



Immobilization of Humic Acid on Bentonite and Its Application for Adsorption of Cs¹³⁷ and Am²⁴¹

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ABSTRACT

In the present work, immobilization of humic acid on bentonite and its application as an adsorbent of Cs¹³⁷ (Cesium) and Am²⁴¹ (Americium) is performed. The parameters studied are rate constant, adsorption capacity, and adsorption energy. This research started with the immobilization of humic acid on a bentonite surface followed by a stability test for immobilization of humic acid at various acidities. Adsorption of Cs¹³⁷ and Am²⁴¹ ions was conducted by first examining the optimum pH giving minimum complexed ions by the soluble fraction of humic acid and maximum adsorbed ions on the adsorbent. While adsorption energy and capacity were determined by the Langmuir isotherm adsorption model. The result shows that the amount of immobilization of humic acid on bentonite is 39.75 % (w/w) at optimum conditions. Immobilization of humic acid was stable up to pH 12.0. For both ions, optimum adsorption occurred at pH 5. At this optimum condition, the adsorption energies of 21.481 kJ.mol⁻¹ and 22.276 kJ.mol⁻¹ for Cs¹³⁷ and Am²⁴¹ are obtained, respectively. The result also shows that adsorption capacity and energy for Am²⁴¹ were higher than that for Cs¹³⁷ which indicates the affinity of Am²⁴¹ for both adsorbents was higher than that of Cs¹³⁷.

INTRODUCTION

Cesium (Cs¹³⁷) and Americium (Am²⁴¹) are the radioactive waste generated from plutonium-fueled power reactors or the result of nuclear weapon explosions. These radioactive can spread to the atmosphere as well as to the soil (Glikson 2017, Meszaros et al. 2016, Snow et al. 2019) and can be very harmful to human health. In the future, these radioactive emissions may increase since more nuclear power plant has been built around the world. Thus it is important to find out a sustainable method to encounter the Am²⁴¹ and Cs¹³⁷ pollution to the atmosphere and or to the soil. One method that can be utilized in controlling water pollution due to heavy metal and radioactive waste pollution is the adsorption method. The adsorption method was first introduced by Cihan et al. (2019). Mojiri et al. (2019) stated that adsorption is one method that can be used to treat waste. Adsorption is a method that is generally based on interactions between metals and functional groups that exist on the surface of the adsorbent that occurs through complex formation interactions and usually occur on solid surfaces that are rich in functional groups such as: -COOH, -OH, and NH (Yang et al. 2019, Kumar & Jiang 2016). The adsorbent that can be used for the purpose is humic acid which can be obtained from peat soil. According to Uda et al. (2017), Indonesia has peatlands of approximately 26.5 hectares, mostly in Kalimantan and Sumatra Island.

Humic acid is a very abundant and essential component in the natural environment and can bind to pollutants, both organic and inorganic pollutants (Ceci et al. 2019). Humic acid is a heterogeneous compound, consisting of many oxygen-containing groups (Boguta et al. 2019, Shi et al. 2018, Zhang et al. 2018). The various functional groups found in humic acid are the -COON, OH enolic, quinone, lactone, ether, and alcohol-OH groups (Zhang et al. 2018, Wu et al. 2019). The main functional groups found in humic acid are carboxylic groups, -OH phenolics and -OH alcoholic, in addition to other groups in minor quantities, such as carboxyl, phosphate, sulfate, amides, and sulfides which all can react with metal ions in solution. Spectroscopic studies show that the -COOH group is a group that plays a vital role in the formation of complexes between metal ions with humic and fulvic acid. Moreover, the interaction also involves OH groups, -C = O and -NH.

Humic acid immobilization has also been reported by Cruz-Zavala et al. (2018), which is by immobilizing humic acid in chitin, by combining humic acid molecules with chitin through electrostatic interactions due to different loads, so we get a combined adsorbent of humic and chitin acids and produce a decrease in humic acid solubility to highly alkaline acidity. To enrich the surface of an inorganic solid through immobilization with functional groups of organic compounds, the solid should have active sides such as

siloxane (-Si-O-Si-), silanol (-SiOH), and aluminol groups (-AlOH) which can be chemically bonded with immobilized organic compounds, besides the solids must also have a large surface area. Fig. 1 shows the reaction mechanism of humic acid-binding in the adsorption process according to Tunega et al. (2019) and Smilek et al. (2017). The reaction mechanism of humic acid-binding in the adsorption process of humic compounds is supporting solids can occur through the reaction between hydrophilic functional groups of humic acid (carboxylic groups) with -OH groups on the surface of the supporting solid

The humic acid molecular structure consists of a set of active groups/micelles that form polymers naturally with the basic structure of the aromatic ring. Because of the very complex structure of humic acid, its structure cannot be stated with certainty and can only be expressed in a hypothetical structure (El-Sayed et al. 2019). Humic and fulvic acids contain groups consisting of oxygen atoms (such as -OH, -COOH, and -C = O) with large concentrations per unit weight, so these compounds are hydrophilic (Ai et al. 2020). Some hypothetical structures of humic acid have been proposed by several researchers, such as Fuch, the German

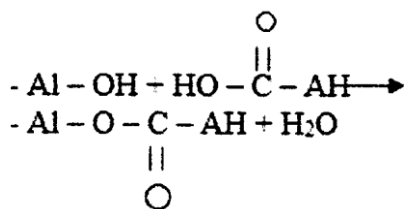


Fig. 1: Reaction mechanism of humic acid-binding in the adsorption process.

scientist, who proposed the structure of humic acid as shown in Fig. 2 (Klucakova & Veznikova 2017).

Another material that can be used as an adsorbent is bentonite. Based on the chemical nature of bentonite as ion exchange, bentonite can be used as an absorber in the treatment of liquid radioactive waste. Bentonite is a designation for commercial quality montmorillonite, with various compositions, but the formula is often stated as $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} + \text{XH}_2\text{O}$. The montmorillonite clay is a 2:1 clay type, a clay structure built by two tetrahedra sheets and one octahedral sheet. Two types of structures have been proposed for montmorillonite namely structures according to (1) Hofmann & Endell, and (2) Edelman & Favajee, as shown in Fig. 3 (Tournassat et al. 2018).

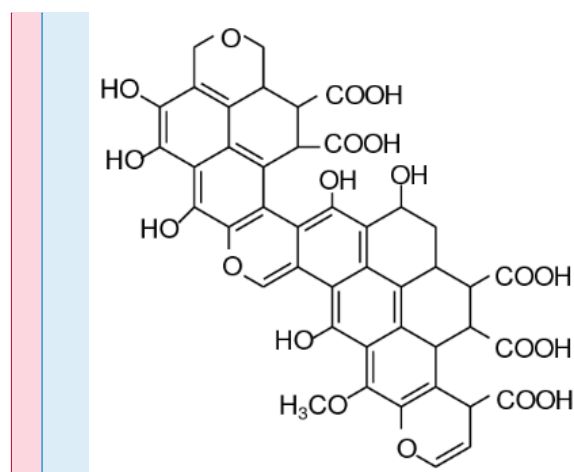


Fig. 2: Hypothetical structure of humic acid according to Fuch.

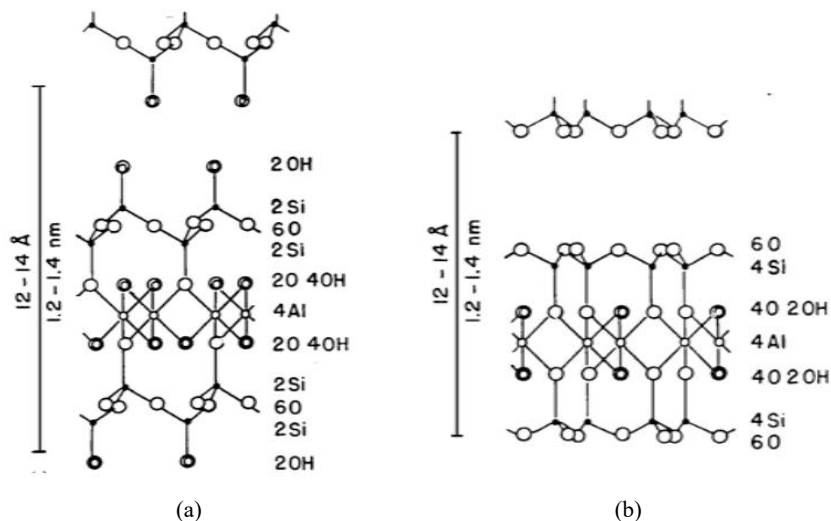


Fig. 3: The model of montmorillonite structure according to a) Edelman & Favajee, b) Hoffman & Endell.

The use of humic acid and bentonite as adsorbents for Cs¹³⁷ and Am²⁴¹ filtration is limited. Thus, the present work aims to investigate the potential use of humic acid from peat land and bentonite as Adsorption material of Cs¹³⁷ and Am²⁴¹. The work investigates the immobilization of humic acid on bentonite and its characteristic in terms of rate constant, adsorption capacity, and adsorption.

MATERIALS AND METHODS

Immobilization of Humic Acid on Bentonite: 60 mg of humic acid fills to three tubes in which the humic acid had been dissolved with 10 mL of 0.01 M NaOH and 100 mg of bentonite, with 0.001 M ion strength variation; 0.010 M and 0.100 M of NaNO₃. Furthermore, a magnetic stirrer was performed to mix the solution for 1 h and allowed to stand overnight. It was then filtered and washed to produce neutral pH. The solid was dried at 66 °C in an oven until a constant weight was obtained. An ultraviolet spectrophotometer analyzed the filtrate at a wavelength of 466 nm.

Identification and Clarification of Adsorbent Functional Groups: To identify and clarify the changes in groups found on bentonite and humic acid, which are immobilized on bentonite with optimal ion strength, 1 mg of each sample was sampled to be dissolved and analyzed using an infrared spectrophotometer.

Investigation of Adsorption of Cs¹³⁷ and Am²⁴¹ as the Function of Acidity: Bentonite or AH-bentonite as much as

0.01 g and 10 mL of 100 ppm CsI³⁷ feed solution with pH of 1 were poured into vial continued with 60 min shaking and allowed to stand overnight. It would produce segregation of deposits and filtrates. The filtrates were analyzed by θ spectrometer. The following steps were conducted in terms of pH 3, 5, 7, and 9. The adsorption test procedure of Am²⁴¹ is similar to that of Cs¹³⁷.

RESULTS AND DISCUSSION

Immobilization of Humic Acid on Bentonite: Fig. 4 shows the immobilization reaction of humic acid on bentonite. The humic acid is a fraction of humic compounds that are insoluble in water solvents under acidic conditions (pH around 2), but it starts to dissolve if the pH of the solution

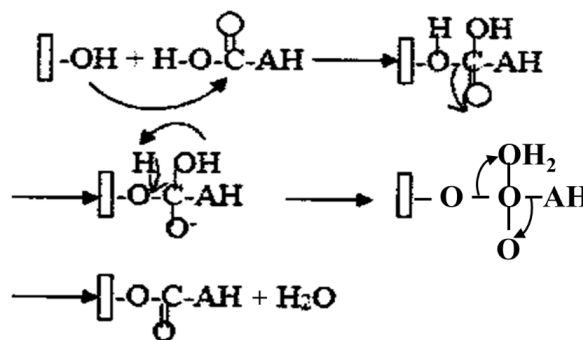


Fig. 4: Immobilization reaction of humic acid on bentonite.

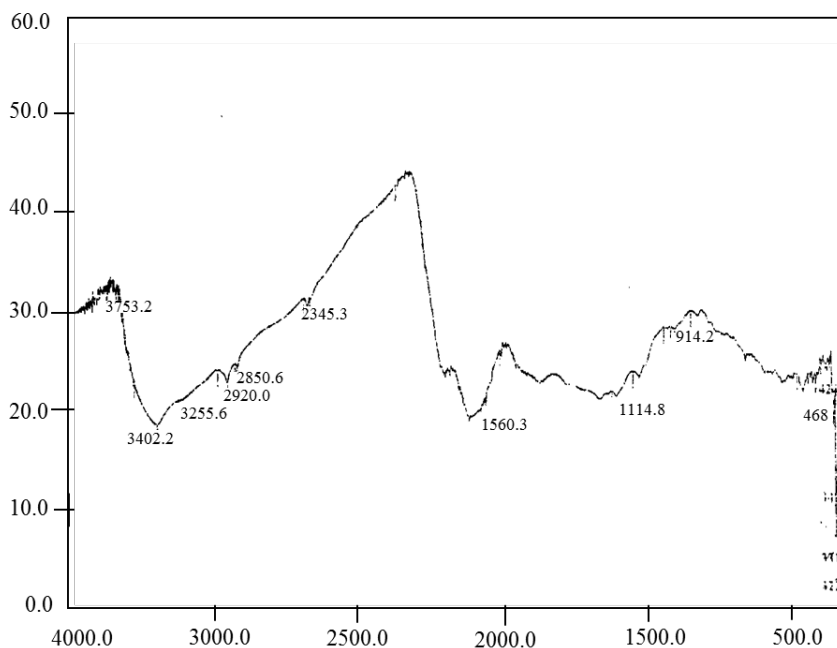


Fig. 5: Humic acid infrared spectra.

is above 2, and dissolves completely at pH above 6. At high pH, functional groups such as $-\text{COON}^-$ and $-\text{OH}$ phenolics from humic acid begin to be ionized, thus, weakening the intramolecular hydrogen bonds of humic acid, repelling inter-ionized groups and also as a result of hydration by water molecules. As a result of the dissolved fraction of humic acid, the interaction of humic acid with metal ions is not solely in the form of adsorption by insoluble fractions of humic acid, but also the interaction of complex formation between metal and dissolved humic acid fraction. Therefore, to study the adsorption of metals by humic acid at high pH, the treatment was applied to reduce the solubility of humic acid at high pH. To reduce the solubility of humic acid, the immobilization of humic acid on the surface of bentonite is carried out. The humic acid-binding reaction mechanism in the process of humic acid immobilization on bentonite occurs between functional groups of humic acid (carboxylic groups) with OH groups on bentonite through nucleophilic substitution reactions as follows. Therefore, bentonite solids that have silanol groups bind with humic acid through OH groups establishing nucleophilic substitution reactions to C atoms in the humic acid COOH groups.

Spectra Characterization: Fig. 5 presents infrared spectra of the humic acid. The spectra indicate widely absorbed

absorption at 3402.2 cm^{-1} wave number shows the OH carboxylic stretching vibration, absorption at 3255.6 cm^{-1} wave number is OH phenol vibration, absorption at 2920.0 cm^{-1} wave number identifies the existence of aliphatic CH stretching vibrations, the absorption at 2850.6 cm^{-1} wavenumber is the methylene group. The OH bending vibration of COOH and the C-O stretching vibration of COOH were identified by the absorption of 1114.8 cm^{-1} wave number. The aromatic group of humic acid was identified by the absorption band at 1560.3 cm^{-1} wave number indicates the presence of $-\text{C}=\text{C}$ aromatic. The OH stretching vibration of $-\text{COOH}$ is confirmed by the appearance of absorption bands at 2345.3 cm^{-1} wave number. The absorption bands of the humic acid infrared spectrum following the infrared spectroscopic data of humic acid, which absorbs 3300 cm^{-1} wavenumbers as a result of the $-\text{OH}$ stretching vibration. The existence of C-H stretching vibrations at 2900 cm^{-1} wavenumbers indicates the presence of C-H aliphatic, and weak absorption bands at wavenumbers around 1500 cm^{-1} indicate the existence of aromatic C = C vibrations.

Meanwhile, Fig. 6 shows a spectrum of bentonite. The graph shows a wide absorption band of 3431.1 cm^{-1} wave number; a sharp band at 1637.5 cm^{-1} ; a wide band at 1028.0 cm^{-1} ; and a sharp band at 916.1 cm^{-1} . It is following the in-

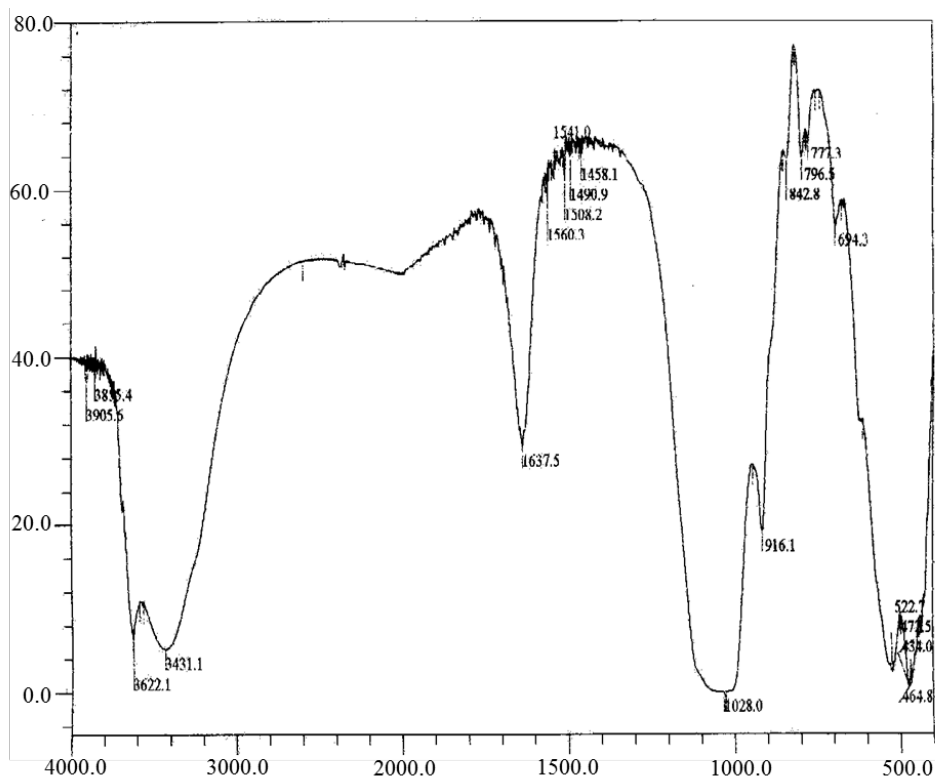


Fig. 6: Bentonite infrared spectra.

frared results of the reference montmorillonite which shows a wide band in the area of about 3420 cm⁻¹ for OH stretching vibrations and a wide band at 1050 cm⁻¹ for Si-O vibrations, bands for OH stretching vibrations, and bandwidth at 1050 cm⁻¹ for Si-O vibrations, sharp bands at wavenumbers 3622.1 cm⁻¹ for free stretching vibrations and sharp bands at 1637.5 cm⁻¹ are OH Stretching vibrations of water molecules and sharp bands at 910-920 cm⁻¹ wavenumber for Al-O vibrations.

Whereas, immobilized humic acid on bentonite spectra is shown in Fig. 7. The infrared spectra of the humic acid adsorbent immobilized on bentonite provide absorption peaks that are somewhat different from the infrared spectra of bentonite, namely the appearance of absorption at 2923.9 cm⁻¹ wavenumbers as CO aliphatic stretching vibrations and 2852.4 cm⁻¹ wavenumbers as methyl group vibrations. It clarifies the presence of humic acid in the adsorbent of

AH-bentonite. The absorption peak at 1035.7 cm⁻¹ wave number shows a decrease in the crystallinity of bentonite due to the immobilization occurrence of humic acid.

Adsorption rate of Cs¹¹⁷ and Am²⁴¹ on a single ion condition: The adsorption equilibrium time needs to be determined to achieve maximum adsorption of adsorbate on the surface of the adsorbent. The shorter the reaction time, the higher the reaction rate. Increasing the interaction time will not increase the amount of metal adsorbed if the adsorption equilibrium has been reached. The value of the adsorption equilibrium constant (K) and the first-order reaction rate (k₁) constant values obtained from calculations with the application of the kinetic model proposed by Chuanjiang et al. (2016) are presented in Table 1.

It can be seen from Table 1, that the value of the first-order reaction rate k₁ for CS¹³⁷ and Am²⁴¹ adsorption using HA-ben-

Table 1: The kinetics constants for Cs¹³⁷ and Am²⁴¹ adsorption (Chuanjiang et al. 2016).

Species	Adsorbent	Kinetics Parameter	
		K ₁ [min ⁻¹]	K [mol.L ⁻¹]
CS ¹³⁷	AH-bentonite	1.2 x 10 ⁻³	2881.8
	Pure bentonite	5.3 x 10 ⁻⁴	1045.8
Am ²⁴¹	AH-bentonite	1.6 x 10 ⁻³	5624.7
	Pure bentonite	9.8 x 10 ⁻⁴	2724.4

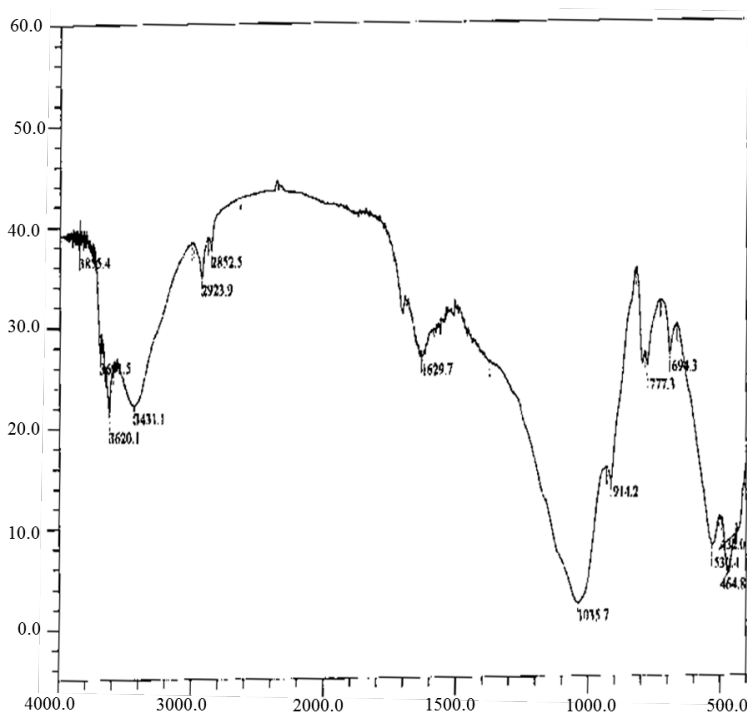


Fig 7: Infrared spectra of immobilized humic acid on bentonite.

tonite adsorbent is higher than pure bentonite adsorbents. It is due to the rich active site of HA-bentonite resulting from immobilized of humic acid on the surface, so HA-bentonite binds more efficiently to metal ions. The -COOH and -OH alcoholic and phenolic groups of humic acid that are immobilized on bentonite give new characteristics to the surface of the adsorbent. Those active groups have a significant role in binding metal ions, whereas, on bentonite, the binding of metal ions is dominantly determined by the presence of silanol (SiOH) groups on the surface of bentonite. The adsorption rate of Am²⁴¹ by the adsorbent of humic acid immobilized on bentonite increased higher compared with Cs¹³⁷. It describes that Am²⁴¹ has a greater affinity compared with Cs¹³⁷ on HA-bentonite. It also can be seen that the adsorption rate of the Am²⁴¹ metal ion is higher than the adsorption rate of Cs¹³⁷ in both adsorbents. The electronegativity (the size of atoms in a molecule to attract electrons to itself) values of Am and Cs are 1.3 Å and 0.86 Å, respectively (Cotton 2014). The electronegativity value of Am is higher than Cs, so the bond between Am and the adsorbent surface-active site has a relatively higher covalent bond. The increased covalent bonds between Am and adsorbents make Am less dissolved and more Am adsorbed on the surface of the adsorbent. Cs with smaller electronegativity form relatively more polar bonds with active sites on the surface of the adsorbent. The effect caused by polarization by cation is the solubility in polar solvents such as water. Therefore, the bond between Cs and immobilized humic acid on bentonite is more polar. It makes Cs easier to dissolve in water, which resulted in more Cs in the solution.

Regarding K values, the adsorption capability of HA-bentonite towards Cs¹³⁷ and Am²⁴¹ is higher compared to bentonite. It is caused by the more prosperous active sites of HA-Bentonite as the result of humic acid immobilization on the bentonite surface. Humic acid, which is rich in the -COOH and -OH groups, both phenolic and alcoholic, will give new characteristics to surfaces that are bound to bentonite. These groups have a high affinity for binding metal ions, so it creates more active sites in binding metals, whereas, in bentonite groups, the silanol groups are responsible for the active sites. The adsorption capability of HA-bentonite adsorbent is higher than Am²⁴¹ compared with Cs¹³⁷ indicated by a higher K value. It occurs because Am²⁴¹ has a greater affinity than Cs¹³⁷ in interacting with the adsorbent. According to Vogel (1961), ions that have a higher charge will have more excellent adsorption capability than the smaller charges. Am³⁺ has a total charge of +3, so the ability to adsorb is higher than Cs⁺ ions whose total charge is only +1.

CONCLUSION

The work on immobilization of Humic Acid on Bentonite

and Its Application for Adsorption of Cs¹³⁷ and Am²⁴¹ has been performed. It can be concluded that the more strength the ion concentration, the larger the immobilization of humic acid on bentonite was, and vice versa. The amount of immobilization of humic acid on bentonite is 39.75 % (w/w) at optimum conditions. Immobilization of humic acid was stable up to pH 12.0. For both ions, optimum adsorption occurred at pH 5. At this optimum condition, the adsorption energies of 21.481 kJ.mol⁻¹ and 22.276 kJ.mol⁻¹ for Cs¹³⁷ and Am²⁴¹ are obtained, respectively. The result also shows that adsorption capacity and energy for Am²⁴¹ were higher than that for Cs¹³⁷ which indicates the affinity of Am²⁴¹ for both adsorbents was higher than that of Cs¹³⁷.

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REFERENCES

- Ai Y., Zhao C., Sun L., Wang X. and Liang L. 2020. Coagulation mechanisms of humic acid in metal ions solution under different pH conditions: A molecular dynamics simulation. *Sci. Total Environ.*, 702: 135072.
- Boguta, P., D'Orazio, V., Senesi, N., Sokolowska, Z. and Szweczek-Karpisz, K. 2019. Insight into the interaction mechanism of iron ions with soil humic acids. The effect of the pH and chemical properties of humic acids. *J. Environ. Manag.*, 245: 367-374.
- Ceci, A., Pinzari, F., Russo F., Persiani, A.M. and Gadd G.M. 2019. Roles of saprotrophic fungi in biodegradation or transformation of organic and inorganic pollutants in co-contaminated sites. *Appl. Microbiol. Biotechnol.*, 103: 53-68.
- Chuanjiang, A., Yang, S., Huang, G., Zhao, S., Zhang, P. and Yao, Y. 2016. Removal of sulfonated humic acid from the aqueous phase by modified coal fly ash waste: Equilibrium and kinetic adsorption studies. *Fuel*, 165: 264-271.
- Cihan, A., Tokunaga, T.K. and Birkholzer, J.T. 2019. Adsorption and Capillary Condensation-Induced Imbibition in Nanoporous Media, *Langmuir*, 35 (29): 9611-9621.
- Cotton, F.A. 2014. *My Life in the Golden Age of Chemistry: More Fun Than Fun*. Elsevier, Amsterdam, The Netherlands
- Cruz-Zavala, A.S., Pat-Espadas, A.M., Rangel-Mendez, J.R., Chazarro-Ruiz, L.F., Ascacio-Valdes, J.A., Aguilar, C.N. and Cervantes, F.J. 2016. Immobilization of metal-humic acid complexes in anaerobic granular sludge for their application as solid-phase redox mediators in the biotransformation of iopromide in UASB reactors. *Bioresour. Technol.*, 207: 39-45.
- El-Sayed, M.E.A., Khalaf, M.M.R., Gibson, D. and Rice, J.A. 2019. Assessment of clay mineral selectivity for adsorption of aliphatic/aromatic humic acid fraction. *Chem. Geol.*, 511: 21-27.
- Glikson, A.Y. 2017. The Breach in the Earth's Radiation Shield. In Glikson, A.Y. (ed), *The Plutocene: Blueprints for a Post-Anthropocene Greenhouse Earth*, Springer, Cham, pp. 39-81.
- Klucakova, M. and Veznikova, K. 2017. Micro-organization of humic acids in aqueous solutions. *J. Mol. Struct.*, 1144: 33-40.

- Kumar, A.S.K. and Jiang, S.J. 2016. Chitosan-functionalized graphene oxide: A novel adsorbent for efficient adsorption of arsenic from aqueous solution. *J. Environ. Chem. Eng.*, 4(2): 1698-1713.
- Meszaros, R., Leelossy, A., Kovacs, T. and Lagzi, I. 2016. Predictability of the dispersion of Fukushima-derived radionuclides and their homogenization in the atmosphere. *Sci. Rep.*, 6(1): 43.
- Mojiri, A., Ohashi, A., Ozaki, N. and Kindaichi T. 2019. Pollutants removal from synthetic wastewater by the combined electrochemical, adsorption, and sequencing batch reactor (SBR). *Ecotoxicol. Environ. Safety*, 161: 137-144.
- Shi, W., Lü, C., He, J., En, H., Gao, M., Zhao, B. and Zhang, Y. 2018. Nature differences of humic acids fractions induced by extracted sequence as explanatory factors for binding characteristics of heavy metals. *Ecotoxicol. Environ. Safety*, 154: 59-68.
- Smilek, J., Sedlacek, P., Lastuvkova, M., Kalina, M. and Klucakova, M. 2017. Transport of organic compounds through porous systems containing humic acids. *Bull. Environ. Contam. Toxicol.*, 98: 373-377.
- Snow, M.S., Ward, J., Olson, J., Bucher, B., Delmore, J., Adamic, M. and Snyder, D. 2019. Carbon-14 content in surface soils near atmospheric and below ground nuclear detonations. *J. Environ. Radioact.*, 11: 208-209.
- Tournassat, C., Tinnacher, R.M., Grangeon, S. and Davis, J.A. 2018. Modeling uranium (VI) adsorption onto montmorillonite under varying carbonate concentrations: A surface complexation model accounting for the spillover effect on surface potential. *Geochim. Cosmochim. Acta*, 220: 291-308.
- Tunega, D., Gerzabek, M.H., Haberhauer, G., Lischka, H., Sole, R. and Aquino A.J. 2019. Adsorption process of polar and nonpolar compounds in a nanopore model of humic substances. *Eur. J. Soil Sci.*, 15: 1-11.
- Uda, S.K., Hein, L. and Surnarga, E. 2017. Towards sustainable management of Indonesian tropical peatlands. *Ecol. Manag.*, 25: 683-701.
- Vogel, J.L. 1961. Authoritarianism in the therapeutic relationship. *J. Consult. Psychol.*, 25(2): 102-108.
- Wu, J., Jiang, R., Lin, W. and Ouyang, G. 2019. Effect of salinity and humic acid on the aggregation and toxicity of polystyrene nano plastics with different functional groups and charges. *Environ. Pollut.*, 245: 836-843.
- Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J. and Gao, B. 2019. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. *Chem. Eng. J.*, 366: 608-621.
- Zhang, Z., Lü, C., He, J., Gao, M., Zhao, B., Zhou, B. and Zhang, Y. 2018. Nature differences of fulvic acid fractions induced by extracted sequence as explanatory factors for binding characteristics of Cu 2+. *Chemosphere*, 191: 458-466.
- Zhang, J., Yin, H., Chen, L., Liu, F. and Chen, H. 2018. The role of different functional groups in a novel adsorption-complexation-reduction multi-step kinetic model for hexavalent chromium retention by undissolved humic acid. *Environ. Pollut.*, 237: 740-746.