IOP Conf. Series: Materials Science and Engineering **298** (2018) 012056 doi:10.1088/1757-899X/298/1/012056

Adsorption of thorium onto soil around coal-fired power plant

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Abstract. A study has been performed to determine the adsorption of Thorium (Th-232) onto three soil sample around Jimah Energy Venture coal-fired power plant located in Jimah, Port Dickson. Parameters that were set constant include soil dosage at 2.5g each; 50 ml of Th-232 solution. Parameters tested for optimum adsorption was based on initial concentration and pH of Th-232, and contact time. Highest percentage removal of Th-232 obtained for sample 1 and 3 at initial concentration of 25 ppm, pH 5 for 140 minutes are 99.69% and 99.98% respectively, while for sample 2, the highest percentage removal obtained at initial concentration of 25 ppm, pH 7 for 120 minutes are 99.92%. Freundlich and Langmuir isotherms were used to determine the adsorption isotherm for Th-232 adsorption. Based on this study, the result can be used as future reference regarding soil capability of adsorbing radionuclide. It is concluded that all soil sample has considerable ability of adsorbing Th-232 from entering the groundwater.

1. Introduction

Coal is one of the largest contributors for power generation in Malaysia. Ramasamy (2012) stated that the estimation for coal demand in Malaysia can be up to 10280MW in 2020. The coal-fired power plant produces huge amounts of fly ash and bottom ash containing natural radionuclides (Pandit *et al,* 2011). When coal is burned into fly ash, uranium and thorium are concentrated at up to 10 times from their original levels (Mara, 2007). The main radiation hazard from solid fallout will result in elevated concentration of natural radionuclide in surface of soils around the power plant (Zakaria et al., 2010). The two principal processes that can contaminate soil from coal industry is through precipitation of airborne dusts and land disposal of uranium or thorium containing wastes (Abdul Rashid et al., 2016). Thorium accumulation in soil can likely cause phytotoxicity and poisoning the food chain (Guo et al., 2008).

This study investigated the adsorption of the Th-232 onto the soil around Jimah coal-fired power plant. Jimah East Power Sdn. Bhd (JEP) is a special-purpose vehicle set up to develop the 2,000MW coal-fired power plant in Jimah, Negeri Sembilan, known as Project 3B (Yee, 2016). The coal-fired power plant is located far from residential area but the surrounding is packed with other industrial activities. According to U.S. Agency for Toxic Substances and Disease Registry, workers are exposed to higher levels of thorium and other radionuclides in certain thorium related industries, as indicated by the measurement of Th-232 exhaled breath of some Th-232 plant workers is indirect evidence of higher thorium intakes. Thorium can increase probability of lung cancer, pancreas, and blood in workers exposed to high levels of it in the air (ASTDR, 2014).

In this study, soil act as the adsorbent of the Th-232. The surface of the soil has net negative charge and radionuclides are attracted from the solution to balance the surface charge by adsorption (Soderlund et al., 2011). Thorium was most soluble in acidic soils and the highest concentrations of dissolved Th and U were found close to the soil surface (Ahmed et al., 2012). Radionuclides mobility in the soil and their availability to be uptake by plants depend on the mineralogical composition and soil texture, pH, organic matter content, cation composition of soil solution and Ca and K concentrations. Soil adsorption capability of Th and U depended on the soil composition and pH of the soil solution (Vandenhove et al., 2007). For example, Vandenhove et al., (2007) observed that soil-liquid distribution coefficients were significantly related to organic matter content and amorphous Fe. Other studies also found that uranium sorption in soils were highly influenced by natural organic matter content, followed by Fe, Mn, and Al oxides content in soil (Bednar et al., 2007). This shows that in suitable condition, soil can become potential adsorbent of Th-232. The result from this study can become future reference in selecting new coal-fired power plants location which can adsorb Th-232 from leaching into the groundwater. Previous studies focuses more on thorium adsorption in wastewater using activated carbon, mesoporous molecular sieves and oxidized carbon nanotubes (Cheng et al., 2014). The lack of study on capability of soil on removing Th-232 around coal-fired power plants is the reason why this study is conducted.

2. Methodology

2.1 Sampling Site

Sample soils were collected at 3 different points around Jimah coal-fired power plant that was located at Port Dickson, Negeri Sembilan. The sampling point is located 2 km from the power plant and the distance between each sampling point was 500 meter. The coordinate of the sampling area is given in Table 1.

Table 1. Coordinate of sampling location.

Sampling point	Latitude	Longitude
Sample 1	2.597517°	101.723235°
Sample 2	2.602260°	101.723496°
Sample 3	2.608739°	101.729737°

3. Sample preparation and analysis

Collected soil samples were air-dried for two to three days, sieved to less than 2 mm size and oven dried overnight at 110 ºC. Next, the soil samples were ground and sieved further for XRD and FTIR analysis to determine the functional groups in soil samples and also the chemical compounds present in the sample. For physical and chemical characteristic of soil samples, analysis for organic content, pH, cation exchange capacity (CEC) and particle size distribution clay were carried out.

3.1 Batch analysis

The adsorption study method was based on US-EPA (1992, 1999) using 50 mL of respective Th-232 concentrations each at 5, 10, 15, 20, and 25 and 40mg/L were mixed with 2.5 g soil in conical flask and the mixture were put on shaker for 24 hours. Next the mixture was filtered from the solid phase and the concentration of Th-232 remaining in the solutions was measured. After optimum initial concentration obtained, the experiment proceed with optimum pH determination at range from 2-10 for 24 hours. Then, at the optimum pH and initial concentration, the adsorption process conducted with different contact time period between 60-140 min.

The concentration of Th-232 in solution determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Percentage of Th-232 removal was calculated using the calculation i) below whereby C_i is the initial concentration and C_f is the final concentration of Th-232.

$$(\%)removal = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

3.2 Adsorption isotherm

Analysis of adsorption was studied using Langmuir and Freundlich equations. Langmuir isotherm assumes that the binding sites is in infinite numbers having the same affinity for adsorption and the adsorption is mono layer and have no interaction between the adsorbed molecules. Langmuir isotherm linear equation to determine adsorption parameters described as below:

$$\frac{1}{q_e} = \frac{1}{q_m} + (\frac{1}{q_m} KL)\frac{1}{Q} \quad (2)$$

where q_e (mg/g) and q_m (mg/g) are the amount of adsorbed Th-232 per unit mass of adsorbent and adsorption capacity, respectively. *KL* was the Langmuir constant, related to the bonding energy between the adsorb ion and adsorbent (L/mg) and C_c is a unadsorbed Th-232 concentration in solution at equilibrium (mg/L).

The Freundlich isotherm used to describe heterogeneous systems and reversible adsorption and is not necessarily to form monolayers. The linear form equation was defined as follows:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (3)$$

where q_e was the amount of adsorb Th-232 per unit weight of soil at equilibrium (mg/g), C_e was the equilibrium concentration of Th-232 (mg/L), K_f was Freundlich constant (mg/g), and $1/n$ was adsorption intensity respectively. *n* is a measurement of the deviation from linearity of adsorption.

4. Result and discussion

4.1 Soil physical and chemical properties

The results of physical and chemical characterization of soils were tabulated in table 2. The organic matter percentage in sample 1 is the highest compared to sample 2 and 3 while the CEC is averagely same in all soil samples. Organic matter occurred by decomposition process of dead organisms from physical and biochemical complex organic matter into simple organic matter as they reverted back to soil. CEC is the capacity of soil surface in holding nutrient composition. High CEC is equal to high organic matter percentage and this is tally with the clay percentage is the highest for sample 1. The average pH of sample soil are between pH 4 and pH 5 which is suitable for Th-232 adsorption onto the soil because Th-232 is most stable in acidic soil condition [4]. The collected soil was categorized as sandy clay loam soil as there were highest percentage of sandy soil compare to silt and clay soil texture (table 2). From XRD result it was found that silica dioxide, SiO_2 percentages are high in all soil samples which are 87%, 85% and 80% respectively and this is concurrent with percentage of clay in each sample. Other mineral present in sample soil are magnesite, hematite, pyrolusite and spinel in less than 12% of each mineral.

Table 2. Soil texture and other physical-chemical properties from three different locations.

Soil Sample	*Organic matter (%)*	*pH*	*Cation exchange capacity (cmol/kg)*	*Sand (%)*	*Silt (%)*	*Clay (%)*
Sample 1	9.82	4.88	0.004	45.99	12.50	28.49
Sample 2	1.30	5.75	0.004	47.20	14.50	27.26
Sample 3	2.85	5.57	0.003	43.46	13.42	21.00

Three different absorption peaks were detected from the FTIR spectrum. The peak at 3651.19 cm^{-1} shows the OH functional group. The adsorption band at 1507.86 cm^{-1} occurred for primary amine N-H functional group while the carboxylic acid (-COOH) group were detected at 1751.01 cm^{-1} wavelength. From the previous study had stated that hydroxyl and carboxylic acid groups played a major role in the adsorption process [9]'.

According to Wu *et. al.* [6], the hydroxyl group is highly effective towards adsorption rate and efficient through the exchange of radionuclide ions. Besides that, the carboxylic acid group adsorption rate is relatively high due to the presence of more negatively charged groups on its surface [19].

4.2 Effect of initial concentration

The effect of initial concentration on Th-232 removal was shown in figure 1. The percentage removal of Th-232 is directly proportional with the increasing of initial concentration from 5 ppm to 25 ppm for all collected samples. The increase in Th-232 adsorption with the concentration can be attributed to the availability of greater surface area and larger number of adsorption site. The maximum percentage removal of Th-232 for sample 1, sample 2 and sample 3 are 99.92%, 99.88%, and 99.95% respectively at initial concentration of 25 ppm.

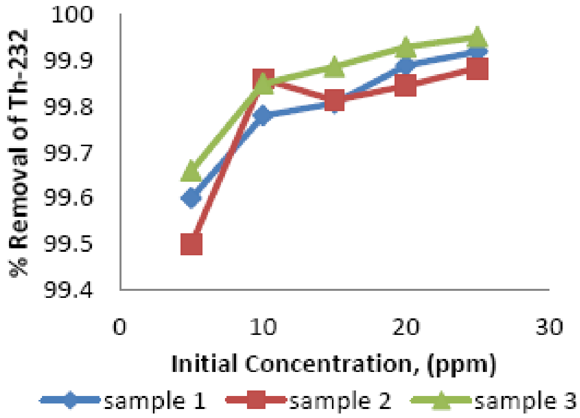

Figure 1. Graph of initial concentration versus percentage removal of Th-232.

4.3 Effect of pH

Figure 2 shows the percentage removal of Th-232 increase from pH 2 to pH 5 before fluctuated at pH above 5. This is due to resistant minerals were decomposed under stronger acidic conditions, and the presence of acid radical ions in soil enhanced the solubility of ThO_2 by forming thorium-sulfate, fluoride and phosphate complexes below pH 7 [16]. The optimum pH 5 was determined for sample 1 and sample 3, but for sample 2 the optimum pH is 7. At acidic condition, the proton of the functional group such as carboxyl, hydroxyl, and amine group in the adsorbent does not dissociate easily and thereby decreases the interaction of Th-232 with the adsorbent. However, when pH increases to 5, due to de-protonation of these functional groups, the increase in negative charge on the adsorbent surface offers more Th-232 adsorption sites and thus increases Th-232 adsorption . The maximum percentage removal of Th-232 is 99.70%, 99.72%, and 99.77% respectively. The maximum adsorption rate due to development negative charged on the surface of adsorbent.

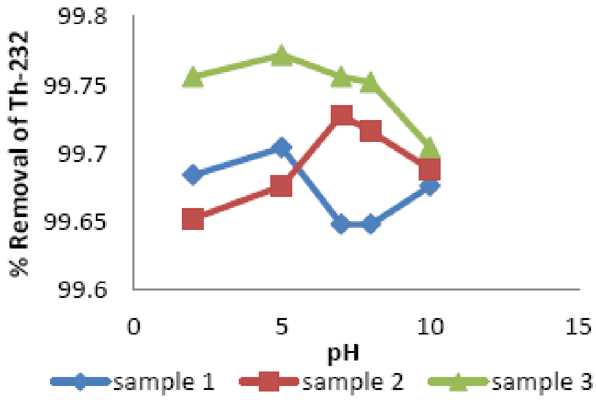

Figure 2. Graph of pH versus percentage removal of Th-232.

4.4 Effect of Contact Time

Figure 3 shows the percentage removal of Th-232 influence by the contact time between adsorbent and Th-232 solution. It can be seen that the percentage removal of Th-232 solutions is increasing in period of 60 to 140 minutes for sample 1 and 3. This happened because there were abundant active sites on the soil surface in early period of adsorption [11]. The equilibrium times of Th-232 by sample 1 and sample 3 occurred at 140 minutes, as the maximum percentage removal of Th-232 are 99.96% and 99.98%. Whereby for sample 2, the optimum contact time is at 120 minutes and it start declining approaching 140 minutes implying to saturation of adsorbent site causing inefficiency in adsorption process as the time extended

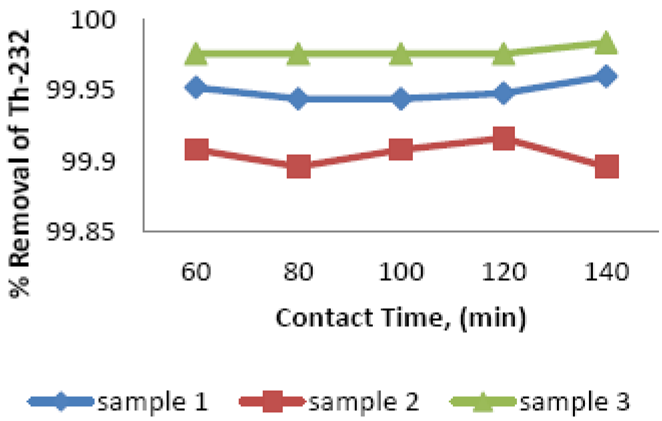

Figure 3. Graph of contact time versus percentage removal of Th-232.

4.5 Isotherm Studies

Based on table 3, it was evident that sample 1 follows Langmuir isotherm as the value of R^2 is closest to 1 compare to the Freundlich isotherm model. Therefore it is suggested that sample 1 adsorption process is homogenous and occurs on one layer only. In this experiment, sample 1 obtained the higher value of K_L indicating high affinity towards adsorbent. Sample 2 and 3 follows Freundlich isotherm as the value of R^2 is closest to 1. Freundlich isotherm suggests that the adsorption process is favourable when the n value is greater than 1 and sample 3 shows a value of n greater than 1. As for sample 2, the n value is less than 1 indicating that the adsorption process is chemical.

Table 3. Langmuir and Freundlich parameters and correlation coefficient for Th-232

Th-232		Langmuir Isotherm			Freundlich Isotherm	
	q_m	K*l*	R^2	n	K*f*	R^2
Sample 1	19.10	0.35	0.1042	0.38	4.25	0.0310
Sample 2	83.02	0.13	0.0968	0.29	36.29	0.2548
Sample 3	86.71	0.05	0.3877	2.19	1.04×10^{-6}	0.4709

5. Conclusion

This study concluded that all soil samples collected have the potential capability of adsorbing Th-232. Several parameters displayed huge part in removal of Th-232. As pH increased the ability to adsorb decrease and so does the extension of contact time as it reached saturation point. Highest percentage removal of Th-232 for sample 1 and 3 obtained at initial concentration of 25 ppm, pH 5 for 140 minutes which are99.69‘% and 99.98% respectively, while for sample 2, the highest percentage removal of Th-232 at initial concentration of 25 ppm, pH 7 for 120 minutes are 99.92%. In addition, all the soil samples have acidic pH which is one of the suitable characteristic of soil on Th-232 adsorption. All collected soil sample have high SiO_2 percentage which means slightly clayey and have the potential in prevention of Th-232 from entering the groundwater. The capability of soil as potential adsorbent for Th-232 is proven based on FTIR result by the presence of three functional groups namely hydroxyl groups, carboxylic groups and amine groups which played a major role in adsorption. From isotherm studies, sample 1 follows Langmuir isotherm while sample 2 and 3 follows Freundlich isotherm. Based on these experiment, all collected soil sample around Jimah coal-fired power plant has considerable ability to adsorb Th-232.

6. References

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Acknowledgment
The authors would like to express gratitude to Ministry of Higher Education for allocating Research Acculturation Grant Scheme (RAGS) 600-IRMI/RAGS5/3(59(2015)) and thank the Universiti Teknologi MARA (UiTM) Shah Alam especially to Faculty of Applied Science, for giving the opportunity and providing facilities to made this study successful.