

STUDY ON THE ADSORPTION CHARACTERISTICS OF COBALT AND CAESIUM FROM A SOLUTION BY USING VIETNAMESE BENTONITE

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Abstract: The radioactive waste produced from the construction of a nuclear power plant is one of the most controversial topics. The resulting radioactive waste in Co-60 and Cs-137 is the most difficult to immobilise. The immobilisation cemented of radioactive waste seems to be the most feasible and safe method. Bentonite is a widely used adsorbent for the immobilisation of various heavy metals. In the near future, a nuclear power plant which is to be built in Vietnam will be an important factor in the safe operation of waste immobilisation. Therefore, the method of degrading complexes of radionuclides and the adsorption of radionuclides onto Vietnamese Bentonite (VNB) has been implemented in this study. Generally, the systems of UV rays and heating with oxidising substances which have been used to degrade complexes of radionuclides have shown some positive results. The experimental results for the adsorption of Co and Cs onto VNB suggested that VNB can be used in the future for large-scale liquid waste treatment due to its low cost, high efficiency and environmentally friendliness.

Keywords: radionuclides; Vietnamese bentonite; adsorption; UV ray; hydrogen peroxide

1. Introduction

During its operation, the NPP releases a large quantity of liquid waste containing radionuclides. The sources of liquid waste include leaked liquid from the primary circuit, the decontamination solution used to decontaminate the equipment of the primary circuit and other waste sources that are collected. Radionuclides that exist in liquid waste include Cs-137, Co-60, Fe-59, Cr-51, Mn-54...[1-4].

In all types of nuclear reactor the solutions that are used to decontaminate equipment containing chemicals are for example alkalis, KMnO_4 , EDTA...[4] in order to form complexes with radionuclides. These complexes are highly soluble in reactor solutions. Liquid waste containing radionuclides has to be stored for a certain length of time to decay. The short-lived radionuclides decay during this storage time, however the longer-lasting radionuclides such as Co-60 and Cs-137 are still present in concentrations above the discharge limit of 1 kBq/l and are not allowed to be discharged into the environment even after several years of storage [4-9].

One of the most effective methods for the treatment of radioactive waste is based on ion exchange and adsorption processes using inorganic ion exchangers. The desirable characteristics of high exchange capacity and favourable selectivity for some radioisotopes have

made certain zeolites quite useful in the treatment of radioactive waste. Natural zeolites, which have been considered for radioactive waste treatment, include mordenite, erionite, chabazite, clinoptilolite and bentonite. Among these, bentonite has received much attention due to its widespread usage, large surface area and high selectivity for some heavy and radiotoxic metals [3, 10].

Bentonite consists predominantly of the mineral montmorillonite - an aluminium hydro silicate. Crystal bentonite consists predominantly of the mineral montmorillonite, an aluminium hydro silicate. Its crystal structure has distinct layers (i.e. a layer lattice, see Fig.1.). The term "bentonite" was first used by Knight in 1889 following a discovery of highly colloidal plastic clay near Fort Benton in the cretaceous bed of Wyoming. Bentonite is a naturally occurring cationic clay, which can be processed or modified to tailor its properties so that it is suitable for various applications and uses. In its pure form or with some chemical additives or modifications, bentonite can be used as a rotary mud, an anticaking medium for certain granular fertilisers, a binding medium in the agglomeration of cattle feed, pesticides or a mineral oil, for filling, oil deodorising, palletising or bleaching, and in civil construction, foundries, and the alkylation of phenols [3, 5-7].

The scope of this study is the identification of degrading and mineralising complex compounds of Co and Cs by using UV ray and heating systems with oxidation substances and also to determine the adsorption efficiency of these radioactive isotopes onto VNB.

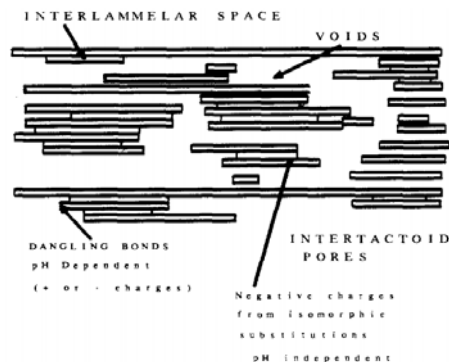


Figure 1: Structure of bentonite [5]

2. Objectives and methodology

2.1. Objectives

In order to extract Co-60 and Cs-137 from radioactive liquid waste, the combined treatment method has been used. This method includes two stages. In the first stage, the complex compounds of radionuclides with EDTA were degraded and mineralised by UV rays and heating with oxidation substances and then in the second stage radionuclides in the form of ions were removed by an adsorption technique using VNB.

First of all, in order to prepare the model solutions in this study, the activity concentrations of the radioactive isotopes of Cs-137 and Co-60 in a typical liquid radioactive waste sample were determined by standard gamma spectrometry using a gamma Műszaki zRt scintillation (NaI) detector. Table 1 shows measurements taken from the liquid waste radioactive sample.

Table 1: Typical radioactive liquid waste sample

Radio-nuclides	Activity concentration [Bq/dm ³] (3/2/2015)	pH	Dry matter [g/l]	Boric acid [g/l]	EDTA [g/l]
Co-60	1.23E+04	12.50	85.23	120	4
Cs-137	2.51E+05				
Σ	2.63E+05				

The concentrations of radioactive elements have been determined by using an AAS iCE 3000 atom absorption spectroscope (Thermo Scientific, USA) with flame air-C₂H₂ at a flow rate of 0.9 l/min.

The chemicals used as analytical standards were all reagent grade or better. Ethylenediaminetetraacetic acid (EDTA), H₃BO₃, NaOH, H₂O₂, CoSO₄, and CsCl were purchased from Merck (Germany). All glassware and

polyethylene bottles were thoroughly washed and then rinsed with ultra-pure water before use.

2.2. Research methodology

2.2.1. Degradation of complex compounds by heating with an oxidation reagent

In the heating system, the degradation of complex EDTA, CoSO₄ & H₃BO₃ was investigated under two sets of conditions:

- T° = 60°C with and without H₂O₂ (30mg/l)
- T° = 90°C with and without H₂O₂ (30mg/l)

Each experiment lasted one hour for three solutions with various concentrations of CoSO₄ (40 mg/l, 20 mg/l and 10mg/l). The samples were withdrawn from the system after regular intervals: 10 min, 30 min and 60 min. These solutions were centrifuged and stirred with VNB for one hour. After that, the solution samples with and without VNB were analysed to monitor their Co concentrations.

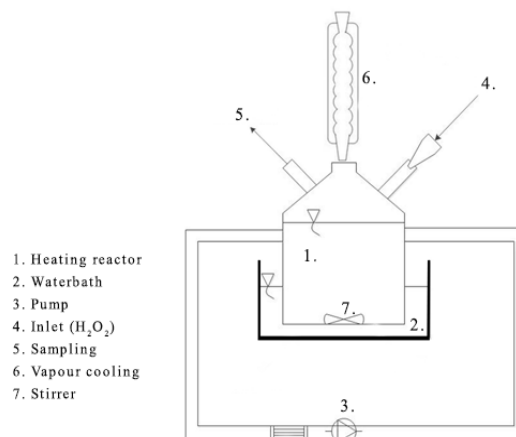


Figure 2: The experimental set-up of the heating system

2.2.2. Degradation of complex compounds by UV rays with oxidation reagents

In the present study, some aspects of the photocatalytic degradation of complex EDTA, CoSO₄ & H₃BO₃ were investigated. The degradation efficiency was studied in detail using a UV ray system within the range of 280-315nm and at 0.15 W/m² (see Fig. 3.) under four sets of conditions as below:

- Only with UV light;
- UV and O₂ (flow rate 70 l/h);
- UV, O₂ and H₂O₂ (3 mg/l);
- UV, O₂ and TiO₂;
- UV, O₂, TiO₂ and H₂O₂ (3mg/l).

Each experiment lasted two hours for the three solutions using various concentrations of CoSO₄ (40 mg/l, 20 mg/l and 10mg/l). The samples were withdrawn from the system after regular intervals: 10 min, 30 min, 60 min and 120 min. These solutions were centrifuged and stirred with VNB for one hour. After

that, the solution samples with and without VNB were analysed to monitor their Co concentrations.

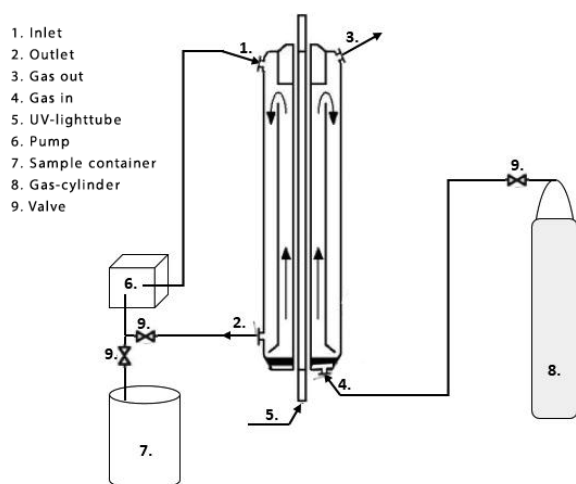


Figure 3: Experimental set-up of the UV ray system

2.2.3. Adsorption of radioactive elements onto VNB

Experiments on the adsorption of Co and Cs onto bentonite have been performed in batches to determine their adsorption times and equilibrium isotherms. 30 ml of radioactive solution with various initial concentrations: for CoSO_4 (10mg/l, 20mg/l, and 40mg/l); and CsCl (60mg/l, and 120mg/l) was stirred with bentonite for 1 hour within a pH range of 12 to 13, depending on the initial concentrations of EDTA and H_3BO_3 in the model solution. Samples were withdrawn at regular intervals, centrifuged and analysed in order to monitor their Co and Cs concentrations.

2.2.4. Adsorption isotherms

To evaluate the adsorption ability of ions onto bentonite, the Langmuir isotherm and Freundlich isotherm models were used in this study. Based on experimental data, the typical parameters of the adsorption process were determined by using the linear regression method.

The Langmuir equation is given by:

$$q_e = q_m k_a C_e / (1 + k_a C_e)$$

Its linear form is $C_e/q_e = (1/q_m)C_e + 1/(k_a q_m)$

where

q_e is the amount of ions adsorbed (mg/g) corresponding to C_e ;

C_e is the equilibrium concentration (mg/l);

q_m is the maximum adsorption capacity (mg/g); and

k_a is the adsorption equilibrium constant.

A plot of C_e/q_e against C_e should indicate a straight line with a gradient of $1/q_m$ and an intercept of $1/(k_a q_m)$

The Freundlich equation is given by:

$$q_e = K_f C_e^{1/n}$$

Its linear form is:

$$\ln q_e = \ln K_f + (1/n) \ln C_e$$

where

K_f and n are constants

3. Results and discussion

3.1. Efficiency of adsorption of radioactive elements onto VNB

For the estimation of the adsorption ability of Co (II) onto VNB, 0.1 g of VNB was stirred with 50 ml of Co (II) solution (8 – 200 mg/l). After equilibrium was achieved, the residual concentration of Co (II) was measured using an AAS iCE 3000 atom absorption spectroscope.

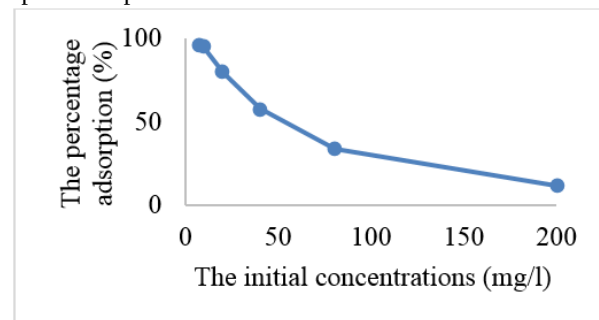


Figure 4: The effect of the initial concentration on the adsorption of Co (II) onto VNB

The effect of initial concentrations on the adsorption of Co (II) by VNB can be seen in Fig. 4. When the initial Co (II) concentration was increased from 8 to 200 mg.l^{-1} the absolute amount of Co (II) adsorbed per unit weight of VNB increased from 2.31 mg.g^{-1} (96.52%) to 6.95 mg.g^{-1} (11.77%). However, the percentage adsorption decreased with increasing initial concentration. The results showed that the removal of Co (II) ions is concentration dependent. At higher initial concentrations, the number of available adsorption sites decreased and hence, the removal of Co (II) ions depends upon the initial concentration.

To determine the optimal reaction time in order to achieve an equilibrium state, test flasks containing the mix of solutions with VNB were stirred for different intervals of time (10 minutes, 30 minutes, 60 minutes, and 120 minutes). The concentrations of Cs ions in the solutions were measured using an AAS iCE 3000 detector?. The reaction time required to achieve an equilibrium state was defined as from when stirring was initiated until the concentration of the solution remained constant. Figure 5 describes the Cs content in the solution after different periods of time.

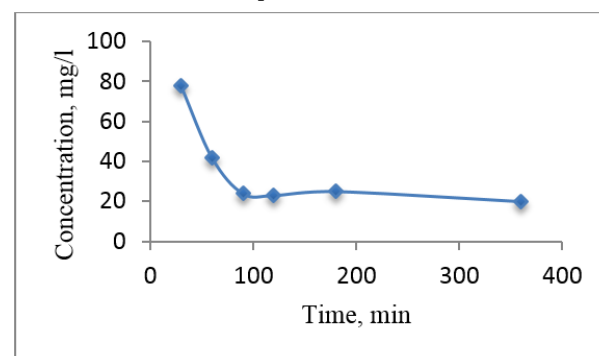


Figure 5: Cs content in the solution after different periods of time

According to Fig. 5, 100 minutes can be considered as the optimal reaction time to achieve the equilibrium state. This optimal time was implemented for the experiments on the adsorption of Cs ions onto VNB.

3.2. Study of the kinetics of the adsorption of radionuclides onto bentonite

3.2.1. Adsorption isotherms of Co

Figure 6 shows that the adsorption isotherm of Co (II) onto VNB could be described by the Langmuir model with a correlation coefficient (R^2) of 0.9791 and a maximum adsorption capacity of 8.15 mg/g. The equilibrium data also corresponded to the Freundlich isotherm with a correlation coefficient (R^2) of 0.964.

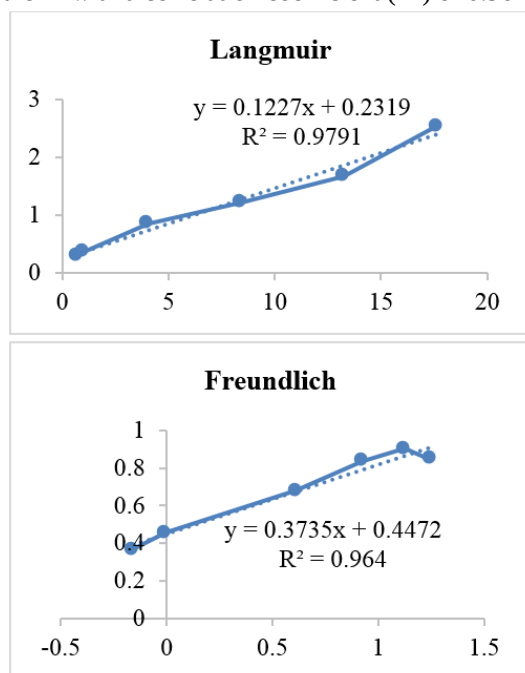


Figure 6: Adsorption isotherms of Co (II) onto VNB

Regarding the 4 experiments on the heating system, only experiment 4 (reaction at a temperature of 90°C with the addition of 30 mg/l of H_2O_2) could reduce the concentration of Co(II), in the other experiments, the Co(II) concentration remained unchanged or showed no significant change. Figure 7 shows that the concentration of Co(II) decreased as time increased within 30 minutes, after that, it practically remained constant. Moreover, initial concentrations also affected the efficiency of removing Co(II), using the initial concentrations of 40, 20 and 10 mg/l, the efficiency of removing Co(II) was 22.23%, 31.53% and 61.72% respectively for samples that were not stirred with VNB, and 22.70%, 43.30%, 67.74% for samples that were stirred with VNB.

Thus, the experimental adsorption capacity of VNB showed that it could adsorb Co (II) (the highest value of adsorption capacity is 8.15 mg/g), but, in the four experiments of the heating system, the efficiency of removing Co(II) with VNB did not show significant differences without VNB. Previous research [1, 3, 5] has shown that bentonite exhibits good adsorption capacities with some organic matter. However, these

results showed that the adsorption ability of EDTA onto bentonite is low, and Co (II) still remains in complex with EDTA, and is only removed when EDTA is completely degraded.

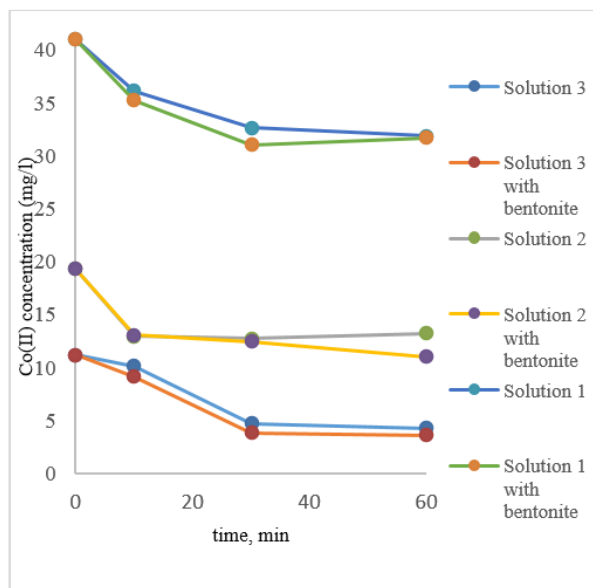


Figure 7: Degradation of Co (II) over different time frames (Ex. 4)

With regards to the UV system, the results from all experiments show that this method was not affected by decreasing Co (II) concentration. Kamal Rekab et al. show that the efficiencies of the UV/TiO₂ and UV/H₂O₂ processes are 67% and 42% under low pH conditions. On the other hand, the degradation efficiency was greater under acidic pH conditions, probably because H₂O₂ mainly dissociates into HO₂⁻ at alkaline pH levels, and the photolytic generation of OH[•] radicals is therefore inhibited. In addition, the nitrogen concentration in EDTA is mainly converted into ammonium, which forms a complex compound with Co (II) [1].

3.2.2. Adsorption isotherms of Cs

Figure 8 shows that the adsorption isotherm of Cs (II) onto VNB could be described by both the Langmuir and Freundlich models with correlation coefficients (R^2) of 0.7924 and 0.8020, respectively. Based on the Langmuir model, the highest value of adsorption capacity is 1.15 mg/g. Thus, the experimental adsorption capacity of VNB showed that it could adsorb Cs (the highest value of adsorption capacity is 1.15 mg/g).

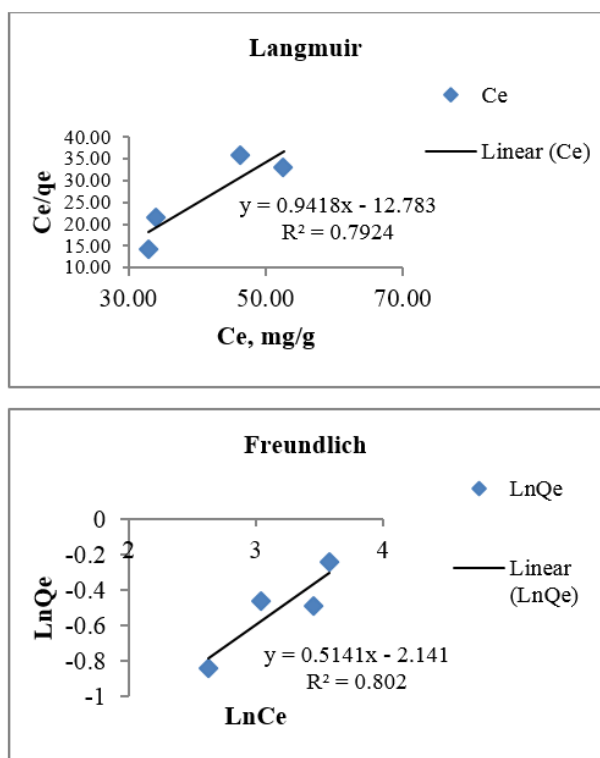


Figure 8: Adsorption isotherms of Cs onto VNB

4. Conclusion

VNB was tested as an adsorbent material for the removal of cobalt and caesium ions from sulphate and chloride waste solutions. The adsorption of Co (II) ions onto VNB followed the pseudo-second-order rate model. The adsorption isotherm of Co was described by the Langmuir and Freundlich models and this shows that the radioactive isotopes can be adsorbed onto VNB with high efficiency. The adsorption isotherm of Cs corresponded more closely to the Freundlich model. In the presence of EDTA in liquid radioactive waste, radioactive isotopes could not be adsorbed onto VNB due to complexes of EDTA with isotopes. Therefore, in this study two pre-treatment systems were implemented to remove EDTA from the liquid waste. The heating system achieved an efficiency of 67% while the UV system did not exhibit satisfactory levels of treatment efficiency. In the future, this study will be continued by upscaling the UV system to include the optimisation of pH values and the effect of ammonium converted from EDTA in order to apply these findings to radioactive liquid waste on a large scale.

Acknowledgement

The author would like to thank the Ministry of Education and Training, Vietnam for funding this research, and the Institute of Radiochemistry and Radioecology at the University of Pannonia for supplying experimental conditions.

REFERENCES

- [1] K. REKAB, C. LEPEYTRE, AND M. DUNAND: H₂O₂ and/or photocatalysis under UV-C irradiation for the removal of EDTA, a chelating agent present in nuclear waste waters, *Applied Catalysis A: General*, 488 (2014), pp.103-110
- [2] H. OMAR, H. ARIDA, AND A. DAIFULLAH: Adsorption of ⁶⁰Co radionuclides from aqueous solution by raw and modified bentonite, *Applied Clay Science*, 44 (2009), pp.21-26
- [3] S.KH. EGAMEDIEV, D.A. NURBAEVA, AND N.G. TASHEMIROVA: Modified bentonite as adsorbents for radionuclides: adsorption of carrier-free radiocobalt-57 on acid modified and calcined bentonite, *International Conference "Nuclear Science and its Application"*, Samarkand, Uzbekistan, September 25-28, 2012, pp.345-346
- [4] IAEA: Modified Combined methods for liquid radioactive waste treatment, Final Report, IAEA-TECDOC-1336, 1997-2001
- [5] J. DALE ORTEGO, M. KOWALSKA, AND D. COCKE: Interactions of montmorillonite with organic compounds-adsorptive and catalytic properties, *Chemosphere*, (1991) VOL 22, NO.8, pp.769-798
- [6] V.V. MILYUIN, AND O.A. KONONENKO: Sorption of Caesium on finely dispersed composite ferrocyanide sorbents, *Radiochemistry*, (2010) VOL 52, NO.3, pp.281-283
- [7] R. TOFALVI, A. SEPSEY, K. HORVATH, AND P. HAJOS: Environmental significance and identification of metal-chelate complexes using ion chromatography, *Hungarian Journal of Industrial Chemistry*, VESZPREM (2011) VOL 39, NO.1, pp.95-99
- [8] J.K. FRERICH, AND U. FLUGGE: High performance catalytic tubular membrane reactors owing to forced convective flow operation, *Hungarian Journal of Industrial Chemistry*, VESZPREM (2005) VOL 33, NO.1-2, pp.31-42
- [9] K. VARGA, AND G. HIRSCHBERG: Accumulation of radioactive corrosion products on steel surface of VVER-type nuclear reactors. II. ⁶⁰Co, *Journal of Nuclear Material*, ELSEVIER (2001) VOL 298, pp.231-238
- [10] A. KOLICS, AND K. VARGA: Study of cobalt sorption on polyethylene, *Journal of Colloid and Interface Science*, (1994) VOL 168, pp.451-457