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The photocatalytic decomposition of microcystin-LR using selected titanium dioxide materials.

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Keywords: TiO_2, photocatalyst, cyanotoxin, microcystin-LR.

Abstract

Microcystins (cyclic heptapeptides) produced by a number of freshwater cyanobacteria are a potential cause for concern in potable water supplies due to their acute and chronic toxicity. TiO_2 photocatalysis is a promising technology for removal of these toxins from drinking water. It is, however, necessary to have a sufficient knowledge of how the catalyst materials cause the degradation of the toxins through the photocatalytic process. The present study reports microcystin degradation products of the photocatalytic oxidation by using a number of commercial TiO_2 powder (P25, PC50, PC500 and UV100) and granular (KO1, KO3, TiCat-C, TiCat-S) materials, so aiding the mechanistic understanding of this process. Liquid chromatography-mass spectrometry analysis demonstrated that the major destruction pathway of microcystin for all the catalysts tested followed almost the same pathway for each of the materials, indicating the physical properties of the catalysts had little effects on the degradation pathway of microcystin-LR.

1. Introduction

Cyanotoxins are a group of naturally produced biomolecules from several genera of cyanobacteria that occur in freshwaters around the world and have been well documented as a potential hazard to human health (Carmichael, 1995; Sivonen, 1996). Microcystins are reported to be the most commonly occurring cyanotoxins found in water, and have been linked with poisonings of animals and humans exposed to contaminated water (Codd et al., 1989). The most commonly detected microcystin is microcystin-LR. Acute exposure can results in hepatic injury and in extreme cases this can prove fatal (Dunn, 1996). One such incident reported from South America resulted in the death of over 50 dialysis patients due to the use of microcystin-contaminated water in their treatment (Dunn, 1996). Exposure to low levels of microcystin in drinking water over a prolonged period may contribute to life threatening illnesses such as primary liver cancer (PLC) through the known tumour-promoting activities of these compounds (Yu, 1994).

Cyanotoxins present in drinking water sources are a serious concern world-wide and may pose a considerable threat to human health, therefore various treatments have been evaluated for their removal (Lawton et al., 1999). Most conventional water treatment systems, however, are not reliable for the elimination of these toxins from potable water (Lawton et al., 1999, Keijola et al., 1988, Lahtik et

al., 1989). One particular challenge with chlorination is the formation of chlorinated by products of microcyctins. This was reported by Merel et al. in their study of the byproducts generated when chorination was used as a treatment process for the removal of microcystin-LR (Merel et al., 2009). The biodegradation of cyanotoxins have also been previously reported (Edwards et al., 2003; Torunska et al., 2008). Edwards et al. reported the half life for the biodegradation of microcystin-LR, -LF and nodularin in water of between 4 and 18 days (Edwards et al., 2003).

TiO_2 photocatalysis has previously been shown to effectively destroy microcystin-LR and related toxins in aqueous solutions even at extremely high concentrations (Robertson et al., 1997, Lawton et al., 1999, Liu et al., 2002). A number of by-products were generated by the photocatalytic oxidation of microcystin-LR and this has enabled the elucidation of some of the possible degradation pathways (Lawton et al., 1999, Liu et al., 2003). Another study has also evaluated the potential toxicity of degradation products using protein phosphatase inhibition assay and brine shrimp bioassay (Liu et al., 2002).

To date, most work performed on the photocatalytic destruction of microcystins has been performed using Degussa P25. In addition to P25, there are a number of commercially available TiO_2 catalyst

materials that could be used for microcystin destruction. This paper reports a study of the destruction of microcystin using a range of commercially TiO_2 photocatalyst powder materials, including Degussa P25. In addition a number of novel granular TiO_2 photocatalysts have also been examined.

2. Materials and Methods.

2.1. Materials

Microcystin-LR was purified from a laboratory culture of *Microcystis aeruginosa* PCC7820 using the procedure previously detailed (Edwards et al., 1996). Titanium dioxide P25 (Degussa), PC50 (Millennium Chemicals), PC-500 (Millennium Chemicals) and UV-100 (Hombikat) were used as received. TiO_2 catalysts KO1, KO3, TiCat-S and TiCat-C are synthesized granular materials supplied by Sachtleben Chemie GmbH and were also used as received. The properties of these catalysts are summarized in Table 1. All solutions were prepared in Milli-Q water and all other reagents and solvents used were of analytical or HPLC grade.

2.2. *Photocatalysis*

Aqueous solutions of microcystin-LR containing 0.1% (w/v) TiO_2 were illuminated in the presence of air with a 480 W xenon lamp (Uvalight Technology Ltd.; spectral output 330-450 nm). The reactions were carried out in glass bottles with constant stirring. The distance from the UV lamp to the surface of the test solution was 30 cm, with an intensity of 11.0 mW cm^{-2} measured using a UV meter (Dr. Honle GmbH, Martinsried, Germany). At timed intervals, samples were taken and centrifuged to remove TiO_2 prior to analysis by LC-MS. The initial concentration of microcystin-LR was 10 μg mL^{-1}.

The reactor experiments were performed in a simple packed bed flow reactor (figure 1). The microcystin solutions (350 ng mL^{-1}) was pumped from a reservoir through a series of five glass columns packed with TiO_2 pellets (TiCat-C), weight 1.80 g per column with a total catalyst surface area exposed to UV light of 6.6 cm^2. The mass of catalyst in the five columns totalled 9.0 g of TiO_2 in weight, 33 cm^2 in surface area exposed to UV light and passing flow length 35 cm. The unit was irradiated with a 480 W xenon lamp, 30 cm distance to glass column of TiO_2. In addition a mirror was positioned 4 cm from the back of the reactor unit to facilitate irradiation of the reverse side of the packed columns. At specific time intervals, the treated solution was collected and analysed using LC-MS as detailed in section 2.3.

2.3. Analysis

The LC-MS system used in the study consisted of Waters Alliance 2690 HPLC Pump connected with Waters 996 PDA and Micromass ZQ Mass spectrometer with electrospray ionisation source. HPLC column was Waters Symmetry 300^{TM} C18 column (5 μm, 2.1 × 150 mm, Waters, USA). The injection volume was between 10-50 μL and the Mobile phase was a gradient elution of water and acetonitrile, both containing 0.05% trifluoroacetic acids (TFA). The gradient elution was programmed as 5-20% of acetonitrile in 10 minute followed by an increase to 80% by 35 minutes. The mass data was

obtained in the positive ion mode by full scanning from m/z 100-1100 with a dwell time of 2 seconds and Select Ion Recording (SIR) acquisition with a dwell time 0.75 seconds. Masslynx software workstation was used for the LC-MS instrument control, data acquisition and data processing.

3. Results and discussion

Previously we reported the destruction of microcystin-LR using Degussa P25 TiO_2 powders (Robertson et al., 1997; Lawton et al., 1999; Cornish et al., 2000; Liu et al., 2002, 2003]. One of the objectives of this study was to evaluate the photocatalytic efficiency of a range of different powder catalysts compared with P25. The photocatalytic degradation of microcystin-LR on the different TiO_2 powders (P25, PC50, PC100, PC500 and UV100) as a function of irradiation times are shown in figure 2. It can be seen that the photocatalytic degradation of microcystin-LR on the five TiO_2 powders was rapid and complete after 100 min irradiation. From the results it is clear that P25 appeared to be the most effective catalyst with greater than 90% of the toxin destroyed within 20 minutes irradiation (835 ng mL^{-1} remained). Within this irradiation period the other catalysts only achieved between 25% to 60% microcystin destruction, with 3961, 4876, 3886 and 7633 ng mL^{-1} of the toxin remaining for PC50, PC100, PC500 and UV100 respectively. Therefore, the effectiveness of the photocatalysts for destruction of microcystin-LR within a 20 minute irradiation, was in the order of P25>PC500>PC50>PC100>UV100. After 100 minutes photocatalysis, however, the order of efficiency changed to PC25>UV100> PC100>PC500> and PC50 due to increased destruction rate of UV 100 and PC 100 over PC 500 and PC 50 (Figure 2.) This observation indicated that the reaction rate during

different phases of photocatalysis was not consistent, but variable. It is interesting to note that the photocatalytic activity of TiO_2 in the degradation of microcystin-LR does not appear to depend on surface area. PC500 and UV100 have significant larger surface area compared to both P25 and PC50 (Table 1), respectively. The photocatalytic activities of PC500 and UV100, however, were similar PC50 and poorer than P25.

Previously we proposed the mechanism of the photocatalytic destruction of microcystin-LR using a Degussa P25 TiO_2 photocatalyst through analysis of the by-products using LCMS (Lawton et al., 1999; Liu et al., 2002, 2003). The degradation products with the various powder photocatalysts examined in this study were explored to determine if there were any differences in the mechanism. Ion extraction techniques were used to establish extracted-ion chromatogram for further characterisation of the byproducts peaks and calculation of peak area. Table 2 shows the peak areas of breakdown products together with their protonated ions and retention times at various time periods of the photocatalytic process. A total of 14 degradation products were detected by LC-MS analysis. The structural assignment of the breakdown products of the photocatalytic destruction of microcystin-LR was based on the analysis of the LC-Mass

196 chromatogram and correspondent mass spectrum of by-products
197 (peaks 1-14) (Liu et al., 2003).
198
199 Based on the LCMS data it was found that for each of the catalysts
200 the breakdown mechanism was similar to that previously reported
201 by us (Liu et al., 2003) for Degussa P25. This involved an initial
202 photoisomerisation of the microcystin, followed by hydroxyl radical
203 attack and subsequent cleavage of the Adda conjugated diene
204 structure. This is then followed by cleavage of the Mdha double
205 bond with subsequent residue oxidation and peptide bond
206 hydrolysis. The LCMS data also suggested that the photocatalytic
207 degradation of microcystin-LR followed the same pathway on all
208 four of the powder catalysts. Figure 3 presents the relative ratios of
209 each of the degradation products generated and from this it is clear
210 that the same breakdown products were generated in similar ratios
211 for each of the powder catalysts examined. In this figure the peak
212 areas correspond to the sum of the each of the 14 products over the
213 100 min from table 2 and not at an individual time.
214
215 When compared to the powder TiO_2 samples discussed above, the
216 granular catalysts (figure 4) displayed much lower photocatalytic
217 destruction efficiencies for microcystin-LR. After 100 minutes
218 photocatalysis, the percentage destruction of microcystin-LR was
219 79%, 75%, 63% and 4% for KO1, KO3, TiCat-C, and TiCat-S

respectively. Studies on physical and chemical characterisations of the catalysts revealed that the granular catalysts showed similar spectroscopic properties with each other (Wood, 2009). The adsorption surface area was similar too for KO3 (41.7 m^2g^{-1}), TiCat-C (40.8 m^2g^{-1}) and KO1 (48.6 m^2g^{-1}), but was substantially higher for TiCat-S (199.6 m^2g^{-1}) (Wood, 2009). It has previously been suggested that adsorption surface area of catalyst might play an important role in photocatalysis efficiency (Hoffman et. al., 1995). Interestingly, the TiCat-S material which had the largest adsorption area displayed the lowest photocatalytic activity for microcystin destruction (figure 4). This observation indicated that photocatalytic efficiency of the granules appeared to be related to not only to their adsorption surface area but also exposure area to UV light. In the reactor filled with granules, the adsorption surface area of catalysts is not equal to its surface area exposed to UV light because the inner matrix of the particle while contributing to surface area and potentially adsorption may be shielded from UV light and hence not activated. Consequently the area exposed to light should be considered together with adsorption area in the case of photoactive granule catalysts. This hypothesis could explain why granules had a lower efficiency than powders in the photocatalytic destruction of the toxin.

While both KO1 and KO3 appeared to be more effective photocatalysts than TiCat-C, it was noted that TiCat-C was a more robust material. While the TiCat-C material remained intact, the KO1 and KO3 materials physically decomposed to powders during the course of the experiments. The utilisation of the TiCat-C catalyst in a basic packed bed flow reactors was investigated as a potential device for larger scale assessment of toxin destruction (figure 1). On photocatalysis in the back bed flow reactor the concentration of microcystin was reduced from an initial concentration of 333 ng mL^{-1} to 23 ng mL^{-1} (Figure 5), which corresponded to greater than 90% toxin destruction. Since the concentration limit of microcystin in drinking water recommended by WHO is 1.0 µg L^{-1} (1 ng mL^{-1}), the microcystin-containing water used in this study was more than 300 fold higher than the limit concentration. It was observed that the slower the flow rates the greater the destruction of microcystin (Figure 5). This is not surprising since at slower flow rates the microcystin solution will be in contact with the photocatalyst longer hence allowing more destruction. From the above observation, it is proposed that in a device to remove microcystin in passing flow, catalyst surface area exposed to UV irradiation and flow duration exposed to photocatalysis appeared to be the most important factors related to efficacy as previously suggested. For this design of reactor air bubbles in the system are not considered to pose a significant problem with the efficiency of the unit. These crucial

267 factors should be to considered in future reactor development. It is
268 important to note that this particular reactor design would not be
269 the optimum configuration and in the up-scaled process. In
270 particular it will be critical to ensure the minimisation of photonic
271 loss due to reflections in any practical process.

4. Conclusions

Each of the photocatalyst materials examined in this study successfully degraded microcystin-LR. In comparing to the four commercial TiO_2 powders the effectiveness for toxin destruction was found to be in the order of P25>PC500>PC50>PC100>UV100. Degussa P25 appeared to be the most effective catalyst with more than 90% microcystin destruction achieved within 20 minutes while each of the other catalysts only destroyed around 25% to 60% of microcystin over the same time frame. It would appear that surface area of the photocatalysts did not influence the photocatalytic degradation of microcystin-LR. The major photocatalytic degradation mechanism for each of the powder catalysts examined appears to follow the same pathway, with isomerisation, hydroxyl radical attack and cleavage of the Adda conjugated diene structure, Mdha double bond cleavage followed by residue oxidation and peptide bone hydrolysis. The physical properties of the selected commercial catalysts had little effects on the degradation pathway of microcystin-LR.

Although the photocatalytic efficiencies of the granular TiO_2 samples appeared to be lower than those of powder catalysts, the great advantage of the granular materials over their powder counterparts would be their applicability in practical water treatment systems. With these materials separation of the catalysts from the treated

water would be much simpler than is the case with powder samples. Furthermore, the lower efficiency of granular materials could be compensated by increasing the quantity of catalyst in the reactor since large quantity of granular materials would be acceptable if isolation is unnecessary.

The simple flow reactor system proved to be an effective test bed unit for the assessment of the granular and powder photocatalysts which will be utilised in the larger scale reactors. In addition it has provided useful detail on the effects of flow rate, contact time and light distribution on the efficiency of the photocatalytic destruction of the microcystins. It is important to emphasize that the results obtained in the simple reactor study are only semi quantitative. Consequently these are initial exploratory observations and further work will be necessary to further elucidate the important parameters that need to be considered in large scale water treatment systems.

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392

393 **Legends for Figures and Tables.**

394 **Figure 1.** Packed Bed Flow Photocatalytic Reactor. 1-Reservoir of
395 water containing microcystins, 2-Pump controlling flow rate. 3-
396 Tubing, 4-Glass column packed with TiO_2 pellets 5-Sample
397 collection point, 6-UV lamp, 480 W xenon lamp (Uvalight
398 Technology Ltd.; spectral output 330-450 nm), 30 cm distance to
399 glass column of $TiO_{2.,}$ 7- Mirror.

400 **Figure 2**. The photocatalytic degradation of Microcystin-LR on TiO_2
401 (P25, PC50, PC500 and UV100) over 100 min irradiation times.

402 **Figure 3.** Total peak area of breakdown products of microcystin-LR
403 during photocatalysis (0-100 min)

404 **Figure 4.** Decomposition of microcystin-LR with granular TiO_2
405 catalysts

406 **Figure 5.** Concentration variation of microcystin-LR (ng mL^{-1})
407 during photocatalysis with flow reactor at flow rates of 5 and 1 mL
408 min^{-1}.

409 **Table 1**. The properties of TiO_2 catalysts.

410 **Table 2.** Peak area (count × 10^6) of by-products of microcystin-LR
411 with photocatalysis with selected TiO_2 catalysts

412
413

414

415

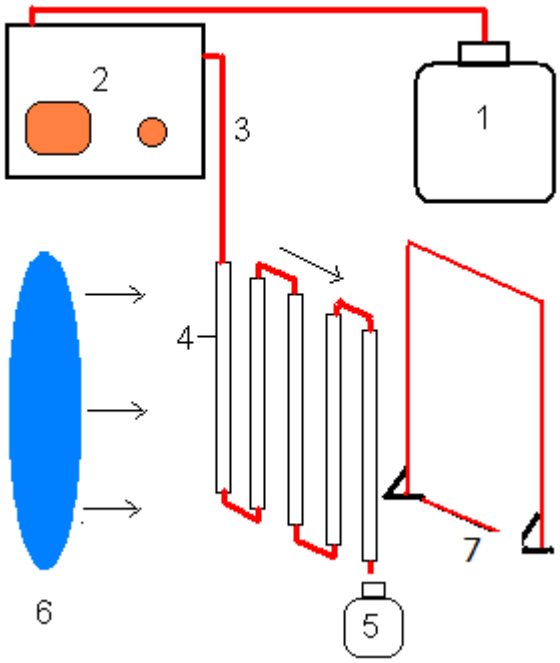

Figure 1.

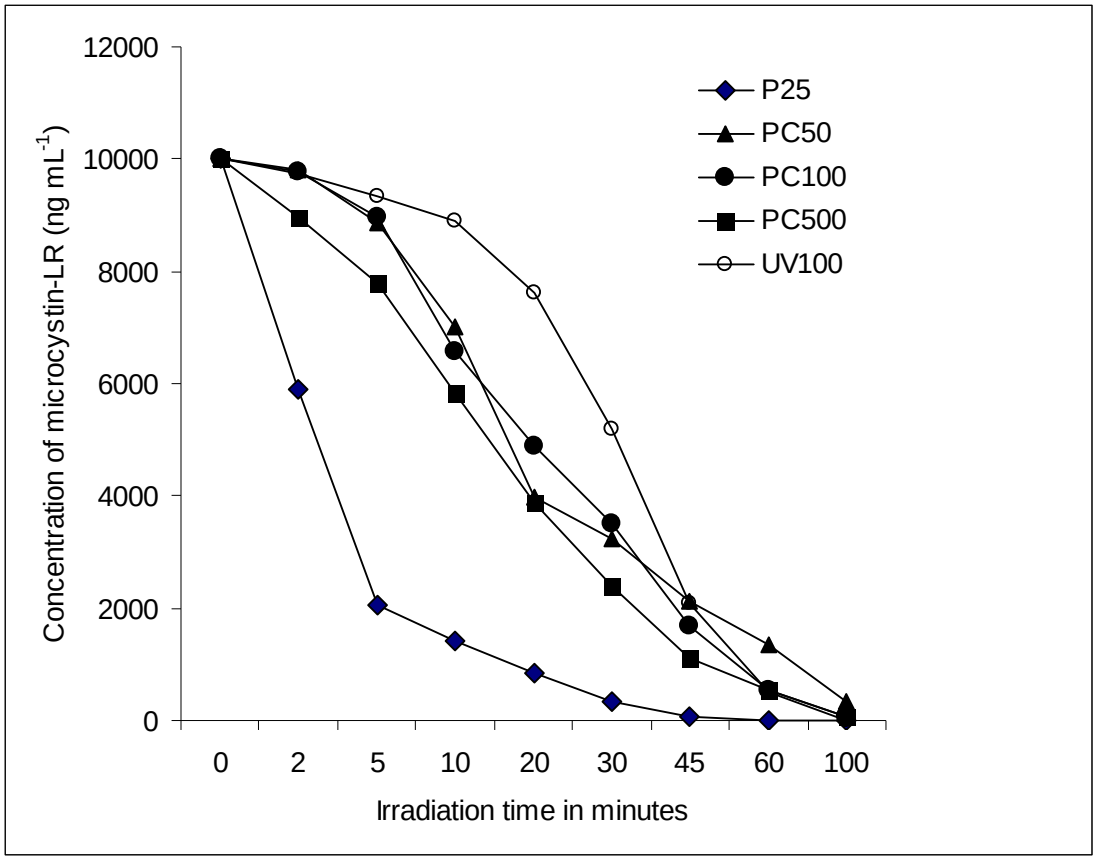
12000
10000
8000
6000
4000
2000
0
Concentration of microcystin-LR (ng mL-1)
0
2
5
10
20
30
45
60
100
Irradiation time in minutes
P25
PC50
PC100
PC500
UV100

Figure 2.

Figure 3.

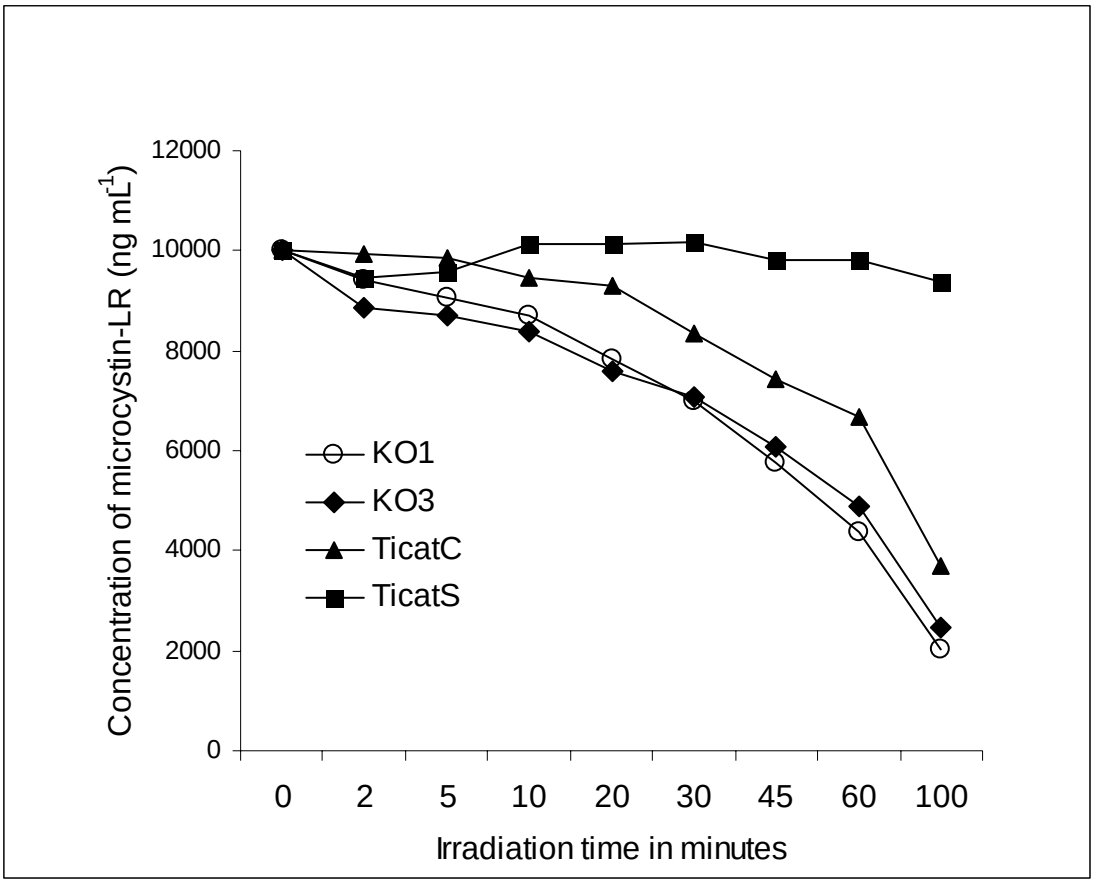
Concentration of microcystin-LR (ng mL-1)
12000
10000
8000
6000
4000
2000
0
KO1
KO3
TicatC
TicatS
0
2
5
10
20
30
45
60
100
Irradiation time in minutes

Figure 4.

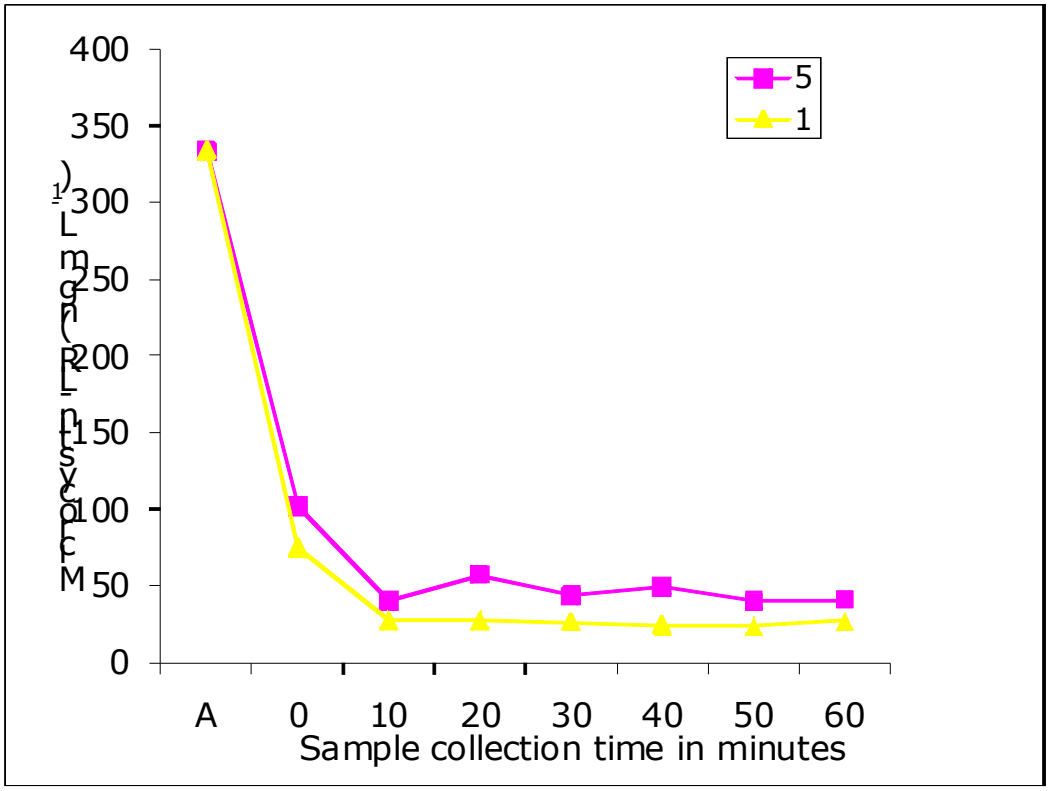
400
350
300
250
200
150
100
50
0
5
1
A
0
10
20
30
40
50
60
Sample collection time in minutes

Figure 5.

442

Catalyst TiO_2	**Anatase**	**Rutile**	**BET Surface Area / $m^2 g^{-1}$**
Degussa P25	75%	25%	50
Millennium PC50	99%	1%	44
Millennium PC500	100%	0%	284
Hombikat UV100	100%	0%	280
KO1	100%	0%	42
KO3	100%	0%	49
TiCat-C	100%	0%	41
TiCat-S	100%	0%	200

443

444 **Table 1**.

Table 2.

TiO_2	Product name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	MCLR
	$[M+H]^+$	272	323 *	495	853	795	783	835	907	175	1029	759	787	965 *	162	996
	Retention time (min)	2.1-2.3	6.7-7.0	8.9-9.1	10.5-10.7	10.5-10.8	10.5-10.8	12.9-13.1	15.5-15.7	16.3-16.4	17.8-20.0	2.3-20.5	20.8-21.0	23.8-24.1	26.5-26.6	21.4-21.8
	Photocatalysis time (min)															
	Original	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Degussa																
	0	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-	391.5
	2	-	-	-	-	0.4	0.5	4.6	0.5	-	0.5	-	-	-	-	279.0
	5	-	-	-	-	0.4	0.7	7.3	1.8	0.7	1.1	0.3	0.8	-	-	176.5
	10	0.2	0.2	0.2	-	0.4	0.7	6.2	2.0	1.1	24.0	0.4	1.4	-	0.9	92.5
	20	0.4	0.3	0.2	-	0.3	0.5	4.6	1.2	2.1	12.9	0.6	1.2	-	1.0	22.1
	30	1.1	0.3	1.0	-	0.2	0.6	3.9	0.8	2.2	0.5	0.3	0.9	-	1.1	2.7
	45	1.0	0.2	0.3	-	0.1	0.2	1.7	0.2	1.1	0.6	0.1	0.2	-	0.9	-
	60	0.3	0.2	-	-	-	-	0.1	-	-	-	-	-	-	-	-
	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PC50																
	0	-	-	-	-	-	-	-	0.4	-	-	-	-	-	-	540.

																2
	2	-	-	-	-	0.4	0.5	4.5	1.5	-	4.2	-	0.3	0.1	-	420.3
	5	0.4	-	-	-	0.3	0.7	6.3	1.6	0.6	16.3	-	0.7	0.1	-	285.4
	10	1.4	0.1	-	-	0.3	0.7	5.5	1.6	1.1	20.6	0.5	1.7	0.2	0.9	109.0
	20	1.9	0.3	0.2	0.2	-	0.4	3.2	1.9	1.5	2.7	0.4	1.5	0.6	2.5	4.4
	30	0.7	0.3	0.3	0.1	-	0.3	2.4	1.7	1.7	2.4	0.2	1.1	-	2.9	0.3
	45	0.4	0.3	0.3	0.1	-	0.1	0.9	0.3	0.5	1.5	-	0.1	-	3.7	0.1
	60	0.2	0.3	-	-	-	-	0.1	0.1	-	-	-	-	-	1.3	-
	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PC500																
	0	-	-	-	-	-	-	-	0.9	-	-	-	-	-	-	1263.4
	2	-	-	-	-	-	0.3	7.1	2.3	-	2.6	0.2	0.3	0.7	-	874.2
	5	-	0.1	-	-	-	0.3	8.3	1.4	-	4.4	1.3	0.7	0.2	-	612.7
	10	-	0.3	-	0.2	-	0.3	8.8	0.6	0.7	14.5	3.2	1.6	0.4	1.0	223.0
	20	-	0.4	-	0.2	-	0.2	6.1	1.0	1.0	3.4	3.3	1.1	0.1	2.6	68.0
	30	-	0.5	-	0.3	-	0.2	3.4	0.8	1.1	3.7	2.6	0.5	0.1	3.1	9.1
	45	-	0.4	-	0.2	-	-	1.6	0.5	0.8	1.0	0.9	-	-	3.2	0.5
	60	-	0.5	-	0.1	-	-	0.4	-	-	0.4	0.1	-	-	1.6	0.1
	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
UV100																
	0	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-	961.9

	2	-	0.1	-	0.1	-	0.2	4.7	0.9	-	18.4	0.2	0.3	0.4	-	505.5
	5	-	0.2	-	0.2	-	0.2	6.9	1.4	-	2.4	0.7	0.4	0.6	0.3	401.9
	10	-	0.4	-	0.2	-	0.1	4.4	1.2	-	5.3	0.9	0.7	0.1	1.1	83.3
	20	-	0.6	-	0.2	-	-	1.4	1.1	0.5	1.6	1.2	0.3	0.1	2.5	2.3
	30	-	0.6	-	0.1	-	-	0.9	1.2	0.4	1.1	1.1	0.1	-	2.9	-
	45	-	0.6	-	0.1	-	-	0.3	0.8	-	0.5	0.4	-	-	2.8	-
	60	-	0.6	-	-	-	-	-	-	-	-	-	-	-	1.3	-
	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* $[M+Na]^+$