

Radiation extinction of slurried TiO_2 as a function of mechanical action and ionic composition of the suspending media: a key factor in the photocatalytic efficiency

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Abstract

Water contaminants can be completely mineralized by UV activated powdered TiO_2 . By recirculating slurried titania through a fluidized bed (FB) of quartz sand, the apparent quantum efficiency of the photocatalyst can be made several fold higher than by just using the suspended powder. Although, in principle, this could be attributed to the re-distribution of the incoming radiation inside the reacting space by the extra scattering centers (the sand grains), and/or the increment of the active catalytic surface through fragmentation of the coalesced TiO_2 powder by the collisions among the sand grains and the titania particles, we have found that the latter effect predominates. However, the ionic composition of the aqueous media also plays a key role (via electrostatic interactions between both particulate solids), causing a higher effective concentration of TiO_2 inside the reactor. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titania suspensions; Fluidized bed; Catalyst particles desaggregation; Photocatalytic efficiency

1. Introduction

It is well known that water contaminants can be photocatalytically oxidized to harmless compounds by an UV activated suspension of powdered TiO_2 . In a previous work we reported that by recirculating slurried titania through a fully illuminated fluidized bed (FB) of quartz sand (an almost diatonic material) the apparent quantum efficiency of the catalyst could be made several fold higher than by just using the suspended powder in the same concentration [1]. We hypothesized that this could be attributed to the re-distribution of the incoming radiation inside the reactor by the ex-

tra scattering centers (the quartz sand grains) and/or an increment of the active catalytic surface through fragmentation of the coalesced ‘flocs’ of the TiO_2 powder via collisions among the sand grains of the FB and the titania particles.

Certainly, when one tries to perform a kinetic modeling of these photoactivated reactions, a key problem to take into account is the correct evaluation of the absorbed radiation inside the heterogeneous reactor. In this regard, it is recognized that the aggregation state of the catalyst particles has a strong influence on the distribution of the radiation field and moreover, it has been reported that the agglomerating tendency of these finely divided catalyst particles in the suspension is strongly dependent on the pH as well as on pumping or stirring procedures [2]. Besides, according to the DLVO theory [3], the coalescence can be a function

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of the ionic composition of the aqueous media, which is expected to change whenever the products of the photocatalytic degradation are ‘mineralized’ (e.g. to hydrogen chloride, in the case of chlorinated hydrocarbons). Within the framework of this theory, the coalescence of colloidal particles depends upon the interplay of attractive van der Waals forces and repulsive electrostatic forces. The surface charge density of the particles is either positive or negative at pHs lower or higher than the point of zero charge (PZC) and as already said, it is also strongly dependent on ionic strength. Lastly, specific ionic adsorption can modify the PZC of the suspended particles as well [4].

Therefore, the two main objectives of this work were (1) to elucidate the reasons for the apparent higher photocatalytic efficiency of the combined slurry-plus-FB as compared to the slurry-only system and (2) to investigate if the presumed mechanical attrition of the titania flocs attributed to the presence of the fluidized quartz sand was appreciable enough, so as to stabilize a given desaggregation state of the photocatalyst, independently of the pH and the ionic composition of the solution. We hoped that, if the latter were the case, the combined FB/slurry system could be a suitable and easy way for disengaging the radiation field distribution inside the reactor from changes in the solution composition, because the optical properties could be made independent of the progress of the mineralization and in turn, the kinetic

modeling of these photocatalytic reactions could be simplified considerably.

Consequently, a research program was carried out to gain further knowledge on how the presence of the fluidized quartz grains affect the optical behavior of the TiO_2 slurry and how this effect might be affected by the ionic composition of the aqueous media. In addition, titania desaggregation was compared with the action of ultrasound waves.

2. Experimental work

2.1. Experimental set-up

The set-up consisted of a recirculating slurry of titania passing through an aluminum cell with two parallel, optically clear, flat Pyrex glass walls (Fig. 1). The outgoing UV radiation after crossing the slurry flowing through the cell, either in the presence or in the absence of a quartz sand FB, was measured in a Optronic OL series 750 spectrophotometer interfaced with a data station. A collimated 360 nm light beam was perpendicularly directed to a small area of the cell flat wall chosen for irradiation, right above the upper end of the FB, when the latter was used. The internal cell thickness, i.e. the distance between the inside surfaces of the reactor walls, was 7.0 mm. A manual ramrod (2) with its cleaning end made of urethane foam was added on top of the cell, to clean up the inner side

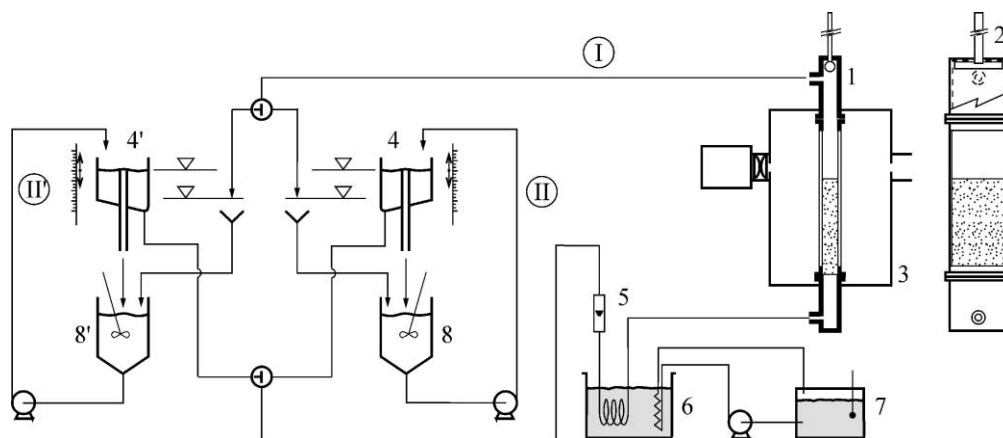


Fig. 1. Experimental set-up: (1) cell; (2) cleaning ramrod; (3) metal housing; (4) gravity-flow reservoir; (5) flow meter; (6) US bath; (7) thermostatic bath; (8) stirred recirculating reservoir. (I) Gravity-flow closed loop. (II or II') Recirculating loop.

of the cell windows whenever required. For measuring, the cell was mounted inside a totally blind, black painted metal housing (3).

A stable FB, at any given expansion, requires maintaining a steady flow. This condition was achieved by means of a constant hydrostatic pressure generation device. It consisted of two types of ‘open-atmosphere’ loops: Loop (I) included the cell (1), a reservoir (4) supported by a jack mechanism for height control, with a centered evacuating tube to set a constant liquid volume of the slurry, a flow meter (5) and a portion of the line submerged into an ultrasonic (US) bath (6) so that the TiO_2 slurry could be exposed at will to US action just before entering the cell. A thermostatic bath (7) was linked to the US bath for temperature control. Loop (II) included a second, stirred reservoir (8), to maintain the homogeneity of the TiO_2 suspension all along the experiments and a peristaltic pump to drive this auxiliary recycling system. Another reservoir (4') containing the same solution used to suspend the TiO_2 in each experiment, raised to the same level of liquid as reservoir (4) to preserve the expansion of the FB and with its own recycling loop (Loop II') was also added for start-up and/or rinsing purposes. A pair of three-way valves was used to switch from slurry to liquid solution and vice versa.

2.2. Materials, methods and experimental procedures

Degussa P25 ($\rho_c = 3.8 \text{ g cm}^{-3}$; $S_g \cong 50 \text{ m}^2 \text{ g}^{-1}$; $d_p = 30\text{--}70 \text{ nm}$; ~ 75 anatase) was used to make the slurry and Aldrich quartz white sand (Cat. no. 27,473-9; $\rho_s = 2.4 \text{ g cm}^{-3}$; $D_p = 250 \mu\text{m}$ (+50–70 mesh) for the FB. Filtered ($0.2 \mu\text{m}$) deionized, distilled water was utilized in all the tests.

Slurries of a standard concentration of TiO_2 (50 mg dm^{-3}) were prepared for each run with, alternatively, four different aqueous solutions: (a) pure water at its natural pH in air (5.5); (b) dilute solution of HCl, pH = 3.5 (c) dilute KCl ($3.16 \times 10^{-7} \text{ mol cm}^{-3}$ same ionic strength as the pH = 3.5 HCl solution); (d) dilute oxalic acid ($5 \times 10^{-7} \text{ mol cm}^{-3}$; pH = 3.4), a widely used model reactant in photocatalytic studies. All the reagents were ACS pure grade.

The outgoing UV radiation through the cell was measured under several different experimental conditions for the circulating P25 slurry: (1) through the

slurry in the absence of a FB inside the cell, either with or without US action; (2) through the slurry in the presence of a FB in the cell, with a bed expansion of five times its unexpanded volume (EX-5) in such way that the light beam crossed the cell through the slurry just above the top of the FB (i.e. no FB along the light beam path). The capacity or fouling of the glass cell windows due to titania/glass adhesive forces was examined by switching from slurry to support solution, to rinse the cell without changing the ionic strength of the media. Lastly, right after this rinsing, the quartz sand grains that made up the FB were flushed from the cell, collected and dried at 393 K. Aliquots were tested for any remaining TiO_2 ‘bound’ to the sand grains owing to the contact with the slurry, by digestion with NH_4SO_4 [1].

Basically, the experimental procedures consisted on the measurement of the outgoing radiation after each one of the following steps: (a) pure liquid solution was recycled through the (I) loop (blank measurement), switching then to (b) slurry circulation (either with or without US action, according to the designated experiment) for 3–5 min, to stabilize the FB (when present), then switching again to (c) pure liquid solution circulation, flowing a minimum of 20-fold the circuit volume in open loop (i.e. discarding the returning solution to rinse the system) which was finally followed by (d) cleaning of the cell windows with the ramrod.

3. Results and discussion

In dealing with heterogeneous media, radiative transport theory uses the radiation extinction concept to give partial but representative account, through the extinction coefficient, of the combined effect of absorption and scattering over the radiation path [5]. At any given wavelength, conventional spectrophotometric measurements can be employed to determine the spectral apparent Napierian extintance, $(\text{ANE})_\lambda$ which operationally can be defined as $(\text{ANE})_\lambda = -\ln(I/I_o)$, where I and I_o represent the outgoing radiation intensities after interacting, respectively, with the participating medium and with a non participating, reference (blank) setting [2].

Our working hypothesis was that mechanical attrition, generated by collisions among the particles of sand and titania, lessens catalyst agglomeration,

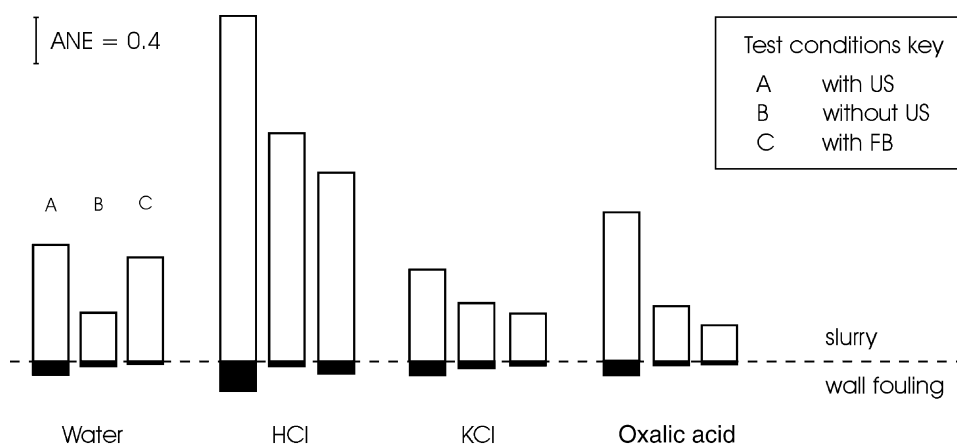


Fig. 2. Apparent Napierian extincance of the powdered TiO_2 slurried in the different solutions, after passing through a five-fold expanded (EX-5) FB of quartz sand.

presumably as efficiently as ultrasound does [2]. Since it is well known that the more desaggregated the titania particles are in the slurry the higher is the radiation extinction they produce, part of the experimental design was specifically aimed at evaluating how the radiation extinction given by slurries immediately after passing throughout FBs of quartz sand (without ultrasound) compare with that of the same slurries after being exposed to the action of ultrasound waves.

Fig. 2 compares the values of $(\text{ANE})_{360\text{ nm}}$ obtained from three types of experiments made with the TiO_2 slurries: (a) slurry exposed to ultrasound, (b) 'natural slurry' (i.e. non-exposed to ultrasound) and (c) the P25 slurry immediately after emerging from a EX-5 FB. Four different ionic solutions (pure water at its natural pH, dilute HCl, dilute KCl and dilute oxalic acid) were used with each of these slurries. The ANE values are given after correcting for glass windows fouling. The latter values, which were obtained by measuring the ANE_{λ} after rinsing the cell with the corresponding support solution, are also shown in Fig. 2. Corrections for windows fouling were carried out by considering that the only observable effect it

produces is an additional extincance that can be subtracted from the measured total ANE [6]. It is clearly observed that the windows fouling for the slurries pre-exposed to US were the most relevant, being the highest for the HCl solution. As regards the amounts of the remaining TiO_2 "bound" to the rinsed sand grains which had been previously in contact with the different slurries, they are indicated in Table 1. Their relevance is discussed in the following paragraphs.

In general, as shown in Fig. 2, the extincance was higher for the US pre-exposed slurries via à vis the 'natural' ones, indicating floc desaggregation induced by the ultrasound action. By focusing now on the slurries right after passing through the FB, it can be observed the following, for pure water, the radiation extincance almost equaled that of the sonicated slurry and was much higher than the one of the 'natural' slurry. This finding is in agreement with our main working hypothesis, namely, that the sand FB acts as an attrition device for the coalesced TiO_2 particles. Nevertheless, for the other ionic solutions the lowest ANEs were recorded for the slurries that had passed through the FB, which appeared to be in contradiction

Table 1

Remaining TiO_2 'bound' to the sand grains put in contact with the slurries of titania dispersed in different solutions

Solution	Pure water	HCl	KCl ($3.16 \times 10^{-7} \text{ mol cm}^{-3}$)	Oxalic acid ($5 \times 10^{-7} \text{ mol cm}^{-3}$)
pH	5.5	3.5	5.5	3.4
TiO_2/sand (mg/g)	0.5	0.25	1.35	2.11

with the previously mentioned results. How can these outcomes be rationalized, then?

As said before, and according to the DLVO theory, the interactions among charged particulate matter (e.g., among the TiO_2 particles and between them and the quartz sand grains) depend upon the interplay of surface-related forces (ionic double layer) and bulk type (van der Waals) attractive forces. The interaction between the double layers ranges from indifference at large distances to increasing repulsion/attraction, as the particles approach. The potential energy associated with these interactions is closely associated to the double layer Gouy–Chapman potential ψ , given by [7]:

$$\psi = \psi_0 e^{-\chi r} \quad (1)$$

where ψ_0 is the surface potential, r the distance from the particle surface radius and χ^{-1} usually represents the ‘double layer thickness’ of a cloud of charged ions around the particle and can be expressed by:

$$\chi = \frac{4\pi}{\epsilon k T} \sum n_i^0 z_i^2 e^2 \quad (2)$$

where n_i^0 the concentration of the i th ion of valence z_i , and e_0 , k and T are the electronic charge, the Boltzman constant and the absolute temperature, respectively. The surface potential depends upon the solution pH, but is a function of specific ionic adsorption as well. The bulk interactions lead to mutual attraction unless the particles get too close, when there is a sharp repulsion.

It has been reported that the PZC (i.e. $\psi_0 = 0$) of anatase in pure water is at pHs between 6.3 and 6.6 [8], whereas for silica it is around 2 [9]. Therefore, for the slurry of P25 in water at pH = 5.5 the titania particles are quite close to their PZC, but still on their positive side of electrical charging, while the quartz particles are negatively charged. So, the TiO_2 particles “repel” among themselves but are attracted by the negatively charged sand grains which are, therewith, surrounded by a “cloud” of titania (Fig. 3.) Therefore, the concentration of slurried titania inside the FB will be higher than in the rest of the flow circuit (I). As a consequence and after a simple mass balance (i.e. the total amount of TiO_2 is either in the slurry or retained in the clouds surrounding the quartz grains) it comes out that a less concentrated slurry than the initial one (and so less radiation extinctive), will flow outside the FB. Thus, the observable ANE of the exiting slurry

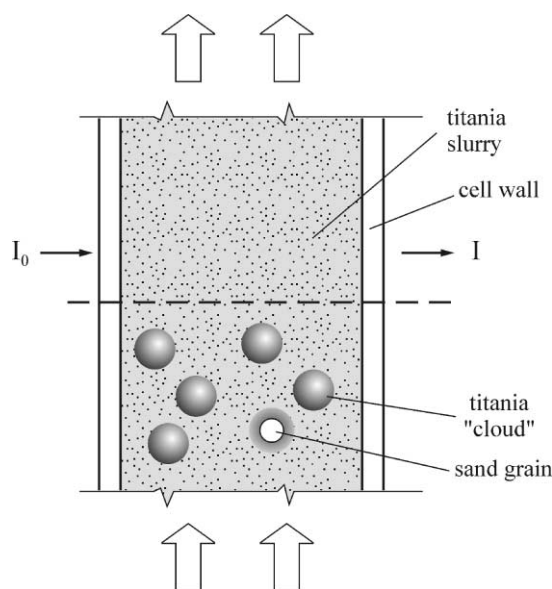


Fig. 3. Schematic diagram of the components of the cell/FB/slurry optical composite when lit across. The light beam is positioned right above the upper end of the five-fold expanded FB (EX-5).

appears smaller than in the absence of the FB grains. In other words, electrostatic effects (which cause accumulation of TiO_2 inside the FB) can counteract by some extent the FB desaggregation effect (which enhances light extinction). Moreover, some of the TiO_2 particles become retained onto the sand grains surface by bulk type (van der Waals) forces, and will remain “bound” even after rinsing with the same slurry support solution (Table 1).

In the pH = 3.5 HCl solution, the titania particles are more positively charged than in pure water (i.e. their inter-particle repulsive forces are higher) so that they have even a lower tendency to coalesce. The higher surface charge density of the TiO_2 particles at this low pH, also explains its lowest retention by the sand grains after rinsing (Table 1).

For the KCl solution a more compressed double layer, as compared to pure water (higher ionic strength, but still natural pH = 5.5) diminishes the repulsive forces among TiO_2 particles therewith favoring their clouding around (and the binding to) the sand grains (Table 1). These combined effects lead to a less concentrated, circulating slurry and override the attrition of the FB upon the titania flocs. A shifting of the ψ_0

of TiO_2 toward less positive values, by specific adsorption of oxalate anions, would explain the behavior of slurries in oxalic acid solution (despite the pH being 3.4) the particles are close to neutral charging, thus favoring coalescence, clouding (less concentrated slurry) and binding to sand grains (Table 1).

In order to correlate the optical behavior shown by the TiO_2 slurries just after emerging from the EX-5 FB, with those of the same slurries inside the FB itself, a new series of tests was carried out, by measuring the outgoing radiation from a fully expanded FB. A bed expansion of seven times the unexpanded volume (from now on, EX-7) was used since, under these conditions, the bed height was enough for the light beam to cross the cell either through the quartz sand-only FB or through the slurry/quartz sand FB particles composite.

For all of the ionic solutions, ANE values were determined using this arrangement, after each of the following steps of experimental conditions: (1) generation of an EX-7 FB, uphold by pure liquid solution circulating through loop I; (2) switching to slurry circulation through the likewise expanded bed and measuring after 3–5 min, once the FB had stabilized again at EX-7; (3) switching for a second time to pure liquid solution, flowing a minimum of 20-fold the circuit volume in open loop (i.e. discarding the returning solution to rinse/clean the system) while upholding now an EX-5 FB (this step was aimed at assessing the impact of windows fouling on light extinction); (4) expanding again the rinsed FB to EX-7 by flowing pure liquid solution for another 10 min; (5) bringing back the FB expansion to EX-5, to examine

if the mechanical cleaning of the windows by sand scraping in the previous step was significant.

In Table 2, the values of ANE obtained after steps 1 to 4 are presented in rows coded (a), (b), (d) and (c), respectively. These values are representative of the light extinction by the corresponding system configurations, namely: (a) bare sand, in the EX-7 FBs, uphold by pure liquid solutions; (b) composites of FB (EX-7)/ TiO_2 slurry, and fouled walls; (c) EX-7 FBs of sand with bound TiO_2 , after having been put in contact with the slurry and rinsed; and (d) windows fouling by titania sticking, after rinsing with the corresponding pure liquid solution at EX-5. The values of ANE measured after step 5 were almost the same as those presented in row (d), indicating that the cleaning of the fouled windows via sand scraping was negligible in all the cases. To clarify matters, a schematic diagram is shown in Fig. 4.

It comes from Table 2 that the radiation extinction of the FB/slurry composite in HCl was the largest, followed by those in KCl, pure water and oxalic acid solution, respectively, in a decreasing order. According to these results and to the electrochemical arguments already put forward, it can be readily concluded that the high extinction power of the system in HCl can be mainly attributed to the natural, low tendency to coalesce of TiO_2 particles in acidic media. Also, the values of ANE in row (c), corresponding to just the FB of sand, with bound TiO_2 but in the absence of slurry, correlate, in general, with those presented in Table 1, i.e. the higher the amount of TiO_2 bound to the sand is, the higher the light extinction by the FB becomes. However, the system in oxalic acid apparently seems

Table 2

Apparent Napierian extinctance of the cell for the monochromated light beam of the spectrophotometer going through the indicated composite systems

Measurement code	System	(ANE) _{360 nm}			
		Solution			
		Water	HCl	KCl	Oxalic acid
(a)	FB (EX-7) of bare sand	2.74	2.96	2.87	2.74
(b)	FB (EX-7) of sand with bound TiO_2 + slurry (+ fouled walls)	3.58	4.90	4.66	3.22
(c)	FB (EX-7) of sand with bound TiO_2 (+ fouled walls)	3.07	3.11	4.09	3.06
Cell walls fouling after rinsing ^a	0.17	0.25	0.76	0.01	

^a The FB was only expanded five-fold (EX-5) to take these measurements.

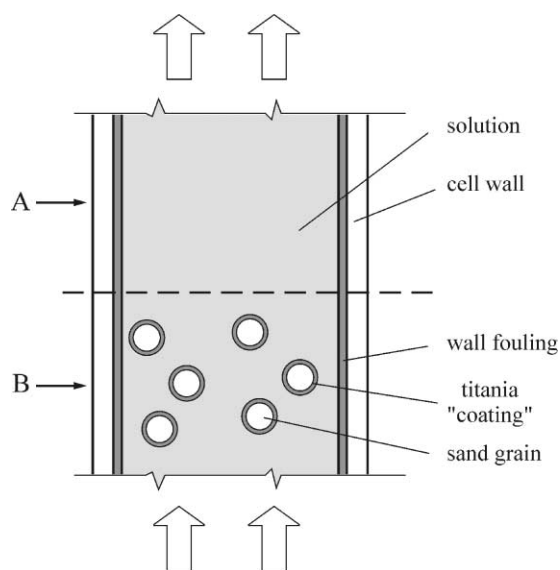


Fig. 4. Schematic diagram of the components of the cell/FB/rinsed slurry optical composite when lit across. (A) Light beam position for the five-fold expanded FB (EX-5). (B) Light beam position for the seven-fold expanded FB (EX-7).

to deny this rule: notwithstanding the quartz sand had the highest loading of 'bound' TiO_2 (Table 1), this system showed the lowest ANE.

Table 2 further shows that fouling of the cell glass windows by TiO_2 adhesion was present in each of the light extinction measurements (row d) and that it was particularly appreciable in the case of KCl solution. In addition, it is clear at this time, that the ANEs measured on the FB/slurry composites are the outcome of the combined effect of scattering and light absorption by the titania slurry, by the FB of quartz sand with bound TiO_2 and by wall fouling. Therewith, we judged necessary to distinguish among all these sources of light extinction, before continuing with further analyses. This was made in a semiquantitative way, by assuming that the combined ANEs by the slurry and of the FB of the sand is additive, i.e. equivalent to the simple summation of the extinctive power of each component of the optical system taken independently.

In the upper side of Fig. 5, the calculated net ANE values of the FB/ TiO_2 slurry composites for all the

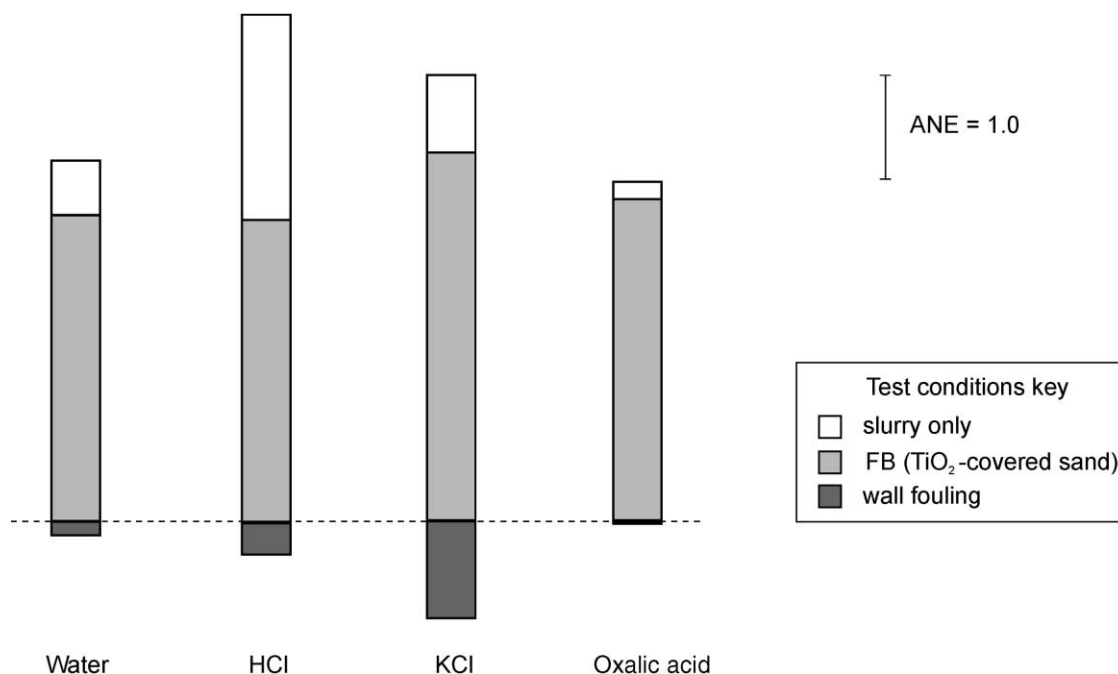


Fig. 5. Apparent Napierian extingtnance of the powdered TiO_2 slurried in the different solutions and of the TiO_2 -covered quartz sand in a seven-fold expanded (EX-7) FB.

ionic solutions are compared, after correcting for cell windows fouling (b–d in Table 2). They are presented as the summation of those assigned to the FB of sand with bound TiO_2 (c–d) and to the slurries (b–c), respectively, from the same Table. For comparison purposes, the values of ANE due to wall fouling only are also included in Fig. 5, lower part.

A fairly good correlation arises when the ANE values of the titania slurries inside the FB in Fig. 5 are compared with those for the same slurries (i.e. equal amounts of titania dispersed in the same ionic solution) observed just over the FB (third bars in Fig. 2). Yet, inside the FB the slurry in the KCl solution appears to have a higher extinction power than the corresponding value in pure water, while the opposite is observed for these slurries examined immediately after emerging from the sand bed. Once more, the more compressed double layers in the KCl solution (as compared to the pure water environment) diminish the repulsive forces among TiO_2 particles, favoring their clouding around the sand grains. The slurry inside the FB (a composite of ‘bulk’ and ‘sand-cloud’ slurried titania) is, then, more concentrated than immediately outside the FB and therefore a higher ANE is observed in the former case.

It further comes out as particularly remarkable that the extinguishing power of the FB of the sand with bound TiO_2 in oxalic acid is about the same as those of the other solution systems (Table 2). Indeed, it is quite likely that, even though this sand had the highest loading of bound titania (Table 1), the surface of the quartz grains became (optically) saturated at or about 1 mg TiO_2/g sand. This loading represents about a monolayer of the P-25 titania powder onto flat spheres of 250 μm of diameter [10]. However, we are more inclined to think that electrostatic effects suffice to give account of the phenomena: charge neutralization by specific adsorption of oxalate anions would favor not only the coalescence of TiO_2 particles in the slurry (notice the low ANE of this slurry in oxalic acid solution, Fig. 5) but also on the surface of the sand grains, throughout the binding process, lessening by this ‘surface agglomeration’ their radiation extinguishing capability [1].

Cell windows fouling by titania sticking to glass (assuming glass surface properties similar to those of quartz) can be explained, also, by the same type of surface/bulk interactions: the positively charged TiO_2

particles would adhere by double layer and bulk forces to the negatively charged glass windows.

4. Conclusions

In a photocatalytic reactor device, an in situ FB of quartz sand can be as effective as ultrasound waves as an attrition device for the coalescing particles of a TiO_2 slurry circulating throughout it. Moreover, as a result of double layer and bulk interactions among the particulate matter (e.g., among the TiO_2 particles and between them and the quartz sand grains) the FB may act as a concentrator for the titania slurry, hence increasing its photocatalytic capacity.

All of this would explain the higher photocatalytic apparent efficiency of a combined slurry/FB versus slurry-only system previously reported by us. Fouling of reactor windows and of the solid surfaces of the containing reaction system by TiO_2 sticking, can be relevant, specially for highly dispersed slurries and should never be ignored in dealing with photocatalytic efficiencies. Not only the aggregation state of the titania photocatalyst but also the concentrating effect of the FB upon the slurry and wall fouling, depend strongly on the ionic composition of the supporting solution.

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