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Application of graphene oxides and graphene oxide-based nanomaterials in radionuclide removal from aqueous solutions

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Abstract With the fast development of nanoscience and nanotechnology, the nanomaterials have attracted multi-disciplinary interests. The high specific surface area and large numbers of oxygen-containing functional groups of graphene oxides (GOs) make them suitable in the precon-centration and solidification of radionuclides from wastewater. In this paper, mainly based on the recent work carried out in our laboratory, the efficient elimination of radionuclides using GOs and GO-based nanomaterials as adsorbents are summarized and the interaction mechanisms are discussed from the results of batch techniques, surface complexation modeling, spectroscopic analysis and theo-retical calculations. This review is helpful for the under-standing of the interactions of radionuclides with GOs and GO-based nanomaterials, which is also crucial for the application of GOs and GO-based nanomaterials in environmental radionuclide pollution management and also helpful in nuclear waste management.

Keywords Graphene oxides · Radionuclides · Sorption · Interaction mechanism · Theoretical calculation · Spectroscopic analysis

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1 Introduction

With the quick development of nuclear science and energy, more and more nuclear power plants have been built and large amounts of nuclear wastes have been generated. In the nuclear fuel cycle options (i.e., from the extraction of uranium for the fabrication of nuclear fuel, the application of nuclear fuel in nuclear power plants, and at last in the spent fuel process to the geological disposal, etc.), it is inevitable to produce large volumes of wastewater con-taining different kinds of long-lived radionuclides, espe-cially some important fission products, lanthanides and actinides, which should be eliminated from the radioactive wastewater before they are discharged into the natural environment [1, 2]. Different kinds of techniques such as sorption, (co)precipitation, ion exchange, solidification, and membrane separation, have been extensively applied to eliminate radionuclides from wastewater [3, 4]. Among these methods, sorption technique has widely been applied in large scale and in real environmental pollution man-agement because of its simple operation, low cost and applications in large scale [5–8]. The application of sorp-tion technique in the removal of radionuclides from large volumes of aqueous solutions has been studied extensively by using batch techniques, and the interaction mechanisms were discussed from the results of surface complexation

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modeling, spectroscopic analysis and theoretical calculations. From the batch sorption results, the interaction mechanism can be postulated from the results, such as outer-sphere surface complexation or ion exchange is mainly ionic strength-dependent and pH-independent whereas inner-sphere surface complexation is mainly pH-dependent and ionic strength-independent. From the surface complexation modeling simulation, the formation of the surface complexes of radionuclides on solid surfaces can be provided and the interaction mechanism may be postulated from the assumption of the species, such as inner-sphere surface complexes, outer-sphere surface complexes, multi-layered surface complexes, surface (co)precipitation, etc. [9, 10]. From the spectroscopy measurements, the species and the microstructures of radionuclides on solid particles at molecular level and the functional groups which form surface complexes with radionuclides can be achieved directly from the spectrum analysis, which are crucial and useful to evaluate the interaction mechanism of radionuclides at solid–liquid interfaces [11, 12]. For example, the X-ray absorption fine structure (XAFS) spectroscopy, which includes X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, is helpful to achieve the microstructures and species at molecular level. The XANES spectra can provide the evidence for the identification of oxidation–reduction state of radionuclides at solid particles directly, whereas the EXAFS spectra can provide the information of specific bonding type, coordination number and the corresponding microstructures at molecular level [13, 14]. The analysis of XAFS spectra is crucial to get the information of the microstructures and the species of radionuclides on solid particles. The time resolved laser fluorescence spectroscopy (TRLFS) can provide the information of the number of water molecules in the first coordination sphere from the analysis of the fluorescence lifetime, which is crucial to identify the formation of outer-sphere or inner-sphere surface complexes [15–19]. From the loss of water molecular number in the sorption process, the interaction mechanism and the binding state of radionuclides at solid/water interfaces can be evaluated. The Raman spectroscopy can identify the molecular structure of radionuclides from the peak position and fundamental vibrations to determine the binding state of the sorption species [20]. The X-ray photoelectron spectroscopy (XPS) can be used to obtain the chemical composition of radionuclides with functional groups, the oxidation states, and bonding relationships of radionuclides with surrounding spheres. The theoretical calculation such as density functional theory (DFT) has shown to be a very useful and powerful tool to describe and evaluate the physical and chemical properties of radionuclide interaction with solid particles [21–27]. From the

binding energies of the radionuclides interaction with different functional groups, one can understand the interaction mechanism of radionuclides and to identify the sorption properties such as physical sorption or chemical sorption, which are helpful to interpret the experimental results. Generally, from the results of batch experiments, advanced spectroscopic analysis and theoretical calculation, one can understand the interaction mechanism of radionuclides at solid-water interfaces clearly.

In recent years, graphene oxides (GOs) and GO-based nanomaterials have attracted multidisciplinary interests because of their unique physicochemical properties such as high surface area, high chemical stability, large pore volume structure and abundant oxygen-containing functional groups [28–35]. These special properties make GOs suitable for efficient elimination of inorganic and organic chemical pollutants from solutions. Zhao et al. [36] firstly synthesized sulfonated GOs and applied the sulfonated GOs as adsorbents to remove organic pollutants in environmental pollution cleanup, and found that the prepared GOs had the highest adsorption capacity in the preconcentration of persistent aromatic pollutants among today's nanomaterials, which was also evidenced from the DFT calculations. They also applied GOs to remove Co(II) and Cd(II) ions from aqueous solutions using batch technique and found that the adsorption capacities were much higher than any related materials currently reported. Most importantly, they found that the presence of humic acid reduced Co(II) and Cd(II) sorption at the applied pH values (i.e., pH < 8), which was quite different to the effect of humic acid on the sorption of heavy metal ions on clay minerals and oxides, suggesting that the GOs provided much more accessible unoccupied sites and functional groups for the binding of metal ions rather than humic acid. The surface adsorbed humic acid occupied parts of sorption sites on GO surfaces, thereby reduced the available sites and functional groups and decreased the sorption capacity [37]. The interactions of radionuclides with GOs and GO-based materials were further studied under different experimental conditions, and the results showed that the GOs and GO-based materials had high sorption capacities in the removal of radionuclides, which was attributed to the large number of oxygen-containing functional groups on the surface or edge sites [38, 39].

From the above mentioned literatures, one can see that GOs and GO-based nanomaterials have high surface areas and large number of functional groups, which are favorable for the preconcentration of radionuclides from aqueous solutions. Although the applications of GOs and GO-based nanomaterials in the elimination of radionuclides from wastewater have been studied extensively, the summary on the interaction mechanisms of radionuclides with GOs is still scarce [34]. In this review paper, mainly based on the