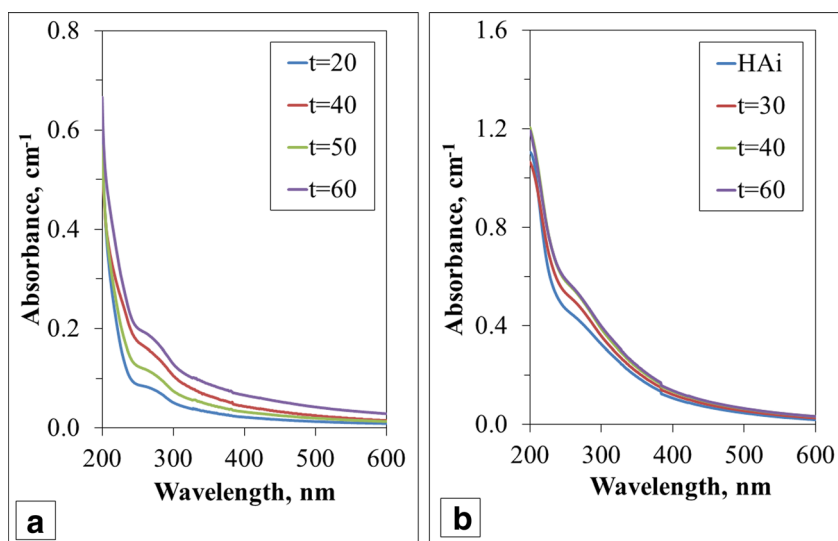
NOM exhibits fluorescence in excitation wavelength range of λ<sub>exc</sub> ~ 200–500 and emission wavelength range of λ<sub>emis</sub> ~ 280–600 nm (Baker et al. 2008) (Fig. 4). Fluorophoric centers could be described as humic-like fluorescence (λ<sub>exc</sub> 220–470 nm and λ<sub>emis</sub> 380–580 nm), fulvic-like (λ<sub>exc</sub> 220–250 nm and λ<sub>emis</sub> 380–580 nm), aromatic proteins I (λ<sub>exc</sub> 220–250 nm and λ<sub>emis</sub> 280–332 nm), aromatic proteins II (λ<sub>exc</sub> 220–250 nm and λ<sub>emis</sub> 332–380 nm), and microbial by-products (λ<sub>exc</sub> 250–470 nm and λ<sub>emis</sub> 280–380 nm (Coble 1996). Based on this regional distribution, EEM fluorescence contour plots related to the OM remaining in the reaction medium was characterized. In the absence of HA, irradiation time dependent elucidation of the EEM contour plots revealed the emergence of microbial by-products and protein-like fluorophores in accordance with the solar photolytic removal of *E. coli*. No formation humic-like and fulvic-like fluorophores were observed as expected. In the presence of humic acid, humic-like and fulvic-like fluorophores were more evident slightly masking the microbial by-products and protein-like fluorophores.

**Characterization of organic matter released by solar photocatalytic treatment of *E. coli***

UV-vis absorbance spectra of OM released by solar photocatalytic removal of *E. coli* in the absence of HA were presented for an irradiation period of 60 min (Fig. 6a). Based on the almost overlapping absorbance decay profiles, UV-vis spectroscopic parameters were evaluated and presented in Table 1.

In the absence of HA upon solar photocatalytic treatment of *E. coli*, slight variations in UV-vis spectroscopic parameters of the released organic matrix were attained as could also be

**Fig. 3** UV-vis absorption spectra of OM released by solar photolytic removal of *E. coli* in the absence of HA (a) and in the presence of HA (b)

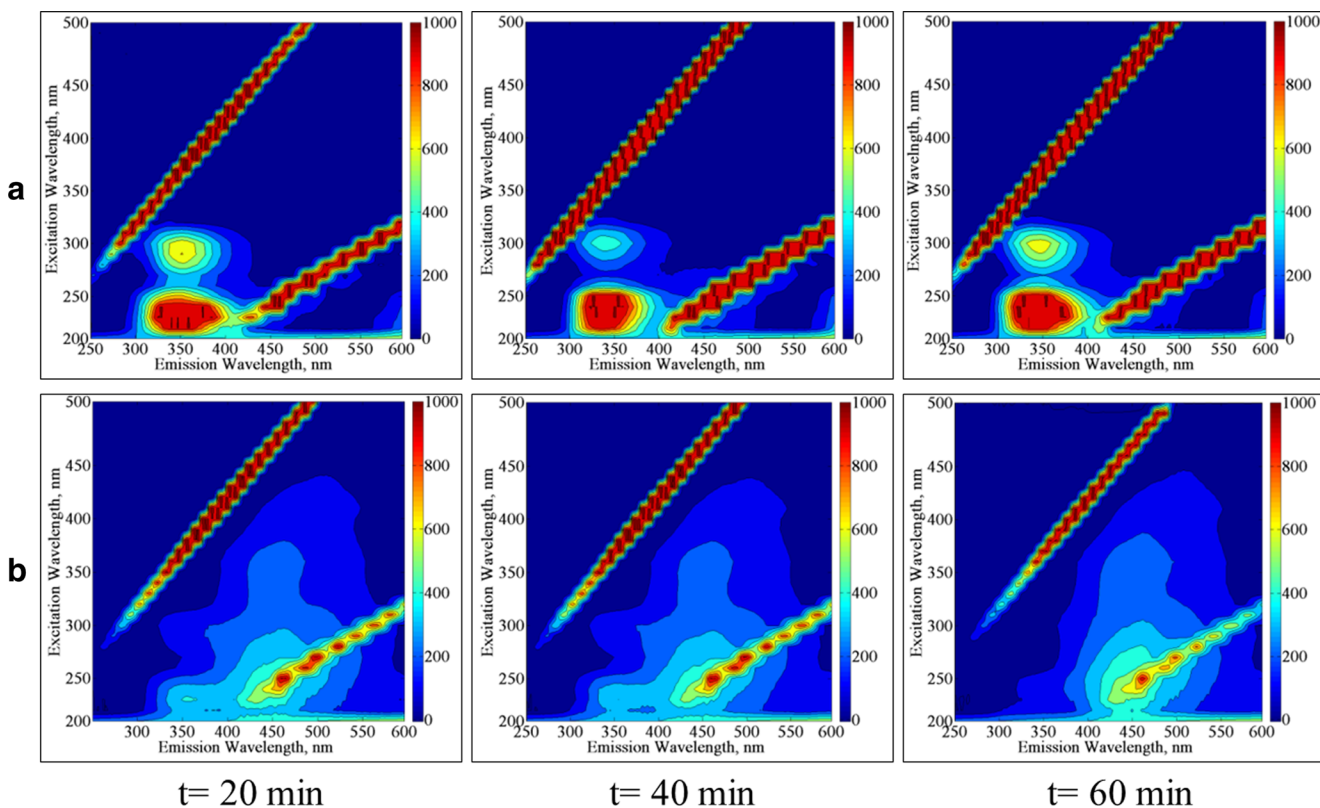


visualized from Fig. 6a. Released organic matter expressed NPOC (mg/L) contents as 4.01, 4.41, and 4.61 upon solar photocatalytic treatment using N-doped, Se-doped, and Se-N co-doped TiO<sub>2</sub> specimens, respectively. Related SUVA values were 1.74, 2.12, and 1.90 L/m mg representing more aliphatic character of the OM (Edzwald et al. 1985).

Comparison of EEM fluorescence contour plots of the OM attained using VLA photocatalysts displayed the emergence of microbial by-products ( $\lambda_{\text{exc}}$  250–470 nm and  $\lambda_{\text{emis}}$  280–

380 nm), protein-like fluorophores ( $\lambda_{\text{exc}}$  220–250 nm and  $\lambda_{\text{emis}}$  280–332 nm), and aromatic proteins II ( $\lambda_{\text{exc}}$  220–250 nm and  $\lambda_{\text{emis}}$  332–380 nm), upon irradiation period of 40 min in comparison to 60 min (Fig. 5a, b).

In the absence of HA, irradiation time dependent elucidation of the EEM fluorescence contour plots revealed the occurrence of microbial by-products and protein-like fluorophores in accordance with a simultaneously taking place of solar photocatalytic degradation of organic matrix and removal of *E. coli*. No



**Fig. 4** EEM fluorescence contour plots of OM released by solar photolytic removal of *E. coli* in the absence of HA (a) and in the presence of HA (b)

**Table 1** Characteristic properties of organic matter present in solution followed by solar photocatalytic treatment of *E. coli*

	UV-vis spectroscopic parameters, cm <sup>-1</sup>				NPOC, mg/L	SUVA, L/m mg	FI
	Color <sub>436</sub>	UV <sub>365</sub>	UV <sub>280</sub>	UV <sub>254</sub>			
In the absence of HA t <sub>irr</sub> 60 min							
N-doped	0.014	0.024	0.065	0.080	4.61	1.74	1.84
Se-doped	0.018	0.029	0.072	0.085	4.01	2.12	1.77
Se-N co-doped	0.017	0.027	0.069	0.084	4.41	1.90	1.74
In the presence of HA t <sub>irr</sub> 120 min							
N-doped	0.039	0.078	0.193	0.238	5.08	4.68	1.00
Se-doped	0.012	0.051	0.130	0.158	4.18	3.78	1.08
Se-N co-doped	0.010	0.031	0.103	0.140	2.86	4.90	1.01

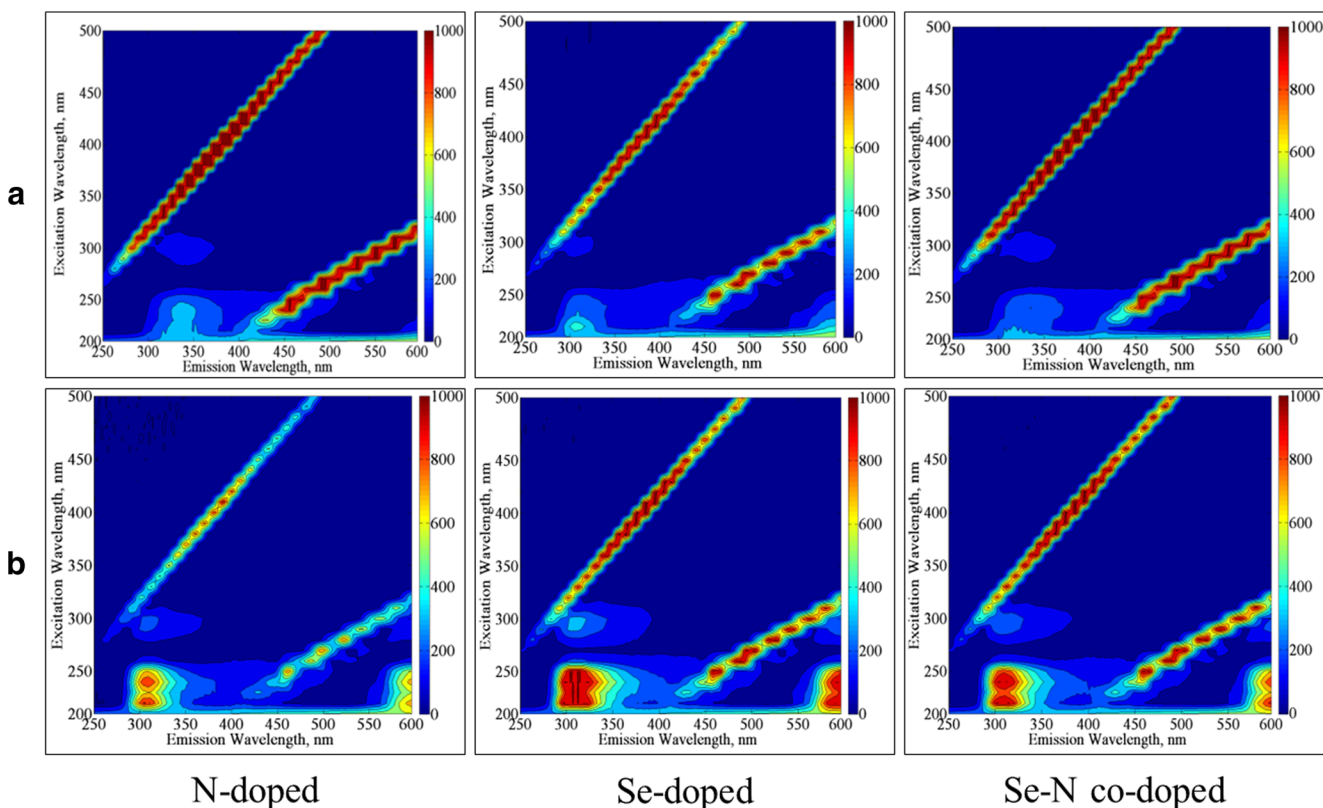
formation of humic-like ( $\lambda_{exc}$  220–470 nm and  $\lambda_{emis}$  380–580 nm) and fulvic-like fluorophores ( $\lambda_{exc}$  220–250 nm and  $\lambda_{emis}$  380–580 nm) were observed as expected.

**Characterization of organic matter produced by solar photocatalytic removal of *E. coli* in the presence of HA (NPOC; 4.87 mg/L)**

The effect of HA on the organic matrix release upon solar photocatalytic removal of *E. coli* was elucidated by UV-vis and

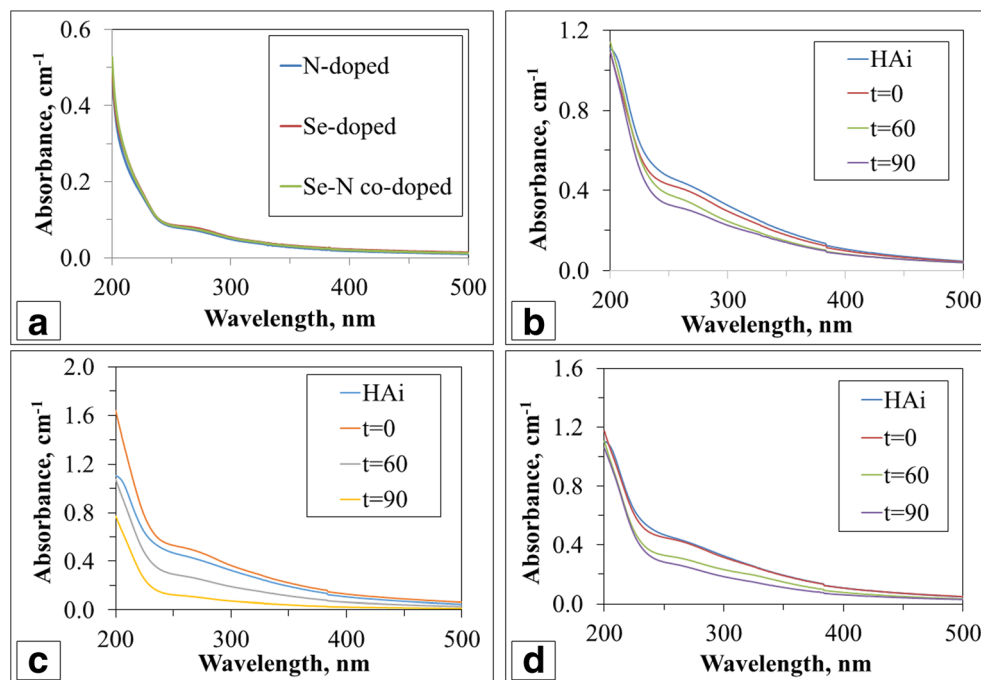
fluorescence spectral features (Fig. 6b–d). In the presence of HA, solar photocatalytic treatment of *E. coli* using N-doped TiO<sub>2</sub> specimen displayed an increasing OM release with respect to irradiation time (t<sub>irr</sub> 0–90 min). Due to the co-presence of HA and as a result of the prevailing competitive adsorption condition, a decrease in all absorbances in the UV-vis wavelength region was observed followed which a consistent decrease was attained with respect to irradiation period.

Following release of OM by *E. coli* through solar photocatalysis, simultaneous degradation of HA resulted



**Fig. 5** EEM contour plots of OM released by solar photocatalytic removal of *E. coli* in the absence of HA for t<sub>irr</sub> 40 min (a) and t<sub>irr</sub> 60 min (b)

**Fig. 6** UV-vis absorption spectra of OM released by solar photocatalytic removal of *E. coli* in the absence of HA (a), in the presence of HA by using N-doped TiO<sub>2</sub> (b), Se-doped TiO<sub>2</sub> (c), and Se-N co-doped TiO<sub>2</sub> (d)



in comparatively different patterns of UV-vis spectral features. Upon irradiation period of  $t_{irr}$  120 min at which complete removal of *E. coli* was attained, UV-vis parameters were evaluated and presented in Table 1.

With respect to the used doped TiO<sub>2</sub>, all of the UV-vis parameters displayed a decreasing order of N-doped TiO<sub>2</sub> > Se-doped TiO<sub>2</sub> > Se-N co-doped TiO<sub>2</sub>. Following solar photocatalytic treatment using N-doped, Se-doped, and Se-N co-doped TiO<sub>2</sub> for the irradiation period of 60 min, SUVA (L/mg) values were 4.68, 3.78, and 4.90, respectively. SUVA values expressed that the remaining organic matrix could be regarded as a mixture displaying both aliphatic and aromatic character (Edzwald et al. 1985).

EEM fluorescence contour plots attained for an irradiation period of 120 min in comparison to the features attained for shorter irradiation periods were shown in Fig. 7a–c. The presence of humic-like ( $\lambda_{exc}$  220–470 nm and  $\lambda_{emis}$  380–580 nm) and fulvic-like ( $\lambda_{exc}$  220–250 nm and  $\lambda_{emis}$  380–580 nm) fluorophores was evident under all irradiation conditions irrespective of the used doped TiO<sub>2</sub> specimen.

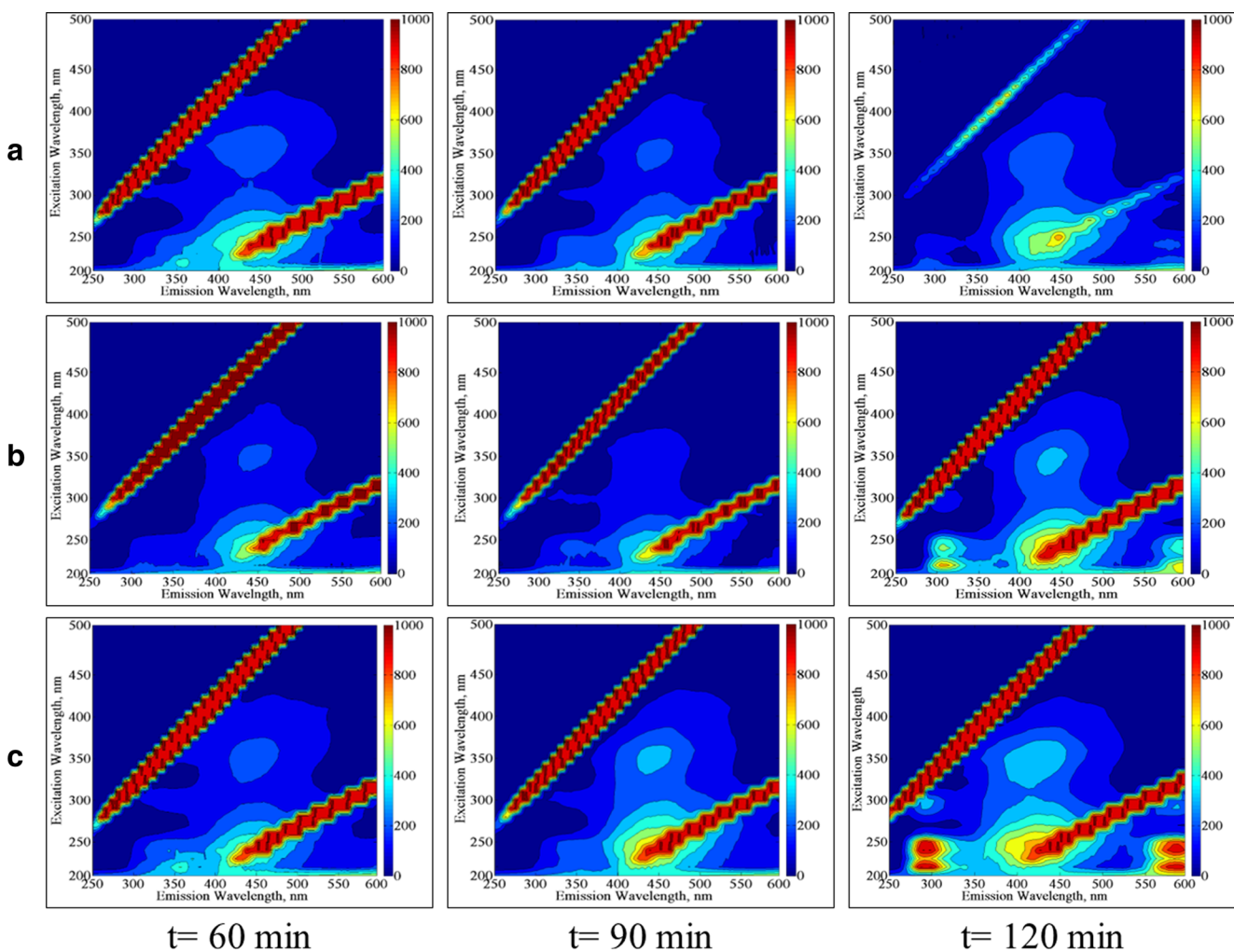
It should also be mentioned that the fluorescence of the protein-like components could be greatly quenched by the humic-like components (Wang et al. 2015). Therefore, presence of humic matter strongly influences the EEM fluorescence features of the OM released through solar photocatalytic disinfection of *E. coli*.

Further assessment was presented in terms of FI in a comparable manner. Upon solar photolysis in the absence of HA FI, 1.68 was observed in comparison to FI as 1.09 in the presence of HA. Upon solar photocatalytic treatment of *E. coli*, fluorescence characteristics of OM displayed FI as

(i) in the absence of HA 1.84 for N-doped TiO<sub>2</sub>; 1.77 for Se-doped TiO<sub>2</sub>, and 1.74 for Se-N co-doped TiO<sub>2</sub> and (ii) in the presence of HA 1.00 for N-doped TiO<sub>2</sub>; 1.08 for Se-doped TiO<sub>2</sub>, and 1.01 for Se-N co-doped TiO<sub>2</sub> as being not significantly different than each other. An inverse relationship was elucidated between FI and aromaticity of humic matter.  $FI \leq 1.4$  represented humic fluorophores of organic matter originating from terrestrial sources whereas  $FI \geq 1.9$  mainly attributed to microbially derived organic material (Sen Kavurmaci and Bekbolet 2014). It could be deduced that masking effect predominantly affected the evaluation by using FI.

#### Solar photocatalytic removal of *E. coli* using undoped TiO<sub>2</sub> P-25

Solar photocatalytic removal of *E. coli* using undoped TiO<sub>2</sub> P-25 was followed both in the absence and presence of HA under identical experimental conditions. *E. coli* removal kinetics revealed rate constants as  $k$  0.140 min<sup>-1</sup> in the absence of HA, whereas in the presence of HA, a retardation effect was attained expressing  $k$  as 0.0986 min<sup>-1</sup>. Evaluation of the rate constants indicated that undoped TiO<sub>2</sub> displayed slower removal rates in the following manner: (i) in the absence of HA: Se-doped TiO<sub>2</sub> > Se-N co-doped TiO<sub>2</sub> > N-doped TiO<sub>2</sub> > undoped TiO<sub>2</sub> and (ii) in the presence of HA: undoped TiO<sub>2</sub> ≥ Se-N co-doped TiO<sub>2</sub> > N-doped TiO<sub>2</sub> > Se-doped TiO<sub>2</sub>. Rincón and Pulgarin also reported an increase in DOC content of a wastewater sample upon photocatalytic treatment by TiO<sub>2</sub> (Rincón and Pulgarin 2004c). However, no detailed characterization of the released OM was assessed.



**Fig. 7** EEM contour plots of OM released by solar photocatalytic removal of *E. coli* in the presence of HA by using N-doped TiO<sub>2</sub> (a), Se-doped TiO<sub>2</sub> (b), and Se-N co-doped TiO<sub>2</sub> (c),  $t_{irr}$  60–120 min

It should also be indicated that neither Se leaching nor formation of NO<sub>3</sub><sup>-</sup> was observed under all experimental conditions.

### Conclusion

Solar photocatalytic performances of mono- and co-doped VLA TiO<sub>2</sub> specimens were investigated using *E. coli* as the indicator organism under neutral pH conditions. Characterization of the released organic material was elucidated both in the absence and presence of humic acid (HA) as a representative of NOM. By solar photolysis, one log inactivation of *E. coli* was achieved both in the absence and presence of HA upon irradiation period of 40 min.

Upon solar photocatalytic conditions, (i) in the absence of HA, six log *E. coli* inactivations were achieved in 60 min irrespective of the dopant type, (ii) in the presence of HA, six log *E. coli* inactivation could only be reached in 60 min

for Se-doped TiO<sub>2</sub> and Se-N co-doped TiO<sub>2</sub> specimens whereas irradiation period of 90 min was required when using N-doped TiO<sub>2</sub>.

Upon use of all doped TiO<sub>2</sub> specimens, emergence of both microbial by-products and protein-like fluorophores was observed for solar photolytic treatment of *E. coli* both in the absence of HA and in the presence of HA that could be regarded as being more pronounced.

Application of solar photocatalysis in the absence of HA resulted in the emergence of both protein-like and microbial by-products-like fluorophores that were evident up to 60 min of irradiation. In the presence of HA, both protein-like and microbial by-products-like fluorophores were evident up to 120 min of irradiation at which non-existence of *E. coli* was observed.

From a general perspective, a retardation effect of HA was observed.

Undoped TiO<sub>2</sub> displayed comparatively slower removal rates in comparison to the doped and co-doped TiO<sub>2</sub> specimens.



Neither Se leaching nor formation of  $\text{NO}_3^-$  was observed under all experimental conditions.

No regrowth of *E. coli* was assessed following solar photocatalysis using selected VLA photocatalysts.

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