

## REMOVAL OF RADIUM-226 FROM RADIUM-CONTAMINATED SOIL USING DISTILLED WATER AND HUMIC ACID: EFFECT OF pH

*Phillip, E., Yasir, M.S., Omar, M., Ibrahim, M.Z., Laili, Z.*

Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor DarulEhsan, Malaysia; UniversitiKebangsaan  
Malaysia, 43000 Kajang, Selangor DarulEhsan, Malaysia

E-mail: esther@nuclearmalaysia.gov.my

### ABSTRACT

Effect of washing solutions' pH on removal of radium-226 from radium-contaminated soil using distilled water and humic acid extracted from Malaysian peat soil was studied by batch washing method. The study encompassed the extraction of humic acid and the washing of radium-contaminated soil using distilled water and humic acid solutions of 100 ppm, both with varying pHs in the range of 3 to 11. The radioactivity concentration of radium-226 was determined by gamma spectrometer. The removal of radium-226 was greater when humic acid solutions were used compared to distilled water at the pH range studied and both washing solutions showed greater removal of radium-226 when basic solutions were used. Nevertheless, comparable removal efficiencies were observed when neutral and highly basic humic acid solutions were used.

### ABSTRAK

Kesan pH larutan pembersihan terhadap penyingkiran radium-226 daripada tercemar dengan radium menggunakan air suling dan asid humik yang diekstrak daripada gambut dikaji melalui kaedah pembersihan kelompok. Kajian melibatkan pengekstrakan asid humik dan pembersihan tercemar dengan radium menggunakan air suling dan asid humik berkepekatan 100 ppm dengan kedua-dua larutan pembersihan dalam julat 3 hingga 11. Kepekatan radioaktiviti radium-226 ditentukan menggunakan alat spektrometer gama. Penyingkiran radium-226 adalah lebih tinggi apabila larutan asid humik digunakan berbanding dengan air suling pada julat pH yang dikaji dan kedua-dua larutan pembersihan menunjukkan penyingkiran radium-226 yang tinggi apabila larutan beralkali digunakan. Namun begitu, keberkesanan penyingkiran yang agaksamadiperhatikan apabila larutan asid humik berpH neutral dan berkealkali tinggi digunakan.

### INTRODUCTION

In Malaysia, historically generated radium (Ra)-contaminated soil was originated from compass dial painting activities that were carried out since the 1960s until 1990s. The radioluminescence paint used for those activities contained radium-226 (Ra-226) as the primary luminescence substance before the discoveries of tritium (H-3) and promethium-147 (Pm-147) (Eisenbud and Gesell, 1997). Ra-226 has a relatively long half-life of approximately 1600 years and being an alpha and gamma emitter (EPA, 2004) it poses an extremely hazardous

effect on human health. Therefore, clean-up of Ra-contaminated soil needs to be carried out to diminish and finally eliminate the detrimental effect of Ra-226.

Interaction between Ra and soil organic matter was discussed by Hansen and Huntington (1969). Soil organic matter contains humic substances (HS) that can be fractionated to humic acid (HA), fulvic acid (FA) and humin (Schnitzer and Khan, 1978), with HA as the main extractable fraction (Koczorowska et al., 2002). HA contains two major acidic functional groups; carboxyl and phenolic, (Choppin, 1988; Stevenson, 1982; Samadfam et al., 1998) that provide binding sites for interactions with other materials such as metal ions (Bowen et al., 1979; Omar and Bowen, 1982) and radionuclides (Marquardt, 2000). As a remarkably heterogeneous ligand (Choppin, 1988; Stevenson, 1982) with polyelectrolytic nature (Samadfam et al., 1998), HA interactions with metal ions and radionuclides are significantly affected by pH (Carlsen, 1989; Stevenson, 1982; Samadfam et al., 1998) due to the changes in the amount of binding sites of HA as pH shifts. The changes in binding sites are due to the alteration of ionization of acidic functional groups in HA molecules (Marinsky et al., 1982; Stevenson, 1982). As pH increases, deprotonation of functional groups also increases thus providing more negatively charged binding sites. Apart from binding sites, changes in pH also affect the structural configuration of HA molecules (Stevenson, 1982; Wood, 1996). With increase in pH, structural configuration of HA molecules changes from a tightly coiled, cross-linked configuration to a more open configuration that favours binding (Bertha and Choppin, 1978) owing to electrostatic repulsion between negatively charged HA molecules (Stevenson, 1982). Besides effect on HA, pH also contributes to speciation of Ra. Ra normally exists in its +2 oxidation state over a wide pH range of 3 to 10 (Smith and Amonette, 2006). Nevertheless, it can also form aqueous complexes such as  $\text{RaOH}^+$ ,  $\text{RaCl}^+$ ,  $\text{RaHCO}_3^+$ ,  $\text{RaCO}_3^0$  (aq) and  $\text{RaSO}_4^0$  (aq) (EPA, 2004; Baeza et al., 2006) at different pH values. Binding of HA molecules with Ra differs with different Ra species.

At different pH, binding of Ra to HA molecules can also be affected by the presence of metal ions such as Al and Fe that are typically found in soil. Stevenson and Vance (1989) stated that HS such as HA can form both soluble and insoluble complexes with Al and that the interactions involved are governed by pH. pH affects the complexation of HA with Al through hydrolysis reactions involving  $\text{Al}^{3+}$  that resulted in the formation of monomeric and polymeric Al species and changes in charge and configurational characteristics of HA (Stevenson and Vance, 1989). The HA – Al complexes also act as pseudocolloid for radionuclides (Choppin, 1988; McCarthy and Zachara, 1989).

In soil washing, one of the main operating variables that determined the efficiency of washing was pH as pH could affect the retention and mobility of pollutants such as metal ions and radionuclides in soil (Reed et al., 1996; Peters, 1999). Besides that, pH could also affect the ability of chelating agents to extract metal ions and radionuclides from soil through numerous mechanisms (Zou et al., 2009).

This study aims at determining the pH-dependence of removal efficiency of Ra-226 from Ra-contaminated soil by using distilled water and HA solutions of varying pH as washing solutions. The pHs of the washing solutions studied ranged from 3 – 11 at room temperature. pH adjustment was done on the washing solution (distilled water and HA solutions) and not on the mixture of washing solution and soil sample. This method was found to

be more practical and easier in terms of implementation of soil washing processes. Washing of contaminated soil with distilled water was important in order to eliminate metal ion and radionuclide fractions that were weakly bound to soil particles or sorbed at easily coordinated sites in the outer surfaces of soil particles (Mann, 1999). Water-removable Ra species were known as water-exchangeable Ra (Cooper et al., 1981) or water-soluble Ra (Goulden et al., 1998). Removal of Ra from soil depended on the solubility of Ra-226 species in water that was controlled by precipitation, co-precipitation and sorption reactions in natural systems (Langmuir and Melchior, 1985; Langmuir and Riese, 1985). Meanwhile, interactions between metal ions or radionuclides and HA molecules depended on pH due to the polyelectrolytic properties of HA (Stevenson, 1982; Carlsen, 1989) and ligand heterogeneity in terms of functional groups content (Stevenson, 1982; Choppin, 1988). Therefore, the washing of Ra-contaminated soil using HA solutions of various pHs was studied in order to evaluate the ability and efficiency of HA in removing Ra-226 species that were tightly bound to the soil matrix. Metal and radionuclides species that were tightly bound to soil matrix could be identified as exchangeable ions, adsorbed ions, precipitated ions, organically-bound ions or insoluble ions that were trapped in soil matrix (Mann, 1999).

## **MATERIALS AND METHODS**

HA used was extracted from peat soil obtained from Bachok, Kelantan. Meanwhile, Ra-contaminated soil was sampled from a former compass dial painting facility site. The Ra-contaminated soil sample had been excavated from the site and transferred to the radioactive waste storage facility at Nuclear Malaysia since year 2000.

Ra-226 standard solutions were obtained from Isotope Products Laboratories (an Eckert & Ziegler Company). Other reagents and chemicals used were of analytical grade from R&M Chemicals or Sigma Aldrich.

### *Extraction of HA from peat soil*

HA was extracted from peat soil according to the acid-base extraction method described by International Humic Substances Society (IHSS). HA stock solutions were prepared by dissolving the extracted solid HA in diluted sodium hydroxide (NaOH) solutions. HA working solutions were prepared by diluting the stock solutions also in diluted NaOH.

### *Preparation of Ra-contaminated soil sample*

The Ra-contaminated soil sample was air-dried at room temperature in a fume hood prior to manual grinding using a ceramic pestle and mortar. The ground soil sample was then sieved using a 2 mm sieve and finally stored in a sealed container for experimental purposes.

### *Elemental and radioactivity characterization of Ra-contaminated soil sample*

Elemental composition of the Ra-contaminated soil sample was determined by NAA (neutron activation analysis) technique. Ra-226 activity concentration of the Ra-contaminated soil sample was analysed by a gamma spectrometer (Oxford Instruments Inc., 30% relative efficiency and 1.9 keV at 1.33 MeV resolution with a CANBERRA n-type hyper-germanium detector (HPGe)).

*pH study*

HA solutions of 100 ppm and distilled water, both with varying pHs in the range of 3 – 11, were used as washing solutions. 1 g of Ra-contaminated soil sample was added to 20 mL HA solution in 100 mL conical flask and agitated using an orbital shaker at 100 rpm for 24 h at room temperature. Preliminary kinetic experiments revealed that equilibrium was established within this period. pH of the soil suspension was also measured. The soil suspension was then centrifuged at 4000 rpm for 10 min and the supernatant was collected by decantation. The collected supernatant was immediately sealed in a plastic container and was left to equilibrate for 20 days before analysis with gamma spectrometer. Precision was established by preparing duplicates for each test. Experiments were repeated with distilled water.

Removal efficiency of Ra-226 was calculated based on the equation

$$\text{Removal efficiency, \%} = \frac{A_0 - A}{A_0} \times 100\%$$

- $A_0$  = Initial Ra-226 activity concentration in Ra-contaminated soil sample, Bq/kg  
 $A$  = Final Ra-226 activity concentration in Ra-contaminated soil sample after Washing, Bq/kg

**RESULTS AND DISCUSSION**

Elemental composition of Ra-contaminated soil sample displayed in Table 1 shows that Al was the major metal present in the soil sample. Meanwhile, gamma spectrometry analysis showed that Ra-226 activity concentration of the soil sample was  $70486 \pm 2935$  Bq/kg.

Table 1

Elemental composition of Ra-contaminated soil sample

<b>Element</b>	<b>ppm</b>	<b>±</b>
Al	54600	1870
Fe	8510	607
K	2500	248
Ti	1930	146
Na	386	42
Zr	275	29
Zn	178	7
Mn	89.5	9.3
Ba	78	21

Figure 1 shows the effect of pHs of distilled water and HA solutions on the removal efficiency of Ra-226 from Ra-contaminated soil sample.

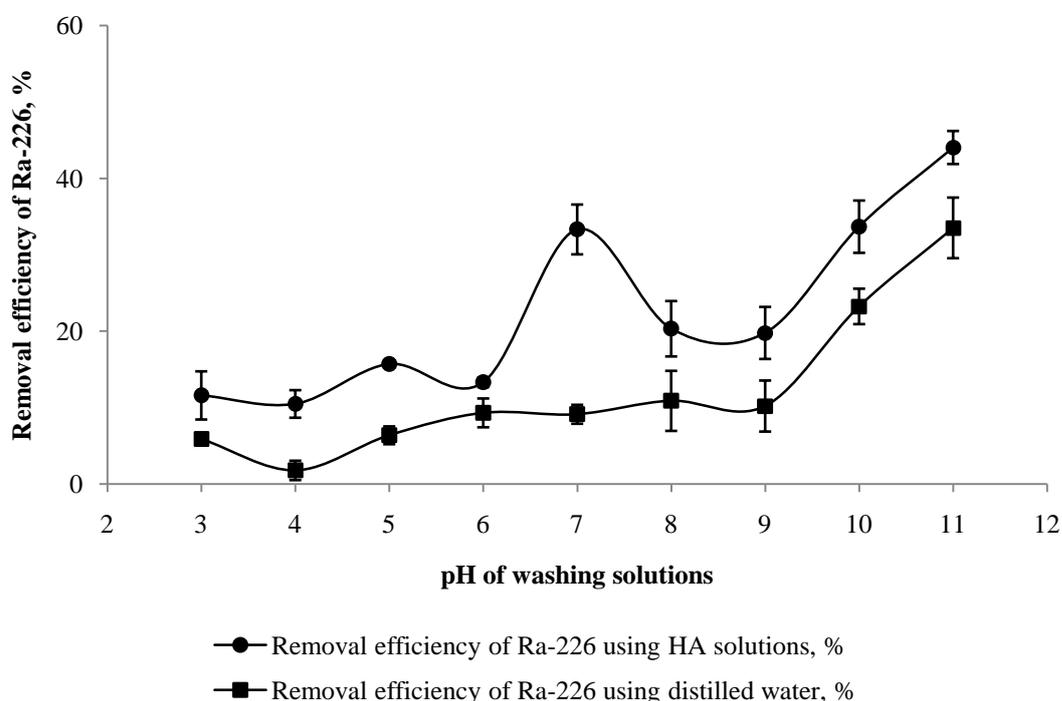


Figure 1 Effect of pH of washing solutions on the removal efficiency of Ra-226 from Ra-contaminated soil sample

In this study, the data obtained for removal efficiency of Ra-226 using distilled water served as baseline data to compare with removal efficiency of Ra-226 using HA solutions, thus to evaluate the ability and efficiency of HA solutions as washing agents. Experimental results showed that batch washings of Ra-contaminated soil sample using distilled water of pH ranged from 3 to 11 were able to remove 2 – 34 % of Ra-226. It was also found that the removal efficiency of Ra-226 increased with the pH of distilled water used.

When distilled water of pH 3 was used, the final pH of the washing system was altered to around 5. The removal efficiency of Ra-226 was approximately  $6 \pm 1$  %. Soluble Ra species present at this pH was mainly  $\text{Ra}^{2+}$  ions (Baeza et al., 2006) that could result from solubilisation of  $\text{RaSO}_4$  or desorption of Ra-226 species from hydrous oxides such as hydrous iron oxides in soil due to oxide solubilisation by  $\text{H}^+$  ions at low pH (Zou et al., 2009). Besides contributing to oxide solubilisation,  $\text{H}^+$  ions also acted as weak competing cations that could replace desorbed Ra-226 species via cation exchange mechanism. As an alkaline earth metal, Ra is chemically analogued to Ba (van Beek et al., 2009) and therefore possesses the same chemical properties as Ba (Henriksen et al., 2002; Comstock, 2010). Thus, Ra species in soil could adsorb to hydrous oxides the same way as Ba species (Carbonell et al., 1999). However, adsorption of Ra onto hydrous iron oxides was not very encouraging (Megumi, 1979) thus resulting in less Ra-226 species being desorbed from the hydrous iron oxides in the Ra-contaminated soil sample. The weak acidic condition at pH 5 also further led to less Ra-226 species being

desorbed from the hydrous iron oxides in the Ra-contaminated soil sample. Besides that, competition between  $\text{Ra}^{2+}$  ions and dissolved Al and Fe species in securing exchange sites in soil matrix (Carbonell et al., 1999) could also lead to the low removal efficiency of Ra-226. Other soluble Ra complexes such as  $\text{RaSO}_4^0$  and  $\text{RaHCO}_3^+$  were also present at this pH (Baeza et al., 2006). The effect of pH could also be explained by incorporating the roles of polyvalent cation such as Al that was present in the Ra-contaminated soil sample. For instance,  $\text{Al}(\text{OH})_3$  precipitates that were starting to form at pH 5 could adsorb Ra-226 species especially  $\text{RaSO}_4^0$  thus resulting in low removal of Ra-226.

The final pHs of the washing systems were altered to around neutral when distilled water in the pH range 4 – 8 was used. Meanwhile, the removal efficiency of Ra-226 was found to be approximately 2 – 11 %. At near neutral pH, soluble  $\text{RaHCO}_3^+$  complex was the dominant Ra species present (Baeza et al., 2006). Besides that,  $\text{Ra}^{2+}$  ions and soluble  $\text{RaSO}_4^0$  complex were also present (Baeza et al., 2006). Removal efficiency of Ra-226 was at its minimum when distilled water of pH 4 was used probably due to maximum adsorption of Ra-226 species especially neutral  $\text{RaSO}_4^0$  complex onto  $\text{Al}(\text{OH})_3$  precipitates. When distilled water of pH 5 – 8 was used, the removal efficiency of Ra-226 remained almost constant.

When distilled water in the pH range 9 – 10 was used, the final pHs of the washing systems were shifted to around 8 at which Ra species in the forms of soluble complexes  $\text{RaHCO}_3^+$ ,  $\text{RaCO}_3^0$ ,  $\text{RaSO}_4^0$  and  $\text{Ra}^{2+}$  ions were present (Baeza et al., 2006). The removal efficiency of Ra-226 obtained was approximately 10 – 23 %. According to Hem (1986), hydroxyl  $\text{Al}(\text{OH})_4^-$  complexes were the dominant Al species formed at pH greater than 7 thus signifying the decrease and finally the end of  $\text{Al}(\text{OH})_3$  precipitates formation. This then led to higher removal of Ra-226 compared to the previous neutral pH as adsorption of Ra-226 species onto  $\text{Al}(\text{OH})_3$  precipitates had ceased.

When distilled water of high alkalinity (pH 11) was used, the final pH of the washing system was maintained at the initial pH of the distilled water. The removal efficiency of Ra-226 was at its maximum at this pH. The increase in removal efficiency with the final pH of washing system corresponded well with the increased solubility of Ra at high pH as discussed by McCready et al. (1980) and Huck and Anderson (1982). At this pH, most of the Ra-226 species present was in the form of soluble  $\text{RaCO}_3^0$  complexes (Baeza et al., 2006). The removal of Ra-226 was balanced by the adsorption of  $\text{RaCO}_3^0$  onto metal precipitate such as ferric sulphate as adsorption of neutral species such as  $\text{RaCO}_3^0$  onto metal precipitate was more favourable at high pH (Valentine et al., 1985; Baeza et al., 2006).

Batch washings of the Ra-contaminated soil using HA solutions in the pH range 3 – 11 resulted in 10 – 44 % of Ra-226 removal. It was also found that the removal efficiency increased with the final pHs of the washing systems and the increase observed was greater compared to when distilled water was used as washing solution. The increase suggested that HA was able to remove Ra-226 species that were strongly bound to the soil matrix that were not removable by distilled water through complexation of deprotonated center (Güngör and Bekbölet, 2010).

The removal efficiency of Ra-226 using HA solutions that increased with pH was probably due to the increase in stability constant of Ra-HA complex as both binding sites and strength increased. Nevertheless, the removal of Ra-226 was also affected by binding of HA molecules with soil matrices and presence of other metal species such as Al that were isolated from the contaminated soil. Al species could interfere the binding of Ra-226 by HA molecules since Al itself could form stable complexes with HA molecules (Stevenson and Vance, 1989).

When HA solutions of particular pHs were shaken with the Ra-contaminated soil sample of neutral pH, the final pHs of the soil washing systems obtained differed from the pHs of the HA solutions used except for HA solutions of pH 7. The final pHs of the washing systems shifted to around 5 – 6.5 when HA solutions in the pH range of 3 – 6 were used. It was found that the removal efficiency of Ra-226 was the lowest at this pH range. At  $\text{pH} < 7$ , acid dissociation of carboxylic functional groups of HA molecules was not favourable (Fukushima, 1996) and could lead to less Ra-226 species being bound to HA molecules. Besides binding to HA molecules, trapping of Ra-226 species by HA aggregates was also not favourable in this weakly acidic pH condition. In very acidic pH condition, HA molecules tended to form supramolecules or aggregates through protonation of carboxylate or phenolate that reduced electrostatic repulsion between molecules and increased formation of intermolecular H-bond (Brigante et al., 2009). Therefore, the temporary trapping of metal ions and radionuclides by HA aggregates were more favourable in very acidic condition (Avena & Wilkinson, 2002). In weakly acidic condition as in the pH range 5 – 6.5, this phenomenon was unlikely to occur. Furthermore, in the pH range 5 – 6.5, the binding of Ra-226 species to HA molecules was low probably due to the coagulation of HA molecules with Al species that was prone to occur in the pH range 4 – 7 (Dempsey et al., 1984). Kaiser et al. (1997) mentioned that the structural surfaces of amorphous  $\text{Al}(\text{OH})_3$  precipitates were suitable for the adsorption of soluble organic substances.

When HA solutions of pH 7 were used, the final pHs of the washing systems were maintained at the same neutral pHs. Meanwhile, the removal efficiency of Ra-226 obtained was approximately  $33 \pm 3 \%$ ; an increase of about 17 – 23 % from the previous pHs. The appreciable increase indicated that greater ionization of HA molecules at higher pH allowed for more binding of Ra-226 species. At pH range 7 – 8, the main functional groups of HA molecules that involved in the interaction with metal ions and radionuclides were deprotonated carboxylic groups, phenolic-OH groups and partially reactive aliphatic-OH groups (Güngör, 2010). Solubility of Al was lowest at pH 6.5 due to the formation of  $\text{Al}(\text{OH})_3$  precipitates and increased with pH due to the formation of  $\text{Al}(\text{OH})_4^-$  ions (Driscoll, 1989). Therefore, at pH 7, the adsorption of neutral Ra-226 species namely  $\text{RaSO}_4^0$  and  $\text{RaCO}_3^0$  onto  $\text{Al}(\text{OH})_3$  precipitates was low due to the decreasing formation of  $\text{Al}(\text{OH})_3$  precipitates and thus more Ra-226 species were available for binding with HA molecules. However, as coagulation of HA with Al that tended to occur at pH 4 -7 (Dempsey et al., 1984), the binding of Ra-226 species to HA molecules was also reduced thus resulting in lower removal efficiency of Ra-226 than anticipated. A notable difference in removal efficiency of Ra-226 between distilled water and HA solution was also observed at pH 7 probably due to high amount of deprotonated functional groups in HA molecules at this particular pH. Besides that, without HA, coagulation of HA with Al did not happen therefore resulting in more Al available for formation of  $\text{Al}(\text{OH})_3$  precipitates. This would consequently lead to the difference in removal efficiency

observed as more neutral species such as  $\text{RaSO}_4^0$  and  $\text{RaCO}_3^0$  could be adsorbed by the  $\text{Al}(\text{OH})_3$  precipitates in the absence of HA.

The final pHs of the washing systems were shifted to around 7.5 when HA solutions in the pH range 8 – 9 were used. Our findings showed that the removal efficiency of Ra-226 at this pH was approximately 13 % lower than at the previous pH 7. At this pH, the Ra-226 species were favourably bound to the deprotonated carboxylic functional groups rather than to the deprotonated phenolic functional groups.

When HA solutions in the pH range 10 – 11 were used, the final pHs of the washing systems were found to be around 8 with the final pHs for HA solutions of pH 11 slightly higher than pH 10. The removal efficiency was higher at this pH compared to near neutral pH and reached its maximum when HA solutions of pH 11 were used. The significant increase in the removal efficiency of Ra-226 in basic conditions suggested the increasing importance of deprotonated phenolic functional groups in binding with Ra-226. Deprotonation of functional groups that increased with pH (Hsieh et al., 2010) encouraged more interaction between HA molecules and Ra-226 species thus leading to increasing removal with pH. Other than amount of binding sites, the removal of Ra-226 was also affected by the binding strength between HA molecules and Ra-226 species that could be explained by the structural changes of HA molecules (Samadfam et al., 1998). In basic condition, HA molecules were more open and linear due to the decrease in intra- and inter-molecular hydrogen bonding (Spark et al., 1997). Therefore, the increase in removal efficiency of Ra-226 in basic pH was due not only to the increase in activity but also accessibility of HA functional groups (Güngör, 2010). Besides that, adsorption of soil organic matter on the surface of soil mineral that decreased with pH (Ganter, 2007) explained the decreasing adsorption of HA molecules onto soil matrix as pH increased. This was due to the effect of pH on the surface charge of multi-charged mineral such as Al and Fe hydroxide at which the surface net charge on the hydrolysed surface was more negative with increasing pH (Sollins et al., 1996; Krull et al., 2003). Therefore, the decreasing adsorption of HA molecules on the soil matrix would consequently lead to higher removal of Ra-226 species from the soil matrix through binding of Ra-226 species with HA molecules.

## CONCLUSION

As far as the pH study is concerned, the data obtained shows that HA solutions are able to remove Ra-226 species from the Ra-contaminated soil sample studied and the removal efficiency observed was greater than when distilled water was used as washing solution. Nevertheless, the difference in removal efficiency observed was about 4 – 24 % with the highest difference noted when washing solutions of pH 7 were used. The efficiency of HA solutions could be attributed to the interactions between functional groups in HA molecules and Ra-226 species. Nonetheless, the efficiency of HA solutions could also be affected by Al species present in the soil. Both washing solutions showed comparable trend in removal efficiency when acidic and basic solutions were used. However, the trend in removal efficiency varied when neutral washing solutions were used.

## REFERENCES

- Avena, M.J. and Wilkinson, K.J., (2002), Disaggregation kinetics of a peat humic acid: Mechanism and pH effects, *Environmental Science Technology* 36:5100-5105.
- Baeza, A., Fernandez, M., Herbanz, M., Legarda, F., Miro, C., and Salas, A., (2006), Removing uranium and radium from a natural water, *Water, Air, and Soil Pollution* 173:57-69.
- Bertha, E.L. and Choppin, G.R., (1978), Interaction of humic and fulvic acids with Eu(III) and Am(III), *J. Inorg. Nucl. Chem.* 40:655-658.
- Bowen, H.J.M., Page, E., Valente, I. and Wade, R.J., (1979), Radio-tracer methods for studying speciation in natural waters, *Journal of Radioanal. Chem.* 48:9-16.
- Brigante, M., Zanini, G. and Avena, M., (2009), Effect of pH, anions and cations on the dissolution kinetics of humic acid particles, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 347:180–186.
- Carbonell, A. A., Pulido, R., DeLaune, R.D. and Patrick, W.H., (1999), Soluble barium in barite and phosphogypsum amended Mississippi River alluvial sediment, *Journal of Environmental Quality* 28:316-321.
- Carlsen, L., (1989), The role of organics on the migration of radionuclides in the geosphere in EUR 12024 EN, Eurooffice.
- Choppin, G.R., (1988), Humics and radionuclide migration, *Radiochim.Acta.* 44-45:23-28.
- Comstock, S., (2010), *Biogeochemistry of Barium: Chemical Properties and Environmental Interactions.* CWR6252, Florida, USA.
- Cooper, M.B., Stanney, K.A. and Williams, G.A., (1981), An Investigation of the Speciation of Radionuclides in Sediments and Soils. Report ARL/TR-039, Australian Radiation Laboratory, Melbourne, Australia.
- Davis, J.A. and Hem, J.D., (1989), The Surface Chemistry of Aluminium Oxides and Hydroxides. In: *The Environmental Chemistry of Aluminium*, CRC Press, Inc., Boca Raton, Florida. 7.
- Dempsey, B.A., Ganho, R.M. and O'Melia, C.R., (1984), The coagulation of humic substances by means of aluminium salts, *J. Am. Water Works Assoc.* 76(141).
- Driscoll, C.T., (1989), The Chemistry of Aluminium in Surface Waters. In: *The Environmental Chemistry of Aluminium*, CRC Press, Inc., Boca Raton, Florida. 9.
- Eisenbud, M. and Gesell, T., (1997), *Environmental Radioactivity. From Natural, Industrial and Military Sources.* 4<sup>th</sup> Edition, Academic Press, UK, 656 pp.
- Frissel, M.J. and Koster, H.W., (1990), Radium in soil. In: *The Environmental Behaviour of Radium*, Vol. 1, Chapter 4-1. Technical Report Series No. 310, IAEA, Vienna.
- Fukushima, M., Tanaka, S., Nakamura, H. and Ito, S., (1996), Acid-base characterization of molecular weight fractionated humic acid, *Talanta* 43:383-390.
- Ganter, C. (2007), *Stabilization of Soil Organic Matter by Mineral Surfaces.* Term Paper in Biogeochemistry and Pollutant Dynamics, M.Sc. Environmental Sciences, ETH Zürich, 1-13.
- Goulden, W.D., Hendry, M.J., Clifton, A.W. and Barbour, S.L., (1998), Characterization of Radium-226 in Uranium Mill Tailings. In: *Tailings and Mine Waste '98*, Balkema, Rotterdam. 561-570.
- Güngör, E.B.Ö. and Bekbölet, M., (2010), Zinc release by humic and fulvic acid as influenced by pH, complexation and DOC sorption, *Geoderma* 159(1-2):131-138.
- Hansen, R.O. and Huntington, G.L., (1969), Thorium movement in Morainal Soils of the High Sierra, California, *Soil Science* 108:257-265.

- Hem, J.D., (1983), Kinetics of Dissolution and Structure of Aluminium Hydroxide Polymers. In: Leaching and Diffusion in Rocks and Their Weathering Products, Augustithis, S.S., Ed., Theophrastus Publications S. A., Athens, 51.
- Henriksen, G., Hoff, P. and Larsen, R.H.,(2002), Evaluation of potential chelating agents for radium, Applied Radiation and Isotopes 56:667-671.
- Hsieh, P.C., Hsu, S.H., Lee, C.L., and Brimblecombe, P., (2010), pH dependence of binding benzo[h]quinoline and humic acid and effects on fluorescence quenching, Environmental Toxicology and Chemistry 29:1696-1702.
- Huck, P.M. and Anderson B., (1982), Leachability of barium-radium sulphate sludges, Kaiser, K., Guggenberger, G., Haumaier, L. & Zech, W. 1997. Dissolved organic matter sorption on subsoils and minerals studied by C-NMR and DRIFT spectroscopy. European Journal of Soil Science 48:301–310.
- Koczorowska, E., Nieloch, M. and Slawinski, J.,(2002), Model radioisotope experiments on the influence of acid rain on Zn-65 binding with humic acid, Nukleonika 47(4):167-172.
- Krull, E. S. and Baldock, J.A.,(2003), Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover, Functional Plant Biology 30(2):207-222.
- Langmuir, D. and Melchior, D., (1985), The geochemistry of Ca, Sr, Ba, and Ra sulfates in some deep brines from the Palo Duro Basin, Texas, Geochim. Cosmochim. Acta 49:2423-2432.
- Langmuir, D. and Riese, A.C., (1985). The thermodynamic properties of radium, Geochim. Cosmochim. Acta 49:1593-1601.
- Mann, J.M., (1999), Full-scale and pilot-scale soil washing, J. Hazard Mater. 66:119-136.
- Marinsky, J.A., Gupta, S. and Schindler, P.J., (1982), A unified physicochemical description of the equilibria encountered in humic-acid gels, J. Colloid Interface Sci. 89:412-426.
- Marquardt, C.M., (2000), Influence of Humic Acids on the Migration Behaviour of Radioactive and Non-Radioactive Substances under Conditions Close to Nature. Final Report BMBF Project No. 02E87958. Forschungszentrum Karlsruhe GmbH, Karlsruhe.
- McBride, M., Sauve, S. and Hendershot, W., (1997), Solubility control of Cu, Zn, Cd, and Pb in contaminated soils, European Journal of Soil Science 48:337–346.
- McCarthy, J.E. and Zachara, J.M., (1989), Subsurface transport of contaminants, Environ. Sci. Technol. 23(5).
- McCready, R.G.L., Bland, C.J. and Gonzales, D.E., (1980), Preliminary studies on the chemical, physical, and biological stability of Ba/RaSO<sub>4</sub> precipitates, Hydrometallurgy 5(2-3):109-116.
- Megumi, K., (1979), Radioactive disequilibrium of uranium and actinium series nuclides in soil, J. Geophys. Res. 84:3677-3682.
- Omar, M. and Bowen, H.J.M., (1982), Separation of methyltin species from inorganic tin and their interactions with humates in natural waters, Journal of Radioanal. Chem. 74(1):273-282
- Peters, W.R., (1999), Chelant extraction of heavy metals from contaminated soil, J. Hazard Mater. 66:151-210.
- Reed, B.E., Carriere, P.C. and Moore, R., (1996), Flushing of a Pb(II) contaminated soil using HCl, EDTA and CaCl<sub>2</sub>, J. Environ. Eng. 121:48-50.
- Samadfam, M., Jintoku, T., Sato, S. and Ohashi, H., (1998), Effect of pH on stability constants of Sr (II) – humate complexes, Journal of Nuclear Science and Technology 35(8):579-583.
- Schnitzer, M. and Khan, S.U., (1972), Humic Substances in the Environment, Marcel Dekker Inc., New York.

- Smith, B. and Amonette, A., (2006), The Environmental Transport of Radium and Plutonium: A Review, Institute for Energy and Environmental Research, Maryland, USA.
- Sollins, P. and Homann, P., (1996). Stabilization and destabilization of soil organic matter: Mechanisms and controls, *Geoderma*74(1-2):65-105.
- Spark, K.M., Wells, J.D. and Johnson, B.B.,(1997). The interaction of humic acid with heavy metals, *Australian Journal of Soil Research* 35:89–101.
- Stevenson, F.J. and Vance, G.F., (1989), Naturally Occuring Aluminium-Organic Complexes. In: *The Environmental Chemistry of Aluminium*, CRC Press, Inc., Boca Raton, Florida. 5.
- Stevenson, F.J., (1982), *Humus Chemistry*, A Wiley-Interscience Publication, John Wiley & Sons , New York.
- EPA (U.S. Environmental Protection Agency), (2004), *Understanding Variation in Partition Coefficient, K<sub>d</sub>, Values. Volume III: Review of Geochemistry and Available K<sub>d</sub> Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium*, USA.
- Valentine, R.L., Splinter, R.C., Horng, J.J. and Nogaj, T.M., (1985), Factors affecting radium reduction in an iron removal process. In: *Proceedings of American Water Works Association Annual Conference*.
- vanBeek, P., Sternberg, E., Reyss, J.L., Souhaut, M., Robin, E., and Jeandel, C., (2009), Ra-228/Ra-226 and Ra-226/Ba ratios in the Western Mediterranean Sea: Barite formation and transport in the water column, *Geochimica Et Cosmochimica Acta*73:4720-4737.
- Wood, S.A., (1996), The Role of Humic Substances in the Transport and Fixation of Metals of economic Interest (Au, Pt, U, V), *Ore Geology Reviews* 11(1-3):1-31.
- Zou, Z., Qiu, R., Zhang, W., Dong, H., Zhao, Z., Zhang, T., Wei, X. and Cai, X.,(2009), The study of operating variables in soil washing with EDTA, *Environmental Pollution* 157:229-236.