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Reformation of the surface of powdered activated carbon (PAC) using covalent organic polymers (COPs) and synthesis of a Prussian blue impregnated adsorbent for the decontamination of radioactive cesium

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ABSTRACT

Prussian blue (PB) is known to selectively adsorb cesium (Cs), with a high adsorption efficiency. However, it is difficult to collect it after adsorption, which increases the risk of secondary environmental pollution. In this study, covalent organic polymers (COPs) were used to reform the surface of powdered activated carbon (PAC) particles in order to stably immobilize PB, with the aim of developing an adsorbent impregnated with PB (COP-PAC-PB). PAC particles reformed with COPs (COP-PAC) were analyzed using TEM (EDS) and FT-IR techniques, and it was found that COPs were successfully synthesized on the surface of COP-PAC particles. COP-PAC-PB particles were synthesized by reacting PAC particles with iron(III) chloride and potassium ferrocyanide solutions in order, to synthesize PB within the pores of COPs (in situ). COP-PAC-PB particles were analyzed using XRD and FT-IR techniques, and peaks showing the general characteristics of PB were observed, which indicated that PB existed on the surface of COP-PAC-PB particles. PB was synthesized on the surface of the non-reformed groups (PAC and Ox-PAC) using the same method. In addition, UV-vis analysis was performed to compare the characteristics of PB desorbed from the non-reformed and reformed groups immediately after synthesizing and washing them. In the non-reformed groups (PAC-PB and Ox-PAC-PB), a large amount of PB was desorbed while they were washed 6 times. For COP-PAC-PB, however, a small amount of PB was desorbed during the first washing, but no desorbed PB was observed thereafter. The maximum Cs adsorption capacity of COP-PAC-PB particles was 19 mg/g, and its removal efficiency of radioactivity cesium (Cs-137, 60 Bq/kg) was 97.3%. In this study, the surface of PAC particles was effectively reformed using COPs, and an adsorbent to which PB was stably immobilized was developed.

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1. Introduction

Recently, a series of earthquakes hit Gyeongju and Pohang in North Gyeongsang Province. As these occurred near nuclear power plants in the region, concerns over the potential for a Fukushimatype nuclear disaster [1] have been raised. In addition, considering that the Republic of Korea is located in Northeast Asia, which is home to a dense cluster of nuclear power plants, it is inevitably

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vulnerable to potential accidents that might occur in nuclear power plants in neighboring countries, creating another source of anxiety [2]. Once radioactive contamination occurs due to an accident in a nuclear power plant, water sources can become contaminated, which may paralyze a state's function; as such, thorough measures to protect water sources are required [3]. Cesium (Cs), one of the radionuclides that are artificially produced in experiments or nuclear reactors, emits a high level of gamma rays (γ), has high solubility, and its half-life is approximately 30 years [4,5]. Once cesium is absorbed into the body, hardly any of it is excreted from the body; it instead remains in muscle tissue, where it poses a deadly threat [6,7]. Methods such as ion exchange, membrane filtration and reverse osmosis are applied to eliminate cesium, but these require additional facilities and result in high maintenance costs [8–10]. It







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is, therefore, necessary to develop practical alternatives. Adsorption has been recognized as an economically feasible method of eliminating particulate cesium dissolved in water in a way that is quick and efficient [10-12]. Research into the development of adsorbents using materials such as natural clay minerals and Prussian blue has been active [13-15].

Among them, Prussian blue (PB), a cheap dark blue pigment, is known to have a high cesium adsorption efficiency, and selectively adsorbs cesium [16,17]. PB has a lattice structure that is similar in appearance to a jungle gym, and it is included in the cyano group. It has metal ions, and K+ ions are included in the lattice structure. As the radius of dissolved cesium ions in water (1.19 Å) is similar to that of K+ ions in the lattice of Prussian blue (1.25 Å), cesium can be selectively adsorbed through selective ion exchange [18,19]. In addition, dissolved cesium ions can be easily adsorbed within the lattice of Prussian blue filled with water molecules joined with a coordinate bond. However, since PB forms colloids in water, it is difficult to collect it after adsorption [20]. To address this issue, research has been conducted into immobilizing and synthesizing PB into certain scaffolds, including alginate, non-woven fabric, chitin sponge and carbon nanotube [21–24]. However, these methods of immobilizing PB reduce the adsorption performance due to the desorption of PB that is immobilized on the surface of scaffolds or captured within them, and cyano compounds cause secondary environmental pollution [25,26]. Earlier studies on the immobilization and synthesis of PB so far have not been focused on desorption. For this reason, it is necessary to conduct research on stable immobilization to prevent PB that is synthesized on the surface of or within adsorbents from being desorbed.

In general, as activated carbon is cost-effective and has a high adsorption efficiency, it has been used as an agent to adsorb pollutants [27–32]. In addition, activated carbon synthesized with materials such as cellulose/Fe3O4, chitosan and polyacrylonitrile is used as an adsorbent to selectively remove certain pollutants [33–35]. Recently, researchers have sought methods of expanding the specific surface area of activated carbon particles by using covalent organic polymers (COPs) that show stability in extreme environments, such as high temperature environments [36]. COPs are high molecules that have a chain structure, and they can be synthesized through the phased exchange reactions of hexahydrotriazine and cyanuric acid chloride, and the immobilization of aromatic nitro and aliphatic amine. Adsorbents of which the surface has been reformed using COPs are synthesized to have a netlike surface on which nanometer-sized pores exist. The adsorbents reformed through this process have a sufficient adsorption surface area. These adsorbents reformed with COPs have a broad specific surface area, and their performance in adsorbing, purifying and storing gases, and adsorbing dissolved materials has been proved [37-39]. In particular, Paul D. Mines (2017) successfully synthesized COP-19 on the surface of granule activated carbon (GAC) particles, and used GAC as an adsorbent for azo dyes, cadmium and iron ions [40].

Thus, in this study, PB that can selectively remove radioactive cesium and COPs were synthesized on the surface of PAC particles. In addition, the adsorption and elution characteristics of PB that was immobilized using COPs were analyzed in order to develop an adsorbent for the rapid and efficient decontamination of radioactive pollutants in water supply sources.

2. Materials and methods

In this study, the surface of powdered activated carbon (PAC) particles was reformed into COP-PAC using covalent organic polymers (COPs), and COP-PAC particles were reacted with iron(III)

chloride and potassium ferrocyanide solutions in order, to synthesize COP-PAC-PB.

2.1. Materials

To synthesize COP-PAC, the following reagents were used: PAC (SAMCHUN), nitric acid (SHOWA, HNO₃, 60%), sulfuric acid (SAM-CHUN, H₂SO₄, 33%), dichloromethane (SAMCHUN, CH₂Cl₂, 99%~~), thionyl chloride (DAEJUNG, SOCl₂, 99%), melamine (SAMCHUN, C₃H₆N₆, 99%), dimethyl sulfoxide (SAMCHUN, (CH₃)₂SO, 99%), diisopropylethylamine (SAMCHUN, C₃H₁₉N, 99%), terephthalaldehyde (Sigma aldrich, C₆H₄(CHO)₂, 99%), acetone (C₃H₆O, 99%) and ethanol (SAMCHUN, C₂H₆O, 70%). To synthesize COP-PAC-PB, iron(III) chloride (SAMCHUN, FeCl₃, 97%) and potassium ferrocyanide (SAMCHUN, K₄Fe(CN)₆· 3H₂O, 99%) solutions were reacted in order *in situ*. CsCl (SAMCHUN, 99%) was used in an adsorption experiment, and Cs-137 (radioactive cesium) was obtained from a standard source solution certified by the Korea Research Institute of Standards and Science (KRISS).

2.2. Synthesis of COP-PAC and COP-PAC-PB

2.2.1. Preparation of PAC reformed with covalent organic polymers (COP-PAC)

Powdered activated carbon (PAC) particles of which the surface was reformed with covalent organic polymers (COP-PAC) were synthesized following the four stages suggested in an earlier study [40]. The first step was to react 20 g of PAC for 24 h in 500 mL of the mixture with 40% nitric acid and 45% sulfuric acid at a ratio of 3 to 1. The reacted PAC was washed with a large volume of distilled water until it reached a neutral pH, and the solution was dried at 110 °C in a vacuum oven for 12 h to synthesize Ox-PAC. The second step was to inject 2.5 g of Ox-PAC into a solution mixed with 400 mL of dichloromethane and 100 mL of thionyl chloride, and to react the solution at 35 °C for 24 h. After that, the solution was rotated and evaporated using a rotary evaporator in order to obtain Thio-PAC from the synthesized compound. The third step is to immediately react 2.5 g of Thio-PAC in a solution mixed with 150 mL of melamine, 2.5 mL of dimethyl sulfoxide, and diisopropylethylamine (melamine was completely dissolved in the solution using an ultrasonic injection method in a water bath), and to react the mixed solution in nitrogen gas at 120 °C for 24 h. Through solid-liquid separation, the PAC particles were washed with dimethyl sulfoxide, triple distilled water and ethanol (three times with each solution), and dried at 110 °C in a vacuum oven for 12 h to synthesize Mel-PAC. In the last step, 500 mg of melamine and 800 mg of terephthalaldehyde were mixed with 150 mL of dimethyl sulfoxide and were completely dissolved through ultrasonic treatment in a water bath in order to synthesize COP-PAC by grafting COPs to PAC particles. After that, 1000 mg of Mel-PAC was mixed with the mixture solution and reacted in nitrogen gas at 150 °C for 48 h. The synthesized COP-PAC was separated from the solution, and was thoroughly washed with dimethyl sulfoxide, acetone, triple distilled water and ethanol in order (three times with each solution). After that, the COP-PAC was dried at 110 °C in a vacuum oven for 12 h.

2.2.2. Prussian blue synthesis and desorption of the reformed PAC group (COP-PAC-PB) and the non-reformed PAC groups (PAC, Ox-PAC)

The PB synthesis method conducted *in situ* was as shown in Fig. 1. First, 5 g each of PAC, Ox-PAC and COP-PAC particles was reacted in 50 mL of iron(III) chloride (FeCl₃) and was magnetically stirred at 100 rpm for one day. The solid and liquid in the mixed solution were separated using a centrifuge (4000 rpm, 10 min).



Fig. 1. Scheme of COP-PAC-PB synthesis(in-situ) process.

After that, the separated solid was mixed with 50 mL of 20 mM potassium ferricyanide, and was reacted for 5 min. Again, the solid and liquid in the mixed solution were separated using a centrifuge (4000 rpm, 10 min), and the solid was washed with triple distilled water several times, and was dried at 60 °C in a drying oven for 6 h. To identify any desorbed Prussian blue (PB) that was synthesized on the particles of the reformed group (COP-PAC) and the non-reformed groups (PAC and Ox-PAC), the PB concentration in solutions was measured during washing and after the adsorption experiment using a UV–Vis spectrophotometer.

2.3. Characterization of COP-PAC and COP-PAC-PB

Using a transmission electron microscope (JEOL, JEM-2010, Japan) operated at 300 kV, the characteristics of the surface of PAC and COP-PAC particles were analyzed, and energy dispersive spectroscopy (EDS) and elemental analysis (Thermo, Flash2000, Germany) were also carried out to identify the content of each element that composed each adsorbent generated in each stage. XRD (Rigaku, SmartLab, Japan) and FT-IR (Thermo, Nicolet iS50) techniques were performed on samples at room temperature, and the spectrum range was 15–75 degrees and 500–3000 cm⁻¹. Using a specific surface area and pore distribution analyzer (BEL, BELSORP-max, Japan), the BET (Brunauer-Emmett-Teller) surface area and average pore size of PAC, COP-PAC and COP-PAC-PB were measured. To identify any desorbed Prussian blue (PB) that was synthesized within the pores of COPs in situ, the desorption characteristics were analyzed using a UV spectrum (BioChrom, Libara S22, USA).

2.4. Adsorption isotherm of cesium by COP-PAC-PB

Prussian blue (PB) was immobilized in situ within the nanometer-sized pores of COPs that were synthesized on the surface of powdered activated carbon (PAC) particles. Every adsorption experiment in this study was conducted at room temperature using a polypropylene falcon tube (15 mL). Using CsCl, a stock solution (1000 mg L-1) was prepared, and it was used after dilution for experiments. COP-PAC-PB (0.01-5 g) was injected to 50 mL of the Cs 10 mg L-1 (ppm) solution and reacted for 24 h, and the Cs adsorption efficiency of COP-PAC-PB was analyzed using ICP-MS (Perkin-Elmer, NexION 350D, USA). To measure the efficiency of COP-PAC-PB in terms of removing radioactive cesium (Cs-137), 200 mL of distilled water that included 600 Bq of radioactive cesium was reacted with 0.1 g of COP-PAC-PB within a radiation detection tube for 24 h. Radiation was measured using a radiation monitor (Nucare, RAD IQ FS200, Korea) in which a 3×3 inch Nal detector, an MCA and a digital MCA are equipped within a 20 mm-thick lead lined storage container.

3. Results and discussion

3.1. Characterization of COP-PAC and COP-PAC-PB

First, powered activated carbon (PAC) particles were reacted and oxidized for 24 h in mixture solution (nitric acid 3: sulfuric acid 1) to synthesize Ox-PAC. Once carboxyls are highly saturated on the surface of PAC particles, they were reacted in a solution mixed with dichloromethane (CH_2Cl_2) and thionyl chloride $(SOCl_2)$ in the ratio of 2 to 1 under the reflux, and were converted into acyl chloride substituents that are extremely reactive. The solvent used in the synthesized Thio-PAC particles was evaporated using a rotary evaporator, and the following process was immediately conducted to prevent the hydrolysis of acyl chloride caused by air or moisture. Thio-PAC was reacted with a dimethyl sulfoxide solution in which melamine was completely dissolved to synthesize Mel-PAC. In this process, the melamine created an amide bond and was grafted on the surface of activated carbon particles that were converted from carboxyls into acyl chlorides. Therefore, shell-form COPs were generated by amine groups in melamine. COP-PAC was successfully synthesized through the growth of melamine which is similar to earlier studies [40]. After synthesis, the COP-PAC was washed to remove monomers and polymers that were not synthesized on the surface of PAC particles. Fig. 2 (a), (b) show the TEM images of the powder activated carbon and synthesized COP-PAC. The analysis of the TEM images showed that PAC particles had a smooth surface. On the other hand, shell-form COPs were synthesized on the surface of COP-PAC particles. The form of the COPs that were successfully grafted on the surface of PAC particles in this study was very similar to that of the COPs used in earlier studies to synthesize GAC particles [40].

Using energy dispersive spectroscopy (EDS) and elemental analysis (EA) techniques, the presence of COPs was identified, and the results were as shown in Table 1. As predicted, PAC was mainly composed of carbon, and it was also found that the content of nitrogen in COP-PAC was very high due to the presence of COP caused by the growth of melamine. Particle analysis showed that carbon accounted for the majority of the PAC particle content, which is similar to the results of EDS analysis. The content of oxygen in Ox-PAC that was oxidized in mixture solution significantly increased, while the content of hydrogen and nitrogen only slightly increased. In the case of Mel-PAC, the content of nitrogen increased due to the grafted melamine, which can be attributed to the addition of amine groups that compose melamine. The content of oxygen slightly decreased, which seems to have been caused by melamine that replaced acyl chloride. The content of nitrogen in COP-PAC was the highest compared to other PAC types reformed in the previous stages, which can be attributed to the fact that the content of nitrogen in COP-PAC was higher than that in Mel-PAC due to terephthalaldehyde and the growth of melamine [40]. The Fourier transform infrared spectroscopy (FT-IR) of those produced in COP



Fig. 2. TEM image of adsorbents. (a) Powder activated carbon, (b) COP-PAC.

Table 1

(a) TEM(EDS) data of PAC and COP-PAC, (b) Elemetal analysis data of COP-PAC Synthesis Products of each steps.

Component	(a) TEM(EDS) analysis (%)		(b) Elemental analysis (%)			
	PAC	COP-PAC	PAC	Ox-PAC	Mel-PAC	COP-PAC
С	90.71	63.61	80.14	45.60	76.64	70.95
Ν	0.93	10.08	0.27	1.12	2.48	8.06
0	3.78	14.13	3.06	16.32	8.95	10.46
Н	_	_	0.58	4.59	0.78	1.96
Other	4.58	12.18	15.92	30.98	12.49	8.55

synthesis stages was analyzed, and the results are as shown in Fig. 3. For Ox-PAC, peaks ascribed to C=O and C-O were observed near 1631 cm⁻¹ and 1064 cm⁻¹, respectively, and the adsorption peak ascribed to C-O was slightly stronger than that ascribed to C=O. Mel-PAC synthesized in the 3rd stage showed correlation with N-H and C-N near 1630 cm⁻¹ and 1209 cm⁻¹, respectively. For the final reformed COP-PAC, multiple peaks were observed near 1706, 1548, 1479, 1354, 1193, 877 and 807 cm⁻¹. The peak patterns were similar to previously studied to those found in the COP-GAC, which indicates that COPs were effectively grafted on the surface of PAC particles [40].



Fig. 3. FT-IR spectra of PAC (black), Ox-PAC (yellow), Mel-PAC (green), COP-PAC (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

As shown in Fig. 1, Prussian blue (PB) was synthesized *in situ* within the pores of COPs that were grafted onto the surface of COP-PAC particles. The results of XRD (PAC, COP-PAC, COP-PAC-PB) and FT-IR(COP-PAC, COP-PAC-PB) analysis were as shown in Fig. 4. In general, peaks that show the characteristics of PB are observed near 17.5 and 35.7 degrees [41]. The XRD of COP-PAC-PB was analyzed, and the peaks of PB were compared to the peak patterns of PAC and COP-PAC, which are marked in black and red, respectively. The peaks of PB were found at similar sites to the results of earlier studies [36,37]. The results indicate that PB was effectively synthesized *in situ*. In order to identify the presence of PB in COP-PAC-PB particles, FT-IR analysis was conducted, and a new adsorption peak ascribed to the cyanide group (C \equiv N) stretching vibration was observed near 2076 cm⁻¹, which shows that PB existed in COP-PAC-PB particles.

Using an N₂ adsorption-desorption isotherm, the BET surface area of PAC, COP-PAC and COP-PAC-PB was analyzed, and the results are as shown in Fig. 5. The specific surface areas of PAC and COP-PAC were 776.82 m² g⁻¹ and 395 m² g⁻¹, respectively. The specific surface area of porous materials is known to be significantly reduced, as they are oxidized in the process of synthesizing COPs. It can be said that this process increases the level of functionality against oxidization on the surface of activated carbon particles. These results can be confirmed in the results of TEM (EDS) and elemental analysis (EA) shown in Table 1. The specific surface area of COP-PAC was higher than that of Ox-PAC, which can be attributed to the fact that the specific surface area of COP-PAC increased as COPs were synthesized on the surface of PACs through the grafting and growth of melamine [40]. The results of a BET analysis in Table 2 indicate that the average pore size of COP-PAC and COP-PAC-PB was higher than that of PAC, which can be attributed to the fact that the wall of fine pores was destroyed in the process of oxidation [39]. The BET surface area of COP-PAC-PB was 290 m² g⁻¹, and the reason for this is that PB was synthesized in situ within the pores of COPs that existed on the surface of PAC particles. Thus, it can be said that the specific surface area of COP-PAC-PB was smaller than that of COP-PAC for this reason.

Immediately after PB was synthesized with PAC, Ox-PAC and COP-PAC *in situ*, each adsorbent was washed 6 times (solid/liquid ratio, adsorbent 0.1 g/distilled water 50 mL). Their samples were analyzed using a UV–Vis spectrophotometer in order to examine the desorption characteristics of PB, and the results of this analysis are as shown in Fig. 6. When the non-reformed groups (PAC and Ox-PAC) were washed for the first and second times, a large amount of PB was desorbed. A low concentration of PB seemed to continue to be desorbed thereafter. On the other hand, PB was not desorbed



Fig. 4. (a) XRD pattern; (b) FT-IR spectra of PAC (black), COP-PAC (red), COP-PAC-PB (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. N_2 adsorption(filled)-desorption(empty) isotherms of PAC (black), COP-PAC (red), COP-PAC-PB (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2			
Results of BET surface	area at 77 K: PAC.	COP-PAC.	COP-PAC-PB.

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	BET surface area (m ² g ⁻¹)	Average pore size (nm)	Total pore volume $(cm^3 g^{-1})$
PAC	776.82	2.1172	0.4112
COP-PAC	395.68	2.3651	0.2349
COP-PAC-PB	289.61	2.3299	0.1687

from the reformed group (COP-PAC). It was found that hardly any PB was desorbed from COP-PAC after being washed 6 times, which indicates that PB was effectively combined and immobilized within the pores of COPs synthesized on the surface of PAC particles without being desorbed. Therefore, it can be said that secondary environmental pollution caused by the desorption of PB can be prevented by applying COP-PAC-PB on site.

The results of the adsorption experiment conducted in this study are as shown in Table 3. PAC-PB and Ox-PAC showed 21% and 25% removal efficiency, respectively, in a cesium solution of 9.91 mg L^{-1} (initial concentration), while COP-PAC-PB showed approximately 86% removal efficiency. These results indicate that



Fig. 6. PB elution after being synthesized when the pure COP-PAC-PB were washed by deionized water.

Table 3

Cesium removal efficiency of COP modified and unmodified adsorbents.

Items	PAC-PB	Ox-PAC-PB	COP-PAC-PB
initial Cs (mg L ⁻¹)	9.91	9.91	9.91
Final Cs (mg L ⁻¹)	7.82	7.45	1.32
Removal rate (%)	20	24.8	86.7

COPs were effectively synthesized on the surface of PAC particles, and that PB was successfully synthesized within the pores of COPs *in situ*. The Cs adsorption isotherm of COP-PAC-PB particles is as shown in Fig. 7. The maximum adsorption capacity of COP-PAC-PB particles was 16.36 mg/g, and equilibrium data was fitted to the Langmuir and Freundlich isotherm models. The Langmuir model assumes that adsorption occurs in certain sites that have equivalent adsorption energy, and its equation is as follows:

$$\frac{1}{q_e} = \frac{1}{bC_e q_m} + \frac{1}{q_m} \tag{1}$$

Here, $C_e (mg L^{-1})$ is equilibrium concentration, and $q_m (mg L^{-1})$ is the maximum adsorption capacity of a single layer. b is



Fig. 7. Isotherm of cesium sorption of COP-PAC-PB fitted by Langmuir and Freundlich model.

Langmuir's constant. The adsorption capacity of a single layer (q_m) and Langmuir's constant (b) are obtained from its intercept and slope, respectively. The Freundlich isotherm adsorption model assumes that the surface of an adsorbent has a spectrum on which different sites are activated by different adsorption energy levels.

$$q_e = k_f C_e^{1/n} \tag{2}$$

Here, K_f is adsorption capacity, and n is a constant describing the intensity of adsorption. The constants of the Langmuir and Freundlich models for COP-PAC-PB are as shown in Table 4. The correlation coefficient (R^2) of the Langmuir isotherm model was 0.9844, higher than that of the Freundlich isotherm model (0.9635). From these results, it can be said that the adsorption of Cs evenly occurs in a single layer within pores [41].

To measure the capacity of COP-PAC-PB to remove radioactive cesium (Cs-137), an adsorption experiment was performed, and the results are as shown in Table 5. COP-PAC-PB (0.2 g) was injected into 200 mL of a solution in which 60 Bq/kg of Cs-137 existed and was reacted for 24 h. Next, the Cs-137 concentration in the solution was measured for 3600 s using a 3×3 -inch Nal detector (Nucare, RAD IQ FS200, Korea) that can analyze nuclides within a 20 mmthick lead lined storage container. The final Cs-137 concentration was 1.62 Bg/kg, down 97.3% from the initial concentration. In addition, the radiation levels in the solution before and after performing the adsorption experiment were described on a spectrum, as shown in Fig. 8. The level before and after adsorption was marked in red and black, respectively. The detector was used under the same conditions. Before and after performing the adsorption experiment, the energy level of the K-40 gamma ray, a natural radioactive nuclide, showed a clear peak (1460 KeV). The energy level of the Cs-137 gamma ray before adsorption (marked in red) showed a clear peak (662 KeV), while the peak (662 KeV) was not clearly observed on the spectrum after adsorption due to the reduced Cs-137 concentration. Therefore, it can be said that Cs-137

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Cs-137 removal performance of COP-PAC-PB.

COP-PAC-PB (g L ⁻¹)	Cs-137 activity (Bq/ kg)		Performance	
	Initial	Final	R(%)	DL
0.2	60	1.62	97.3	5.73



Fig. 8. Spectrum quantitative analysis of Cs-137 solution (red) and decontaminated solution by COP-PAC-PB (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

was efficiently adsorbed and removed by the injected COP-PAC-PB.

4. Conclusion

The aim of this study was to develop an adsorbent to which Prussian blue (PB) is stably immobilized to remove radioactive cesium (Cs). To this end, the surface of powdered activated carbon (PAC) particles was reformed using covalent organic polymers (COPs) to synthesize COP-PAC, and PB was synthesized within the pores of COPs in situ in order to develop an adsorbent that can stably remove radioactive cesium without any desorbed PB. Using TEM (EDS) and elemental analysis (EA) techniques, it was confirmed that COPs were effectively synthesized, and the results of XRD and FT-IR analyses also indicated that PB existed within COP-PAC-PB particles. PB was synthesized with the non-reformed groups (PAC and Ox-PAC) and the reformed group (COP-PAC) using the same method, and solutions used to wash them were sampled after washing them in order to identify the characteristics of PB desorbed from the synthesized adsorbents. Each solution used to wash them was analyzed using an UV-Vis spectrophotometer, and no peak that shows the characteristics of PB was found in the COP-PAC-PB after washing 6 times. Therefore, it can be said that PB was successfully immobilized within the pores of COPs that were synthesized in situ. From these results, it can be concluded that the secondary environmental pollution caused by discharged PB particles (that adsorbed radioactive cesium) can be prevented by applying COP-PAC-PB as an adsorbent on site. The maximum Cs adsorption capacity of COP-PAC-PB particles was 19 mg/g, and this was confirmed using two isotherm models. It was found that the

Table 4
Langmuir isotherm and Freundlich isotherm parameters for cesium adsorption onto the COP-PAC-PB

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	q _m (mg/g)	K _L (L/mg)	R ²	$K_F([mg/g] \cdot [mg/L])$	1/ <i>n</i>	R ²
303	16.36	0.1530	0.9844	6.8212	0.5088	0.9635

data were fitted better to the Langmuir adsorption model. An adsorption experiment was also performed to measure COP-PAC-PB's radioactive cesium (Cs-137) removal efficiency. Using a radiation detector, the radiation levels before and after the experiment were measured. The initial radiation level was 60 Bq/kg, and, after adsorption, the level was reduced to 1.62 Bq/kg, down by 97.3%. Based on these results, it can be concluded that COP-PAC-PB can be used effectively as an adsorbent in the process of decontaminating water polluted with radioactive cesium on site. To identify the additional adsorption characteristics of COP-PAC-PB, it will be necessary to examine changes in its adsorption efficiency in the presence of competitive ions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2019.01.154.

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