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Deterioration of activated carbon by oxidants, contaminants, and carbon regeneration

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ABSTRACT

Activated carbon (AC) is widely used for removing organic contaminants; however, its finite adsorption capacity may limit the long-term use. Oxidation regeneration of saturated AC is one of the effective measures to recover the adsorptive capacity of AC, even though the deterioration of AC during the regeneration is common. In this study, advanced oxidation process (Fenton combined persulfate system, $Fe^{2+}/H_2O_2/S_2O_8^{2-}$) was used to regenerate the saturated AC, the mechanisms of AC deterioration were evaluated, and the interactions of oxidants, contaminants, and AC during the adsorption/regeneration processes were investigated. The results indicate that the oxidants mainly functions on the AC surface, resulting in the deterioration of AC along with the destruction of the sorbed contaminant (e.g., trichloroethylene in this study). Deterioration of AC exposed fresh carbon to the surface, however, such emergence of the fresh carbon to the AC surface does not seem to increase the AC adsorption capacity. Iron precipitation on the surface of AC was also observed during the adsorption/regeneration process, however, it can be partially removed from the surface of AC along with the carbon deterioration.

Keywords: Activated carbon; Hydrogen peroxide; Persulfate; Ferrous; Interactions

1. Introduction

Activated carbon (AC) is an effective adsorbent for removing a wide array of dissolved organic contaminants from drinking water [1]. When AC is used to adsorb hazardous compounds, it becomes a hazardous waste that should be treated or disposed of properly [2]. Regeneration of AC upon the saturation of its adsorptive capacity allows the contaminants to transform into less toxic byproducts and re-establish the adsorptive capacity of AC [3–5]. Methods used to regenerate saturated AC include advanced oxidation processes (AOPs) such as biological treatment, electro-chemical treatment, and wet oxidation, etc. [4,6–8]. In case of AOPs, Fenton's reaction (Fe^{2+}/H_2O_2), persulfate

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reaction ($Fe^{2+}/S_2O_8^{2-}$), and Fenton combined persulfate reaction ($Fe^{2+}/H_2O_2/S_2O_8^{2-}$) are the most common AOPs used for regenerating saturated AC [2,9,10].

The adsorbed contaminants are mainly distributed on the surface and pores of AC [11]. The contaminants that are transformed and oxidized during AC regeneration include those that were desorbed or diffused from the AC's surface and pores (which were directly removed or transformed to intermediate products) [12]. However, the desorbed and diffused contaminants only account for a small portion of the total adsorbed contaminants on AC [13]. Therefore, it can be deduced that the AC regeneration proceeds mainly toward the contaminants that are adsorbed on its surface and pores, which means that the reaction between oxidants and AC is inevitable during the transformation and oxidation of contaminants [14].

Although it may seem that the reactions between oxidants and AC will result in the deterioration of AC [15–17], research involving AC regeneration mainly focuses on the restoration of AC's adsorption capacity and the protection of its chemical and physical characteristics [18,19]. Furthermore, the interactions of oxidants, contaminants, and AC during regeneration, especially in regards to the contaminants removal process, warrant further studies.

To better understand the AC regeneration and deterioration processes, trichloroethylene (TCE) was selected as the target contaminant and the $Fe^{2+}/H_2O_2/S_2O_8^{2-}$ reaction was used to regenerate the saturated AC. The adsorption/regeneration process was carried out in three cycles. Techniques such as scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS) were used to investigate the shifts of the AC characteristics during the process, including the chemical and physical properties, surface area, pore size and volume, elements variation, etc. The argon ion-bombardment technology of XPS was applied to study the cross section of AC at different depths (20, 40, 60, 80, and 100 nm from the surface to the inner structure) to investigate the distribution of oxidants and contaminants during the adsorption/regeneration process.

2. Materials and methods

2.1. Materials

All chemicals used in this study were prepared with ultrapure water from a Millipore system. Granular AC (20–40 mesh, obtained from Sigma-Aldrich, USA), trichloroethylene (C_2HCl_3, TCE ≥ 98%), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, ≥99%), hydrogen peroxide (H_2O_2, ≥30%), sodium persulfate ($Na_2S_2O_8$, ≥98%), benzoic acid (C_6H_5COOH, ≥98%), p-hydroxybenzoic acid ($C_7H_6O_3$, ≥98%), and ascorbic acid ($C_6H_8O_6$, ≥98%) were of analytical reagent grade and obtained from Beijing Chemical Works (Beijing, China).

2.2. Experiment design

All trials were performed in batch mode and in non-buffered solutions under ambient room temperature (~22°C). The initial pH and TCE concentration were 7 ± 0.2 and 30 mg/L, respectively. The initial pH of samples was adjusted with H_2SO_4 (1 mol/L) and NaOH (1 mol/L). All 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 an adjustable flow rate (150 rpm) using a magnetic stirrer. Experiments, including controls, were setup in triplicate. Ascorbic acid was used to terminate the radical reactions.

The adsorption experiments were conducted in 2 L TCE solutions (30 mg/L) with 1 g AC. Three times adsorption was selected in the experiments because that it not only can achieve high TCE removal efficiency but also can have enough TCE adsorbed in AC.

AC was first saturated by TCE before being freeze-dried to help it regenerate. Oxidants were added in accordance to the molar ratio of $TCE/Fe^{2+}/H_2O_2/\ S_2O_8^{2-} = 1.00/9.00/56.63/76.25$ (the ratio of oxidants was chosen based on our previous study [20], based on the amount of the adsorbed TCE. The adsorption/regeneration cycles were repeated three times. AC from the control, saturation, first regeneration cycle, second regeneration cycle, and third regeneration cycle were analyzed by SEM, EDS, and XPS (including argon ion-bombardment with depths of 20, 40, 60, 80, and 100 nm, respectively) to identify AC's surface, pore, and inner space characteristics. Concentrations of TCE and chloride were also analyzed during the reactions.

2.3. Analytical methods

TCE was analyzed by using a GC-6820 with a headspace autosampler (HP 7694E, Agilent, USA), an FID detector, and a 30 m × 0.53 mm DB-5 capillary column (film thickness 1.5 μm). Dissolved iron ions (Fe) were analyzed by ICP-OES (Spectroblue, Germany). The value of pH was determined by using a Sartorius PB-10 pH meter (Sartorious, Germany). TCE was finally oxidized to water, carbon dioxide, and chloride during the regeneration (1 molar TCE can generate three molar chloride), which means that chloride can present the oxidized amount of TCE. Chloride was determined by silver nitrate titration (0.01 mol/L) by using an automatic potentiometric titrator (Metrohm 877 Titrino plus equipped with Metrohm 801 stirrer, Switzerland). An S-4800 field emission scanning electron microscope (Hitachi, Japan) and an Escalab 250Xi X-ray photoelectron spectrometer (Thermo Scientific, USA) were used to assess the surface structure 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. AC deterioration and iron precipitation during adsorption/regeneration

The surface characteristics of AC during different reactions are presented in Fig. 1. The surface of the original AC was relatively smooth and few attachments were found (Fig. 1a). Due to the collisions and abrasion during the adsorption process, ashes on AC's surface and pores were removed, which resulted in the opening of partial pores and the increase of AC's surface area (Fig. 1b; Table 1). Furthermore, some attachments formed on the saturated

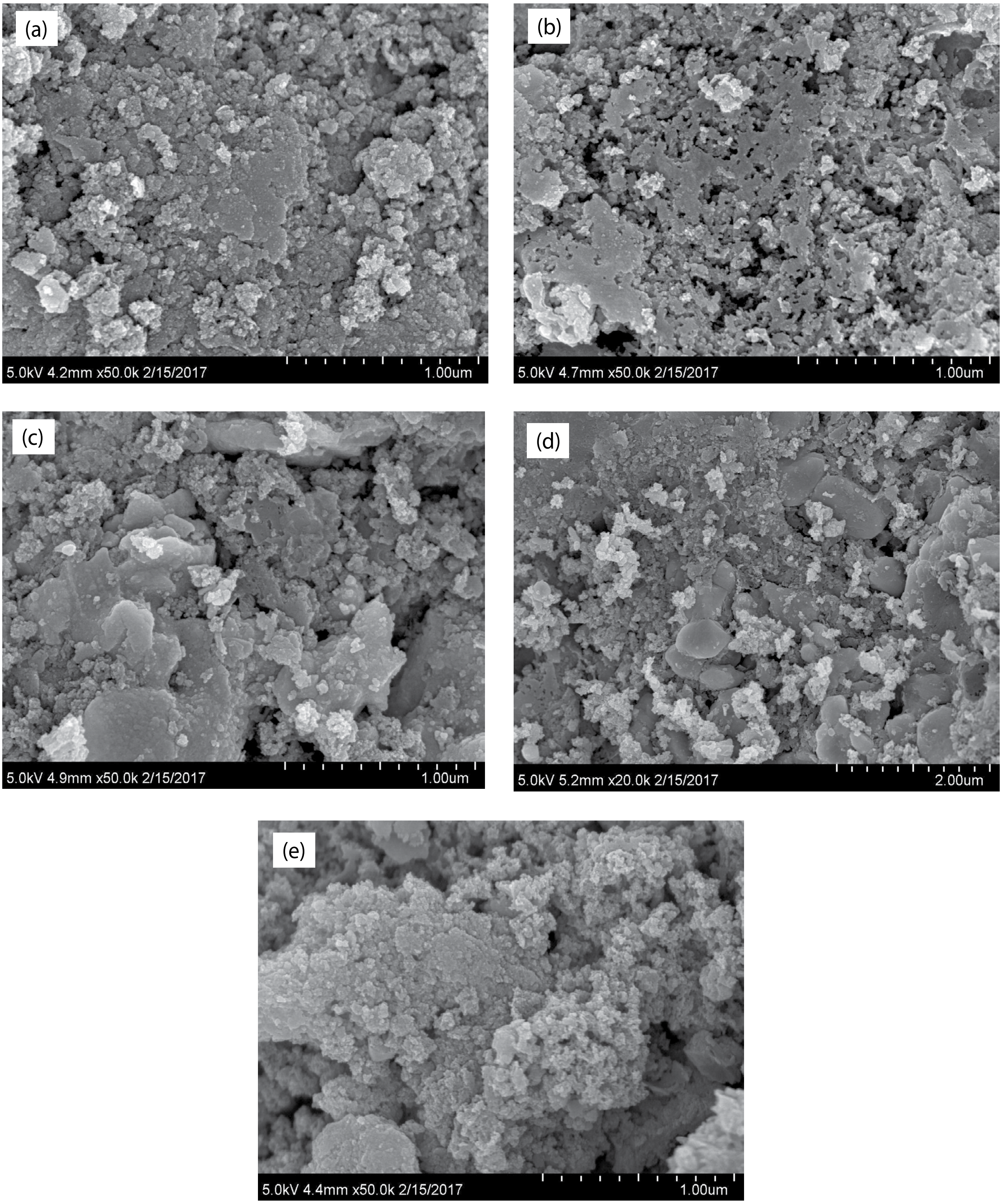

Fig. 1. AC surface characteristics (a: original AC; b: saturated AC; c: the first regeneration cycle AC; d: the second regeneration cycle AC; e: the third regeneration cycle AC).

Table 1
AC surface area change

Category (surface area, m²/g)	Original AC	Saturated AC	First cycle AC	Second cycle AC	Third cycle AC
BET	310.54	339.43	141.45	230.34	240.11
Langmuir	604.98	742.34	357.66	556.93	593.24
t-Plot micropores	231.21	226.41	84.32	133.93	129.75
t-Plot external	79.33	113.02	57.13	96.41	110.36

AC's surface. It seemed that the iron precipitation started to accumulate on the AC's surface after the first regeneration cycle (Fig. 1c); however, such accumulation of iron decreased during the second regeneration cycle (Fig. 1d), but significantly rebound during the third regeneration cycle (Fig. 1e).

This accumulation–reduction–re-accumulation of iron indicates that AC surface deterioration might have occurred during regeneration, which resulted in iron precipitation removal and partial loss of carbon mass.

Surface carbon loss was obvious during AC's regeneration process. As shown in Table 2, an estimated 19.79% of carbon loss occurred after the first regeneration cycle, suggesting that AC deterioration took place immediately. As a result of the deterioration of AC, new carbon was exposed at the AC surface, resulting in partially increase AC's surface area (Table 1).

In spite of surface C loss during the oxidant regeneration of AC, precipitation of oxidized iron on the AC surface was also evident, and it could have offset the total mass loss of AC. As illustrated in Fig. 2a, the mass loss of AC in the control group was about 20%, vs. 15% in the experimental group.

Carbon plays an important role in AC's adsorption capacity [21,22]. The deterioration of AC surface leads to carbon loss and decreases its adsorption capacity. As shown in Fig. 2b, the deterioration of AC mainly occurred on its surface. For example, the surface C content of the original AC's surface (depth of 0 nm) was about 90%, and decreased to about 80% after the first and second regeneration cycles. Surface C content increased to about 92% after the third regeneration process, indicating that the oxidant removed the oxidized iron deposited on the AC surface and exposed more fresh carbon. Since TCE is mainly adsorbed at the AC surface and shallow pores, the change of the surface C contents is expected to influence its adsorption capacity to TCE and presumably other contaminants.

Iron precipitation formed during the regeneration mainly existed in solutions or was adsorbed onto the carbons. AC surface iron precipitation can be removed either through solubilization, which results in the increase of Fe ion concentration, or by oxidation, which could contribute to carbon loss on AC.

In Fig. 3, no increase in Fe ion concentrations in solutions was observed after the AC regeneration, suggesting that no Fe was dissolved into water. When looking at the Fe amounts on AC's surface, we found that compared with the original and saturated AC, the accumulation of iron in the first regeneration cycle was significant (Table 2). In the first regeneration cycle, Fe content increased from 0.54% (original AC) and 0.82% (saturated AC) to 2.15% (the first regeneration cycle AC), indicating that the accumulation of iron occurred. It can be observed that Fe content decreased in the second and third regeneration cycle along with a C loss of 45.92%–36.09%, suggesting that AC deterioration caused by oxidants might have resulted in iron precipitation removal from AC's surface. The new carbon content that was exposed

Table 2
Elements contents

Elt.	Original AC (wt.%)	Saturated AC (wt.%)	First cycle AC (wt.%)	Second cycle AC (wt.%)	Third cycle AC (wt.%)
C	72.51	65.71	45.92	36.09	47.43
N	0.00	0.00	0.00	0.00	0.00
O	8.79	7.88	23.63	26.54	25.42
Na	0.16	0.92	0.54	0.81	0.46
Al	2.32	5.02	12.46	13.26	7.33
Si	12.53	17.79	12.88	17.13	15.25
P	1.15	1.06	1.36	1.55	0.87
S	0.80	0.14	0.49	0.64	0.56
Cl	0.17	0.28	0.50	1.03	0.09
Ti	1.03	0.37	0.06	0.93	0.88
Fe	0.54	0.82	2.15	2.03	1.71
Total	100.00	100.00	100.00	100.00	100.00

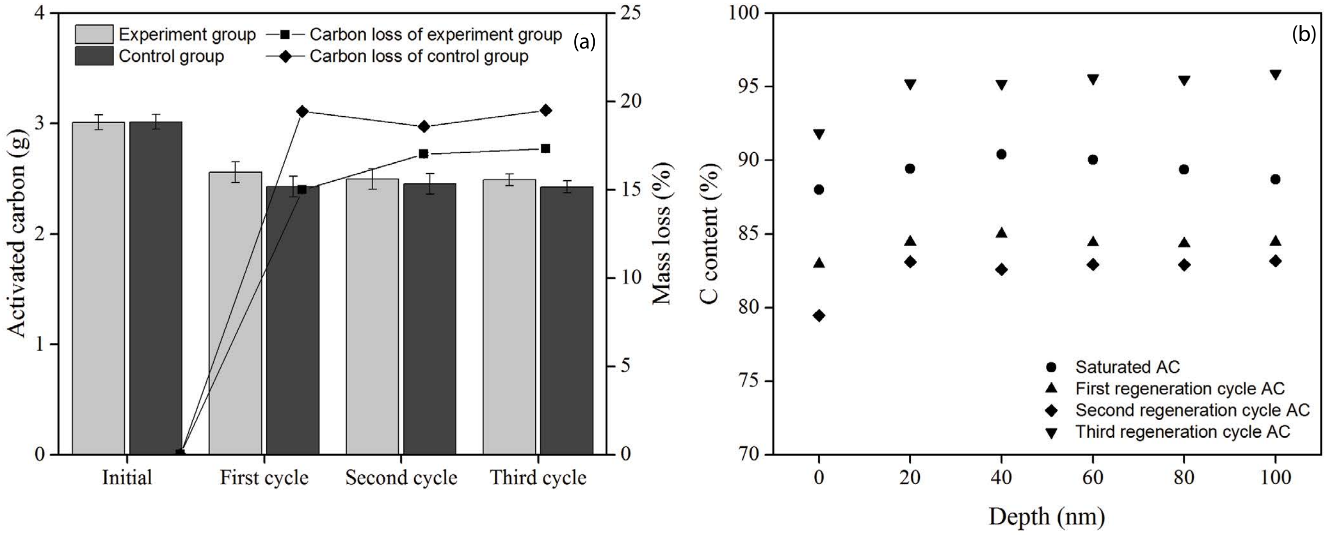

Fig. 2. AC mass loss (a) and the distribution of C in AC (b).

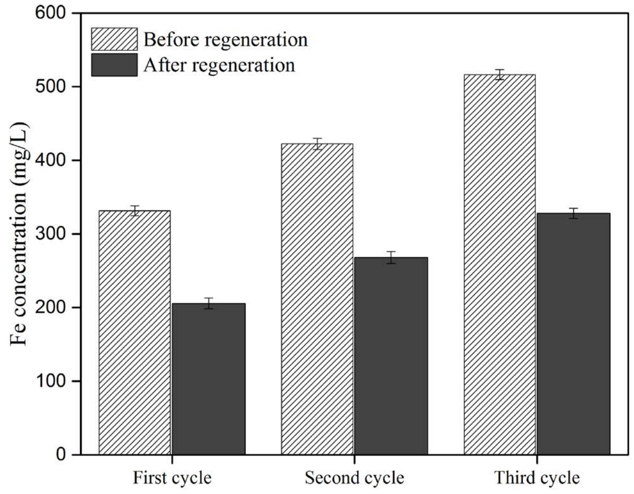

Fig. 3. Variation Fe concentrations in solutions during regeneration.

aided in AC's adsorption capacity and provided the sites for iron precipitation to re-accumulate.

It was significant that the distribution of iron precipitation occurred not only on AC's surface, but also diffused into the inner parts of AC (Table 3). However, as shown in the second and third regeneration cycles (Table 3), iron precipitation only accumulated on the surface of AC after regeneration, which might have aided in the deterioration of AC's surface and resulted in the destruction of AC's pore structures.

Overall, iron precipitation accumulated and carbon deterioration occurred during AC's adsorption/regeneration process. Carbon deterioration resulted in carbon loss and the exposure of new carbon at the surface, however, AC's adsorption capacity did not increase.

3.2. Interactions of contaminants, oxidants and AC

Chloride (Cl) content can represent the distribution of TCE sorbed on AC. In the original AC, Cl concentration was relatively low, and it increased from 0.17% to 0.28% through the adsorption process (Table 2)—theoretically, the removal of TCE during the regeneration process led to this Cl content decrease. However, Cl contents in the first and second regeneration cycles increased significantly (Table 2). This phenomenon might have been attributed to the fact that the adsorbed TCE was much higher than oxidized TCE during the first and the second regeneration cycles, resulting in the increase of Cl contents on AC's surface, as shown in Fig. 4a.

Since the adsorbed TCE was mainly distributed on AC's surface and inner parts, the proportion of TCE on different parts of AC during the adsorption/regeneration process was

Table 3
Distribution of Fe elements

Depth (nm)	Saturated AC (%)	First cycle AC (%)	Second cycle AC (%)	Third cycle AC (%)
0	0.23	2.15	2.03	2.71
20	0.78	0.74	0.00	0.00
40	0.00	0.84	0.00	0.00
60	0.00	0.90	0.00	0.00
80	0.94	0.96	0.00	0.00
100	0.87	0.91	0.00	0.00

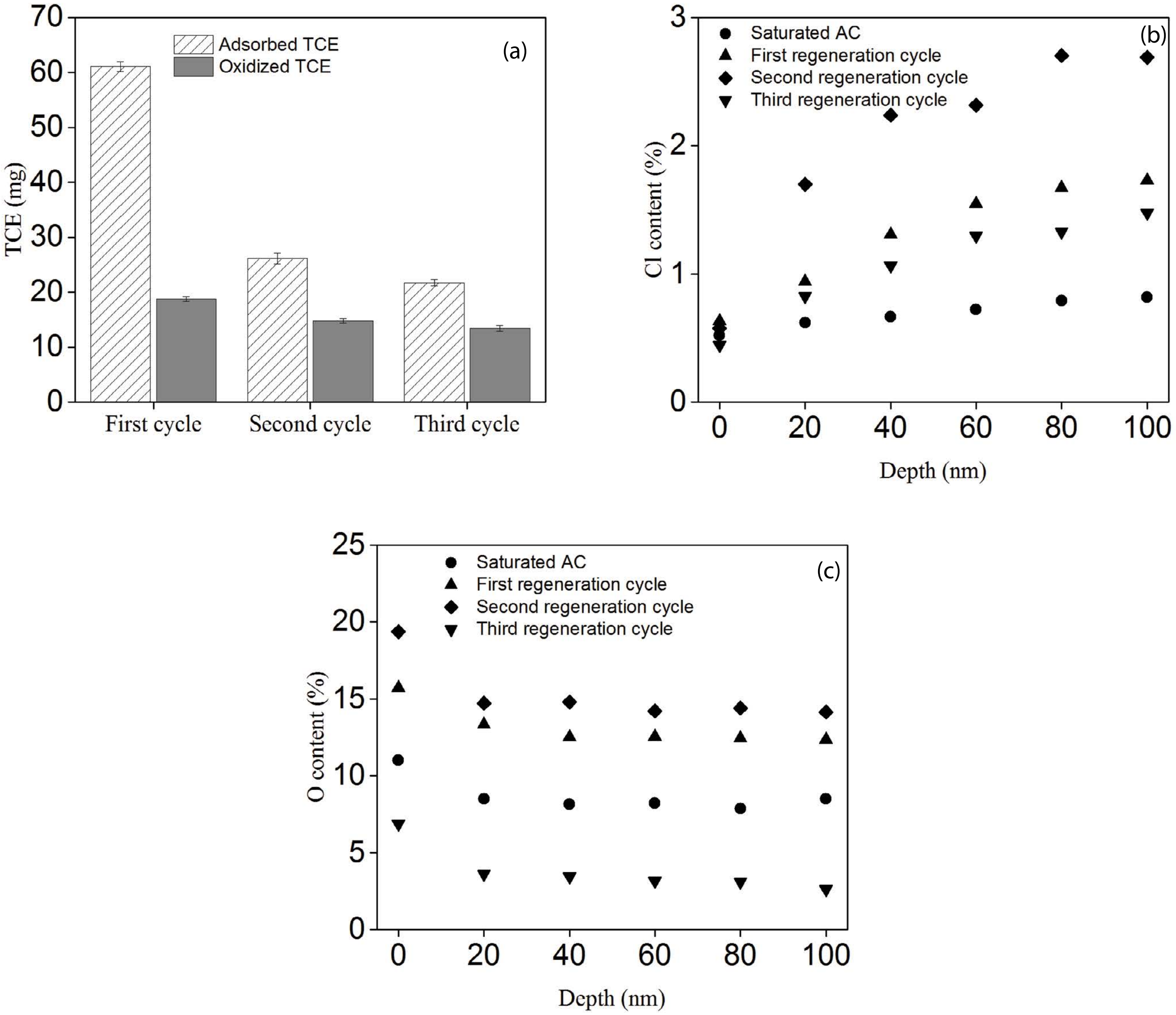

Fig. 4. Adsorbed and oxidized TCE amount (a), distribution of TCE in AC (b), distribution of O in AC (c).

a key factor in evaluating regeneration efficiency. Overall, the distribution of TCE concentration increased from the surface to the inner parts (Fig. 4b), suggesting that TCE was mainly distributed in AC's inner parts. It could also be observed that Cl contents increased significantly in the first and second regeneration cycles, especially in the inner (0–100 nm) parts. In comparison with the increased Cl on the surface, which indicated that the removal of TCE occurred mainly on AC's surface rather than the inner parts, the decrease of Cl content in the third regeneration cycle might have been due to the deterioration of AC surface, resulting in a decrease in adsorbed TCE and carbon loss.

Because of the oxidation regeneration process, O contents (elemental O) increased significantly in the first and second regeneration cycles. The distribution of O contents indicated that since O contents on AC's surface were higher than that in the inner parts, the oxidants mainly acted on AC's surface (Fig. 4c). Even so, it seemed that the oxidants still acted on the inner parts of AC, which was supported by the increase of O contents (in the depth of 20–100 nm) in the first and second regeneration cycle. The decrease of O contents in the third regeneration cycle signified that the deterioration of AC had occurred. On the other hand, the oxidized products could block pores and that prevented continuous penetration of oxidants later in the regeneration cycles.

In general, TCE concentrations increased from the surface to the inner parts of AC and the removal of TCE mainly occurred on its surface. Oxidants acted on both the surface and inner parts of AC, however, as aforementioned, the deterioration of AC and the removal of TCE mainly occurred on the surface.

4. Conclusion

Oxidant-regeneration of AC may be a destructive process that could result in the deterioration of AC. Since ferrous iron is commonly used as the catalysis for oxidation such as Fenton's reaction, the precipitation of oxidized iron tend to accumulate on the AC. However, it can be partially removed along with the carbon deterioration. Adsorbed TCE distributes on both the surface and inner pores of AC. The interactions of oxidants and AC mainly occur on the surface of AC, resulting in its deterioration and release of certain sorbed constituents, such as oxidized iron, and expose fresh carbon to the surface. However, such emergence of the fresh carbon to the AC surface does not seem to increase the AC adsorption capacity.

Acknowledgments

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