

Cite this: *RSC Adv.*, 2018, 8, 16834

Effects of calcium ion and pH on the adsorption/regeneration process by activated carbon permeable reactive barriers

Shengpin Li,^{ab} Wenpeng Li,^a Honghan Chen,^b Fei Liu,^{†*b} Song Jin,^{cd} Xiulan Yin,^a Yuejun Zheng^a and Boyang Liu^b

Activated carbon (AC) is widely used in groundwater remediation, more specifically, for the activated carbon permeable barriers (AC-PRBs). However, the long-term use of AC-PRBs is limited by the AC's adsorption capacity. In this work, a Fenton-combined persulfate system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$) was used to treat activated carbon that was saturated with organic compounds, such as trichloroethylene (TCE), to promote the oxidation of the adsorbed contaminants and the regeneration of AC. The effect of pH and the calcium ion (Ca^{2+}) were investigated during AC's adsorption/regeneration. The results showed that under certain reaction conditions ($\text{TCE}/\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ molar ratio of 1.00/9.00/56.63/76.25), acidic pH conditions ($\text{pH} = 3$) favored the adsorption/regeneration process of AC, yielding a regeneration efficiency of 26.28% on average in three regeneration cycles. The presence of Ca^{2+} , even in relatively low concentrations, seemed to decrease HO^\bullet generation and AC's adsorption capacity.

Received 6th March 2018

Accepted 17th April 2018

DOI: 10.1039/c8ra01961d

rsc.li/rsc-advances

1 Introduction

Activated carbon (AC) is widely used in groundwater remediation and wastewater treatment, thanks to its high surface area and porous structure, which can physically adsorb a variety of contaminants, especially in terms of its interaction with volatile organic compounds (VOCs).^{1–7} AC has been used as an adsorbent for organic contaminants in a range of permeable reactive barriers (PRBs),^{8,9} especially for the remediation of groundwater contaminated by chlorinated organic compounds.¹⁰ To better utilize the AC-PRBs, differently designed structures of the PRBs were investigated and applied in groundwater remediation.¹¹ PRB offers the potential for low-cost remediation, taking advantage of the passive groundwater flow to bring the contaminants in contact with the reactive materials in the barrier.^{12,13} However, AC-PRBs are limited by AC's adsorption capacity.

The regeneration of AC can transform the contaminants into less toxic byproducts, re-establish the adsorptive capacity of the carbon for the target chemicals, and increase its lifespan.¹⁴

Several methods have been studied for the regeneration of AC saturated with organic contaminants. The advanced oxidation process (AOPs) is one of the most promising methods to treat aqueous effluents containing organic contaminants.^{15,16} Available AOP approaches to regenerate AC include Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), persulfate oxidation ($\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$) and a Fenton-combined persulfate system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$).^{15,17,18}

The results of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system in the regeneration of AC saturated with organic compounds were promising.^{19–21} In particular, both H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system can be catalyzed by Fe^{2+} to avoid the consumption of $\text{SO}_4^{\bullet-}$ by excess Fe^{2+} and improve the production of the hydroxyl radical (HO^\bullet).^{22,23} Furthermore, the pH of the reaction environment was decreased as a result of $\text{S}_2\text{O}_8^{2-}$, which would favor the reaction and avoid iron precipitation.²⁴

Despite the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system's promising results, the adsorption/regeneration processes are known to be affected by several environmental factors, including pH, temperature, salinity and chemical composition,²⁵ particularly,²⁶ which play an important role in the efficiency of oxidants. Moreover, pH and Ca^{2+} alter the surface charge and polarity of AC, resulting in different adsorption properties for contaminants.²⁷ The adsorption capacity of AC is strongly unfavored by a high O content. In an alkaline environment, the O amount in the surface of the AC increased and resulted in a decrease of its adsorption capacity.^{27,28} Iron ion (Fe^{2+} and Fe^{3+}) concentrations played an important role in the oxidation ability of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system, and are strongly affected by pH. Kilduff and Karanfil²⁹ pointed out that the increasing concentrations of Ca^{2+} lead to a decrease in trichloroethylene (TCE) adsorption by

^aChina Institute of Geo-Environment Monitoring, Beijing 100081, P. R. China^bBeijing Key Laboratory of Water Resources and Environmental Engineering, China University of Geosciences, Beijing 100083, P. R. China. E-mail: feiliu@cugb.edu.cn^cDepartment of Civil and Architectural Engineering, University of Wyoming, 1000 East University Avenue, Laramie, Wyoming 82071, USA^dAdvanced Environmental Technologies LLC, 4025 Automation Way, Suite F4, Fort Collins, Colorado 80525, USA[†] Present address: Haiyang Mailbox, China University of Geosciences, Beijing, No. 29 Xueyuan Road, Haidian District, Beijing 100083, P. R. China. Tel.: +86-151-20086112; fax: +86-010-82321081.

activated carbon. Heo *et al.*²⁶ stated that the solution ionic strength, mainly with cations (*i.e.* Ca^{2+} , Mg^{2+} , Na^+), affects the TCE adsorption on granular activated carbon from synthetic groundwater. Ca^{2+} in groundwater easily precipitates and complexes, which might have a negative effect on the efficiency of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system. Previous research into AC regeneration by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system mainly focused on the re-establishment of AC's adsorption capacity, but the effects of pH and Ca^{2+} on the regeneration are still under debate.

In order to reveal the interactions of pH, Ca^{2+} , AC and oxidants during the regeneration process of AC, the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system was used to regenerate the AC saturated with TCE, and the effects of pH and Ca^{2+} on the adsorption/regeneration process of AC were investigated. The adsorption/regeneration process of AC was conducted in three cycles to evaluate the variation of AC's adsorption capacity. Both physical and chemical AC properties, such as BET surface area and chemical composition during the adsorption/regeneration process, were evaluated. The significance of the study will provide some insights in the application of AC-PRBs in groundwater remediation; furthermore, environmental factors (pH and Ca^{2+}) that affect the adsorption/regeneration process of AC-PRBs are discussed, which can help us to understand the mechanisms of AC regeneration and support the sustainable use of AC-PRBs in groundwater.

2 Materials and methods

2.1 Chemicals

All the chemicals used in this study were prepared with ultra-pure water from a Millipore system. Granular AC (20–40 mesh) was purchased from Sigma-Aldrich and used as the adsorbent for TCE. Trichloroethylene was the selected contaminant (C_2HCl_3 , TCE $\geq 98\%$). Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99\%$), hydrogen peroxide (H_2O_2 , $\geq 30\%$) and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 98\%$) were used as the oxidation system to regenerate saturated AC. Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, $\geq 98\%$) was used as a radical scavenger to capture HO^\bullet . *p*-Hydroxybenzoic acid ($\text{C}_7\text{H}_6\text{O}_3$, $\geq 98\%$) was the product of benzoic acid and HO^\bullet , and was used as a standard material for HO^\bullet detection. Calcium chloride (CaCl_2 , $\geq 96\%$) was used to adjust the concentration of Ca^{2+} during the experiment. H_2SO_4 and NaOH were used to adjust the pH in the experiment. Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, $\geq 98\%$) was used to terminate the radical reactions during the regeneration process. Chemicals were all analytical grade reagents and obtained from Beijing Chemical Works (Beijing, China).

2.2 Experiment design

All the experiments were conducted in batch mode and in non-buffered solutions under ambient room temperature. The initial pH of samples was adjusted with H_2SO_4 (1 mol L^{-1}) and NaOH (1 mol L^{-1}). All the experiments were conducted in a 2 L conical flask with a Teflon coated plug and a magnetic stirring apparatus. The reaction liquid was stirred with a magnetic stirrer that had an adjustable agitation rate (150 rpm).

Experiments, including controls, were set up in triplicate. The ascorbic acid was used to terminate the radical reactions. Adsorption three times was selected in the experiments because a 3 times adsorption not only achieves a high TCE removal efficiency, but also enough TCE can be adsorbed in AC. 479 samples were taken in the experiments, including the effect of pH on TCE removal and HO^\bullet generation tests (147 samples), the effect of pH on the adsorption/regeneration and iron loss tests (108 samples), the effect of pH on AC's surface characters (4 samples), the effect of Ca^{2+} concentrations on TCE removal and HO^\bullet generation tests (168 samples), the effect of Ca^{2+} concentrations on the adsorption/regeneration and iron loss tests (48 samples) and the effect of Ca^{2+} on AC's surface characters (4 samples).

2.2.1 Effect of pH on the adsorption/regeneration process of AC. To investigate the effect of pH on the AC adsorption process, kinetic tests were conducted. The adsorption experiments were conducted in 2 L of TCE solutions (30 mg L^{-1}) with 1 g of AC while the initial pH was adjusted to 3, 7 and 9. TCE concentrations were analyzed from 5 mL samples of the reaction solution that were mixed in a 10 mL borosilicate vial containing 1 mL of ascorbic acid (0.1 mol L^{-1}) at for 10, 30, 60, 120, 180, 240, 360, 480, 720 and 1440 minutes.

In the regeneration process of AC, the adsorption process was conducted first, while the solution pH was fixed at 7, the reaction time was selected for 12 h (according to the results from kinetic tests when the adsorption equilibrium was achieved). The adsorption processes were conducted 3 times to help the AC saturate (not fully saturated), the saturated AC was then freeze-dried to help regeneration. Based on the adsorbed TCE amount, the solution's pH was adjusted to 3, 7 and 9, respectively; oxidants with a TCE/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ molar ratio of 1.00/9.00/56.63/76.25 (obtained from our previous study) were then added. The adsorption/regeneration cycle was repeated 3 times. TCE, HO^\bullet , and chloride concentrations were analyzed during the reactions.

2.2.2 Effect of Ca^{2+} on the AC adsorption/regeneration process. To investigate the effect of Ca^{2+} on the AC adsorption process, kinetic tests were conducted under a pH of 7. The adsorption experiments were conducted in 2 L of TCE solutions (30 mg L^{-1}) with 1 g of AC while the initial Ca^{2+} concentration was adjusted to 0.01, 0.05 and 0.1 mol L^{-1} . An aliquot of 5 mL of the reaction solution was sampled and combined in a 10 mL borosilicate vial containing 1 mL of ascorbic acid (0.1 mol L^{-1}) for 10, 30, 60, 120, 180, 240, 360, 480, 720 and 1440 mins. The TCE concentration was analyzed.

For the regeneration process of AC, the adsorption process was conducted first ($\text{Ca}^{2+} = 0 \text{ mol L}^{-1}$), while the solution pH was fixed at 7, and the reaction time was selected for 12 h. The adsorption processes were conducted 3 times to help the AC saturate (not fully saturated), the saturated AC was then freeze-dried to help regeneration. Based on the adsorbed TCE amount, the Ca^{2+} concentration in the solution was adjusted to 0.01, 0.05 and 0.1 mol L^{-1} , and then the oxidants added with a TCE/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ molar ratio of 1.00/9.00/56.63/76.25. The adsorption/regeneration cycle was repeated 3 times. TCE, HO^\bullet and chloride concentrations were analyzed during the reactions.



2.3 Analytical methods

TCE was analyzed by using an Agilent GC-6820 with a headspace autosampler (HP 7694E), a FID detector and a 30 m × 0.53 mm DB-5 capillary column (film thickness 1.5 μm). The total iron ion (Fe) amounts were analyzed by ICP-OES (Spectroblue, Germany). The value of pH was determined by using a Sartorius PB-10 pH meter. In order to investigate the HO• concentrations, benzoic acid was selected as the radical scavenger.³⁰ Benzoic acid and *p*-Hydroxybenzoic acid were determined by using an Agilent 1220 HPLC that was equipped with a ZORBAX SB-Aq column (5 μm, 4.6 × 150 mm) and HPLC-UV detection at 240 nm. Chloride was determined by Silver nitrate titration (0.01 mol L⁻¹) by using an automatic potentiometric titrator (Metrohm 877 Titrino plus equipped with a Metrohm 801 stirrer, Switzerland). An Escalab 250Xi X-ray photoelectron spectrometer (Thermo Scientific, USA) was used to assess the surface element change of the AC. Pore size and volume were determined by using an ASAP2020 physical adsorption instrument (Micromeritics Instrument Corp, USA).

3 Results and discussion

3.1 Effect of pH on AC adsorption/regeneration process

The variation of pH resulted in a change of the AC's surface charge and affected the adsorption properties.²⁷ As presented in Fig. 1, adsorption/regeneration cycles were conducted three times under different pH conditions. The left Y-axis of Fig. 1 represents the TCE amount that adsorbed or oxidized

during the adsorption/regeneration cycles, the right Y-axis of Fig. 1 represents the regeneration efficiency of TCE during the adsorption/regeneration cycles. TCE was finally oxidized to chloride during the regeneration (1 molar TCE can finally generate 3 molar chloride; no intermediates were detected), which means that chloride can represent the oxidized amount of TCE. The generated chloride divided by 3 was the oxidized TCE amount (in a molar ratio). The regeneration efficiency was expressed as eqn (1). It was observed that the Fe²⁺/H₂O₂/S₂O₈²⁻ system was very efficient in oxidizing TCE that adsorbed on the surface of AC (eqn (2) and (3)). During the first regeneration cycle, 30.22%, 29.29% and 33.98% of the TCE was mineralized to chloride under different pH conditions of 3, 7 and 9, respectively (Fig. 1). However, during the second and the third regeneration cycles, the regeneration efficiency of AC decreased to 26.75% and 21.87% with a pH of 3. Due to the decrease in TCE adsorption with a pH of 7 and 9 (Fig. 1), the regeneration efficiency of AC increased to 42.52% and 44.01% with a pH of 9, decreased to 17.04% and then increased to 30.41% with a pH of 7.

$$\text{AC regeneration efficiency (\%)} = \frac{\text{Cl}_{\text{generation amount}}^-}{3 \times \text{TCE}_{\text{adsorbed amount}}} \times 100 \quad (1)$$

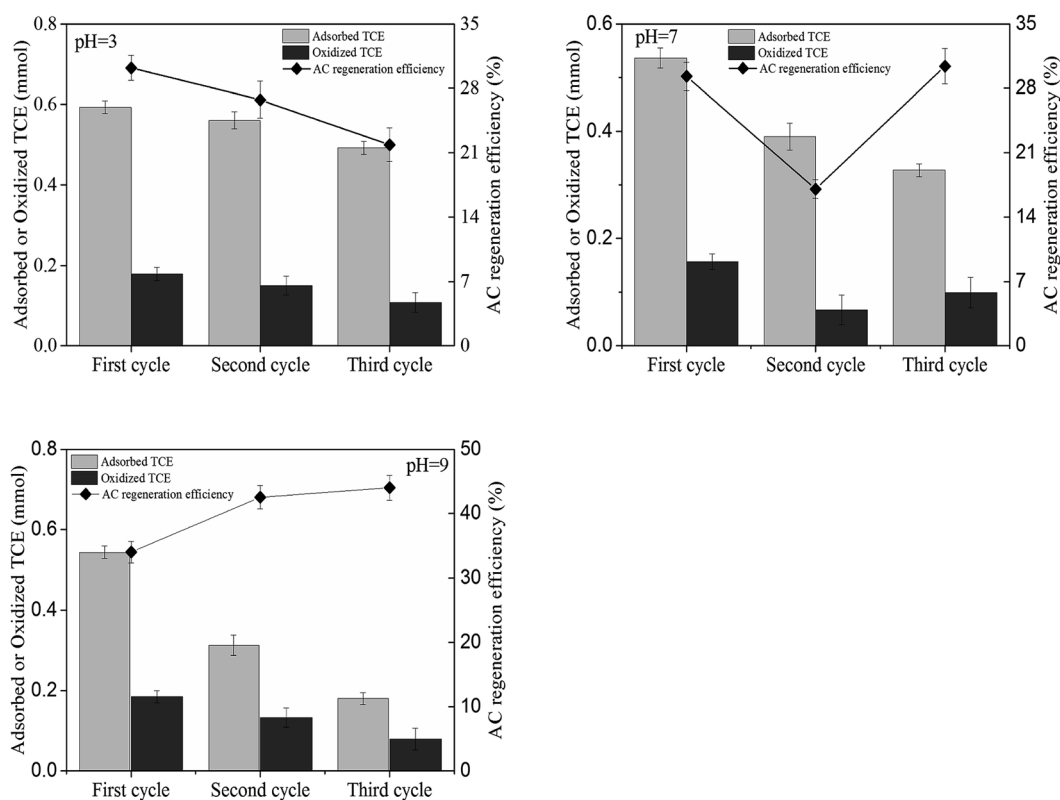
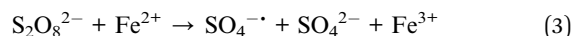


Fig. 1 Effect of pH on the adsorption/regeneration process of AC.



Although the highest regeneration efficiency of AC was achieved with pHs of 7 and 9, the adsorption capacity of AC decreased after regeneration. In comparison, at pH 3 the adsorption capacity of AC was stable, indicating that a low pH was favorable for AC's long-term adsorption/regeneration (Fig. 1).

The TCE adsorption capacity is strongly unfavored by a high O content; in fact, the presence of O made the AC surface more polar and, consequently, decreased the adsorption capacity of AC.^{27,28} In an alkaline environment, the O amount in the surface of the AC increased and resulted in a decrease of its adsorption capacity. As shown in Fig. 2, with pH increasing, the adsorbed TCE on AC decreased, and it can be observed that the highest TCE adsorption occurred at pH = 3, confirming that an acidic condition is favorable for the adsorption process of AC (Fig. 2). The HO[•] concentration represented the efficiency with which the oxidized TCE was adsorbed on the AC's surface during the regeneration process. Because of the initial addition of persulfate, an acidic condition was created, so there was little change in HO[•] generation with pH at 3, 7 and 9 (Fig. 2), suggesting that the Fe²⁺/H₂O₂/S₂O₈²⁻ system possessed a high oxidation ability with pH ranging from 3 to 9.

Iron ions (Fe²⁺ and Fe³⁺) played an important role on the surface character of AC and the oxidation ability of the Fe²⁺/H₂O₂/S₂O₈²⁻ system; however, iron precipitation might adversely impact the oxidants and the adsorption capacity of AC. Iron precipitation was mainly determined by pH and the iron concentration. Despite the adjustment of pH by persulfate, iron precipitation was inevitable during the reaction. As presented in Fig. 3, the iron losses with pH = 3, 7 and 9 in the first regeneration cycle were 14.94%, 22.24% and 24.35%, respectively. However, it was obvious that the input iron of the oxidation systems decreased at pHs of 7 and 9, indicating that the adsorption capacity of AC decreased, which resulted in a decrease of adsorbed TCE on AC. For a pH of 9, there was a significant iron loss during regeneration compared with pHs of 3 and 7, suggesting that an alkaline environment is favorable

for iron precipitation. Though the pH of 7 possessed a better iron loss control, considering the stability of AC's adsorption capacity, pH 3 is more suitable for the adsorption/regeneration process of AC.

The effect of pH on the physico-chemical characteristics of AC was investigated. Acidic conditions not only exhibited good iron loss prevention (Fig. 3), they also resulted in the highest adsorption capacity of AC (Fig. 1). Table 1 presents the element changes under different pH conditions, and it can be observed that after the regeneration, the Fe contents were 2.38%, 0.87% and 0.73% for pH 3, 7 and 9, respectively. Due to the high AC adsorption capacity in the acidic condition (pH 3), the addition of the oxidant amount was higher, resulting in an increase of iron content in the surface of AC (Table 1). Compared with the initial AC, the accumulation of iron on the AC surface was significant, especially at pH = 3. It can be observed that the Fe content increased at pH 3 (from 0.32% to 2.38%) in comparison with 0.87% and 0.73% at pH 7 and pH 9, respectively. The chloride content (representing the TCE content) increased from 0.14% to 0.58%, 1.44% and 1.53% at pH 3, pH 7, and pH 9, respectively. The contents of Cl under pHs of 3, 7 and 9 were 0.58%, 1.44% and 1.53%, respectively, suggesting that acidic pH conditions with the least Cl reservation favored TCE removal. However, acidic pH conditions promote contaminant removal by the Fe²⁺/H₂O₂/S₂O₈²⁻ system, which could result in a mass loss of the AC.

The surface area of the AC during regeneration under different pH conditions showed that acidic conditions were more favorable for the protection of the AC surface area (Table 2). However, there was an approximately 32.85% decline in the BET surface area of the AC that occurred at pH 3 after three regeneration cycles, which was attributed to iron accumulation and carbon mass loss of the AC surfaces.³¹

In general, despite iron precipitation, the loss of carbon mass and the decrease of AC surface area, high adsorption and removal of TCE during the regeneration suggested that an acidic pH favored AC's adsorption/regeneration process.

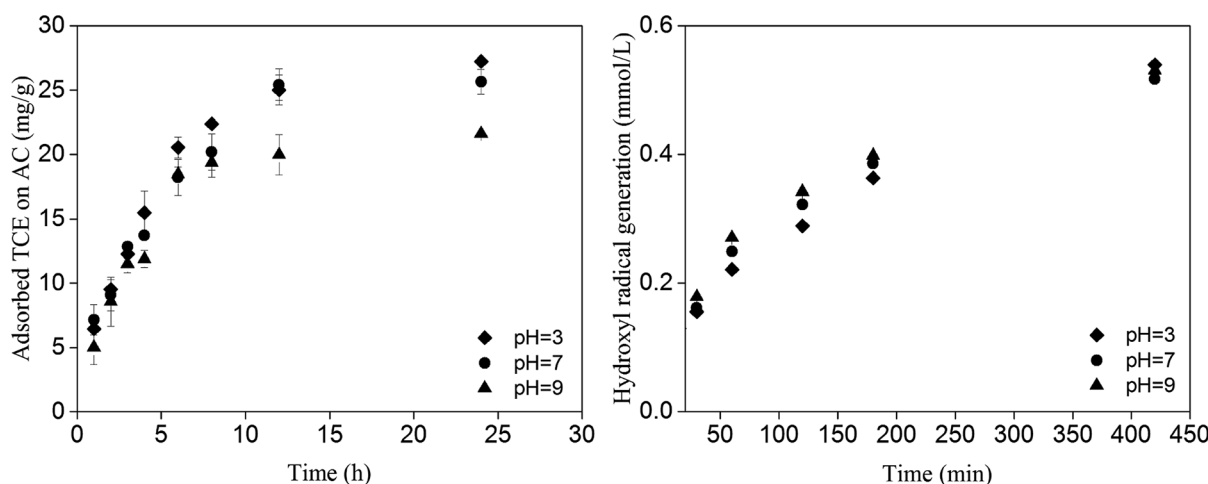


Fig. 2 Effect of pH on TCE removal and HO[•] generation.



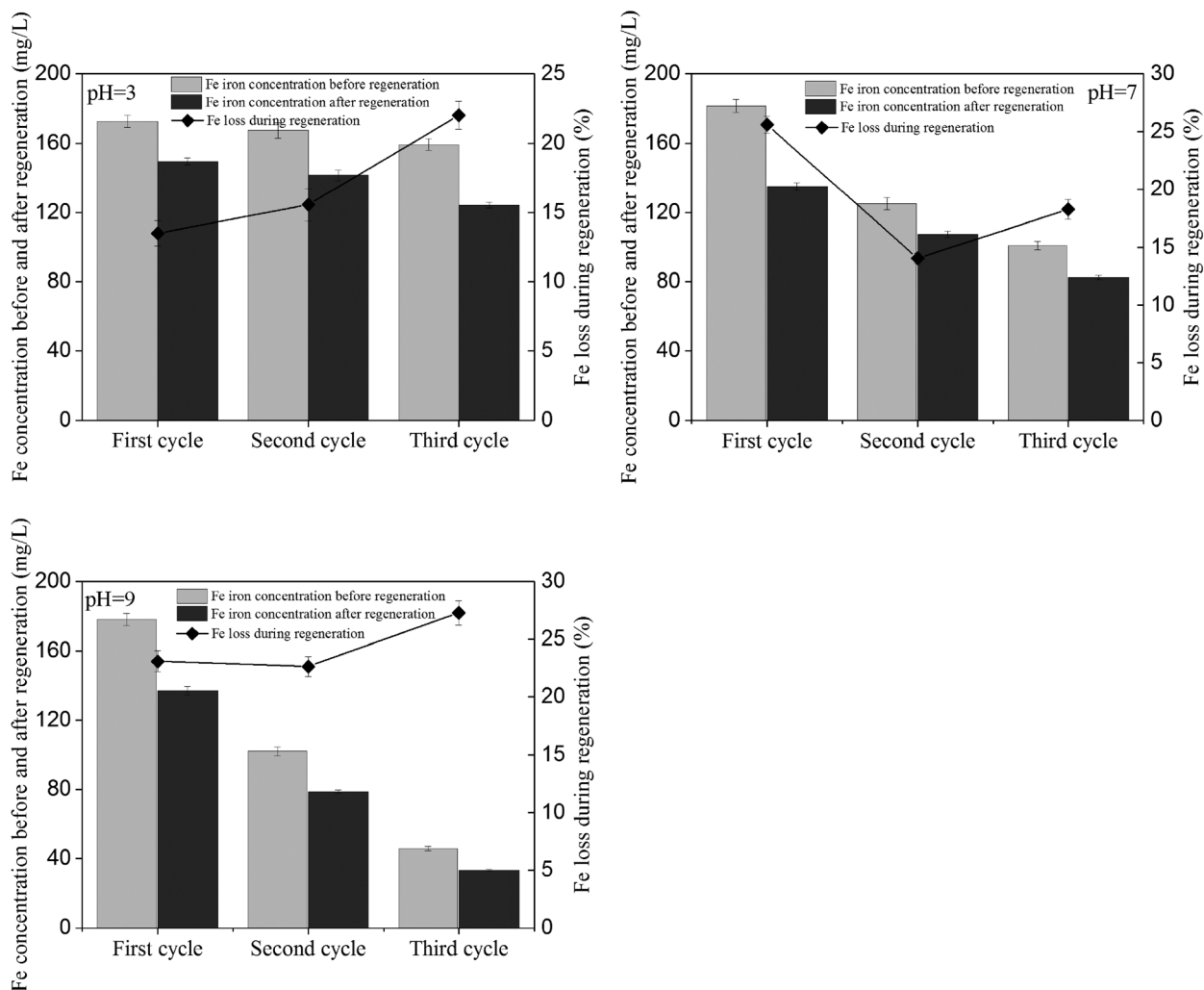


Fig. 3 Effect of pH on iron loss.

3.2 Effect of Ca^{2+} on AC adsorption/regeneration process

Due to its relatively low solubility in compound form, Ca^{2+} in groundwater easily precipitates and complexes. It was widely accepted that pH and ionic strength do not affect the adsorption

of uncharged organic compounds on activated carbon.^{27,32} However, the influence of the presence of Ca^{2+} in solutions on the adsorption capacity of AC and the oxidation ability of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system is still a debated subject. It is widely known that CaSO_4 and CaCO_3 easily precipitate in groundwater; apparently, SO_4^{2-} and CO_3^{2-} are the products of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system. It is possible that due to the presence of Ca^{2+} , the adsorption capacity of AC may be affected.

As presented in Fig. 4, two adsorption/regeneration cycles were conducted. During the first adsorption/regeneration cycle, TCE removal decreased obviously when Ca^{2+} was present. It was apparent that during the second adsorption/regeneration cycle, even though the regeneration of AC was carried out, it had difficulty in removing TCE in the presence of Ca^{2+} conditions. This indicated that Ca^{2+} could play an important role not only in AC's adsorption capacity, but also in its regeneration process. The reasons might owe to the combination of Ca^{2+} with other ions, especially for SO_4^{2-} and CO_3^{2-} , which generate from $\text{S}_2\text{O}_8^{2-}$ (eqn (3)) and TCE degradation, respectively, which easily precipitate on the surface of the AC and affect the adsorption capacity of it, resulting in a decrease in TCE removal in the second cycle.

Table 1 AC element changes under different pH conditions after regeneration

Elements	Initial AC (wt%)	Final AC (pH = 3) (wt%)	Final AC (pH = 3) (wt%)	Final AC (pH = 9) (wt%)
C	70.84	45.76	56.67	61.31
N	0.00	0.00	0.00	0.00
O	9.48	28.24	28.55	28.79
Na	0.13	0.15	0.10	0.17
Al	1.31	9.35	0.99	0.90
Si	15.57	12.35	6.83	2.62
P	0.91	0.82	1.46	1.47
S	0.52	0.11	1.83	2.36
Cl	0.14	0.58	1.44	1.53
Ti	0.77	0.26	1.28	0.11
Fe	0.32	2.38	0.87	0.73



Table 2 AC surface area change under different pH conditions after regeneration

Category ($\text{m}^2 \text{g}^{-1}$)	Initial AC	Final AC (pH = 3)	Final AC (pH = 7)	Final AC (pH = 9)
BET surface area	637.41	437.99	433.92	418.07
Langmuir surface area	1267.26	1001.43	988.03	949.33
<i>t</i> -plot pore area	452.07	269.41	272.33	265.33
<i>t</i> -plot external surface area	185.34	168.59	234.21	152.74

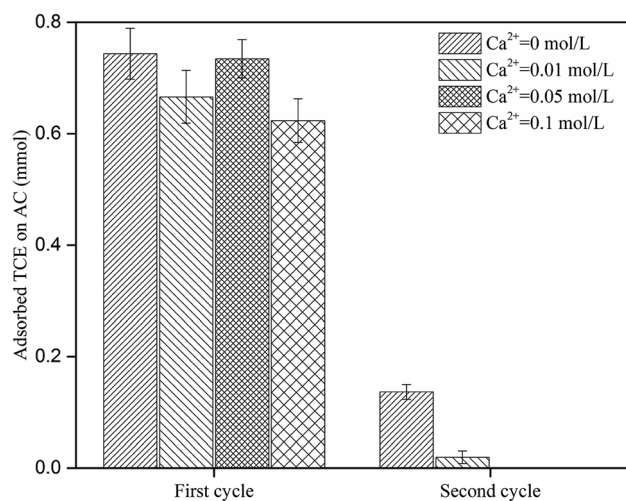
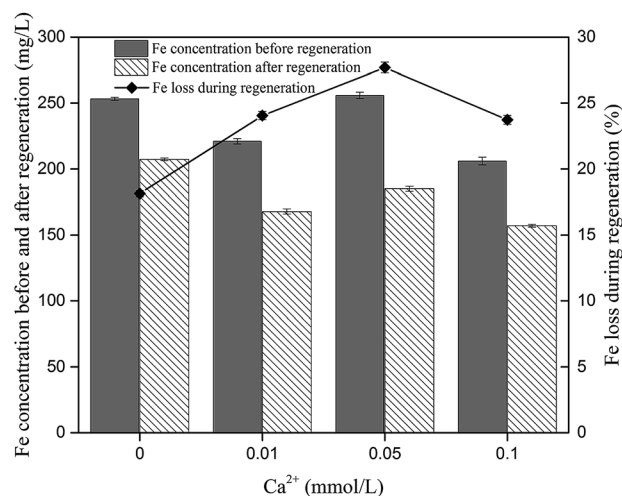
Fig. 4 TCE removal in different Ca^{2+} concentrations.

Fig. 6 Variation of Fe ion concentrations during regeneration.

The presence of Ca^{2+} also showed an influence on the oxidation ability of oxidants, the adsorption capacity of AC, and the formation of iron ions in solution. When Ca^{2+} was present, the generation of HO^\bullet decreased significantly, as Fig. 5 shows. Without Ca^{2+} in the regeneration process, the generation of HO^\bullet was much higher than that with Ca^{2+} present, suggesting that Ca^{2+} decreased the oxidation ability of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system. As with the variation of AC's adsorption capacity when Ca^{2+} was present, it can be observed that the amount of

adsorbed TCE on the AC decreased obviously (Fig. 5). Compared with the reaction system without Ca^{2+} , the adsorption of AC decreased as the Ca^{2+} concentration increased, indicating a negative effect of Ca^{2+} on the adsorption capacity of AC.

The iron loss during the regeneration of AC is presented in Fig. 6. Compared with the input Fe concentration before regeneration, the Fe concentration decreased significantly after regeneration. Even without the presence of Ca^{2+} , iron loss also

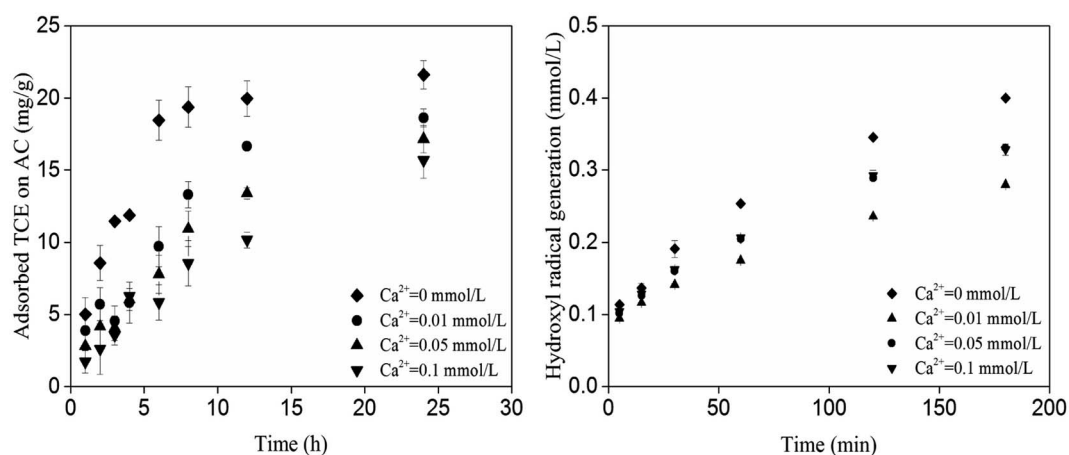
Fig. 5 Effect of Ca^{2+} concentrations on TCE removal and HO^\bullet generation.

Table 3 The AC elements change under different Ca^{2+} concentrations after regeneration

Elements	Initial AC (wt%)	$\text{Ca}^{2+} = 0 \text{ mmol L}^{-1}$ (wt%)	$\text{Ca}^{2+} = 0.01 \text{ mmol L}^{-1}$ (wt%)	$\text{Ca}^{2+} = 0.05 \text{ mmol L}^{-1}$ (wt%)	$\text{Ca}^{2+} = 0.1 \text{ mmol L}^{-1}$ (wt%)
C	70.84	75.57	69.89	59.25	49.32
N	0.00	0.00	0.00	0.00	0.00
O	9.48	6.70	19.94	27.36	28.78
Na	0.13	0.32	0.29	0.72	0.99
Al	1.31	8.13	0.89	7.98	5.90
Si	15.57	6.39	1.80	15.62	12.38
P	0.91	0.87	1.46	1.48	0.89
S	0.52	0.23	1.34	0.56	0.15
Cl	0.14	0.51	2.63	2.64	0.69
Ti	0.77	0.36	0.43	0.46	0.23
Fe	0.32	0.91	0.34	0.42	0.66

Table 4 AC surface area under different Ca^{2+} conditions after regeneration

Category ($\text{m}^2 \text{ g}^{-1}$)	Initial	$\text{Ca}^{2+} = 0 \text{ mmol L}^{-1}$	$\text{Ca}^{2+} = 0.01 \text{ mmol L}^{-1}$	$\text{Ca}^{2+} = 0.05 \text{ mmol L}^{-1}$	$\text{Ca}^{2+} = 0.1 \text{ mmol L}^{-1}$
BET surface area	637.41	457.21	447.50	395.35	450.81
Langmuir surface area	1267.26	1033.59	999.60	927.88	995.31
<i>t</i> -plot pore area	452.07	269.63	286.04	242.84	294.75
<i>t</i> -plot external surface area	185.34	187.59	161.46	152.51	156.06

happened. The iron loss at Ca^{2+} concentrations of 0.01, 0.05 and 0.1 mmol L^{-1} were 24.05%, 27.68% and 23.73%, respectively, compared with the control (without Ca^{2+}) in which 18.14% of iron loss occurred in the absence of Ca^{2+} . Iron loss increased when Ca^{2+} was present, which indicated that Ca^{2+} precipitation formed by Ca^{2+} promoted the iron loss during the regeneration process of AC.

It can be observed that in the presence of Ca^{2+} , the mass loss of C increased after the regeneration of AC (Table 3). The C content on the surface of the AC was 75.57% without Ca^{2+} , compared with that of 69.89%, 59.25% and 49.32% under Ca^{2+} concentrations of 0.01, 0.05 and 0.1 mmol L^{-1} , respectively. The C content was directly related with the adsorption capacity of the AC, further indicating that Ca^{2+} can decrease the AC's adsorption capacity. The content of iron in the AC surface decreased in the presence of Ca^{2+} , suggesting that the complexation of Ca^{2+} and Fe ions mainly occurred in solution rather than on the AC surface. The Cl level increased substantially on the surface of the AC in the presence of Ca^{2+} , proving that Ca^{2+} decreased the regeneration efficiency of AC.

Comparing the AC surface area with and without Ca^{2+} , it was found that Ca^{2+} did not influence the surface area of the AC (Table 4). Looking at the change of the AC's surface area and Fe content, it can be inferred that the complexation of Ca^{2+} and Fe ions occurred in solution and then reduced the iron precipitation on the AC's surface. Furthermore, the consumption of HO^{\bullet} in the presence of Ca^{2+} eliminated the deterioration of the AC surface structure.

Overall, the influence of Ca^{2+} , even at low concentrations, appeared to be evident on the HO^{\bullet} generation and the AC adsorption capacity and regeneration.

Based on the results obtained from the experiments, it can be concluded that AC-PRB is a valuable approach for ground-water management. It requires refinement, as several environmental factors played a negative effect on the PRBs, including pH and Ca^{2+} , but it has the advantages of an immediate organic contamination removal followed by a sustainable use that employs the adsorption/regeneration process.

4 Conclusion

Under certain reaction conditions ($\text{TCE}/\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ molar ratio of 1.00/9.00/56.63/76.25), compared with the pHs of 7 and 9, the adsorption capacity of AC under pH 3 decreased less after regeneration, indicating a sustainable use of AC-PRBs under an acidic pH condition. Even though the iron precipitation, C mass loss, and the decrease of the AC surface area were higher under a pH of 3, a high adsorption and removal of TCE during the regeneration suggested that an acidic pH favored AC's adsorption/regeneration process. The presence of Ca^{2+} , even at low concentrations, could decrease HO^{\bullet} generation and AC adsorption capacity. Ca^{2+} or precipitation formed by Ca^{2+} promoted the iron loss during the regeneration process of AC, which resulted in iron precipitation in solutions rather than on the surface of the AC. Moreover, the consumption of HO^{\bullet} in the presence of Ca^{2+} eliminated the deterioration of the AC surface structure.

Conflicts of interest

There are no conflicts to declare.



Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC) (41272268), the Special Fund for Public Interest research support by the Ministry of Environmental Protection (201309001-3), the Fundamental Research Funds for the Central Universities, and China Scholarship Council (201506400018) and National Grade Geological Environment Monitoring and Forecast (121201014000150003).

References

- 1 T. n. Dobre, O. C. Pârvolescu, G. Iavorschi, M. Stroescu and A. a. Stoica, *Ind. Eng. Chem. Res.*, 2014, **53**, 3622–3628.
- 2 D. T. Tefera, M. Jahandar Lashaki, M. Fayaz, Z. Hashisho, J. H. Philips, J. E. Anderson and M. Nichols, *Environ. Sci. Technol.*, 2013, **47**, 11700–11710.
- 3 A. D. Luz, S. M. d. A. Guelli Ulson de Souza, C. da Luz, R. V. d. P. Rezende and A. n. A. Ulson de Souza, *Ind. Eng. Chem. Res.*, 2013, **52**, 7896–7911.
- 4 J. Zhang, W. Zhu, M. Makkee, B. Van der Linden, F. Kapteijn and J. Moulijn, *J. Chem. Eng. Data*, 2001, **46**, 662–664.
- 5 Y.-f. Su, Y.-l. Cheng and Y.-h. Shih, *J. Environ. Manage.*, 2013, **129**, 361–366.
- 6 K. S. Walton, C. L. Cavalcante Jr and M. D. Levan, *Adsorption*, 2005, **11**, 107–111.
- 7 Y.-C. Chiang, P.-C. Chiang and C.-P. Huang, *Carbon*, 2001, **39**, 523–534.
- 8 B. Bone, Review of UK guidance on permeable reactive barriers, *2012 Taipei International Conference on Remediation and Management of Soil and Groundwater Contaminated Sites*, Taipei, Taiwan, 2012, pp. 611–768.
- 9 M. Turner, A. Sogorka, N. Dave, M. Duchene, B. Dwyer, D. Hubble, L. Kessel, W. Khan, J. Liskowitz and P. Lurk, *Technical/Regulatory Guidelines: Permeable Reactive Barriers: Lessons Learned/New Directions*, 2005.
- 10 A. Erto, I. Bortone, N. A. Di, N. M. Di and D. Musmarra, *J. Environ. Manage.*, 2014, **140**, 111–119.
- 11 I. Bortone, A. Erto, G. Santonastaso, A. D. Nardo, M. D. Natale and D. Musmarra, *Desalin. Water Treat.*, 2015, **55**, 3231–3240.
- 12 L. Carniato, G. Schoups, P. Seuntjens, T. Van Nooten, Q. Simons and L. Bastiaens, *J. Contam. Hydrol.*, 2012, **142–143**, 93–108.
- 13 B. M. Patterson, M. E. Grassi, B. S. Robertson, G. B. Davis, A. J. Smith and A. J. McKinley, *Environ. Sci. Technol.*, 2004, **38**, 6846–6854.
- 14 S. G. Huling, P. K. Jones, W. P. Ela and R. G. Arnold, *Water Res.*, 2005, **39**, 2145–2153.
- 15 L. C. Toledo, A. C. B. Silva, R. Augusti and R. M. Lago, *Chemosphere*, 2003, **50**, 1049–1054.
- 16 A. Cabrera-Codony, R. Gonzalez-Olmos and M. J. Martín, *J. Hazard. Mater.*, 2015, **285**, 501–508.
- 17 A. Hutson, S. Ko and S. G. Huling, *Chemosphere*, 2012, **89**, 1218–1223.
- 18 Q. Chen, H. Liu, Z. Yang and D. Tan, *J. Mater. Cycles Waste Manage.*, 2017, **19**, 256–264.
- 19 S. Li, M. Li, X. Luo, G. Huang, F. Liu and H. Chen, *Environ. Sci. Pollut. Res.*, 2016, **23**, 402–407.
- 20 N. Yan, F. Liu and W. Huang, *Chem. Eng. J.*, 2013, **219**, 149–154.
- 21 P. A. Block, R. A. Brown and D. Robinson, Novel activation technologies for sodium persulfate in situ chemical oxidation, *Proceedings of the Fourth International Conference on the remediation of chlorinated and recalcitrant compounds*, 2004, pp. 24–27.
- 22 C. Liang, C. J. Bruell, M. C. Marley and K. L. Sperry, *Chemosphere*, 2004, **55**, 1213–1223.
- 23 C. Liang, C.-F. Huang, N. Mohanty, C.-J. Lu and R. M. Kurakalva, *Ind. Eng. Chem. Res.*, 2007, **46**, 6466–6479.
- 24 M. Usman, P. Faure, K. Hanna, M. Abdelmoula and C. Ruby, *Fuel*, 2012, **96**, 270–276.
- 25 A. Erto, R. Andreozzi, A. Lancia and D. Musmarra, *Appl. Surf. Sci.*, 2010, **256**, 5237–5242.
- 26 J.-H. Heo, D.-H. Lee, D.-C. Koh and H.-W. Chang, *Geosci. J.*, 2007, **11**, 229–239.
- 27 C. Moreno-Castilla, *Carbon*, 2004, **42**, 83–94.
- 28 J. S. Mattson and H. B. Mark, *Activated carbon: surface chemistry and adsorption from solution*, M. Dekker, New York, 1971.
- 29 J. E. Kilduff and T. Karanfil, *Water Res.*, 2002, **36**, 1685–1698.
- 30 M. E. Lindsey and M. A. Tarr, *Chemosphere*, 2000, **41**, 409–417.
- 31 R. G. Arnold, P. K. Jones, S. G. Huling and W. P. Ela, *J. Environ. Eng.*, 2005, **131**, 287–297.
- 32 S. Mukherjee, S. Kumar, A. K. Misra and M. Fan, *Chem. Eng. J.*, 2007, **129**, 133–142.

