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Sorption Behavior of Molybdenum (IV) Onto Commercial Acidic Alumina Surface

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ABSTRACT

The study investigated the adsorption behavior of molybdate on acidic alumina at different pH values, contact times, initial molybdenum concentrations, and reaction temperatures. The batch capacity of the commercial acidic alumina was determined by batch method at 25 °C from 0.005 M sodium molybdate solution and was found to be 45 mg /g. The sorption data was fitted to the Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) sorption isotherms, and the mean sorption energy was found to be 9.243 kJ/mol. For the kinetic analysis, the Lagergren equation was applied, and the pseudo-second-order kinetic model offered excellent data fitting for molybdenum uptake. The standard enthalpy was found to be -6.2 kJ/mol after calculating the thermodynamic constants. The calculated ΔG° were -12.42, -12.635, and -13.126 kJ mol⁻¹ at all experimental temperatures. While the standard entropy was found to be 20.67 J mol⁻¹. The results show that the sorption process is exothermic and spontaneous, with a higher degree of ion freedom.

INTRODUCTION

^{99m}Tc is the most often used medical isotope of all radioisotopes, with a wide range of uses, including cancer and cardiology. It is molybdenum's "daughter" isotope, Mo-99, which is used in 80–85% of the roughly 30 million nuclear medicine diagnostic procedures performed annually [1]. Brookhaven National Laboratory created the first ⁹⁹Mo/^{99m}Tc generator in 1958. Most ⁹⁹Mo/^{99m}Tc generators use column chromatography to chemically separate the parent and daughter isotopes [2].

The parent radioisotope (⁹⁹Mo) can be obtained by irradiating metallic molybdenum or molybdenum oxide (MoO₃) with neutrons, or by irradiating ²³⁵U with thermal or fast neutrons. In the first case, ⁹⁹Mo is created together with other fission products, which requires separation via various processes. In the second case, just a minor amount of ⁹⁸Mo is converted to ⁹⁹Mo [3-5]. As a result, the radioactivity of ^{99m}Tc eluted from ⁹⁹Mo generated by molybdenum irradiation is limited in generator columns. ⁹⁹Mo/^{99m}Tc generators are formed by adsorbing ⁹⁹MoO₄²⁻ ions onto chromatographic alumina columns, requiring high-activity molybdenum-99 radioisotope from ²³⁵U fission [6]. As it decays, the pertechnetate, TcO₄⁻, is less strongly bonded to alumina

and can be eluted with a saline solution (0.9% NaCl)[7]. Goldberg et al. (2008) investigated molybdenum adsorption by aluminum oxide, finding maximum adsorption at low pH and decreasing rapidly above pH 5. The Mo (IV) adsorption mechanism of alumina is a ligand exchange with hydroxyl ions [1, 2, 8, 9, 10]. The ligand exchange mechanism allows ions to be specifically adsorbed by creating complexes on the inner surfaces of spheres[7]. These complexes lack water molecules and shift the point of zero charge (PZC) of minerals to an acidic pH value[11-15]. Molybdenum adsorption reduces alumina's PZC, favoring specific adsorption. Studying ionic strength's effects on anion adsorption helps distinguish between inner and outer surface complexes. Between the oxide adsorbent and the surface functional group, the external spherical surface complexes contain at least one water molecule [16].

This study investigates the kinetic and thermodynamic characteristics of ⁹⁹Mo radioisotope sorption from aqueous solution on commercial acidic alumina, focusing on molybdate adsorption mechanisms, to aid in the production of technetium-99m generators, considering initial concentration, reaction temperature, and pH values.

EXPERIMENTAL

All chemicals were acquired from E. Merck (Germany), and the majority were of the GR/AR grade. The particle size of Al_2O_3 was 0.063-0.200 mm (90 active acidic I for column chromatography 70-230 mesh ASTM). Sodium molybdate, $\text{Na}_2^{99}\text{MoO}_4$, with high specific activity in aqueous solution, was produced as a fission product at the Radioisotopes Production Facility (RPF) of the Atomic Energy Authority in Cairo, Egypt. Aqueous ^{99}Mo with low specific activity was prepared by coupling high specific radioactivity ^{99}Mo with natural Na_2MoO_4 solution. The Al_2O_3 resin was first pretreated by soaking it in water for 24 hours. The resin was rinsed with water before being activated with a 2 mole/L HCL acid solution and then rinsed with distilled water to neutralize and remove fine particles. Finally, the resin was dried to constant mass in a drying oven at 50°C . ^{99}Mo (VI) radioisotope absorption was measured as a function of concentration by contacting 10 mL of a Mo-99 radioisotope solution with 100 mg of sorbent for 24 hours at 25°C in a thermostatic shaker bath. Aqueous solutions containing 1×10^{-4} to 5×10^{-2} M Mo as Na_2MoO_4 were utilized. After equilibration, the solution was removed and filtered with a syringe equipped with a 0.22 μm pore-size PVDF membrane filter (Millipore). Blank tests indicated that the filter does not absorb Mo-99.

The amount of ^{99}Mo radioactivity left in the aqueous solution was determined using a germanium detector. Mo-99 was identified by measuring its 739 Kev-ray. Each sample's Mo-99 radioactivity was adjusted for decay. The amount of radionuclide uptake was stated in terms of a distribution coefficient, K_d , which was defined as follows:

$$K_d = \left(\frac{A_o - A_s}{W} \right) / \left(\frac{A_s}{V} \right) \quad \text{ml/g} \quad (1)$$

Where:

A_o and A_s indicate the aqueous phase activity (mCi) before and after equilibration, respectively; W is the sorbent's dry weight (g); and V represents the aqueous phase volume (mL).

Equation (2) was used to estimate the amount of molybdenum ions adsorbed per 1 g of Al_2O_3 (mg/g):

$$q_o = \frac{C_o - C_e}{m} \times V \quad (2)$$

where C_o and C_e initial and equilibrium concentration of Mo(VI) ions, mg/mL, respectively; V volume of the solution, mL; m the mass of the adsorbent, g.

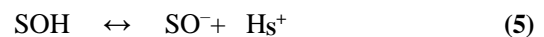
The degree of the adsorbed Mo(VI), (Mo) (%), from solutions for different pH was calculated by Equation (3):

$$\text{Adsorbed (Mo) \%} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

RESULTS AND DISCUSSIONS

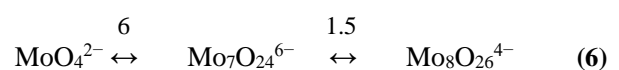
3.1. The influence of HCl acid concentration

According to the surface complex formation model (SCF) [17], cations and anions are adsorbed in solution at different pH values. This model suggests that the surface functional groups of hydrous oxide can be represented as a single weak diprotic acid by the following surface reactions.



Where H^+ denotes the proton activity at the solid surface and the symbol (SO^-) denotes the active surface site. Hence, raising the pH value of the solution causes protons to be released from the surface, exposing more negative sites (SO^-) that can bind more cations. By contrast, lowering the pH exposed more positively charged sites for the binding of additional anions by protonating the acid alumina on the surface. The effect of acid concentration on the adsorption of ^{99}Mo (VI) radioisotope onto acid alumina was studied at varying HCl acid concentrations ranging from 1×10^{-5} to 5×10^{-1} mole/liter while the initial concentrations remained constant at 1×10^{-4} mole/liter, and the results are shown in Figure 1 in terms of uptake percent against acid concentration.

As shown in Figure 1, the effect of pH on ^{99}Mo (VI) radioisotope sorption on alumina was difficult to determine. The sorption effectiveness of Mo (VI) improves with lowering pH value until it reaches a maximum of 2.5, then falls with rising HCl acid concentration up to 0.5 M. The varied forms of molybdenum species and the different surface structures of alumina at different pH values are thought to be the cause. In an acidic media, acid activates alumina, increasing the sorption efficiency of anion molybdenum species. The maximum sorption uptake occurred in acidic conditions with pH values 2.5-3.0. According to the following equilibrium, this might be attributed to the formation of polyanionic species with greater molybdenum content per unit charge, such as $\text{Mo}_7\text{O}_{24}^{6-}$ or $\text{Mo}_8\text{O}_{26}^{4-}$ [15]:



Furthermore, at higher pH levels, OH^- will compete as an anion with molybdate adsorption onto the surface of acid alumina.

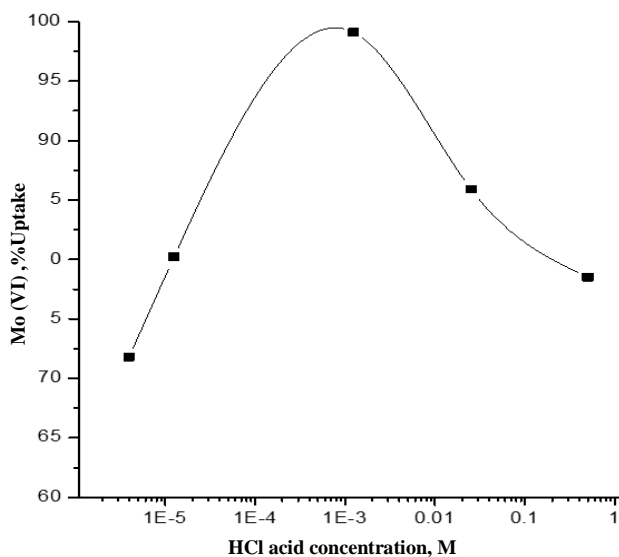


Fig. (1): Uptake of 1×10^{-4} M Mo(VI) onto acid alumina as a function of acid concentration at 25 °C

3.2. The influence of Mo (VI) concentration

Figure 2 illustrates the effect of initial molybdate, (MoO_4^{2-}), concentration on the percentage of molybdenum-99 radioisotope ions that adsorb onto acidic alumina surface in 0.031 M HCl (pH 2.5). As shown in Figure 2, the molybdenum absorption uptake reduces modestly with increasing concentration up to 0.005 M, then drastically drops up to 0.5 M. The saturation of the exchange sites caused the absorption to be independent of MoO_4^{2-} concentration at beginning concentrations above 0.01 M. Based on the above data, The batch capacity of the commercial acidic alumina for Mo(VI) was determined by batch method at 25 °C from 0.005 M sodium molybdate in HCl acid solution (pH2-3) and was found to be 45 mg /g.

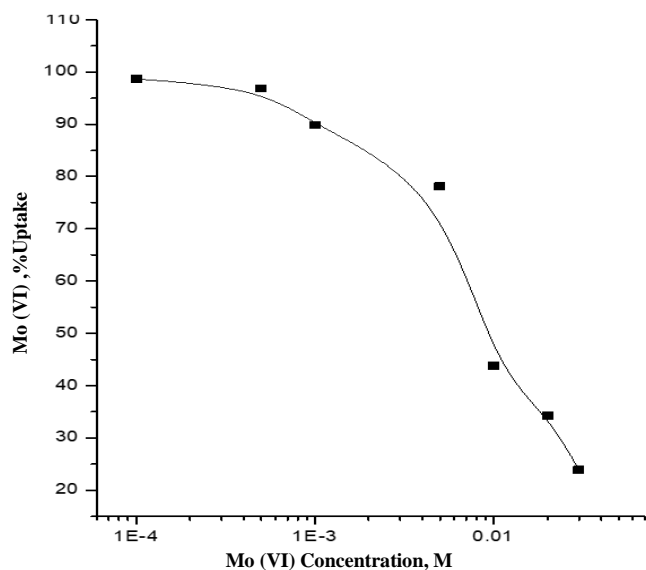


Fig. (2): Variation of the uptake present of Mo (VI) onto alumina as a function of Mo (VI) concentration from HCL acidulation at 25+1 °C

3.3. The Influence of Contact Time

Figure 3 demonstrates the influence of contact time on ^{99}Mo (VI) radioisotope sorption on alumina. It is observed that the adsorption of ^{99}Mo (VI) radioisotope rises as the shaking time increases up to 120 minutes. At 25 °C, the maximum sorption efficiency was 80.5%. After 120 minutes of shaking at 25 °C, a saturation plateau was established. As a result, 120 minutes was selected as the optimum shaking time for all subsequent studies.

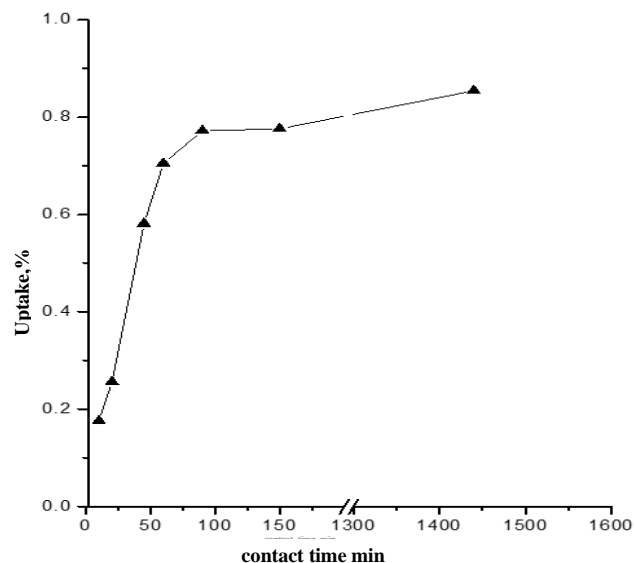


Fig (3): Effect contact time on 5×10^{-3} M Mo(VI) sorption onto acid alumina surface from HCl acid solution (pH2) and 25+1 °C

3.4. Models of sorption isotherms

At a constant temperature of 25 °C, the Langmuir, Freundlich, and D-R isotherm models are employed to illustrate the specific connection between the equilibrium concentration of ^{99}Mo (VI) radioisotope and its sorption degree on the surface of acidic alumina.

3.4.1. The Langmuir model

Adsorbing species form a single monolayer and occupy only free adsorption sites, all adsorption sites are equal, adsorbing species do not interact with one another, and the adsorption process is the same for all species, according to the Langmuir model.[2, 18, 19]. Adsorption occurs at particular homogenous areas on the adsorbent and is employed efficiently in several monolayer adsorption methods. This is the linear form of the Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K} + \frac{C_e}{Q_o} \quad (7)$$

Where: q_e is the equilibrium amount of adsorbate adsorbed (mg) per unit mass of adsorbent (g), C_e is the concentration of adsorbate in equilibrium solution (mg/L), and q_0 (mg/g) and k (L/mg) is the adsorbent's maximum sorption capacity and the sorption energy coefficient, respectively.

As the Mo (IV) concentration increased, the absorption of Mo (IV) was investigated in a batch manner, as shown in Figure 4. The linear plot's correlation coefficient ($R_2 = 0.986$) is rather excellent. The maximum sorption capacity (q_0) and sorption energy coefficient (k) of alumina at 25 °C were calculated to be 69.93 mg/g and 1.1721 L/mg, respectively, based on the slope and intercept of the linear plot.

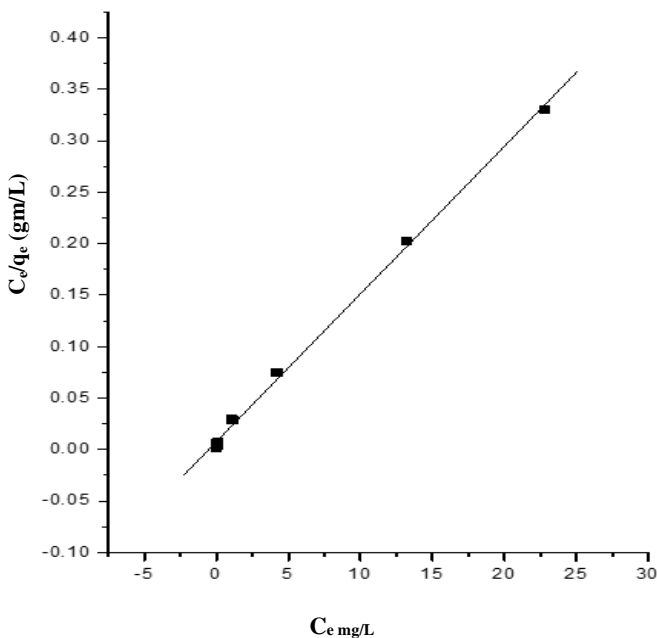


Fig. (4): Linear plot of langmuir isotherm of Mo (VI) ions sorption onto alumina from HCL acid at 25°C

The main features of the Langmuir isotherm may be expressed in terms of the dimension less constant separation factor R_L :

$$R_L = \frac{I}{1 + kC_0} \quad (8)$$

Where C_0 (mg/L) is the initial adsorbate concentration and k is the Langmuir constant (L/mg). The R_L value has four probabilities: $0 < R_L < 1$ for favorable sorption; $R_L > 1$ for unfavorable sorption; $R_L = 1$ for linear sorption; and $R_L = 0$ for irreversible sorption [20-22]. The fluctuation of the separation factor (R_L) with initial Mo concentration is seen in figure 5. The fact that the R_L values were in the 0-1 range indicates that Mo sorption on acid alumina is favorable.

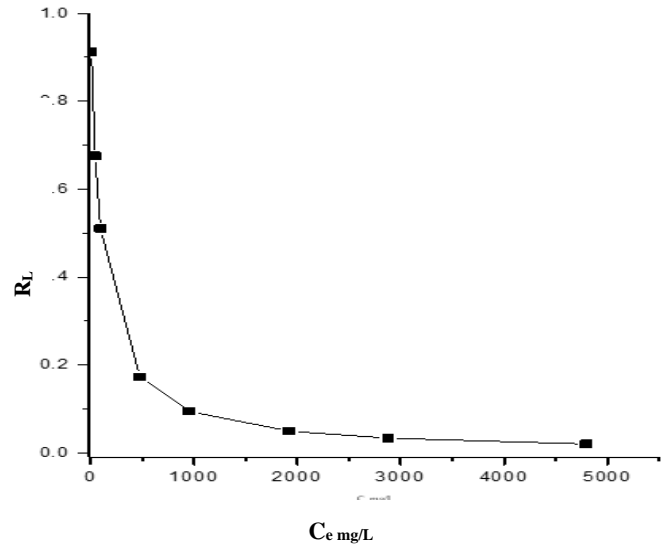


Fig. (5): Variation of separation factor (R_L) as function of initial Mo (VI) concentration

3.4.2 Freundlich model

Sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model is represented in linear form as follows:

$$\log q_e = \log K_f + 1/n \log C_e \quad (9)$$

Where $1/n$ is the heterogeneity factor, a constant associated with surface heterogeneity or sorption intensity, and K_f is the Freundlich constant (mg/g), which quantifies the sorption capacity of the adsorbent. The linear plot of the Freundlich isotherm of Mo (VI) radioisotope sorption on acidic alumina is shown in Figure 6. The correlation coefficient value of the Freundlich model ($R_2 = 0.9957$) is greater than that of the linear plot of the Langmuir isotherm was determined to be less suitable. Positive sorption conditions are indicated by a value of $1/n$ less than [18, 19, 20, 24].

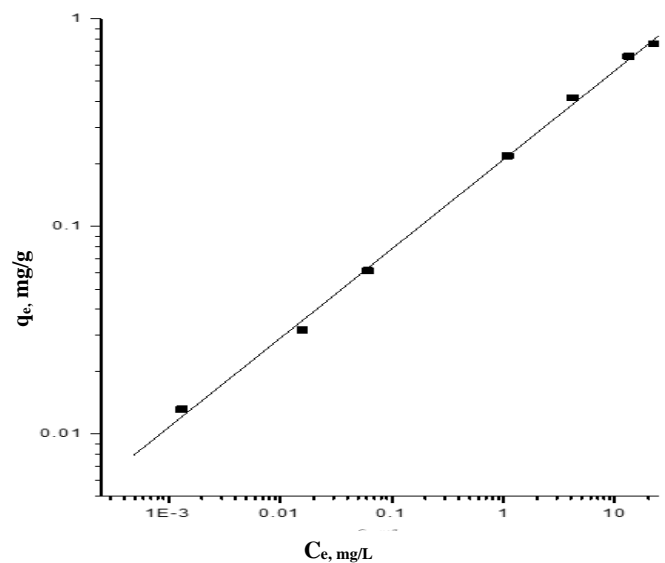


Fig. (6): Log-log plot of Freundlich is isotherm of Mo(Vi) ions sorption alumina from HCL acid solution 25°C

3.4.3 D-R model

Additionally, the D-R model [20, 23, 25, 26] was given the equilibrium data to ascertain the kind of sorption (chemical or physical). The following equation represents the D-R isotherm in its linear form:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (10)$$

Where β is the sorption energy constant (mol^2/J^2), which is proportional to the average energy of sorption per mole of the sorbate as it is transported to the solid's surface from an infinite distance in the solution [20, 25]. Where q_e is the quantity of Mo adsorbed onto per unit dose of acid alumina (mole/g), q_m is the theoretical monolayer sorption capacity (mole/g), and ε is the Polanyi potential, which is characterized as:

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (11)$$

Where T is the temperature of the solution (K) and R is the gas constant, which equals 8.314 J/mol K. The D-R parameter can be used to calculate the mean sorption energy, E (kJ/mole), as shown below.

$$E = 1 / \sqrt{-2\beta} \quad (12)$$

Chemical and physical sorption are explained by the mean sorption energy value. The E values of chemical and physical sorption are 8–16 kJ/mole and 1–8 kJ/mole, respectively [20, 23, and 25]. Mo sorption on acid alumina involves chemisorption, as evidenced by the E value (9.152 kJ/mole), which was determined to be in the 8–16 kJ/mole range (Figure 7).

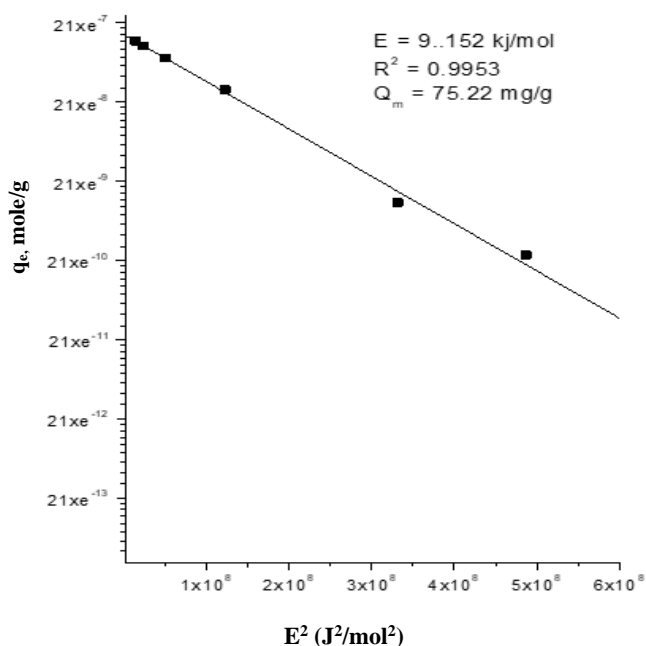


Fig. (7): D-R isotherm plot of Mo (VI) ions sorption on alumina

Table (1): isotherm model constants for sorption of Mo (VI) from aqueous solutions onto acid alumina at $25 \pm 1^\circ\text{C}$.

Langmuir isotherm			Freundlich isotherm		
K_L (Lmg^{-1})	q_{\max} (mg/g)	R^2	K_F (mg/g)	$1/n$	R^2
1.1808	69.93	0.986	0.667	0.434	0.994

Sorption kinetics were examined using Lagergren's pseudo-first-order, pseudo-second-order, and diffusion models. Lagergren's equation for first-order kinetics is written as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

Where q_t represents the amount of adsorbate adsorbed (mg/g) at time t and k_1 represents the rate constant (min^{-1}). Figure 8 shows pseudo-first-order kinetics displayed at 25°C .

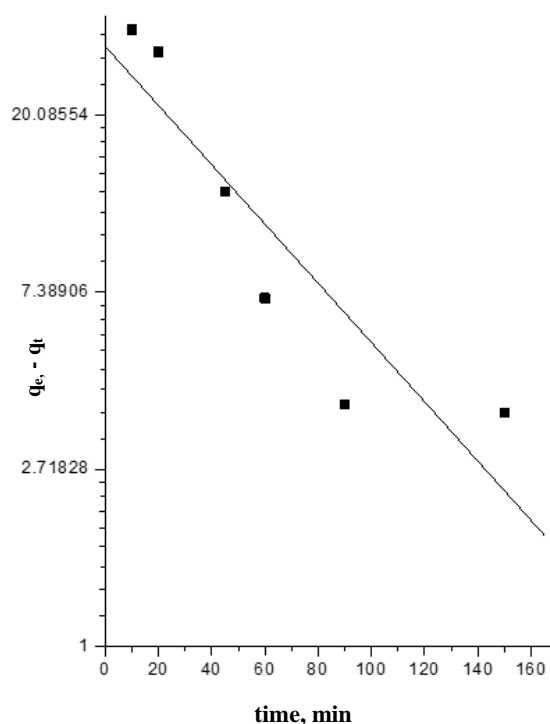


Fig. (8): Pseudo-first order kinetic plot for Mo(VI) sorption onto alumina from HCl acid solution (pH1.5) at $25 \pm 1^\circ\text{C}$

Pseudo second-order model is represented as [27]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} t \right) \quad (14)$$

k_2 denotes the rate constant (g/mg min). Figure 9 shows a pseudo-second-order kinetic plotted at 25°C .

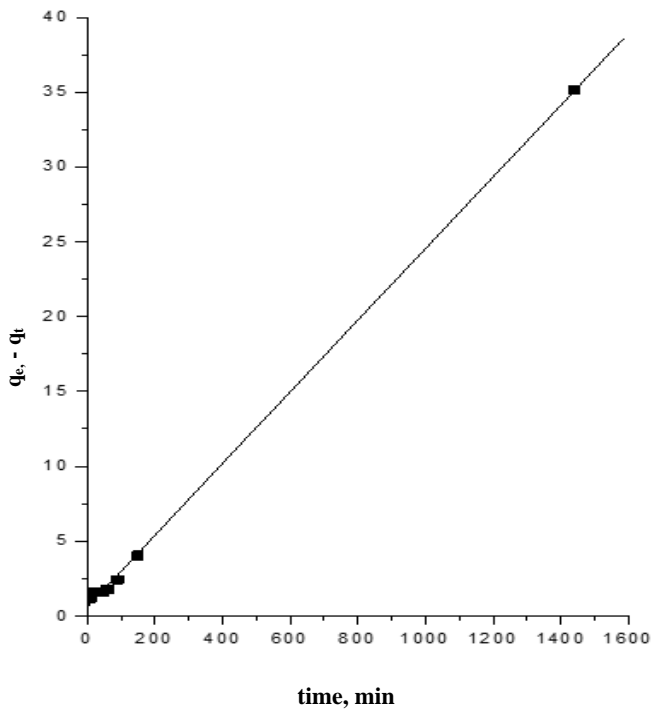


Fig. (9): Pseudo-Second order kinetic plot for Mo(VI) sorption onto alumina from HCl acid solution (pH1.5) at 25±1°C

Table (2). Comparison of sorption rate constants, estimated q_e , and correlation coefficients for pseudo-first-order and pseudo-second-order rate equations.

pseudo-first-order			pseudo-second-order		
k_1 (min ⁻¹)	R ²	q_e (mg/g)	k_2 (g.mg ⁻¹ .min ⁻¹)	R ²	q_e (mg/g)
- 0167	0.8237	1.2207	0.0084168	0.9993	41.45

3.6. Thermodynamic parameters

Thermodynamic parameters are critical criteria for determining the efficiency of molybdenum ion uptake at different temperatures, clarifying thermodynamic feasibility, and confirming the nature of the sorption process. To investigate the effect of temperature on the ability of acid alumina to sorb ⁹⁹Mo radionuclides from their aqueous media, experiments were carried out at varied temperatures of 298, 313, and 333 °K. The results demonstrate that the absorption percent of ⁹⁹Mo increases with increasing system temperature, and that temperature elevation improves ⁹⁹Mo radionuclide sorption efficiency, implying that the examined sorption processes were endothermic. Furthermore, the increase in sorption efficiency with increasing temperature can be explained using the Van't Hoff equation [28] based on thermodynamic factors such as enthalpy change (ΔH°), entropy change (ΔS°), and Gibbs free energy (ΔG°):

$$K_c = \frac{q_e}{c_e} \quad (15)$$

$$\ln K_c = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{RT} \right) \quad (16)$$

$$\Delta G^\circ = -RT \ln K_c \quad (17)$$

Where:

T is the absolute temperature in degrees Kelvin; ΔS° is the entropy change (J.mol⁻¹.K⁻¹); ΔH° is the enthalpy change (J.mol⁻¹); and ΔG° is the Gibbs free energy change (J.mol⁻¹).

The slope and intercept of the linear plot of $\ln K_c$ vs $1/T$, illustrated in Figure 10, were used to calculate the values of ΔH° and ΔS° . The shift in standard free energy ΔG° with negative values for -12.42, -12.63, and -13.126 kJ/mole at 25, 40, and 60 °C implies that radioactive molybdenum sorption by acidic alumina is spontaneous. The change in the standard enthalpy, ΔH° , is -6.24 kJ/mol. The negative ΔH° shows that radioactive molybdenum sorption by acidic alumina is exothermic. The intercept of Figure 10 was also used to get the value of ΔS° . The value of ΔS° was found to be 20.67 J. / K. mol, and a positive value indicates that sorption increases the degree of freedom of ions and also indicates the stability of surface sorption.

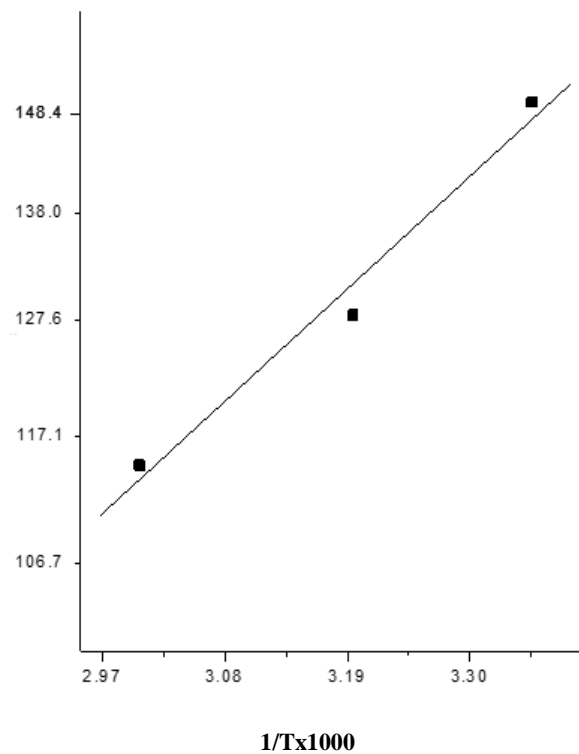


Fig. (10): variation of equilibrium constant (k_c) as a function of temperature

CONCLUSIONS

The adsorption process of Molybdenum on acidic alumina was investigated, and the results indicated that the sorption process is dependent on the pH values, contact times, initial molybdenum concentrations, and reaction temperatures. The maximum K_d values of 5×10^{-3} M Mo (VI) in HCl acid solution onto acidic alumina was attained at pH 2.5. The batch capacity of commercial acidic alumina for Mo (VI) was identified and found to be 45 mg /g. The sorption of molybdenum follows the pseudo-second-order kinetic model and the Langmuir isotherms. Molybdenum sorption occurs exothermically and spontaneously, with higher levels of ion freedom.

REFERENCE

- [1] El Shafei G.M.S., Moussa N. A. and Philip C. A., (2000) Association of molybdenum ionic species with alumina surface, *J. Coll. Interf. Sci.*, 228(1), 105-113.
- [2] Sanjit K., (2008) Surface structure and reactivity of iron oxide-water interface *Developments in Earth and Environmental Sciences USA*, 1stEdn, Elsevier, 1-29.
- [3] Boyd RE. (1982) Technetium-99m generators—The available options. *The International Journal of Applied Radiation and Isotopes*. 33(10):801-809.
- [4] Monroy-Guzman F, Rivero Gutiérrez T, López Malpica IZ, Hernández Cortes S, Rojas Nava P, Vazquez Maldonado JC, et al. (2012) Production optimization of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ zirconium molybdate gel generators at semi-automatic device: DISIGEG. *Applied Radiation and Isotopes*.;70(1):103-111.
- [5] Seifert S, Wagner G, Eckardt A. (1994) Highly concentrated [$^{99\text{m}}\text{Tc}$] pertechnetate solutions from (n, γ) $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators for nuclear medical use. *Applied Radiation and Isotopes*.;45(5):577-579.
- [6] Lavi N. (1978)The study of conditions for the preparation and application of $^{99}\text{Mo}-^{99\text{m}}\text{Tc}$ generators starting from irradiated molybdenum metal. *Journal of Radioanalytical Chemistry*.;42(1):25-34.
- [7] Rohadi A., (2014) Mechanism of ^{99}Mo adsorption and $^{99\text{m}}\text{Tc}$ elution from zirconium-based material in $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator column using neutron-irradiated natural molybdenum, *Jada. Nucl. Chem.*, 303(2), 1481-1483,.
- [8] Goldberg S., Cliff T. J., Donald L. D. S., and Scott M. L., (2008) Mechanism of molybdenum adsorption on soils and soil evaluated using vibrational spectroscopy and surface complexation modeling, *J. Develop. Ear. Environ. Sci.*, 7, 235-266.
- [9] Goldberg S., (2010) Competitive adsorption of molybdenum in the presence of phosphorus or Sulphur on Gibbsite, *J. Soil Sci.*,175(3), 105-110.
- [10] Alexandra Yu. Kurmysheva Marina D. Vedenyapina , Stanislav A. Kulaishin , Pavel Podrabinnik ,NestorWashington Solís Pinargote , Anton Smirnov , Alexander S. Metel , José F. Bartolomé and Sergey N. Grigoriev (2023) (Adsorption Removal of Mo(VI) from an Aqueous Solution by Alumina with the Subsequent Regeneration of the Adsorbent, *Int. J. Mol. Sci.*, 24, 8700.
- [11] Nan X., Christos C., and Washington B., (2006) Adsorption of molybdate and tetra thiomolybdate onto pyrite and goethite: Effect of pH and competitive anions, *J.Chemos.* 62(10), 1726-1735.
- [12] Sarkar A. and Sar P, (2015)Horizontal gene transfer of *Ars Genes*: A possible source of arsenic dissemination in subsurface environment, *J. Environ. Res. Develop.*, 9(3A), 803- 812.
- [13] Singh B. K. and Nema P., (2015) Removal characteristics of para-chlorophenol from aqueous solution by fly ash, *J. Environ. Res. Develop.*, 9(3A), 864-871.
- [14] Ran B., (2015) Removal of Pb (II) ions by using modified anionic ion exchanger, Amberlite IRA-400, *J. Environ. Res. Develop.*, 9(3A), 744-754,.
- [15] Ramachandra H., Akshatha A., and Sundara J. (2016) Understanding the effects of copper sulfide in transformer insulation by different chemical and analytical techniques, *J. Environ. Res. Develop.*, 10(4), 621- 634.
- [16] Prasad K. S., Peter B. M. and Donald C. G., (2002) Adsorption of molybdenum onto anatase from dilute aqueous solutions, *J. App. Geochem.*, 17(5), 649-656.
- [17] Bertoni F.A., Medeot A.C., González J.C., Sala L.F., and Bellu S.E., (2015) Application of green seaweed biomass for Mo(V)I sorption from contaminated waters, Kinetic, thermodynamic and continuous sorption studies, *J.Coll. Interf.Sci.* 15, 122-132.
- [18] H.E. Ramadan, M.A. El-Amir, M. Mostafa (2022) " Adsorption studies of molybdate(VI)— ^{99}Mo onto nano zirconium hydroxide gel" *Applied Radiation and Isotopes* 181, 110092.

- [19] E.A. Azooz, H.E. Ramadan, M. A. Abd Elaal, M. A. El-Amir, M. A. EL-Absy, W. H.Mahmoud (2023)"Kinetic and Thermodynamic Parameters of ^{99}Mo Sorption on Zirconia Nanoparticles Prepared By Hydrothermal Method" *Egypt. J. Chem.* Vol. 66, No. SI: 13 pp. 187 - 197.
- [20] K. Saltalı, A. Sarı, M. Aydın, (2007) Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, *J.Hazard. Mater.* 141, 258–263.
- [21] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, (1966) Pore- and solid diffusion kinetics in fixed-bed adsorption under constant-pattern condition, *Ind. Eng. Chem. Fundam.* 5, 212–223.
- [22] Y.S. Ho, C.T. Huang, H.W. Huang, (2002) Equilibrium sorption isotherm for metal ions on tree fern, *Process. Biochem.* 37, 1421–1430.
- [23] A. Sarı, M. Tuzen, D. Cıtak, M. Soylak, (2007) Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution, *J. Hazard. Mater.* 148, 387–394.
- [24] D. Karadag, Y. Koc, M. Turan, B. Armagan, (2006) Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite, *J. Hazard. Mater. B* 136, 604 – 609.
- [25] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, (1947) Sorption and structure of active carbons. I. Adsorption of organic vapors, *Zh. Fiz. Khim.* 21, 1351–1362.
- [26] K. Saltalı, A. Sarı, (2006) Sorption capacity and thermodynamic properties of natural Turkish (Resadiye) bentonite for the removal of ammonium ions from aqueous solution, *Adsorp. Sci. Technol.* 24, 749–760.
- [27] Y.S. Ho, G. McKay, (1999) Pseudo-second order model for sorption processes, *Process Biochem.* 34, 451–465.
- [28] Murray J. W. and Dillard J. G., (1979) The oxidation of cobalt (II) adsorbed on manganese dioxide. *Geochim. Cosmochim. Acta* 43, 781-787.