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Extensive adsorption of the lighter homologue tellurium of polonium from wastewater using porous silver layer deposited stainless steel mesh

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ABSTRACT

Polonium-210 is a key radioactive hazard for accelerator driven sub-critical system, in which the lead-bismuth eutectic is used as coolant and spallation target. To solve its potential pollution problems produced under accident conditions, the lighter homologue tellurium was utilized to replace it in the present research. Quantitive study and structural characterization of tellurium adsorption by Stainless steel-Ni-Cu-Ag multiple-layer mesh (SNCA) were discussed as well. The results indicated that the tellurium accumulation ascended with rising copper electroplating current density due to the increase of silver coating. The Te(IV) accumulated by naked stainless steel mesh was negligible, and the granular silver coating had a stronger adsorption ability than the flat layer after contacting for 64 h. The results suggested the high dependence of tellurium accumulation on the available surface area of silver layer. The tellurium accumulation rose at first and gone down later with the increasing of iodine ions, which resulted from the joint effects of competitive adsorption between I^- and TeO_3^{2-}, the reduction of iodine ions and the refinement of silver particles. The SEM-EDS showed a smoky tellurium precipitation formed between silver particles. Elemental mapping imaging depicted completely identical spatial distributions of silver and tellurium, revealing the selective adsorption of Te(IV) by silver. Besides, the XPS demonstrated that the spontaneous deposition of Te(IV) and the oxidation-reduction reaction between silver and Te(IV) both play important roles in removal of tellurium from aqueous solution.

1. Introduction

Accelerator driven sub-critical system (ADS) has been regarded as a potential powerful tool for the treatment of nuclear waste. The development programs and researches on ADS have been launched in Russia, America, Japan (Sasa et al., 2004) and European Union (Abderrahim et al., 2010). China also initiated the ADS research project in 2011 (Wu et al., 2014a, 2015a, 2016; Wang et al., 2015) and carried out extensively studies on conceptual design (Wu and FDS Team, 2006; Wu and FDS Team, 2008; Wu et al., 2011), technical exploration (Qiu et al., 2000), application development (Wu et al., 1999, 2015b; Wu and FDS Team, 2009) and so on. The lead-bismuth eutectic (LBE) had been selected as one of the most promising coolants and spallation target materials for ADS due to its excellent neutronics, thermal-hydraulics and inherent safety characteristics (Wang et al., 2015). However, some issues should be taken into consideration with the development of LBE-cooled reactors, for instance, the isotopes of polonium that produced by proton-induced spallation reaction and neutron capture reaction on bismuth (Neuhausen et al., 2004). Polonium-210 (Po-210), which decays by emission of α particles with an energy of 5.5 MeV and a half-life of 138.38 days (Rizzi et al.,. 2014), is vital to be concerned for the radiation protection in LBE-cooled reactors. It would spread to aqueous solution once heat exchanger crevasse or severe nuclear meltdown accidents happen in reactors. And as we know, it can also enter into the human body through drinking water and food chain if the polluted water discharged into environmental without treatment. Po-210 would accumulate essentially in kidney, spleen and liver and then cause irreversible damage

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to these organs due to their complete adsorption of the α particle energy. The maximum permissible activity of Po-210 for once human intake being regulated by the International Commission on Radiological Protection (ICRP) is only 0.74 kBq, equivalent to a particle weighing 4.5×10^{-12} g. Nevertheless, the Po-210 activity in the LBE for 15 MW target circuit after 1 year operation is estimated to be ~10^4Ci (Yefimov et al., 1997), which is 12 orders of magnitude higher than the maximum permissible intake. Therefore, in order to enhance the emergency response capability and prevent the serious radioactive pollution, it is necessary to develop an effective filter to remove polonium from radioactive wastewater. However, to our best knowledge, there are no documented works that aims at polonium removal from aqueous solution except the studies on its accumulation behavior in living organisms (Stewart and Fisher, 2003; Cherrier et al., 1995; LaRock et al., 1996; Skwarzec and Fabisiak, 2007; Carvalho and Fowler, 1993).

Tellurium (Te) is a lighter homologue of Po in chalcogen group. Even though its melting point and boiling point are somewhat higher than those of Po, it was also widely used as a surrogate in published work, such as the characteristic investigation of Po removal from liquid LBE in Buongiorno's and Ermolaev's reports (Buongiorno et al., 2004; Ermolaev et al., 1998). As indicated in the literature, the polonium in aqueous solution is mainly tetravalent (Po(IV)) (Starik et al., 1964). And Te(IV) and Po(IV) have high similarity in the chemical behavior (Ayala et al., 2012). Apart from these, the Po isotopes are radioactive and Te has non-radioactive isotopes, which can be handled more easily. Accordingly, the Te(IV) solution was used in place of Po-containing aqueous solution in this work.

With the diversified development of material, the studies on novel metals that contain hybrid nanocomposites and nanostructures have received more attention in the past few years (Xing et al., 2016a,b), especially the silver. And due to its unique properties, the silver decorated composites have been widely researched in anti-bacteria (Zhang et al., 2011a), conduction (Wu et al., 2014b), catalyst (He et al., 2012), sensing (Zhao et al., 2013; Zhan et al., 2014) and surface field enhance (Dutta et al., 2013). Besides, silver possesses good corrosion resistance and high chemical stability. Its hybrid nanocomposites are always used in wastewater treatment (Dubey et al., 2014; Fan et al., 2015; Jiao et al., 2015a). And the porous architecture is now considered to be an optimum choice because of its novel characteristics, such as large surface area, low cost and small density. For example, Tifeng Jiao's group fabricated the porous structured composite hydrogel materials of acrylic acid-AgNPs, which demonstrated good removal capacities for congo red, rhodamine B and methylene blue (Hou et al., 2016). Notably, due to the good mechanical strength, these three-dimensional porous materials could be separated from aqueous solution easily after reaction. It can be expected that the suitable silver porous material with high mechanical strength will be promising for water treatment. In our studies, 316L stainless steel mesh was selected as the supporting matrix, and the filter deposited with a porous silver layer was fabricated for Te(IV) removal. Nickel was first electroplated to avoid the oxidation of steel. And then, Copper transition layer was electroplated to enhance the adhesion between silver and the matrix. The effect of copper electroplating current density, silver deposition time, contact time and iodine ionic strength on Te(IV) adsorption by silver loaded stainless steel mesh were investigated through batch technique. The pH was fixed at 1.0 to ensure the solubility of Te(IV) in aqueous solution. To illustrate accumulated Te(IV) by SNCA and the mechanisms involved, scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) were utilized.

2. Materials and methods

2.1. *Preparation of silver loaded stainless steel mesh*

Stainless steel meshes with diameter of 30 mm were sonicated in industrial detergent and 5 wt% sodium hydrate solution for 30 min, respectively. To remove the oxide film on the stainless steel wires, They were washed in dilute acid solution at the temperature of 60 °C for 15 min. Then, in turn, the meshes were treated in the solutions of $FeCl_3$ and H_2SO_4 to achieve a smooth and polished surface. After cleaning, Ni film was electroplated on the stainless steel meshes in aqueous solution of $NiCl_2$ at 0.21 A/dm^2, followed by electro-deposition of copper from $CuSO_4$ solution at a certain current density. The resulting meshes were pre-treated in an aqueous $AgNO_3$ solution (marked as $AgNO_3$-1) for 10 min. And then Ag layer was electroless-plated in another aqueous solution of $AgNO_3$ (marked as $AgNO_3$-2) for the desired time, in which sodium tartrate was used as reducing agent. To avoid oxidation, The obtained Stainless steel-Ni-Cu-Ag multiple-layer meshes (SNCAs) were stored in acetone for further use. The main compositions of the $AgNO_3$ -1 and $AgNO_3$-2 solutions are listed in Table 1.

2.2. *Chemicals*

All of the chemicals, such as sodium hydrate, hydrochloric acid (37% w/w), ferric chloride, sulphuric acid (98% w/w), nickel chloride hexahydrate, copper sulphate pentahydrate, silver nitrate, sodium sulphite, potassium dihydrogen phosphate, ammonium hydroxide (28% w/w), sodium tartrate, potassium iodide, nitric acid (68% w/w), and tellurium power (99.999% purity), were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and were used as received. High purity deionized water (18.2 MΩ cm) obtained from an ultrapure water polishing system (Kertone, UK) was used in all experiments.

The Te(IV) solutions were prepared by dissolving the ultrafine tellurium powder in a minimum of nitric acid (Andrews and Johnson, 1976). Then, the solution was evaporated to expulse nitric acid and diluted with 1 M HCl solution to give a 1 mg/ml Te(IV) solution. The resulting stock solution of Te(IV) was progressively diluted to desired concentration and was stored below pH 1.0. And NaOH was used to adjust the pH.

2.3. *Batch adsorption experiments*

2.3.1. *Effect of copper electroplating current density*

For the SNCAs used in this experiment, the Cu film was electroplated at current densities of 0.21 A/dm^2, 0.28 A/dm^2, 0.35 A/dm^2 and 0.50 A/dm^2, respectively, and the silver was deposited on the surface of Cu coating for 1.5 h. After that, the obtained SNCAs were cast into high borosilicate glass tubes filled with 25 ml of 100 μg/ml Te(IV) at room temperature. The pH of the systems was adjusted to 1.0 with negligible volume of 5 M and 0.5 M NaOH. After contacting for 24 h, the meshes were separated and the solutions were determined for the residual tellurium. Mesh-free controls were run concurrently in all experiments to ensure that the Te(IV) accumulated on the wall of the tubes was excluded.

Table 1
The main composition of immersion silver and silver electroless plating solutions.

$AgNO_3$ -1 (mol/L)		$AgNO_3$ -2 (mol/L)	
$AgNO_3$	0.03	$AgNO_3$	0.06
Na_2SO_3	1.98	NH_4OH	0.56
KH_2PO_4	0.44	$C_4H_4Na_2O_6$	0.26