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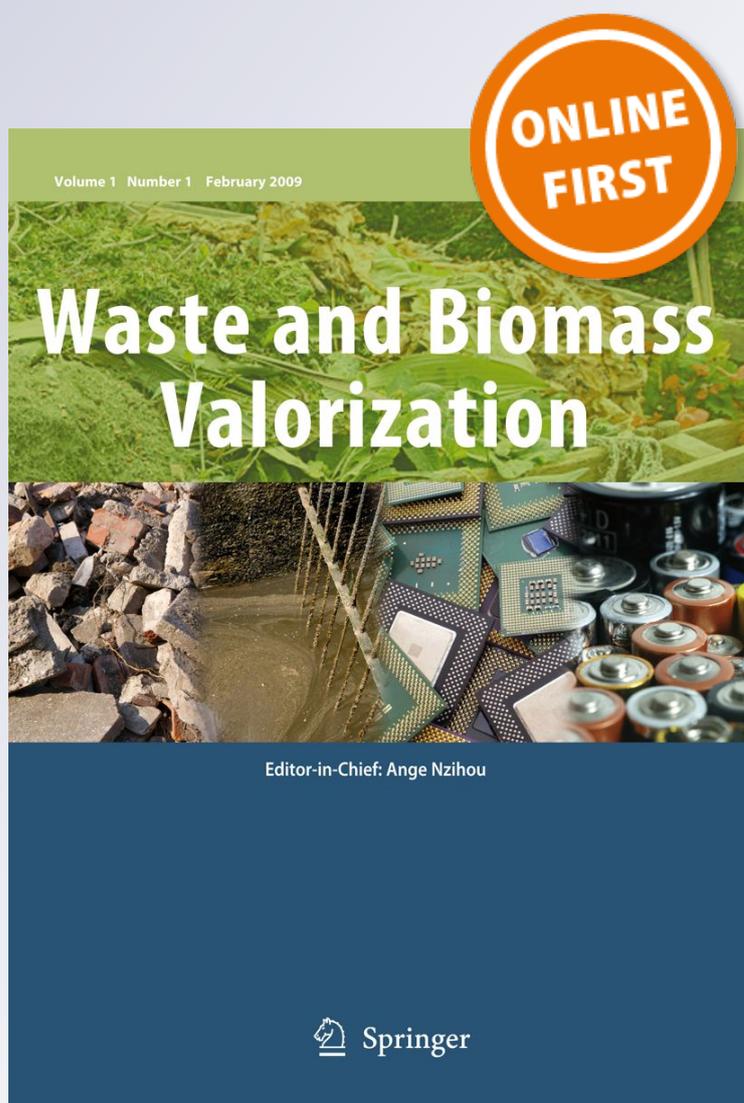
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# Adsorption and Photocatalytic Degradation Kinetics of Pharmaceuticals by TiO<sub>2</sub> Nanowires During Water Treatment

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**Abstract** The adsorption and photocatalytic degradation of 15 different pharmaceuticals in the presence or absence of UV was comparatively studied using titanium dioxide (TiO<sub>2</sub>) anatase and rutile nanowires as well as commercially available TiO<sub>2</sub> (P25) nanoparticles. Both anatase and rutile nanowires were grown under environmentally benign hydrothermal conditions. The kinetic adsorption studies demonstrate adsorption is usually complete within 20–40 min. The nanomaterials evaluated differed in photocatalytic efficiency by compound, with the UV-exposed anatase-phased nanowires being more effective at degrading venlafaxin, atorvastatin, ibuprofen, naproxen, gemfibrozil, lincomycin, norfluoxetine, diclofenac, and trimethoprim, while the rutile-phased nanowires were more effective for fluoxetine and norfluoxetine. The sole exposure to 265 nm UV leads to effectively decay sulfamethoxazole (SFX) and atrazine. Intermediate analysis unveils a higher mineralization of SFX is obtained with TiO<sub>2</sub> photocatalytic degradation compared to the photolysis with a UVC at 254 nm. These initial studies provide mechanistic insight into the effectiveness of TiO<sub>2</sub> nanowires and nanoparticles for treatment of surface and drinking waters containing trace pharmaceutical residues.

**Keywords** TiO<sub>2</sub> nanowire · Surface adsorption · Photocatalytic degradation · Pharmaceuticals

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## Introduction

A rapidly growing urban population, and the associated increases in municipal wastewater effluent (MWW) discharges, have led to multiple challenges for urban waterways. These challenges can be broadly summarized as an increasing demand for sufficient quantities of adequate quality raw drinking water, in the face of simultaneous declining or fluctuating quantities of increasingly polluted surface water adjacent urban areas [1–3]. As wastewater treatment plants were not designed to remove pharmaceuticals and personal care products (PPCPs) from their effluents, many residues of these compounds can be detected in MWW, and ultimately, surface water bodies serving as raw drinking water sources [1, 2, 4]. Although PPCP residues are only detected in very small concentrations, public mistrust of drinking water from municipal sources remains high. Traditional techniques to disinfect raw drinking water such as chlorine dioxide are largely ineffective at removing many recalcitrant PPCPs, while advanced oxidation and reverse osmosis systems are very effective, but limited by high cost [5, 6]. The increasing cost includes high prices of replaced components and the maintenance required special trained skills. For the majority of drugs, removal by conventional biological treatments also seems inefficient, since they are found in significant amounts in sewage treatment plant (STP) effluents and surface water [1, 2, 4, 7–9]. Therefore, a cost-effective treatment with simple operating and minimized maintenance is still desired. Advances in nanotechnology are generating novel materials with unique surface-active properties which may be beneficial in removing PPCPs from raw water sources [3, 8, 10–12].

TiO<sub>2</sub> is a wide band semiconductor material with a gap of 3.2 eV for anatase and 3.0 eV for rutile [13]. TiO<sub>2</sub> is a

chemically inert, bio-compatible and cost-effective material. For water treatment  $\text{TiO}_2$  nanowire/nanotubes possess superior performance than  $\text{TiO}_2$  nanoparticles since the separation of  $\text{TiO}_2$  nanoparticles from treated water is energetic costly [13].  $\text{TiO}_2$  nanowires and/nanotubes can form free-standing membranes and thereby minimize the release of nanomaterials in effluents [3, 14, 15]. Three kinds of degradation are reported with  $\text{TiO}_2$  nanowire membranes: surface adsorption [12], ultrafiltration [14, 16, 17] and photocatalytic degradation [3, 16]. However, the effect of  $\text{TiO}_2$  nanowire membranes on pharmaceuticals degradation is not systematically established [3–6]. Furthermore, in comparison with extensive studies on the application of  $\text{TiO}_2$  anatase nanowires for water treatment the investigation on the photocatalytic degradation with  $\text{TiO}_2$  rutile nanowires is very rare [11].

In this work we compared surface adsorption and photocatalytic degradation of three kinds of titanium dioxide ( $\text{TiO}_2$ ) nanomaterials, namely, anatase nanowires, rutile nanowires and P25 nanoparticles. A series of experiments demonstrated these nanomaterials, to varying degrees depending on PPCP properties, effectively removed these bioactive pollutants from water through both surface adsorption and photocatalytic degradation mechanisms.

## Materials and Methods

### Nanomaterial Synthesis and Characterization

Titanium dioxide ( $\text{TiO}_2$ ) nanowires were synthesized by modified hydrothermal growth techniques.  $\text{TiO}_2$  anatase nanowires were grown in a 10 M alkaline solution with Ti foil as a Ti source [3] while  $\text{TiO}_2$  rutile nanowires were grown on a glass substrate in the strong acidic solution with titanium butoxide as a Ti source [18]. The suspension of nanowires from alkaline solution were obtained by centrifugal separation and then washed in 0.1 M HCl solution and deionization water for several times till the pH value of washed water is neutral. The rutile nanowires were washed in deionization water first for 24 h before being cleaved from substrates. The fabricated nanowires were ground into fine powder and annealed at 700 °C for 2 h for experimental characterization. Commercially available  $\text{TiO}_2$  P25 nanoparticles were used for comparison.

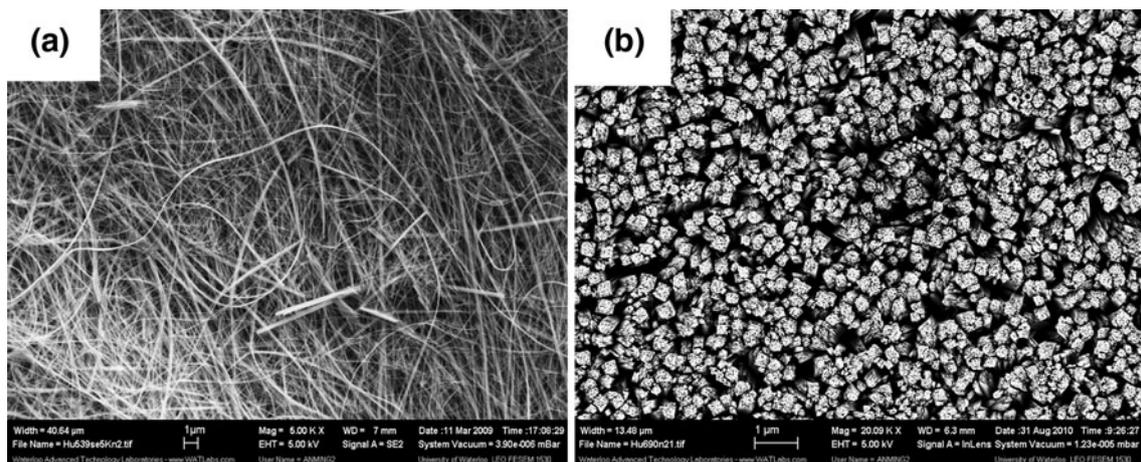
The phase and microstructure of fabricated nanowires were examined by X-ray diffractometer, Raman microscope (Renishaw inVia microscope equipped with 488 nm Ar ion laser) and scanning electron microscopy (SEM). The specific area was determined by the Brunaur–Emmett–Teller (BET) method using the  $\text{N}_2$  adsorption data (Quantachrome Instruments NOVA 2200).

### Surface Adsorption and Photocatalytic Degradation

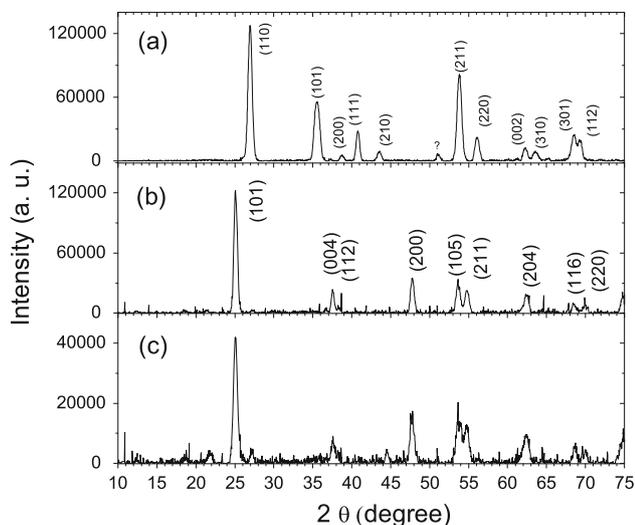
The surface adsorption experiments were carried out by dispersing prepared nanomaterials into 100 ml spiked pharmaceutical solutions with an initial concentration of 200 ppb for each pharmaceutical (phosphate buffer solution, pH = 7.4) in the dark at room temperature (22 °C) where adsorption was accelerated by magnetic stirring. A pharmaceutical mixture included 15 compounds was prepared and these compounds were chosen on the basis of literature survey, which displays that these compounds are extensively presented in ground water, wastewater and/or drinking water [1–3]. For comparison, the added mass of each kind of nanomaterials was kept as 100 mg. Photocatalytic degradation was assessed by the presence or absence of UV irradiation with a low pressure mercury lamp at an intensity of  $2.7 \times 10^{-4}$  W/cm<sup>2</sup> with a few emission lines mainly at 264 and 365 nm. The added mass of nanomaterials were set at 100 mg. To research surface adsorption the solution was first stirred in the dark for 1 h. Solid phase microextraction (SPME) and HPLC–MS/MS (Agilent 1100 LC and AB Sciex 3200 Q-Trap) techniques were employed to determine the PPCP concentrations and intermediates in the solution. The wash solvent was 20 %  $\text{H}_2\text{O}$ : 20 % methanol: 60 % isopropyl alcohol. The mobile phase was 95 %  $\text{H}_2\text{O}$ : 5 % methanol: 0.1 % acetic acid. The C18 column was used. Mass analysis was conducted in positive mode electrospray ionization over a mass range of 50–280 m/z.

## Results and Discussion

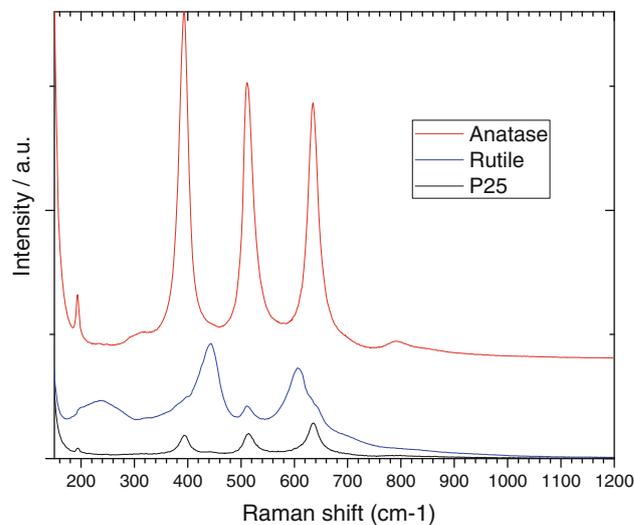
Figure 1 shows SEM images for (a) entangled  $\text{TiO}_2$  nanowires grown in strong alkaline solution and (b) highly oriented  $\text{TiO}_2$  nanowires grown in an acidic solution. The length of entangled  $\text{TiO}_2$  nanowires is around 100–400  $\mu\text{m}$ . The diameter is around 10–30 nm. The aligned nanowires with a square appearance in cross-section possess a side of 20 nm to 50 nm. The length ranges from 1 to 3  $\mu\text{m}$ . As shown in Fig. 2 X-ray diffraction patterns confirm that (a) entangled nanowires can be indexed by the anatase phase while aligned nanowires can be indexed by the rutile phase after annealing at 700 °C. For comparison, the diffraction patterns of P25 are also shown in Fig. 2c. It is clear that P25 includes two phases: anatase and rutile. Specific areas for three nanomaterials are 16.709 m<sup>2</sup>/g for anatase nanowires, 13.988 m<sup>2</sup>/g for rutile nanowires and 50.694 m<sup>2</sup>/g for P25, respectively. Figure 3 shows the Raman features of three kinds of  $\text{TiO}_2$  nanomaterials. Typical modes of  $\text{TiO}_2$  anatase phase at 197, 399, 515 and 639 cm<sup>-1</sup> can be founded in the anatase nanowires while 445, 609.8 cm<sup>-1</sup>, a superposition mode at 512 cm<sup>-1</sup> and a



**Fig. 1** SEM images for TiO<sub>2</sub> nanowires grown in **a** an alkaline solution and **b** acidic solution



**Fig. 2** XRD patterns of three kinds of TiO<sub>2</sub> nanomaterials: **a** nanowires grown in an acidic solution, **b** nanowires fabricated in the alkaline solution, and **c** commercially available P25 nanopowder



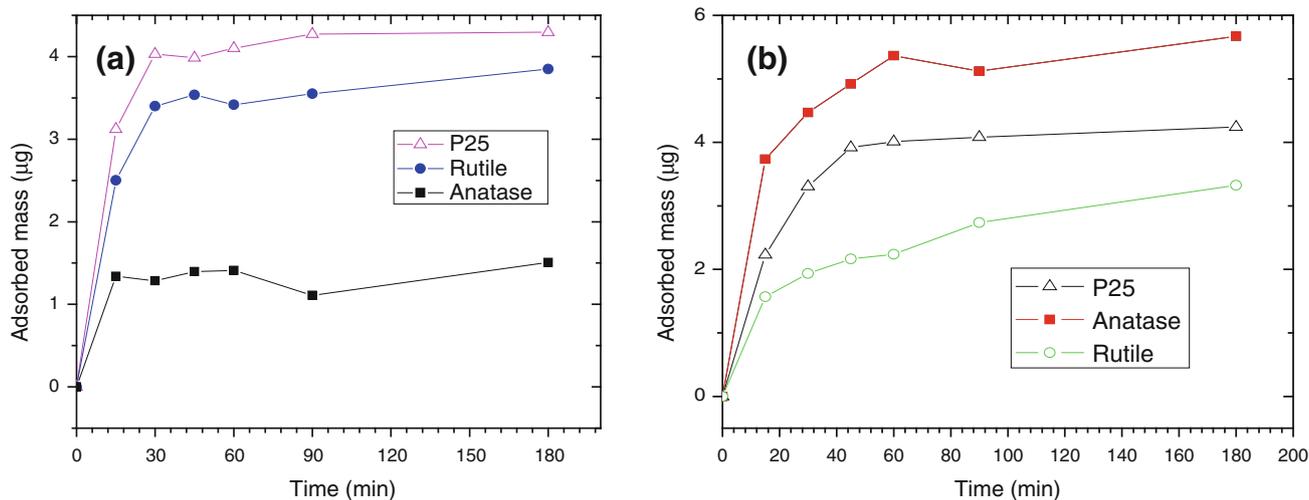
**Fig. 3** Raman spectra for three kinds of TiO<sub>2</sub> nanomaterials. The laser excitation is 488 nm

multi-photon mode at 235.5 cm<sup>-1</sup> can be observed in rutile phase. P25 mainly shows the anatase modes since the dominant component is anatase. These results are consistent with previous reports [19–21].

Figure 4 illustrates the surface adsorption kinetics of (a) fluoxetine and (b) naproxen on three kinds of TiO<sub>2</sub> nanomaterials, namely, TiO<sub>2</sub> anatase nanowires, rutile nanowire and P25 nanoparticles. It is evident that the adsorption gradually reaches an equilibrium after 20–40 min. Since the total mass of each pharmaceuticals is 20 μg the saturation is one of intrinsic properties of nanomaterials. Figure 4 also displays that the selected adsorption of different drugs by variable nanomaterials, i.e., at the same mass, P25 strongly adsorbs fluoxetine while anatase nanowires are mostly effective to adsorb naproxen. According to the specific surface area determined

by BET method, rutile is most effective to adsorb fluoxetine in per unit of surface area. The saturated adsorption of fluoxetine is given as 2.034 μg/m<sup>2</sup> for rutile, 0.918 μg/m<sup>2</sup> for anatase and 0.806 μg/m<sup>2</sup> for P25. For naproxen the saturated adsorption per unit of surface area is 1.296 μg/m<sup>2</sup> for rutile, 3.518 μg/m<sup>2</sup> for anatase and 0.784 μg/m<sup>2</sup> for P25. There is a significant enhancement of surface adsorption by nanowires relative to the commercial P25 nanoparticles.

Figure 5 clearly illustrates that photocatalytic degradation is dependent on individual physicochemical characteristics of each PPCP and the interacting nanomaterial, as verified by the differential degradation of (a) venlafaxine, (b) fluoxetine and (c) sulfamethoxazole. Additional experimentation demonstrated UV-exposed anatase-phased nanowires were more effective at degrading atorvastatin,



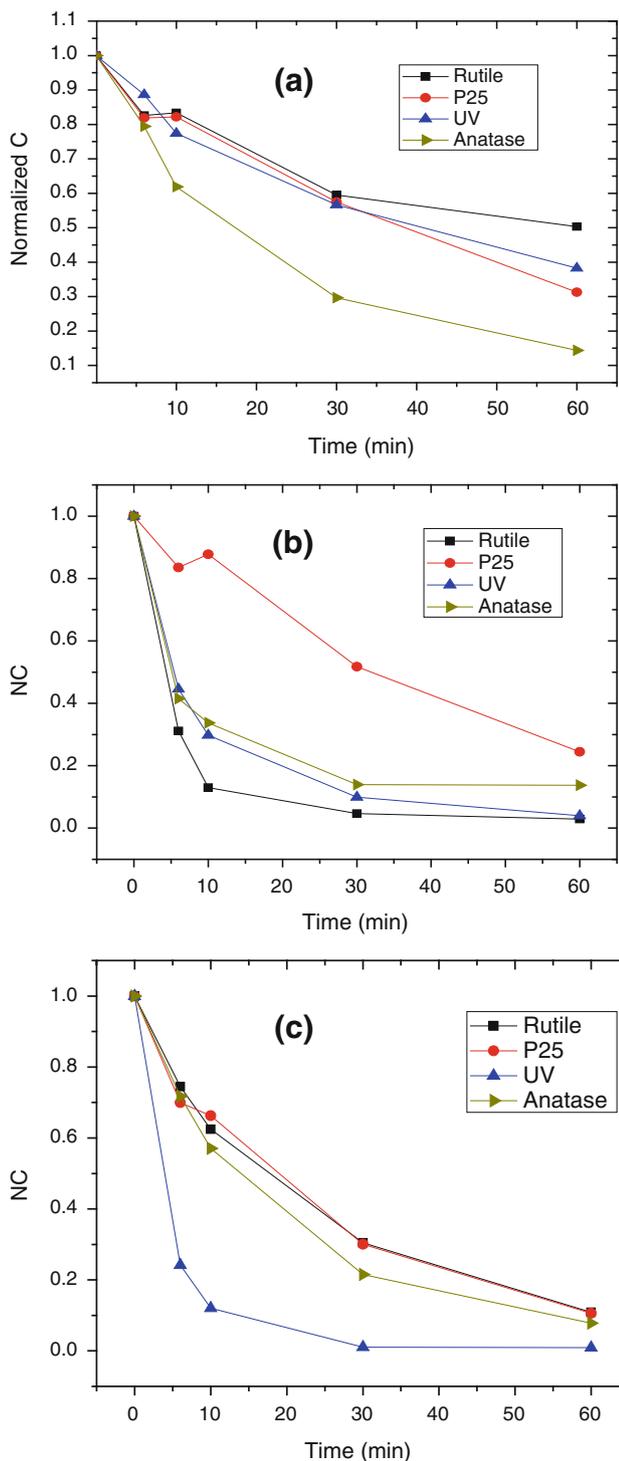
**Fig. 4** Adsorption kinetics of **a** fluoxetine and **b** naproxen at 100 ml aquatic solution dispersed with one of 100 mg nanomaterials: either P25, rutile nanowires or anatase nanowires

ibuprofen, naproxen, gemfibrozil, venlafaxin, lincomycin, declofenac, and trimethoprim, while the rutile-phased nanowires were more effective for fluoxetine and nor-fluoxetine. The sole exposure to UV was more effective in degrading sulfamethoxazole and atrazine. The preferred degradation is consistent with the selected surface adsorption since at per unit of surface area anatase is effective for naproxen and rutile is more effective to adsorb fluoxetine. It is widely accepted that UV excitation leads to the generation of electron-hole pairs on the  $\text{TiO}_2$  nanomaterial surface. These charges will react with water molecules and result in  $\text{OH}^*$  radicals.  $\text{OH}^*$  radicals oxidize pharmaceutical molecules and make the latter decompose and mineralize.  $\text{OH}^*$  are transient species so that the photocatalytic degradation only occurs in the vicinity of nanomaterial surface. Therefore, the degradation is strongly influenced by surface adsorption. For sole UV exposure, it has been found that pharmaceuticals with amine bonds, such as, sulfamethoxazole, are photolyzed easily by 254 nm UV photons [22]. Meanwhile, drug molecules with amide bonds are more resisted for photolysis [22]. This can be explained why atrazine is also sensitive to photolysis since it also has amine groups. It is important to point out that although sulfamethoxazole and atrazine are UV photolyzed they may only be transferred to other intermediates.

Figure 6 shows the kinetic analysis of photocatalytic and photolytic degradation of venlafaxine, fluoxetine and sulfamethoxazole in case of the fastest decay shown in Fig. 5. It is notable that the venlafaxine photocatalytic degradation follows a pseudo first order mechanism with an apparent rate constant of  $0.0375 \text{ min}^{-1}$  at  $R^2$  value of 0.996. For fluoxetine and sulfamethoxazole the initial concentration very quickly decays to a trace amount within half an hour. However, the data within 20 min can be well

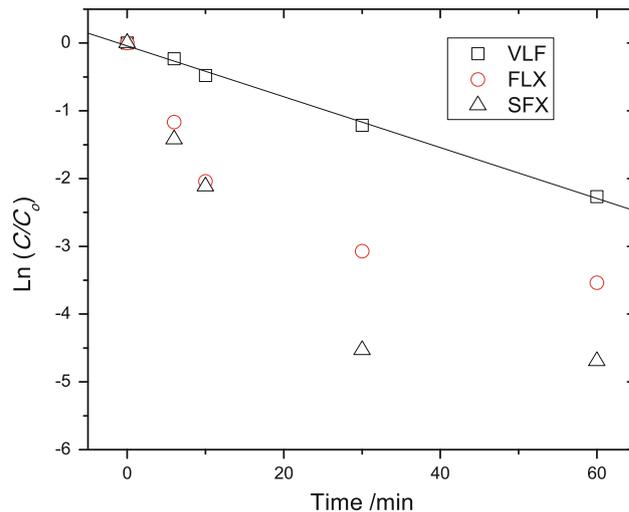
fitted by the pseudo first order formula and yield a very fast decay rate at around of  $0.2/\text{min}$ , which is in agreement with the reported range of  $0.170\text{--}0.375 \text{ min}^{-1}$  [23].

The UV photolysis of pharmaceuticals can produce even more toxic products [5, 24]. To assess the degradation fates of sulfamethoxazole (SFX) the further investigation with LC/MS/MS is carried out. Figure 7 shows the retention curve of SFX with a flow rate of 0.6 ml/min. Although the current experimental conditions do not allow separate each component, the intermediates can be still identified from the mass spectra. Figure 8 shows the mass spectra of intermediates at the retention time of 4.07 min for two kinds of degradations: with 254 nm UV light and  $\text{TiO}_2$  anatase excited by 254 nm light at 30 min and 90 min, respectively. The SFX molecule is identified at 254.1 m/z. A quasimolecular ion at 269.2 m/z can be assigned to  $[\text{M}-\text{OH}]^+$  [25, 26], where M is SFX molecule. Two degradation paths,  $99 + 173$  and  $115 + 156$  m/z can be clearly observed. These assignments agree with previous studies [25, 26]. However, the ion abundance in case of  $\text{TiO}_2$  photocatalytic degradation for these determined ions is remarkably lower than these in UV degradation. This indicates that although UV photolysis leads to a similar spectra (similar intermediates) as  $\text{TiO}_2$  photocatalytic degradation the latter displays a higher level of mineralization. This also coincides with a lower concentration of SFX at  $\text{TiO}_2$  with 90 min illumination. The calculated specie of  $\text{C}_7\text{H}_{10}\text{N}_3\text{O}_3\text{S}$  at 215 m/z is also identified [25], which could form a pair with 73 m/z ions dissociated from mother specie at 288 m/z, equal to a water molecule attached to a quasi-molecule ion at 269 m/z [25]. A new channel is founded at  $196 + 59$  m/z, which could directly rupture from SFX. To further confirm these transformation pathways the separated experiment with these intermediates is needed. The mass spectra at the

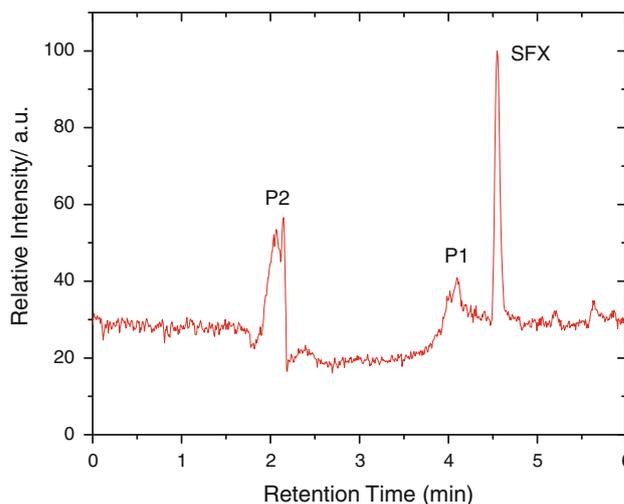


**Fig. 5** Normalized concentration of pharmaceuticals, **a** venlafaxine, **b** fluoxetine, and **c** sulfamethoxazole as a function of UV exposure time with or without different nanomaterials

retention time at 2 min display almost identical features for variable experiment conditions, indicating a worse resolution. For the simplicity we omit the analysis of these spectra.



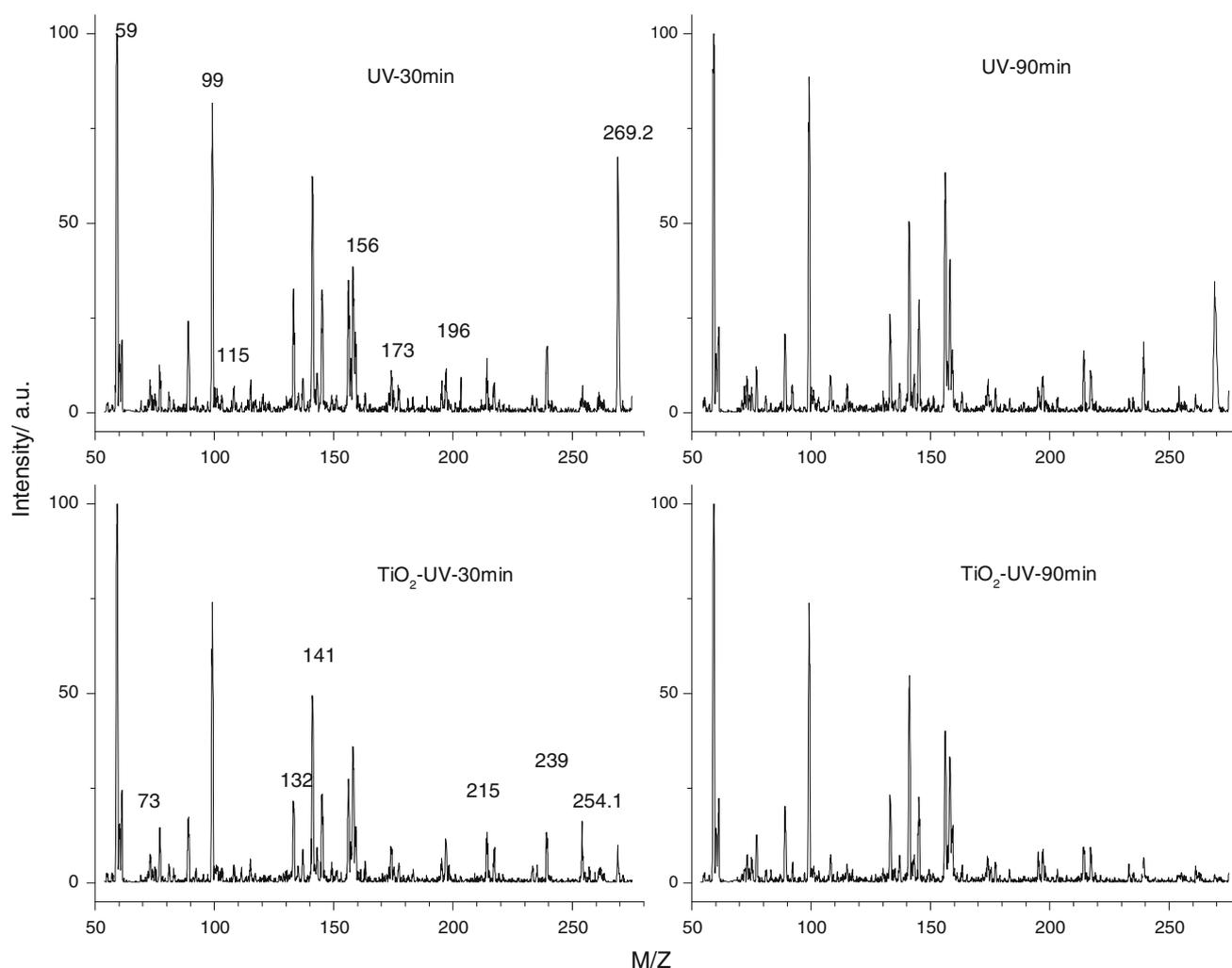
**Fig. 6** Kinetic analysis of three drugs at the fastest decay cases shown in Fig. 5



**Fig. 7** Retention spectra of sulfamethoxazole degradation with TiO<sub>2</sub> nanowires excited with 254 nm UV light

### Conclusion

Two removal mechanisms have been identified as significant for aqueous pharmaceutical solutions interacting with a variety of nanomaterials: surface adsorption and photocatalytic degradation. It is unveiled that the photocatalytic degradation is correlated to surface adsorption, i.e., an effective surface adsorption resulting in a quick degradation. For surface adsorption, TiO<sub>2</sub> nanowires are considerably more effective than commercial TiO<sub>2</sub> nanoparticles, while photocatalytic degradation effectiveness varies on a PPCP and nanomaterial-specific basis. Intermediate analysis displays a higher mineralization can be obtained in photocatalytic degradation with TiO<sub>2</sub> nanomaterials compared to UVC photolysis.



**Fig. 8** HPLC-mass spectra of intermediates of sulfamethoxazole degradation with and without TiO<sub>2</sub> under UV illumination at 254 nm for 30 and 90 min, respectively

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