Treatment of Trichloroethylene by Adsorption and Persulfate Oxidation in Batch Studies

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For remediation of trichloroethylene (TCE) contaminated groundwater, activated carbon (AC) has been used to adsorb and reduce the TCE concentration and to manage contaminant migration. Additionally, AC may also act as an activator of the electron-transfer mediator in activating persulfate anion (S₂O₈²⁻) to generate sulfate radical (SO₄²⁻) for contaminant destruction. The objective of the present research was to examine the combined use of AC and persulfate to treat TCE. The degradation of persulfate in the presence of AC follows a first-order kinetic behavior, and the faster persulfate degradation is observed when elevated AC dosage is used. Higher initial persulfate concentration results in a decrease of the persulfate degradation rate. Upon persulfate oxidation, the AC surface properties are altered including: an increase in acidity of surface concentration, a decrease in pH_pzc, and a slight decrease in the surface area. The results of a study of adsorption kinetics and isotherms suggest that the adsorption behavior for the original AC fits the pseudo-second-order kinetic model while the pseudo-first-order kinetic model is suitable for predicting oxidized AC performance. During the persulfate oxidation of TCE with AC as an activator, studies show that TCE removal can be a net result of adsorption and oxidation, in which a partial mineralization of TCE to release chloride occurs.

1. Introduction

Chlorinated solvents such as trichloroethylene (TCE) are widely used as an ingredient in industrial cleaning solutions and as a universal degreasing agent. TCE is one of the most frequently detected volatile organic contaminants in groundwater in the United States. For the purification of groundwater TCE contamination, an in situ remediation method known as permeable reactive barriers (PRBs) may be designed to reduce mass flux of the down gradient residual contamination by contaminant removal occurring within the barrier. Among reactive materials used in PRBs, activated carbon (AC) has been used to manage contaminant migration through direct sorption control. AC with a high surface area and porous structure is widely used as an adsorbent, catalyst, and catalyst support. Adsorption of contaminants onto the AC can be regarded as preconcentration of contaminants for further treatment. The adsorption capacity of AC does not rely only on its pores but also on its chemical composition. Several types of oxygen functional groups are important in influencing the surface characteristics and adsorption behavior. Moreover, AC also has been used in heterogeneous catalysis as a direct catalyst. Catalytic effects in ozone and peroxide oxidation of toxic organic contaminants in the presence of AC have been successfully demonstrated. The potential of AC as a catalyst support has also been an alternative use in a variety of environmental applications. For example, AC-supported Pt, Cu, and Fe have been developed and demonstrated in catalytic peroxide oxidation for wastewater treatment.

One of the oxidants recently used for the in situ chemical oxidation (ISCO) remediation of subsurface contamination via advanced oxidation processes is the activated persulfate (S₂O₈²⁻) reaction, which is based on the generation of the strong sulfate radical oxidant (SO₄²⁻) to destroy a variety of organic contaminants. Some of the properties of persulfate anion that make it attractive for the ISCO application are: high water solubility (730 g L⁻¹), no odor, effective oxidation capability over a wide range of pH, and lower affinity to soil organics. The sulfate radical has been extensively studied as an intermediate radical oxidant in the thermal-, metal (Me)-, and photochemical-activated decomposition of persulfate.

Thermal activation

S₂O₈²⁻ + heat → 2SO₄²⁻ (1)

Metal activation

S₂O₈²⁻ + Meⁿ⁺ → SO₄²⁻ + Me⁽ⁿ⁺¹⁾ + SO₄²⁻ (2)

Photochemical activation

S₂O₈²⁻ + e⁻ → SO₄²⁻ + SO₄²⁻ (3)

Additionally, it has been suggested that AC containing oxygen functional groups may act as a catalyst of the electron-transfer mediator and generate catalytic decomposition of hydrogen peroxide. Because the structure of persulfate is a symmetrically substituted derivative of hydrogen peroxide and a more stable ISCO oxidant than peroxide, if the persulfate is used instead of peroxide, the AC may enable the decomposition of persulfate, with releases of organic radicals and sulfate radicals during the radical propagation processes. The following predicted reaction mechanisms are assumed to result:

AC surface−OOH + S₂O₈²⁻ → SO₄²⁻ + AC surface−OO⁻ + HSO₄⁻ (4)

AC surface−OH + S₂O₈²⁻ → SO₄²⁻ + AC surface−O⁻ + HSO₄⁻ (5)

As illustrated above, the combined effects of AC adsorption and persulfate oxidation of TCE have not been studied in a systematic manner. The purpose of this study was to investigate the potential simultaneous operation of AC adsorption and...
persulfate oxidation for treating a model TCE contaminant. Therefore, the study involves objectives including: (1) decomposition of persulfate on the AC and characterization of the AC surface upon oxidation; (2) effects of AC surface properties on TCE adsorption; and (3) the activated oxidation of TCE with persulfate using AC.

2. Materials and Methods

2.1. Chemicals. Water used for preparation of TCE containing solutions was purified by a Millipore reverse osmosis (RO) purification system. The chemicals used were purchased from the following sources: TCE (>99.5%), sulfuric acid (>99.8%), and nitric acid (>65%) were purchased from Fluka; n-pentane (min. 99.9%) was purchased from Tedia; sodium thiosulfate pentahydrate (min. 99.5%), sodium chloride (min. 99.8%), sodium nitrate (>99.0%), sodium hydroxide (min. 99.0%), and potassium bromide (spectroscopic grade) were purchased from Riedel-deHaën; sodium persulfate (min. 99.0%) and hydrochloric acid (min. 37%) were purchased from Merck. A commercial activated carbon Calgon Filtrasorb 400 (F400), a bituminous-coal-based carbon, was obtained from Calgon Carbon Corporation.

The activated carbon was purified by an acid washing procedure (5% HCl) to remove impurities present and then rinsed with RO water in accordance with the procedure of Cao et al.8 Thereafter, AC was dried at 105 °C for 1 h prior to storage in a desiccator. Note that the notation AC was used to represent the original carbon which was acid-washed.

2.2. Experimental Procedure. 2.2.1. Degradation of Persulfate on the Activated Carbon. The experiments were conducted in 1 L volumetric flasks that were capped and stirred at a constant temperature of 20 °C. Two sets of experiments were run to study the effect of AC dosages (1–5 g L\(^{-1}\)) and sodium persulfate concentrations (1–5 g L\(^{-1}\)). Note that the experimental results labeled OAC1–OAC5 were the products of AC which was oxidized with 1–5 g L\(^{-1}\) of sodium persulfate, respectively. The pH of the RO water was initially adjusted to pH 3 (note: because the presence of persulfate in water usually results in acidic pH, the fixed initial solution pH was adjusted for all experiments) with sulfuric acid before adding reactants. The pH was monitored using a ROSS pH combination electrode and a pH/ion meter (Thermo Orion 720A+). During the reaction, the concentration of persulfate was monitored by iodometric titration of 2 mL aliquots.19 After the reaction, all the AC was washed with RO water several times and dried in an oven at 50 °C for preservation and subsequent analysis of surface properties. BET surface area and pore volumes were...
determined by N2 adsorption at 77 K (Micrometritics ASAP 2020, high surface area and porosimetry analyzer). The point of zero charge (pHzpc) for AC surfaces was measured by the mass titration method as described by Noh and Schwarz.20 The boehm titration method was used to determine the acidity and basicity of AC.21 The surface morphology and chemical composition of AC was analyzed using JEOL JSM-6700F scanning electron microscope (SEM) equipped with an Oxford Energy 400 X-ray energy dispersive spectrometer (EDS). Fourier transform infrared (FTIR) spectroscopy analysis of the AC was performed on a JASCO FTIR 4100 spectrometer. The dried samples were mixed with finely divided KBr at a ratio of 3:100, and FTIR spectra were recorded at a resolution of 4 cm\(^{-1}\).

### Table 1. Surface Characteristics of the Original and Oxidized Carbons

<table>
<thead>
<tr>
<th>adsorbent</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>pHzpc (m(^{-1}))</th>
<th>total acidity (mmol g(^{-1}))</th>
<th>total basicity (mmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>930</td>
<td>7.5</td>
<td>0.47</td>
<td>1.37</td>
</tr>
<tr>
<td>OAC5</td>
<td>815</td>
<td>2.4</td>
<td>2.52</td>
<td>0.95</td>
</tr>
</tbody>
</table>

2.2.2. Adsorption Kinetics and Isotherms. The TCE solution (100 mg L\(^{-1}\), pH 3) was prepared by adding the required amount of pure TCE and stirred for 12 h in a 1.3 L heavy-wall plain pressure reaction flask (IWAKI 7740 glass). The flask was placed in a temperature-controlled chamber at 20 °C, and the top of the flask was covered and clamp-sealed with a flat Teflon reaction head containing Teflon-lined septum ports. For determining the kinetics of the adsorption process, AC doses of 0.5 and 1 g L\(^{-1}\) and an OAC5 dose of 0.5 g L\(^{-1}\) were utilized. At each designated time interval, solution was withdrawn through a septum port by a 5 mL gastight syringe (SGE gastight syringe, fitted with a push-button luer lock valve) and filtered using a PTFE filter (0.2 µm, Toyo stainless syringe holder) for TCE analysis in duplicate. A 2.5-mL aliquot was placed in a 5 mL brown bottle and extracted with 1.5 mL pentane. The extraction vials were shaken for 5 min on a vortex shaker (Thermolyne type 65800) and then equilibrated for 5 min. The TCE extract was measured by gas chromatography/flame ionization detector (Agilent 6890N) in accordance with operational conditions reported by Liang et al.14

Equilibrium isotherm experiments were conducted using the bottle point method. The TCE solution (100 mg L\(^{-1}\), pH 3) was prepared in a 2 L borosilicate reservoir (Schott Puran) equipped with a Teflon stopper and valved bottom outlet. The solution was then added to a series of 120 mL amber brown reaction bottles with no head space in which different AC or OAC5 doses between 0.2 and 1 g L\(^{-1}\) were initially added. Upon equilibration (magnetic stirring for 24 h and determined based on the adsorption kinetic experiment), samples were taken by a gastight syringe through the septa using a 5 mL gastight syringe and filtered for TCE analysis in accordance with the procedure described above.

2.2.3. Oxidation Experiments with AC/S\(_2\)O\(_8\)\(^{2-}\). In order to elucidate the sorption, oxidation, and activation behavior during the course of the TCE degradation reaction, experiments were separated into two systems (i.e., systems A and B). For comparison purposes, the experimental procedure for system A is...
similar to that described for the adsorption kinetic experiment with the exception that as soon as the AC (1 or 5 g L$^{-1}$) and TCE were mixed, the reaction was initiated by the addition of sodium persulfate (2 g L$^{-1}$). At each designated time interval, 10 mL of solution was withdrawn and used for TCE and persulfate analysis.

System B was a study of the distribution of TCE between aqueous and sorbed phases and chloride concentration as a function of reaction time. The preparation for these experiments was similar to the procedure described in the equilibrium isotherm experiments with the exception that after addition of persulfate into the TCE solution, the resulting mixture (TCE/$\text{S}_2\text{O}_8^2^-$, pH 3) was added to a series of 40 mL brown bottles containing 5 g L$^{-1}$ AC and the bottles were shaken on a reciprocating shaker (IKA 260) at 160 rpm. At each sampling interval, two sample bottles were removed from the shaker and analyzed for TCE and chloride in solution. Chloride ions (i.e., endproduct upon TCE mineralization) were analyzed by a Metrohm 790 ion chromatograph coupled with a conductivity detector using a Metrosep A Supp 5 column. The residual AC was filtered, and approximately 0.2 g of AC was weighed and immediately placed in 5 mL brown bottles containing 2 mL pentane for subsequent 2 min extraction at 1400 rpm on a vortex shaker. All experiments were performed in duplicate to ensure the reproducibility of experimental results, and averaged data
were presented. Control tests in the absence of persulfate were carried out in parallel.

3. Results and Discussion

3.1. Degradation of Persulfate on Activated Carbon. The degradation of persulfate in the presence of AC is shown in Figure 1a and b. It can be seen that the degradation followed a first-order kinetic behavior ($R^2 > 0.95$). The rate constants as a function of AC and persulfate dosages are presented in Figure 1c, and varying rate constants are almost linearly correlated with the variables (i.e., AC and persulfate dosages). When the AC dosage increases, the faster persulfate degradation was observed, as opposed to the decrease of the persulfate degradation rate while increasing the persulfate concentration. These results are similar to other studies investigating peroxide degradation on AC, which reported that the decomposition rate of peroxide is of first-order with respect to the hydrogen peroxide and increased proportionally to the amount of AC added. Khalil et al. also indicated that decomposition of peroxide on the AC may be ascribed to the activated carbon’s physicochemical characteristics such as: porosity and surface chemical nature. Furthermore, it was assumed that the interaction of peroxide and AC involves primary exchange of an oxonium-hydroxyl group (e.g., AC surface $\text{C} – \text{OH}_2^+\text{OH}^-$) with a hydrogen peroxide anion to form acidic functional groups (e.g., AC surface $\text{C} – \text{OH}_2\text{OOH}^-$). Therefore, functional groups present on the AC may also play a role in both the electrostatic and dispersive interactions with persulfate anion. Oxidation of the AC surface usually decreases the $\pi$-electron density and thus reduces the AC’s dispersive adsorption potential. Analysis of surface structures and chemical components by SEM and EDS for AC and OAC are illustrated in Figure 2, and BET surface area, $p_H$, total acidity and basicity are presented in Table 1. It is evident that the surface structure of AC does not exhibit significant changes by persulfate oxidation (see Figure 2) and considerable numbers of pores remain after persulfate oxidation.

However, oxidation resulted in a decrease in the surface area by approximately 12%. Additionally, introduction of functional groups on the AC surface after oxidation can be demonstrated from a decrease in $p_H$, an increase in the acidity of surface concentration, and an associated decreased basicity. These trends match those studies obtained by peroxide and persulfate oxidation of AC, which demonstrated the formation of acidic functional groups (e.g., ethers, lactones, carboxyls, and quinines) on the AC surface. The identification of various forms of acidic functional constituents in AC has also been analyzed by FTIR, and the results of infrared spectra are illustrated in Figure 3. The assignment of the absorption bands is made based on similar stretching frequencies with molecular organic compounds, and it can be seen that after oxidation the spectrum for the OAC samples shows a pronounced band centered at $1120 \text{ cm}^{-1}$ with a shoulder at $1220 \text{ cm}^{-1}$. These wave numbers are characteristics of oxygen containing organic functional groups and assigned to the $\text{C} – \text{O}$ asymmetric stretching modes of the ether or ester. Additionally, the presence of ether-oxygen (ascribed to $\text{C} – \text{O}$ single bonds) at $1300 – 1000 \text{ cm}^{-1}$ is usually used to explain why more oxygen than can be accounted for is observed in the functional groups of AC. These possible oxygen functional groups are classified as acidic functional groups, and therefore, the FTIR results obtained are consistent with Boehm analysis.

3.2. Adsorption Kinetics and Isotherms. In order to study the kinetics and transient behavior of AC adsorption processes, the adsorption capacity variation along with reaction time was...
Liberated (eq 7) Lagergren-based kinetic models and intraparticle measured and pseudo-first-order (eq 6) and pseudo-second-order kinetic models representing the initial adsorption stages where rapid adsorption occurs are illustrated in Figure 4b and c, and the rate constants with the correlation coefficients are presented in the tables. It was observed that the pseudo-second-order model provides the best correlation ($R^2 = 0.999$) for the AC adsorption process (see Figure 4b) while the pseudo-first-order model fits better for the OAC adsorption process. Ho indicated that when the initial concentration of solute is low, then the adsorption process obeys the pseudo-second-order model. Conversely pseudo-first-order models can be applied to higher initial concentrations. Therefore, it can be explained that due to a reduction of OAC5 adsorption capacity, the aqueous TCE concentration in the OAC5 system is relatively high in comparison to that in the AC adsorption system in the presence of the same amount of adsorbent in aqueous solution. With the determined kinetic models, the equilibrium capacity and the initial adsorption rate can be obtained from the model. For example, the calculated $q_e$ values based on the pseudo-second-order model for 0.5 and 1.0 g AC L$^{-1}$ and also for 0.5 g OAC5 L$^{-1}$ based on the pseudo-first-order model are 188, 103, and 63, respectively, which are approximate to the experimental values (see Figure 4a–c).

Figure 4d shows the plot of $q_t$ versus $t^{1/2}$ using the intraparticle diffusion model to investigate the diffusion controlled adsorption system. Since the plots are not linear over the first 6 h of the adsorption, this indicates that the intraparticle diffusion starts with a rapid transport within macropores as seen step 1 in Figure 4d (a higher $k_{diff}$ value), then gradual adsorption in the smaller meso- and micropores (step 2), and finally reaches equilibrium (step 3). Also, the intercept of C (see Figure 4d step 1, intercept on y-axis $q_t$ values) provides information about the thickness of boundary layer; the larger the intercept, the greater the boundary layer. It can be seen that the OAC5 shows a lesser degree of boundary layer control (the plot nearly passes through the origin) which means that the intraparticle diffusion can be a rate-controlling step.

The amount of TCE adsorbed is determined as a function of the equilibrium concentration at a constant temperature, which was analyzed by two adsorption isotherms Langmuir (eq 9) and Freundlich (eq 10).

$$ q_e = \frac{abC_e}{1 + bC_e} \quad (9) $$

$$ q_e = KC_e^{1/n} \quad (10) $$

where $q_e$ is the amount of TCE adsorbed per unit weight of AC (mg g$^{-1}$); $C_e$ is the concentration of TCE solution at equilibrium (mg L$^{-1}$); $a$ is the maximum adsorption capacity, and $b$ is the constant related to the free energy of adsorption (L mg$^{-1}$); $K$ is a relative indicator of adsorption capacity, and $1/n$ describes the intensity of the reaction.
Figure 5 shows the adsorption isotherm, and parameters obtained are presented in Table 2. The equilibrium adsorption \( q_e \) increases with the decrease in the amount of adsorbent used. In general, both models seemed to describe both AC and OAC5 adsorption behavior well based on similar \( R^2 \) values within the concentration range studied. However, when comparing adsorption parameters between AC and OAC5, the Langmuir maximum monolayer adsorption capacities (i.e., parameter \( a \)) are similar while the decrease of the \( b \) parameter values indicated lower energy of adsorption for the OAC5. In a similar trend, the decreased Freundlich parameter \( K \) indicated a lower adsorption capacity and the increased \( 1/n \) value presented the lower intensity of the adsorption reaction for the OAC5. The change in this adsorption behavior of AC resulting from persulfate oxidation could mainly be due to two factors such as the following: (1) a consequence of an increase in the number and density of acidic functional groups (a.k.a., a decrease in \( \pi \)-electron density) and (2) a decrease in the volume of micropores. Moreover, since water adsorption is very sensitive to the presence of acidic functional groups on the AC surface, these functional groups can act as primary centers which attract water adsorption via hydrogen bonding and thus block the adsorption sites.

3.3. Oxidation Experiments with AC/S\( _2 \)O\(_8\)^2-. The experiment of TCE degradation by persulfate in the presence of AC was conducted in comparison to the TCE removal from aqueous phase by only adsorption. The results obtained are shown in Figure 6 (system A). As can be seen, the experiments with adsorption alone exhibit faster TCE removal for two different AC doses than the observation in the presence of both persulfate and AC. Oxidation of AC, as expected (see the discussion in section 3.1), caused introduction of AC surface oxygen functional groups which may decrease the amount of TCE adsorbed. However, it has to be mentioned here that in the course of the simultaneous adsorption and oxidation processes, TCE can be destroyed even though TCE adsorption is reduced. The persulfate decomposition can still be described with the pseudo-first-order rate expression in the presence of TCE. However, the persulfate decomposition rate constants in the presence of both TCE and AC obviously decreased in comparison to that obtained from the presence of the AC only experiment (i.e., \( k_{obs,PS} = 2.25 \times 10^{-2} \) min\(^{-1} \) in the presence of TCE and 5 g AC L\(^{-1} \) (see Figure 6b) compared to \( k_{obs,PS} = 3.29 \times 10^{-2} \) min\(^{-1} \) in the presence 5 g AC L\(^{-1} \) (see Figure 1c). This phenomenon is similar to the results from other studies using AC in catalyzing peroxyde for contaminant destruction, which reported that, due to a consequence of contaminant adsorption, the available surface area of AC for the decomposition of oxidant (e.g., peroxyde or persulfate) would possibly be reduced.

In order to differentiate the effect of adsorption and activation on the removal of TCE, Figure 7 shows the results obtained in the system B experiment. Even though the overall reaction time is longer than that of system A due to a slower mixing action for system B, the trend of TCE removal (Figure 6a and b vs Figures 7a and b) is the same by adsorption and oxidation. It should be noted that, in general, strongly dissociated salts such as sodium and sulfate ions are not appreciably adsorbed by activated carbon. However, as can be seen in Figure 7a, the presence of an equivalent molar concentration of Na\(_2\)SO\(_4\) (8.4 mM), which dissociated into sodium and sulfate ions and simulated the persulfate decomposition end-products, appeared to result in complete TCE adsorption at a faster rate. This result was most likely due to a salting-out effect which decreased the solubility of the nonpolar compounds and increased the number of molecules which entered into the carbon solid phase in a zero head space environment and therefore reduced the time necessary to reach equilibrium. Figure 7c shows the results obtained in terms of TCE degraded, sorbed, and remaining in solution and chloride liberated. Control tests of TCE alone and in the presence of persulfate exhibit little loss of TCE. The fraction of TCE at 5 g AC L\(^{-1} \) obtained at 48 h by analyzing both aqueous and sorbed TCE reveals a 99% mass balance, i.e., 90% sorbed and 9% remaining in solution (see Figure 7c). It can be seen that approximately 40% of the TCE was in the solution at \( t = 12 \) h while 30% of the TCE was degraded, and the associated chloride liberated was 18%. Note that it is assumed that the complete mineralization of 1 mol of TCE releases 3 mol of chloride (i.e., [Cl\(^-\)]\(_{max} = 3[\text{TCE}]_0\)). Subsequently, the fraction of TCE degraded was gradually increased (i.e., up to ~55%) along with the decrease of the aqueous TCE concentration. Complete mineralization to liberate chloride was not attained, and almost unchanged fractions of chloride and sorbed TCE were observed. It is apparent that unidentified byproducts would be generated and have not yet been discovered in the present study. In such a system using AC in activating persulfate, observations of TCE removal in these experiments can be regarded as a net result of both adsorption and oxidation. Nevertheless, when the persulfate/TCE mixture is in contact with AC, TCE can be partially destroyed by oxidation rather than by physical adsorption mechanisms alone. Hence, it is possible to conclude that the AC is active for persulfate activation and TCE is being transformed through oxidation (e.g., SO\(_4^{2-}\) as speculated in eqs 4 and 5).

4. Conclusions

The degradation kinetics of persulfate over AC can be described by first-order degradation behavior, and the rate constant increases with the increase of AC dosage. It was found that the variation of AC surface properties caused by persulfate oxidation include the increase of acidity concentration, a reduced \( pH_{pzc} \), the decrease of AC surface area, and the alteration of TCE adsorption kinetic behavior. Hence, these changes lead to a reduction in adsorption capacity and a weakened intensity of the adsorption reaction, which are related to removal of \( \pi \)-electrons from the AC matrix by persulfate oxidation. Even though the increased number of acidic groups on the AC surface resulted in weaker adsorption interactions between TCE and AC, the presence of AC could activate persulfate to destroy TCE during the course of simultaneous adsorption and oxidation reactions. The degradation of TCE in the combined oxidation and adsorption system, compared to those of TCE removal by adsorption only, exhibits potential TCE destruction by the AC activated persulfate oxidation and suggests an alternative for the removal of organic contaminants.

Acknowledgment

This study was partially funded by the National Science Council (NSC) of Taiwan under project number of 96-2221-E-005-017-MY3.

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*Received for review* February 6, 2009  
*Revised manuscript received* June 10, 2009  
*Accepted* July 17, 2009  
IE900841K