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Notes

Photocatalytic studies using a very low surface area catalyst: TiO_2 over $CaCO_3$ from waste shell (*Pomacea canaliculata*) in paraquat degradation

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Calcination of shell waste and subsequent processing resulted in $CaCO_3$ powder that was used as the catalyst support for $TiO_2/CaCO_3$ catalyst. The catalyst has been characterized by scanning electron microscopy, BET measurements, X-ray diffraction, UV-visible diffused reflectance spectroscopy and Fourior transform infrared spectroscopy to elucidate the catalyst's properties. The TiO_2 over $CaCO_3$ catalyst has been used as a photocatalyst in paraquat removal under optimized conditions of calcination temperature, TiO_2 loading method, loading content of Ti component, loading content of TiO_2 in the catalyst and light irradiation. The results show that all the experimental parameters significantly affect paraquat removal efficiency of the catalyst. The calcination temperature and TiO_2 loading method show the most significant effect.

Keywords: Photocatalysts, Titania, Calcium carbonate, Paraquat degradation

Calcium carbonate is one of the most promising materials for various applications such as catalyst in transesterification[1-4], adsorbent for poisonous organic compounds or heavy metals[5-7] and is even used as a catalyst support[8-9], since it is very cheap and abundant in nature (found as limestone) and some sources are renewable (waste material consisting of $CaCO_3$ such as egg shell, animal bone or sea shells). In the last decade, many research groups and factories have used chemical reactions leading to the development of $CaCO_3$ with specific particle size, high porosity and with the removal of residual organic matter, undesirable odours and microorganisms. They could then be applied for use as catalysts or adsorbents.

The removal of high toxicity of organic compounds such as dyes, carcinogenic compounds, herbicides or insecticides, includes many processes, such as adsorption, photodegradation, oxidation or specific chemical reactions. One of the most powerful and well-known methods used to reduce the amount of contaminated organic compounds is their photodegradation or photocatalysis. Photodegradation occurs under light irradiation with the addition of catalyst. According to literature reports, in general catalysts could be recycled and showed high level of organic compound removal ability[10-12]. The main component used to operate as the catalyst is TiO_2.

TiO_2 is an excellent photocatalytic material because it exhibits characteristic properties of nontoxicity, high photocatalytic activity, high stability, strong oxidation ability, low energy consumption and is economical[13-15]. TiO_2 is a semiconductor material, and has a band gap energy of about 3.25 eV (Supplementary data, Fig. S1) which can interact with the UV range[16-17]. The excitation of an electron from the conduction band to the valence band and the generation of free electron (e^-) and hole (h^+) occurs after the TiO_2 is irradiated with UV light. A pair of e^- and h^+ were then transferred to the degradation reaction of the poison target compound. The photocatalysis takes place either on the catalyst surface or in the solution.

One reason for the deactivation of the photocatalyst is the agglomeration of TiO_2 particles[18-20]. Researchers have overcome this limitation by implanting the TiO_2 particles over various supports [21-23]. Kumar *et al.*[21] synthesized TiO_2 supported over graphene oxide using microwave activation. They found that the nanoparticles of TiO_2 were dispersed over the graphene sheet. The photoactivity of the prepared material was higher than that of pure TiO_2. Askari *et al.*[22] studied the photoproperty and photoactivity of TiO_2 over multiwall carbon nanotube (MWCN) using a UV-vis spectrophotometer. It was found that TiO_2/MWCN could adsorb light over a wider wavelength range compared to pure TiO_2. The ability to remove methylene blue was studied for various TiO_2 based compounds, which showed that TiO_2/MWCN exhibited higher activity than TiO_2 powder. Yu *et al.*[23] synthesized TiO_2 deposited over fumed silica using tetrabutyl titanate as a precursor. The SEM images of TiO_2/fumed silica samples showed a narrow sized distribution of TiO_2 over the silica surface. The photoactivity for methyl orange degradation using TiO_2/fumed silica sample was found to be higher than that using pure TiO_2.

In the present study, we prepared TiO_2 deposited over $CaCO_3$ as a photocatalyst for paraquat degradation, which was monitored using voltammetry. This material was prepared by sol-gel method and the catalyst was characterized by FTIR, BET measurement, XRD, UV-vis diffused reflectance spectroscopy and SEM.

Experimental

Preparation of $CaCO_3$ was carried out as follows; waste shells of *Pomacea canaliculata* were collected from rice fields after the harvest season (Ban Khamreang, Ampur Kantarawicha, Mahasarakham Province, Thailand) during April 2017. The shells were washed to totally remove any residual soil, and then dried naturally for one day. The clean and dry shells were soaked in 0.01 M NaOH for 12 h, washed with distilled water and dried under sunlight for one day. The shells were crushed in a motar and calcined at 600 °C for 2h at a heating rate 10 °C/min. The calcined shells were then crushed into a powder to obtain pure $CaCO_3$ (labeled as $CaCO_3$-600). The $CaCO_3$ was then used as a catalyst support for Ti compound.

The Ti compound was loaded onto $CaCO_3$ by the sol-gel method. The $CaCO_3$ powder was mixed with tetratitanium isoproproxide (TTIP) in propanol and then a few drops of DI water was added. The mixture was continuously stirred for 30 min. The pH of the solution was adjusted to 1 using 9.6 M HCl and the reaction mixture stirred for another 2 h. The mixture was filtered and washed with water. The solid powder was collected and transferred to a muffle furnace and heated at 300 °C for one hour. The final product obtained was labeled as Ti/$CaCO_3$-600-300 and used as the catalyst.

Pure TiO_2 was prepared by a similar method but without the addition of $CaCO_3$.

For the preparation of Ti/$CaCO_3$ catalyst by calcination method, the starting materials i.e., TTIP and $CaCO_3$ powder (calcined at 600 °C) were added to propanol. The mixture was then transferred to the crucible and finally heated at 400 °C for 1 h.

The photoactivity of the Ti/$CaCO_3$ catalyst was monitored by paraquat degradation reaction. The catalyst was loaded in a batch reactor using 400 ppm of paraquat from highly purified paraquat (99.99%, Sigma-Aldrich). However, the pH of the 400 ppm paraquat was adjusted to 7 before the start of the reaction using NaOH/ HCl solution. After the catalyst was added to the paraquat solution, paraquat removal occurred. The reaction mixture was stirred and left for 30 min under sunlight. Then, the reaction mixture was centrifuged for 5 min at 5000 rpm. The supernatant was reserved for voltammetry measurement (Autolab PGSTAT204; Metrohm), which was used to analyze the residual paraquat.

For light irradiation, the batch reactor was kept in a sealed wooden box that was connected to two UV lamps inside (power of one lamp = 11 W or 160 mA).

The sample for voltammetric measurements was prepared by taking 1 mL of the supernatant and 10 mL of phosphate buffer (pH about 7.4), the resultant solution was taken in a voltammetry chamber and then stirred (at level 1; Autolab PGSTAT204; metrohm) for 2 min. The potential of residual paraquat was measured thereby. This technique is quite well known and shows high reliability for the detection of amount of paraquat, as reported in literature[24-25].

Surface properties such as BET surface area, average pore diameter and pore volume were calculated using an Autosorb-1 Gas Sorption system (Quantachrome Corporation). The X-ray diffraction (XRD) patterns of the as-prepared catalysts were also studied. The XRD profiles were obtained using a D8 Advance: Bruker BioSpin AG instrument in the range 2θ between 0–80°. The SEM images of the catalyst were obtained using a JEOL-1230 (Becthai) to provide the surface morphology. In this study, Fourier transform infrared spectrometry (FTIR) was also used to examine the surface of the functional groups of the prepared catalyst using a Perkin-Elmer (Spectrum One) spectrometer equipped with a mercury-cadmium-telluride (MCT) detector in the wave number range between 400–4000 cm^{-1}. The diffuse reflectance UV-vis spectra of the catalysts were recorded in air at 200–800 nm using a Shimadzu 3600 UV-vis spectrophotometer.

Results and discussion

A comparison of the surface properties of the studied catalysts is presented in Table 1. The information shows that all the samples exhibit a very low surface area in both pure support powders ($CaCO_3$ and TiO_2) and Ti/$CaCO_3$ catalysts. The surface area of $CaCO_3$ was very low at about 1 m^2/g and that of pure TiO_2 was about 12 m^2/g. After the Ti compound was loaded onto the $CaCO_3$ (Ti/$CaCO_3$ catalyst), the surface area of the catalyst was between that of pure $CaCO_3$ and pure TiO_2 (between 1-12 m^2/g). The effect of annealing temperature over the $CaCO_3$ support and Ti/$CaCO_3$ catalysts was studied and the

Table 1 — Physico-chemical properties of studied catalysts

Catalyst	Method	Heating temperature (°C)[a]	S_{BET} (m^2/g)	Pore volume (mL/g)	Average pore size (Å)
TiO_2	Sol-gel	400	12.634	0.203	39.061
Pure $CaCO_3$	Calcination	600	1.294	0.051	149.977
2%Ti/$CaCO_3$-300-400	Sol-gel	300, 400	1.781	0.029	19.099
2%Ti/$CaCO_3$-600-400	Sol-gel	600, 400	1.852	0.030	19.092
2%Ti/$CaCO_3$-900-400	Sol-gel	900, 400	1.591	0.011	15.236
2%Ti/$CaCO_3$-600-200	Sol-gel	600, 200	1.513	0.035	19.161
2%Ti/$CaCO_3$-600-400	Sol-gel	600, 400	2.736	0.052	19.082
2%Ti/$CaCO_3$-600-400	Calcination	600, 400	0.954	0.017	17.036
2%Ti/$CaCO_3$-600-500	Sol-gel	600, 500	2.789	0.082	19.126
10%Ti/$CaCO_3$-600-400	Sol-gel	600, 400	2.529	0.046	19.133
50%Ti/$CaCO_3$-600-400	Sol-gel	600, 400	11.151	0.163	32.767

[a]Temperature used during $CaCO_3$ preparation and during Ti compound deposition.

results showed that the surface of the catalysts changed by increasing the average pore size and reducing the surface area. However, the Ti/$CaCO_3$ catalysts prepared by the sol-gel method show better surface area and average pore size compared to the Ti/$CaCO_3$ catalysts prepared by only the calcination method. The level of TiO_2 loading was compared (2–50% Ti/$CaCO_3$ catalysts), and it is indicated that increasing the Ti component could enhance both the surface area and reduce the average pore size.

The composition of the crystalline phase of the support and the catalyst under various conditions is presented in Fig. 1. The XRD profiles of the Ti/$CaCO_3$ catalyst at different $CaCO_3$ calcination treatments (between 300 and 900 °C) is given in Fig. 1(a). The XRD profiles of pure TiO_2 and pure $CaCO_3$ (calcined shell at 600 °C) were compared with that of the Ti/$CaCO_3$ catalyst. The XRD profile of pure $CaCO_3$ exhibited a very sharp and intense peak at 2θ about 29°, characteristic of $CaCO_3$[26-29]. Moreover, there are a series of intense peaks with respect to $CaCO_3$. However, there is a tiny but clear peak found at 2θ about 28 and 32° assigned to CaO, which is formed due to expulsion of CO_2 from the sample. It confirmed that the support involved in our study was $CaCO_3$ with a trace of CaO and there was clearly no $Ca(OH)_2$ present. For the Ti/$CaCO_3$ catalyst, prepared at a calcination temperature of 900 °C (labelled as Ti/$CaCO_3$-900-400), the phase of the support changed to CaO. In these XRD profiles, there was an absence of a TiO_2 peak, which indicates a very low amount of TiO_2 loading on the $CaCO_3$ (2% wt).

The calcination temperature was varied between 200 to 500 °C during Ti deposition over Ti/$CaCO_3$ catalysts, as shown in Fig. 1(b). It showed that this range of temperature could not affect the phase of the $CaCO_3$. Ti loading during the preparation of catalyst does not affect the catalyst crystallinity Fig. 1(c).

Finally, the TiO_2 content added up to 50% wt of the catalyst (Fig. 1(d)) and the broad peak centered at 2θ about 27° of the XRD profile over only 50% Ti/$CaCO_3$ sample is the characteristic peak of TiO_2 as found in the XRD pattern of bare TiO_2. It confirmed that the Ti species in the Ti/$CaCO_3$ was in the form of TiO_2.

The FTIR spectra were recorded to investigate the surface groups over the pure TiO_2 and $CaCO_3$ compared to the 2% Ti/$CaCO_3$ catalyst (Supplementary data, Fig. S2a). The spectra show similar patterns with broad peaks at 3400– 3500cm^{-1} corresponding to the vibrational stretching of the surface OH bond[30]. The peak at about 1400– 1500cm^{-1} was assigned to the H-O-H bending vibrational bending of adsorbed water and the bending vibrational of the –OH surface group on the catalyst surface[31]. The intense peak at about 1400 cm^{-1} of the Ti/$CaCO_3$ catalyst was related to the –OH surface group, indicating that the catalyst surface was covered with mainly –OH groups.

The UV-vis diffuse reflectance spectra of the TiO_2 and Ti/$CaCO_3$ (Supplementary data, Fig. S2b), exhibits absorption peaks at about 500 nm with a red shift in the Ti/$CaCO_3$ catalyst. The peak area was related to the light absorption by the sample which confirmed that the Ti/$CaCO_3$ catalyst could absorb more photons than the pure TiO_2 at wavelengths lower than 1000 nm.

The SEM images and the SEM-EDX of the Ti/$CaCO_3$ catalyst calcined at 200 °C and 400 °C, respectively are given in Fig. 2. The non-uniform

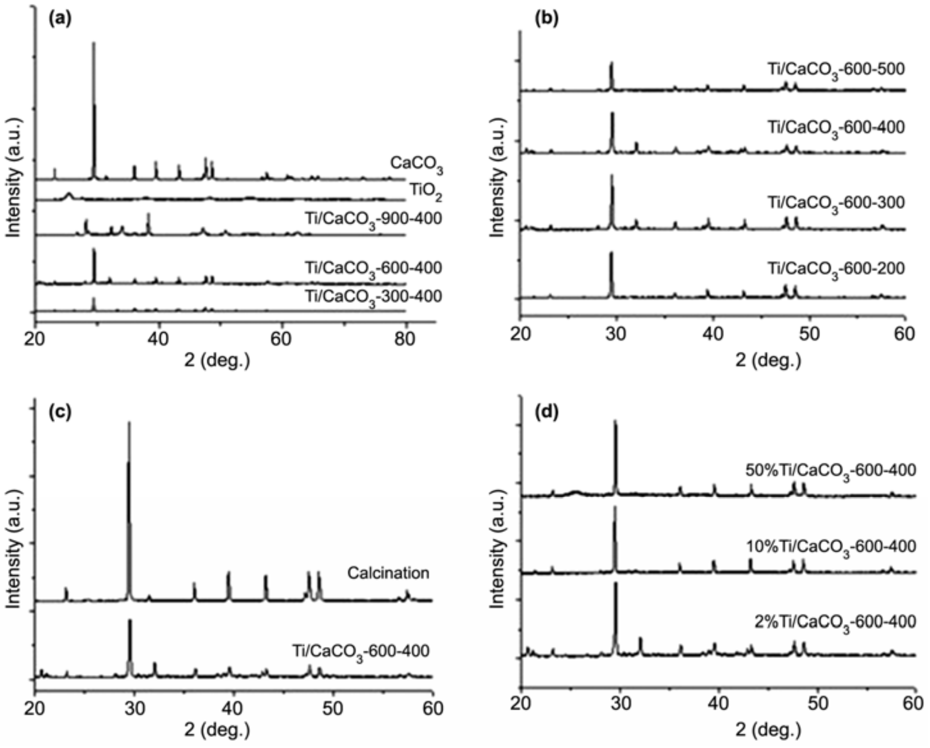


Fig. 1 — XRD diffraction patterns of various solids at (a) different calcination temperatures of CaCO$_3$ support, (b) different calcination temperatures for Ti loading step, (c) different preparation methods, and, (d) different Ti loadings in Ti/CaCO$_3$ catalysts.

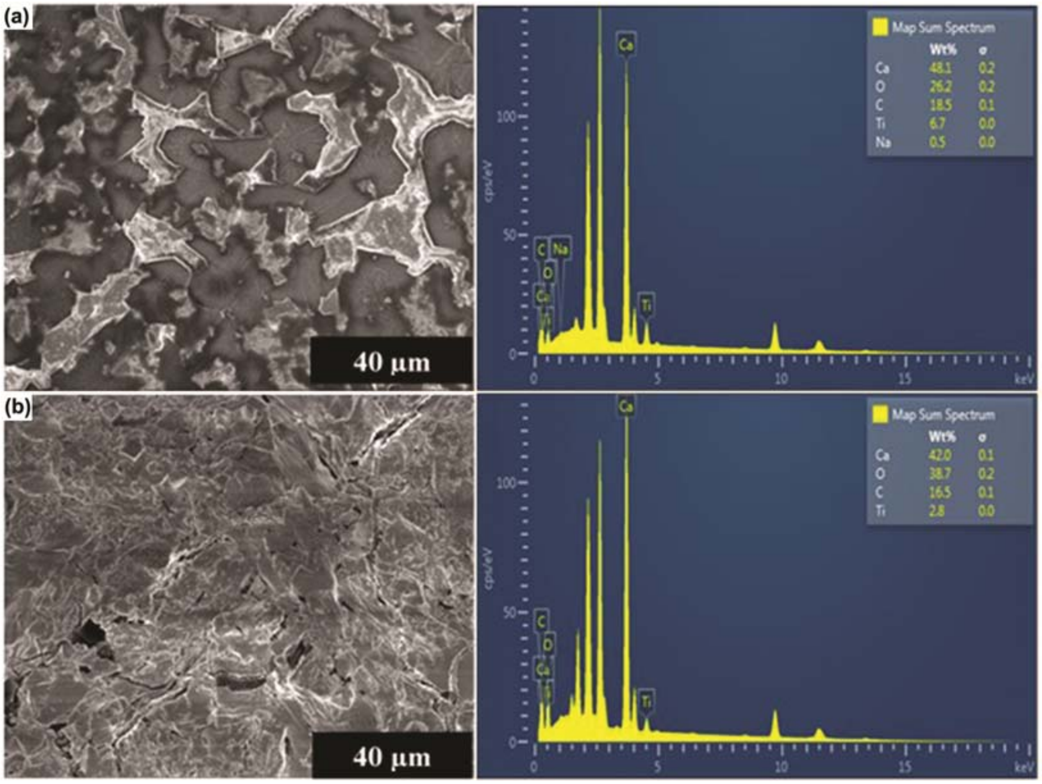


Fig. 2 — SEM image of Ti/CaCO$_3$ catalyst prepared via sol-gel method at different calcination temperatures of (a) 200 °C and (b) 400 °C.

sharp peak of the obtained sample calcined at 200 °C contained Na composition at about 0.5% wt which was very low when compared to other elements. On the other hand, the sample which was calcined at 400 °C had no trace of Na. However, the Na peak was observed as a little bump in SEM-EDX profiles. Therefore, a more precise technique such as atomic adsorption spectroscopy (AAS) must be used for confirmation. The SEM-EDX suggests that the main components of the obtained catalysts were Ca, O, C and Ti element. The amount of the Ti component was close to the loaded amount (2% wt). The surface of powder Ti/$CaCO_3$ catalyst has great homogenity with some porosity (Fig. 2(a) and Fig. 2(b)).

The SEM images of the Ti/$CaCO_3$ catalysts with different loadings (2% and 10% wt) is given in Fig. 3. It clearly shows that lower porosity is found in the high Ti component % loading content (Table 1).

The photoactivity of the Ti/$CaCO_3$ catalysts under different conditions for paraquat removal is given in Supplementary data, Fig. S3(a)-(f). The effect of heating temperature for $CaCO_3$ preparation was examined at 300, 600 and 900 °C, it was then used as support for TiO_2 (the catalyst activity is shown in Fig. S3(a)). It can be seen that the optimum heating temperature for the waste shell was 600 °C. Scheme 1(a) showed that CaO was formed on the Ti/$CaCO_3$-900-400 catalyst, whereas the Ti/$CaCO_3$-300-400 catalyst showed presence of both $CaCO_3$ and $Ca(OH)_2$. The Ti/$CaCO_3$-600-400 catalyst showed the presence of only $CaCO_3$. This suggests that the suitable form of Ca compound from the waste shell for Ti/$CaCO_3$, was $CaCO_3$. Higher light absorption by Ti/$CaCO_3$ as compared to TiO_2 reaffirms the presence of $CaCO_3$ as the suitable form (Fig. S2(b)). Moreover, the heating temperature during the Ti component loading in autoclave was also studied at 200, 300, 400 and 500 °C and the results are shown in Fig. S3. It showed that the Ti/$CaCO_3$ sample procured at 400 °C is the best catalyst because it could remove higher levels of paraquat than other samples. Therefore, the optimum temperature for Ti component loading on $CaCO_3$ (with autoclave) was 400 °C. From the SEM/SEM-EDX imaged and Table 1, it is seen that greater porosity in the Ti/$CaCO_3$-600-400 catalyst could enhance catalytic activity.

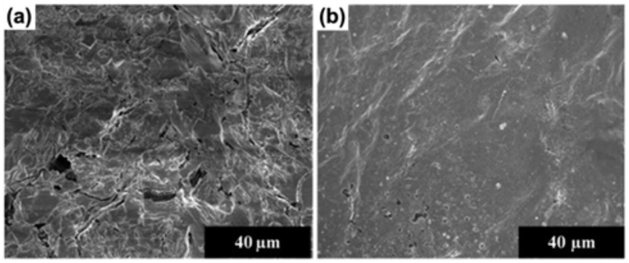
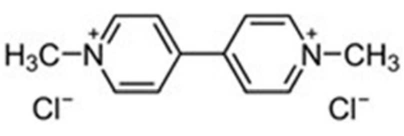


Fig. 3 — SEM image of Ti/$CaCO_3$ catalyst prepared via sol-gel method with different Ti loadings of (a) 2% and (b) 10%.



Scheme 1

The sol-gel method is found to be suitable for Ti/$CaCO_3$ catalyst synthesis (Fig. S3(c)). This could be explained by the higher surface area and smaller total pore volume of the resulting catalyst. When the catalyst loading was varied between 1–10 g/L, higher catalytic activity was observed for higher catalysts loadings (Fig. S3(d)). In the present study, catalyst content higher than 10 g/L could not be added because the separation of the catalyst from the reaction solution was not sufficient. Upon separation the solution still contained a tiny amount of catalyst, which affected the paraquat analysis.

The amount of Ti component over the $CaCO_3$ support was examined and the results show that 2% wt Ti was the optimum level for preparing the Ti/$CaCO_3$ catalyst (Fig. S3(e)). This may be explained by the better Ti component dispersion on the $CaCO_3$ surface. Finally, the effect of light irradiation was observed and it is suggested that the Ti/$CaCO_3$ catalyst under solar light irradiation could remove paraquat in higher amounts than that under other conditions (Fig. S3(f)). UV-vis diffuse reflectance spectra confirmed that the Ti/$CaCO_3$ could adsorb more light in the region of visible light as compared to bare TiO_2.

Thus, Ti/$CaCO_3$ catalyst could act as a photocatalyst that could interact with solar light. Therefore, the mechanism of the reaction proceeds via free radicals normally found in active species such as superoxide radical ($\bullet O_2^-$), hydroxyl radical (•OH) or hydroperoxide radical ($\bullet HO_2$)[32]. The free radical involved in the reaction could be used as a key species to indicate the possible mechanism. Thus, the photodegradation of paraquat was performed under the addition of various free radical scavengers or free radical generators as shown in Supplementary data, Fig. S4. The additional solutions were $AgNO_3$, *tert*-butyl alcohol (TBA), *p*-benzoquinone (BQ), H_2O_2 and EDTA. The BQ, TBA and $AgNO_3$ were added to capture the $\bullet O_2^-$, $\bullet$OH and photoelectrons (e^-) respectively. The H_2O_2 and EDTA solutions were the free radical generators used to produce the ·OH and e^- for the reaction. The activity of the catalyst in Supplementry data Fig. S4 clearly showed that the express respectively of activities of the reactions with $AgNO_3$ and TBA addition were both pretty low. Both $AgNO_3$ and TBA and were reacted with the free e- and $\cdot OH^-$. This results indicated that these two species (free e- and $\cdot OH^-$) are important for the paraquat degradation. This was confirmed by the reaction processes under H_2O_2 and EDTA. These two reactions exhibited higher catalytic activity as compared to the normal reaction without any added reagent. This suggested that the higher content of ·OH (produced by H_2O_2) and free e^- (produced from EDTA) could enhance the activity and were the key species for paraquat degradation. FTIR spectrum (Fig. S2(a)) shows that in case of Ti/$CaCO_3$, a very intense peak for the –OH surface group is observed. Upon BQ addition, the activity was comparable to the normal reaction (about 40% removal). The BQ was trapped in the $\cdot O_2^-$ species and it could be turned to $\cdot HO_2$, which does not affect the activity of Ti/$CaCO_3$ catalyst. Apparently, there may be other reactive species involved in addition to those mentioned above, in the paraquat degradation using the Ti/$CaCO_3$ catalyst.

Proposed mechanism

The mechanism of paraquat photodegradation in the presence of under the Ti/$CaCO_3$ under UV light is proposed as follows:

Light irradiation step:

$$TiO_2 + h\nu\ (UV) \rightarrow TiO_2\ (e_{CB}^- + h_{VB}^+) \quad \ldots (1)$$

Hole reacted with water:

$$TiO_2\ (h_{VB}^+) + H_2O \rightarrow TiO_2 + \cdot OH_{ads} + H^+ \quad \ldots (2)$$

Hole reacted with OH^-:

$$TiO_2\ (h_{VB}^+) + OH^- \rightarrow TiO_2 + \cdot OH_{ads} \quad \ldots (3)$$

Paraquat (PQ) degradation:

$$PQ + \cdot OH_{ads} \rightarrow \text{degradation product} \quad \ldots (4)$$

$$PQ + TiO_2\ (h_{VB}^+) \rightarrow \text{oxidation products} \quad \ldots (5)$$

$$PQ + TiO_2\ (e_{CB}^-\ ) \rightarrow \text{reduction products} \quad \ldots (6)$$

A similar mechanism has been proposed for some TiO_2 based catalysts used in photocatalytic degradation[18,33]. The $CaCO_3$ support is suitable for this catalyst system because it is a basic compound and produces more OH^- in the reaction solution that could enhance the reaction in eqn 3. This could be the reason that with a very low surface area, Ti/$CaCO_3$ catalyst (few m^2/g) could express good photoactivity (with more than 50% removal of paraquat).

In summary waste shells were used to prepare a catalyst support for the loading of Ti. The preparation parameters, such as calcination parameter of dried shell, calcination temperature of Ti loading step, Ti content as well as effect of light irradiation, were evaluated. Results confirm that the very low surface area catalyst could reduce the amount of paraquat in solution (more than 50%). This could be explained by higher light absorption by Ti/$CaCO_3$. The optimum conditions of preparation include: calcinations of waste shells at 600 °C, Ti loading step with calcination at 400 °C, Ti loaded at 2% wt and under UV irradiation. Furhter, radical testing suggested that the paraquat degradation in the presence of Ti/$CaCO_3$ catalysts occurred through $\bullet$OH. This was also supported by the results of FTIR spectra.

Supplementary Data

Supplementary data associated with this article, are available in the electronic form at http://www.niscair.res.in /jinfo/ijca/IJCA_57A(XX)1358-1364_SupplData.pdf.

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