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Removal of metals and organics in a chemical decontamination process solution: Laboratory and semi-pilot scale experiments

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Abstract

In this study the system of adsorbents and an oxygen source was considered in order to remove metal species and organic compounds existing in a chemical decontamination process solution. It was observed in the laboratory experiments that adsorption and degradation of metal species and organic compounds were dependent on the solution pH value. The results of the semi-pilot scale decontamination experiments showed that metal species were removed mostly by adsorption on the surface of the adsorbent, while organic compounds were degraded by the chemical oxidation of radical reaction in the presence of hydrogen peroxide. It was shown in the laboratory and the semi-pilot scale experiments that metal species and organic compounds could be removed by adsorption and chemical oxidation using an oxygen source (H_2O_2) with adsorbent (activated carbon) with high removal efficiencies.

Keywords: Activated carbon; Adsorption; Degradation; Decontamination process

1. Introduction

Organic compounds and metal species are found in many effluent streams including industrial effluents, wastewater, chemical process streams and others [1–3]. Biodegradation is one of the methods generally employed for degradation of organic compounds and their complexes of metal species. However, it was reported that their degradation rates were low in the mild experimental conditions [4,5]. Chemical oxidation or chemical conversion is considered as one of the alternatives for enhancement of degradation rates of organic compounds using chemical oxidants. Of chemical oxidants, hydrogen peroxide is accepted as one of the effective ones due to decomposition by highly reactive radicals in the presence of iron salts and/or supported iron oxides. The hydroxyl radical is believed to be an intermediate product of the interaction of hydrogen peroxide with ferrous and ferric ions and iron oxides on the surface of activated carbon [6,7]. Since activated carbon is a carbonaceous material having a high porosity and a high surface area, they have been extensively used as catalyst/catalyst support as well as adsorbent in a variety of industrial and environmental applications (i.e., the purification and chemical recovery operations as well as removal of organic compounds and metal species) [2,8–12].

The study focuses on the removal of metal species and organic compounds existing in decontamination process solution. Decontamination means the removal of contaminated oxide films or oxide deposits from the surfaces of pipes, pumps, valves and heat exchangers in the various systems of water-cooled reactors such as pressurized water reactor (PWR) and boiled water reactor (BWR). Decontamination methods are classified with three types, i.e., electrical, chemical or mechanical one. Of methods, chemical decontamination is considered to be the most effective method [13]. The process involves dissolution of the radioactive contaminants themselves or the matrix (oxide films or deposits), which are trapped by chelating agents. Proper chemical decontaminating agents consisting of ethylenediaminetetraacetic acid (EDTA) and oxalic acid are often used to remove metal oxides such as magnetite (Fe_3O_4), nickel ferrite ($NiFeO_4$), hematite (Fe_2O_3) and chromium oxides in the chemical decontamination methods [14,15].

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The chemical decontamination process in the previous study was developed for decontamination of components in the PWRs in Korea, which consists of four consequent steps including oxidation, reduction, dissolution and decomposition/cleanup steps. The metal oxides consisting of Fe, Cr and Ni were synthesized based on the metal compositions existing in the primary systems of a Korean PWR for the development of the chemical decontamination process [14]. In the oxidation step, the oxidant mixture of $KMnO_4$ and H_3PO_4 dissolves mainly oxides of chrome among metal oxides as the first step of the chemical decontamination process.

The products of MnO_2 and $HMnO_2$ are reduced in the subsequent step (the reduction step). In order to dissolve metal oxides, the chemical decontaminating agents are used in the dissolution step, one of the important ones to determine the effectiveness of the chemical decontamination process [13].

As a final step in the chemical decontamination process, dissolved oxides of metal species and organic compounds existing in the chemical decontaminating agent are removed in the decomposition/cleanup step. In order to increase the effectiveness of the chemical decontamination process, it is necessary to remove remaining organic compounds and metal species in the process solution. Of commercialized decontamination processes, organic compounds and metal complexes are decomposed by hydrogen peroxide and UV source in the chemical oxidation reduction decontamination (CORD) process [13]. In the developed decontamination process, organic compounds and their metal complexes in the chemical decontamination process are removed by adsorption and chemical degradation in the presence of an oxygen source (hydrogen peroxide) on the surface of adsorbent (activated carbon) [10]. It is suggested that the chemical reaction rate increases due to radical reaction during the decomposition step [3]. In the present study, the adsorption tendencies and removal of metal species and organic compounds were investigated in the laboratory experiments. And, their removal efficiencies were estimated through chemical decontamination experiments using a semi-pilot scale equipment.

2. Experimental

The adsorption isotherm of Fe was investigated in this study since it has the highest concentration level among three metal components (Fe, Cr and Ni) existing in the synthesized metal oxides [14]. Adsorption on activated carbon was measured at a room temperature by increasing initial concentration as a form of $Fe(NO_3)_3{\cdot}9H_2O$ [16]. The adsorption competition experiments for metal species were carried out with increasing Fe(III) concentration at a constant concentration of Cr(III) and Ni(II) (0.02 M). Both solutions of Cr(III) and Ni(II) were prepared by using corresponding nitrate forms, $Cr(NO_3)_3{\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$, respectively. The pH effects of the amount of adsorption on the activated carbon were investigated within the pH ranges between 2.5 ± 0.2 and 5.5 ± 0.2. In addition, different concentrations of $Na_2EDTA{\cdot}2H_2O$ were prepared for the equilibrium isotherm experiments of organic compounds. Degradation experiments of organic compounds were carried out in the presence of H_2O_2 or H_3PO_4. All the chemicals for the above laboratory experiments were purchased from Aldrich, USA.

Table 1
Experimental conditions for the semi-pilot scale chemical decontamination process

Process step	Experimental condition	pH range	
		Initial	Final
Oxidation step	$KMnO_4$ 70.2 g (0.05%) H_3PO_4 63 cm^3 (0.025%) Metal oxide 30.3 g	2.1	2.5
Reduction step	Oxalic acid 281.3 g (0.2%)	2.3	2.5
Dissolution step	Na_2EDTA 702.2 g (0.5%) Oxalic acid 284.6 g (0.2%)	2.6	2.7
Decomposition/cleanup step			
Decomposition	Activated carbon 5 L	2.4	2.8
Cation exchange	DOWEX 650 C 5 L	1.8	2.9
Anion exchange	DOWEX 550 A 5 L	2.5	6.1

The semi-pilot scale decontamination equipment was operated with the experimental conditions, shown in Table 1. Operation volume of the reaction tank in the equipment is 140 L. Detailed specifications of the equipment are found elsewhere [17]. All the chemicals for the equipment experiments were obtained from Junsei Chemical, Japan. The chemical decontaminating agent consisting of Na_2EDTA and oxalic acid were used in order to dissolve metal oxides consisting of Fe, Cr and Ni during the dissolution step of the decontamination process. In addition, 0.03 wt% of hydrogen peroxide was supplied in the presence of H_3PO_4 and the solution was circulated through the activated carbon tower in the decomposition step. The industrial grade granular activated carbon was used as adsorbent in the activated carbon tower for the decomposition step. The ion exchange resins, DOWEX 650C and 550A, were purchased from Dow Chemical, USA as forms of H^+ and OH^-, respectively.

The surface properties of activated carbon were characterized from nitrogen adsorption isotherm at 77 K using a Micromeritics ASAP 2010 [18]. Concentration of organic compounds was analyzed with total organic carbon using a total organic carbon analyzer, Multi N/C 3000 (Analytik Jena AG, Germany) after filtration with 0.45 μm membrane filters. Also, concentrations of metal species were analyzed using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES), Optima 4300 DV Perkin-Elmer. The deposition of metal species on the adsorbent surface was observed using an energy dispersive X-ray (EDX) analytical spectrometer (Kevex Sigma Gold, USA) connected to a field emission scanning electron microscope (S-4700, Hitach, Japan).

3. Results and discussion

3.1. Physical properties of the activated carbon and adsorption isotherms

The surface properties of the activated carbon were characterized with nitrogen adsorption and the adsorption–desorption

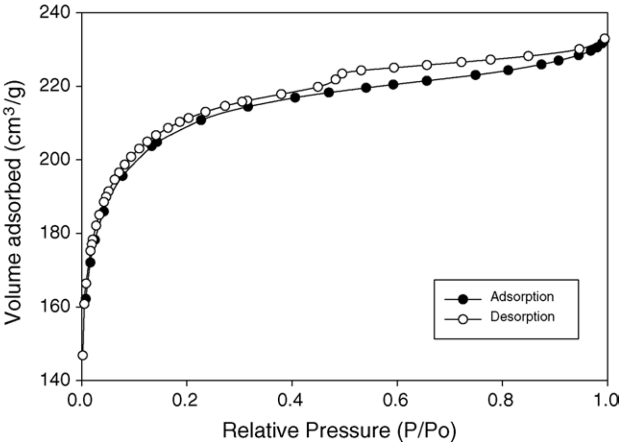


Fig. 1. N_2 adsorption–desorption isotherms for the fresh activated carbon.

isotherm is shown in Fig. 1. The curve in the figure resembles the type I isotherm according to the BDDT (Brunauer, Deming, Deming and Teller) theory. It is known that the major uptake occurs at low relative pressures due to formation of highly microporous materials [19–22]. Difference between adsorption and desorption isotherms was observed at the relative pressure (p/p_o) of 0.4. The characteristic values related to surface properties were summarized at the column of AC0 in Table 2. As shown in the table, the surface area of the microstructure of the activated carbon was 1.81 nm by the BET isotherm. Also, the micropore surface area was estimated as 797 m^2/g.

Of three metal species, the adsorption amount of Fe on the activated carbon was measured and the adsorption isotherm of Fe was described using the Freundlich equation. The Freundlich equation for the equilibrium isotherm is

$$q_e = k(C_e)^{1/n} \tag{1}$$

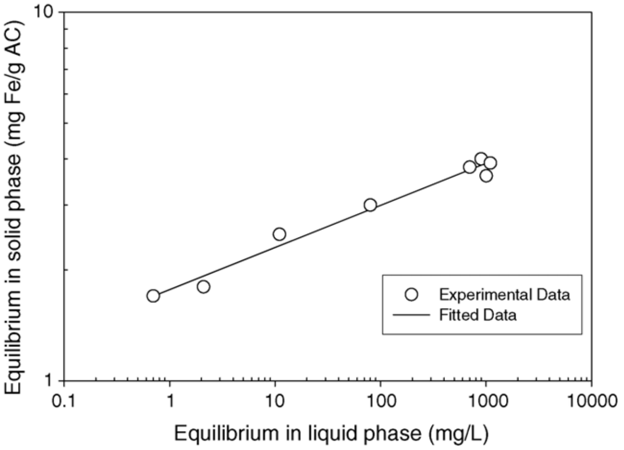
$$\ln q_e = \ln k + \left(\frac{1}{n}\right) \ln(C_e) \tag{2}$$

where q_e is the adsorbed amount on unit weight of adsorbent (mg/g AC), C_e the equilibrium concentration in the liquid (kg/m^3) and k and $1/n$ are the Freundlich constants. The result of the adsorption isotherm for Fe is shown in Fig. 2(a). From the fitted curve, the value of k and $1/n$ was determined to 1.40 and 0.18, respectively. In the results of the isotherm of organics in the solution of Na_2EDTA, the adsorption isotherm of organics was also fitted the Freundlich equation, as shown in Fig. 2(b).

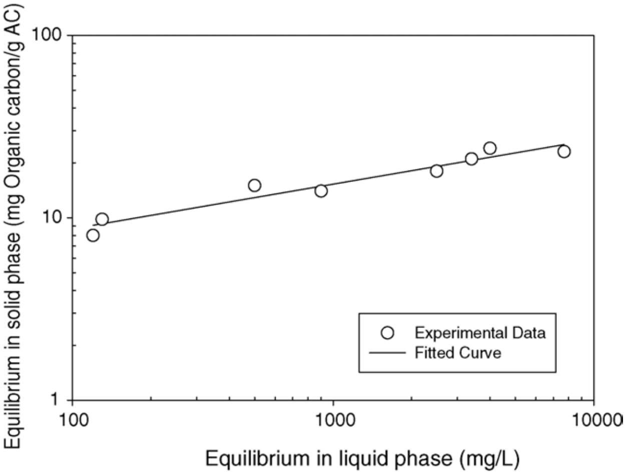
Table 2
Characteristic values for surface properties of activated carbon

	AC0[a]	Used AC[b]
Area		
BET surface area (m^2/g)	797	678
Micropore surface area (m^2/g)	782	666
External surface area (m^2/g)	14	13
Pore diameter (BET) (nm)	1.81	1.80
Pore volume (BET) (cm^3/g)	0.33	0.28

[a] AC0: fresh activated carbon.
[b] Used AC: activated carbon used in the decomposition step.



(a) Fe



(b) Na_2 EDTA

Fig. 2. Adsorption of: (a) Fe and (b) Na_2EDTA on the activated carbon.

The Freundlich constants, k and $1/n$, were estimated to be 2.04 and 0.28, respectively.

3.2. Adsorption and degradation of metals and organic compounds

The pH effects on the adsorption of a metal species (Fe) were investigated and the results are shown in Fig. 3. The amount of Fe adsorption on the adsorbent increased with increasing pH values, the adsorbed amount of Fe being dependent on the solution pH. The least adsorption amount was observed as 2.4 mg Fe/g AC at the pH value of 2.5. It is thought that the lesser amount adsorbed at acidic pH values in the figure is related to increase in competition between protons and metal species for the surface sites of the activated carbon [23,24].

It is known that the adsorption of metal species can be affected by different metal species as well as the solution pH [24]. The adsorption aspect of Fe on the activated carbon was investigated in the both binary systems of Fe/Cr and Fe/Ni and the results are shown in Fig. 4. The adsorption amount of Fe increased with increasing the equilibrium concentration of liquid phase. In the case of Cr and Ni, their adsorption amounts decreased

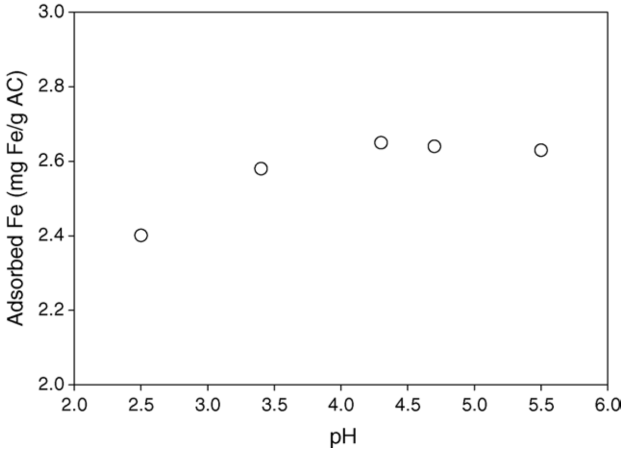


Fig. 3. Adsorption of Fe on the activated carbon as a function of the solution pH.

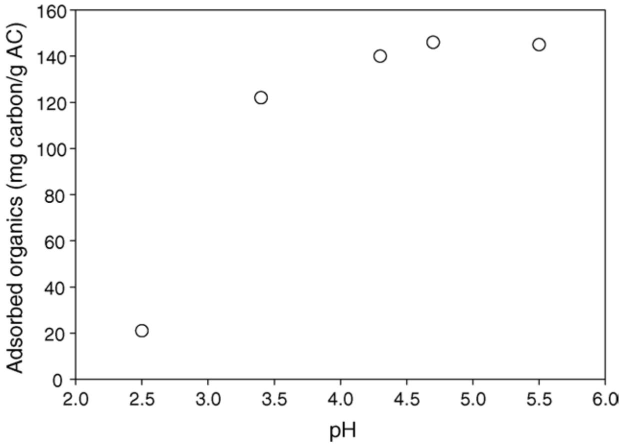


Fig. 5. Adsorption of organic compounds on activated carbon as a function of the solution pH.

with increasing concentration of liquid phase. It is interesting that the adsorbed amount of Cr and Ni on the activated carbon was the least (0.2 mg/g AC) when the equilibrium of Fe in the liquid phase was increased up to 1000 mg/L. The results imply that Fe has the highest adsorption capacity independent of metal species in the solution, which may be related to the highest charge density among three metal species [25].

Fig. 5 showed the adsorption tendencies of Na_2EDTA with different pH values. A significantly lower adsorbed amount of organic compounds was observed when the solution pH became acidic. Different adsorption of EDTA on the adsorbent according to solution pH conditions can be understood by consideration of the different chemical properties of EDTA. That is, the specific adsorption of anionic type with one or several functional groups of EDTA is bounded by formation of the inner-sphere complexation with adsorbent. The small adsorption of EDTA at low pH values is related to a binuclear complex with proton. Meanwhile, the adsorbed amount increased with increasing pH values, which can be explained by a mononuclear complex [26–28].

The effects of H_2O_2 and H_3PO_4 concentrations on the degradation of organic compounds were investigated with increasing concentrations and the removal efficiencies of organic compounds are shown in Fig. 6. The removal efficiency increased with increasing H_2O_2 concentrations increased up to 0.3 wt% at a constant concentration of H_3PO_4 (0.025 wt%) and the values remained at 55% even with increasing concentrations (see Fig. 6(a)). Also, organic removal efficiency with increasing concentration of H_3PO_4 was estimated at a concentration of H_2O_2 (0.3 wt%), and the results are shown in Fig. 6(b). The degrada-

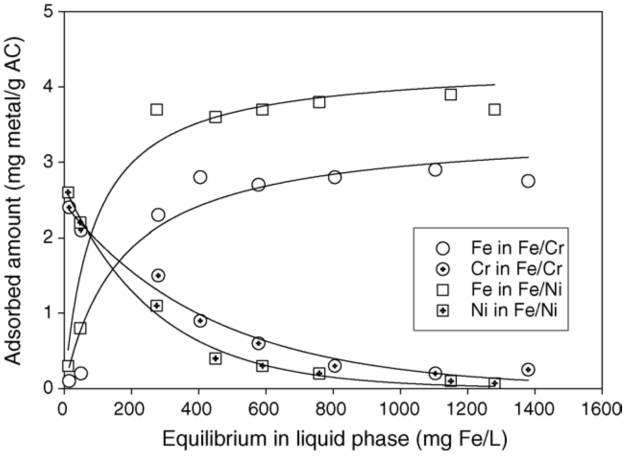


Fig. 4. Fe adsorption behaviors on the activated carbon in both binary systems.

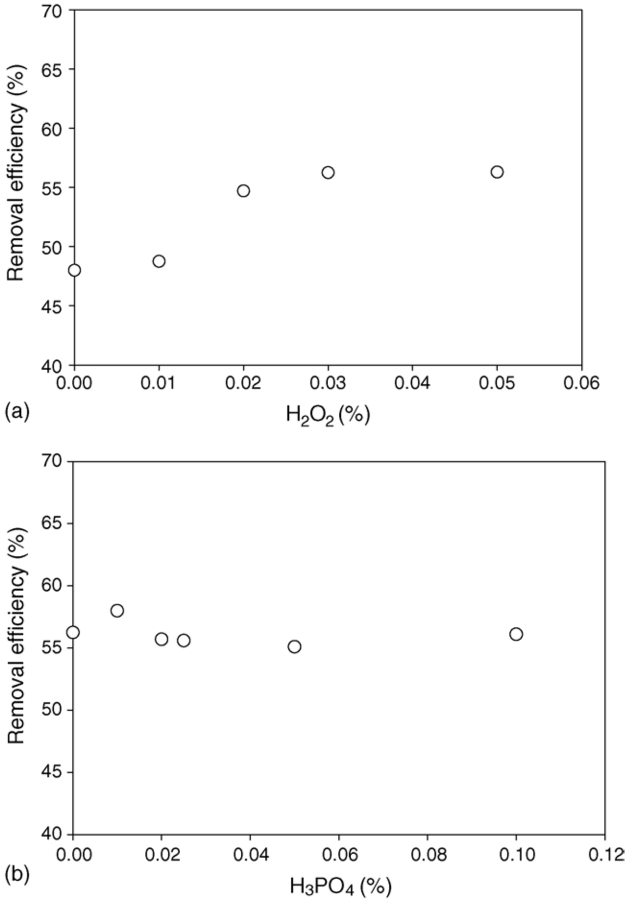


Fig. 6. Influence of: (a) H_2O_2 and (b) H_3PO_4 concentrations on the organic compound removal.

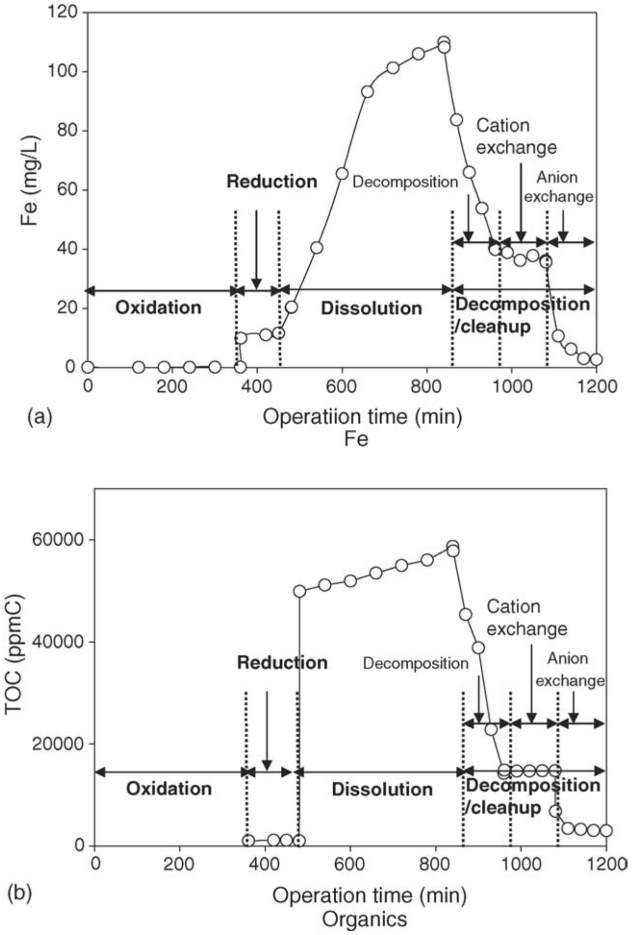


Fig. 7. Concentration changes of: (a) Fe and (b) organics during the semi-pilot scale decontamination experiment.

tion aspects showed the independency of the acid concentration, the value representing a similar value as 56%. The results imply that the organic removal could be enhanced by an oxygen source (H_2O_2) in acidic conditions and that it was affected by concentration of H_2O_2 rather than H_3PO_4.

3.3. Semi-pilot scale decontamination experiments

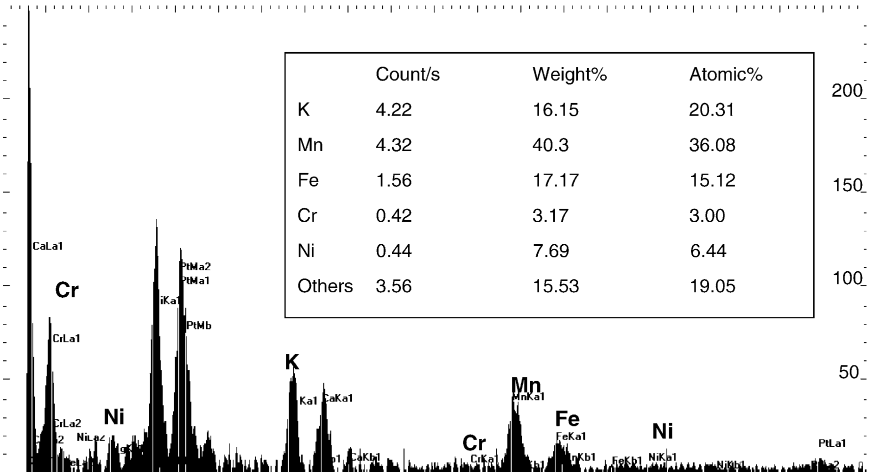
After the adsorption and degradation aspects of metal species and organic compounds were investigated through the laboratory experiments, the chemical decontamination experiments were performed in the semi-pilot scale decontamination equipment with four consequent steps (oxidation, reduction, dissolution and decomposition/cleanup step). During the semi-pilot operation, changes of metal species and organic compounds were observed with elapsed operation time. Fig. 7(a and b) illustrates concentration changes of Fe and organics for four consequent steps. The dissolved concentration of Fe increased by a reductant (oxalic acid) as a form of oxalate metal complex (see Fig. 7(a)) after Fe was slightly dissolved in the oxidation step. Then, Fe concentration increased up to maximum concentration (109.9 mg/L) in the dissolution step. In the following decomposition step, it decreased to 40.3 mg/L showing a removal efficiency of 63.3%. Furthermore, the remaining metals and metal complex with organics were removed using cation exchange and anion exchange resins. The final concentration of Fe was measured at 2.7 mg/L, the total removal efficiency representing 97.5%. In the case of organic compounds, oxalic acid was supplied as a reductant in the reduction step and then the decontaminating agent during the dissolution step, showing the dissolved concentration to be 59,500 ppm C (see Fig. 7(b)). Also, the dissolved organics were removed in the decomposition step using H_2O_2 and activated carbon. The removal of organic compounds was 75.0% in the decomposition step and 95.0% in the total chemical decontamination process.

Table 3
Removal efficiencies of metal species in the semi-pilot scale experiments

	Metal species				
	Fe	Cr	Ni	K	Mn
Concentration (mg/L)					
Dissolution step, at final	109.9	24.6	13.9	245.4	243.5
Decomposition step, at final	40.3	14.4	8.1	204.6	225.1
Removal efficiency (%)					
Decomposition step	63.3	37.2	41.5	16.7	7.5
Total	97.5	97.9	99.5	92.9	99.8

Table 3 shows the removal of metal species in the decomposition step and the total decontamination process based on the results of the semi-pilot scale decontamination experiments. The total removal efficiencies of all the metal species except for K represented up to 97% or more in the decontamination process. The metal species of Fe showed the highest value (63.3%) during the decomposition step, while those of Cr and Ni were 37.2 and 41.5%, respectively. The highest removal efficiency of Fe is expected from the highest adsorption capacity, shown in Fig. 4. Adsorption on the surface of activated carbons can be estimated based on laboratory experiments shown in Fig. 3. The estimated result at the solution pH of 2.5 shows that 7855 mg of Fe in the operation volume was removed during the decomposition step, which is 94.1% of the total removed amount. It was shown in the results that most of metal species were removed mainly be adsorption on the surface of the activated carbon. The adsorption of metal species on the activated carbon after the decomposition step was observed using the SEM-EDX and the result is shown in Fig. 8.

In the case of the organic compounds, 75.0% were removed during in the decomposition step and the removal efficiency of the total chemical decomposition process was 95.0%. Considering the adsorbed amount at pH 2.5 based on the laboratory experiment in Fig. 5, the estimated result shows that only 0.9% of total organic carbons were removed by adsorption on the adsorbent surface during the decomposition step. It is suggested that the organic compounds were removed mostly by chemical oxidation followed by decomposition of gases, even though compositions and concentrations of gas components were not measured during the semi-pilot scale decontamination experiments. It is assumed that the chemical reaction enhanced due to the production of hydroxyl radicals in the presence of Fe during the decomposition step after adsorption on the surface of the activated carbon [3,4].



	Count/s	Weight%	Atomic%
K	4.22	16.15	20.31
Mn	4.32	40.3	36.08
Fe	1.56	17.17	15.12
Cr	0.42	3.17	3.00
Ni	0.44	7.69	6.44
Others	3.56	15.53	19.05

Fig. 8. SEM-EDX image showing adsorption of metal species on activated carbon.

It was shown through the laboratory and semi-pilot scale experiments that the metals and organic compounds could be removed by adsorption on the surface and chemical conversion using an oxygen source and adsorbents. The adsorption of metal species and organic compounds on the surface on the adsorbent can affect the surface properties, especially the microporous structures [4]. The second and third columns in Table 2 represent the activated carbon surface characteristic values (the surface area, pore diameter and pore volume) between the fresh activated carbon (AC0) and the activated carbon used in the decomposition step (used AC). The results showed that adsorption of the metal species and organic compounds changed the surface properties of the activated carbon, thus reducing surface area, pore diameter and pore volume. The total surface area was reduced from 797 to 678 m^2/g after the decomposition step. In addition, the surface area and the volume of microporous structures were decreased compared with the characteristic values of the fresh activated carbon.

It was observed through the semi-pilot scale decontamination experiments that metal species in the chemical decontamination process solution were removed by adsorption on the surface of the activated carbon, while organic compounds were degraded by chemical conversion. In the study, the remaining metal species and organic compounds in the chemical decontamination process solution were removed up to values above 95% in the system of H_2O_2 and activated carbon, thus increasing the effectiveness in the decontamination process.

4. Conclusions

In this study, the system of an oxygen source (hydrogen peroxide) with an adsorbent (activated carbon) was considered to remove metal species and organic compounds existing in the chemical decontamination process through the laboratory and semi-pilot scale experiments. Adsorption and degradation of metal species and organic compounds in the laboratory experiments were dependent on the solution pH values. The results of the semi-pilot scale decontamination experiments represented that most of metal species of the chemical decontamination process were removed by adsorption on the surface of the activated carbon. Meanwhile, organic compounds were degraded by chemical conversion due to radicals in the presence of hydrogen peroxide. The results of the laboratory and the semi-pilot scale experiments showed that metals and organic compounds existing in the chemical decontamination process solution could be removed by adsorption of adsorption/chemical conversion using hydrogen peroxide with activated carbon.

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