

Removal of radioactive cesium from liquid waste by zeolite

Aamir Abdullah Mohammed^{1*}, Hayder Saleem Hussain¹, Salam Khudhair Abdullah²

1- Department of Physics, College of Science, University of Baghdad, Iraq (amir.aljebori@yahoo.com)

2- Ministry of Science and Technology, Baghdad, Iraq

Article Information

Received: 01/02/2020

Accepted: 05/04/2020

Keywords:

Cesium-137, Zeolite, Langmuir, Freundlich, Adsorption.

Abstract

A radioactive fluid waste polluted with cesium-137 from Al-Tuwaitha site -south of Baghdad-Iraq is used in this paper. Commercial zeolite is used as a sorbent material in the present work for the removal of radioactive cesium-137. The removal efficiency for radioactive liquid was 96.43 % with 2 h mixing time, 0.04 g sorbent mass and pH=6.8 and at room temperature. The Freundlich and Langmuir isotherm models were found to represent the experimental results well and these results are more consistent with Freundlich model than Langmuir model.

Introduction

Through the last years, the increase of urbanization, populations, industrialization and human activities have been increasing the environmental pollution in the world [1]. Numerous human exercises have produced unsuitable degrees of radioactive materials, for example, Cs-137 (in number beta-gamma producer) with half-life of around 30 years [2-4]. The radioactive materials are release into the earth through the release of nuclear fluid waste, nuclear weapon testing and nuclear mishaps, for example, in Fukushima, which defiled soil, water and air. [5-7].

There are a few techniques utilized to treat radioactive wastewater, for example, "flocculation, ion exchange, evaporation, and adsorption" [8,9]. Adsorption has obtained increasing attention because of its advantages in wastewater treatment [10]. Adsorption can bring down the utilization of organic solvents in order to make the activity procedure easier and more secure. Tremendously utilized adsorption materials incorporate "zeolite, vermiculite, and crystalline silicotitanate" [11-13]. Adsorption is fiercely utilized and considered a most dominant technique as indicated by the minimal effort, simple system, effective, and plenitude [14]. Zeolites are consider of the most remarkable ion exchange means and available naturally [15,16].

Zeolites are tetrahydrate aluminosilicate system with exceptionally open three-dimensional structures. Zeolites are chiefly included of $[\text{SiO}_4]^{-4}$ and $[\text{AlO}_4]^{-5}$ [15], have pores of uniform size $(3-13) \times 10^{-10}$ m [17]. Cavities and channels are found inside Zeolite structures; they structure about half of the all out volume permit cations, for example, such as $(\text{Na}^+, \text{K}^+,$

Ca²⁺ and Mg²⁺) and water particles to be held inside zeolites structure. These cations have a high level of ability to move and capacity to exchange with different cations. Besides, the inner structure of the zeolite allows for uniform arranged pores. These structural properties make it a valuable adsorbent for metallic particles and water fume [16,18].

Materials and Methods

Zeolite has been used in this work as a sorbent material to removal cesium-137. The microstructure of the materials was studies utilization "scanning electron microscope" supplemented with EDX Unit. Many factors affecting removing efficiency such as time, weight of zeolite, pH and initial concentration were studied in separated experiments at room temperature. A qualitative analysis of radionuclides was done in gamma spectrometry analysis using high-purity germanium detector (HPGe) with 65 % relative efficiency and 1.95 keV energy resolutions at 1.33 MeV of Co-60 isotope.

The batch method was utilized to study the sorption of ¹³⁷Cs ions on zeolite sorbent. Five samples with different activity concentrations were used to study sorption isotherm. Two adsorption isotherm models used frequently are the Langmuir and Freundlich [19].

The linear Langmuir Eq. is [20, 21]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (1)$$

where, q_e is the measure of material adsorbed at balance; C_e is the concentration at balance; q_m & b are Langmuir constants.

The Freundlich Eq. is [22]:

$$\log(q_e) = \left(\frac{1}{n}\right) \log(C_e) + \log(K_f) \quad (2)$$

where; (K_f, n) are Freundlich constants.

The percentage adsorption is calculated as follows [23, 24]:

$$Removal\ Eff. = \frac{C_o}{C_o - C_e} \times 100\ \% \quad (3)$$

where C_o is the initial concentration.

Results and discussion

The figure 1 shows the SEM micrograph of the commercial zeolite sample. The particles size seems to be less than 5 μ m. Table 1 shows elements analysis of commercial zeolite sample based on the EDX spectrum as shown in figure 2, where the Si/Al ratio was 0.985(\approx 1).

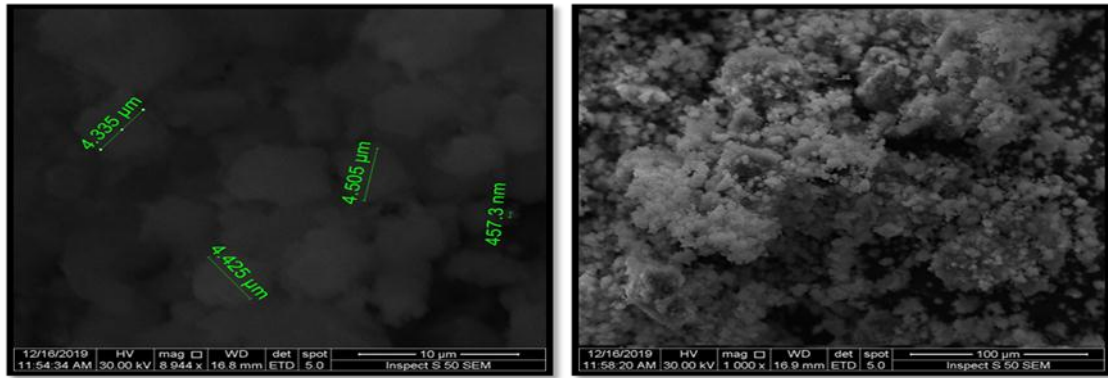


Fig. 1: SEM micro image of commercial zeolite samples.

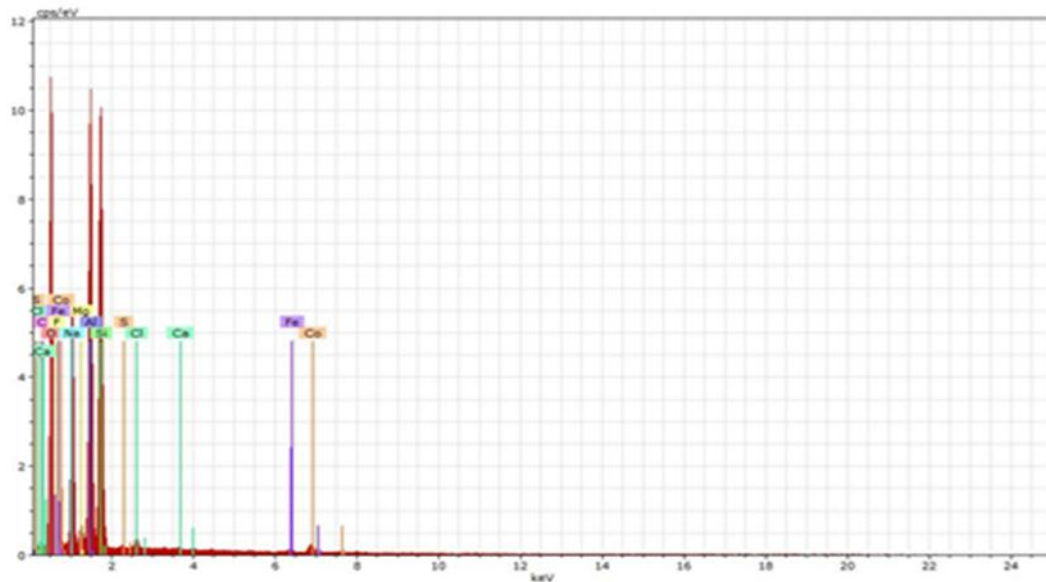


Fig. 2: EDX spectrum of commercial zeolite samples.

Table 1: Elements analysis of zeolite sample based on the EDX spectrum.

Element	Weight (%)
O	52.03
Na	14.68
Al	13.11
Si	12.91
C	4.21
Mg	1.32
Co	0.70
Cl	0.36
F	0.32
Fe	0.19
S	0.09
Ca	0.07
Total	100

Effect of Parameters on Adsorption Process: Factors affecting on the removal efficiency of radioactive ^{137}Cs from the fluid waste such as (mixing time, weight of zeolite, pH, and activity concentration) is shown below.

Time: The impact of mixing time on the removal efficiency of the cesium-137 isotope in liquid waste has been studied, where five time values were chosen (0.5, 1, 2, 2.5 and 3) h with a constant zeolite weight and pH= 6.8. Figure 3 explains the impact of mixing time on the activity, where the activity decrease with increasing mixing time and the balance time was 2 hours. Figure below also shows that the radioactivity of radioactive cesium in the solution decreases dramatically during the first half hour of mixing time with zeolites, due to the fact that adsorption occurs at the beginning and the ion exchange occurs between the ions existing in the fluid and the adsorbent substance where the ions transported from the solution occupy most of the cavities on the surface of the adsorbent material, therefore, with increasing time, the decrease in the value of radioactivity is small and almost stabilizes at a time of two hours or so-called equilibrium time.

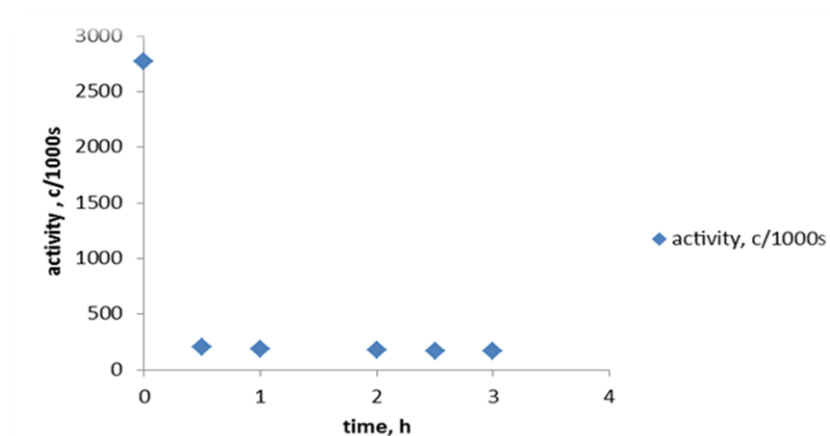


Fig. 3: Impact of mixing time on the activity.

Weight: Five values of zeolite weight were chosen (0.005, 0.01, 0.02, 0.03, 0.04) g, with a constant mixing time (2 h) and pH=6.8. Figure 4 explains the impact of the weight of the zeolite as an adsorbent material on the removal efficiency, as it is clear that the removal efficiency was good for the weights (0.01, 0.02, 0.03 and 0.04) g and that the highest removal efficiency was at the weight 0.04 g of the adsorbent material.

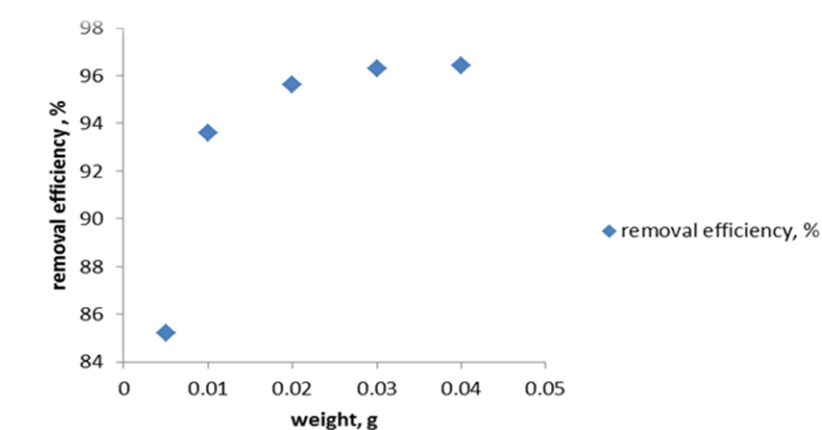


Fig. 4: Impact of weight on the removal efficiency.

pH: The impact of pH of liquid waste on the removal efficiency has been studied, where five values of pH were chosen (2, 4, 6.8, 8, and 10) with weight (0.04 g) and contact time (2 h). Figure 5 shows increasing the removal efficiency with increasing pH until pH=6.8, then it decreases by increasing the pH. At low pH amount, abundance H^+ existing in fluid contends with the studied element ions for active locations which causes less element ions removal and negative surface hydroxyl groups begins to take place. Subsequently, the surface has a low net negative charge (at neutral or near-neutral pH values) because of the increase in positively charged surfaces. On the other hand, as the fluid pH increases, the number of negatively charged locations increases this favors the sorption of element cations and their hydroxides, forming surface metal complexes. The best removal efficiency was at pH=6.8.

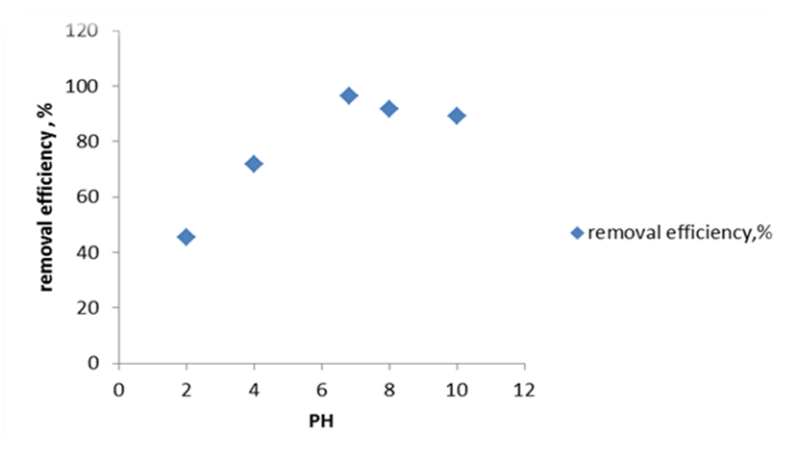


Fig. 5: Impact of pH on the removal efficiency.

Activity concentration: The plot of removal efficiency versus initial activity concentration with (time 2 h, pH= 6.8 and weight 0.04 g) is explain in figure 6. The removal efficiency increases with the increase in the initial concentration and then gradually stabilizes with the increase in concentration.

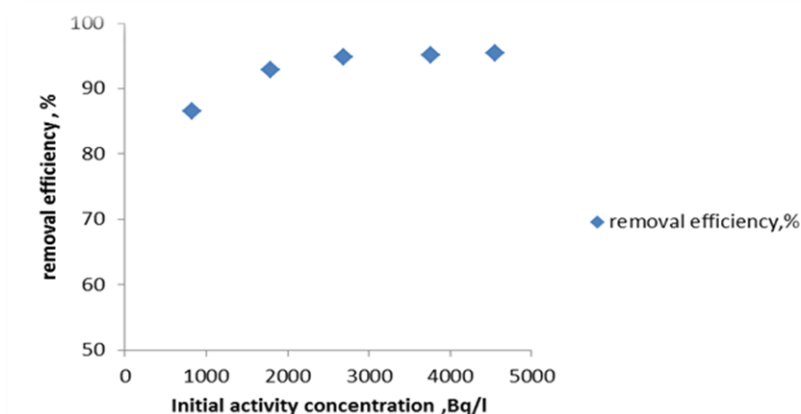


Fig. 6: Impact of initial activity concentration on the removal efficiency.

Equilibrium isotherms:

The most widely recognized balance isotherm models utilized in adsorption tests are Langmuir and Freundlich adsorption models as shown in figures 7 and 8.

The figure 7 shows the linear relationship of the isotherm Langmuir model, which includes the rapport between the balance concentration and the measure of adsorbed material at balance.

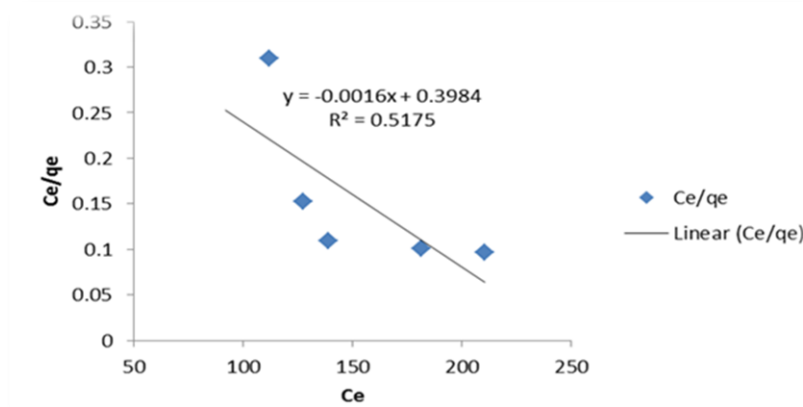


Fig. 7: Langmuir plot of C_e/q_e vs. C_e for the adsorption of cesium onto zeolite.

The figure 8 shows the linear relationship of the isotherm Freundlich model, which includes the rapport between the balance concentration and the measure of adsorbed material at equilibrium ($\log q_e$ vs. $\log C_e$).

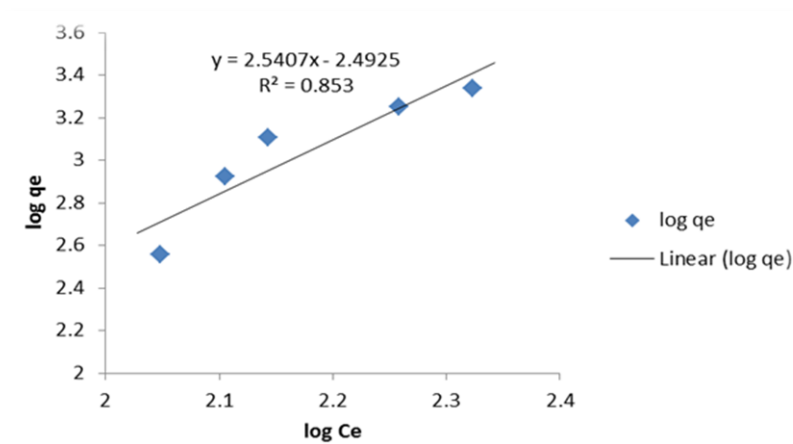


Fig. 8: Freundlich plot for the adsorption of cesium onto zeolite.

The constants of each model and their correlation coefficients are explained in Table (2). The values of linear correlation coefficients (R^2) were (0.5175 and 0.853) for Langmuir and Freundlich isotherm models respectively.

Table 2: Equilibrium isotherm model constants and correlation coefficients.

Isotherm model	Isotherm model constant				Linear correlation coefficient (R^2)
	q_m	b	n	K_f	
Langmuir	-625	-0.004016			0.5175
Freundlich			0.393592	0.082703	0.853

Conclusion

According to the results obtained in the adsorption process study of Cs-137 on commercial zeolite, we can conclude that:

1. The zeolite used in this study was found to be an effective and low-cost adsorbent for the adsorption of Cs-137 ions from fluids.
2. The pH of fluid, mixing time, zeolite weight, and initial activity concentration have an effect on the removal efficiency.
3. Optimum conditions were found at pH 6.8, time 2h and weight 0.04 g.
4. The removal efficiency is directly proportional to the initial concentration.
5. Freundlich model has better correlation coefficient than Langmuir model. This shows that the rapport between the concentration of balance and the measure of adsorbed material is weak according to the Langmuir model while it is strong according to the Freundlich model. This means that the Freundlich equilibrium isotherm represents the practical results well.

References

1. Rasmeey, A. H., Aboseidah, A. A., & Youssef, A. K. (2018). Application of Langmuir and Freundlich Isotherm Models on Biosorption of Pb²⁺ by Freez-dried Biomass of *Pseudomonas aeruginosa*. *Egyptian Journal of Microbiology*, 53(1), 37-48.
2. Tiwari, D., Prasad, S. K., Yang, J. K., Choi, B. J., & Lee, S. M. (2006). Inorganic and bio-materials in the removal/speciation of radiocesium and radiostrontium: an overview. *Environmental Engineering Research*, 11(2), 106-125.
3. Hui, K. S., Chao, C. Y. H., & Kot, S. C. (2005). Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. *Journal of Hazardous Materials*, 127(1-3), 89-101.
4. International Atomic Energy Agency, (2011). Final report of the international mission on remediation of large contaminated areas off-site the Fukushima Dai-ichi, NPP. Japan.
5. Zheng, J., Aono, T., Uchida, S., Zhang, J., & Honda, M. C. (2012). Distribution of Pu isotopes in marine sediments in the Pacific 30 km off Fukushima after the Fukushima Daiichi nuclear power plant accident. *Geochemical Journal*, 46(4), 361-369.
6. Honda, M. C., Aono, T., Aoyama, M., Hamajima, Y., Kawakami, H., Kitamura, M., ... & Saino, T. (2012). Dispersion of artificial caesium-134 and-137 in the western North Pacific one month after the Fukushima accident. *Geochemical Journal*, 46(1), e1-e9.
7. Nakamaru, Y., Ishikawa, N., Tagami, K., & Uchida, S. (2007). Role of soil organic matter in the mobility of radiocesium in agricultural soils common in Japan. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 306(1-3), 111-117.
8. Rahman, R. O., Ibrahim, H. A., & Hung, Y. T. (2011). Liquid radioactive wastes treatment: a review. *Water*, 3(2), 551-565.
9. Radhi, F. M. (2017). Development of treatment process for radioactive - contaminated soil. PhD thesis, college of science, university of Baghdad.
10. Ali, I. and Gupta, V.K. (2006). Advances in water treatment by adsorption technology. *Nature protocol*, 1 (6), 2661-2667.
11. Mysore, D., Viraraghavan, T., & Jin, Y. C. (2005). Treatment of oily waters using vermiculite. *Water Research*, 39(12), 2643-2653.

12. Miller, J. E., & Brown, N. E. (1997). *Development and properties of crystalline silicotitanate (CST) ion exchangers for radioactive waste applications* (No. SAND-97-0771). Sandia National Labs., Albuquerque, NM (United States).
13. Johnson, C. D., & Worrall, F. (2007). Novel granular materials with microcrystalline active surfaces—Waste water treatment applications of zeolite/vermiculite composites. *Water research*, 41(10), 2229-2235.
14. Streat, M., Patrick, J. and Perez M. (1995). Sorption of phenol and parachlorophenol from water using conventional and novel activated carbons. *Water research*, 29 (2), 467-472.
15. Xu, R., Pang, W., Yu, J., Huo, Q., & Chen, J. (2009). *Chemistry of zeolites and related porous materials: synthesis and structure*. John Wiley & Sons.
16. Allen, ER, and Ming, D.W. (1995). Recent progress in the use of natural zeolites in agronomy and horticulture. International committee on natural zeolites, Brockport, New York, USA, 477-490.
17. Gao, N., Kume, S. and Watari, K. (2005). Zeolite-carbon composites prepared from industrial wastes :(I) Effects of processing parameters. *Materials science and engineering: A*, 399 (1), 216-221.
18. Dyer, A. (1988). An introduction to zeolite molecular sieves.
19. Khayyun, T. S., & Mseer, A. H. (2019). Comparison of the experimental results with the Langmuir and Freundlich models for copper removal on limestone adsorbent. *Applied Water Science*, 9(8), 170.
20. Ho, Y. S. (2003). Removal of copper ions from aqueous solution by tree fern. *Water research*, 37(10), 2323-2330.
21. Kumar, K. V. Subanandam, K., Ramamurthi, V. and Sivanesan S. (2005). Solid liquid adsorption for wastewater treatment: principle design and operation. College of technology, Anna university, Chennai-India, 41 (5), 1198-1202.
22. Ho, Y. S., Porter, J. F., & McKay, G. (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water, air, and soil pollution*, 141(1-4), 1-33.
23. Mohammad, S.J. (2017). Preparation of Fe: Mn binary oxides nanostructures for water treatment. PhD thesis, College of Science -University of Baghdad.
24. Jorfi, S., Ahmadi, M.J., Pourfadakari, S., Jaafarzadeh, N., Soltani, R.D.C. and Akbari, H. (2017). Adsorption of Cr (VI) by natural clinoptilolite zeolite from aqueous solutions: isotherms and kinetics. *Polish journal of chemical technology*, 19 (3), 106-114.

إزالة السيزيوم المشع من النفايات السائلة بواسطة الزيولايت

عامر عبدالله محمد*1، حيدر سليم حسين1، سلام خضير عبدالله2

1- قسم الفيزياء، كلية العلوم، جامعة بغداد، العراق (amir.aljebori.yahoo.com)

2- وزارة العلوم والتكنولوجيا، بغداد، العراق

البحث مستل من أطروحة دكتوراه الباحث الأول

معلومات البحث:	الخلاصة:
تاريخ الاستلام: 2020/02/01 تاريخ القبول: 2020/04/05	استخدمت في هذا البحث النفايات المشعة السائلة الملوثة بالسيزيوم -137 والموجودة في موقع التويثة الذي يقع جنوب بغداد. استخدم الزيولايت التجاري كونه مادة مازة لازالة السيزيوم المشع حيث كانت النسبة المئوية لكفاءة الازالة 96,43 % عند زمن خلط مقداره 2 ساعة، ووزن 0,04 غرام للمادة المازة والاس الهيدروجيني pH=6.8 وفي درجة حرارة الغرفة. تم استخدام نموذجي لانكماير وفريندلش لدراسة ايزوثيرمات الامتزاز حيث وجد ان نموذج فريندلش يمثل النتائج بشكل جيد.
الكلمات المفتاحية:	
سيزيوم-137، زيولايت، لانكماير، فريندلش، امتزاز	