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## Water purification in a solar reactor incorporating TiO<sub>2</sub> coated mesh structures

Amer S. El-Kalliny, Alireza H. Rivandi, Sibel Uzun, J. Ruud van Ommen, Henk W. Nugteren, Luuk C. Rietveld and Peter W. Appel

### ABSTRACT

The rate of photocatalytic oxidation of contaminants in drinking water using an immobilized catalyst can be increased by properly designing the catalyst structure. By creating a solar reactor in which meshes coated with TiO<sub>2</sub> were stacked, we demonstrated that degradation of humic acids with four superimposed stainless steel meshes was up to 3.4 times faster than in a single plate flat-bed reactor. Incorporation of TiO<sub>2</sub> coated mesh structures resulted in a high specific photocatalytically active surface area with sufficient light penetration in the reactor, while the coated area for one mesh was 0.77 m<sup>2</sup> per m<sup>2</sup> projected area. This brought the photocatalytic efficiency of such reactors closer to that of dispersed-phase reactors, but without the complex separation of the very fine TiO<sub>2</sub> particles from the treated water.

**Key words** | humic acid, immobilized TiO<sub>2</sub>, mesh structure, photocatalysis, solar reactor, water purification

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### INTRODUCTION

Heterogeneous solar photocatalysis uses solar UV light in the range between 300 nm and 400 nm to photo-excite the catalyst in contact with water and in the presence of oxygen (Malato *et al.* 2009) to generate hydroxyl radicals (OH). TiO<sub>2</sub> is the most-used photocatalyst because of its biological and chemical inertness, photo-stability, availability, and non-toxicity (McCullagh *et al.* 2011). The largest exposed active

catalyst surface area, relative to the reactor volume, can be obtained in a so-called dispersed-phase reactor. However, a complex and expensive separation step is required to remove the fine catalyst particles from the water. This can be avoided by using immobilized photocatalyst reactors (Feitz *et al.* 2000; Malato *et al.* 2009; McCullagh *et al.* 2011). For efficient contaminant degradation such reactors require a large reactor surface with low throughput because of their low catalyst surface to reactor volume ratio. The degradation potential can be increased by changing the configuration of such reactors. Zhang *et al.* (2004) reported that the rate of

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degradation with a corrugated plate was a factor 1.5 faster than with the flat-plate for the same exposed reactor area. More complex configurations can be used to increase even further the catalyst surface to reactor volume ratio. However, although the catalyst surface to reactor volume ratio may increase, light penetration in the reactor can then become a limiting factor (Feitz *et al.* 2000; Dijkstra *et al.* 2001).

TiO<sub>2</sub> coatings were successfully applied on various materials of different surface areas such as ordinary glass and borosilicate glass (Parra *et al.* 2004; Fujishima *et al.* 2008; Zhang *et al.* 2012), cellulose fibres (Goetz *et al.* 2009), and stainless steel (Yanagida *et al.* 2006). To optimize the active catalyst surface to reactor volume ratio as well as light penetration and light distribution, a novel reactor was developed containing a stack of TiO<sub>2</sub> coated meshes (El-Kalliny *et al.* 2014). Stainless steel woven meshes were used as catalyst support material and TiO<sub>2</sub> coatings were applied by electrophoretic deposition (EPD) using a commercial sol gel (O5100) as a stable suspended electrolyte. In this paper, the TiO<sub>2</sub> coated mesh reactor was used to study the adsorption and solar photocatalytic degradation efficiency of humic acids (HA) as a model compound for surface water contaminants. The performance of the catalyst structure was investigated at different scales, including a batch system in a beaker and a recirculating flow fixed-bed reactor. Results were compared with those obtained with a similarly coated flat-plate reactor of the same size.

## EXPERIMENTAL METHODS

### Preparation of the immobilized TiO<sub>2</sub> catalyst

Immobilization of the TiO<sub>2</sub> photocatalyst on grade 304 stainless steel woven meshes and flat plates was done using the EPD technique described in El-Kalliny *et al.* (2014). Meshes had a wire diameter of 0.355 mm and an aperture diameter of 0.915 mm, resulting in an open area of 52%. Flat plates were 2 mm thick and had the same dimensions as the rectangular mesh sheets (32 cm × 19 cm).

### Fixed-bed reactor and photocatalytic activity evaluation

The batch experiments with small circular meshes (ø 5.5 cm) were carried out in 250 mL Pyrex glass beakers (internal

diameter 7 cm) using a magnetic stirrer (IKA, RT15) with a stirring rate of 550 rpm. The meshes were placed on top of each other and separated by 2-mm-thick silicone rubber rings. The temperature was kept at  $32 \pm 1$  °C by using a recirculation cooler (Julabo, FL300). This temperature is a simulation for the temperature of the system subjected to solar light. Working solutions of HA were prepared from a 1,000 mg·L<sup>-1</sup> stock solution of HA sodium salt (Sigma Aldrich). The HA sodium salt was dissolved in aerated deionized water and filtered through a 0.45 µm syringe-driven filter unit (Millex) to remove suspended solids (0.03 g·L<sup>-1</sup>).

The schematic view of the fixed-bed photocatalytic reactor is presented in the Supplementary Data (Figure S1), available with the online version of this paper. The body of the reactor was made of Perspex and the cover was 4-mm-thick borosilicate glass. UV solar light (300–400 nm) transmission of this cover, measured by Xenocal UV-sensor (Atlas), was 92.9%. Four mesh layers (32 cm × 19 cm) were placed in the reactor, separated by 2-mm-thick silicone rubber spacers. Water recirculated and entered into the reactor from the short side (19 cm width) by a peristaltic pump (Minipuls 3, Gilson) with a maximum flow rate of 200 mL·min<sup>-1</sup>, corresponding to a hydraulic retention time through the reactor of 3.25 min. These conditions showed that there were no dead zones in the reactor with a good mixing as clarified by the color injection method. This method showed that mixing occurred within 10 s, which is a very short time compared with the reaction retention time of about 1 hour. Mixing of outlet water was done in a separate container by a magnetic stirrer. In the flat plate reactor experiment, the flat plate of 32 cm × 19 cm coated with TiO<sub>2</sub> was placed instead of mesh layers. The chamber of a SUNTEST XXL+ (Atlas) equipped with three Xenon lamps irradiating solar light (65 J·m<sup>-2</sup>·s<sup>-1</sup> intensity in the range of 300–400 nm) was used for both systems.

### Adsorption experiments of HA in the dark

Before HA degradation experiments under solar light could be done, adsorption experiments of HA on TiO<sub>2</sub> coated films over stainless steel woven meshes were carried out in the dark. The adsorption experiments were carried out with 100 mL and 2 L of HA solution of the desired concentrations in batch and in recirculating flow fixed-bed systems,

respectively, at constant temperature 32 °C ±1 °C. The adsorbed amount of HA ( $q_t$ , mg·m<sup>-2</sup>) on the coated meshes was determined by:

$$q_t = \frac{(C_o - C_t)V}{A_S} \quad (1)$$

where  $C_o$  (mg·L<sup>-1</sup>) is the concentration of HA at  $t_o$ ,  $C_t$  (mg·L<sup>-1</sup>) is the concentration of HA at  $t_t$ ,  $V$  (L) is the volume of the HA solution, and  $A_S$  (m<sup>2</sup>) is the surface area of the stainless steel woven mesh coated by the photocatalyst.  $A_S$  is half the value of the total surface area of the mesh ( $A_{\text{Mesh}}$ ) as the TiO<sub>2</sub> film was coated on one side of the mesh which was facing the anode in the EPD process. Hence:

$$A_S = \frac{1}{2} A_{\text{Mesh}} = \frac{1}{2} L\pi D \quad (2)$$

where  $L$  (m) is the total length of the wire from which the mesh is made and  $D$  (m) is the diameter of the wire. No corrections for the wire diameter due to the coating were carried out as it was small compared with the diameter of the virgin wire. The length of the wire was determined by:

$$L = \frac{4W}{\rho\pi D^2} \quad (3)$$

where  $W$  (kg) is the weight of the wire mesh and  $\rho$  is the density of the stainless steel (7,977 kg·m<sup>-3</sup>). By weighing a mesh, the surface area of that mesh was calculated knowing its wire diameter (0.355 mm according to the manufacturer). The 5.8 cm diameter disk used in the batch experiments weighed 2.88 g, so its coated surface area was 20.3 cm<sup>2</sup> for a projected area  $A_P$  of 26.4 cm<sup>2</sup>. The coated area was thus 0.77 m<sup>2</sup> per m<sup>2</sup> projected area.

Because of the grid structure of the mesh, there was wire overlap at the contact points. From basic geometrical considerations it can be calculated that for the given wire diameter and mesh aperture the overlap was 16.25% of the total wire surface. The exposed coated surface area  $A_S$  was therefore corrected accordingly.

The adsorption experiments were carried out in the dark for different starting concentrations in the range of 6 mg·L<sup>-1</sup> to 14 mg·L<sup>-1</sup>. Assuming that the adsorption kinetics of HA

onto the TiO<sub>2</sub> film on the meshes follows a pseudo-first-order Lagergren kinetic model, the amount of HA adsorbed at equilibrium ( $q_e$ ) can be obtained from curve-fitting of the data to the equation of that model (Qiu et al. 2009; Zhao et al. 2010):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

where  $q_e$  (mg·m<sup>-2</sup>) and  $q_t$  (mg·m<sup>-2</sup>) are the amounts of HA adsorbed at equilibrium and at time  $t$  (min), respectively, and  $k_1$  (min<sup>-1</sup>) is the pseudo-first-order rate constant. The adsorbed amount at equilibrium,  $q_e$  (mg·m<sup>-2</sup>), can be obtained through the empirical equation proposed by Freundlich (Zhao et al. 2010):

$$q_e = K_f C_e^n \quad (5)$$

where  $K_f$  (L·m<sup>-2</sup>, in case of  $n = 1$ ) is the Freundlich isotherm constant and is a measure of adsorptive capacity, and  $n$  determines the intensity of adsorption.

Precise experimental determination of both  $q_e$  and  $C_e$  is difficult because of mass conservation; both are related to the initial concentration of HA in the solution ( $C_o$ ). By combining Equations (4) and (5) and substituting  $C_o$  for  $C_e$ , with an assumption that  $q_e$  is  $C_o$ -dependent in order to simplify the calculations, the amount of HA adsorbed  $q_t$  at  $t_t$  can be obtained by the following equation:

$$q_t = K_f C_o^n (1 - e^{-k_1 t}) \quad (6)$$

## Analytical methods

The HA concentration was determined by the UV absorption at 254 nm, which is representative of the aromatic moieties. This was done with a Hach Lange DR 5,000 spectrophotometer as described in El-Kalliny et al. (2014).

## Solar radiation evaluation

The intensity of the UV solar light (300–400 nm) was measured with a Xenocal UV-sensor with a resolution of 0.1 J·m<sup>-2</sup>·s<sup>-1</sup>. The exposed energy  $Q_{UV,N}$  (kJ·L<sup>-1</sup>) is the

total radiation energy absorbed per unit volume in the reactor from the beginning of an experiment up to a given time (Bandala et al. 2002; Sichel et al. 2007) and it was determined by Malato et al. (1999) as:

$$Q_{UV,N} = Q_{UV,N-1} + \Delta t_n I_N \frac{A_P}{V} \quad (7)$$

with

$$\Delta t_n = t_n - t_{n-1} \quad (8)$$

where  $t_n$ (s) is the experimental time for each sample,  $I_N$  ( $\text{kJ}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) is the intensity of solar UV<sub>300-400 nm</sub> irradiation projected on top of a mesh layer during the time interval  $t_n$ ,  $A_P$  ( $\text{m}^2$ ) is the projected area for the mesh layer,  $N$  is the number of the mesh layers, and  $V$  (L) is the reactor volume. In the case of a first-order reaction, the reaction rate is expressed in units of  $\text{mg}\cdot\text{kJ}^{-1}$  of UV irradiated on the catalyst surface, as the exposed energy was used instead of time to describe the process.

$I_N$ ,  $A_P$ , and  $V$  were taken into account by calculating  $Q_{UV,N}$  for each mesh and the total absorbed energy in the reactor was obtained by adding the values of all the mesh layers.  $I_N$  in UV<sub>300-400 nm</sub> on top of the  $N^{\text{th}}$  mesh ( $N$  is an integer  $\geq 1$ ) for the small-scale batch system was determined by El-Kalliny et al. (2014):

$$I_N = I_0(1-r)^{(N-1)}e^{-\epsilon CNd} \quad (9)$$

where  $I_0$  ( $\text{kJ}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) is the intensity of light on top of the water surface,  $r$  (dimensionless) is the fraction of light absorbed by each mesh, assuming that there is no back or forth reflection from the mesh layers (El-Kalliny et al. 2014),  $\epsilon$  is the extinction coefficient of HA at  $\lambda$  from 300 nm to 400 nm ( $\epsilon_{\text{HA},254 \text{ nm}} = 0.0717 \text{ L}\cdot\text{mg}^{-1}\cdot\text{cm}^{-1}$ ),  $C$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the HA concentration, and  $d$  (cm) is the separation distance between the meshes. The transmission of UV<sub>300-400 nm</sub> through 1 cm of HA ( $10 \text{ mg}\cdot\text{L}^{-1}$ ), measured by the Xenocal UV-sensor, is equal to 0.77 and consequently the  $\epsilon_{\text{HA},300-400 \text{ nm}}$  is equal to  $0.027 \text{ L}\cdot\text{mg}^{-1}\cdot\text{cm}^{-1}$ . Through Equation (9), the HA light absorption is taken into account, where the HA concentration is homogeneously distributed over the reactor (El-Kalliny et al. 2014).

For the large-scale fixed-bed reactor, the separators were taken into account and the intensity of solar UV<sub>300-400 nm</sub>  $I_N$  ( $\text{kJ}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) on top of the  $N^{\text{th}}$  mesh was determined by:

$$I_N = I_0(1-r)^{(N-1)}\left(\frac{A_T - A_{\text{Sep}}}{A_T}\right)e^{-\epsilon CNd} \quad (10)$$

where  $A_T$  ( $\text{m}^2$ ) is the total area of the mesh layer, and  $A_{\text{Sep}}$  ( $\text{m}^2$ ) is the area of the separator that blocks the light.

The applicability of the Langmuir–Hinshelwood (LH) model gives an interpretation for the mechanism of the photocatalytic degradation of HA using coated meshes. The reaction rate in exposed energy  $Q$  is obtained by using the LH expression given by Kumar et al. (2008):

$$r = \frac{-dC}{dQ} = \frac{k_r K_{\text{LH}} C}{1 + K_{\text{LH}} C} \quad (11)$$

where  $k_r$  is the rate constant of photochemical reaction, and  $K_{\text{LH}}$  is the adsorption coefficient of HA onto the catalyst during the irradiation period. If the LH obeys pseudo-first-order kinetics, then  $r$  and  $k_r$  are in  $\text{mg}\cdot\text{kJ}^{-1}$  and  $K_{\text{LH}}$  is in  $\text{L}\cdot\text{mg}^{-1}$ . The reaction rate  $r$  is represented as a function of the initial concentration of HA ( $C_0$ ) as follows:

$$r_0 = k_{\text{app}} C_0 = \frac{k_r K_{\text{LH}} C_0}{1 + K_{\text{LH}} C_0} \quad (12)$$

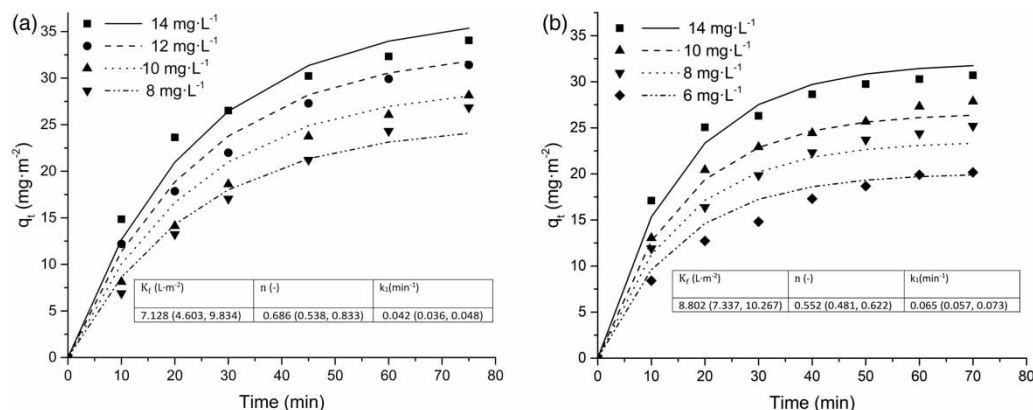
The parameters  $k_r$  and  $K_{\text{LH}}$  were predicted by linearizing Equation (12) as follows:

$$\frac{1}{k_{\text{app}} C_0} = \frac{1}{k_r} + \frac{1}{k_r K_{\text{LH}} C_0} \quad (13)$$

## RESULTS AND DISCUSSION

### Adsorption of HA on coated meshes

Figure 1 shows  $q_t$  ( $\text{mg}\cdot\text{m}^{-2}$ ) as a function of contact time for the small and large mesh structures in the batch system and in the recirculating flow fixed-bed reactor, respectively. The data show a strong increase in  $q_t$  during the first 20 minutes, levelling off thereafter to a saturation value at



**Figure 1** | Adsorption kinetics of HA onto: (a) small coated meshes in the batch reactor and (b) large coated meshes in the recirculating flow fixed-bed reactor for initial concentration  $C_0$  varying between 6 and 14 mg·L<sup>-1</sup>. The lines are obtained by curve-fitting of the measured data according to Equation (6).

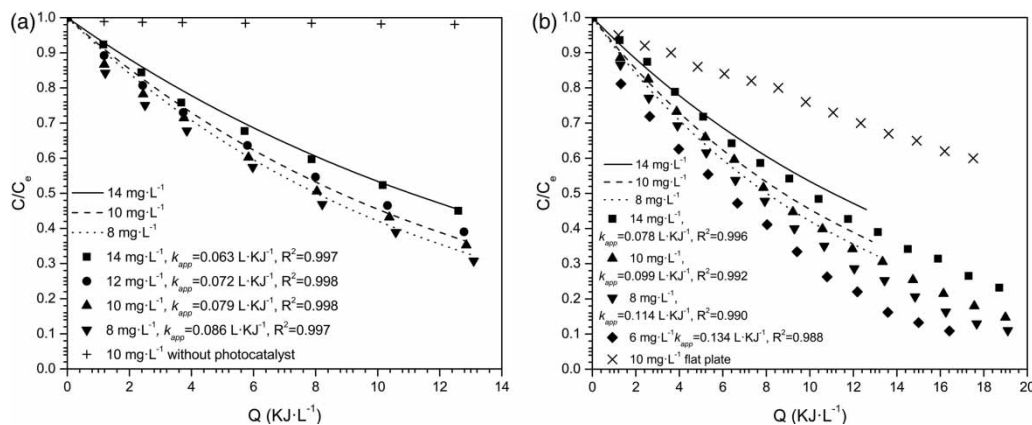
equilibrium. Figure 1 shows that the adsorption capacity increased with increasing  $C_0$ . This is an indication of the presence of sufficient active sites per unit volume that can acquire and adsorb HA molecules with increasing  $C_0$ . The values of  $K_f$ ,  $n$ , and  $k_1$  (from Equation (6)) were obtained by least-square-fitting of the experimental measurements and the resulting curves are drawn for different  $C_0$  in Figure 1. The good fit shows that the adsorption kinetics of HA onto the TiO<sub>2</sub> film coated on the meshes are well-described by the combination of the pseudo-first-order kinetic model and the Freundlich adsorption model (Equation (6)). Therefore, probably a multilayer of adsorbed molecules was formed on the catalyst surface and saturated the adsorption sites. The values of the constants and the corresponding 95% confidence level intervals are inserted in Figure 1. The fit has  $R^2$  of 0.964 and 0.961 with the root-mean-square deviation equal to 1.43 and 1.17 for the small meshes and the large meshes, respectively. The  $K_f$  for the recirculating flow fixed-bed reactor was slightly higher than for the batch system. This reflected a difference range of 7%–14% of calculated  $q_e$  values (Supplementary Data, Table S1, available with the online version of this paper). It was found that the calculated  $q_e$  (via Equation (5)) for small meshes ranged from 44.12 to 30.05 mg·m<sup>-2</sup> for small meshes and ranged from 37.78 to 27.74 mg·m<sup>-2</sup> for large meshes with  $C_0$  values of 14–8 mg·L<sup>-1</sup>. The similarity between the two systems in the behaviour of HA adsorption over the meshes suggests that up-scaling of the mesh structure is feasible. Further, the higher value of the kinetic constant  $k_1$  suggests that there were no mass transfer

limitations in the recirculating flow fixed-bed reactor compared with the well-stirred batch system.

### Solar photocatalytic degradation of HA

Before starting photocatalytic degradation experiments, the systems were preconditioned for 2 h in the dark to attain adsorption equilibrium. When exposure to solar light started, the HA concentration was equal to the  $C_e$ . Therefore, in Figure 2, the decrease of HA concentration due to exposed solar energy  $Q$  (in kJ·L<sup>-1</sup>) is given as  $C/C_e$  for different  $C_0$  values. An additional photolysis experiment was done in the batch reactor by irradiating a HA solution of 10 mg·L<sup>-1</sup> without any photocatalyst present. The results in Figure 2(a) show that no noticeable degradation of HA occurred up to 12.5 kJ·L<sup>-1</sup> of solar energy irradiation without the catalyst. However, when applying the small coated meshes, HA concentrations were reduced to less than half of those when solar irradiation started. By using a flat plate in the fixed bed reactor at an initial HA concentration of 10 mg·L<sup>-1</sup> the solar photocatalytic degradation of HA was 3.4 times lower than in the case of the coated mesh structure at the same exposed energy (Figure 2(b)). Even though the light intensity was not homogeneously distributed over the expanded surface area ( $A_S$  for four coated meshes was increased from 1 m<sup>2</sup> to 3 m<sup>2</sup>, see above), the attenuation factor was still higher than 3, indicating that a more spatial distribution of light over the surface was beneficial. Not only were more active sites of TiO<sub>2</sub> photocatalyst available on the mesh structure than on the





**Figure 2** | (a) Solar photolysis of HA (10 mg·L<sup>-1</sup>) and solar photocatalytic degradation of HA with different initial concentrations ( $C_0$ ) using coated meshes in the batch reactor; (b) solar photocatalytic degradation of HA with different initial concentrations ( $C_0$ ) using coated meshes and a flat plate in the fixed-bed solar photocatalytic reactor. Lines represent the pseudo-first-order kinetics of HA degradation for small meshes. These lines are presented also in (b) to show the extent of deviations between the two systems.

flat plate for the same volume of water, but these sites were also more efficient due to better light distribution. Fujishima *et al.* (2008) already showed that the catalyst efficiency increases by immobilization on a large surface area support, due to an increase in the surface-area-to-volume ratio (Fujishima *et al.* 2008). That the mesh structure allowed a high light penetration and distribution in the reactor was reported earlier (El-Kalliny *et al.* 2014), but now it is also shown that this translates into increased photodegradation of HA.

In order to investigate the dependence of photocatalytic degradation on the adsorption step by checking the applicability of the LH model, it is essential to calculate the apparent rate constants ( $k_{app}$ ) for the removal of HA for different initial HA concentrations (Equation (12)). The relations between  $\ln(C)$  and the exposed energy ( $Q$ ), including light absorption, resulted in straight lines for different  $C_0$ . The slopes of these lines represent the apparent rate constants  $k_{app}$ . These pseudo-first-order rate constants are inserted in Figure 2 together with their correlation coefficient  $R^2$ , which is always greater than 0.98. The  $k_{app}$  was calculated for the first stage of the photocatalytic reaction. In this stage, the concentration of HA is predominant relative to the by-products. Accordingly, the rate of reaction depends on the HA concentration, not on by-products. Therefore, the simplified form of the LH model (Equation (12)) was used. Consequently, the experimental data are fitted to the pseudo-first-order kinetic model, as shown in Figure 2. It is noticeable that  $k_{app}$  for the degradation of

HA in the fixed bed reactor is higher than that in the glass beaker reactor, as is shown in Figure 2. This can be attributed to wall effects of the beaker from absorbing or transmitting part of the incident solar UV light, resulting in a lower captured light energy than calculated. The experimental results show that the  $k_{app}$  decreases with increasing  $C_0$  of HA. This is consistent with what was reported previously by Li *et al.* (2002) for the degradation of HA by a TiO<sub>2</sub> suspension. As the amount of light absorbed by the HA solution was taken into consideration (see Equations (9) and (10)), therefore, this behaviour could be due to the higher number of adsorbed HA molecules (i.e.  $q_e$ ) at a high HA  $C_0$ . These HA molecules may block some active sites on the TiO<sub>2</sub> surface, which are responsible for the production of active radicals. Hence, the number of produced  $\cdot\text{OH}$  decreases with increasing HA  $C_0$ , leading to a slower rate of photodegradation. This indicates that availability of  $\cdot\text{OH}$  is rate-limiting by hindering the reaction of HA with the produced  $\cdot\text{OH}$ .

The  $k_{app}$  for the degradation of HA by coated meshes was 3.4 times higher than that over a flat plate at the same absorbed energy, the same projected area, and at the same initial HA concentration of 10 mg·L<sup>-1</sup>.

The validation of LH kinetics for photodegradation of HA with the glass beaker reactor and with the fixed-bed solar reactor can be done by checking the linearity of the relation of  $1/r_0$  versus  $1/C_0$ . The high correlation coefficients ( $R^2 = 0.969$  and  $0.998$  for small and large meshes, respectively) show that the photocatalytic degradation of HA

using TiO<sub>2</sub> coated over the woven meshes obeyed the LH model. According to this model, the rate of reaction ( $r$ ) is proportional to the fraction of the catalyst surface that is covered by HA. This gives an indication that HA molecules are first adsorbed onto the photocatalyst surface and then decomposed (i.e., the photocatalytic reaction mainly occurs on the catalyst surface and not in the bulk of the solution), which is consistent with previous studies (Bekbolet et al. 2002; Li et al. 2002). The actual rate constant ( $k_r$ ) of the reaction, as obtained from Equation (13), for large coated meshes in the recirculating flow fixed-bed reactor (1.495 mg·kJ<sup>-1</sup>) was close to that for small coated meshes in the batch system (1.462 mg·kJ<sup>-1</sup>), which proves that up-scaling was feasible.

## CONCLUSIONS

- The adsorption kinetics of HA onto TiO<sub>2</sub> film coated over stainless steel woven meshes obeyed pseudo-first-order adsorption kinetics according to the Freundlich adsorption isotherm.
- The degradation kinetics of HA using small coated meshes in the batch reactor and large coated meshes in the recirculating flow fixed-bed solar reactor obeyed the LH kinetic model.
- Up-scaling of mesh size was possible as was shown by the comparable adsorption and photodegradation kinetics for the two investigated reactor sizes.
- The photocatalytic degradation of HA in a solar reactor with four superimposed stainless steel meshes was 3.4 times faster than the flat-plate reactor. This brought the photocatalytic efficiency of such reactors closer to that of dispersed-phase reactors without the complex separation of the TiO<sub>2</sub> photocatalyst.

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