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Preparation and performance of integrated photocatalyst adsorbent (IPCA) employed to degrade model organic compounds in synthetic wastewater

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Abstract

An integrated photocatalyst adsorbent (IPCA) system was prepared for the purpose of removing organic pollutants from wastewater. Its efficiency to remove some representative compounds from the most frequently occurring water contaminants commonly treated by activated carbon was tested on laboratory scale. The IPCA formulation was built using TiO_2 as the photoactive component and a non-carbon family of adsorbents (zeolites) as the adsorbents, all supported on an inert base (glass beads). The IPCA offers a competitive alternative treatment to the activated carbon because its photoactive component permits multiple regeneration of the adsorbent while integration on the support makes the IPCA mechanically robust and easy to handle in the reactor systems. The study included the search for the best candidates for the role of the IPCA components, optimum proportions among them, and suitable pre-treatment procedures to achieve the maximum efficiency of the IPCA material. IPCA with the composition beads:P25:zeolite:silica gel = 73:1:3:23 was found to be optimal for the purposes in this research. The choice of the zeolite in this composition was determined by the contaminant of interest. A combination of acid-wash, sonication, and calcination procedures applied to the precursors enhanced photodegradation efficiency of the IPCA by a factor of 1.5.

1. Introduction

Heterogeneous photocatalysis has been evaluated as a potential technology in applications related to liquid phase pollution control processes [1–3]. Among the metal oxide semiconductors suitable for photocatalytic processes, TiO_2 in its anatase form is the most widely used because of its high photocatalytic activity, availability and chemical/photocorrosion stability in all reaction conditions [4,5]. However, most of commercially available TiO_2 suffers from its nanosized particle dimensions that require a difficult catalyst-recovery stage, which in turn significantly decreases the overall efficiency of the process. As a result, much effort has been focused on developing supported titania catalysts that can offer high efficiency combined with better recovery properties. Various attempts have been made to select appropriate supports for titania photocatalysts for degradation of pollutants from wastewater. Most often, silicon oxide-based materials, such as glass fibers or beads, quartz, sand, and silica gel have been chosen [6–8].

Despite the potential of TiO_2 photocatalysis, it has not yet been successfully implemented on a large scale. Major limitations arise from the requirement for near UV light and the fact that the intrinsic quantum yields of titania are low leading to a high-energy requirement to drive lamps. Those problems were attacked in this study by the development of an integrated photocatalyst adsorbent (IPCA) that supports TiO_2 on a zeolite-based adsorbent thus, achieving pre-concentration of target compounds near TiO_2. Since quantum yields on TiO_2 increase almost linearly with concentration [9,10], pre-concentration of organics allows reduction in energy requirements. In addition, pre-concentration of organics from solution (three-dimensional problem) onto the surface (two-dimensional) decreases the length of diffusion towards active sites and may maximize the contact between the reactant, catalyst, and photons. At the same time, TiO_2 content is controlled so that all available photons emitted at a given intensity are utilized.

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This study aimed at formulating the optimum composition of an IPCA material using a TiO_2 catalyst and a non-carbon family of adsorbents (zeolites) as the main ingredients that were to be supported on an inert base (glass beads) for the purpose of removing organic pollutants from wastewater. The study included the selection of the best candidates for the role of the IPCA components from the list of the most promising commercially available and locally prepared compounds. Efforts have also been made in this study to find the optimum ratio between the selected IPCA components in order to achieve the maximum efficiency of the IPCA material. Specific pre-treatment procedures such as acid wash, sonication, calcination were applied to the IPCA components prior to manufacturing of the final composite material with the goal of further improving the IPCA performance. Finally, the IPCA matrix has been manufactured on laboratory scale and its physical properties were characterized using SEM, X-ray diffraction (XRD) and BET analyses. The IPCA performance was studied on the basis of the efficiency of removal of some representative compounds that were chosen from the families of the most frequently occurring water pollutants such as aromatics including BTEX series (represented by *o*-xylene), aromatic alcohols (represented by phenol), ketones (acetophenone) and organo-chlorine compounds (dichloromethane and mono-chloroacetic acid).

2. Experimental

2.1. Materials

Titanium dioxide (P25 grade) was a gift from Degussa Corporation; zeolites ZSM-5, silicalite I (S-115) and zeolite Y were purchased from Zeolyst International; white cement (90% $3CaO\cdot SiO_2$ + $2CaO\cdot SiO_2$ + $3CaO\cdot Al_2O_3$ and 4–6% $CaSO_4\cdot 2H_2O$) was purchased from Inland Cement; porous glass beads (SIRAN^{TM} carriers) were purchased from JAEGER Biotech Engineering Inc.; colloidal silica (40 wt.% silica suspension in water) and model organic pollutants (acetophenone, phenol, *o*-xylene, dichloromethane, mono-chloroacetic acid) were purchased from Aldrich and used as received. A titania sol–gel was synthesized from titanium isopropoxide solution via the acid-catalyzed sol–gel technique according to literature methods [11]. Zeolites TS-16 and ARC-142 were synthesized locally. Zeolite TS-16, an analogue of ZSM-5 zeolite, was prepared in the laboratory using a lower cost templating agent. Zeolite ARC-142 was prepared at Alberta Research Council by affixing TiO_2 on silicalite-I and designated accordingly as the ARC-142 material.

The IPCA structure was based on the 'golf ball' concept where porous glass beads were used as the support on which TiO_2 and a specific zeolite were attached in the surface pores with a binding agent. By impregnating TiO_2/zeolite composition in the caverns of a porous glass support, the IPCA ma-
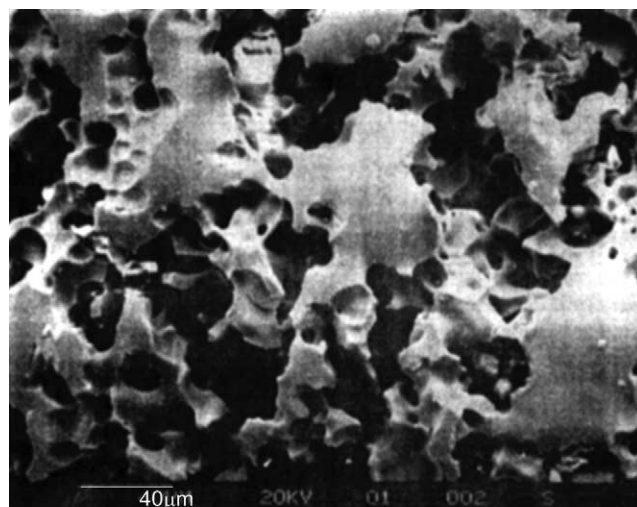
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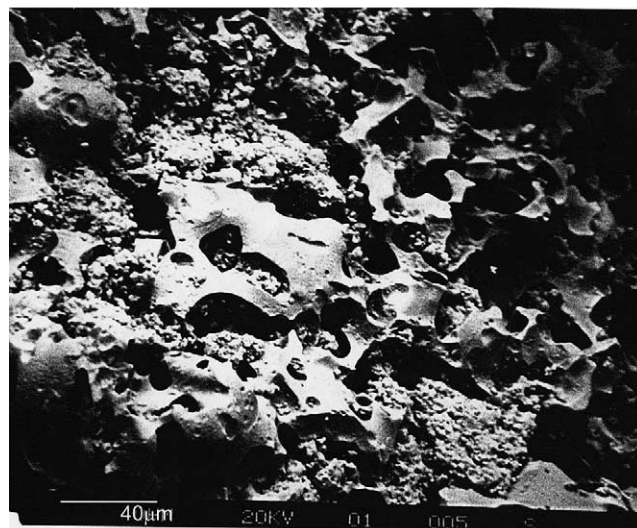
(b)

Fig. 1. SEM images of: (a) porous glass beads and (b) titania and zeolite loaded on the beads.

terial has been made mechanically robust and easy to handle in the reactor systems. Synthesis of the IPCA included the following steps. Appropriate amounts of TiO_2 and zeolite were mixed together and dispersed uniformly in a known volume of colloidal silica gel binder. A known weight of porous glass beads was stirred into the three-component solution. The mixture was dried slowly under ambient conditions, then at 100 °C. Solid granules were separated by gentle crushing and screened to obtain a narrow size distribution. Finally, prepared IPCA was washed several times to remove remaining fines. Fig. 1 depicts SEM images of the pure glass beads and beads with IPCA materials supported on them.

Pre-treatment of titania and zeolite powders, which involved acid-wash, sonication and calcinations procedures, was performed either separately or after combination with each other but prior to attaching the components to the

porous glass beads. The acid-wash procedure was performed as follows: each component was mixed with 0.5 M HCl solution at a weight ratio of 1:20 (solid:acid) and heated while stirring for at least 1 h in the 85–95 °C temperature range. The suspension was then centrifuged, solids separated, and dried at 100 °C. Next, a similar procedure was repeated taking distilled water instead of HCl. Sonication pre-treatment was performed in an Aquasonic bath (model P250D) at 60 °C for at 1 h. For the thermal pre-treatment of the components, the solids were calcined in a high temperature oven (Hotpack Inc.) at various temperatures (250, 350, 450, 550 and 650 °C) for 3 h.

2.2. Dark adsorption and photocatalysis experiments

Adsorption experiments were carried out in a dark chamber in rotating Pyrex test tubes containing 30 ml of contaminant solution along with a known weight of IPCA. Irradiation experiments were performed in the same rotating tubes containing the catalyst and either the remaining contaminant solution or aqueous media added to the vials after decantation of the remaining contaminant solution. Irradiation was achieved using a 40 W fluorescent bulb with average intensity of 4×10^{-8} einstein/s (2.4×10^{16} photons/s) entering the test tube with emission centered at 350 nm.

2.3. Analyses and data treatment

For physical characterization of TiO_2 and zeolite, powder X-ray diffraction patterns were recorded using Cu Kα1 radiation ($\lambda = 1.54056$ Å) on a Rigaku Multiflex X-ray diffractometer. Diffraction patterns were recorded over the 2θ range of $20°$–$60°$ for TiO_2 and $3°$–$60°$ for TiO_2 attached to a zeolite. The average particle size, XS, of crystallites was estimated using Scherrer equation:

$$\text{XS (nm)} = \kappa \lambda / \text{FWHM} \cos \theta \tag{1}$$

where κ is a shape factor of the particle (0.9 was set for spherical shape) and FWHM (full-width at half-maximum) is the peak width at half-height expressed in radians.

The BET surface area measurements on TiO_2 and zeolite were performed on an AUTOSORB-1 apparatus (Quantachrome Corp.) with liquid nitrogen as the adsorption gas at 77.35 °K (-195.8 °C). Prior to the experiments, samples were degassed at 100 °C for at least 3 h. During the measurement, nitrogen adsorption data was collected when the pressure reached almost 10% of the saturation pressure corresponding to monolayer coverage. The volume of adsorbed nitrogen was normalized to standard temperature and pressure (STP). The relative pressure (P/P_o) was recorded in the range of 0.1–0.3.

Examination of TiO_2 and zeolite distribution on the surface of the support was performed on Kevex SEM (Cambridge Stereoscan 250) operated at 20 kV. The instrument was linked to an Analytical Spectrometer 6100 data processor.

High-performance liquid chromatography (HPLC) was employed for monitoring photoproducts and intermediates throughout the experiments. The instrument was Waters 600 equipped with a C_{18} column. Mobile phase was a mixed solvent containing acetonitrile and deionized water (50%:50%) with flow rate equal to 1.00 cm^3/min. The effectiveness of photodegradation of organics was evaluated by comparing chromatograms before and after timed intervals of irradiation to ascertain changes.

Photodegradation processes of the organic compounds were adequately fitted by a pseudo-first-order kinetic treatment in the presence of IPCA catalyst studied in this work. Loss of the model pollutant was fitted to the following logarithmic expression:

$$\log[C]_t = -kt + \log[C]_0 \tag{2}$$

where $[C]_0$ and $[C]_t$ represent the concentration of the substrate in solution at the time zero and time t of illumination, respectively, and k represents the apparent rate constant in s^{-1}. This is an empirical rate law reflecting a complex of factors including competition between the primary substrate and intermediates.

3. Results

3.1. Best candidates for the role of IPCA components

For the purpose of comparative assessment of various IPCA compositions, a base IPCA formulation consisting of Degussa P25 titania and S-115 zeolite attached to the glass beads with silica gel (beads:P25:S-115:silica gel = 56:3:11:29) was established as a reference point against which all the other compositions were compared. Preliminary evaluation of performance of the reference IPCA formulation towards model pollutants chosen in this study is reflected in Table 1. It can be seen that chloro-organics were the slowest to respond to the IPCA treatment as might be expected from a preferred reductive (versus oxidative for hydrocarbons) mechanism of initial reaction steps. Xylene, on the other hand, was the most promising compound to be degraded by the photocatalytic method. The most suitable candidates for the role of the catalyst, adsorbent, and binder were tested next. In the following study, the

Table 1
Relative adsorption and degradation efficiencies of the reference IPCA material (beads:P25:S-115:silica gel = 56:3:11:29) towards model pollutants

4.8 mWh/cm² irradiation at 350 nm in the tube with contaminant solution under rotation	Adsorption (mg/g IPCA)	Degradation (%)
o-Xylene	4.2	52
Acetophenone	6.2	24
Phenol	2.1	20
Mono-chloroacetic acid	0.6	5
Dichlorometane	2.9	1.6

number of contaminants was narrowed down to the middle range present in Table 1 and extreme cases of xylene and dichloromethane were excluded.

3.1.1. Zeolites as adsorbents

Representatives from ZSM-5 and Faujasite families of zeolites were chosen for the role of the adsorbent in the IPCA matrix based on preliminary evaluation performed in the laboratory. Current study focused on commercially available zeolites: ZSM-5, silicalite I (S-115), and zeolite Y as well as locally synthesized systems, TS-16 and ARC-142. Zeolites ZSM-5 ($SiO_2:Al_2O_3$ = 50, 280) and Y ($SiO_2:Al_2O_3$ = 12, 30, 60, 80) were investigated to take into account different $SiO_2:Al_2O_3$ ratio, known to be one of the major factors affecting zeolite adsorptivity.

Trials of the IPCA materials prepared with the selected zeolites show that as expected, adsorption capacity for the substrates used in this work increased with the increase of the Si:Al ratio (Table 2). On the other hand, photoactivity of the IPCA seems to be inversely proportional to its adsorption efficiency. A similar observation was made earlier [12]. It can be concluded that a specific zeolite is optimal for each family of organic pollutants. For instance, zeolite Y or ZSM-5 seemed to be better choices when readily adsorbed substrate such as acetophenone was used as the model contaminant, while S-115 emerged as a more suitable adsorbent for phenol/chloroacetic acid contaminated water.

3.1.2. Degussa P25 versus sol–gel titania catalysts

Comparison of the IPCA materials, which were manufactured using either the particulate TiO_2 (Degussa P25) or the catalyst produced in situ via the acid-catalyzed sol–gel technique, was performed. Four different IPCA formulations were prepared based on these two types of TiO_2 with two different zeolites, S-115 and TS-16. In addition to these four samples, one more sample where sol–gel titania played the role of both the binder and catalyst was prepared. In the last case, the weight of the formulated IPCA material was adjusted so as to contain the same amount of TiO_2 as in the other samples.
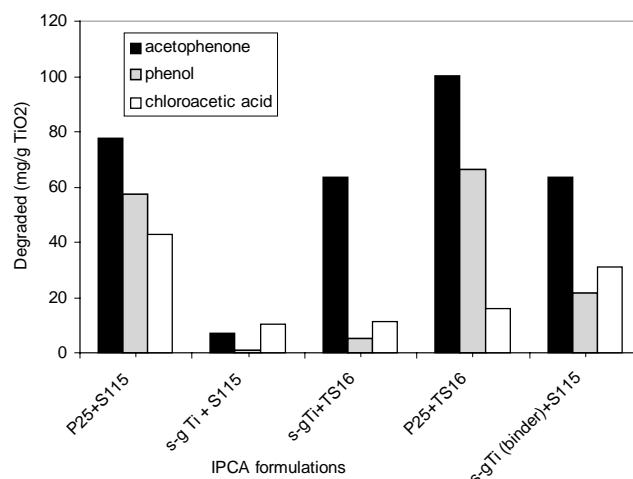

Fig. 2. Photocatalytic degradation of acetophenone, phenol, and chloroacetic acid using IPCA materials prepared from different variations of P25 or sol–gel titania along with S-115 or TS-16 zeolites.

Results shown on Fig. 2 indicate that particulate TiO_2 (P25) exhibited higher photocatalytic efficiency than the sol–gel-based titania for most of the cases.

3.1.3. Binders

The main requirement for the binder in a photocatalytic matrix is adhesion maintained over an extended period of time without loss of photocatalytic activity. Several binders have been extensively used by different researchers for the purpose of attaching photocatalytic particles on their respective supports, examples include organic/inorganic adhesives, various polymers, silicon-modified resins, polysiloxanes, colloidal silica, titania sols, etc. [13,14].

In this study, white cement, sol–gel titania and colloidal silica were employed to attach the main components onto the glass beads. Except for titania, these binders were transparent to UV radiation, inert, and their appearance was not altered during photocatalyst operation. Samples were analyzed for efficiency of model organics removal and long-term stability. The latter was estimated by loss of catalyst activity
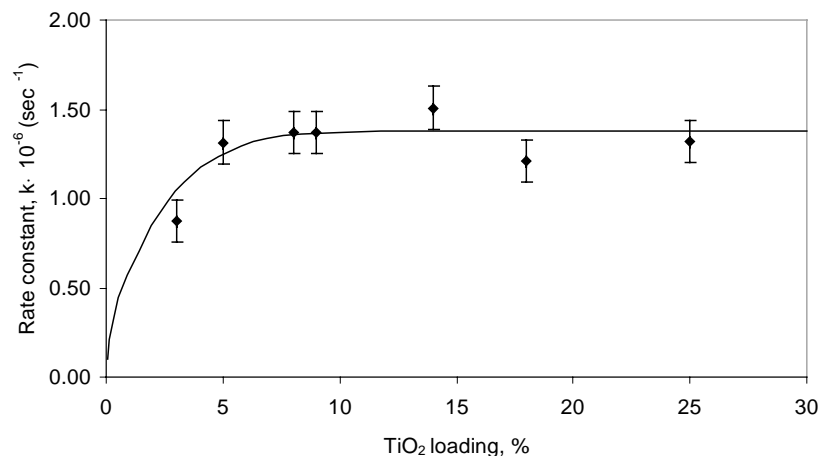
Table 2
Relative adsorption and degradation efficiencies of the reference IPCA material loaded with different zeolites towards the model pollutants

IPCA loaded with different zeolite	Acetophenone		Phenol		Mono-chloroacetic acid	
	Adsorption (mg/g zeolite)	$k \times 10^{-4}$ (s^{-1}) per g TiO_2)[a]	Adsorption (mg/g zeolite)	$k \times 10^{-4}$ (s^{-1}) per g TiO_2)[a]	Adsorption (mg/g zeolite)	$k \times 10^{-4}$ (s^{-1}) per g TiO_2)[a]
Zeolite Y (Si:Al = 12)	42.5	2.8	1.3	2.6	4.1	6.0
Zeolite Y (Si:Al = 30)	52.7	2.5	1.9	2.7	3.9	5.7
Zeolite Y (Si:Al = 60)	59.5	1.7	2.0	0.9	5.1	2.8
Zeolite Y (Si:Al = 80)	68.0	1.5	2.5	0.9	5.2	2.3
ZSM-5 (Si:Al = 50)	31.8	7.6	12.5	2.9	4.7	3.1
ZSM-5 (Si:Al = 280)	69.2	2.5	17.8	2.2	5.1	2.5
S-115 (no Al_2O_3)	71.7	1.6	20.2	2.0	5.2	0.2
TS-16	60.9	1.8	13.0	3.1	4.1	1.5
ARC-142	22.7	0.3	7.9	0.5	0.8	0.5

[a] Pseudo first-order apparent rate constant re-calculated per gram of titania.

Fig. 3. Photoactivity of the IPCA with varying TiO$_2$content, based on the reference composition for the case of acetophenone degradation.

and also by visual inspection for production of fines after seven days rotation in water.

Throughout the study, catalysts with colloidal silica binders showed superior contaminant degradation efficiency. For example, the amount of phenol loss after 1-day UV irradiation in 100 ppm phenol solution was 58, 47 and 22 mg/g TiO$_2$ for colloidal silica, white cement and sol–gel titania binders, respectively. In addition, more light scattering indicating the presence of more fines in suspensions was found in the cases of white cement and sol–gel titania than in the case of colloidal silica gel as a binder. It should be noted however, that in the case where sol–gel titania was used both as the catalyst and binder (Fig. 2), it performed comparably to silica gel binder when chloroacetic acid was used as the test compound.

3.2. Optimum IPCA composition

3.2.1. TiO$_2$ loading

Photocatalytic efficiency of the IPCA was found to increase with the increase of Ti content in the sample up to a certain limit and then no further significant change in activity was observed (Fig. 3). This observation is similar to earlier results [15] suggesting the following features. First, at low loading, TiO$_2$ develops a thin film on the surface of the composite catalyst. Second, the adsorbed molecules on the surface may frequently reach the light activated sites at this low loading. Third, once all photons are absorbed by TiO$_2$, no further increase can occur.

3.2.2. Zeolite loading

According to Fig. 4 , adsorption capacity of the IPCA increased with the increase of zeolite content in the catalyst. On the contrary, photodegradation rate slowed with the increase in zeolite loading. Decrease in degradation efficiency may be explained by the increase of the diffusion pathway for organic molecules as available zeolite surface

is increased. An optimum loading of 11% zeolite on IPCA was suggested, balancing both adsorption and degradation efficiencies.

3.2.3. Overall loading on support

The total loading of all of the components (titania/zeolite/binder) on the glass beads was varied from 7 to 44% and the IPCA performance was analyzed in terms of its adsorption/degradation efficiency as well as its stability and resistance to attrition. Total weight of IPCA was adjusted in each sample so as to have equal amount of TiO$_2$ and zeolite for the comparison of their photocatalytic activity. Adsorption and degradation efficiencies were found to be optimal at ca. 15% loading of titania/zeolite/binder on the support. Tests on stability and resistance to attrition were performed under rotation for 7-days. Catalyst activity and production of fines were monitored for each batch. Minimum loss to fines (1% compared to 9% for the highest loading) and no change of the photocatalytic activity was found at the IPCA composition based on the 15% loading of titania/zeolite/binder on the glass beads.

Thus, the following IPCA composition was chosen as optimal—beads:P25:zeolite:silica gel = 73:1:3:23 where the choice of zeolite was determined by the contaminant of interest.

3.3. Pre-treatment of components

Pre-treatment effects on TiO$_2$ and zeolite powders were investigated in order to enhance the photodegradation efficiency of the IPCA. First, each one of the three procedures (acid-wash, sonication, and calcination at several different calcination temperatures—250, 350, 450, 550 and 650 °C for 3 h) was executed separately from the other pre-treatment options on titania only, then on zeolite only and finally on their mixture. No significant improvement in the activity of the IPCA material was found when the pre-treatment procedures were applied to a single component. However, when
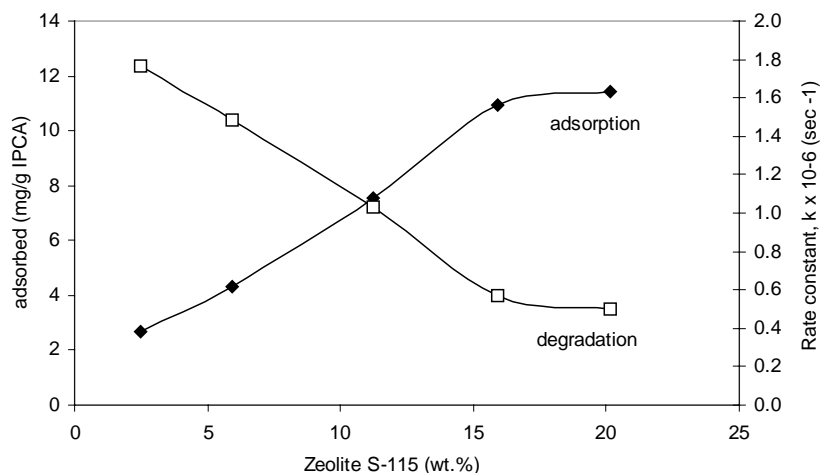
Fig. 4. Effect of zeolite content on adsorption and degradation behavior of the reference IPCA formulation in the case of acetophenone.

it was applied to the titania/zeolite mixture, an improved IPCA performance was observed. Fig. 5 represents a comparison of the degradation efficiency of the initial IPCA with no pre-treatment (dried at 100 °C) and pre-treated IPCA calcined at different temperatures. Perhaps, pre-treatment of the mixtures resulted in better integration of the two components and more bond formation by dehydration between TiO_2 and zeolite surface –OH groups. In order to better characterize the IPCA material, XRD and BET analyses were performed.

3.4. XRD and BET analysis

X-ray diffraction patterns were monitored for acid-treated P25 and S-115 mixtures to identify the temperature range at which phase transformation from anatase to rutile took place. Phase contributions were calculated for each sample from peak area. Rutile TiO_2 started to form at 550 °C.

It was hard to estimate the particle size of the anatase attached with zeolite, since overlap with zeolite reflections was pronounced. Qualitative estimation of peak broadening

of the powder diffraction pattern up to 450 °C indicated that crystal growth was prevented and P25 was dispersed in the sample. Above 450 °C, crystal growth was observed as more rutile started to form (Table 3).

BET surface area measurements were performed from nitrogen adsorption data. Acid-treatment of P25 increased specific surface area, BET surface areas of untreated and acid-treated P25 were found to be 50.43 and 72.86 m²/g, respectively. Table 3 summarizes the properties derived from nitrogen adsorption data. The total surface area of zeolite/TiO_2 was decreased after titania loading. Also, there is a hint that with increase in calcination temperature of the acid-treated titania/zeolite mixture, BET surface area increased. Fig. 6 shows the volume of nitrogen adsorbed at several relative pressures P/P_o for different heat-treated samples. Physical characterization of the pre-treated P25 and S-115 mixture by XRD and BET measurements also supported this feature. Samples treated at 450 °C exhibited higher BET surface area and XRD diffraction patterns showed more rutile formation after treatment at this tem-
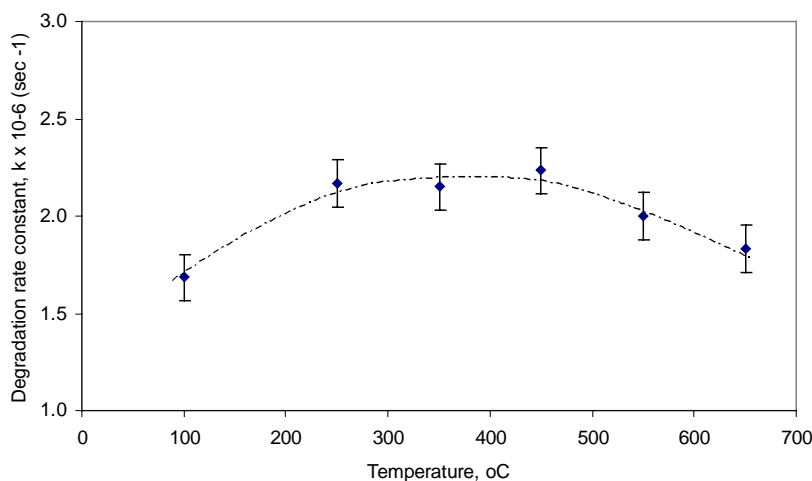

Fig. 5. Performance of untreated IPCA and the IPCA with pre-treated P25 and S-115 at different calcination temperatures after 1-day UV irradiation using 100 ppm acetophenone solution. The data point at 100 °C represents the IPCA heated at this temperature with no pre-treatment method applied on it.

Table 3
Data from XRD and BET analyses

Sample	Apparent particle size (nm)	FWHM[a] (radian)	BET surface area[b] (m^2/g)
S-115	43	0.21	339
S-115 (acidified)	–	–	338
P25	20	0.411	50
P25 (acidified)	20	0.403	72
P25 + S-115 (acidified, calcined, 150 °C)	42	0.214	305
P25 + S-115 (acidified, calcined, 250 °C)	45	0.2	319
P25 + S-115 (acidified, calcined, 350 °C)	38	0.229	312
P25 + S-115 (acidified, calcined, 450 °C)	31	0.27	344
P25 + S-115 (acidified, calcined, 550 °C)	44	0.206	–
P25 + S-115 (acidified, calcined, 650 °C)	46	0.199	–

[a] FWHM: full-width at half-maximum height measured at $2\theta = 25.4°$ for P-25 and $2\theta = 7.9°$ for S-115.

[b] Specific surface area estimated from standard BET equation, i.e., $1/w((P_o/P) - 1) = (1/w_m C) + ((C - 1)/w_m C)(P/P_o)$, where w and w_m represent the amount of gas adsorbed at a relative pressure P/P_o and the maximum amount of adsorbate constituting a monolayer coverage and C is a BET constant.
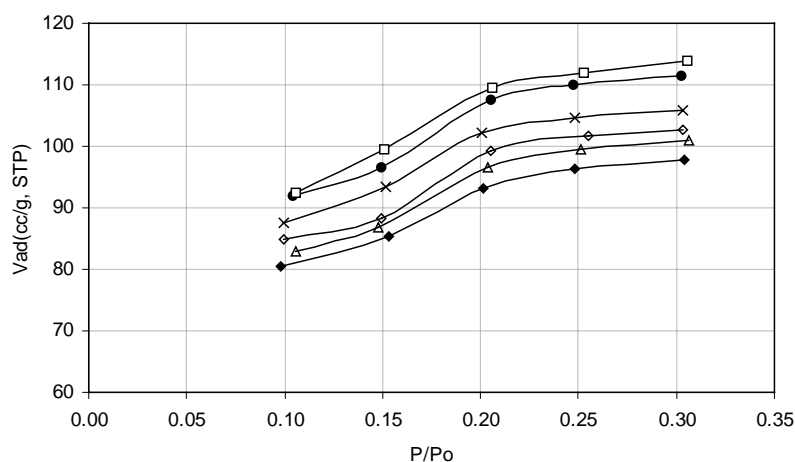

Fig. 6. BET isotherm plot of acidified samples calcined at different temperatures: (●) S-115, no calcination, (◆) P25 + S-115, no calcination, (△) P25 + S-115 (150 °C), (×) P25+S-115 (250 °C), (◇) P25 + S-115 (350 °C) and (□) P25 + S-115 (450 °C).

perature. As rutile TiO$_2$ is inefficient for photocatalysis, photoactivity decreased at higher temperatures.

4. Conclusions

A combination of the three pre-treatment procedures were developed where TiO$_2$ and zeolite powders were first acid-washed separately as described earlier, then combined together for sonication and thermal treatment in the 250–450 °C range. The IPCA material manufactured from the pre-treated titania/zeolite mixture showed an average increase in its performance by a factor of 1.5. The choice of zeolite proved to be a significant variable. However, the optimum choice was clearly a function of the organic contaminant target.

References

[1] D.F. Ollis, Chemistry 3 (2000) 405.
[2] D.D. Dionysiou, G. Balasubramanian, T. Suidan, A.P. Khodadoust, I. Baudin, M. Laine, Water Res. 34 (2000) 2927.
[3] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1523.
[4] X.Z. Li, H. Liu, L.F. Cheng, H.J. Tong, Environ. Sci. Technol. 37 (2003) 3989.
[5] J.E. Lopez, W.J. JakobyA, Air Waste Manage. Assoc. 52 (2002) 1206.
[6] A. Blazkova, I. Csolleova, V.J. Brezova, Photochem. Photobiol. A 113 (1998) 251.
[7] S. Chen, X. Liang, J. Zhao, L. Wang, M. Zhao, J. Environ. Sci. 9 (1997) 278.
[8] L.J. Alemany, M.A. Banares, E. Pardo, F. Martin, M. Galan-Fereres, J.M. Blasko, Appl. Catal. B 13 (1997) 289.
[9] G. Waldner, M. Pourmodjib, R. Bauer, M. Neumann-Spallart, Chemosphere 50 (2003) 989.
[10] D.A. Friesen, J.V. Headley, C.H. Langford, Environ. Sci. Technol. 33 (1999) 3193.
[11] M.A. Anderson, M.J. Gieselman, Q.J. Xu, Membr. Sci. 39 (1988) 243.
[12] T. Hisanaga, K. Tanaka, J. Hazard. Mater. B 93 (2002) 331.
[13] Murasawa, Sadao, Murakami, Hajime, Fukui, Yasuro, Watanabe, Mitsuru, Fujishima, Akira, Hashimoto, Kazuhito, US Patent 6,277,346 B1, 2001.
[14] Kimura, Nobuo, Yoshimoto, Tetsuo, US Patent 6,407,033, 2001.
[15] Y. Xu, C.H. Langford, J. Phys. Chem. 99 (1995) 11501.