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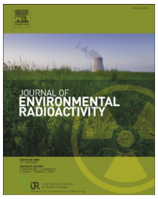

Electrokinetic removal of radionuclides contained in scintillation liquids absorbed in soil type Phaeozem

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ABSTRACT

Control samples of scintillation liquids – Phaeozem soil mixtures were prepared with different scintillation liquids as the support electrolyte, Install Gel® XF, (Ultima Gold AB™ and Ultima Gold XR™), to construct the polarization curves, and to select the cell potential with the highest mass transfer to remove ^{24}Na (15 h) and ^{99m}Tc (6 h) as radiotracers from polluted Phaeozem soil. During the electrokinetic treatment (EKT), the removal of radionuclides contained in scintillation liquids absorbed in Phaeozem soil, liquid phase was characterized by Gas Chromatography coupled with a Flame Ionization Detector (GC-FID) and Fourier Transform Infrared Spectrometry (FTIR), solids by FTIR, before and after the application of cell potential. In this sense, the support electrolyte was selected based on the highest current generated (1 mA), as in the case of scintillation liquid 50% Ultima Gold XR™ + 50% Water (1:1), which was used for 6 h in the presence of a mesh and a titanium rod, as anode and cathode, respectively. Finally, the removal percentage accumulated in the liquid phase after the EKT of Phaeozem soil polluted by ^{99m}Tc was 61% close to the anode after 4 h. It was also 61% for ^{24}Na close to cathode after 2 h, and after 4 h it was 71.8%.

1. Introduction

There are many uses of radioactive materials which improve or facilitate human activities or the quality of life of people. These uses are demonstrated in different fields of technology, ranging from power generation to supply entire cities or areas, to medical and industrial uses, and even smoke detectors in buildings. All these applications generate radioactive wastes that may represent risks to the environment or to human beings; therefore it is necessary to pay special attention to the management of radioactive waste (Abdel et al., 2011; Radiation Safety General Regulations, 1988). Treatment process selection for this waste depends upon its radiological and physicochemical properties and the quantity (IAEA, 2001; Adenot et al., 2005; Chang, 2001). In the case of liquid radioactive wastes as scintillation liquids (mixtures of non-polar organic solvents such as toluene, xylene, pseudocumene; scintillators such as naphthalene, 2,5-diphenyloxazole, and surfactants), solvents, oils and diverse biological fluids that are generated in nuclear research centers, medical centers or industries and considered as radioactive organic liquid wastes, these may present radioactive and chemical or biochemical hazards requiring treatments to separate or remove the radioactive material, or to chemically or biochemically destroy hazardous components. Processes such as incineration, wet oxidation, acid digestion, electrochemical oxidation, distillation or absorption can be applied to treat radioactive organic liquid (IAEA, 1992, 2001). The objective is to reduce the volume of radioactive waste which requires storage, transport, conditioning and land disposal, or the elimination of the organic components to enhance compatibility of the treated waste with secondary conditioning processes.

The treatment of organic liquid radioactive waste with absorbents has been routinely used to convert the liquid to a solid form. Absorbents such as sawdust, cotton, polypropylene, mica, clays, diatomaceous earth, or alkyl styrene polymer have been used for this treatment. Absorption is a simple and cheap technique to reduce the risk of a possible environmental hazard from radioactive liquid dispersion. However, the suitability of absorption alone for

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the solidification of organic liquid wastes is only moderate, because organic material is not destroyed, the waste volume is increased and the waste form has no special integrity, and can be readily dispersed in air or water if the product container is breached (IAEA, 1992, 2001).

Liquid organic radioactive waste, generated in research and medical establishments, constituted particularly by scintillation liquids that contained U-238 (4.468×10^9 y), Th-232 (1.41×10^{10} y), Tl-204(3.7 y) or Na-22 (2.6 y), was absorbed on soil type Phaeozem during the 70's and 80's in Mexico, in order to convert it to a less hazardous form during interim storage. However, these wastes are considered as mixed wastes because they contain hazardous organic solvents in addition to the radioisotopes. Therefore, these wastes must be re-treated to remove radionuclides from the liquid-soil matrix and to reduce their volume.

Among the treatments used for these kinds of wastes is electrochemical treatment. Electroremediation, also known as electrokinetic remediation (EKR) process is classified as a physicochemical technology by the electrochemical transformation or destruction of organic and inorganic wastes. The main advantages of the electrochemical treatment are (NEA, 1999): low temperatures, conversion to an aqueous waste stream that is easy to treat, does not have the problems of off-gas cleanup that are associated with incineration, can be carried out for small batches of waste using simple bench top equipment and the capacity to remove organic and/or inorganic pollutants by applying direct electric current to the soil (Vázquez et al., 2007) with or without the presence of metal oxidizing agents like Ag(II)/Ag(I), Ce(IV)/Ce(III), Co(III)/Co(II), etc., in pilot and commercial scale systems (Adenot et al., 2005; Chang, 2001; Prabhakaran et al., 2009; Farmer et al., 1991) or radioactive species as ^{137}Cs, ^{90}Sr, ^{60}Co, ^{238}U among others from both saturated and unsaturated soils, sludges and sediments (Virkutytea et al., 2002; Hamed et al., 1991). The efficiency of pollutant removal using EKR depends on many factors such as the kind of electrode material or support electrolyte (Yeung et al., 1996; Cox et al., 1996) to develop the EKT in a one-dimension (1D) array, having only one anode (+) and one cathode (−) separated by the polluted soil, or a two-dimensional system (2D) with a *x-y* axis electrode array (Méndez et al., 2012; Pérez et al., 2013; Reddy et al., 2001). In addition, several flushing solutions have been investigated, such as water, acids, bases, chelating agents, alcohol, and other additives (Chaiyaraksa and Sriwiriyanuphap, 2004), or adsorbents like graphite which is regenerated (Brown and Roberts, 2007), boron-doped diamond (BDD) electrodes in presence of sonication (Taylor et al., 2009) or transuranic oxides (PuO_2) (Chiba et al., 1995). Therefore, in this paper we show the electrokinetic removal of ^{22}Na and ^{99}Tc contained in scintillation liquids absorbed on soil type Phaeozem.

2. Materials and methods

2.1. Materials

The soil type Phaeozem used in this study was mixtures of clay and sand, which had crystalline forms as quartz, albite calcium, montmorillonite, tridymite and magnesium hornblende with elemental compositions of oxygen, aluminum, silica, potassium, calcium, titanium and iron. This kind of soil had a real density between 2.16 and 2.41 g mL^{-1}, a pH close to 7.0, an electrical conductivity less than 2 dS m^{-1}, organic matter content less than 5%, and moisture content less than 4%.

In order to simulate the radioactive wastes constituted by scintillation liquids absorbed into soil, control samples of scintillation liquids – soil mixtures were prepared with three scintillation liquids: Install Gel® XF (pH = 5.20, electrical conductivity = 0.0414 μS cm^{-1}), Ultima Gold AB™ (pH = 5.75, electrical conductivity = 1.563 μS cm^{-1}) and Ultima Gold XR™ (pH = 4.61, electrical conductivity = 0.0088 μS cm^{-1}). These scintillation liquids are mainly constituted of 1,2-dimethyl propoxy benzene, 2,5-diphenyloxazole, tributyl phosphate, p-xylene, 2-(2-butoxyethoxy) ethanol, 1,2-diisopropyl naphthalene and 2,6-diisopropyl naphthalene as shown in Table 1.

Ten different support electrolytes were prepared with these scintillation liquids as shown in Table 2: (a) 100% ULTIMA GOLD XR™, (b) 50% ULTIMA GOLD XR™ + 50% water (1:1), (c) 100% INSTAL GEL® XF, (d) 100% ULTIMA GOLD AB™, (e) 100% thinner, (f) 100% water, (g) 25% ULTIMA GOLD XR™ + 75% thinner, (h) 50% ULTIMA GOLD XR™ + 50% thinner, (i) 25% ULTIMA GOLD XR™ + 25% water + 50% thinner, and (j) 25% ULTIMA GOLD XR™ + 12.5% water + 50% thinner.

2.2. Electrochemical analysis of ^{22}Na and ^{99}Tc contained in scintillation liquids absorbed in Phaeozem soil

The polarization curves and EKT were developed using a cylindrical electrochemical cell containing the polluted soil with an iron cylinder as the cathode and a titanium mesh as the anode, which were connected in the top of electrodes to a power supply (Matrix Technology Inc, model MPS-3003D). The cell was covered with acrylic to eliminate the loss of gases and radioactive material during the EKT, which were collected in a gas trap.

To define the experimental conditions of the EKT for the radioactive wastes previously described, control samples of scintillation liquids (SL) – soil mixtures were prepared with the scintillation liquids reported in Table 1 as the support electrolyte and the polarization curves were constructed using a power supply (Matrix Technology Inc.) to select the potential with the highest mass transfer.

From the polarization curves, cronoamperometries were developed using 60 g of soil without mesh in the described electrochemical cell before adding between 29 and 34 g of a mixture of the support electrolytes shown in Table 2 and manually mixing the samples. These mixtures were maintained for 18 h at laboratory temperature (293 K) with the intent to stabilize the ions in the water present in the pores formed by the particles of Phaeozem soil. After this time, the cronoamperometries were developed by applying 1, 3, 5, 7, 9, 11, 13, 15 or 25 V for 1 h to the Phaeozem soil + SL and measuring the current every 10 min during the experiment to construct the polarization curves (current vs. potential).

To normalize the results, the current was divided by the electroactive geometrical area (Trasatti and Petrii, 1991), which was calculated with the capacitive current of the double layer, which was applied to each electrode according to Equation (1).

$$i = \left(\frac{dq}{dt}\right)\left(\frac{dE}{dE}\right) = \left(\frac{dq}{dE}\right)\left(\frac{dE}{dt}\right) = C_{dl}(\nu) \quad (1)$$

The data were obtained from cyclic voltammetry experiments at different scan rates ($\nu = 0.020$, 0.040, 0.060, 0.080, 0.100, 0.120, 0.140, 0.160, 0.180 and 0.200 V s^{-1}), using a windows potential ± 10 mV around the equilibrium potential. The standard capacitance (C_{st}) used to evaluate the area was 60 μF cm^{-2} to the roughness of electrode (Trasatti and Petrii, 1991). Hence, the i_{cap} was calculated by Equation (2):

$$i_{cap} = \left(\frac{\left|i^a_{cap}\right| + \left|i^c_{cap}\right|}{2}\right) \nu s\ (\nu) \quad (2)$$

Where i^a_{cap} is the anodic capacitive current and i^c_{cap} is the cathodic capacitive current. The slope of the linear relationship is the