

OPTIMIZATION STUDY FOR REMOVAL OF RADIUM-226 FROM RADIUM-CONTAMINATED SOIL USING HUMIC ACID

(Kajian Pengoptimuman Penyingkiran Radium-226 Daripada Tanah Tercemar Radium
Dengan Menggunakan Asid Humik)

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Abstract

This study discusses the various parameters involved in the removal of radium-226 from radium-contaminated soil using humic acid extracted from Malaysian peat soil. The parameters studied included the contact time, the pH and the concentration of humic acid solution and the liquid/solid ratio. The optimum removal efficiency of radium-226 was achieved after 24 hours of agitation. Further agitation did not contribute to any increase in the removal efficiency of radium-226. Meanwhile, the removal efficiency of radium-226 was optimum when the humic acid concentration was 100 ppm. The greatest removal efficiency of radium-226 was obtained using highly basic humic acid solutions of pH 10 – 11. Humic acid solutions of basic pH 8 – 9 resulted in comparable removal efficiency to humic acid solutions of pH 7. Nevertheless, acidic humic acid solutions showed the lowest removal efficiency of radium-226. For the purpose of this study, humic acid solutions of pH 7 were used throughout the study. A ratio of 20 mL humic acid solution to 1 g soil sample was found as the optimum value. Any further increment in the ratio did not contribute to the removal efficiency of radium-226.

Keywords: Radium-226, Humic Acid, Contact time, pH, Concentration, Liquid/solid ratio

Abstrak

Kajian ini membincangkan pelbagai parameter yang terlibat dalam penyingkiran radium-226 daripada tanah tercemar radium dengan menggunakan asid humik yang diekstrak daripada tanah gambut Malaysia. Parameter yang dikaji termasuk masa sentuhan, pH dan kepekatan larutan asid humik serta nisbah cecair/pepejal. Penyingkiran optimum radium-226 dicapai selepas tempoh 24 jam goncangan. Masa goncangan yang lebih lama tidak menyumbang kepada sebarang peningkatan dalam keberkesanan penyingkiran radium-226. Sementara itu, penyingkiran radium-226 adalah optimum apabila asid humik berkepekatan 100 ppm digunakan. Keberkesanan penyingkiran yang paling tinggi dicapai apabila larutan asid humik berkepekatan tinggi dalam pH 10 – 11 digunakan. Larutan asid humik berkali dengan pH 8 – 9 menunjukkan keberkesanan penyingkiran yang sama dengan larutan asid humik berpH 7. Walaubagaimanapun, larutan asid humik yang berasid menunjukkan keberkesanan penyingkiran radium-226 yang paling rendah. Untuk tujuan kajian ini, asid humik berpH 7 digunakan sepanjang kajian. Nisbah 20 mL larutan asid humik kepada 1 g sampel tanah pula didapati sebagai nilai optimum. Sebarang pertambahan dalam nisbah larutan asid humik kepada sampel tanah tidak menyumbang kepada keberkesanan penyingkiran radium-226.

Kata kunci: Radium-226, Asid humik, Masa sentuhan, pH, Kepekatan, Nisbah cecair/pepejal

Introduction

One of the past activities that contributes to the generation of radium (Ra)-contaminated soil is luminous dial painting using radioluminescence paint that contains mixtures of radioactive and luminescent crystalline materials [1]. The radioluminescence paint used radium-226 (Ra-226) as the primary radioactive material before the discoveries of tritium (H-3) and promethium-147 (Pm-147) [2]. In Malaysia, such activity that was actively been

carried out since the 1960s until 1990s had left the processing sites, especially the soil being contaminated with Ra-226. Being an alpha and gamma emitter [3] with relatively long half-life of 1600 years, Ra-226 has been known to be extremely hazardous to the environment as well as human health. Therefore, removal of Ra-226 from the Ra-contaminated soil is vital to ensure that the hazardous effect of Ra-226 can be eliminated.

Various removal methods can be explored including the application of natural material such as humic substances extracted from soil organic matter. Humic acid (HA), the main extractable fraction of humic substances [4], has been found to interact with metal ions [5, 6] including radionuclides [7, 8]. Over the years, interaction between HA and radionuclides has been extensively studied [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. Laili et al. [22] in particular has discussed the influence of HA on the removal of Ra from aqueous solution by adsorption of Ra ions onto coir pith. The interaction between HA and other molecules or ions is due to the presence of binding sites provided by its functional groups in particular carboxyl and phenolic groups [17, 23, 24].

As a remarkably heterogeneous ligand [17, 23] with polyelectrolytic nature [24], the interaction of HA with other molecules and ions is significantly affected by various parameters. This paper describes the various parameters involved in the removal of Ra-226 from Ra-contaminated soil using HA as removal agent. Parameters investigated include contact time, pH and concentration of HA solution and liquid/solid ratio.

Experimental

Materials

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 in Malaysia. 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

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) solution. 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 (27°C) in a fume hood prior to manual grinding. 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 neutron activation analysis (NAA) technique. Ra-226 activity concentration of the Ra-contaminated soil sample was analysed by a gamma spectrometer equipped with a CANBERRA n-type hyper-germanium detector (HPGe) (30% relative efficiency and 1.9 keV resolution at 1.33 MeV) from Oxford Instruments Inc. together with Genie 2K software for spectrum analysis.

Removal of Ra-226

The removal study was carried out in a batch method by agitating 50 mL polyethylene tubes containing 1.00 g soil sample and a measured volume of HA solutions of certain pH and concentration at a speed of 100 rpm at room temperature (27°C) for a given time. The suspensions were then centrifuged at 4000 rpm for 10 minutes. The precipitates were removed leaving the supernatants for Ra-226 analysis. The collected supernatants were sealed in 50 mL bottles and kept at room temperature (27°C) for at least 21 days before counting to allow secular equilibrium of Ra-226 with their respective decay products. Ra-226 analyses were performed using a gamma spectrometry system. For the purpose of this study, the determination of Ra-226 activity was performed based on indirect measurement of gamma ray at energy line 609 keV. The contact time ranged from a period of 2 to 96 hours (HA =

pH 7, 100 ppm, L/S = 20). Meanwhile, the pH of HA solutions investigated were in the range of 3 to 11 (contact time = 24 hours, HA = 100 ppm, L/S = 20). For the concentration experiments, five different concentrations (25, 50, 75, 100, 125 and 150 ppm) of HA solutions were chosen (contact time = 24 hours, HA = pH 7, L/S = 20). Finally, the liquid/solid ratio experiments were conducted by using 10, 20, 30 and 40 mL of HA solutions giving liquid/solid ratios of 10, 20, 30 and 40 respectively (contact time = 24 hours, HA = pH 7, 100 ppm).

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

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

A_o = Initial Ra-226 activity in Ra-contaminated soil sample, Bq

A = Final Ra-226 activity in Ra-contaminated soil sample after removal, Bq

Results and Discussion

Contact time

Contact time is a vital parameter in any desorption study of metals from soil as desorption itself is a kinetic equilibrium process [25]. Therefore, a study investigating the effect of contact time on the removal efficiency of Ra-226 from the Ra-contaminated soil sample was carried out and the results obtained are shown as semi-log plot in Figure 1. It was found that the removal efficiency of Ra-226 ranged from 4 – 24 %. Initially, increase in contact time did not affect the removal efficiency of Ra-226. Nevertheless, a progressive increase in removal efficiency of Ra-226 was observed as contact time increased to 24 hours. Further agitation however did not lead to any changes in the removal efficiency of Ra-226. The relatively long contact time required to reach maximum removal efficiency implied that Ra-226 was strongly bound to soil matrix via adsorption [26, 27, 28], precipitation and co-precipitation [29]. The fact that the adsorption of Ra is the strongest among all other alkaline earth metal [3] supported the strong binding of Ra-226 to the soil matrix. For the purpose of this study, contact time of 24 hours was selected as the optimum value.

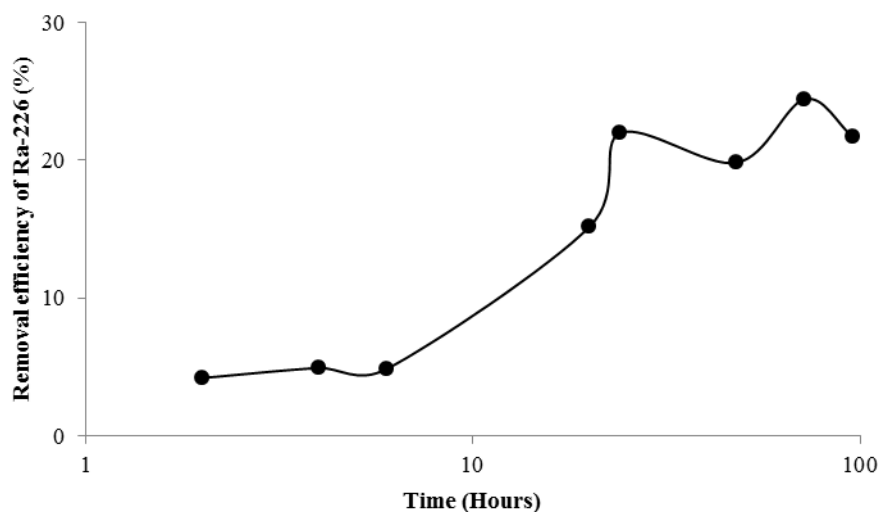


Figure 1: Effect of contact time on removal efficiency of Ra-226 from Ra-contaminated soil sample (HA = 100 ppm, pH 7, L/S = 20 mL/g)

Concentration of HA

HA solutions of different concentration were used in the removal study and the results obtained are shown in Figure 2. The removal efficiency of Ra-226 was the lowest when the concentration of HA was below 100 ppm as there was not much HA molecules present. The removal efficiency observed was almost constant with an increase of only 3 – 6 % from the condition when the HA was absent. Nevertheless, as the concentration of HA reached 100 ppm, higher removal efficiency of Ra-226 was observed. Further increase in the concentration of HA however resulted in a slight decrease in the removal efficiency of Ra-226.

The effect of different concentration of HA on the removal efficiency of Ra-226 could be explained by applying the diffusion phenomenon discussed by Wu and Nofziger [30]. According to Wu and Nofziger [30], diffusion coefficient of a solute in a dilute solution was regarded as constant. Therefore, in dilute HA solution (below 100 ppm), the diffusion coefficient of HA molecules could be considered as constant. Consequently, similar rate of transfer of HA molecules in HA solutions of different concentration (below 100 ppm) was achieved leading to less interaction between Ra-226 and HA molecules and finally resulting in the constant removal efficiency observed. Higher removal efficiency of Ra-226 achieved when HA solution of 100 ppm was used was probably due to the increase of flux from the Ra-226 – HA complexes. Nevertheless, further increase in the concentration of HA that eventually led to increase in viscosity could retard the mass transfer of Ra-226 – HA complexes thus resulting in decrease of removal efficiency of Ra-226. For the purpose of this study, 100 ppm was chosen as the optimum concentration of HA solution.

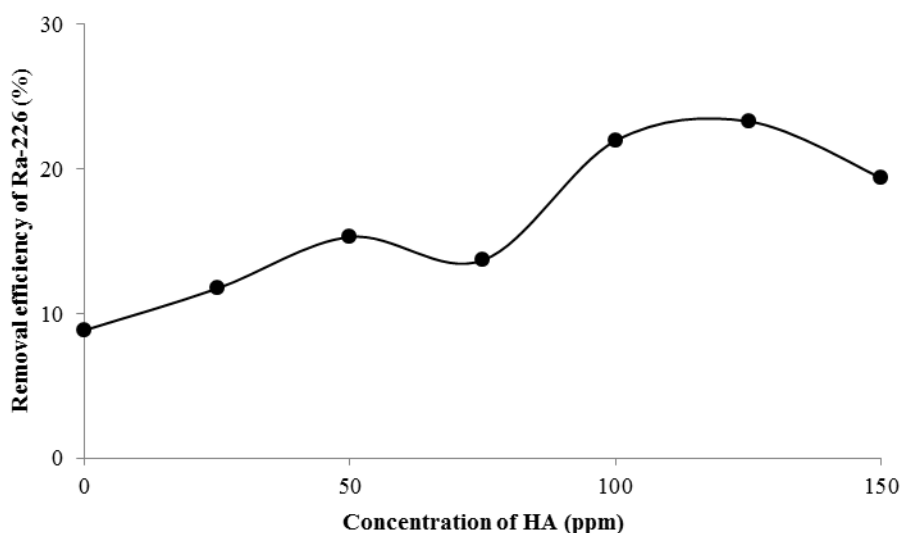


Figure 2: Effect of concentration of HA on removal efficiency of Ra-226 from Ra-contaminated soil sample (Contact time = 24 hours, pH 7, L/S = 20 mL/g)

pH of HA

Another important parameter was pH as pH could affect the retardation and mobility of metal ions and radionuclides in soil [31, 32]. Besides that, pH could also affect the removal capability of removal agent such as chelating agent to extract contaminants from soil through numerous mechanisms [25]. Interaction between metal ions and radionuclides with HA depended on pH due to the polyelectrolytic properties of HA [14, 17] and its ligand heterogeneity in terms of content of functional groups [17, 23]. Therefore, a study investigating the effect of HA

solutions of different pH on the removal efficiency of Ra-226 from the Ra-contaminated soil sample was carried out. The results obtained are shown in Figure 3.

The removal efficiency of Ra-226 using HA solutions of pH in the range 3 – 11 resulted in 11 – 44 % of Ra-226 removal. The efficiency was found to increase with the pH of HA solutions used. The increasing trend of the removal efficiency could be due to increase in the stability constants of the Ra-226 – HA complexes as the number and strength of the binding increased. Nevertheless, the removal efficiency of Ra-226 could be affected by Al that was present in the contaminated soil sample as Al could form stable complexes with HA [33].

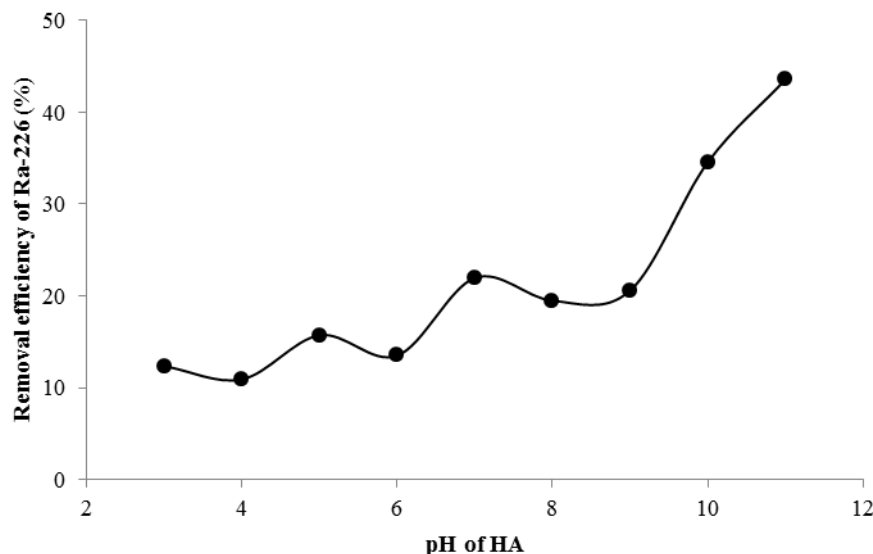


Figure 3: Effect of pH on removal efficiency of Ra-226 from Ra-contaminated soil sample (Contact time = 24 hours, HA = 100 ppm, L/S = 20 mL/g)

It was also found that the pH of the soil suspensions differed from the initial pH of the HA solutions used except for the HA solutions of pH 7, with pH tended to shift towards near neutral pH. HA increased the buffering capacity of the contaminated soil sample and permitted the soil neutral pH to stay stable. The removal efficiency of Ra-226 was the lowest when acidic HA solutions in the range 3 – 6 were used. The resulting pHs of the soil suspensions were approximately 5.0 – 6.5. Those findings could be due to less HA molecules available for binding with Ra-226 species as ionization of carboxylic functional groups of HA molecules was not favourable at pH < 7 [34]. Besides that, trapping of Ra-226 species by HA aggregates was also not favourable at this pH condition as temporary trapping of metal ions and radionuclides by HA molecules tended to occur at highly acidic condition [35]. Furthermore, the coagulation of HA molecules with Al species that was prone to occur in the pH range 4 – 7 [36] could lead to less binding of HA molecules with Ra-226 species. Increased removal efficiency of Ra-226 was observed when HA solutions of pH in the range 7 – 9 were used. The resulting pHs of the soil suspensions were around neutral thus allowed more ionization of HA molecules than at the acidic pH condition. At pH 7, the adsorption of neutral Ra-226 species namely RaSO_4^0 and RaCO_3^0 [37] 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. The removal efficiency of Ra-226 was high when HA solutions of pH in the range 10 – 11 were used and reached its maximum when HA solutions of pH 11 were used. The resulting pHs of the soil suspensions were found to be around 8. The greater removal efficiency in basic condition suggested the increasing importance of

deprotonated phenolic functional groups of HA molecules in binding with Ra-226 as pH increased. The higher removal efficiency at basic condition could also be explained by the accessibility of HA functional groups [38] as HA molecules were more open and linear due to the decrease in intra- and inter-molecular hydrogen bonding [39]. Besides that, adsorption of soil organic matter on the surface of soil mineral that decreased with pH [40] explained the decreasing adsorption of HA molecules onto soil matrix as pH increased thus allowed more mobile HA molecules for interaction with Ra-226.

For the purpose of this study, HA solutions of pH 7 were used throughout the study due to several reasons. Addition of acidic and basic reagents was not required as the prepared HA solutions were initially of neutral pH. The neutral resulting HA solutions containing removed Ra-226 did not cause any acidic or basic toxic materials emission. Besides that, the neutral resulting HA solutions also did not require any further treatment as highly acidic and basic washing solutions.

Liquid/solid ratio

Liquid/solid ratio was also another important parameter in the removal of Ra-226 from the Ra-contaminated soil sample. The results of the removal study conducted using varying liquid/solid ratios are presented in Figure 4. Different soil samples had their own requirements in terms of critical level at which almost all of their mobile metal ions could be extracted or removed; above this critical level, only slight increase in extraction or removal could be anticipated. In this study, dose was defined as moles of HA used for treating 1 g soil and the dose was directly correlated to the liquid/solid ratio if the concentration of HA was fixed. Therefore, as the liquid/solid ratio increased so did the dose. The results obtained showed that the removal efficiency of Ra-226 increased as liquid/solid ratio increased but only up to a ratio of 20 mL/g. The progressive increase in removal efficiency of Ra-226 observed at low liquid/solid ratio (below 20 mL/g) indicated that the dose of HA was less than the soil requirement. Meanwhile, further increase in the ratio higher than 20 mL/g did not result in any increment of removal. The almost constant removal of Ra-226 at liquid/solid ratio higher than 20 mL/g implied that the soil requirement had been exceeded.

For the purpose of this study, a liquid/solid ratio of 20 mL/g was chosen as optimum value.

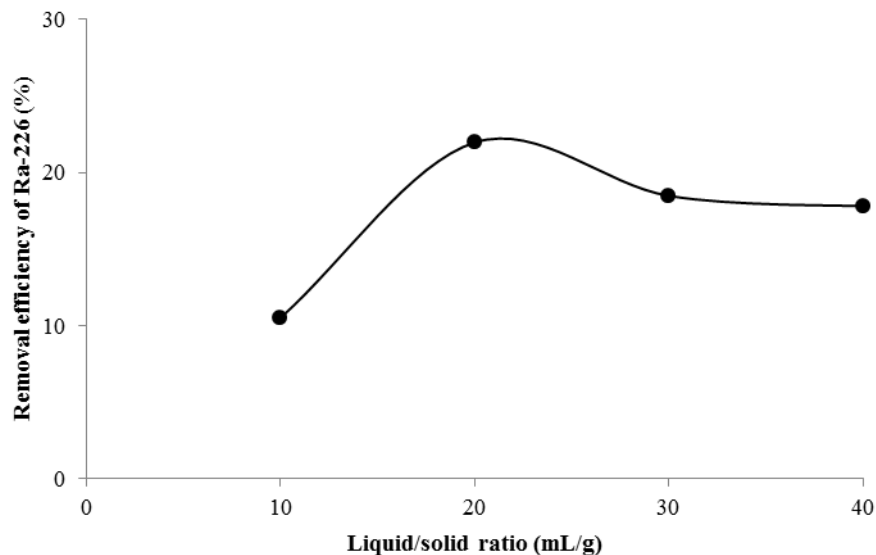


Figure 4: Effect of liquid/solid ratio on removal efficiency of Ra-226 from Ra-contaminated soil sample (24 hours, HA = pH 7, 100 ppm)

Conclusion

From this study, it was concluded that HA extracted from peat soil could be used as removal agent in removing Ra-226 from Ra-contaminated soil sample and the removal efficiency depended on parameters such as contact time, concentration of HA, pH of HA and liquid/solid ratio. The relatively long contact time of 24 hours required to reach optimum removal efficiency indicated that Ra-226 was tightly bound to soil matrix. Diffusion phenomenon was used to describe the effect of concentration of HA. HA with concentration of 100 ppm resulted in optimum removal efficiency. At lower concentration, the removal efficiency was also lower and remained constant due to constant diffusion coefficient of HA molecules in dilute HA solutions. At higher concentration, the removal efficiency trend observed was due to retardation of mass transfer of Ra-226 – HA complexes. HA solutions of highly basic pH of 10 – 11 resulted in the highest removal efficiency followed by HA solutions of pH 7 – 9. Meanwhile, HA solutions of acidic pH showed the lowest removal efficiency of Ra-226. The trend observed could be due to increasing deprotonation of HA molecules as pH increased. Nevertheless, the removal efficiency could also be affected by Al present in the contaminated soil sample. For the purpose of this study, HA solutions of pH 7 were used throughout the study. As for liquid/solid ratio, the increase in ratio did not necessarily increase the removal efficiency especially when the soil requirement had been exceeded. In this study, at optimum contact time of 24 hours using HA solutions of optimum concentration 100 ppm and pH 7 with optimum liquid/solid ratio of 20 mL/g, the resulting removal efficiency of Ra-226 obtained was recorded as 22 %.

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