Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 23-24, 2019

Organic Nanocrystals for Efficient Uranium Sorption

Kangwoo Jin[a], Jinkyu Park [b], Jayeon Bae[a], Jinhee Park[a*]
[a]*Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology (DGIST), 333 Techno Jungang-daero, Dalseong-gun, Daegu, 42988, South Korea*
[b]*Nuclear Chemistry Reseach Division, Korea Atomic Energy Research Institute, 989-111.Daebok-daero, Yeseong-gu, Daejeon, 34057, South Korea*
[*]*Corresponding author: jinhee@dgist.ac.kr*

1. Introduction

It is well-known that the operation of nuclear power plants results in the emission of nuclear wastes in the forms of nuclear fuel effluents and gaseous radioactive wastes. Given the environmental effects and toxicity of radioactive nuclides, the removal of them has been essential for developing sustainable energy sources.

So far, diverse materials and techniques have been suggested as radioactive nuclides sorbents. Nevertheless, the poor capacities of candidate materials are unsatisfactory owing to their limited adsorption sites [1,2]. In the present work, organic nanocrystals (ONCs) functionalized with carboxyl and hydroxyl groups which have a strong affinity with uranyl ions were synthesized. Combining perylene diimides (PDIs) or naphthalene diimide (NDIs) scaffolds and –COOH or –OH groups (considered as adsorption sites) facilitate the formation of highly packed structures owing to quadrupolar π systems [3].

N,*N*'-di-(phenyl-3,5-dicarboxylic acid)-perylene-3,4,9,10-tetracarboxylic acid diimide (T-PR), and *N*,*N*'-di-(phenyl-2-hydroxy-4-carboxylic acid)-perylene-3,4,9,10-tetracarboxylic acid diimide (L-PR-OH) were synthesized for U(VI) adsorption. The NDI derivative *N*,*N*'-di-(phenyl-3,5-dicarboxylic acid)-naphthalene-1,4,5,8-tetracarboxylic acid diimide (T-NP) was also synthesized in order to investigate the effects of different π-π stacking moieties on the U(VI) adsorption capacities [4]. For clarity, the ONCs prepared from T-PR, L-PR-OH, and T-NP are denoted as T-PR-ONC, L-PR-OH-ONC, and T-NP-ONC, respectively.

We have observed that these ONCs exhibit superior U(VI) adsorption capacities and stability in aqueous solutions. Some of the parameters were used to determine the adsorption mechanism including U(VI) adsorption isotherm, kinetic and selectivity.
Furthermore, to utilize the ONCs in real-world applications, selective adsorption of U(VI) in the mixture with other metal cations was conducted.

2. Methods and Results

2.1 Synthesis and characterization of ONCs

The well-known anhydride-amine condensation reaction was adapted to synthesize desired functional groups [5]. For the synthesis of PDI and NDI derivatives, imidazole and DMF were used as solvents, respectively.

Since imidazole strongly interacts with carboxyl groups via hydrogen bonding, ONCs containing imidazole were also obtained and names as (T-PR(IM)-ONC) and (L-PR-OH(IM)-ONC), respectively. We confirmed ratios of L-PR or T-PR to imidazole using NMR spectra and elemental analysis. The T-PR:imidazole and L-PR-OH:imidazole ratios in T-PR(IM)-ONC and L-PR-OH(IM)-ONC were 1:2 and 2:1, respectively. To afford imidazole-free ONCs, the thorough washing process with hot water was required. Nano rod-like shapes and their micro-crystalline structures of ONCs are shown by FE-SEM.

2.2 U(VI) adsorption isotherm studies

pH 5.0 solutions corresponding to a series of U(VI) concentrations were prepared. Then, ONCs added to the U(VI) solution. The mixture was stirred for 5 h. the resultant solution centrifuged. the supernatant collected and measured by inductively coupled plasma mass spectrometry (ICP-MS) to analyze the remaining metal quantity in the solution.

The Langmuir or Langmuir-Freundlich isotherm models are applied to the experimental data and explain the sorption at isothermal conditions [4]. The Langmuir isotherm describes the adsorption of adsorbates onto ideal flat surfaces with the assumption uptake is given as a saturated monolayer. The Langmuir–Freundlich isotherm is an extended assumption of the Langmuir isotherm that describes multi-site adsorption on heterogeneous surfaces well.

Initially, concerning the theoretical adsorption capacities, T-NP-ONC was expected as the most efficient sorbent among the ONCs. However, the TNP-ONC adsorption capacity was exceeded by the T-PR(IM)-ONC and L-PR(IM)-ONC at pH 5 and interestingly, the adsorption capacities of T-PR(IM)-ONC and L-PR-OH(IM) were comparable. These results imply that hydroxyl groups and carbonyl groups also acted as adsorption sites as well as carboxyl groups.

2.3 U(VI) adsorption kinetics tests

For monitoring kinetics, ONCs added to a fixed concentration of U(VI) solutions. Then, the mixture stirred for 7h. After the different exposure times (10, 30 min and 1,2,4 and 7h), the aliquot solutions were collected. The aliquot solutions were centrifuged and the U(VI) concentrations in the supernatants were evaluated by ICP-MS.

U(VI) uptakes as a function of exposure time were obtained and fitted by three kinetic models, i.e., pseudo-second-order kinetics, pseudo-first-order kinetics, and intraparticle diffusion kinetics. Among these, pseudo-second-order kinetics presents the highest coefficient of determination, denoted R^2, implying that chemisorption is the rate-controlling step for U(VI) adsorption by these materials.

2.4 U(VI) adsorption selectivity studies

Selectivity toward U(VI) in simulated nuclear industrial effluent was examined. The effluent contains a variety of metal ions (Gd^{3+}, Sm^{3+}, Nd^{3+}, Ce^{3+}, La^{3+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+}). The increasing of pH results in extended selectivity of U(VI) ions over other cations. L-PR-OH-ONC and T-NP-ONC were able to get rid of U(VI) from the simulated effluent at pH 6. T-PR-ONC presented lower U(VI) removal efficiency at pH 6. The result was in contrast with the case in the pure U(VI) solution. Moreover, when simulated sea water, containing 3 ppm U(VI) is added to the ONCs, T-PR(IM)-ONC and T-NP-ONC removed c.a. 70% U(VI). But only approximately a half amount of U was removed by L-PR-OH(IM)-ONC, suggesting that hydroxyl groups are less eligible for removal of U from high-ionic-strength solution.

2.5 U(VI) adsorption-pH dependency studies

The carboxyl groups binding with the imidazole residues in T-PR(IM)-ONC and L-PR-OH(IM)-ONC, diminish the pH dependency of U(VI) adsorption.

The pH dependency of the U(VI) adsorption was tested for all ONCs. Similar to previously reported sorbents, the UO_2^{2+} adsorptions of the ONCs were subjected to the pH of the solution.

In neutral or basic solutions, carboxylic acids were deprotonated. Once a proton apart from carboxylic acid, their solubility increase in aqueous solution. Thus, T-PR, L-PR-OH, and T-NP cannot maintain self-assembled nanostructures. This gives rise to the overall uptake capacity increases with pH from 2 to 5. Carboxylic acids easily undergo proton exchange with UO_2^{2+} by forming $UO_2^{2+}(COO^-)_2$ complexes. Meanwhile, uptake by T-PR(IM)-ONCs and L-PR(IM)-ONCs is almost consistent over the pH range 3–5. The imidazole forms hydrogen bonds with the carboxylic acid group and thus accelerates the deprotonation of the carboxylic acid, even at low pH, resulting in pH-independent U(VI) uptake.

3. Conclusions

In conclusion, we successfully synthesized ONCs containing highly dense packed U(VI) adsorption sites. These ONCs showed that outstanding UO_2^{2+} adsorption capacities.

Specifically, T-PR(IM)-ONC, comprising four carboxyl groups and remained imidazole was found to be independent on the various pH conditions.

Even in simulated nuclear industrial effluent and simulated sea water, ONCs can effectively isolate U(VI).

We reported that that ONCs are one of the promising candidates for the remediation of U-contaminated environments.

REFERENCES

[1] L.M. Camacho, S. Deng, R.R. Parra, Uranium removal from groundwater by natural clinoptilolite zeolite: Effects of pH and initial feed concentration, J. Hazard. Mater., 175, pp. 393-398, 2010.

[2] J. Qu, W. Li, C.Y. Cao, X.J. Yin, L. Zhao, J. Bai, Z. Qin, W.-G. Song, Metal silicate nanotubes with nanostructured walls as superb adsorbents for uranyl ions and lead ions in water, J. Mater. Chem., 22, pp. 17222-17226, 2012.

[3] L. Wang, F. Luo, L.L. Dang, J.Q. Li, X.L. Wu, S.J. Liu, M.B. Luo, Ultrafast high-performance extraction of uranium from seawater without pretreatment using an acylamide- and carboxyl-functionalized metal-organic framework, J. Mater. Chem. A., 3, 13724-13790, 2015.

[4] A.J. Cairns, J.A. Perman, L. Wojtas, V.C. Kravtsov, M.H. Alkordi, M. Eddaoudi, M.J.Zaworotko, Supermolecular Building Blocks (SBBs) and Crystal Design: 12-Connected Open Frameworks Based on a Molecular Cubohemioctahedron, J. Am. Chem. Soc., 130, pp. 1560-1561 2008.

[5] P.K. Sukul, D. Asthana, P. Mukhopadhyay, D. Summa, L. Muccioli, C. Zannoni, D.Beljonne, A.E. Rowan, S. Malik, Assemblies of perylene diimide derivatives with melamine into luminescent hydrogels, Chem. Commun., 47, pp. 11858-11860, 2011.