Humic acid provenance influence to the adsorption capacity in uranium and thorium removal

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Abstract. It is common knowledge that humic acid is organic compound without certain chemical composition since it is derived from different organic materials. Further this raises question whether the different humic acid sample used could lead to different adsorbent properties e.g. adsorption capacity. To address the problem, this paper is aimed to clarify the relation between the provenances of humic acid and synthesized adsorbent properties especially adsorption capacities by quantitative and qualitative functional groups determination including discussion on their effect to the metal ion adsorption mechanism using three humic acid samples. Two commercial samples were derived from recent compost while the other extracted from tertiary carbonaceous mudstone strata.

1. Introduction
Environmental pollution caused by the release of heavy metal or radioactive elements needs serious attention, especially in developing countries. To resolve the problems, the removal of these pollutants from the wastewater is stipulated as mandatory. Several technologies have been proposed for pollutant removal including electrochemical treatment, chemical separation, liquid-liquid separation, intracellular sequestration e.g. phytoextraction and solid phase extraction. Among these techniques, solid liquid separation or adsorption is considered as the most promising due to its advantages including versatility, cost effective [1] and ability to manage the low concentration pollutant [2].

Numerous adsorbent had been proposed to remove heavy metals and radioactive elements, but unfortunately most of these adsorbents are not available for wide scale operation due to complicated and high cost synthesis procedure. This problem inspired the researchers to synthesize low cost adsorbents using widely and inexpensive materials, including humic acid. Humic acid is major organic component in soil, coal and peat, also could be found in aquatic environment e.g. lakes and sea water [3]. Humic substance could be classified based on solubility into fulvic acid (FA, soluble fraction), humin (HUM, insoluble fraction) and humic acid (HA, soluble only in basic solution). According to standard protocol, HA and FA are extracted from soil using strong basic solution (sodium or potassium hydroxide), and HA further is separated from FA through precipitation by changing the pH of solution to acidic. HA has ability to bind metal ions due to the presence of functional group such as carboxyl and hydroxyl, which act as ligand [4].

Several HA based adsorbent had been reported [1, 5-9]. In these reports, only single HA sample was used and this evokes the question whether the different HA sample used could lead to different adsorbent properties e.g. adsorption capacity. This concern rose due to common knowledge that HA is organic compound without certain chemical composition since it is derived from different organic materials. To put this indecision into rest, this paper is aimed to clarify the relation between the provenances of HA and synthesized adsorbent properties especially adsorption capacities by quantitative and qualitative functional groups determination including discussion on their effect to the metal ion adsorption mechanism.
2. Material and Method

2.1. Humic acid samples

Three HA sample used in this research, 2 of them are commercial HA obtained from Acros Organic, USA (HA-AC) and Wako Chemical, Japan (HA-WK) and the other was extracted from carbonaceous mudstone of tertiary coal strata, Mesuji, Lampung, Indonesia (HA-MJ). Before used further, these HA samples were purified according to the protocol by Koopal et al. [10]. In brief, 10 g HA was dissolve in 1 L sodium hydroxide 0.1 M and stirred for 12 h. Mineral and undissolved materials were separated from supernatant by centrifugation. HA in supernatant phase was precipitated by changing the pH to 2 using hydrochloric acid and finally the HA was recovered by centrifugation and dried at 50°C.

2.2. Functional group determination

HA functional groups were determined by titration method according to Khil’ko et al. [11]. Total acidity (exchangeable proton) was quantified using barium method. Weighed HA sample was introduced into flask containing 50 ml barium hydroxide 0.1 N, stirred for 18 h and settled for 4 days. Five ml supernatant solution was taken and diluted to 100 ml using boiled distillate water. This mixture was titrated by 0.1 N hydrochloric standard solutions by using phenolphthalein indicator to detect the end point. Blank titration was also carried out using distillate water instead of HA sample. Total acid acidity was calculated using following equation (1).

\[
[H^+] = \frac{(V_0 - V_{HCl})M_{HCl}V_{Ba}}{mV_a}
\]  

(1)

Where \([H^+], V_0, V_{HCl}, M_{HCl}, V_{Ba}, m, V_a\) are total acidity (mequiv/g), volume of hydrochloric acid used for blank solution titration (ml), volume of hydrochloric acid used for HA sample solution titration, hydrochloric acid concentration (mequiv/ml), initial volume of barium hydroxide (ml), HA in aliquot portion (g) and aliquot volume used for each titration (ml), respectively.

In carboxylic determination, weighed HA sample was mixed with 10 ml sodium acetate 0.1 M and 40 ml boiled distillate water. The mixture was homogenized at 100°C for 40 min. The precipitate formed was filtered and washed thoroughly using 100 ml boiled distillate water and liberated acetic acid was titrated using potassium hydroxide 0.05 N, using phenolphthalein indicator to detect end point. Carboxylic content was calculated using following equation.

\[
[COOH] = \frac{V_{KOH}M_{KOH}V_1}{mV_2}
\]  

(2)

Where \([COOH], V_{KOH}, M_{KOH}, m, V_1\) and \(V_2\) are carboxylic content (mequiv/g), volume of potassium hydroxide used for titration (ml), potassium hydroxide concentration (mequiv/ml), HA in each aliquot portion (g), total volume (152 ml) and aliquot volume for each titration (ml), respectively. The hydroxyl content \([OH]\) of HA sample was obtained by subtraction of total acidity with carboxylic content (3).

\[
[OH] = [H^+] - [COOH]
\]  

(3)

2.3. Adsorption capacity determination

Adsorption capacity of each HA sample was carried out using batch method. Before used further in the experiments, HA needs to be stabilized by attaching it to the silica gel particle through silylation process according to Prado et al. [12] as shown in Figure 1. This step was necessary considering HA
solubility in aqueous phase. The adsorbent synthesized using HA-AC, HA-WK and HA-MJ are referred as SiHA-AC, SiHA-WK and SiHA-MJ, respectively.

![Diagram](https://example.com/diagram)

**Figure 1.** Silylation process to attach HA on silica gel surface (modified from Prado et al. [12])

Batch experiment to determine adsorption capacity was done by equilibrating 10 mg of SiHA adsorbent with 5 ml uranyl (UO$_2^{2+}$) or thorium (Th$^{4+}$) 250 mg/L (pH 3). The mixture was equilibrated for 24 h and supernatant solution was separated by centrifugation. Optimum parameters such as pH, solid-liquid ratio, uranyl or thorium concentration and equilibrium time for adsorption studies were set according to the previous research [9]. Uranyl and thorium concentration in liquid phase before and after equilibration were measured spectrophotometrically using Arsenazo III as chromogenic reagent using Jasco V-530 UV/Vis spectrophotometer. Adsorption capacity was calculated using following equation (4).

\[
q = (C_0 - C_E)\frac{V}{m}
\]

where q, C$_0$, CE, V and m are adsorption capacity (mmol/g), uranyl or thorium initial concentration (mmol/L), uranyl or thorium equilibrium concentration (mmol/ml), volume of liquid phase (ml) and adsorbent added (g), respectively.

2.4. **Humic acid and adsorbent characterization**

HA and Si-HA characterization were carried out using FT-IR in order to determine the functional group present in the surface of HA and SiHA, also to clarify the differences among three HA samples and SiHA adsorbents. Other characterization is SEM to reveal the morphology of HA and adsorbent particle, also to confirm the silica gel surface modification by humic acid. FT-IR data was obtained using Jasco FT/IR 4100 spectrometer by the KBr method with a wavelength range of 400 to 4000 cm$^{-1}$, while surface morphology was captured using Hitachi S-2400 scanning electron microscope operated at 15 kV after gold coating in Graduate School of Environmental Science, Hokkaido University.
3. Results and discussions

3.1. Humic acid samples and their purification

HA as previously explained is derived from organic material (especially plant material) degradation [13]. Generally, commercial HA is extracted from compost (recent age) i.e. HA-AC and HA-WK, while HA-MJ was extracted from organic matter of carbonaceous mudstone with tertiary age (2.58 – 65 million years ago). The organic matter had been through biodegradation process by microorganism in early phase and sedimentation or diagenesis (temperature and pressure) in advance phase. Since derived from compost, organic matter as precursor only experienced biodegradation while HA-MJ, besides decomposition by microorganism, the organic matter had been subject to high temperature and pressure. Advance phase would affect HA structure through cracking process of organic compound with high molecular mass [14] into product with lower mass, and it is assumed that HA-MJ would have lower molecular mass and more functional group due to cracking process (Figure 2).

![Figure 2. Cracking of humic substance through increasing pressure (P) and temperature (T)](image)

3.2. Functional group determination

Functional group determination (total acid and carboxylic) was carried out while hydroxyl was obtained from the subtraction of total acidic by carboxylic fraction. The results are shown in Table 1.

| Sample    | Total acidity (meq/g) | Carboxylic (meq/g) | Hydroxyl (meq/g) |
|-----------|-----------------------|--------------------|------------------|
| HA-AC     | 5.35±0.16             | 3.54±0.05          | 1.81             |
| HA-WK     | 4.47±0.00             | 2.37±0.06          | 2.10             |
| HA-MJ     | 4.73±0.00             | 4.48±0.11          | 0.24             |
| SiHA-AC   | 4.59±0.00             | 0.28±0.00          | 4.31             |
| SiHA-WK   | 3.86±0.06             | 0.44±0.03          | 3.42             |
| SiHA-MJ   | 4.23±0.00             | 0.28±0.05          | 3.95             |

Table 1 shows significant difference in case of total acidity (total exchangeable proton) for two commercial HA samples while HA-MJ value of total acidity close to the value of HA-WK. Total acidity for each HA sample mostly contributed by carboxylic functional group. In this respect there is contrast between commercial humic acid (HA-AC and HA-WK), which carboxylic group contributed 66% and 53% respectively to the total acidity compared to the value of HA-MJ. In the tertiary humic acid sample, 95% of total acidity comprise of carboxylic acid. This is probably caused by...
biodegradation and advance process (diagenesis), which leads the ester or fatty acid of organic material as HA precursor were transformed (cracked) into carboxylic acid (Figure 2).

After modification of HA by silica gel to form SiHA adsorbent, the total acidity decrease around 15% from the original HA sample values. As predicted, carboxylic content in each adsorbent significantly decrease (90 % of initial value), since this group reacted with amine group during silylation process (Figure 1) to form peptide bonding which attached the humic acid to the silica gel surface. Interestingly, the hydroxyl group was increasing after HA modification. This is due to the presence of hydroxyl of silanol group on the surface of silica gel (Figure 1).

3.3. Adsorption capacity determination

Adsorption capacity of HA modified silica gel to remove uranyl and thorium from aqueous solution using batch method had been carried out and the results are shown in Table 2.

Table 2. Adsorption capacity of HA modified silica gel (SiHA). Carb and hyd mean carboxylic and hydroxyl capacity for each ion, respectively

| Adsorbent | UO$_2^{2+}$ (mmol/g) | Carb. UO$_2^{2+}$ (mmol/g) | Hyd. UO$_2^{2+}$ (mmol/g) | Th$^{4+}$ (mmol/g) | Carb. Th$^{4+}$ Hyd. Th$^{4+}$ (mmol/g) |
|-----------|----------------------|-----------------------------|-----------------------------|-------------------|------------------------------------------|
| SiHA-AC   | 0.10 ±0.01           | 0.14                        | 2.16                        | 0.14± 0.00        | 0.07                                      | 1.08                                       |
| SiHA-WK   | 0.07 ±0.00           | 0.22                        | 1.71                        | 0.13 ±0.00        | 0.11                                      | 0.86                                       |
| SiHA-MJ   | 0.11 ±0.02           | 0.24                        | 1.98                        | 0.18 ±0.18        | 0.07                                      | 0.96                                       |

Based on Table 2, all HA modified silica gel adsorbents had more affinities toward thorium than to uranyl ions, which are shown by the capacity values. For each ion species, HA-MJ modified silica gel (SiHA-MJ) possesses highest capacity compared to the both commercial HA modified adsorbent. Interestingly, statistic analysis using t-test two-sample assuming unequal variance revealed insignificant difference among three HA acid sample used for uranyl and thorium removal in terms of adsorption capacity. Stochiometrically, by using functional group data in Table 1 and adsorption capacity for uranyl and thorium in Table 2, the maximum theoretic capacity of each adsorbent could be calculated. To bind a uranyl ion, the adsorbent has to provide two carboxylic or two hydroxyl groups and in the case of thorium, four carboxyl or hydroxyl are required to bind a thorium ion (Figure 3).

Based on dissociation constant data, carboxyl would release proton at pH 4.28 [15], while hydroxyl which consists of phenolic or silanol would be dissociated at higher pH at basic condition between 10 and11, hence in this experiment condition (pH 3), it could be said that only carboxyl group plays important role in binding mechanism. Based on carboxyl capacity for uranyl ion in Table 2, the carboxyl capacity is higher compared to uranyl ion adsorbed. This indicated that not all carboxyl groups on the adsorbent could bind uranyl ion due to incomplete dissociation at pH 3. In contrast with thorium, carboxyl capacity is lower compared to the adsorption capacity, which inferred that all carboxylic had been bound to thorium ion, and fraction of thorium ion was bound electrostatic ally to the hydroxyl group. According to these results, it could be hypothesized that two interaction mechanisms occurred: ion exchange and electrostatic force. Interaction to bind uranyl ion was exclusively contributed by ion exchange, while in the case of thorium, the interaction was dominated by ion exchange and to lesser extent contributed by electrostatic force. The ability of thorium ion to form electrostatic binding is partly caused by ionic radii and charge factors [5, 8].
**Figure 3.** Possible adsorption mechanism, bonding between ligand (functional group) and target ion (uranyl and thorium), double red dot and red arrow signify the electrostatic interaction and ion exchange respectively.

**Figure 4.** SEM image of unmodified silica gel (top) and humic acid modified silica gel (SiHA, bottom)
3.4. Humic acid and adsorbent characterization

Characterization using FT-IR and SEM was done to confirm the adsorbent formation by comparing the raw materials (silica gel and HA) with the product (SiHA adsorbent). The results of SEM characterization are shown in Figure 4.

Figure 4 show the difference between silica gel and SiHA in terms of surface morphology. Silica gel shows smooth surface morphology and the modification is marked by surface encrustation. FT-IR was done to prove the presence of certain functional group and to confirm the surface modification. The results in Figure 5 show that silica gel (SiO$_2$) reveals the peak at 796 cm$^{-1}$ (tetrahedral silica matrix), adsorption at 1080 cm$^{-1}$ (Si-O bonding) and 954 cm$^{-1}$ (silanol functional group). HA modified silica gel (SiHA) spectra confirm that SiHA is hybrid material between HA and silica gel through the presence of carboxyl group (3500-3800 cm$^{-1}$) of HA, while silica gel spectra are still retained at 796 and 1080 cm$^{-1}$. Two commercial HA samples based on Figure 5 show no significant deference in terms of FT-IR spectra.

![Figure 5. FT-IR spectra of Silica gel, SiHA-AC, HA-AC and HA-WK](image)

4. Conclusions

Three commercial humic acids had been purified and used in adsorbent synthesis. The adsorbents were used in uranyl and thorium removal. Based on titration analysis, total acidity for each HA sample mostly contributed by carboxylic functional group. In this respect there is contrast between commercial humic acid (HA-AC and HA-WK), compared to the value of HA-MJ. After modification of HA by silica gel to form SiHA adsorbent, the total acidity decrease and as predicted, carboxylic content in each adsorbent significantly decrease by 90 % of initial value, while hydroxyl group was increasing due to the presence of hydroxyl of silanol group on the surface of silica gel. All SiHA adsorbents had more affinities toward thorium than to uranyl ions. For each ion species, HA-MJ modified silica gel (SiHA-MJ) possesses highest capacity compared to the other adsorbents. However, statistic analysis using t-test two-sample assuming unequal variance revealed insignificant difference among three HA acid sample used for uranyl and thorium removal in terms of adsorption capacity. Stochiometrically, by using functional group data, it could be hypothesized that two interaction mechanisms occurred. Interaction to bind uranyl ion was exclusively contributed by ion exchange, while in the case of thorium, the interaction was dominated by ion exchange and to lesser extent...
contributed by electrostatic force. Characterization using FT-IR and SEM confirmed the adsorbent formation, while FT-IR reveals no significant deference between HA samples.

Acknowledgement
The research is supported by MEXT scholarship of Japan for foreign students and under supervision of Kazuhiro Toyoda of Graduate School of Environmental Science, Hokkaido University. All instrumentation and characterization were performed in Graduate School of Environmental Science, Hokkaido University.

References
[1] Anirudhan T S, Bringle C D, Rijith S 2010 J. Environ. Radioactiv. 101 267-76
[2] Gasser M S 2007 Sep. Purif. Technol. 53 81-8
[3] Stevenson F J 1994 Humus Chemistry: Genesis, Composition, Reactions New York: John Wiley & Sons
[4] Davies G, Fataftah A, Cherkasskiy A, Ghabbour E A, Radwan A, Jansen S A, Kolla S, Paciolla M D, Buermann W, Balasubramanian M, Budnick J, Xing B 1997 J. Chem. Soc. Dalton Trans. 4047-60
[5] Erdogan S, Merdivan M, Hamamci C, Akba O, Baysal A 2004 Anal. Lett. 37 2565-75
[6] Prado A G S, Miranda B S, Dias J A 2004 Colloids and Surf A: Physicochem. Eng. Asp. 242 137-43
[7] Seki H, Suzuki A 1995 J. Colloid Interf. Sci. 171 490-4
[8] Khalili F, Al-Banna G 2015 J. Environ. Radioact. 146 16-26
[9] Prasetyo E, Toyoda K 2016 J. Radioanal. Nucl. Chem. 310 69-80
[10] Koopal L K, Yang Y, Minnaard A J, Theunissen P L M, Riemsdijk W H V 1998 Colloids and Surf. A: Physicochem. and Eng. Asp. 141 385-95
[11] Khil’ko S L, Koytun A I, Rybachenko V I 2011 Solid Fuel Chemistry 45 337-48
[12] Prado A G S, Miranda B S, Dias J A 2004 Colloids and Surf. A: Physicochem. and Eng. Asp. 242 137-43
[13] Ponomarenko E V, Anderson D W 2001 Canadian Journal of Soil Science 81 285-97
[14] Diessel C F K 1992 Coal-Bearing Depositional Systems Berlin: Springer
[15] Andjelkovic T, Perovic J, Purenovic M, Blagojevic S, Nikolic R, Andjelkovic D, Bojic A 2006 Eclet. Quim. 31 39-46