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Simultaneous lanthanides and surfactants micelles removal from aqueous outflows by complexation and sol–gel chemistry

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ABSTRACT

A two-step process was developed to achieve a complete treatment of aqueous liquid wastes containing lanthanides, as nuclear fission products surrogates, and micelles. In a first step, complexation of lanthanides with organo-phosphorous ligands in an aqueous bulk phase was investigated. This complexation tends to make the complexed ion go from the bulk phase to the vicinity of the micelles because of the increase in hydrophobicity. Then, in a second step the simultaneous removal of micelles and lanthanides was performed using a sol–gel process, making a mainly inorganic powder final waste suitable to the field of nuclear industry. The effect of the hydrophobicity of ligands was then studied in a solution containing amphiphilic block copolymers micelles. The results showed both lanthanides and micelles removal close to 100% for systems with high enough hydrophobicity. For instance, the most efficient removal were reached for ligands with at least six atoms of carbons in the hydrophobic chain.

1. Introduction

Nuclear industries deal with different types of waste aqueous outflows. It is necessary to remove the whole pollution from these outflows to avoid unwanted rejections in environment. In some nuclear sites, these outflows are contaminated by penalising organic substances and elements with residual radioactivity. The organic substances are mainly organic solvents used in nuclear processes such as tributylphosphate (TBP) that is used in Purex® process as Uranium and Plutonium complexing agent. These organic solvents generally strongly stick to the metallic surfaces and can pollute materials and pipelines forming a thin organic radioactive layer. Therefore, some treatment processes were developed to clean the metallic surfaces using surfactant micellar solutions. Indeed, surfactants are well known to solubilize hydrophobic compounds [1] due to their ability to form micelles in solution [2]. Past studies showed that Pluronic P123 exhibited enhanced TBP solubilisation properties [3]. This amphiphilic triblock copolymer family was therefore chosen as surface active agents in decontamination cleaning solutions. After use, those solutions have to be treated in order to incorporate radioactivity in specific solid conditioning matrices such as concrete or glass. This incorporation is easier when radioactive wastes are solid. That's the reason why, actually, liquid wastes coming from decontamination cleaning solutions are currently evaporated before incorporation in conditioning matrixes.

The study presented in this paper describes a more environmentally friendly alternative process that is replacing evaporation of large water amount steps with simple filtration steps. We simplified the initial outflow considering a solution containing only P123 surfactants and radionuclides surrogates in aqueous medium. This choice was driven by the fact that radionuclides initially present in TBP are released in the water pseudophase of the micellar solution during the cleaning treatment. This is due to changes of physico-chemical properties during this step. For instance, concentration of nitric acid in the cleaning solution is not so high, and the oil/water ratio is really lower than for U and Pu extraction step described by Purex® process. That is why the system is not favourable anymore for ion/TBP complexation in the cleaning solution. Therefore, the ideal model effluent was assumed to be a micellar solution containing radionuclides without any specific interaction between ions and surfactants due to the uncharged nature of Pluronic P123. One of the main scientific challenges of this work was based on the use of organic ligands with specific properties to make ions move from the water pseudophase to the micelles pseudophase. Then, once the radionuclides were in the micelles close vicinity, a sol–gel process was applied to

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precipitate those surfactant aggregates in an inorganic matrix as explained in Fig. 1.

Finally we used lanthanides as radionuclides surrogates for practical reasons [4]. The ion migration from bulk phase to micelles was done thanks to slightly water-soluble phosphorus based organic ligands. This lanthanide complex migration is due to the loose of hydrophilicity of the ligand when phosphate or phosphonic acid group is bonded to lanthanide ion. Therefore, the hydrophobicity of the complex is greater than the ligand and the most suitable environment for this compound is not aqueous bulk anymore, but the vicinity of the micelles. This family of complexing agents is widely known in coordination chemistry and one of the most common ligand used to form complexes with lanthanides is the bis-(2-ethylhexyl)-phosphoric acid, named HDEHP or DEH2PA [5].

After the complexation of lanthanides and their migration towards the micelles environment, a sol–gel process is used. The aim is to concentrate micelles and complexes in solution and make them coprecipitate in a silica matrix at room temperature. Indeed, Pluronic P123 is known to specifically interact with silica precursor such as tetraethylorthosilicate (TEOS) [6]. It is known that this surfactant induces silica precipitation within hexagonal structure since the discovery of the mesoporous silica SBA-15 [7]. The point of this study is to use this property in our reference outflow. The final purpose is to simultaneously remove all pollutions, surfactants and radionuclides, from the outflow and form a solid waste, as it is summed up in Fig. 1.

Furthermore, the final waste produced with the procedure described in Fig. 1 is silica powder based. This kind of waste is very suitable to glass conditioning matrices since silica enters in the glass composition. Indeed, nowadays the nuclear wastes are treated to be buried and to resist rough conditions and the actual nuclear matrices used to confine wastes are glass or cement depending on radioactivity level. Hence, wastes such as silica powder would highly facilitate the incorporation in existing nuclear matrices. Therefore, the process described in this work improves nuclear waste management.

2. Experimental

2.1. Chemicals

P123 is an amphiphilic triblock copolymer with the following structure, EO_{20}–PO_{70}–EO_{20} where EO and PO are respectively ethylene oxide and propylene oxide. It was purchased from Sigma Aldrich (average molecular weight of 5800) and was used after purification (see Supporting Information). The lanthanides salts $La(NO_3)_3{\cdot}6H_2O$–$Nd(NO_3)_3{\cdot}6H_2O$ for respectively Lanthanum and Neodymium, were purchased from Sigma Aldrich with 99.9% of purity and used as received. The ligands ethyl-phosphonic acid (EPA), butyl-phosphonic acid (BPA), hexyl-phosphonic acid (HPA), octyl-phosphonic acid (OPA) and bis-(2-ethylhexyl)-phosphoric acid (HDEHP) were also purchased from Aldrich and used as received.

2.2. Samples

The samples were prepared by dissolving the required products in a 0.1 mmol L^{-1} nitric acid solution prepared in milliQ. The operating temperature was room temperature. All the samples were filtrated before measurements with an acrylic membrane Versapor® (cut-off threshold of 1.2 μm). For all the experiments, Neodymium was chosen as the referent lanthanide.

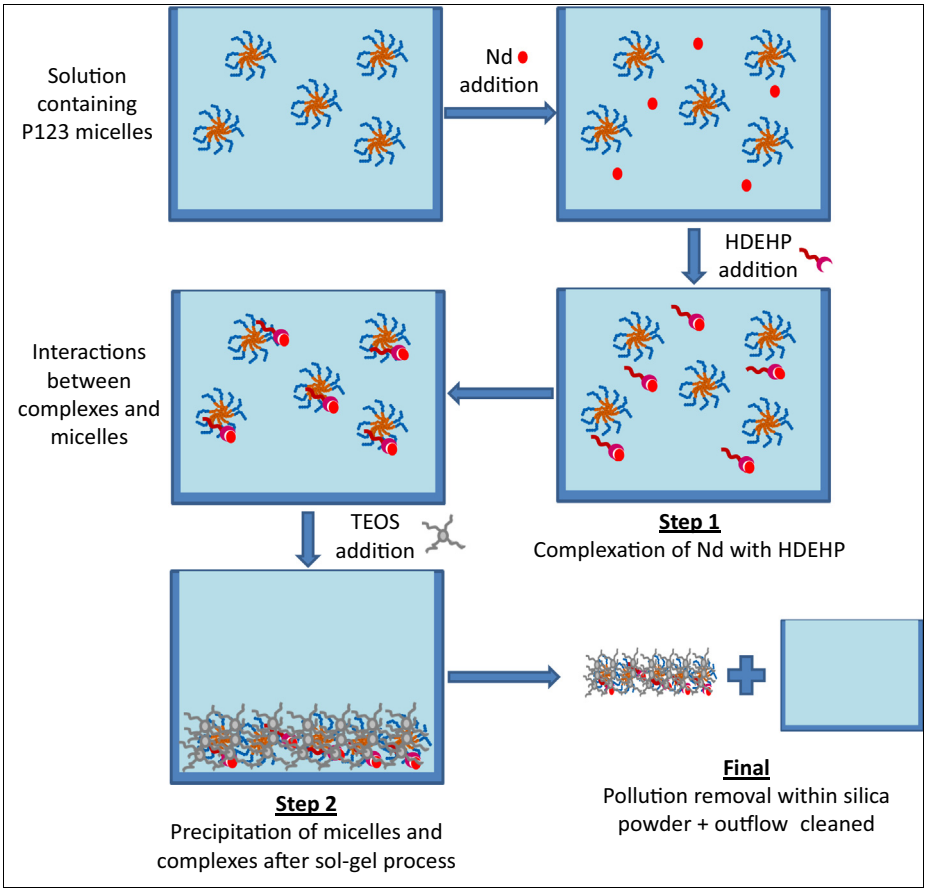

Fig. 1. Summary of the treatment process proposed in this paper for the removal of micelles and lanthanides simultaneously.