Trapping and decomposing of color compounds from recycled water by TiO\textsubscript{2} coated activated carbon

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Abstract

Five types of commercially available activated carbons (ACs) were coated with TiO\textsubscript{2} nanoparticles prepared using a sol–gel method. Color and trace organics remaining in the actual treated effluent were adsorbed by TiO\textsubscript{2} coated ACs. The absorbed organic compounds were then decomposed using a photocatalytic process, and the ACs were regenerated for reuse. The efficiency of the process was assessed by the characterization of true color and A\textsubscript{254} (the organics absorption at the wavelength of 254 nm) at the beginning and the end of the experiment. The effects of UV light source, UV irradiation time, hydrogen peroxide and ultrasound on the efficiency of photocatalytic regeneration were also investigated. Significant differences in the efficiency were observed between uncoated ACs and TiO\textsubscript{2} coated samples. Among the 5 types of ACs tested, AC-3, AC-4 and their coated ones achieved better efficiency in color and A\textsubscript{254} removal, with around 90% or more color and A\textsubscript{254} being removed within 1 h of treatment. The data obtained in this study also demonstrated that the photocatalytic process was effective for decomposing the adsorbed compounds and regenerating the spent TiO\textsubscript{2}/AC-3. Finally, it was found that this regeneration process could be greatly enhanced with the assistance of H\textsubscript{2}O\textsubscript{2} and ultrasound by reducing the required regeneration time.

1. Introduction

As drinking water is becoming a more scarce resource in Australia, the demand for treating and reusing the effluent has been greatly increased. However, color and non-biodegradable trace organics present in the treated wastewater from sewage treatment plants (STPs) can affect the options for disposal or recycling water. Color is sometimes a concern because aesthetics impacts on public acceptance of recycling.

Adsorption by activated carbon (AC) has been used successfully for the advanced (tertiary) treatment of municipal and industrial wastewater (EPA, 2000; Coelho et al., 2006; Arerachakul et al., 2007; El-Sharkawy et al., 2007). The main disadvantage of such methodology is that the saturated AC must be regenerated before reuse (Sheintuch and Matatov-Meytal, 1999). Moreover, the spent carbon itself may have to be handled as a hazardous waste at the end of the treatment (Sheintuch and Matatov-Meytal, 1999; Coelho et al., 2006; Arerachakul et al., 2007). Therefore, decomposition of the adsorbed organics and regeneration of the adsorbent is a very critical step to the cost-effective use of AC in water treatment. Several methods have been used to regenerate activated carbon (Sheintuch and Matatov-Meytal, 1999). High temperatures promote the drying and loss of highly volatile compounds below 200 °C, vaporization and decomposition of unstable compounds at temperatures between 200 and 500 °C, and the pyrolysis of non-volatile adsorbates at temperatures over 500–700 °C (Sheintuch and Matatov-Meytal, 1999).

Heterogeneous photocatalysis, an advanced method that can effectively oxidize a wide range of organic compounds at ambient conditions, is an attractive alternative for the degradation of the organics and regeneration of spent carbons. In recent years, applications to environmental cleanup have been one of the most active areas in the heterogeneous photocatalysis (Legrini et al., 1993; Hoffmann et al., 1995; Zou et al., 2005; Zou and Zhu, 2007). Photocatalytic oxidation can be used to regenerate spent AC adsorbent and destroy organic adsorbates simultaneously (Liu et al., 1996). The advantages of heterogeneous photocatalysis over other AC regeneration methods include (Crittenden et al., 1993, 1997; Hoffmann et al., 1995; Malato et al., 2001): (1) It can destroy a wide variety of organic compounds; (2) No post-treatment is needed since the organic pollutants can be mineralized into non-toxic by-products such as H\textsubscript{2}O, CO\textsubscript{2}, and mineral acids; (3) The
process can be performed at low temperature; (4) It can be promoted by solar radiation, resulting in low energy cost; (5) On-site regeneration of spent adsorbent and destruction of adsorbed organic material is provided; (6) The loss of adsorbents due to attrition and burn-off which occurs in thermal regeneration is less.

Coating TiO2 photocatalyst on the surface of AC combines the advantages of both techniques (Crittenden et al., 1997; Khan et al., 2002), i.e. on one hand, AC works as the support of nanosized TiO2 photocatalyst and concentrates the pollutants and intermediates around the TiO2; on the other hand, the TiO2 photocatalyst can destroy the pollutants thus regenerating the AC in situ. A variety of coating methods for the synthesis of TiO2 supported on AC, such as impregnation (Crittenden et al., 1997; Harada et al., 1999; Tao et al., 2005), chemical vapor deposition (Lei et al., 1999), sol–gel method (Carpio et al., 2005), boil deposition (Lu et al., 1999), impregnation–desiccation (Liu et al., 2004), and dip-coating method (Suri et al., 1999; Jeong et al., 2004), have been reported. In general, TiO2 with anatase crystalline structure exhibits higher photocatalytic activity than those with other types such as rutile and brookite (Stafford et al., 1997; Herrmann, 1999; Yamazaki et al., 1999). It is commonly accepted that to obtain anatase TiO2, high temperature (>400°C) calcination is required (Hu and Yuan, 2005). This limits the use of TiO2 as a coat incorporating with AC as it which has poor heat resistance in oxygen containing atmosphere. Some researchers (Li et al., 2006; El-Sharkawy et al., 2007) heat treated TiO2 coated AC at high temperature in inert atmosphere such as in N2 flow to obtain TiO2 in anatase phase. However, this method is not practical since only very small amounts of catalyst are possible prepared in one batch and the operating costs using nitrogen purging gas are high. Therefore, it is very important to develop an alternative process of loading anatase TiO2 on the surface of AC, which could operate at lower temperature, i.e. 200°C to prevent the carbon loss and easily produce a large quantity of absorbent/catalyst using an ambient furnace.

Despite that photocatalysis has shown to be adequate for the destruction of a wide variety of organic compounds, in some cases the complete mineralization is only attained very slowly and the efficiency of the process, in terms of energy consumption, is advantageous only for very dilute effluents (Herrmann et al., 1993; Legrini et al., 1993; Hoffmann et al., 1995). In order to improve the overall performance of the photodegradation process, heterogeneous photocatalysis has been combined with physical process such as ultrasound (Shirgaonkar and Pandit, 1998; Stock et al., 2000; Davydov et al., 2001; Ragaini et al., 2001; Théron et al., 2001; Mrowetz et al., 2003; Peller et al., 2003), or chemical reagents such as ozone (Zou and Zhu, 2008; Sánchez et al., 1998; Kopf et al., 2000; Wang et al., 2002) and hydrogen peroxide (Bahnemann et al., 2007; Saquib et al., 2008; Singh et al., 2007). The combined process can: (i) increase the efficiency and decrease the reaction time in respect to the individual operations; (ii) reduce the cost in respect of heterogeneous photocatalysis alone, generally in terms of UV light energy (Augugliaro et al., 2006). However, most of studies have been carried out in artificial aqueous systems containing only one compound used as model molecule. Only few studies (Zou and Zhu, 2008) were conducted on actual wastewater. Investigations in actual wastewater containing both natural organic matter (NOM) and residuals from biological treatment process, therefore, would be of a great importance for advancing the processes for real applications.

The objective of this study is to investigate the technical feasibility of using photocatalytic oxidation for the degradation of the organics in oxygen containing atmosphere by using a muffle-furnace technique. The uncoated AC samples were also treated following the same procedures as a control. The estimated TiO2 loadings for TiO2/AC-1, TiO2/AC-2, TiO2/AC-3, TiO2/AC-4 and TiO2/AC-5 were 1.4, 1.5, 1.5, 1.7 and 1.3 wt. %, respectively.

Adsorption experiments were conducted using a recirculating system, which comprised an adsorption column (40 cm long and 5.5 cm in diameter), a circulating pump and a storage tank. For each adsorption experiment, 50 g adsorbent (AC or TiO2/AC) were used to treat 1.0 L effluent sample for 60 min. The adsorption column packed with adsorbent was flown with effluent from the storage tank by a peristaltic pump (Masterflex 7592-45, Cole-Parmer, USA) at a certain circulation flow rate. All the adsorption

Table 1

| Characterization of STP non-chlorinated effluent sample. |
|-----------------|-----------------|
| Parameter       | Value           |
| pH              | 6.8             |
| True color, Pt-Co Units | 107            |
| A254 (UV absorption), cm⁻¹ | 0.36           |
| COD (chemical oxygen demand), mg/L | 35.9         |

2. Experimental and methods

2.1. Materials

The water sample (Table 1) used for this study was non-chlorinated effluent sampled from Melbourne’s STP by the authorized operator. The high performance size exclusion chromatography (HPSEC) profile (Fig. 1) showed that color-causing organic compounds in the effluent sample with a wide range of molecular weights, i.e. 400–10 000. The effluent samples were filtered using Whatman No. 1 filter papers prior to adsorption treatment. Five commercially available activated carbons (Table 2) used in the experiments were washed with deionized water (Millipore) and were dried in an oven at 105°C overnight. Titanium butoxide (Ti(OCH2)4, 97%) and hydrogen peroxide (H2O2, 35 wt. % solution) were purchased from Aldrich. Ethanol (Ajax Finechem, Australia) and nitric acid (68.5–69.5%, BDH Chemicals, Australia) were obtained from the chemical store of Victoria University, Australia. All these chemicals were used as received without further purification.
experiments were carried out at room temperature. Effluent samples were taken from the outlet of the adsorption column for analysis.

The spent TiO$_2$/AC adsorbents were photocatalytically regenerated by UV alone, or by a combined UV and H$_2$O$_2$ or ultrasound for a certain time, and were then oven dried at 105 °C for 3 h. The UV panel used for regeneration consisted of six 18 W UV-A (NEC Blacklight Lamp) or UV-C lamps (NEC Germicide lamp) (Zou and Zhu, 2008). An ultrasonic bath (U-lab Instruments, Australia) was used in this study for ultrasonic filtration treatment. H$_2$O$_2$ solution used for regeneration was prepared by diluting 35 wt. % H$_2$O$_2$ solution with deionized water. After the regeneration, the recovered adsorption ability was carried out in a recovery test, where 5 g regenerated adsorbent was used to treat 50 mL effluent sample for 60 min. The treated water samples were then analyzed and compared with those treated by the virgin adsorbents.

2.4. Analyses

Measurements of true color, A$_{254}$ and COD were carried out with a spectrophotometer (HACH DR5000, USA). All samples were first filtered by 0.45 μm filter paper to remove suspended particles. True color was measured at 455 nm using Pt-Co standard method (Method 8025, HACH). A$_{254}$ was determined at a wavelength of 254 nm against organic-free water (Method 10054, HACH), and the results were reported in absorbance per centimeter (cm$^{-1}$). The chemical oxygen demand (COD) was measured by colorimetric determination method (Method 8000, HACH).

HPSEC was used to analyze the profile of the organic compounds in the effluent sample. HPSEC separates organic constituents based on a differential permeation process, according to molecular weight (size) (Chow et al., 2006). Organic compounds are adsorbed on a porous resin and then differentially eluted. The molecular weight (size) (Chow et al., 2006). Organic compounds are adsorbed on a porous resin and then differentially eluted. After the regeneration, the recovered adsorption ability was carried out in a recovery test, where 5 g regenerated adsorbent was used to treat 50 mL effluent sample for 60 min. The treated water samples were then analyzed and compared with those treated by the virgin adsorbents.

3. Results and discussion

3.1. BET results

Table 3 listed the BET surface area, total pore volume and average pore size of ACs before and after the TiO$_2$ coating. There were some differences in BET surface area between five uncoated AC samples, and all of them had significant high surface area ($854$–$1053$ m$^2$/g). The TiO$_2$ coating did not significantly reduce the BET surface area or the total pore volume of the ACs. This indicated that the porous structure of ACs was well retained after coating with TiO$_2$ and most of the TiO$_2$ was coated onto the external surface of ACs (Yuan et al., 2005). As the size of TiO$_2$ particles was a few nanometres, as seen by TEM (Fig. 2), which was bigger than the size of micropores of ACs (<2 nm), they may be capable of entering the mesopores and large micropores of ACs (El-Sheikh et al., 2004).

3.2. Results of adsorption experiments

3.2.1. Removal of color and A$_{254}$ by different adsorbents

The differences in the efficiency of color and A$_{254}$ removal by different adsorbents are compared in Figs. 3 and 4, respectively.

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**Table 2**

Activated carbon samples used in this study.

<table>
<thead>
<tr>
<th>AC sample</th>
<th>AC-1</th>
<th>AC-2</th>
<th>AC-3</th>
<th>AC-4</th>
<th>AC-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product code</td>
<td>EA1000</td>
<td>208EA</td>
<td>G51000</td>
<td>GA1000N</td>
<td>207E4</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Activated Carbon Technologies Pty Ltd, Australia</td>
<td>Filchem Australia Pty Ltd, Australia</td>
<td>Activated Carbon Technologies Pty Ltd, Australia</td>
<td>Activated Carbon Technologies Pty Ltd, Australia</td>
<td>Filchem Australia Pty Ltd, Australia</td>
</tr>
<tr>
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<td>Coal</td>
<td>Coal</td>
<td>Coal</td>
<td>Coal</td>
</tr>
<tr>
<td>Configuration/Form</td>
<td>Extruded pellets</td>
<td>Granules</td>
<td>Granules</td>
<td>Granules</td>
<td>Extruded pellets</td>
</tr>
<tr>
<td>Size</td>
<td>3 mm</td>
<td>6 × 12 mesh</td>
<td>6 × 12 mesh</td>
<td>6 × 12 mesh</td>
<td>4 mm</td>
</tr>
</tbody>
</table>

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**Fig. 1.** HPSEC profile of the organic compounds in the effluent sample.

**Fig. 2.** TEM image of TiO$_2$ nanoparticles.
Five tested AC samples showed significant differences in the reduction of both color and A254 absorbance values. The reduction rates of both color and A254 by AC-1 were the lowest with only around 30% color and A254 removal after 60 min treatment. For the processes using AC-3 and AC-4, however, the reduction rates of both color and A254 were greater than 90%. This is because that the adsorption capacity of ACs is not only influenced by their physical or porous structure, but also strongly depends on other factors such as surface chemical properties, adsorbate characteristics (molecular weight, polarity, pH, molecular size, functional groups) and solution conditions (pH, adsorbate concentration, presence of other possible adsorptives) (Radovic et al., 1997; Haghseresht et al., 2002; Bansal and Goyal, 2005). Due to the presence of imperfection or partially burnt graphic and crystallites, the disturbances in the elementary microcrystalline structure of activated carbons cause a variation in the arrangement of electron clouds in carbon skeleton and thus resulting in the creation of unpaired electrons and incompletely saturated valences. This affects the adsorptive properties of ACs, especially for polar and polarizable compounds (Bansal and Goyal, 2005).

It can also be seen from the figures that the coating of TiO2 onto AC support had almost no negative impact on the adsorption performances of all tested TiO2/AC samples. This confirmed that the TiO2 was mainly loaded onto the external surface of ACs, as suggested by the BET results (Table 3). The TiO2/AC-3 and TiO2/AC-4 samples still achieved the highest performance among five TiO2/AC samples.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-1</td>
<td>952</td>
<td>0.53</td>
<td>2.2</td>
</tr>
<tr>
<td>TiO2/AC-1</td>
<td>894</td>
<td>0.49</td>
<td>2.2</td>
</tr>
<tr>
<td>AC-2</td>
<td>1053</td>
<td>0.65</td>
<td>2.5</td>
</tr>
<tr>
<td>TiO2/AC-2</td>
<td>983</td>
<td>0.56</td>
<td>2.3</td>
</tr>
<tr>
<td>AC-3</td>
<td>894</td>
<td>0.56</td>
<td>2.5</td>
</tr>
<tr>
<td>TiO2/AC-3</td>
<td>859</td>
<td>0.54</td>
<td>2.5</td>
</tr>
<tr>
<td>AC-4</td>
<td>912</td>
<td>0.51</td>
<td>2.2</td>
</tr>
<tr>
<td>TiO2/AC-4</td>
<td>906</td>
<td>0.51</td>
<td>2.2</td>
</tr>
<tr>
<td>AC-5</td>
<td>936</td>
<td>0.67</td>
<td>2.8</td>
</tr>
<tr>
<td>TiO2/AC-5</td>
<td>861</td>
<td>0.55</td>
<td>2.6</td>
</tr>
</tbody>
</table>

3.2.2. **Effect of treatment cycles on the removal of color and A254**

The effect of TiO2 on the adsorption capacity of AC and the performance of TiO2/AC-3 and TiO2/AC-4 samples in the reduction of color and A254 were further investigated by performing multiple treatment cycles on the same amount of adsorbent (50 g) at a circulation flow rate of 0.6 L/min. 1.0 L effluent was treated for 1 h for each cycle. After each treatment cycle, the treated effluent was emptied from both adsorption column and storage tank, and then the storage tank was filled with another 1.0 L untreated effluent for the next treatment cycle until ten treatment cycles were completed. Water samples were taken from the outlet of the adsorption column at the end of each treatment cycle for analysis. The reduction rates of color and A254 against treatment cycle are plotted in Figs. 5 and 6, respectively. It was found that the efficiencies of color removal and A254 reduction for all tested samples decreased when more treatment cycles were conducted. This was reasonable because the adsorption capacity of the adsorbents decreased after prolonged usages. The results also showed that there were only slight differences in the reduction of both color and A254 absorbance between the uncoated and TiO2 coated AC samples, confirming that the loading of TiO2 had no strong influence on the adsorption capacity of the adsorbents. Significant differences in the reduction of both color and A254 absorbance between TiO2/AC-3 and TiO2/AC-4 samples, however, were observed during multiple cycle treatments. The performance of TiO2/AC-3 was much better than that of TiO2/AC-4, indicating that this absorbent was the best candidate for the removal of color and trace organics remained in the actual treated wastewater among five tested TiO2 coated AC adsorbents, and it was therefore chosen for further studies on regeneration.

![Fig. 3. Color removal rate for the different adsorbents, treatment time – 60 min, circulation flow rate – 0.6 L/min, effluent – 1.0 L, adsorbent – 50 g.](image)

![Fig. 4. Reduction rate of A254 absorbance for the different adsorbents, treatment time – 60 min, circulation flow rate – 0.6 L/min, effluent – 1.0 L, adsorbent – 50 g.](image)

![Fig. 5. Variation of the color removal rate with treatment cycle using different adsorbents, circulation flow rate – 0.6 L/min, adsorbent – 50 g, 1 h treatment time and 1.0 L effluent for each cycle.](image)
3.3.2. Effect of circulation flow rate on the removal of color and \(A_{254}\)

The reduction rates of both color and \(A_{254}\) for the TiO\(_2\)/AC-3 sample were examined at two different circulation flow rate (0.3 and 0.6 L/min) and the results are compared in Figs. 7 and 8, respectively. It can be seen that the circulation flow rate of the reactor did not significantly affect the efficiency of the process for both color and \(A_{254}\) removal.

3.3. Degradation of adsorbed organics and regeneration of TiO\(_2\)/AC-3

3.3.1. Photocatalytic regeneration of TiO\(_2\)/AC-3

After the fresh AC-3 and TiO\(_2\)/AC-3 used for ten treatment cycles (Section 3.2.2), the spent adsorbents were regenerated by 16 h UVC irradiation supplied by six 18 W UV-C lamps (NEC Germicide lamp). 5 g of the fresh or UVC treated adsorbent was mixed with 50 mL effluent for the color removal test. Treated effluent samples were withdrawn for analysis after the end of 1 h adsorption. Fig. 9 shows the color removal rates of the original and UVC regenerated TiO\(_2\)/AC-3 samples. The color removal rate of the used sample prior to UVC regeneration was also included in the figure for comparison. The color removal capacity of the used TiO\(_2\)/AC-3 sample was significantly improved after regeneration (65.4%) compared to that prior to regeneration (48.3%) and was close to that of the fresh one (68.2%). This indicated that the capacity of the used TiO\(_2\)/AC-3 was nearly recovered completely after photocatalytic regeneration by 16 h UVC irradiation.

It is commonly accepted that in catalytic processes including photocatalysis using crystalline TiO\(_2\), the dispersion of catalyst has a direct relation with its catalytic efficiency (Przepiórski et al., 2001). Therefore, catalyst with finer particle sizes should have a higher activity in catalytic processes. It is also known that the efficiency of photocatalytic degradation of organic compounds could be enhanced by anchoring of photoactive catalysts on suitable support (Yamashita et al., 2000), particularly that with large surface area such as activated carbons (Crittenden et al., 1997; El-Sheikh et al., 2004). The adsorption of pollutants on AC support increases its concentration around supported TiO\(_2\); its diffusion to TiO\(_2\) and thereby promotes the photocatalytic process (Crittenden et al., 1997; Khan et al., 2002). On the other hand, high surface area and well-developed porosity of AC enhances the dispersion of TiO\(_2\) particles on AC support (Lee et al., 2004; Subramani et al., 2007). The XRD results revealed that anatase phase TiO\(_2\) particles (major peaks at 25.4°, 38.0°, 48.0°, 54.7°, 63.1°) has formed after 2 h heat treatment of TiO\(_2\) sol at 200 °C, although the degree of crystallinity was not very high (Fig. 10). The peak appeared at 27.4° was assigned to be TiO\(_2\) rutile phase, while the signal at 31.0° was ascribed to TiO\(_2\) brookite traces. However, no crystalline TiO\(_2\) phase was detected by XRD for TiO\(_2\)/AC-3. This was possibly due to high dispersion of TiO\(_2\) nanoparticles on AC support. The high performance of photocatalytic regeneration observed in this study for TiO\(_2\)/AC-3 suggested that certain amount of crystalline phase TiO\(_2\) nanoparticles could be loaded with high degree of dispersion on the surface of AC.

3.3.2. Effect of UV light source on regeneration of TiO\(_2\)/AC-3

UV light source is an important factor in photocatalytic reaction. To evaluate the influence of UV light source on the efficiency of regeneration and UVC regenerated adsorbents, adsorbent – 5 g, treatment time – 1 h, effluent – 50 mL.

Fig. 6. Variation of the \(A_{254}\) reduction rate with treatment cycle using different adsorbents, circulation flow rate – 0.6 L/min, adsorbent – 50 g, 1 h treatment time and 1.0 L effluent for each cycle.

Fig. 7. Effect of circulation flow rate on color removal rate, TiO\(_2\)/AC-3 – 50 g, 1 h treatment time and 1.0 L effluent for each cycle.

Fig. 8. Effect of circulation flow rate on \(A_{254}\) reduction, TiO\(_2\)/AC-3 – 50 g, 1 h treatment time and 1.0 L effluent for each cycle.

Fig. 9. Comparison of the color removal rate between the original, used without UVC regeneration and UVC regenerated adsorbents, adsorbent – 5 g, treatment time – 1 h, effluent – 50 mL.
photocatalytic regeneration, the used TiO\textsubscript{2}/AC-3 was irradiated by short wave (UVC, same as that used above) or long wave (UVA) light (Zou and Zhu, 2008) for 16 h. The amount of adsorbent, volume of effluent and experimental procedures for static adsorption experiments were kept the same as those used in Section 3.3.1. Fig. 11 shows the differences in the efficiency of regeneration between long wave and short wave UV light. The sample regenerated under UVC achieved 10% more in the efficiency for color removal than that obtained by UVA regenerated sample. UVC was therefore chosen as the light source for further investigations in this study.

3.3.3. Effect of UV irradiation time on regeneration of TiO\textsubscript{2}/AC-3

Photocatalytic regeneration of used TiO\textsubscript{2}/AC-3 was conducted at different UV irradiation time to investigate the effect of UV irradiation time. As shown in Fig. 12, the color removal rate of regenerated TiO\textsubscript{2}/AC-3 increased significantly with an increase of the UV irradiation time but remained almost unchanged after 16 h of irradiation. This indicated that an irradiation time of 16 h was considered to be the suitable duration for photocatalytic regeneration of used TiO\textsubscript{2}/AC-3 under UVC.

3.3.4. Regeneration of TiO\textsubscript{2}/AC-3 by photocatalysis combined with UV/H\textsubscript{2}O\textsubscript{2} treatment

Hydrogen peroxide has been used in the industrial effluent treatment for detoxification of cyanide, nitrite and hypochlorite, for the destruction of phenol aromatics, formaldehyde, and removal of sulfite, thiosulfate and sulfide compounds (Gogate and Pandit, 2004a). However, since hydrogen peroxide itself is not an excellent oxidant for many organic pollutants, it must be combined with UV light, salts of particular metals or ozone to produce the desired degradation results (Pera-Titus et al., 2004). Because of its inherent advantages (i.e. no sludge formation, significant reduction in COD at relatively short reaction times and easy handling), the H\textsubscript{2}O\textsubscript{2}/UV system remained the advanced oxidation process (AOP) most often applied for the treatment of hazardous/refractory pollutants found in water or wastewater (Alaton et al., 2002). This AOP is based on the formation of hydroxyl radicals (HO\textsuperscript{•}) by means of the photolysis of hydrogen peroxide and the rate of generation of free radicals is significantly enhanced in the combination of hydrogen peroxide with UV light (Gogate and Pandit, 2004b; Pera-Titus et al., 2004). The main reactions of the system have been reported in literature (Glaze et al., 1992; Pera-Titus et al., 2004).

In this study, the used TiO\textsubscript{2}/AC-3 was photocatalytically regenerated with the addition of H\textsubscript{2}O\textsubscript{2} under UVC irradiation. The H\textsubscript{2}O\textsubscript{2} solution (1 vol. %) used for the experiments was prepared from 35 wt. % H\textsubscript{2}O\textsubscript{2} solution (Aldrich). UVC irradiation was supplied by the same UV unit as used above. The color removal rate of regenerated TiO\textsubscript{2}/AC-3 is depicted in Fig. 13, as a function of treatment time. The color removal rate increased gradually with increasing the irradiation time in the presence of H\textsubscript{2}O\textsubscript{2}, and reached the same level within a shorter time period of regeneration (3–4 h) (Fig. 13) as that obtained by 16 h photocatalytic regeneration using UVC alone (Fig. 12). This indicated that the time of photocatalytic regeneration of TiO\textsubscript{2}/AC-3 could be significantly reduced by the addition of H\textsubscript{2}O\textsubscript{2}.

It is well known that the degradation of organic matters in photocatalytic oxidation process is mainly due to the formation of HO\textsuperscript{•} radicals. As discussed earlier in this section, under UV irradiation,
the addition of hydrogen peroxide can greatly enhance the generation of free radicals, and thus accelerated the photocatalytic oxidation reaction.

3.3.5. Effect of ultrasonic treatment on photocatalytic regeneration of TiO\textsubscript{2}/AC-3

Photocatalytic regeneration of used TiO\textsubscript{2}/AC-3 with an assistance of ultrasound was also investigated. During the regeneration process, the used TiO\textsubscript{2}/AC-3 was mixed with deionized water in a beaker and was ultrasonically treated in an ultrasonic bath under UVC irradiation. It was interesting to note that the assistance of ultrasound can further reduce the time of the regeneration process (Fig. 14). The adsorption capacity of used TiO\textsubscript{2}/AC-3 for color removal was completely recovered after 30 min of regeneration by a combined process of ultrasound and UV irradiation (Fig. 14).

Ultrasonic irradiation has been used to treat waters and wastewaters, which is known as sonochemical treatment. Sonoochemical treatment is based on the use of low to medium frequency (20–1000 kHz) and high-energy to catalyze the destruction of organic pollutants, and can be operated at ambient conditions without the addition of extra chemicals. The chemical effects of ultrasound in aqueous solution are due to the propagation of a pressure wave, which leads to the occurrence of cavitation phenomenon, i.e., nucleation, growth and collapse of bubbles in the liquid (Augugliaro et al., 2006). The collapse of the bubbles induces localized supercritical conditions: high temperature and pressure (more than 5000 K and 1000 atm) (Suslick, 1988), electrical discharge and plasma effects. Under these extreme conditions, active species such as H\textsuperscript{+} and HO\textsuperscript{•} radicals are produced through the cleavage of dioxygen and water molecules (Kotronarou et al., 1991).

HO\textsuperscript{•} radicals are capable of attacking the organic compounds in water and can also interact with the oxygen present in the system to form peroxide radicals (HO\textsubscript{2}) and H\textsubscript{2}O\textsubscript{2}.

It was noted that heterogeneous photocatalysis and ultrasonic irradiation could cause degradation of organic pollutants in water by the same species, notably HO\textsuperscript{•} radicals. Similar to the combined photocatalysis and ozonation process (Zou and Zhu, 2008), a synergistic effect was also observed when photocatalysis was combined with ultrasound (Davydov and Smirniotis, 2000; Davydov et al., 2001). The greatly enhanced regeneration efficiency of used TiO\textsubscript{2}/AC-3 by ultrasonic treatment observed in this study may be attributed to the sonophotocatalytic synergistic effect, which can possibly be justified by the following reasons:

(1) Heterogeneous photocatalytic process:

Under the irradiation of UV, organic molecules adsorbed on the external surface of TiO\textsubscript{2}/AC-3 were degraded by a photocatalytic oxidation route as discussed extensively in our previous work (Zou and Zhu, 2007).

(2) Mechanical effects of ultrasound wave:

During the ultrasonic treatment, the photocatalytic process can be enhanced by mechanical effects caused by the ultrasonic waves, such as particle size reduction, increased mass transfer and surface cleaning, which hindered the blocking of the catalyst active sites by reaction intermediates (Augugliaro et al., 2006). Ultrasound may also mechanically remove the adsorbed organic molecules from the inner pores of TiO\textsubscript{2}/AC-3.

(3) Chemical effects of ultrasound:

For the photocatalytic process, the acceleration of reactions was determined not only by mechanical effects of ultrasound irradiation as described above, but also by chemical effects. Under ultrasound irradiation, the presence of solid particles in the aqueous system enhanced the cavitation phenomenon (Suslick, 1990; Jensen, 1996) as the microbubbles tend to break up into smaller ones thus increasing the total number of regions of high temperature and pressure. As a consequence, the number of hydroxyl radicals formed in the system increases thus improving the oxidation capacity of the system. It was also suggested by some authors (Théron et al., 1999; Mrowetz et al., 2003) that the accumulation of hydrogen peroxide in the aqueous phase might be another main reason for the sonophotocatalytic synergistic effect. In fact, hydrogen peroxide is produced by both photocatalysis and sonolysis in water: under photocatalysis H\textsubscript{2}O\textsubscript{2} is formed mainly by the reduction of adsorbed dioxygen by conduction band electrons (Hoffman et al., 1994), while sonolysis of water produces H\textsubscript{2}O\textsubscript{2} as a result of recombination between hydroxyl radicals produced by the implosion of cavitation bubbles (Wu et al., 1999).

4. Conclusions

This study presented the results of treating actual STP effluent by an adsorption process using TiO\textsubscript{2} coated activated carbons. The regeneration of the spent adsorbent was conducted by photocatalysis alone, or aided by H\textsubscript{2}O\textsubscript{2} or ultrasonic irradiation under UV light. Five types of TiO\textsubscript{2} coated activated carbons were compared for the color and A\textsubscript{254} reduction efficiencies. It was found that the TiO\textsubscript{2}/AC-3 and TiO\textsubscript{2}/AC-4 could significantly remove color and organic matters (around 90% of reduction) within 1 h treatment time. The adsorbent regeneration experimental results indicated that the photocatalytic process has been efficient in the degradation of adsorbed organics and regeneration of used TiO\textsubscript{2}/AC-3. The efficiency of the photocatalytic regeneration was significantly enhanced with the aid of H\textsubscript{2}O\textsubscript{2} or ultrasonic treatment.

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References


