

Evaluating the Efficiency of Various Reactive Media Removing Uranium from Groundwater

Beatriz Carbonell¹, Elena Torres¹, Antonio Garralón¹, Belén Buil¹, María Jesús Turrero¹
¹CIEMAT

Avda. Complutense 40, Madrid, Spain
beatriz.carbonell@ciemat.es; elena.torres@ciemat.es

Abstract –Leachate seepage from uranium-contaminated tailings and sites from past uranium mining and milling activities remains a concern because it can contaminate surrounding groundwater, requiring assessment and remediation. Among the various clean-up techniques used to remediate these sites, Permeable Reactive Barriers (PRBs) stand out as a sustainable and cost-effective alternative for the remediation of contaminated groundwater. The objective of the present work is to evaluate the suitability of different reactive media for uranium removal as a first step for the deployment of a pilot-scale PRB in U-contaminated sites in Spain. For this purpose, several reactive materials were selected: activated carbon, Zero Valent Iron (ZVI), iron oxides, phosphates and clays. Batch equilibrium tests were conducted for 7 days at room temperature, using a concentration of 2g/l of reactive material and water with U concentration of $4560 \pm 1000 \mu\text{g/L}$, thus testing the behaviour of the materials under the physicochemical conditions of a contaminated medium. The adsorption capacity and removal efficiency of each reactive material were evaluated. Phosphates and activated carbon proved to be the most suitable options, both technically and economically.

Keywords: Permeable reactive barrier (PRB), groundwater, uranium, activated carbon, zero valent iron, iron oxides, phosphates, clays.

1. Introduction

Uranium concentrations in natural waters is generally low, although higher concentrations can be found in felsic zones, areas associated with U mining, and in the vicinity of NORM industries. The reason for this is that uranium in aqueous solution can be easily dissolved, transported and precipitated by slight changes in the environment, e.g. changes in pH, chemistry or redox, which would lead to environmental contamination problems. Uranium contamination of water poses a threat to human and environmental health due to its radioactivity and chemical toxicity. In this regard, the World Health Organization (WHO) has recommended that the maximum concentration of uranium in drinking water be limited to $30 \mu\text{g/L}$ [1]. Any site with a uranium concentration above this limit requires effective remediation. For this purpose, Permeable Reactive Barriers (PRBs) represent an environmentally friendly and sustainable remediation technology, developed as a passive in situ method for the treatment of contaminated plumes [2], and save energy compared to other conventional methods. PRBs are installed across the flow path of contaminated water. Adsorption and precipitation of contaminants within the barrier occurs through various physical, chemical, or biological processes depending on the reactive infill. The long-term performance of the barrier is an unknown factor in this type of system, and the reduction of barrier permeability due to the accumulation of reaction by-products or surface passivation can significantly affect its effectiveness [3], [4].

A variety of reactive materials for using as PRBs are currently available for uranium removal, such as zero-valent iron, activated carbon, zeolite, phosphates, etc. [5]. However, many of these materials exhibit some limitations, such as their cost or availability. The objective of the present work was to evaluate the uranium removal performance of different reactive media, under certain physicochemical and chemical conditions. The materials tested were: activated carbons, zero valent irons (ZVI), iron oxides, phosphates and clays.

2. Materials and methods

2.1. Activated carbon

The properties of activated carbon (AC) are due to its high adsorption capacity, radiation stability and purity. ACs can be produced from almost any carbonaceous material. Agricultural products or their derivatives are an important and

economical source for the production of carbon adsorbents. In this work, olive pits were used as starting material for the production of AC, without and with $ZnCl_2$ as chemical agent, in a 1:1 ratio following [6], [7]. High purity commercial activated carbon powder EssentQ[®] from Scharlau was also tested.

2.2. Zero Valent Iron (ZVI)

ZVI is the most widely used media in both laboratory studies and full-scale applications due to its high reduction potential in most systems [8], [9], [10]. On the other hand, ZVI nanoparticles have a high surface area, which makes them efficient and cost-effective in the remediation of contaminated waters, although their frequent aggregation reduces their effectiveness [11]. Therefore, different technologies have been developed that use porous materials as mechanical support to reduce aggregation, for example, natural clays such as illite, a stable clay with high loading capacity and low cost, as well as a good adsorbent to remove contaminants in solution [4]. For this work, ZVI supported on illite (I-ZVI) was synthesized as Fe:illite mass ratio of 1:1. It was prepared by reduction with sodium borohydride on ferric iron using an illite from a Spanish deposit as support material and ZVI powder with a purity of 99% and a maximum particle size of 60 μm from Good Fellow[®]. The whole process was carried out under N_2 atmosphere to avoid iron oxidation following [8], [9]. Three other mixtures were tested, one with stevensite and the other with the olive pit activated carbon described in section 2.1, both maintaining the 1:1 ratio.

2.3. Iron oxides

Many other iron-based materials have been used to adsorb or reduce U(VI), for example, Fe (II) and Fe (III) oxyhydroxides [11]. For this work, three iron oxides have been tested: (1) oxidized ZVI to form ferric oxide, which is subsequently synthesized to form oxidized ZVI supported on illite, following the description in section 2.2., and (2) synthetic magnetite with a purity of 99.9 % and a particle size between 1 and 5 μm from Atlantic Equipment Engineers.

2.4. Phosphates

Apatite is also a material used for uranium removal [12]. It is found naturally in soils and sediments, being the main mineral component of phosphate rocks. Also, hydroxyapatite is the main inorganic constituent of vertebrate bone tissue. As part of the present work, two types of phosphates were used: (1) commercial hydroxyapatite with a particle size less than 200 nm from Sigma-Aldrich, and (2) natural hydroxyapatite from a fragment of animal bone that was crushed and sieved to a particle size less than 50 μm .

2.5. Clays

Clay minerals are cost-effective and readily available materials that can be used to solve the uranium problem [13]. Their potential for uranium removal is mainly due to their high adsorption capacity. For this work, three clays have been tested: illite from a Spanish deposit (as in previous sections), commercial vermiculite supplied by Scharlau, and commercial stevensite distributed by Tolsa S.A. under the trade name Minclear 100. All materials are crushed and sieved, obtaining a particle size lower than 50 μm .

2.6 Batch experiments

According to the values measured in U-mining zones, a water with a concentration of $4560 \pm 1000 \mu g/L$ has been considered for the tests, the range intended to reflect the high variation related to the natural evolution of natural systems. The high variation being related to the natural evolution of the system. To quantify the uranium adsorption or precipitation of each reactive material, experimental tests were carried out under ambient conditions by batch technique. All laboratory-prepared materials were sieved to a particle size under 50 μm . A volume of 50 mL of the uranium solution was taken and 0.1 g of each reactive material was added to it; then, the adsorbent dosage was fixed in 2g/L. The mixtures were agitated for seven days. Then, the mixed solutions were filtered through a 0.22 μm membrane. The concentration of uranium in solution was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The efficiency of uranium removal (R) was calculated according to the following equation (Eq. 1):

$$R(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium metal concentration in the solution (mg/L), respectively.

3. Results and discussion

Fig. 1 illustrates the uranium removal efficiencies of the five reactive media.

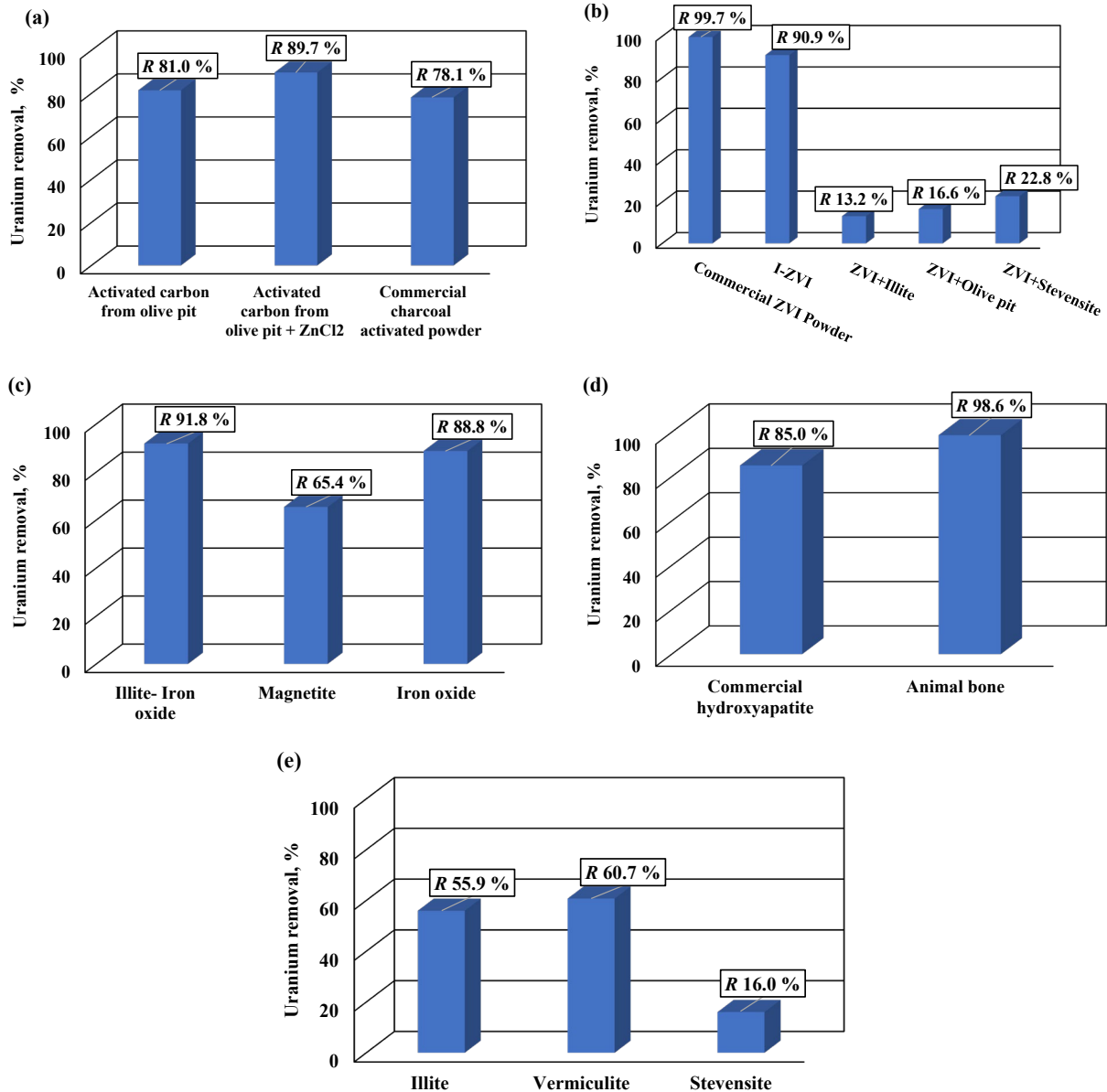


Fig. 1: Uranium removal (%) with (a) activated carbons, (b) zero valent irons, (c) iron oxides, (d) phosphates and (e) clays. (reactive material concentration, 2 g/L)

The adsorption efficiencies of activated carbon from olive pit, activated carbon from olive pit with ZnCl₂ and commercial charcoal activated powder were found to be 81.0%, 89.7% and 78.1%, respectively. Fig. 1, (a). Regarding to the zero valent

iron group, adsorption efficiencies of the commercial ZVI powder (99.7%) and laboratory-prepared I-ZVI (90.9%) were significantly higher than supported ZVI materials. Fig. 1, (b). In relation to iron oxides group, the lowest percentage of uranium removal (65.4%) was obtained with magnetite. The laboratory-prepared materials, iron oxide and illite-iron oxide, showed similar results, between 88.9% and 91.8%. Fig. 1, (c). Uranium removal rates of commercial hydroxyapatite and animal bone were higher than 85% Fig. 1 (d).

The clay group showed the lowest values in uranium removal rates, below 60% Fig. 1, (e).

The clay group showed the lowest uranium removal rates, with percentages ranging from 16% to 61% removal, which is considered insufficient for further study. An additional problem with the use of clay materials would be the consolidation processes that would lead to a reduction in barrier permeability due to the accumulation of by-products. Finally, the hydraulic conductivity of the backfill material must be higher than that of the aquifer, but the use of clay minerals as backfill material may lead to aggregation of the particles, which would lead to a decrease in the hydraulic conductivity of the barrier.

Another important requirement for the material selection is its stability. The reactive material must remain active for long periods and be stable against changes in redox potential, temperature or pressure. In this sense, the main drawback of ZVI and iron oxide groups, despite their high uranium removal rates, is their redox-sensitive behaviour, a key aspect in natural media. Another disadvantage to the use of these materials is the potential exposure to nanoparticles by inhalation. It has been reported that nZVI particles are adsorbed by cells and also cause cell death and DNA damage.

A critical factor in the selection of materials is their availability and cost. The construction of a hypothetical permeable reactive barrier will require large quantities of materials at reasonable prices. Activated carbons and phosphates, both of which have good uranium removal rates, can be produced at the lowest cost.

4. Conclusions

The selection of the reactive media to be used as a filler in a permeable reactive barrier should be based on the following characteristics: good uranium retention rates, stability, availability and cost, hydraulic conductivity, and environmental compatibility. Clays were excluded due to their low uranium removal efficiency and possible future consolidation problems. On the other hand, although ZVI showed the highest uranium removal rates, its strong dependence on changes in redox potential, coupled with the risk of handling nanomaterials, makes it not a selected medium for futures studies. The same disadvantages were found for iron oxides.

Among the uranium removal rates, activated carbon and phosphate groups showed good efficiencies, in several cases exceeding 80% removal at 2g/l concentrations. Furthermore, their availability and low cost underscore the attractiveness of these materials for uranium remediation. Activated carbon can be produced from almost any carbonaceous material. Agricultural by-products are an important and economical source, with the added benefit of contributing to a circular economy. For the phosphate group, a cheap, available and affordable alternative would be the use of NPK fertilizers or bones.

In view of the above, proposals for further study of materials that could be used as fillers for a permeable reactive barrier are those belonging to the groups of activated carbons and phosphates.

Acknowledgements

The authors thank all the members of the Hydrogeochemistry Group for their contributions to various aspects of the paper.

References

- [1] WHO, Guidelines for Drinking-water Quality: fourth edition incorporating the first addendum. ISBN 978-92-4-154995-0. 631 pp.
- [2] R. Naidu and V. Birke, Permeable Reactive Barrier. Sustainable groundwater remediation, CRC Press, 2015.
- [3] E. Torres, A. Escribano, M.J. Turrero, B. Buil, P. L. Martín, "Opciones para el tratamiento de zonas contaminadas por radionucleidos", Anales de química, vol.105(2), pp. 112-119, 2009.

- [4] E. Torres, P. Gómez, “Permeable Reactive Barriers (PRBs) for environmental site remediation”, *The Handbook of Environmental Remediation: Classic and Modern Techniques*. Chapter 7, 2020.
- [5] F. Obiri-Nyarko, S. J. Grajales-Mesa, G. Malina, “An overview of permeable reactive barriers for in situ sustainable groundwater remediation”, *Chemosphere*, vol.111, pp. 243-259, 2014. [Online]. Available: <http://dx.doi.org/10.1016/j.chemosphere.2014.03.112>
- [6] C. Kütahyalı, M. Eral, “Selective adsorption of uranium from aqueous solutions using activated carbon prepared from charcoal by chemical activation”, *Separation and Purification Technology*, vol.40, pp. 109-114, 2004 [Online]. Available: <https://doi.org/10.1016/j.seppur.2004.01.01>
- [7] C. Kütahyalı, M. Eral, “Sorption studies of uranium and thorium on activated carbon prepared from olive stones: Kinetic and thermodynamic aspects”, *Journal of Nuclear Materials*, vol.396, pp. 251–256, 2010. [Online]. Available: <https://doi.org/10.1016/j.jnucmat.2009.11.018>
- [8] C. Jing, Y. Li, R. Cui, J. Xu, “Illite-supported nanoscale zero-valent iron for removal of ²³⁸U from aqueous solution: characterization, reactivity and mechanism”, *Journal of Radioanalytical Nuclear Chemistry*, vol.301, pp. 859-865, 2015. [Online]. Available: DOI:10.1007/s10967-014-3850-2
- [9] C. Jing, S. Landsberger, Y.L. Li, “The application of illite supported nanoscale zero Valente iron for the treatment of uranium contaminated groundwater”, *Journal of Environmental Radioactivity*, vol. 175-176, pp. 1-6, 2017. [Online]. Available: <https://doi.org/10.1016/j.jenvrad.2017.04.003>
- [10] X. Zhang, S. Lin, X. Lu, Z. Chen, “Removal of Pb(II) from water using synthesized kaolin supported nanoscale zero-valent iron”, *Chemical Engineering Journal*, vol. 163, pp. 243-248, 2010. [Online]. Available: <doi:10.1016/j.cej.2010.07.056>
- [11] Anwei Chen, Cui Shang, Jihai Shao, Jiachao Zhang, Hongli Huang, “The application of iron-based technologies in uranium remediation: A review”, *Science of the Total Environment*, vol.575:1, pp. 291–1306, 2016. [Online]. Available: <http://dx.doi.org/10.1016/j.scitotenv.2016.09.211>
- [12] Krestou, A. Xenidis, D. Panias, “Mechanism of aqueous uranium (VI) uptake by hydroxyapatite. *Minerals Engineering*”, vol.17, pp. 373–381, 2004. [Online]. Available: <https://doi.org/10.1016/j.mineng.2003.11.019>
- [13] K. De Pourcq, C. Ayora, M. García-Gutiérrez, T. Missana, J. Carrera, “A clay permeable reactive barrier to remove Cs-137 from groundwater: Column experiments”, *Journal of Environmental Radioactivity*, vol. 149, pp.36-42, 2015. [Online]. Available: <https://doi.org/10.1016/j.jenvrad.2015.06.029>