



Feasibility study on an oxidant-injected permeable reactive barrier to treat *BTEX* contamination: Adsorptive and catalytic characteristics of waste-reclaimed adsorbent

Si-Hyun Do, Yong-Jae Kwon, Sung-Ho Kong*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

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ABSTRACT

The adsorptive and catalytic characteristics of waste-reclaimed adsorbent (WR), which is a calcined mixture of bottom-ash and dredged-soil, was investigated for its application to treating *BTEX* contamination. *BTEX* adsorption in WR was 54%, 64%, 62%, and 65%, respectively, for a 72 h reaction time. Moreover, the catalytic characteristics of WR were observed when three types of oxidation systems (i.e., H_2O_2 , persulfate (PS), and $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{oxalate}$) were tested, and these catalytic roles of WR could be due to iron oxide on its surface. In PS/WR system, large amounts of metal ions from WR were released because of large drops of solution pH, and the surface area of WR was also greatly reduced. Moreover, the *BTEX* that was removed per consumed oxidant ($\Delta C_{\text{rem}}/\Delta \text{Ox}$) increased with increasing PS. In $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{oxalate}$ with WR system, the highest *BTEX* degradation rate constants (k_{deg}) were calculated as 0.338, 0.365, 0.500 and 0.716 h^{-1} , respectively, when 500 mM of H_2O_2 was used, and the sorbed *BTEX* on the surface of WR was also degraded, which suggests the regeneration of WR. Therefore, the oxidant-injected permeable reactive barrier filled in WR could be an alternative to treating *BTEX* with both adsorption and catalytic degradation.

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1. Introduction

Permeable reactive barriers (PRBs) have been known to be a passive and cost-effective alternative to conventional pump-and-treat in the remediation of contaminated groundwater [1,2]. Modifications to PRBs have been studied to evaluate the use of alternative materials as filling media [3–7] and the design of physical, chemical, and biological processes for PRBs [6–9]. Various types of filling materials (i.e., zero-valent iron (ZVI), activated carbon, fly ash, zeolite, waste green sand, and peat) have been tested for groundwater remediation [3–7] and the filling material has generally been determined by both the properties of contaminants (e.g., organic [6–10] or inorganic [3,5,11]) and reaction mechanisms (e.g., degradation [6,8,10] or adsorption [3,7–9]).

Benzene, toluene, ethylbenzene, and xylene (*BTEX*) are the major compounds at contaminated-groundwater sites, and various remediation technologies have been applied to remove these [7–9,12]. The dominant mechanisms for *BTEX* removal with PRB technology have either been biological degradation or physical adsorption [7–9]. Rendering aerobic conditions in biological degradation of *BTEX* by using oxygen-release materials (i.e., those

mainly consisting of mixtures of CaO_2 or MgO_2 , cement, and sand) has been suggested to modify PRB for long-term efficiency [8], but limitations with PRB in bioremediation such as that with inoculation or electron acceptor/nutrient supply and biomass attachment/detachment, cannot be avoided [9]. The application of various types of adsorbents and modifications to these have been investigated [13–16] to physically adsorb *BTEX* and waste materials as potential adsorbents have recently attracted a great deal of attention because they contribute to reducing costs in waste disposal [16]. Even though this adsorption process has been applied to remove contaminants from aqueous phases, a method that can maintain adsorption capacity is required for long-term efficiency [16].

Hydrogen peroxide (H_2O_2) or persulfate (PS) have been used to degrade organic contaminants in soil and groundwater [17–21], and the addition of chelating agents with either a homogeneous or heterogeneous Fenton system have increased both the oxidant yield and the degradation rate at neutral pH [22,23]. Moreover, H_2O_2 and PS have been tested for the regeneration of adsorbents [24–26], and H_2O_2 can be catalyzed by adsorbents to degrade contaminants [27,28].

Our overall objective was to develop an oxidant-injected PRB system to remove *BTEX*, and this study investigated to what extent waste-reclaimed adsorbent (WR) could be applied to both *BTEX* adsorption and the catalytic degradation of *BTEX* with oxidants

* Corresponding author. Tel.: +82 2 2220 0489; fax: +82 2 2293 8551.
E-mail address: shkong@hanyang.ac.kr (S.-H. Kong).

(i.e., PS, H₂O₂, and H₂O₂/Fe(III)/oxalate). All experiments were conducted at neutral pH, and the possibility of WR regeneration is also discussed along with the degradation of sorbed BTEX. Moreover, the morphology of WR and metal ions in solution were checked with BET, SEM, and ICP analysis after oxidation was carried out.

2. Materials and methods

2.1. Materials

Benzene was purchased from Yakiri Pure Chemicals, ethylbenzene from Junsei Chemicals, and toluene and xylene from Carlo Erba Reagenti. Dichloromethane for extracting BTEX was purchased from Fisher Scientific. Two types of oxidants were prepared by dissolving sodium persulfate (Na₂S₂O₈, Sigma–Aldrich) and diluting hydrogen peroxide (H₂O₂, Junsei Chemicals). Iron (III) sulfate hydrate (Fe₂(SO₄)₃·xH₂O, Sigma–Aldrich) and sodium oxalate (Na₂C₂O₄, Junsei Chemicals) were used for iron chelates. Ammonium thiocyanate (NH₄SCN) and ferrous ammonium sulfate (FeSO₄(NH₄)₂SO₄·6H₂O) were purchased from Sigma–Aldrich, and sulfuric acid (H₂SO₄) and titanium (IV) sulfate hydrate (Ti(SO₄)₂·nH₂O) were purchased from Junsei Chemicals.

Waste-reclaimed adsorbent (WR) was treated by the center for resource processing of solid wastes at Kyonggi University. The manufacturing processes for WR were started by pulverizing raw materials (70% bottom ash from a power plant and 30% dredged soil) until they were below 150 μm. After that, they were molded with a pelletizer into spheres, which were dried at 110–120 °C for 48 h and then calcined in a rotary kiln at 1125–1150 °C for 15 min. The BET surface area of WR was 14.56 m² g⁻¹, and the inductively coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 4300DV) results revealed that the main chemical components of WR were 53.12% SiO₂, 17.33% Al₂O₃, 12.65% C (element carbon), and 6.80% Fe₂O₃.

2.2. Experimental procedures

All reaction samples were prepared in duplicate, and the average value was used for analysis. The initial pH of all solutions was adjusted to 7.0 by adding 5 N of NaOH or 1 N of HNO₃. The benzene, toluene, ethylbenzene, and xylene solutions were prepared by adding the required volume of pure chemicals and stirring them for 12 h in a 2.8 L stainless-steel reactor with no headspace. WR (particle sieved: 4.75–9.60 mm) was washed 10 times in deionized water (DI water) with a resistivity of 18 mΩ cm (Millipore system, Young-Lin Co., Korea), then dried at 105 °C for 1 day and stored in a desiccator. The amount of WR was 2.5 g (i.e., the average volume of WR was 1.6 ± 0.1 mL when *n* = 6) and 40 mL of solution (i.e., total volume of both contaminant and oxidant solutions) were poured into a glass vial (i.e., the actual volume of the glass vial was 45.4 ± 0.5 mL when *n* = 7). The concentrations of benzene, toluene, ethylbenzene, and xylene were fixed at 100 mg L⁻¹, and two concentration levels of oxidants (10 and 500 mM) were used. Iron chelate for the H₂O₂/Fe(III)/oxalate experiment was prepared by mixing ferric iron and oxalate at a ratio of 1:6 (Fe(III):oxalate = 5:30 mM) for 1 h at pH 7.0, and then H₂O₂ solution was added. Investigating either the optimum ratio of Fe(III):chelating agent or the types of chelating agent was beyond the scope of the present work. Experimental systems were prepared including controls (only contaminants), WR/contaminants, oxidants/contaminants, and WR/oxidants/contaminants, and they were then mounted on a shaking incubator (LPN-0201F-S, Hanbaek ST.) at 200 rpm and 25 °C for the degradation reaction. Moreover, control II (i.e., contaminants with Fe(III)/oxalate) was used and additional experiments (i.e., contaminants with Fe(III)/oxalate/WR)

were also conducted to see how Fe(III)/oxalate affected BTEX removal.

2.3. Analytical methods

The modified method of extraction, which assumed there were no concentration gradients in diffusion layers, was designed to analyze BTEX in both the aqueous and the sorbed phases. At each sampling time, 5 mL of the aqueous sample was extracted with 5 mL of dichloromethane for 1 min of vortex mixing (TTS3, IKA), and the amount of BTEX in the 5 mL sample solution was defined as *M*_{aque}. After that, an additional 30 mL of the aqueous sample was removed. The second extraction was conducted for BTEX in both the aqueous and the sorbed phase (*M*_{aque+sorbed}); the remaining 5 mL of the aqueous sample and WR were extracted together with 5 mL of dichloromethane for 4 min of vortex mixing followed by 20 min of sonication (8510R-DTH, Banson), and it was centrifuged for 10 min. Therefore, the amounts of sorbed BTEX (*M*_{sorbed}) were calculated by *M*_{aque+sorbed} - *M*_{aque}. The extracted BTEX was analyzed with an HP-6850 gas chromatograph equipped with a flame ionization detector. It was equipped with a capillary column (J&W scientific, Model HP-5: 30.0 m × 530 μm × 0.88 μm), and the injector and detector temperatures were respectively maintained at 200 and 340 °C. The oven temperature started at 40 °C, which was held for 2 min, ramped at 10 °C min⁻¹ to 100 °C followed by ramping at 40 °C min⁻¹ to 280 °C, and held again for 2 min at 285 °C. Nitrogen was the carrier gas and a split ratio of 10:1 was used. The colorimetric method (Milton Roy Spectronic 20⁺) was used to detect either hydrogen peroxide at 467 nm [29] or persulfate at 450 nm [30]. The pH was measured with a pH-200L meter (ISTEK). The Brunauer–Emmett–Teller (BET, BELSORP-mini) technique and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS, JEOL JSM-6330F) were used for surface analysis. The metal ions in solution (i.e., total soluble Fe, Ca(II), Mg(II), and Al(III)) were checked with inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 4300DV).

3. Results and discussion

3.1. Adsorption of BTEX in system containing WR

Fig. 1 plots BTEX adsorption by WR (the error bars in the figures were calculated with the absolute value ($|X - x_i|$) where *X* is the average value and *x_i* is the sample value.). The control indicated a

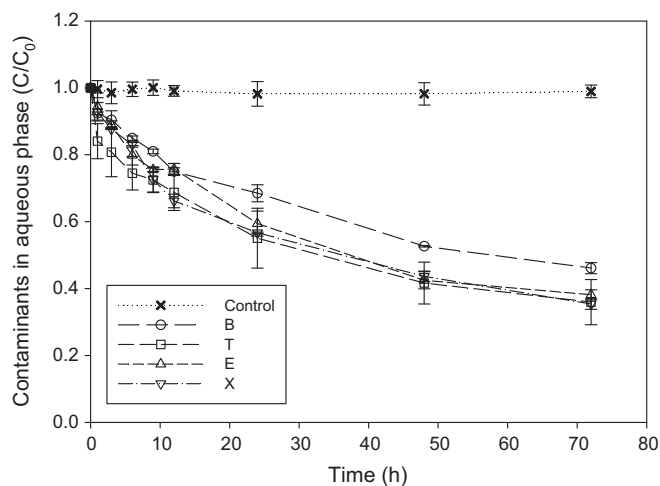


Fig. 1. BTEX adsorption on WR at neutral pH (*[B]* = *[T]* = *[E]* = *[X]* = 100 mg/L, WR = 2.5 g).

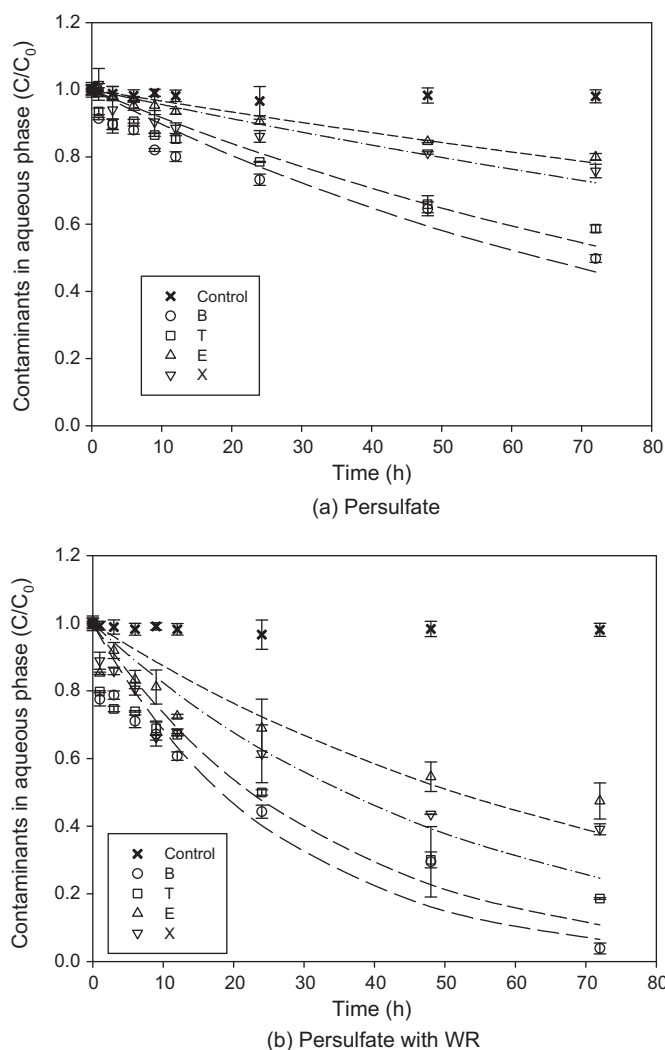


Fig. 2. Removal of BTEX by (a) PS and (b) PS/WR ([PS] = 10 mM, WR = 2.5 g).

negligible loss of *BTEX* for the 72 h reaction time, and *BTEX* adsorption by WR at neutral pH were 54%, 64%, 62%, and 65%, respectively. The order of uptakes on activated carbon for the 72 h of reaction time (i.e., equilibrium was approximately reached) was reported to be $X > E > T > B$, which indicated that the uptakes decreased with water solubility and increased with molecular weight [13]. The order of uptakes on surfactant-modified zeolite (SMZ), on the other hand, were $B > T > E > X$. This was due to the partition mechanism, which was reversely proportional to the octanol-water partition coefficients of *BTEX*, where the values of *B*, *T*, *E*, and *X* were 2.13, 2.69, 3.15, and 3.15–3.20, respectively [31]. Therefore, WR could be defined as material that had a high adsorption capacity for low water solubility and high molecular weight.

3.2. Removal of BTEX by oxidation systems with/without WR

Along with the adsorption ability of WR, its catalytic characteristics were evaluated when three oxidation systems (i.e., PS, H_2O_2 , and $H_2O_2/Fe(III)$ /oxalate) were applied to *BTEX* degradation. PS itself in the 10 mM PS system (Fig. 2) degraded *B*, *T*, *E*, and *X* to 50%, 41%, 20%, and 24%, respectively, and PS with WR (PS/WR) removed *BTEX* from the aqueous phase as 96%, 81%, 53%, and 61%, respectively. The existence of WR in the 10 mM H_2O_2 system (Fig. 3(a) and (b)) also increased the removal of *BTEX*. Xylene was the contaminant that was most likely removed from the aqueous phase in the

H_2O_2 system while this was benzene in the PS system. Because of iron chelate, 10 mM of H_2O_2 with the iron chelate system (Fig. 3(c) and (d)) demonstrated that more *BTEX* was removed from the aqueous phase than that from the others, and the removal rates were increased further with WR. In addition, the loss of *BTEX* in control II (i.e., contaminants with iron chelate) was negligible, and the additional experiments (i.e., contaminants with iron chelate/WR) indicated that iron chelate did not affect *BTEX* adsorption on WR (Table S1. in supplementary data). Therefore, these results indicated that both persulfate and H_2O_2 were catalyzed by WR and the combination of iron chelate and WR could remove the most *BTEX* from the aqueous phase.

Table 1 lists several parameters: the first-order rate constant for *BTEX* removal (k_{rem}), $\Delta C_{rem}/\Delta Ox$ (i.e., the removed contaminant per consumed oxidant), the percentages of residual oxidant, and the final pH. Moreover, *BTEX* removal with high concentration of oxidants (500 mM) is also tabulated.

As summarized in Table 1, the increasing concentration of oxidant increased the removal rates of *BTEX*. The highest removal rate constants (k_{rem}) were predicted in H_2O_2 /iron chelate/WR, and the values for *BTEX* corresponded to 0.422, 0.437, 0.600, and $0.988\ h^{-1}$. In addition, a high residual concentration was observed when a high concentration of oxidant was used, and a relatively low residual concentration was observed when oxidants were catalyzed by WR. The dimensionless value of $\Delta C_{rem}/\Delta Ox$ in Table 1 indicated that the increasing concentration of oxidant increased the value of $\Delta C_{rem}/\Delta Ox$ in the PS system while it decreased the value of $\Delta C_{rem}/\Delta Ox$ in H_2O_2 with/without the iron chelate system. The results from the PS system suggested that the consumption of PS could be directly proportional to the removal of *BTEX*, and the PS system could become an effective method of remediation if the appropriate activation processes were provided. Persulfate could generally be catalyzed by UV radiation, heat, and transition metal ions (i.e., mainly Fe(II), iron chelates, and metal oxide with Fe(II)) [20,30,32–35]. Therefore, if sufficient activation processes were provided and the destruction of sulfate radicals by unwanted reactions was prevented through to the end of the reaction, PS could degrade *BTEX* dramatically and completely [20]. However, $\Delta C_{rem}/\Delta Ox$ decreasing as the concentration of H_2O_2 with/without iron chelate increased could be due to the relatively low stability of H_2O_2 (i.e., relatively high self-decomposition properties) and the relationship between decomposing H_2O_2 and the production of hydroxyl radicals (OH^\bullet) [18,36,37]. Because H_2O_2 decomposition was not a suitable parameter for producing hydroxyl radicals [36,37], the assumption used in the present study (i.e., the consumed H_2O_2 was equal to the highly reactive species that was produced, hydroxyl radicals (OH^\bullet)) could be inaccurate. Moreover, when H_2O_2 concentration was high (i.e., $>1\%$), a series of propagation reactions was promoted, and various reactive species (e.g., perhydroxyl radicals (OOH^\bullet), superoxide anions ($O_2^{\bullet-}$), and hydroperoxide anions (OOH^-)) were generated [18]. These reactions could also have concealed the consumed H_2O_2 that was involved in degrading *BTEX*. Even though the values of $\Delta C_{rem}/\Delta Ox$ decreased, *BTEX* removal rates increased as the concentration of H_2O_2 increased.

In addition, the final pH in the PS/WR system was as low as 2.2–2.5 regardless of the PS concentrations. Moreover, the final pH in the H_2O_2 /iron chelate/WR system was 5.8–6.3 when the initial pH in all systems was adjusted to 7.0. Because of the low final pH in PS, the effect on metal ion compositions in solution after the reaction (i.e., 10 mM oxidants for 72 h reaction times at initial pH of 7.0) was checked and this is summarized in Table 2.

The results in Table 2 indicated that the amounts of dissolved metal ions (i.e., total soluble Fe, Ca(II), Mg(II), and Al(III)) for H_2O_2 were similar to those for the control (DI water). However, the amounts of all tested metal ions in the PS system were higher than

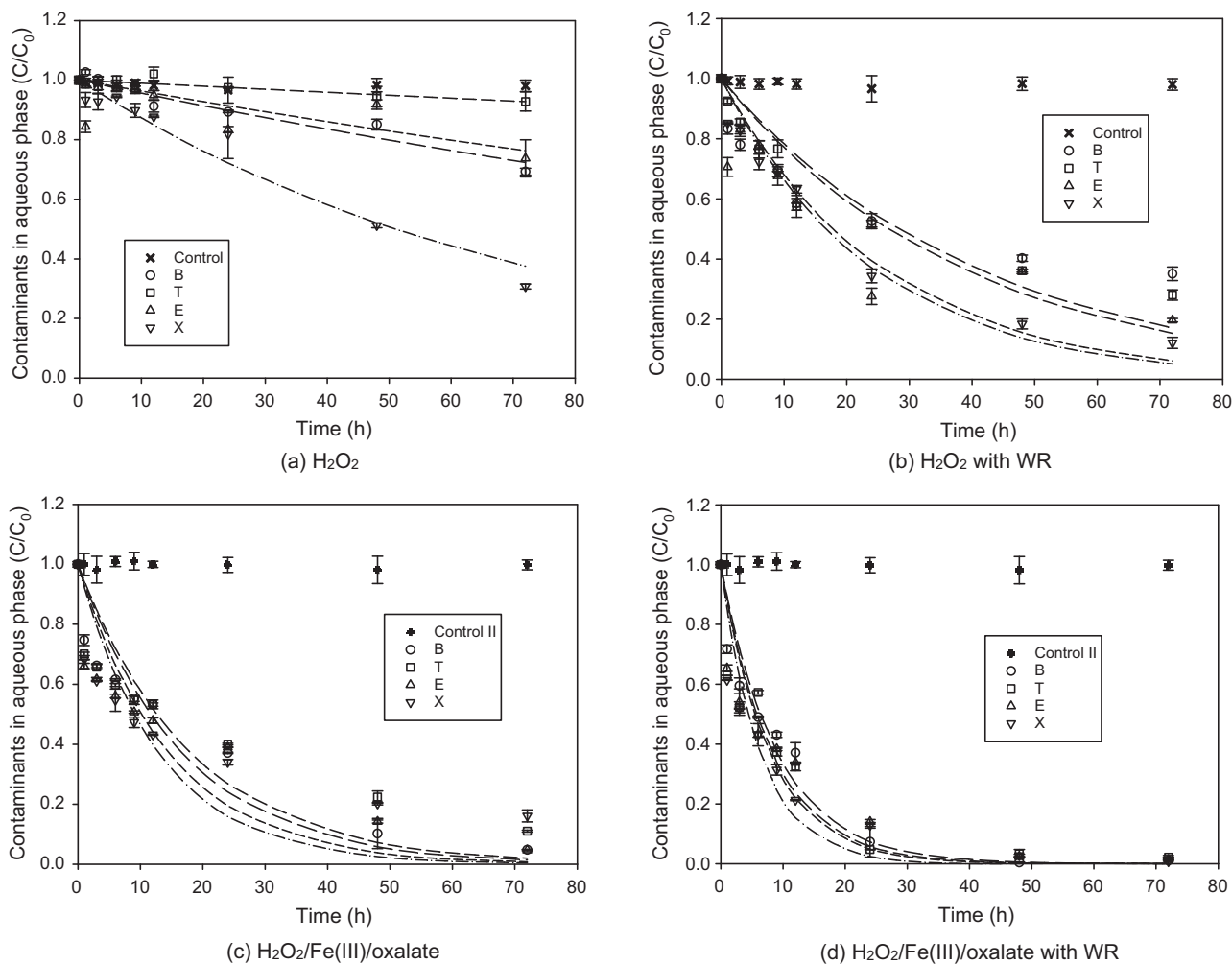


Fig. 3. Removal of BTEX by (a) H_2O_2 , (b) $\text{H}_2\text{O}_2/\text{WR}$, (c) $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{oxalate}$ and (d) $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{oxalate}/\text{WR}$ ($[\text{H}_2\text{O}_2] = 10 \text{ mM}$, $\text{WR} = 2.5 \text{ g}$, $[\text{Fe(III)}]:[\text{oxalate}] = 5 \text{ mM}:30 \text{ mM}$).

Table 1

Parameters (first-order rate constants for BTEX removal, $\Delta C_{\text{rem}}/\Delta \text{Ox}$, percentages of residual oxidants and final pH) in oxidation systems with/without WR.

| | | $k_{\text{rem}}^a, \text{h}^{-1} (\Delta C_{\text{rem}}/\Delta \text{Ox}^b)$ | | | | Residual oxidants ^c (%) | pH ^d |
|--|---------------------|--|--------------|--------------|--------------|------------------------------------|-----------------|
| | | B | T | E | X | | |
| (1) Without WR | | | | | | | |
| PS | 10 mM | 0.011 (0.10) | 0.009 (0.07) | 0.003 (0.03) | 0.005 (0.03) | 35 | 4.6 |
| | 500 mM | 0.091 (0.13) | 0.221 (0.18) | 0.126 (0.13) | 0.120 (0.13) | 99 | 3.2 |
| H_2O_2 | 10 mM | 0.005 (0.57) | 0.001 (0.11) | 0.004 (0.35) | 0.014 (0.93) | 93 | 5.6 |
| | 500 mM | 0.070 (0.04) | 0.057 (0.03) | 0.075 (0.03) | 0.170 (0.04) | 97 | 4.3 |
| $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{oxalate}$ | 10 mM ^e | 0.059 (0.33) | 0.055 (0.26) | 0.068 (0.24) | 0.077 (0.21) | 63 | 5.5 |
| | 500 mM ^e | 0.252 (0.05) | 0.239 (0.04) | 0.399 (0.04) | 0.670 (0.05) | 96 | 5.5 |
| (2) With WR | | | | | | | |
| PS | 10 mM | 0.038 (0.15) | 0.031 (0.11) | 0.013 (0.06) | 0.019 (0.07) | 17 | 2.5 |
| | 500 mM | 0.173 (0.19) | 0.284 (0.20) | 0.156 (0.14) | 0.126 (0.11) | 99 | 2.2 |
| H_2O_2 | 10 mM | 0.025 (0.08) | 0.026 (0.08) | 0.039 (0.08) | 0.041 (0.08) | 1 | 6.0 |
| | 500 mM | 0.140 (0.01) | 0.134 (0.01) | 0.171 (0.01) | 0.354 (0.01) | 83 | 4.6 |
| $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{oxalate}$ | 10 mM ^e | 0.109 (0.13) | 0.120 (0.11) | 0.126 (0.10) | 0.156 (0.10) | 3.3 | 6.3 |
| | 500 mM ^e | 0.422 (0.01) | 0.437 (0.01) | 0.600 (0.01) | 0.988 (0.01) | 81 | 5.8 |

^a First-order rate constant for BTEX removal.

^b Defined dimensionless term (mM/mM), which is total removed contaminant per consumed oxidant.

^c Values are average percentage of remaining oxidants.

^d Final pH, which are average value of B, T, E, and X experiments.

^e Presented concentrations are for hydrogen peroxide, and ratio of Fe(III):oxalate is fixed as 1:6 = 5:30 mM.

Table 2
Metal ions dissolved from waste-reclaimed adsorbent into solution after reaction.

| | Metal ion compositions (mg L ⁻¹) | | | |
|---|--|--------|--------|---------|
| | Total soluble Fe | Ca(II) | Mg(II) | Al(III) |
| Control (DI water) | 0.07 | 16.81 | 3.61 | 0.00 |
| Persulfate | 22.50 | 54.03 | 9.19 | 35.04 |
| H ₂ O ₂ /iron chelate | 234.84 | 0.62 | 3.05 | 2.67 |
| H ₂ O ₂ | 0.12 | 16.51 | 3.42 | 0.07 |

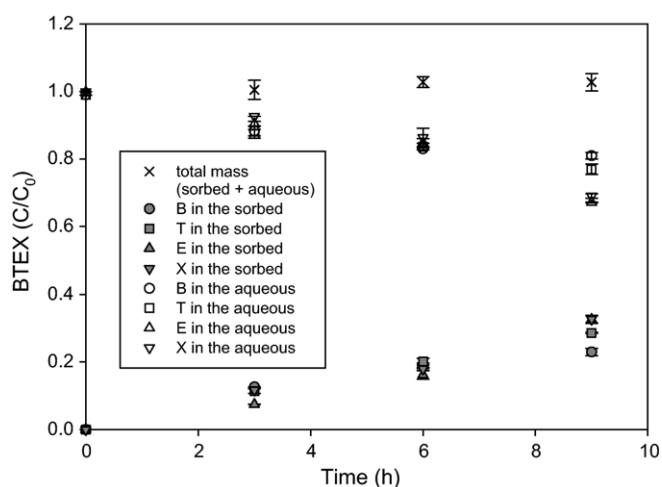


Fig. 4. BTEX distributions in systems containing only WR ([contaminants]=100 mg/L, WR=2.5 g).

those in the control. Therefore, this could indicate an incongruous combination of PS and WR, and ways of sustaining the pH of the solution should have been applied when WR was used with PS. Al(III) was higher in the H₂O₂/iron chelate system but Ca(II) was lower than that in the control. Moreover, the amounts of Fe in solution indicated that approximately 45 mg kg⁻¹ of Fe was adsorbed on WR when no precipitation of Fe and no dissolution of Fe from WR were assumed. Therefore, the higher catalytic degradation by the H₂O₂/iron chelate system might be due to the association of Fe on the surface of WR. In addition, because of the tremendous amounts of total Fe in the H₂O₂/iron chelate system, appropriate amounts of iron should be determined before it is applied.

3.3. Sorbed and catalytic degraded BTEX

Fig. 4 plots the sorbed BTEX in the system only containing WR and it indicated that the sorbed BTEX was gradually increased to 0.37–0.52 mg g⁻¹ for a 9 h reaction time (i.e. approximately 30% BTEX removal from the aqueous phase). Fig. 5 plots the degraded and sorbed BTEX in oxidation systems with WR when 500 mM of the oxidants were used. The closed symbols in the figures represent BTEX in the sorbed phase and the open symbols represent

Table 3
First-order rate constants (k_{deg}) and $\Delta C_{deg}/\Delta O_x$ for BTEX degradation in oxidation systems with WR.

| | k_{deg}^a, h^{-1} ($\Delta C_{deg}/\Delta O_x^b$) | | | |
|---|---|--------------|--------------|--------------|
| | B | T | E | X |
| PS/WR | 0.158 (0.19) | 0.245 (0.19) | 0.130 (0.13) | 0.105 (0.11) |
| H ₂ O ₂ /WR | 0.094 (0.01) | 0.086 (0.01) | 0.135 (0.01) | 0.221 (0.01) |
| H ₂ O ₂ /Fe(III)/oxalate/WR | 0.338 (0.01) | 0.365 (0.01) | 0.500 (0.01) | 0.716 (0.01) |

^a First-order rate constant for BTEX degradation.

^b ΔC_{deg} implied degraded contaminant, and values of consumed oxidant were adapted from Table 1.

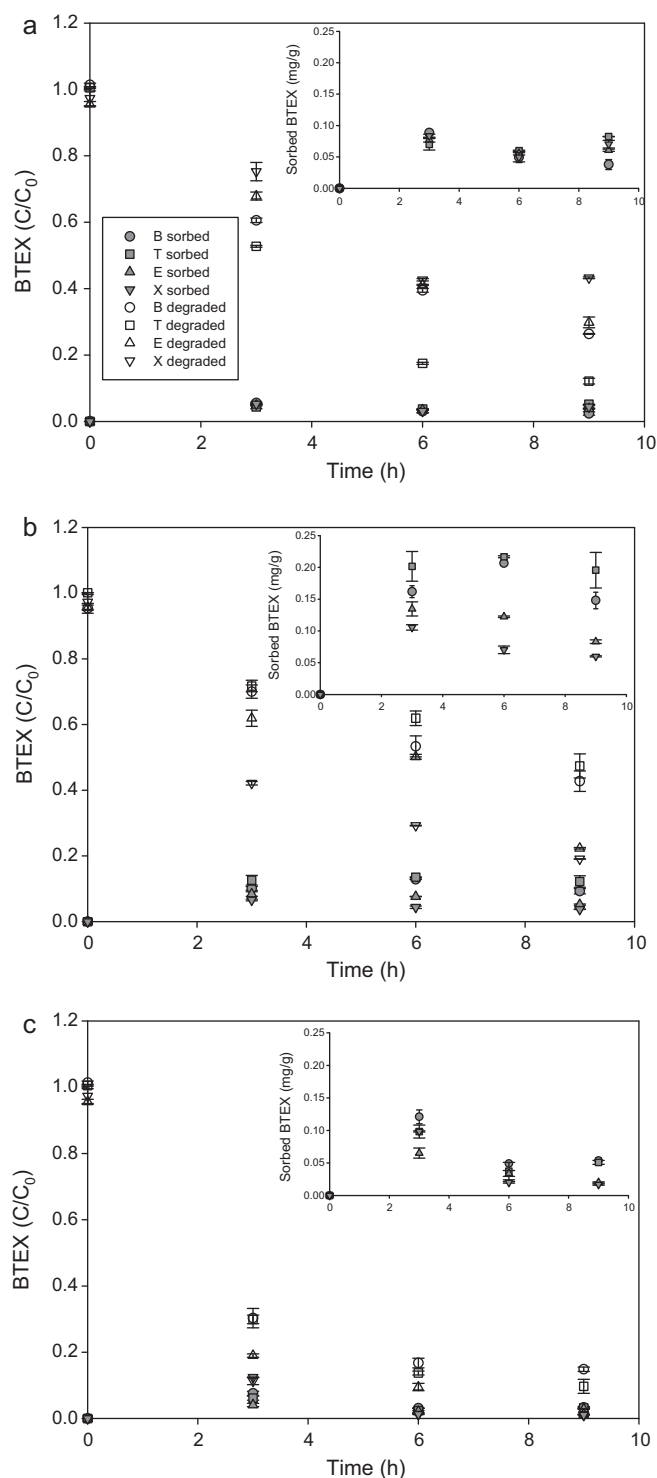


Fig. 5. BTEX degradation and adsorption in systems containing (a) PS/WR, (b) H₂O₂/WR and (c) H₂O₂/Fe(III)/oxalate/WR ([oxidants]=500 mM, WR=2.5 g, The embedded figures showed the sorbed BTEX as mg g⁻¹).

the degraded BTEX in the aqueous phase (i.e. subtraction of BTEX in the sorbed phase from BTEX in the aqueous phase). The tested oxidants (H₂O₂, PS, and H₂O₂ with iron chelate) degraded BTEX well when they catalyzed by WR. Moreover, in both PS/WR and H₂O₂/WR, some of the contaminants sorbed on WR (i.e., specifically benzene in PS/WR, and both ethylbenzene and xylene in H₂O₂/WR) were reduced, but the sorbed BTEX generally seemed to be constant after a 3 h reaction time. However, it can clearly be seen that the

amount of sorbed *BTEX* in H_2O_2 /iron chelate/WR was reduced. This could indicate that the addition of activators like iron chelate was necessary to degrade the sorbed *BTEX* and to regenerate WR.

There are two possible explanations for the degradation of the sorbed organic contaminants. The first is that the sorbed contaminant was directly degraded by oxidants with catalysis [38], and the second is that as the degradation sites were fundamentally different from the sorption sites, desorption of the sorbed contaminants should have occurred preferentially [28,39]. Liang and Chen [40] proposed that the desorption of sorbed benzene was a primary step for persulfate to oxidize in terms of the process for activated carbon regeneration, but the direct oxidation of sorbed benzene was achieved when catalysis (i.e., FeS_2) was added to that system. The present study did not clearly reveal whether the sorbed *BTEX* was directly degraded or the sorbed *BTEX* was degraded after desorption. However, the sorbed *BTEX* was obviously degraded by those oxidants, especially by the H_2O_2 /iron chelate/WR system.

The degradation rate constants (k_{deg}) and the degraded contaminants per consumed oxidants ($\Delta C_{\text{deg}}/\Delta \text{Ox}$) in oxidation systems with WR are presented in Table 3.

Compared to Table 1, this indicated that the degradation-rate constants are smaller than the removal-rate constants. Moreover, degradation-rate constants in the oxidation systems containing WR were higher than the rate constants in only the oxidant systems, which confirmed the catalytic characteristics of WR in those oxidants. Because of the high concentration of oxidants, the surface characteristics of WR were also evaluated.

After 9 h reaction times with 500 mM oxidants, the BET surface area of the control (i.e., DI water), PS, H_2O_2 , and H_2O_2 /iron chelate were 12.08, 1.44, 10.53, and 9.91 $\text{m}^2 \text{g}^{-1}$, respectively, and this indicated that the surface area of WR was dramatically reduced in the PS system. SEM-EDS analysis of both the external and internal surfaces (see Fig. S1. in the supplementary data) indicated that Fe (iron) on the external surface disappeared and sulfur (S) was observed on the internal surface in the PS system. However, Fe on both the external and internal surfaces was increased in the H_2O_2 /iron chelate system. It has been reported that PS degraded diesel more with the association of Fe on metal oxides than only with metal oxides [35]. Similar to these previous results, the existing Fe on WR could increase the reactivity of H_2O_2 .

Based on the presented results, a permeable reactive barrier with a periodic injection of oxidants, possibly H_2O_2 with iron chelate, could be an alternative to remediate *BTEX* contamination (see Fig. S2. in the supplementary data for schematic design of PRB with an oxidant injection system).

4. Conclusions

The adsorptive and catalytic characteristics of waste-reclaimed adsorbent (WR) were investigated for *BTEX* removal. *BTEX* adsorption on WR was 54%, 64%, 62%, and 65%, respectively, for a 72 h reaction time, and the catalytic degradation of *BTEX* was observed when oxidants were used with WR. The drop in solution pH, the reduced WR surface area, and the dissolution of metal ions from WR should be considered in the PS/WR system. The highest rate of *BTEX* removal was observed in the H_2O_2 /Fe(III)/oxalate/WR system, and the sorbed *BTEX* was also degraded, which could indicate the possibility of WR regenerating. On the basis of these results, the application of WR could provide an advantage in reducing waste disposal, and the periodically injecting oxidants into a permeable reactive barrier filled with WR could be an alternative to *BTEX* remediation, even though the optimum conditions including the determination of iron chelate should be quantitatively identified.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.115.

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