

# Regeneration of granular activated carbon saturated with acetone and isopropyl alcohol via a recirculation process under H<sub>2</sub>O<sub>2</sub>/UV oxidation

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## Abstract

This study examines a water-based system, coupling an adsorber and a photoreactor, for regeneration of granular activated carbon (GAC) saturated with acetone and isopropyl alcohol (IPA). Through water recirculation the regeneration reaction was operated in both intermittent and continuous ultraviolet illumination modes. With a periodic dosage of hydrogen peroxide not only was regeneration efficient but it was also catalyzed by GAC in the adsorber. The concentrations of acetone, solution chemical oxygen demand (COD), pH and organic residues on GAC surfaces were measured during regenerations. Both pH and solution COD were found to correlate with regeneration completion as measured by organic residue on GAC surfaces in four regeneration cycles with acetone. Solution pH decreased to the acidic values and then returned to near its original value when organic residues were 0.085–0.255 mg/g GAC, that is, destruction efficiency of adsorbed acetone on the GAC surface was more than 99%. Likewise, solution COD became low (<100 mg/l) at regeneration completion. The pH variation pattern was then applied to another four cycles of regeneration with IPA, and successfully reflected the timing of complete regeneration. The final levels of organic residue on GAC surfaces were between 0.135 and 0.310 mg/g GAC in each of four regeneration cycles, each of which had been stopped based on the measurements of pH and solution COD. Furthermore, nearly the same batch of GAC could be repeatedly used with little changes in physicochemical properties in each of eight cycles: adsorptive capacities were  $95 \pm 7$  mg acetone/g GAC and  $87 \pm 3$  mg IPA/g GAC, and breakthrough time was  $0.86 \pm 0.05$  for acetone and  $0.78 \pm 0.03$  h for IPA. An economic assessment of the system showed that the operating cost was about 0.04 USD for treating every gram of acetone in the air.

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## 1. Introduction

Activated carbon (AC) is widely used as an adsorbent of organic contaminants dispersed in waste streams because of its porous structure and large surface area. Typically, its granular form is used in packed beds for flow through continuous operations. These beds can be operated in series to fully saturate the lead column, while the second column in series is then used to capture the breakthrough contaminants. As more and more stringent regulations on air/water discharges are being implemented, traditional technologies based on adsorption are increasingly being applied to processes with low levels of volatile organic compound discharges, such as spraying, surface coating and device cleaning processes. Adsorption is able

to achieve final discharges which are guaranteed to comply with emission requirements. As soon as the bed is saturated, the carbon is regenerated for another cycle of operation.

The traditional methods for regenerating spent activated carbon are purge desorptions, such as steam or pressure swing/purge desorptions, in combination with a cooling system to recover the organic as a liquid. There are other potentially destructive techniques, such as thermal, wet oxidation [1,2], supercritical fluid [3] and electrochemical regenerations [4]. Chemical regeneration, such as wet oxidation and supercritical fluid regenerations, can be carried out by decomposing the adsorbates using oxidizing chemical agents under subcritical or supercritical conditions. However, the large investment in high pressure and temperature equipment which is necessary makes these methods rather expensive [5]. Thermal regeneration is the most extensively used technology to regenerate spent activated carbon [6–8]. It typically involves heating the spent carbon at high temperatures in rotary kiln or multiple hearth furnaces to decompose the

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adsorbates and reactivate the carbon [9,10]. However it requires very high energy and causes considerable carbon loss (5–15%) due to attrition, burn-off and washout [6,9]. These methods often require special treatment facilities; regeneration is difficult to conduct in situ, so spent activated carbon must be unloaded and shipped to outside regeneration units, which produces additional pollution and costs. For these reasons, a number of alternative activated carbon regeneration methods which can be conducted under ambient conditions in situ are being researched.

Advanced oxidation processes (AOPs) are promising chemical oxidation technologies. They involve the generation of highly reactive hydroxyl radicals,  $\bullet\text{OH}$ , to initiate a series of chain reactions for pollutant degradation. Many refractory organics such as phenol are decomposed first into hydroxylated intermediates, to carboxylic acids [11,12] and then ultimately to nontoxic forms such as  $\text{Cl}^-$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [13,14]. Suri et al. [15] treated effluent steam condensate, which was from a steam regeneration unit, with a photocatalyst ( $\text{Pt-TiO}_2$ ). They observed that mineralization was effective (52–100%) for chlorinated hydrocarbons (carbon tetrachloride, tetrachloroethylene, *p*-dichlorobenzene, *o*-chlorobiphenyl) as measured by  $\text{Cl}^-$  production, but only 16% of methyl ethyl ketone was mineralized. AOPs, such as ozonation, hydrogen peroxide/ozonation ( $\text{H}_2\text{O}_2/\text{O}_3$ ), Fenton's reagent, and hydrogen peroxide under ultraviolet illumination ( $\text{H}_2\text{O}_2/\text{UV}$ ), have also been used to regenerate activated carbon [16–19], without significant loss of the carbon's adsorption characteristics [6,18,20]. Activated carbon in these reactors was observed to be able to enhance advanced oxidation [19,21–23], because of its ability to produce free radicals during interactions with hydrogen peroxide and ozone [24,25]. Lucking et al. [26] also observed that the oxidation of 4-chlorophenol by activated carbons together with hydrogen peroxide ( $\text{AC}/\text{H}_2\text{O}_2$ ) could be achieved; they attributed this to the graphitic structures [27] and iron content of activated carbons.

This present work examines an in situ recirculation system, which couples an  $\text{H}_2\text{O}_2/\text{UV}$  photoreactor to an adsorber with saturated granular activated carbon (GAC) for regeneration. Acetone and isopropyl alcohol (IPA) are chosen as representative organic adsorbates, since they are water soluble and commonly used in industrial operations. Recirculating water between the adsorber and the photoreactor can desorb organics from the GAC surface into water. To provide sufficient hydroxyl radicals for regeneration reactions, multiple  $\text{H}_2\text{O}_2$  dosage is adopted [14,12]. It is anticipated that, as more GAC surface area becomes available through water recirculation, the oxidation of desorbed organics will be enhanced via GAC catalysis in the adsorber.

Various parameters have been used to determine the ending point of the regeneration reactions. Lin and Lai [16] used color disappearance for dye wastewater under activated carbon/ozonation and Toledo et al. [18] used the chloride production of chlorinated adsorbates under Fenton's reagent reactions. Mourand et al. [17] used the disappearance of the chlorinated pollutants and the chloride concentration for  $\text{O}_3/\text{H}_2\text{O}_2$ . However, information about organic residues on activated carbon surfaces to confirm complete regeneration was lacking in these experiments. In this study, an alternative control parameter

is proposed. Because hydrocarbons with carbonyl and hydroxyl groups, such as phenol, are mineralized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  via acid intermediates, it is anticipated that the pH variation could reflect the mineralization reaction in which organic intermediates are converted into carbon dioxide and  $\text{CO}_2$  escapes from the reacting mixture; the pH variation could be used to promptly determine the ending point of advanced oxidation when solution chemical oxygen demand (COD) was low [28]. This work will not only use solution COD and pH to indicate the timing of complete regeneration, but will also measure organic residues on GAC surfaces as parallel information for confirmation of reaction completion. pH would be a more readily measurable parameter during the course of regeneration for process engineers to determine when regeneration was complete.

## 2. Experimental methods

### 2.1. Materials

Hydrogen peroxide was obtained from Fluka Chemical (35% w/w). Acetone and IPA were obtained from Aldrich Chemical Co. and used without further purification. The reagents for COD measurements [29] were all standard analytical reagents and the analyses were conducted using a Photometer SQ300 spectrophotometer purchased from Merck Taiwan Ltd. The charcoal-based activated carbon (from Sigma Chemical) was sieved to a uniform size of 8–10 mesh, washed with 2N NaOH to improve the polarity of the GAC surface, and then washed repeatedly with reverse osmosis (RO) water until the pH of the filtrate was the same as the pH of the water and then dried overnight in an oven at 120 °C for use. The iron content (3.8 mg/g) in the washed GAC and iron ions (0.3 mg/l) leached during regenerations were measured with an absorption spectroscopy (Solaar M6).

### 2.2. Apparatus

The adsorber (diameter 15 mm, length 175 mm) and the photoreactor (80 mm in diameter and 350 mm in height) were both acrylic columns. At the center of the photoreactor was a germicidal UV lamp at 254 nm with 15 W and 32 mW/cm<sup>2</sup> of UV light output at one meter from the lamp (Atlantic Ultraviolet Corp., USA), and on the top was a needle valve, which was opened and closed occasionally to keep the process at ambient pressure. The measurements of acetone and IPA were conducted in a Chrompack CP9002 gas chromatograph (GC) with a flame ionization detector (FID) and a column of Carbowax, 0.53 mm × 60 m capillary column from Restek Corp. The oven temperature was programmed from 50 °C (for 2 min) to 120 °C (for 2 min) at a rate of 10 °C min<sup>-1</sup>. The injector and detector temperatures were both set at 150 °C. The amount of organics remaining on the adsorbent was measured using a gas chromatography–mass spectrometry (GC–MS, Trace GC/Trace MS, Thermo Finnigan, Austin, TX, US) with library: Nist Mass Spectral Search Program version 1.6d. The mass spectrometer was equipped with an electron impact ion source and a quadrupole analyzer. The system was controlled by X'calibur software. A Rtx-5MS sil capillary fused silica column

(30 m × 0.25 mm i.d. × 0.25 μm film thickness, Restek, Bellefonte, PA, US) was used for GC separation in the conditions of oven from 30 °C (for 5 min) to 100 °C (for 10 min) at a rate of 5 °C min<sup>-1</sup> and injector at 200 °C.

### 2.3. Procedures

#### 2.3.1. Adsorption

To obtain spent carbon, dry air containing 1500 ppmv of acetone or IPA was continuously passed through an adsorber with 10 g of GAC at 1.0 l/min at room temperature until outlet concentration was almost equal to the inlet. The effluent was sampled periodically for acetone/IPA analysis. Then the breakthrough curve was plotted to obtain breakthrough time (when the ratio of outlet concentration to the inlet: 0.05) and the quantity of adsorbate on the adsorbent was recorded from the weight difference, i.e., adsorption capacity (mg adsorbate/g GAC).

#### 2.3.2. Desorption and oxidation

As soon as the GAC in the adsorber was saturated, the adsorber was connected to the photoreactor with 1.7 l of RO water. The desorption was allowed to proceed by recirculating water between the adsorber and the photoreactor at a liquid flow rate of 2 l/min. Oxidation was initiated at different modes by irradiating the recirculating water in the photoreactor (UV/H<sub>2</sub>O<sub>2</sub>) and in the adsorber with an initial dosage of 3.3 g of H<sub>2</sub>O<sub>2</sub> (35%) and then at further varying time intervals. Samples were withdrawn at preset time intervals for the analyses of acetone/IPA, pH, or COD to determine the extent of oxidative regeneration. When regeneration reaction was stopped, based on solution COD level (<100 mg/l, the wastewater discharge standard of the EPA, Taiwan) and pH variation pattern [28], the regenerated carbon was separated: 0.5 g were used for extraction to ensure that complete regeneration had occurred and the remainder was then dried in an oven at 120 °C and weighed for another cycle of operation. This cycle was operated eight consecutive times by using the same recirculating water. The adsorption capacity and breakthrough time of the regenerated GAC might reasonably vary in each cycle, and this would change the initial loading (or adsorption capacity) of acetone or IPA on the GAC and in turn their initial concentration ( $C_0$ ) in the regeneration solution. The detailed initial information is shown in the figures and their captions. The first four cycles were to regenerate GAC saturated with acetone and the other four were with IPA. In addition, GAC-absent experiments were conducted in the recirculation process to isolate the catalytic effects of GAC/H<sub>2</sub>O<sub>2</sub> for comparison. Acetone and IPA were individually added to the photoreactor directly for oxidation. For the GAC absent experiments, the oxidant (H<sub>2</sub>O<sub>2</sub>) dosage was 3.3 g of H<sub>2</sub>O<sub>2</sub> (35%) every 2 h.

#### 2.3.3. Extraction of organics and analysis

The 0.5 g of regenerated GAC sample were extracted with 15 ml of hexane for 3 h in the extraction flask. The extract was analyzed by a GC/MS to determine the residual organic species present on the carbon surfaces to ensure that complete regeneration had occurred.

## 3. Results and discussion

### 3.1. preliminary observations regarding desorption at various solution pHs

Prior to the regeneration experiment, desorption in the recirculation process was examined at solutions of pH 4, 7 and 10 with an initial acetone loading of 95 mg/g on the GAC in the adsorber. The changes in acetone concentration in the water recirculating between the adsorber and the photoreactor were measured. Provided that desorption is a pseudo first-order process with an effective mass transfer constant  $k_f$ , data analysis showed that  $k_f$  of acetone was about 0.034, 0.037 and 0.023 min<sup>-1</sup> for solutions of pH 4, 7 and 10. The desorption rate was found to be higher when the GAC was in an acidic solution [30], in which about 85% of acetone adsorbate was desorbed from the adsorbent into the bulk solution in 2 h. (The reacting mixture pH of hydrocarbons with carbonyl and hydroxyl groups under the oxidation of H<sub>2</sub>O<sub>2</sub>/UV has been previously reported to be within the acidic range [11,12,19,28].) The preliminary results suggest that the natural changes in pH during regeneration reactions tend to increase the desorption rate. Hence, the working pH of all desorption/oxidation (regeneration) reactions will not be controlled at a particular value in this work.

### 3.2. Desorption/oxidation reactions

The GAC regeneration process was performed in two modes: continuous and intermittent UV modes. Periodic oxidant addition was adopted to aid the oxidation reactions. Fig. 1 demonstrates the results of the first two regeneration cycles with the intermittent UV mode and Fig. 2 the other two with the continuous UV mode. The initial acetone loading and the final level

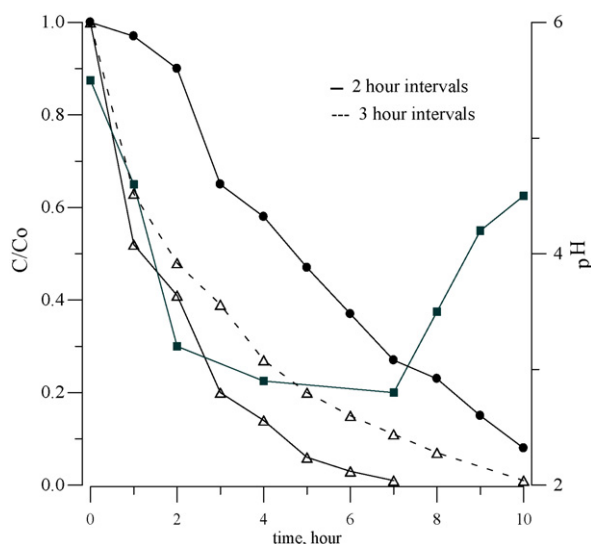


Fig. 1. pH and normalized concentrations of acetone and COD vs. time in the intermittent UV mode with 2 and 3 h intervals of H<sub>2</sub>O<sub>2</sub> addition. (Δ) Acetone concentration, (●) normalized COD and (■) pH. The initial desorbed acetone concentration  $C_0$ : 600 mg/l (COD<sub>0</sub>: 1324 mg/l).

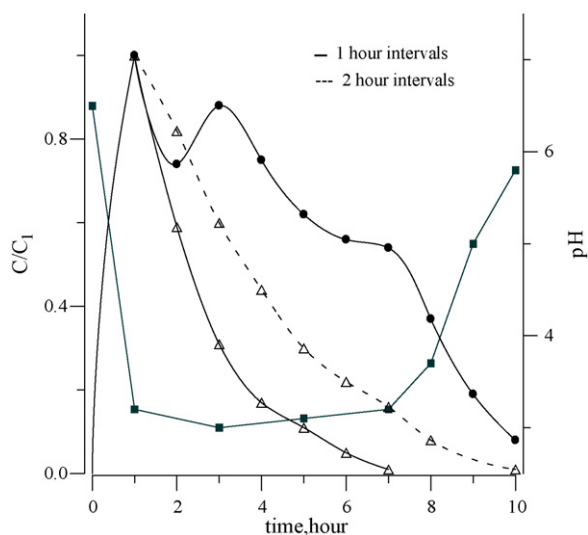


Fig. 2. pH and normalized concentrations of acetone and COD vs. time in the continuous UV mode with 1 and 2 h intervals of  $\text{H}_2\text{O}_2$  addition. ( $\Delta$ ) Acetone concentration with  $C_1$ : 340 mg/l at time = 1 h; ( $\bullet$ ) normalized COD with  $\text{COD}_1$ : 840 mg/l at time = 1 h and pH ( $\blacksquare$ ).

of organic residue on the GAC in each of four regeneration cycles are shown in Fig. 3.

The intermittent UV mode is when photo-oxidation starts after desorption recirculation for 2 h. It was found that it took about 10 h at 3 h intervals of oxidant addition and 7 h at 2 h intervals to completely remove acetone molecules from the reaction mixture (Fig. 1). To almost completely remove COD ( $\text{COD} < 100$  mg/l) from the reaction mixture, the reaction with two hour intervals took about 10 h, while with 3 h intervals, the COD trend was similar (data not shown), but it took 12 h.

The continuous UV mode is when desorption of the adsorbate on saturated GAC in the adsorber and photo-oxidation in the photoreactor is initiated simultaneously. The removal of acetone from the reaction mixture took about 7 h at 1 h intervals of

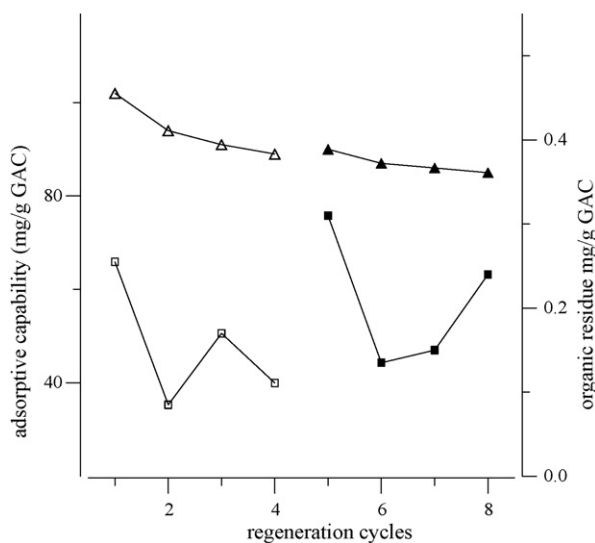


Fig. 3. Adsorption capabilities of acetone ( $\Delta$ ) and IPA ( $\blacktriangle$ ) in each of eight regeneration cycles, and their corresponding acetone ( $\square$ ) and IPA ( $\blacksquare$ ) residues on the GAC surface.

oxidant addition and 10 h at 2 h intervals (Fig. 2). COD accumulation in the reaction mixture was observed in this mode. For nearly complete mineralization within 10 h this mode of reaction required more frequent dosage intervals than the previous mode.

These experiments were run to almost complete mineralization ( $\text{COD} < 100$  mg/l) with continued treatment within 10 h by varying time intervals of  $\text{H}_2\text{O}_2$  addition. From the trends of acetone degradation curves in Figs. 1 and 2, it was observed that the more frequent the dosage (3.3 g of  $\text{H}_2\text{O}_2$  in this work), the faster the reaction; and the intermittent mode was faster than the continuous. Nonetheless, if the reaction time is of concern, further trials to optimize the reaction parameters, such as  $\text{H}_2\text{O}_2$  dosage and UV intensity, would be necessary.

### 3.3. Indicator of complete regeneration

When regeneration reactions were stopped based on COD levels ( $< 100$  mg/l), GC/MS analyses showed that the acetone remaining on GAC surfaces was 12.9, 4.3, 8.6 and 5.6 ppm (g/g hexane), which are equivalent to 0.255, 0.085, 0.170 and 0.111 mg/g GAC, respectively, as shown in Fig. 3. The destruction efficiency of acetone adsorbed on the GAC surface was more than 99%. No other organics were found in the GC/MS chromatograms. The pH and the COD trends (Figs. 1 and 2) show that in both regeneration modes, reaction mixture pH decreased first from the initial value to the acidic range, and then returned to near its original value when solution COD was low, regardless of the frequency of oxidant addition. This finding is very similar to that of a previous work [28], which indicated that this pH variation pattern is able to indirectly indicate the ending point of advanced reaction. The same pH pattern is also applicable to determine the time of regeneration completion in this in situ recirculation process, and it is more readily measurable than solution COD and organic residues on the GAC surface. The adsorption amount and breakthrough time of the regenerated GAC for each of the regeneration cycles was  $95 \pm 7$  mg acetone/g GAC and  $0.86 \pm 0.05$  h. The variation during four cycles of adsorption/regeneration was still within a reasonable range, which shows that using solution COD as an indicator of regeneration completion was successful.

### 3.4. IPA regenerations by using pH as a process control parameter

Using pH as a process control parameter was then applied to another four regeneration cycles of GAC saturated with IPA, by using almost the same batch of GAC. The initial loading and final level of organic residue in each cycle are also shown in Fig. 3. The first two cycles were with the intermittent UV mode and the other two with the continuous UV mode. The degradation trends of IPA are similar to those of acetone in Figs. 1 and 2 and the results in each mode were the same; only typical experimental results are presented in Fig. 4. The pH and COD curves showed that solution pH rebounded from the acidic range to near its original value when solution COD was low. To ensure that complete regeneration had been achieved when the reaction mixture pH turned around at low COD levels, organic residues



on these regenerated GAC surfaces were also measured. IPA residue was found to be 0.135–0.310 mg IPA/g GAC as shown in Fig. 3, which implies that >99% destruction of the adsorbed IPA was achieved. No other organics on the GAC surface were detected in the GC/MS chromatograms. The results confirmed that using pH as a control parameter had been successful in indicating regeneration completion. The adsorptive amount and breakthrough time of the regenerated GAC for each regeneration cycle were  $87 \pm 3$  mg IPA/g GAC (Fig. 3) and  $0.78 \pm 0.03$  h (data not shown). The variation during four cycles of adsorption/regeneration was also within a reasonable range, which shows that the oxidation in the regeneration process had little effect on the reusability of the regenerated granular activated carbon over eight cycles of acetone and IPA regenerations.

### 3.5. Catalytic effects of GAC

An interesting intermediate molecule was incidentally found during regeneration with IPA. The GC retention time and the MS chromatography suggested that the major intermediate molecule was acetone. Its generation with respect to time is shown in Fig. 4, where the trend of IPA disappearance was found closely to match that of acetone generation. It is believed that this dehydrogenation involves the abstraction of hydrogen atoms by  $\cdot\text{OH}$  free radicals from the hydroxyl group ( $-\text{OH}$ ) of IPA ( $\text{CH}_3\text{COHCH}_3$ ) molecules to form the corresponding acetone ( $\text{CH}_3\text{COCH}_3$ ) molecules [31,32]. Although IPA disappearance rates in both modes were much faster than those of acetone (Figs. 1 and 2), COD degradation was not as fast as expected. This is attributed to the intermediate molecule acetone being produced during IPA regenerations.

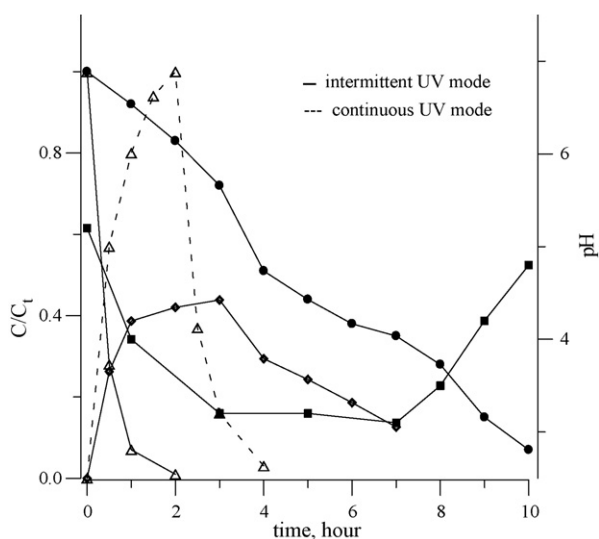


Fig. 4. pH and normalized concentrations of IPA and COD vs. time in the intermittent and continuous UV modes with 2 h intervals of  $\text{H}_2\text{O}_2$  addition.  $C_t$ , maximum concentration at time  $t$  during reaction; ( $\Delta$ ) IPA concentration, ( $\bullet$ ) solution COD and ( $\blacksquare$ ) pH. The initial concentration  $C_0$ : 450 mg/l,  $\text{COD}_0$ : 1100 mg/l for the intermittent mode and  $C_2$ : 340 mg/l at time = 2 h for the continuous mode. ( $\diamond$ ) The concomitant acetone concentration as IPA degraded in the intermittent UV mode with  $C_3$ : 191 mg/l at time = 3 h.

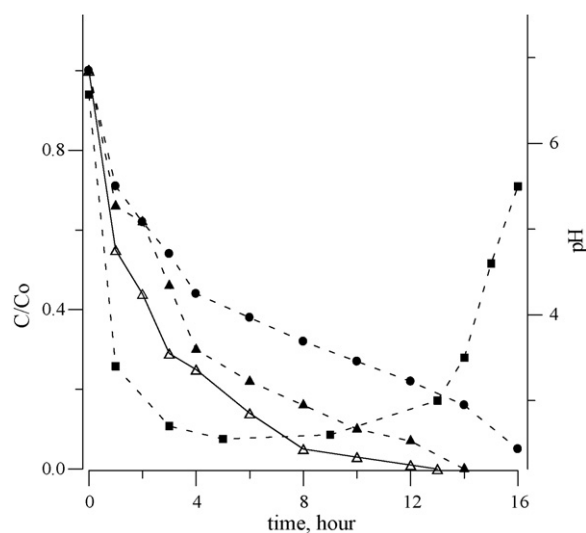


Fig. 5. pH and normalized concentrations of IPA, acetone and COD vs. time under  $\text{H}_2\text{O}_2/\text{UV}$  oxidation with GAC absent in the adsorber. ( $\Delta$ ) IPA concentration with  $C_0$ : 410 mg/l; ( $\blacktriangle$ ) acetone concentration with  $C_0$ : 446 mg/l. ( $\blacksquare$ ) pH and ( $\bullet$ ) COD with  $\text{COD}_0$ : 990 mg/l in the acetone reaction mixture.

First-order regression kinetics was applied to the combinative oxidation system in the intermittent UV mode. The rate constants obtained were:  $0.626 \text{ h}^{-1}$  ( $R^2$ : 0.975) for acetone removal, and  $0.2399 \text{ h}^{-1}$  ( $R^2$ : 0.945) for its corresponding mineralization (Fig. 1), and  $2.30 \text{ h}^{-1}$  ( $R^2$ : 0.992) for IPA (Fig. 4). Comparison experiments, presented in Fig. 5, were also performed to study the degradations of aqueous acetone and IPA (GAC absent in the adsorber) in this recirculation process. The trends of solution COD and pH of acetone degradation confirmed the finding of a previous work: the reaction mixture pH decreased first from the initial value to the acidic range, and then returned to near its original value when solution COD was low [28]. The rate constants calculated with first-order regression were:  $0.23 \text{ h}^{-1}$  ( $R^2$ : 0.975) for acetone removal and  $0.139 \text{ h}^{-1}$  ( $R^2$ : 0.91) for its mineralization, and  $0.363 \text{ h}^{-1}$  ( $R^2$ : 0.987) for IPA. The correlations of fit constants ( $R^2$ ) for the regressions of the data associated with each experiment are all greater than 90%. This indicates a good statistical fit and that the first-order model appears to be an appropriate model for tracking the degradations of acetone/IPA molecules in this combined oxidation treatment system with multiple dosage of oxidant addition. It is also shows that the oxidations with GAC present in the adsorber yielded higher rate constants than those with GAC absent: about 2.72 times faster for acetone and 1.73 times faster for its mineralization; 6.34 times faster for IPA. Therefore, GAC in the adsorber exhibited a good catalytic effect on the regeneration reaction, while it was regenerating in this process.

The enhancement could be explained by two hypotheses. One is that the catalytic activity of GAC in the regeneration process is the result of the release of iron from the GAC. The leached iron ions as homogeneous catalysts initiate Fenton reactions for enhancement. This explanation, however, can be excluded because the iron found in the aqueous solution after a reaction time of 10 h was less than 0.3 mg/l. Another hypothesis is that, as described earlier, the catalytic activity is arising from GAC as a

Table 1  
List of material and power used, and cost estimation for GAC regeneration on a recirculation process under H<sub>2</sub>O<sub>2</sub>/UV oxidation

Parameters <sup>a</sup>	Consumption (per 1000 m <sup>3</sup> air) <sup>b</sup>
GAC (0.52 USD/kg)	21 g
H <sub>2</sub> O <sub>2</sub> (0.193 USD/kg)	0.2772 kg
Reaction time	168 h
Electric power (0.069 USD/kWh)	2.64 kWh
UV lamp life (1.55 USD/800 h)	22%
Total cost	0.59 USD

<sup>a</sup> Numbers in parentheses are unit prices. The electricity is the local price (Taiwan).

<sup>b</sup> Air of 16.1 mg acetone/m<sup>3</sup> is assumed.

heterogeneous catalyst with available graphitic surface area for H<sub>2</sub>O<sub>2</sub> decomposition, which then enhances organics oxidation by producing free radicals [24,26,27]. The experimental results showed that the intermittent UV mode, due to 85% desorption having occurred in the previous 2 h, had more available GAC surface area than the continuous mode; its reaction was faster and no COD accumulation was observed in the regeneration solutions in Figs. 1 and 4. However, acetone may be completely oxidized, or partially oxidized to organic intermediates, which are more polar in nature; the adsorption of these reaction intermediates on the GAC surface was slower. This can be seen from the accumulated COD in the reaction mixture at the early stage of the mineralization reaction in Fig. 2. But later the reaction became faster when the GAC had more available surface area for catalysis. As is well known, these mechanisms are too complex to characterize, involving adsorption, desorption and oxidation, which occurred simultaneously in the combined system under GAC/H<sub>2</sub>O<sub>2</sub>/UV oxidation. But, as the desorbed adsorbate and COD in the regeneration solution were progressively reduced, the organics on the adsorbent surface was desorbed into the bulk liquid phase to maintain equilibrium distribution between both phases, and then more GAC surface area became available for H<sub>2</sub>O<sub>2</sub> decomposition and enhancing oxidation reactions. At the end, when solution COD was very low (<100 mg/l), organic residue on the GAC was also found to be very low.

### 3.6. Economic evaluation of oxidative GAC regeneration

As described earlier, adsorption is particularly well suited to treating large volumes of gases with very dilute pollutant levels and it guarantees the removal of contaminants down to trace levels; in this analysis, pollutant concentration is presumed to be 10 mg carbon/m<sup>3</sup> air, which is equivalent to 16.1 mg acetone/m<sup>3</sup> air. Table 1 summarizes the operating material required for processing 1000 m<sup>3</sup> air with 16.1 mg acetone/m<sup>3</sup> air. At the rates achieved in the present work with 2 h intervals of H<sub>2</sub>O<sub>2</sub> addition in the intermittent mode, this would result in about 21 g of GAC consumption at an adsorption capability of 95 mg acetone/g adsorbent and eight cycles of adsorption/regeneration for each batch of adsorbent. It would also require 168 h of regeneration time and 0.2772 kg H<sub>2</sub>O<sub>2</sub> addition to accomplish almost complete COD removal in the regeneration process. In addition to reagents and power, the deterioration of the UV lamp was

also considered a consumption item, the cost of which was estimated by multiplying the total irradiation time as a fraction of the life time of a lower pressure 15 W UV mercury lamp (800 h) by its unit price. Accordingly, the total operating cost of regenerating the spent GAC for processing 1000 m<sup>3</sup> of the waste air with 16.1 mg acetone/m<sup>3</sup> air, was found to be 0.59 USD, which is also equivalent to ~0.04 USD per gram of acetone in the air. Furthermore, the process also provides a convenient process control (pH) parameter in the regeneration process and the water is reusable.

## 4. Conclusion

The recirculation process was successfully applied to regenerate the spent GAC saturated with acetone and IPA. The levels of organic residue on GAC surfaces were between 0.085 and 0.255 mg/g GAC in four cycles of regeneration with acetone, each of which showed that regeneration was complete when regeneration had been stopped based on solution COD. A consistent pH variation pattern was observed during these regenerations: reaction solution pH decreased first from the initial value to the acidic range, and then returned to near its original value when solution COD was low, regardless of the frequency of oxidant addition and regeneration modes. The pattern was successfully applied to represent the timing of complete regeneration of GAC saturated with IPA for another four cycles. When solution pH rebounded from the acidic to near its original values, organic residue on GAC surfaces was 0.135–0.310 mg/g GAC, which implies that >99% of IPA destruction was achieved. Results from all experimental runs also revealed that:

1. The desorption rate in the recirculation process was higher at acidic pH values, in which about 85% of acetone was desorbed from the adsorbent into the bulk solution in about 2 h.
2. Periodic oxidant addition was found feasible to aid regeneration and lead almost to complete oxidation. The results found from regenerations with acetone in the intermittent and the continuous UV modes were: the more the dosage the faster the reaction. The former mode was faster, which took 10 h to almost completely remove COD with 2 h intervals of oxidant addition, while the latter mode was slower, requiring 1 h intervals.
3. A first-order model was used to describe the behavior of acetone and IPA degradations under multiple doses of oxidant in the intermittent UV mode. It was found that the oxidations with GAC present in the adsorber yielded higher rate constants than with GAC absent: about 2.72 times faster for acetone removal and 1.73 times faster for its mineralization; 6.34 times faster for IPA. GAC present in the adsorber exhibited a good catalytic effect on the degradation reaction, while it was regenerating. Oxidative regeneration not only took place in the combined oxidation process, but was also enhanced due to the GAC presence in the adsorber.
4. It is hypothesized that the catalytic activity of GAC is arising from GAC as a heterogeneous catalyst with available graphitic surface area for H<sub>2</sub>O<sub>2</sub> decomposition to produce

more free radicals for oxidation. The experimental results showed that the intermittent UV mode, due to 85% desorption having occurred, had more available GAC surface area than the continuous mode; its reaction was faster. However, even though COD accumulated in the reaction mixture in the early stages of mineralization in the continuous UV mode, the reaction became faster later when the GAC had more available surface area for catalysis.

5. The adsorption capacity and breakthrough time of the regenerated GAC for each of four regeneration cycles with acetone was,  $95 \pm 7$  mg acetone/g GAC and  $0.86 \pm 0.05$  h, while for another four cycles of IPA, it was  $87 \pm 3$  mg IPA/g GAC and  $0.78 \pm 0.03$  h. The variation was within a reasonable range, which shows that the regeneration had little effect on the physicochemical properties of the reused GAC over eight cycles in the recirculation process.
6. The regeneration reaction for the intermittent UV mode requires less oxidant to achieve GAC regeneration within a certain time interval. Therefore it is a more economically advantageous mode than the continuous. It was also adopted for economic analysis of the water-based regeneration process. The operating cost was about 0.04 USD for treating every gram of acetone in the air.
7. Compared to other regeneration processes, this water-based regeneration process has the following advantages: it can be conducted in situ, it provides a convenient process control parameter, namely pH, for regeneration with hydrocarbons containing carbonyl and hydroxyl groups and the GAC and the water are reusable.

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