Nucl. Sci. and Tech, Vol.5, No. 2 (2015), pp. 39-46

Nuclear Science and Technology

Journal homepage: https://jnst.vn/index.php/nst

Study on treatment of radioactive liquid waste from uranium ore processing by the use of nano oxide ferromagnetic

Vuong Huu Anh, Nguyen Van Chinh, Nguyen Ba Tien,
Doan Thi Thu Hien, Luu Cao Nguyen

Institute for Technology of Radioactive and Rare Elements – Vietnam Atomic Energy Institute
48, Lang Ha st., Dong Da, Hanoi
Email:vhuuanh82@yahoo.com.vn

Abstract: Nano oxide ferromagnetic Fe_3O_4 KT wich was produced by the Military Institute of Science and Technology were used to adsorbed heavy metal elements in liquid waste. In this report, the nano oxide ferromagnetic Fe_3O_4 KT with the particle size of 80-100nm and the specific surface area of 50-70m^2/g was applied to study the adsorption of radioactive elements in the liquid waste of uranium ores processing. The effective parameters on adsorption process included temperature, stirring rate, stirring time, the pH value of the solution, the initial concentration of uranium in solution were investigated. The results showed that the maximum adsorption capacity for uranium of the nano Fe_3O_4 KT was 53.5 mgU/g with conditions such as: room temperature, stirring speed 120 rounds/minute, the pH value of solution was 8, stirring time about 2 hours . From the results obtained, nano Fe_3O_4 KT was tested to treatment real liquid waste of uranium ore processing after removing almost heavy metals and a part of radioactive elements by preliminary precipitation at pH 8. The results were analyzed on the ICP-MS and α, β total activity equipment, the solution concentration after treatment suitable for Vietnamese Technical Regulation on industrial wastewater QCVN 40: 2011 (concentrations of heavy metals; total activity of α and β).

Keywords: *nano oxide ferromagnetic Fe_3O_4 KT, adsorption, uranium*

I. FOREWORD

In the nuclear fuel cycle, waste of uranium ore processing exists in different forms. Among them, the wastes are mainly in liquid, solid. These wastes often have very low radioactivity but have large volumes and the long half-life of the radionuclides. Therefore, if neglected treatment and good management, it would be very dangerous source of emissions to the environment and humans. The purpose of the handling of wastes from the production of uranium is studied to remove, stabilize, secure storage of wastes containing radioactive elements such as uranium, thorium, radium is radioactive for protection the environment and human. In liquid waste treatment technology of hydrometallurgical process uranium ore, many methods have been introduced, such as community precipitate with $BaCl_2$, ion exchange, membrane filter ... and adsorption methods. The methods of liquid waste treatment mentioned above are the advantages and limitations of its own. In methods of liquid waste treatment of hydrometallurgical uranium ore processing, the precipitation method is commonly used, but the drawbacks of of the method is the precipitation pH value is high ($pH \geq 10$) but still not reduce the concentration of radioactive elements down to the required level. With a high pH value, the concentration

https://doi.org/10.53747/jnst.v5i2.192
Received 22 December 2014, accepted 24 June 2015

of Ca^{2+} or Na^{+} as precipitating agent in water often becomes very high, not recommended discharge to the environment.. The application of advanced materials, especially nano materials for liquid waste treatment in general and in particular radioactive liquid waste are thriving and gradually replace the older technology.

The objective of the article:

Founding the appropriate technology conditions for the application of nano oxide iron to treat the liquid waste from uranium ore processing. Proposing a feasible technological process for treatment of liquid waste from uranium ore processing to meet the discharge criteria into the environment of QCVN 40:2011.

The contents of the article:

- Overview document of identity, application of nano oxide iron materials to be used for sewage treatment of uranium ore processing;
- Survey of affective factors for the adsorption capacity of nano Fe_3O_4 KT for uranium in the sample preparative solution;
- Test on the real liquid radioactive waste of uranium ore processing;
- Comparison of two types of nano applications from Vietnamese nano oxide ferromagnetic ($NiFe_2O_4$, Fe_3O_4) and 2 types of Slovakian nano oxide ferromagnetic ($NiFe_2O_4$, Fe_3O_4) to treat radioactive waste of uranium ore processing;

- Proposing a technological process to apply nano oxide ferromagnetic to the treatment for liquid waste of uranium ore processing.

II. EXPERIMENT AND RESULTS

Researching method is the study of adsorption process in static conditions (working in batches). After the pH value of the research solution was adjusted to the appropriate value, filtered and added the nano magnetite adsorbent was into the limpid solution. The solution was stirred or shaked. After a time, the radioactive elements and heavy metals in solution was adsorbed on nano ferromagnetic materials. The separation solid - liquid phase is easy made by using magnets. The uranium adsorption capacity of nano magnetite was shown by the adsorption process efficiency:

$$\eta = \frac{A_i - A_e}{A_i} * 100\% \qquad (1)$$

η – Adsorption process capacity;

A_i - Uranium content in the solution before adsorption;

A_a - Uranium content in the solution after adsorption.

In the experiment, uranium content in the solution was analyzed by photometric method on colorimetric Jenway 6300 spectrophotometer.

Chemical, equipment and measuring instruments:

- Agitator with controled speed (Heidol RZR 2020);

- pH meter (Handulab pH11- SCHOTT);

- Scales (Precisa xt220A); Oven (Memmert 800); Permanent magnets

- Colorimeter Jenway 6300 Spectrophotometer; Analyzer total radioactivity α, β: MPC-2000; ICP-MS analyzer (Analysis Centre - Institute for Technology of Radioactive and Rare)

- Pure Salt UO2 (NO3) 2.6H2O, Fe3O4 (KT, VN); Uranium acetate salt: pure UO2 (CH3COO) 2.2H2O

- HCl, pure NaOH, pure CaO, the liquid waste of uranium ore processing.

Case contents

To accomplish the proposed objectives, on the basis of the review of radioactive waste and the method for waste treatment, we choose the method using Vietnamese nano oxide ferromagnetic materials Fe_3O_4 KT to study the possibilities uranium adsorption capacity of infusion solutions (uranium acetate solution) by means of mixing batch to get the experimental parameters, then tested the ability to remove the radioactive elements in the real liquid waste treatment of uranium ore processing.

A. Investigation effect of technology parameters to the uranium adsorption capacity of nano oxide ferromagnetice materials in the sample solution preparation (using pure salt $UO_2(CH_3COO)_2.2H_2O$ to prepare liquid experiments).

Based on experience and research materials, The speed of stirring 120 rounds / minute was chosen.

Nano oxide ferromagnetic materials used as a laboratory chemical parameters - in accordance with Table I below:

Table I: Characterization of 4 types of nano oxide ferromagnetic materials

Number	Materials	Type	Particular size (nm)	Specific surface area (m^2/g)
1	Fe_3O_4	Viet Nam	80 - 100	50 - 70
2	$NiFe_2O_4$	Viet Nam	70 - 90	60 - 80
3	Fe_3O_4	(Slovakia)	20 - 30	100 - 110
4	$NiFe_2O_4$	(Slovakia)	15 - 20	100 – 120

a. Investigated the effect of mixing time on uranium adsorption capacity of nano magnetite:

The solutions for experiments were prepared from standard uranium salt. The time of each experiment was changed which the period of 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours.

The dependence on contact time to adsorption processing is shown in Fig 1.

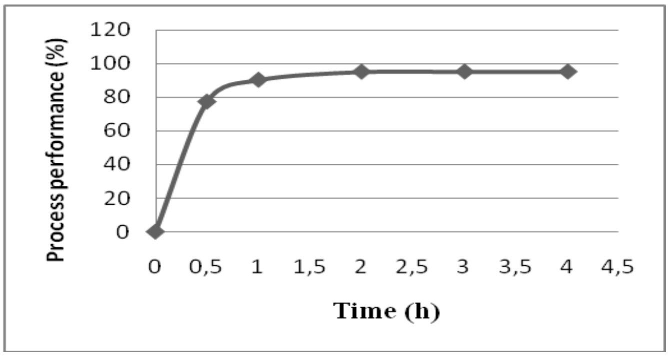

Fig. 1. The dependence of adsorption processing on time

(T= room temperature, n_k=120 rounds/minute, $U_{initial}$=5.15 mg/L, m_{oxit}=0.1g)

Comment: The data from Figure 1 revealed that uranium uptake reached equilibrium after mixing time about 2 hours. The uranium sorption efficiency was constant after increased mixing time from 3 to 4 hours.

b. Investigated the effect of pH value of the solution on the uranium adsorption capacity of nano oxide ferromagnetic materials

The experiments were conducted with uranium acetate standard salt solution. The pH value of the solutions was changed with values: 6.5; 7; 7.5; 8; 8.5; 9 with the stirring time of 2 hours.

The dependence on pH of adsorption performance of material is shown in Figure 2

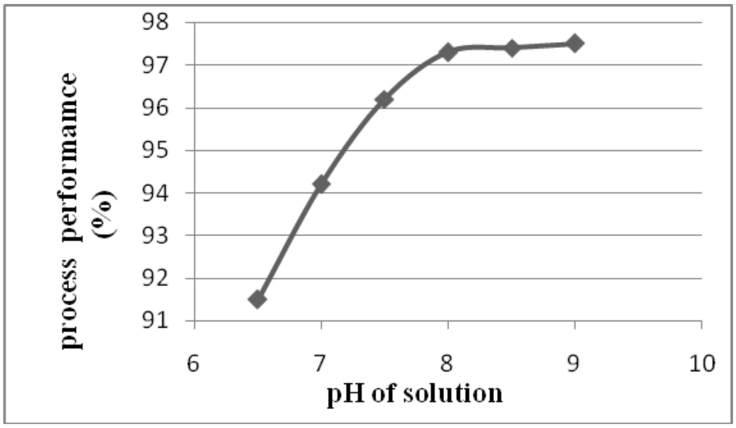

Fig. 2. The dependence of adsorption performance of material on pH to
(T= room temperature, n_k=120 rounds/minute, $U_{initial}$=5.15 mg/L, m_{oxit}=0.1g)

Comment: The data from Fig 2 revealed that the highest sorption efficiency (97.3%) could be observed on pH value of 8 with mixing time about 2 hours.

c. Investigate the influence of uranium concentration in solution on the adsorption capacity of nano oxide ferromagnetic

The research team conducted experiments with standard uranium acetate with saline concentration values (mg / l) are 2.58; 5.15; 7.73; 10.3; 12.88; 15.45 in stirring period of 2 hours and the amount of nano oxide ferromagnetic is 0.1g.

The dependence on initial uranium concentration of adsorption capacity of the material is shown in Figure 3.

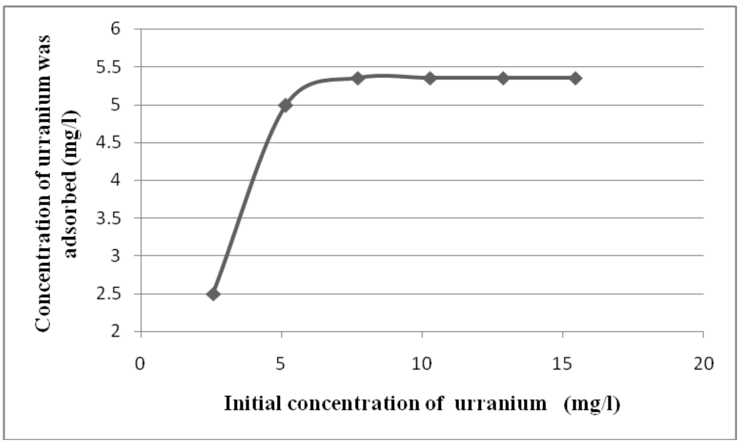

Fig. 3. The dependence of adsorption capacity of the material on initial uranium concentration to
(T= room temperature, n_k=120 rounds/minute, $U_{initial}$=5.15 mg/L, m_{oxit}=0.1g)

Comment: The data from Fig 3 revealed with mixing time about 2 hours, the pH value of 8 could be maximum adsorbed initial Uranium concentration 5.35mg on 0.1g nano Fe_3O_4 KT 100708 (expression clearly on experimental 3). However, the uranium adsorption efficiency was not increased with increasing continuous uranium concentration.

B. Experimental adsorption capacity of nano magnetite materials in real liquid radioactive waste from uranium ore processing.

Real sample of liquid radioactive waste was taken from the Central laboratory for processing of radioactive ore at Institute for Technology of Radioactive and Rare Elements. Liquid waste has pH = 2.2 and the composition of liquid waste was showed in table II

Table II. Compositions of initial liquid waste solution from uranium ore processing

Number	Elements	Concentration	Unit	Analysis Method
1	Fe	1536.4	mg/l	ICP-MS
2	Al	1454.4	mg/l	ICP-MS
3	Cr	4.12	mg/l	ICP-MS
4	Mn	1046.8	mg/l	ICP-MS
5	Mg	287.2	mg/l	ICP-MS
6	Zn	278.84	mg/l	ICP-MS
7	As	8.856	mg/l	ICP-MS
8	U	154.4	mg/l	ICP-MS
9	Total activity α	2988.01	Bq/l	MPC-2000 measure total activity α,β
10	Total activity β	29696.96	Bq/l	MPC-2000 measure total activity α,β

The data from Table II revealed that liquid waste from uranium ore processing have the low of pH value, the high content of heavy metal concentration and total activity α, β.

After adjusting pH of the liquid waste with a solution by lime ($Ca(OH)_2$) to pH 8.0 and separated solid – liquid by filtration. Solution after precipication and filtering at pH = 8.0 has composition as follows:

Table III. Compositions of liquid waste solution after preliminary precipitate at pH 8

Number	Name of Elements	Concentration	Unit	Analysis method
1	Fe	20.76	mg/l	Jenway 6300 Spectrophotometer
2	U	4.75	mg/l	Jenway 6300 Spectrophotometer
3	Total activity α	57.86	Bq/l	MPC-2000 measure total activity α,β
4	Total activity β	575.07	Bq/l	MPC-2000 measure total activity α,β

Comments: the data from Table III revealed that heavy metal concentrations and total activity α, β after preliminary precipitate in pH 8 were still higher than Vietnamese discharge environment standards QCVN 40: 2011.

From the solution was preliminary precipitated at pH 8.0 , the nano oxide ferromagnetic material was added into liquid waste to deep treatment of uranium ore processing (The concentration of Fe_3O_4: 1 gram; Liquid waste volume: 1 liter; Adsorption temperature: room temperature; Adsorption time: 2 hours; Stirring speed: 120 rounds / minute).

Table IV. Compositions of liquid waste after Preliminary precipitate and deeply treatment by nano magnetite material

Number	Elements	Concentration	Unit	Analysis method
1	Fe	0.542	mg/l	ICP-MS
2	Al	0.66	mg/l	ICP-MS
3	Cr	0.001	mg/l	ICP-MS
4	Mn	0.009	mg/l	ICP-MS
5	Mg	0.23	mg/l	ICP-MS
6	Zn	0.025	mg/l	ICP-MS
7	As	0.006	mg/l	ICP-MS
8	U	0.014	mg/l	ICP-MS
9	Total activity α	0.097	Bq/l	MPC-2000 measure total activity α,β
10	Total activity β	0.985	Bq/l	MPC-2000 measure total activity α,β

Comments: The data from Table IV revealed that liquid waste from uranium ore processing after preliminary precipitate and deeply treatment by nano ferromagnetic material was reached discharge environment standard of QCVN 40:2011.

C. Comparing the applicability of 4 different materials for the liquid waste treatment of uranium ore processing

The research team examined the adsorptive capacity of 4 different materials and tested them with liquid waste from uranium ore processing wich was preliminary precipitated at pH 8. The results are given in the following table:

Table IV. Adsorption capacity of differently materials

Number	Materials	Type	Particular size (nm)	Specific surface area (m^2/g)	Adsorption capacity (mg/g)
1	Fe_3O_4	Vietnam	80 - 100	50 - 70	53.5
2	$NiFe_2O_4$	Vietnam	70 - 90	60 - 80	58.5
3	Fe_3O_4	Slovakia	20 - 30	100 - 110	82.2
4	$NiFe_2O_4$	Slovakia	15 - 20	110 - 120	86.5

Table V. Compare the results of treatment of 4 categories materials

Number	Materials	Type	Weight materials (g)	The total activity of α (Bq/l)	The total activity of β (Bq/l)
1	Fe_3O_4	Vietnam	1	0.097	0.985
2	$NiFe_2O_4$	Vietnam	1	0.089	0.865
3	Fe_3O_4	Slovakia	0.5	0.092	0.95
4	$NiFe_2O_4$	Slovakia	0.5	0.085	0.876

Comment: From the data shows a comparison between two kinds of Vietnam and two types of Czechs that these of Czechs have higher usability. But the main solution is the cost of this kind almost double the price of 2 Vietnamese types. So, the material Vietnamese NiFe2O4 was selected for application to handle liquid waste for uranium ore processing.

D. Proposed technology process for the application of nano oxide ferromagnetic materials to treat liquid radioactive waste from processing of uranium ores

The applicability of nano oxide ferromagnetic material for adsorption uranium from uranium solution and uranium ore processing uranium was assessed. Propose process treatment liquid waste from uranium ore processing with the application of nano oxide ferromagnetic was submited.

From an examination of the affective parameters to the adsorption of nano oxide ferromagnetic for uranium solution and test for real liquid waste of uranium ore processing. We have a proposed process using of nano oxide ferromagnetic to handle liquid waste from the of uranium ore processing.

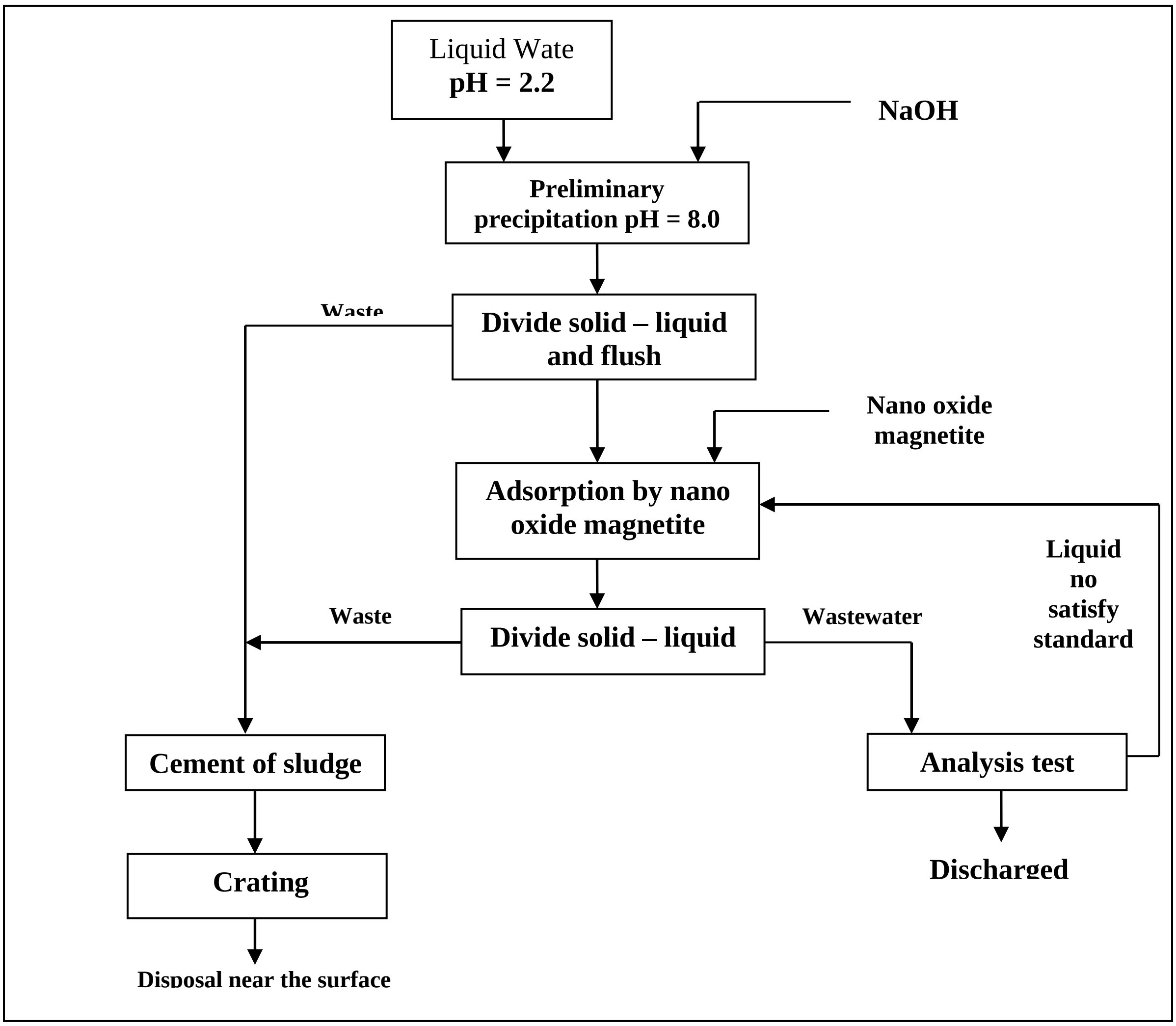

Fig.4. Technology process for treatment liquid radioactive waste generated from uranium ores processing.

CONCLUSIONS

1. The effective parameters of adsorption processing using nano oxide ferromagnetic was tested with simulated uranium solution: temperature, stirring rate, stirring time, the pH value of initial uranium concentration.

2. The radioactive elements adsorption capacity of nano oxide ferromagnetics were applied onreal liquid waste solution from uranium ore hydrometallurgical processing. After treatment, treated liquid waste reached the discharge criteria to the environmental of QCVN40:2011.

RECOMMENDATION

1. Due to the conditions and duration of the study are limited, the theme did not studied completely the adsorption of uranium from waste solution by nano oxide ferromagnetic.

2. The theme did not study elution processing regeneration nano oxide ferromagnetic after adsorption and have not survey the continuous adsorption column method.

Thus, in the next time, the theme need to research uranium adsorption with nano oxide ferromagnetic and desorption processing. The adsorption of nano oxide ferromagnetic for the radioactive nuclides and other heavy metals were expanding studied of in liquid waste.

REFERENCES

[1] Cao Hung Thai, “Introduction fuel cycle, management and disposal of radioactive waste”, Institute for Technology of Radioactive and Rare Elements, 2006.

[2] Nguyen Dinh Trieu, “Documentation of physics analytical methods and physical chemistry”.

[3] Than Van Lien, “Hydrometallurgical uranium”, Publisher of Vietnam National University, 2004.

[4] National technical Regulation on industrial wastewater, Ministry of Natural Resources and Environment of the Socialist Republic of Vietnam, QCVN 40:2011.

[5] Standard 4397:1987

[6] James D. Navratil, Archive of Oncology; 9(4):257-60 “Advances in treatment methods for uranium contaminated soil and water”, 2001.

[7] James D. Navratil, Vol. 5 (5): 697-702, "Chemistry of Iron Ferrites and Their Application for Wastewater and Acid Mine Water Treatment”, 2010.

[8] James D. Navratil and Andrew C.Akin, “Mine water treatment using magnetite and iron ferrites”, 2009.