



# Oxidatively modified carbon as efficient material for removing radionuclides from water



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## ABSTRACT

There is a constant need to develop advantageous materials for removing radioactive waste from aqueous systems. Here we propose a new carbon-based material prepared by oxidative treatment of various natural carbon sources. The as-prepared oxidatively modified carbon (OMC) has an oxygen-rich surface, and retains its particulate granular texture. It has relatively low cost and can be used in traditional filtration columns. The sorption ability of OMC toward several metal cations is demonstrated. It is especially efficient toward Cs<sup>+</sup> cations, the species that are among the most difficult to remove from the waters at the Fukushima nuclear plant.

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## 1. Introduction

Radioactive waste imposes a serious problem to modern society, threatening life and health of many worldwide. The accidental releases of radioactive waste from military or civil nuclear activities can contaminate large areas, as it happened in 1957 at Kyshtym, or in 1986 in Chernobyl, both in the former USSR. The recent accident at the Fukushima nuclear power plant in Japan underscores the magnitude of the problem [1]. Currently, hundreds of thousands tons of water contaminated by radionuclides are stored in massive tanks on the plant site awaiting efficient methods of purification. Among the radionuclides most difficult to remove from water is <sup>137</sup>Cs<sup>+</sup> [1]. The ease with which radionuclides can be removed from water decreases in the order of trivalent, divalent to monovalent metal cations. While trivalent elements can be almost quantitatively removed by numerous known absorbents, the sorption of monovalent <sup>137</sup>Cs<sup>+</sup> remains an enormous challenge [1–4]. Sorption with porous minerals [5–12], and ion-exchange media [13] are among the most effective methods for the Cs<sup>+</sup> removal.

One type of materials effectively sorbing Cs<sup>+</sup> are synthetic ferrocyanides [11,12]. However, these materials suffer from their

nanometer or micrometer scale size that makes them difficult to be used in large-size continuous systems [12]. This is why they need to be immobilized in suitable organic or inorganic matrices [12]; this additionally increases their cost. Among the known Cs<sup>+</sup> sorbents that found practical implementation are synthetic zeolites [5–10]. However, the relatively high cost of synthetic zeolites lowers their performance-to-cost ratio. In addition, after sorption, Cs<sup>+</sup> cannot be removed from ferrocyanides and zeolites as easy as from the ion-exchange resins. Thus, the spent materials need to be compartmentalized and stored along with sorbed radionuclides until their near complete decomposition by the natural radioactive decay.

From this perspectives, carbon-based materials have advantages over the minerals. In practice, after sorption, carbon can be burned in a nuclear furnace leaving only radioactive ash, which results in an ultra-small volume of radioactive waste. Alternatively, carbon-based materials can be regenerated and be used in a new purification cycle. But traditional carbon-based absorbents such as activated carbon and charcoal are not efficient scavengers of metal cations. While being effective in gaseous phases and for removing some organic contaminants from water, they do not efficiently bind metal cations from aqueous solutions. For this purpose, the carbon surface needs to be decorated with oxygen functional groups.

Recently, the method of removing radionuclides by graphene oxide (GO) was reported [14–18]. GO was demonstrated to be very efficient toward several trivalent and divalent metal cations due to

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the presence of oxygen functional groups, and due to its high surface area. In particular, GO was efficient in removing  $^{90}\text{Sr}^{2+}$  from the sea water [14,15]: another challenge at the Fukushima nuclear power plant [15]. However, the sorption of monovalent  $^{137}\text{Cs}^+$  was not as good as that for  $^{90}\text{Sr}^{2+}$  [15]. In general, the affinity of GO toward monovalent metal cations is lower [15,19]. In addition, the usage of GO as a sorbent suffers from the difficulties with the practical implementation: in water, GO forms a stable colloidal solution, which is difficult to separate by common methods. Another problem, preventing application of GO in general, is its high cost. Thus, new materials are needed for purifying water from metal cations. This new material should be as efficient in sorption as GO, but significantly cheaper. Also it should be easily separable from water to be cost-effective in practical implementation. Ideally, it should have a granular particulate texture to be able to be used as a stationary phase in traditional sorption columns.

Here we propose a new material which we term oxidatively modified carbon (OMC) that possesses both low cost and an ability to be easily separated from water. OMC can be prepared from various forms of carbon by treatment with strong oxidants in concentrated acid media under conditions similar to those for the preparation of GO [20–23]. This treatment generates numerous oxygen functional groups on the surface of the existing pores, making the surface chemically similar to that of GO. Unlike GO, OMC is three-dimensional, and it does not exfoliate. While GO production from graphite requires three to six weight equivalents (wt equiv) of  $\text{KMnO}_4$  per one part of graphite [20,23], production of OMC requires only 0.9 to 1.2 wt equiv of  $\text{KMnO}_4$ . Moreover, oxidative treatment can also be effected by a  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture, completely avoiding the use of  $\text{KMnO}_4$ . After oxidation, carbon retains its particulate nature; the reaction mixture is not thickened. Subsequently, the reaction requires  $7\times$  less  $\text{H}_2\text{SO}_4$  compared to that needed for GO production. Finally and most importantly, during the purification steps, separation of as-prepared OMC from the acidic waste waters can be conducted by simple filtration. This makes the cost of OMC  $\sim 10\times$  lower than that of GO.

Various natural carbon sources can be used for OMC preparation. Depending on the source, the resulting OMCs possess different sorption effectiveness toward different metal cations. In this report we show that two widely different carbon sources can be used in generating OMC for the sorption of metal cations. The first carbon source is a commercial product distributed by MiSWACO company as an additive to drilling fluids used in the oil industry. It is a black powdery carbon material, called C-seal-F. The second carbon source is a unique mineral called “shungit” naturally occurring in the north-western part of the Russian Federation, and mined in millions of tons annually. In addition to the amorphous carbon representing petrified non-graphitized organic deposits, shungit contains the inorganic mineral phase [24]. The inorganic phase consists mostly of silicon dioxide in the form of cryptocrystalline quartz or amorphous silica, with the second most abundant component aluminum oxide [24]. The two phases are evenly dispersed in the form of the nanoscale-sized cross-inclusions. The composition of the mineral varies broadly depending on the exact mining area [24]. The carbon content varies from 98.5% through 28.1%. The sample we tested is on the low-carbon-content end with  $\sim 40\%$  of carbon, and  $\sim 60\%$  of the inorganic part. We will refer to these two carbon sources as C1 and C2, respectively. The OMC samples made from the two sources will be labeled as OMC1 and OMC2, respectively.

We developed two different oxidation methods to prepare OMC: first with the use of  $\text{KMnO}_4$  in sulfuric acid media, and second with the use of the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  system. The two oxidation methods used toward the same carbon source yield similar OMC products. With C1, the  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  method gave a slightly more oxidized

OMC product compared to the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  method. With C2 both methods gave equally oxidized OMC products. The sorption performance of two OMC samples made from the same carbon source with the use of the two different methods was in the range of the experimental error. This is why, in this work, we show the data obtained with the use of only one particulate method toward the one carbon source: the  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  method used toward C1, and the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  method used toward C2.

## 2. Experimental part

### 2.1. Materials

Sulfuric acid was from “Shchekinoazot” Trading House, LLC, Russia; nitric acid was from CJSC “TatHimProduct”, Russia; potassium permanganate was from MCD Company, Russia. The carbon source C1 was grade C-seal-F from MiSWACO company, USA. The carbon source C2 was a sample of the mineral coal mined in the Karelia region, Russia. Only non-radioactive metal cations were used in this study.

### 2.2. Characterization

The scanning electron microscopy (SEM) images were acquired with a field-emission high-resolution scanning electron microscope Merlin from Carl Zeiss at accelerating voltage of incident electrons of 5 kV and a current probe of 300 pA. The X-ray photoelectron spectroscopy (XPS) spectra were acquired in a UHV chamber of the multi-technique surface analysis system Phoibos 100/150 from SPECS. The Mg  $K\alpha$  X-ray source operated at 12.5 kV and 250 W was used. A pass energy of 30 eV (step size of 0.5 eV) was used for wide range scans; pass energy of 20 eV (step size of 0.1 eV) was used for high resolution measurements. All spectra were analyzed by using the CasaXPS software. The powder X-ray diffraction (XRD) was acquired with Bruker D8 Advance with Cu  $K\alpha$  irradiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the Bragg-Brentano geometry; the rate was  $0.18^\circ/\text{min}$ ; the range of  $2\theta$  angle was from  $7^\circ$  through  $57^\circ$ ; the step was  $0.015^\circ$ . The thermogravimetric analysis (TGA) data was collected with the Q50 analyzer from TA Instruments in Ar atmosphere with the heating rate of  $10^\circ/\text{min}$ . The content of metal cations was determined with the ionically coupled plasma mass spectrometer (ICP MS) “iCAP Qc” from Thermo Fisher Scientific.

### 2.3. Preparation of OMC

To prepare OMC1, we first prepared the 88.6% sulfuric acid by diluting 150 g 96% commercial sulfuric acid with 12.5 g DI water. The diluted acid was cooled to the room temperature. 10.0 g of C1 were introduced into the 88.6% sulfuric acid with stirring. Potassium permanganate ( $\text{KMnO}_4$ ) was introduced in two portions of 6.0 g each with a 1 h interval. The reaction mixture was continuously stirred for 12 h after the last  $\text{KMnO}_4$  portion. Next, the reaction was quenched with 500 mL DI water, and the diluted reaction mixture was filtered to separate OMC1 from the acidic waste. The OMC1, collected from the filter, was redispersed in 500 mL DI water, stirred for 30 min with a magnetic stirrer, and the dispersion was filtered to separate the purified OMC1. The above mentioned purification procedure was repeated  $4\times$ . The filtrate was always transparent and colorless indicating that very little submicron-scale particles were dispersed in water, and that carbon did not crush to smaller fragments even with magnetic stirring. After the 5th washing, the pH of the filtrate was  $\sim 5$  indicating removal of practically all the sulfuric acid. The as-prepared OMC1 was dried in open air until no change in weight was registered. The 13.49 g of the product was obtained.

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