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

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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 a single 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 varying pH in the range between 3 to 11. Activity of radium-226 was determined by gamma spectrometer. In the pH range studied, the removal of radium-226 was greater when humic acid solutions were used compared to distilled water. Greater removal of radium-226 was obtained using highly basic pH washing solutions compared to neutral and acidic solutions.

Keywords: distilled water, humic acid, pH, radium-226, soil

INTRODUCTION

In Malaysia, generated radium (Ra)-contaminated soil was historically originated from compass dial painting activities that were carried out since the 1960s until 1990s. The radium containing paint used in dial painting contained Ra as the primary radioactive material before the discoveries of tritium and promethium-147 (Eisenbud and Gesell, 1997). The hazard of Ra lies in the risk poses by its daughter products especially radon (Rn). The hazard of Ra in soil is especially important since emanation of Rn in soil organic matter is much greater than emanation from minerals (Greeman and Rose, 1996). Therefore, remediation of Ra-contaminated soil needs to be carried out to mitigate the adverse effect of Ra.

Remediation of soil contaminated with inorganic contaminants including radionuclides is not as extensively explored as organic contaminants (Boardman et al., 2000). Nonetheless, remediation of such soil is vital since inorganic contaminants especially radionuclides cannot be degraded or destroyed. Prolong exposure to radioactive hazard can then occur. Remediation of contaminated soil is usually performed based on 3 categories of technologies namely immobilization, destruction and extraction (Boardman et al., 2000). Extraction technologies involve the extraction and/or separation of contaminants from soil matrix and include technique like soil washing (Boardman et al., 2000). Soil washing can be performed by chemical leaching and extraction using complexants, acids and alkalis to transfer contaminants from soil into aqueous solution (Bayliss and Langley, 2003).

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Studies on removal of Ra from soil using synthetic extractants had been reported by several authors (Frissel and Köster, 1990; Greeman et al., 1999; Misra et al., 2001; Sklifasovskaya et al., 2009). Nevertheless, application of environmental friendly natural extractant is still anticipated. One of the promising natural materials used in remediation of contaminated environment is humic substances (HS) as discussed by Perminova and Hatfield (2005). HS is one of the main organic constituents in soil organic matter (Stevenson, 1982) and 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 RaOH\(^+\), RaCl\(^+\), RaHCO\(_3\)\(^+\), RaCO\(_3\)\(^0\) (aq) and RaSO\(_4\)\(^0\) (aq) (EP A, 2004; Baeza et al., 2006) at different pH values.

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 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 determine the efficiency of washing is pH as pH can affect the retention and mobility of pollutants such as metal ions and radionuclides in soil (Reed et al., 1996; Peters, 1999). Besides that, pH can also affect the ability of chelating agents to extract metal ions and radionuclides from soil through numerous mechanisms (Zou et al., 2009).

This study aimed at observing the effect of pH of washing solutions (distilled water and HA solutions) on the removal of \(^{226}\)Ra from Ra-contaminated soil. pH of the washing solutions studied ranged from 3 – 11. Washing of contaminated soil with distilled water was important in order to isolate metal 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). Meanwhile, washing of contaminated soil with HA solutions was intended to extract metal and radionuclides species that were tightly bound to 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

Materials

Extraction of humic acid from peat soil

HA was extracted from peat soil obtained from a peat swamp located in Kampung Beris Lalang, Bachok, Kelantan, east coast of Peninsular Malaysia. The peat soil was classified as hemic/fibric peat with woody characteristics, mainly formed from mangrove tree litters (Ibrahim et al., 2009).

HA was extracted from peat soil according to the acid-base extraction method described by Swift (1996) with minor modifications as performed by Ibrahim et al. (2008; 2009). Prior to extraction, the peat soil was air-dried at room temperature, ground and sieved using a 2.0 mm sieved. HA stock solution was prepared by dissolving the extracted solid HA in diluted sodium hydroxide (NaOH) solution. HA working solution of 100 ppm was prepared by diluting the stock solution also in diluted NaOH. In this study, HA solution of concentration 100 ppm was used as earlier study had found that optimum removal of $^{226}$Ra from the Ra-contaminated soil sample was achieved at this concentration (Phillip et al., 2012).

Preparation of Ra-contaminated soil sample

Ra-contaminated soil was sampled from a former compass dial painting facility site in Peninsular Malaysia. The compass dial painting facility was in operation since 1960s and ceased its operation in 1990s. Upon its decommissioning, Ra-contaminated soil was excavated from the site and transferred to the radioactive waste storage facility at Nuclear Malaysia in 2000. The Ra-contaminated soil was since regarded as radioactive waste and pending for proper disposal.

The Ra-contaminated soil was air-dried at room temperature in a fume hood prior to manual grinding using a ceramic pastel and mortar. The ground soil sample was then sieved using a 2.0 mm sieve and finally stored in a sealed container for experimental purposes.

pH of the Ra-contaminated soil sample in water suspension was determined based on the method suggested by Jones (2000). 5 g of the Ra-contaminated soil sample was stirred with 5 g of deionized water for approximately 5 seconds. The soil-water suspension was left standing for 10 minutes. pH the soil-water suspension was then recorded using a calibrated pH meter. Result was reported as water pH ($pH_w$). Experiments were repeated 3 times.

Chemicals and apparatus

All chemicals used in this study were of analytical grade. $^{226}$Ra standard solution was obtained from Isotope Products Laboratories (an Eckert & Ziegler Company). A $^{226}$Ra standard solution of activity concentration 3.7878 Bq/mL was prepared. Gamma spectrometry measurement showed that the nett activity of the $^{226}$Ra standard solution was given as 0.116 cps. Other reagents and chemicals used were
of analytical grade from R&M Chemicals or Sigma Aldrich. Orbital shaker (PROTECH 719 Model), centrifuge (Hettich Zentrifugen ROTINA 38 Model) and pH meter (HANNA Instruments pH 211 Model) were used in this study. Meanwhile, a CANBERRA n-type hyper-germanium detector (HPGe) gamma spectrometer (30% relative efficiency and resolution of 1.9 keV at 1.33 MeV from Oxford Instruments Inc.) was used for measuring the $^{226}$Ra activity concentration in supernatant and soil samples. The gamma spectrometry system that was equipped with Genie 2000 gamma analysis software was calibrated using a customized gamma multinuclides standard source solution that included $^{241}$Am, $^{109}$Cd, $^{57}$Co, $^{60}$Co, $^{51}$Cr, $^{137}$Cs, $^{113}$Sn, $^{123m}$Te and $^{88}$Y with known activities prepared by Isotope Products Laboratories, USA. The energy calibration was carried out the same manner as described by Omar et al. (2004). An accurate efficiency calibration curve of the system was therefore achieved to quantify the $^{226}$Ra activity in the experimental samples.

**Effect of pH**

In this study, HA solutions and distilled water were used as washing solutions. pH of the washing solutions were adjusted to desired values in the range between 3 – 11 prior to mixing with the Ra-contaminated soil samples. This method was found to be more practical and easier in terms of implementation of soil washing processes. Effect of washing solutions’ pH on the removal of $^{226}$Ra from the Ra-contaminated soil was investigated by batch washing method. Only single washing was performed. Approximately 1g of Ra-contaminated soil sample was added to 20mL HA solution and agitated using an orbital shaker at 100rpm for 24h at room temperature. Earlier study (Phillip et al., 2012) revealed that a liquid/solid ration of 20mL/g resulted in optimum removal of $^{226}$Ra. It also reported that equilibrium was established within a contact time of 24 hours. pH of the soil-HA suspension was also measured. The soil-HA suspension was then centrifuged at 4000rpm for 10 min and the supernatant was collected by decantation. The collected supernatant was immediately sealed in a 50mL cylindrical container and was left to equilibrate for at least 21 days to ensure secular radioactive equilibrium between $^{226}$Ra and its daughter, $^{214}$Bi, before measuring with gamma spectrometer. Precision was established by preparing triplicates for each test. Experiments were repeated with distilled water.

**Measurement of $^{226}$Ra**

In this study, the determination of $^{226}$Ra activity concentration was based upon indirect measurement from a line of a $^{226}$Ra daughter isotope; the 609keV line of $^{214}$Bi. The 609 keV line of $^{214}$Bi was selected due to the absence of interference from natural radionuclide as well as the high yield of gamma ray produced.

The Ra-contaminated soil sample of approximately 30g was weighed and sealed in a 30mL cylindrical container and kept for 30 days to attain equilibrium among the $^{226}$Ra daughters. 3 sets of the Ra-contaminated soil sample were prepared. Both the Ra-contaminated soil samples and the supernatant samples obtained from the pH experiments were counted using the gamma spectrometer for about 87000 seconds to obtain better counting statistics.
Calculation of $^{226}$Ra activity concentration in supernatant samples

The removal of $^{226}$Ra from the Ra-contaminated soil sample was calculated using equation 1

$$\text{Removal of } ^{226}\text{Ra (\%)} = \frac{A_{\text{supernatant}} (\text{Bq})}{A_{\text{soil}} (\text{Bq})} \times 100\% \quad \text{(Equation 1)}$$

where, $A_{\text{supernatant}}$ and $A_{\text{soil}}$ were activities of $^{226}$Ra in supernatant and soil samples respectively.

Meanwhile, the values of $A_{\text{supernatant}}$ and $A_{\text{soil}}$ were given by equation 2 and 3 respectively

$$A_{\text{supernatant}} (\text{Bq}) = C_{\text{supernatant}} (\text{Bq/mL}) \times V_{\text{supernatant}} (\text{mL}) \quad \text{(Equation 2)}$$

$$A_{\text{soil}} (\text{Bq}) = C_{\text{soil}} (\text{Bq/g}) \times m_{\text{soil}} (\text{g}) \quad \text{(Equation 3)}$$

where, $C_{\text{supernatant}}$ and $C_{\text{soil}}$ were activity concentrations of $^{226}$Ra in supernatant and soil samples respectively. $V_{\text{supernatant}}$ referred to volume of supernatant and $m_{\text{soil}}$ indicated mass of the contaminated soil sample used.

The activity concentration of $^{226}$Ra, $C$, in the supernatant samples was determined based on direct comparison method. The activity of $^{226}$Ra (count per second, cps) obtained for the supernatant samples was converted to activity concentration of $^{226}$Ra (Bq/mL) based on equation 4.

$$C_{\text{supernatant}} (\text{Bq/mL}) = \frac{\text{cps nett}_{\text{supernatant}}}{\text{cps nett}_{\text{standard}}} \times C_{\text{standard}} (\text{Bq/mL}) \quad \text{(Equation 4)}$$

cps nett was obtained by the following equation 5.

$$\text{cps nett}_{\text{supernatant}}/\text{standard} = \text{cps}_{\text{supernatant}}/\text{standard} - \text{cps}_{\text{blank}} \quad \text{(Equation 5)}$$

$C_{\text{standard}}$ was obtained from the $^{226}$Ra standard solution prepared earlier.

RESULTS AND DISCUSSION

Gamma spectrometry measurement showed that the $^{226}$Ra activity concentration of the Ra-contaminated soil sample was 70486 ± 2935 Bq/kg. Meanwhile, pHw of the Ra-contaminated soil sample was recorded as 6.91 ± 0.01.

In this study, distilled water and HA solutions of varying pH were used as washing solutions to remove $^{226}$Ra from the Ra-contaminated soil. Table 1 shows the pH of the washing solutions used as well as the pH of the soil-washing solutions suspension.
Our findings revealed that the pH of the soil-distilled water suspension differed from the pH of the distilled water used except when distilled water of pH 7 and 11 were used.

Table 1: pH of distilled water and HA solutions and washing solutions used as well as the pH of the soil-washing solutions suspension

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In this study, the data obtained for removal of $^{226}$Ra using distilled water served as baseline data to compare with removal of $^{226}$Ra using HA, thus to evaluate the ability and efficiency of HA solution as washing agent. Fig. 1 shows the effect of pH of distilled water and HA solutions on the removal of $^{226}$Ra from the Ra-contaminated soil sample.

Fig.1: Effect of pH of washing solutions on removal of $^{226}$Ra from Ra-contaminated soil sample
As shown in Fig. 1, batch washings of the Ra-contaminated soil sample using distilled water of pH ranged from 3 to 11 were able to remove 1 – 35 % of $^{226}$Ra. The removal of $^{226}$Ra generally increased with the pH of the soil-distilled water suspension.

When distilled water of pH 3 was used, the pH of the soil-distilled water suspension was around 5. The removal of $^{226}$Ra was approximately 6 ± 1 %. Soluble Ra species present at this pH was mainly Ra$^{2+}$ (Baeza et al., 2006). Other soluble Ra complexes such as RaSO$_4^0$ and RaHCO$_3^+$ were also present at this pH (Baeza et al., 2006). Carbonate species such as HCO$_3^-$ and CO$_3^{2-}$ present in the soil could originate from the dissolution of carbonate mineral or CO$_2$ in the atmosphere. The presence of these soluble Ra species could result from solubilisation of RaSO$_4$ or desorption of $^{226}$Ra from soil matrix and hydrous metal oxides in soil. The low solubility of RaSO$_4$ in water (Wang et al., 1995) could have led to the low removal of $^{226}$Ra obtained. Meanwhile, the low removal of $^{226}$Ra could also be due to the low desorption of $^{226}$Ra from the soil matrix and hydrous metal oxides in soil.

Competition between $^{226}$Ra and Al and Fe species in securing exchange sites in soil matrix (Carbonell et al., 1999) could have led to less Ra being adsorbed onto the soil matrix and eventually caused less desorption of $^{226}$Ra. As an alkaline earth metal, Ra is chemically analogued to Ba (Beek et al., 2009) and therefore possesses the same chemical properties as Ba (Henriksen et al., 2002; Comstock, 2010). Therefore, 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). As a result, less $^{226}$Ra species were being desorbed from the hydrous iron oxides in the Ra-contaminated soil. Hydrous metal oxides such as hydrous iron oxides could solubilise due to oxide solubilisation by H$^+$ ions at low pH (Zou et al., 2009).

However, in this study, the weak acidic condition at pH 5 led to less $^{226}$Ra species being desorbed from the hydrous iron oxides. Therefore, desorption of $^{226}$Ra from the hydrous iron oxides did not contribute much to the removal of $^{226}$Ra. 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, Al(OH)$_3$ precipitates that were starting to form at pH 5 could adsorb $^{226}$Ra species especially RaSO$_4^0$ thus resulting in low removal of $^{226}$Ra. Nevertheless, the weak acidic condition caused slight dissolution of Al (Lindsay and Wathall, 1989) that could balance the formation of Al(OH)$_3$ precipitate. As a result, comparable removal of $^{226}$Ra with washing system of neutral pH was observed.

When distilled water of pH 4 was used, the pH of the soil-distilled water suspension was around 6.5. The removal of $^{226}$Ra was at its minimum when distilled water of pH 4 was used probably due to maximum adsorption of $^{226}$Ra species onto Al(OH)$_3$ precipitates. Driscoll (1989) mentioned that the minimum solubility of Al was detected at pH 6.5.

The pH of the soil-distilled water suspension was around neutral when distilled water in the pH range 5 – 8 was used. Meanwhile, the removal of $^{226}$Ra was approximately 7 – 12 %. At near neutral pH, soluble RaHCO$_3^+$ complex was the dominant Ra species present (Baeza et al., 2006). Besides that, Ra$^{2+}$ and soluble RaSO$_4^0$ complex were also present (Baeza et al., 2006). When distilled water of pH 5 – 8 was used, the removal of $^{226}$Ra was found to increase from the previous pH 4. At pH higher than 6.5, Al(OH)$_4^-$ hydroxyl complexes started to form (Lindsay and Wathall, 1989) and these complexes did not interrupt the removal of $^{226}$Ra.

When distilled water in the pH range 9 – 10 was used, the pH of the soil-distilled water suspension was around 8 at which Ra species in the forms of soluble complexes RaHCO$_3^+$, RaCO$_3^0$, RaSO$_4^0$ and Ra$^{2+}$ions were present (Baeza et al., 2006). The removal of $^{226}$Ra obtained was approximately 11 – 24 %.
According to Hem (1983), hydroxyl $\text{Al(OH)}_4^-$ complexes were the dominant Al species formed at pH greater than 7 thus signifying the decrease and finally the end of $\text{Al(OH)}_3$ precipitates formation. This then led to higher removal of $^{226}\text{Ra}$ compared to the previous neutral pH as adsorption of $^{226}\text{Ra}$ species onto $\text{Al(OH)}_3$ precipitates had ceased.

When distilled water of high alkalinity (pH 11) was used, the pH of the soil-distilled water suspension was maintained at pH 11. The removal of $^{226}\text{Ra}$ was at its maximum at this pH. The increase in the removal of $^{226}\text{Ra}$ with the pH of the soil-distilled water suspension corresponded well with the increased solubility of Ra at high pH as discussed by McCreary et al. (1980) and Huck and Anderson (1982). At pH 11, most of the $^{226}\text{Ra}$ species present were in the form of soluble $\text{RaCO}_3^0$ complexes (Baeza et al., 2006). The removal of $^{226}\text{Ra}$ was balanced by the adsorption of $\text{RaCO}_3^0$ onto metal precipitate such as ferric sulphate as adsorption of neutral species 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 11 – 44 % of $^{226}\text{Ra}$ being removed. When HA solutions of particular pH were agitated with the Ra-contaminated soil samples, the pH of the soil-HA suspension differed from the pH of the HA solutions used except for HA solutions of pH 7 as shown in Table 1. The removal of $^{226}\text{Ra}$ generally increased with the pH of the soil-HA suspension. The removal of $^{226}\text{Ra}$ was also slightly higher by 5 – 13 % using HA solutions compared to distilled water. Thus suggesting that HA was able to remove $^{226}\text{Ra}$ species from the soil matrix that were not removable by distilled water. The removal of $^{226}\text{Ra}$ using HA solutions that increased with the pH of the soil-HA suspension was probably due to the increase in stability constant of the Ra/HA complexes. Nevertheless, the removal of $^{226}\text{Ra}$ could be affected by binding of HA molecules to soil matrices as well as interference from other metal species such as Al that were present in the contaminated soil. Al species could interfere the binding of $^{226}\text{Ra}$ with HA molecules since Al itself could form stable complexes with metal precipitate was more favourable at high pH (Valentine et al., 1985; Baeza et al., 2006).

The pH of the soil-HA suspension was around 5 – 6.5 when HA solutions in the pH range of 3 – 6 were used. It was found that the removal of $^{226}\text{Ra}$ was the lowest at this pH range. At pH < 7, acid dissociation of carboxylic functional groups of HA molecules was not favourable (Fukushima, 1996) and therefore could lead to less $^{226}\text{Ra}$ species being bound to HA molecules. Trapping of $^{226}\text{Ra}$ species by HA aggregates was also not favourable in this weakly acidic pH condition. Avena and Wilkinson (2002) also mentioned that the temporary trapping of metal ions and radionuclides by HA aggregates were more favourable in very acidic 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). In weakly acidic condition as in this study, the trapping of $^{226}\text{Ra}$ was unlikely to occur. Moreover, the unfavourable binding of $^{226}\text{Ra}$ with HA molecules could 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 $\text{Al(OH)}_3$ precipitates were suitable for the adsorption of soluble organic substances.

When HA solutions of pH 7 – 9 were used, the pH of the soil-HA suspension was around neutral. Meanwhile, the removal of $^{226}\text{Ra}$ was approximately 19 – 22 %. The increase in the removal of $^{226}\text{Ra}$ from previous pH indicated that greater ionization of HA molecules at higher pH (Hsieh et al., 2010) allowed for more binding of $^{226}\text{Ra}$. 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 and Bekbölet, 2010). A
notable difference in removal of $^{226}$Ra between distilled water and HA solution was also observed at HA solution of pH 7. Coagulation of HA with Al that tended to occur at pH 4 - 7 (Dempsey et al., 1984) resulted in less formation of Al(OH)$_3$ precipitate and thus more soluble $^{226}$Ra species were available in the supernatant.

When HA solutions in the pH range 10 – 11 were used, the pH of the soil-HA suspension was around 8 with the pH of the soil-HA suspension for HA solutions of pH 11 slightly higher than pH 10 (Table 1). The removal of $^{226}$Ra was higher at this pH range compared to near neutral pH and reached its maximum when HA solutions of pH 11 were used. The significant increase in the removal of $^{226}$Ra in basic condition suggested the increasing importance of deprotonated phenolic functional groups of HA molecules in binding with $^{226}$Ra. Deprotonation of functional groups that increased with pH (Hsieh et al., 2010) encouraged more interaction between HA molecules and $^{226}$Ra species eventually leading to increasing removal of $^{226}$Ra with pH. Other than the amount of binding sites, the removal of $^{226}$Ra was also affected 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 higher removal of $^{226}$Ra in basic pH was due not only to the increase in activity but also accessibility of HA functional groups (Güngör and Bekbölet, 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 $^{226}$Ra species from the soil matrix through binding of $^{226}$Ra with HA molecules.

**CONCLUSION**

As far as the pH study is concerned, the data obtained shows that HA solutions are able to remove $^{226}$Ra 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 the removal of $^{226}$Ra was only about 5 – 13 % when only single washing was performed. The highest difference in the removal of $^{226}$Ra was 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 $^{226}$Ra species. Nonetheless, the efficiency of HA solutions could also be affected by Al species present in the soil.

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