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Determined of Equilibrium Adsorption Isotherm Model Pertechnetate Oxoanion Onto Activated Carbon

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Abstract

Four well-known isotherm models were applied to investigate the adsorption process mechanism in the removal of radioactive $^{99m}TcO_4^-$ from aqueous solution by using activated carbon as adsorbent. According to R^2 values, the experimental data is found to be suitable for the four isotherm models. However, when the adsorption capacities of the experimental and isotherm models are compared, it was seen that the Langmuir (L) and Temkin (T) are best suited to the experimental data. The maximal monolayer adsorption capacity value founded from L isotherm model is 3170 μCi.g^{-1}. The dimensionless separation factor (R_L) value indicating a favorable adsorption experiment is 0.126. At the same time, the value of n obtained from F isotherm was found to be 1.72. Therefore, it can be said that active carbon is suitable for this adsorption process. The heat of adsorption process from T isotherm model was estimated to be 724 J/mol and the mean free energy from Dubinin-Radushkevic (D-R) isotherm model was estimated to be 13.4 J/mol. According to these data, it can be said that the adsorption process is realized by physical adsorption. The results showed that the activated carbon is a successful adsorbent for the removal of radioactive $^{99m}TcO_4^-$ from aqueous solutions.

Keyword: Radioactive Substance, Activated Carbon, Isotherm, Adsorption

Aktif Karbon Üzerine Perteknetat Oksoanyonunun Denge İzoterm Modelinin Belirlenmesi

Öz

Adsorbent olarak aktif karbon kullanılaarak, sulu çözeltierden radyoaktif $^{99m}TcO_4^-$ adsorpsiyonunda adsorpsiyon prosesinin mekanizmasını araştırmak için iyi bilinen dört izoterm modeli uygulandı. R^2 değerlerine göre, deneysel verilerin dört izoterm modeli için de uygun olduğu bulundu. Ancak, deneysel ve modellerden hesaplanan adsorpsiyon kapasiteleri karşılaştırıldığında, deneysel verilere en uygun izoterm modellerinin Langmuir (L) ve Temkin (T) olduğu görülmüştür. L izoterm modelinden elde edilen maksimum tek katmanlı adsorpsiyon kapasitesi değeri 3170 μCi.g^{-1}'dir. Uygun bir adsorpsiyon deneyini gösteren boyutsuz ayırma faktörü (R_L) değeri 0.126'dır. Aynı zamanda, F izoterminden elde edilen n değerinin 1.72 olarak bulunmuştur. Bu yüzden, adsorbentin bu adsorpsiyon prosesi için uygun olduğu söylenebilir. Adsorpsiyon proses ısısı T izoterm modelinden 724 J/mol olarak ve ortalama serbest enerjinin Dubinin-Radushkevic (D-R) izoterm modelinden 13.4 J/mol olarak tahmin edilmiştir. Bu verilere göre, adsorpsiyon sürecinin fiziksel adsorpsiyon ile gerçekleştiği

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söylenebilir. Sonuçlar, aktif karbonun, sulu çözeltilerden radyoaktif $^{99m}TcO_4^-$ 'ün uzaklaştırılması için başarılı bir adsorbent olduğunu gösterdi.

Anahtar Kelimeler: Radyoaktif madde,Aktif Karbon,İzoetrm Modeli,Adsorpsiyon

Introduction

Nuclear medicine is a scientific discipline that includes diagnostic imaging and treatment applications through radioactive compounds that can participate in various biochemical and physiological processes in the human body. People can take the radiation from medical treatments, as well as from the cosmic rays of the sun as part of life. Many different radioactive substances are used in the diagnosis of human disease. However, lately, the technetium, a radioactive element, has been widely used for the treatment of humans. Tc is one of the hazardous nuclear wastes detected in contaminating groundwater and sediment [1].

Technetium (Tc), which is present in nanogram quantities in uranium ores in the earth, can be obtained artificially by cosmic ray reaction with Mo, Ru and Nb in nuclear reactors. Tc was first synthesized by Perrier et al. in 1937 by bombarding molybdenum with a neutron (**Fig. 1**) [2].

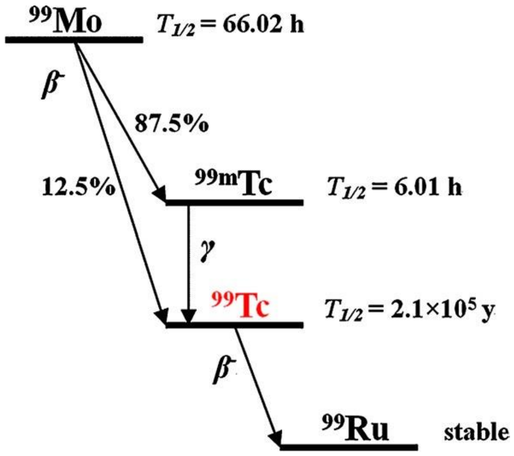

Fig. 1. *Decay scheme of ^{99}Mo.*

As can be seen in **Fig. 1**, the most stable radioactive isotope of Tc is ^{99m}Tc with a half-life of 6 hours. ^{99}Tc is a pure β^- emitter with the maximum decay energy of 0.294 MeV. Therefore, it can be measured by radiation counting [3-5].

^{99m}Tc emits gamma rays and decays to ^{99}Tc. ^{99m}Tc has been widely used for medical diagnosis and medical research since its first application in the hospital in 1960 [6]. The thermal fission of plutonium-239 and uranium-235 produces a ^{99}Technetium with an efficiency of 6% [7].

When ^{99}Tc and 0.9% NaCl solution are mixed, sodium pertechnetate solution, isotonic, colorless, clear, sterile, a

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pyrogenic and ready to inject, is obtained. Sodium pertechnetate solution can be applied directly to the patient for diagnosis [8]. Since pertechnetate oxoanion, $^{99m}TcO_4^-$, is soluble, it creates very significant environmental hazards in groundwater [9].

Because of the weak adsorption of $^{99m}TcO_4^-$ in various environmental media, Tc is considered to be one of the most mobile radionuclides in the environment. The presence of long-lived radionuclides such as ^{99}Tc presents a challenge in the management of radioactive waste. Immobilization of ^{99}Tc should be carried out before long-term and permanent disposal processes. Thus, ^{99}Tc removal methods are required without producing larger volumes of waste [10].

The United States Environmental Protection Agency (USEPA) has identified a maximum level of pollutants of 0.04 milisievert (mSv) per year for β and γ radioactivity from artificial radionuclides such as 99Tc in drinking water [11].

As a result of epidemiological studies, it has been found that if this value is exceeded in the human body, it will cause cancer. In order not to produce nuclear waste in a very large volume, it is necessary to reduce their level [10].

The removal of 99Tc from contaminant groundwater is a difficult process due to the presence of other present anions. Various materials have been investigated for the removal of Tc [1].

Some of the adsorbents reported in the literature to remove $^{99m}TcO_4^-$ are as follows: alumina and goethite [12], stibnite [13], elemental iron [14], pyrhotite, pyrite and magnetite [15-16], organophilic bentonites [17-18] and various synthetic resins and sponges[19-20].

Activated carbon is the trade name for carbonaceous products having large surface area and porosity. It is made from carbon-based material by its thermal decomposition in a furnace using a controlled atmosphere and heat. The density and surface area of activated carbons are generally larger than 0.2 $g.mL^{-1}$ and 400±1600 $m^2.g^{-1}$ respectively [21]. Activated carbon as an adsorbent has been proposed for the removal of radioactive $^{99m}TcO_4^-$ from aqueous solution at room temperature.

The aim of this study was to determine the adsorption isotherm in the removal of the radioactive $^{99m}TcO_4^-$ from aqueous solution by using activated carbon as adsorbent.

Material And Methods

Materials

In present study, radioactive $^{99m}TcO_4^-$, was supplied by Ataturk University Faculty of Medicine Department of Nuclear Medicine. From this department, $^{99m}TcO_4^-$ solutions at the desired values were provided for each experiments. The activated carbon was purchased from local markets. Activated carbon samples' particle sizes set to +0.2–0.18, +0.18–0.15, +0.15-0.125 and +0.125–0.063 mm, by various sieves. All reagents used were of analytical grade.

Methods

The experiments were performed by the batch adsorption technique. In the experiments, the temperature, the optimum pH, the particle size, the stirring speed, adsorption equilibrium time andthe adsorbent mass were kept constant as 25 ^oC, 8, +0.15-0.125 mm, 700 rpm, 15 min. and 0.5 $g.L^{-1}$, respectively.

1mL, 0.39-1.56mCi.mL^{-1} $^{99m}TcO_4^-$ solutions were taken and completed to 500 mL with deionized water. Thus, $^{99m}TcO_4^-$ solutions at 0.78-3.12 mCi.L^{-1} activities were obtained. The pH values were adjusted by the addition of appropriate quantities of 0.1 M NaOH or 0.1 M HCl solutions with a digital pH-meter (model Thermo Orion 3 Star pH meter).

Adsorption experiments were carried out at controlled temperature and mixing speed in a jacketed reactor system with a volume of 700 mL. After predetermined time intervals, the resulting mixture was filtered. The radioactivity of $^{99m}TcO_4^-$ in the final solution was measured by using a dosimetry.

Adsorption capacity, q_e (mCi.g^{-1}), was found from Eq. (1)

$$q_e = \frac{(C_i - C_e)}{C_e}\frac{V}{m} \quad (1)$$

where, C_i and C_e (mCi.L^{-1}) are the $^{99m}TcO_4^-$ activity at the initially and residually, respectively. V (L) is the solution volume and m (g) is the adsorbent mass.

Adsorpiton Isotherms

In the adsorption processes carried out in aqueous solutions, four isotherm models are widely used. These models are Langmuir (L), Freundlich (F), Temkin (T) and Dubinin-Radushkevich (D-R).

The Langmuir isotherm describes the formation of a monolayer adsorbate on sites in the adsorbent quantitatively, and then there are no multiple layers after this layer. Thereby, it is the most important equation that give information about the adsorbed molecules and their distribution between solid and liquid phase at equilibrium. The parameters in isotherm equations give information about surface properties, adsorption mechanisms and affinities of the adsorbent. The Langmuir isotherm's essential characteristics can be expressed with a dimensionless equilibrium parameter (R_L). The R_L values indicate the type of the isotherm (unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$)).

The Freundlich isotherm is generally used to define adsorption properties for the heterogeneous surface and assumes that adsorption occurs in regions with different adsorption energy. If n value is between 1 and 10, the adsorbent is suitable for adsorption.

The Temkin isotherm is generally applied to explain adsorbate–adsorbent interactions. It is characterized by a homogenous distribution of binding energies.

The Dubinin-Radushkevich isotherm is mostly tested to explain the adsorption mechanism and nature (especially on porous adsorbents) with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted well to the high solute activities and the intermediate range of concentrations data. The Isotherm model equations are given in **Table 1.**

Table 1. *Isotherm models (I.M.) commonly used in aqueous solutions.*

I.M.	Mathematical Equations	Eq.	Ref.
L	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \times q_m}, R_L = \frac{1}{1+K_L C_0}$	(2)	[22]
F	$\ln(q_e) = \ln(K_f) + \frac{1}{n} \times \ln(C_e)$	(3)	[23]
T	$q_e = B_T \times \ln(K_T) + B_T \times \ln(C_e)$ $B_T = RT/b_T$	(4)	[24]
D-R	$\ln(q_e) = \ln(q_m) - \beta_{DR} \times \varepsilon^2$ $\varepsilon = R_g \mathrm{T} \ln\left(1 + \frac{1}{C_e}\right)$ $E = \frac{1}{\sqrt{2\beta_{DR}}}$	(5)	[25]

Results and Discussion

The data obtained from the adsorption of the technetium solutions prepared at different initial concentrations with the activated carbon are presented in **Table 2**.

Table 2. *The data obtained from experiments (25 ^oC, 700 rpm, +0.15-0.125 mm, 8 pH, 15 min. and 1 $g.L^{-1}$)*

C_0 (μ $Ci.L^{-1}$)	C_e (μ $Ci.L^{-1}$)	$q_{e.exp}$ (μ $Ci.g^{-1}$)
780	125	655
1560	320	1410
2340	590	1750
3120	960	2160

Four well-known isotherm models presented in **Table 1** were applied to investigate the adsorption process mechanism in the removal of the radioactive $^{99m}TcO_4^-$ from aqueous solution by using activated carbon as adsorbent. From Eq. 2, when the plot Ce versus Ce/qe is plotted, the values of q_m and K_L are found from the intercept and slope of linear relation. The other isotherm constants in Eq. 3-5 can be calculated in the same way. The R^2, isotherm constants and adsorption capacity calculated from model for the isotherm models are given in **Table 3** and **Fig. 2-5**.

Table 3. *Isotherm parameters and R^2 values of equilibrium isotherm models for the $^{99m}TcO_4^-$ adsorption onto activated carbon at 25 ^0C.*

Parameters of isotherm models		$q_{e.calc.}$ ($\mu Ci.g^{-1}$)
Langmuir		
q_m ($\mu Ci.g^{-1}$)	3170	684
K_L(L. g^{-1})	0.0022	1310
R_L	0,126	1791
R^2	0.995	2151
Freundlich		
K_f [(μCi.g-1)	42.87	
((L. $g^{-1})^{-1/n}$]		710
n	1.72	1226
R^2	0.980	1750
		2323
Temkin		
K_T (L. g^{-1})	0.02	663
B_T (J.mol^{-1})	724	1344
R^2	0.996	1787
		2139
Dubinin-Radushkevich		
β_{DR} ($mol^2.kj^{-2}$)	2783	642
q_m ($\mu Ci.g^{-1}$)	1900	1609
E (kj.mol^{-1})	0.0134	1809
R^2	0.974	1865

According to the isotherm Freundlich equation n value is 1.72 and the K_f value is 42.87, it shows that the activated carbon is a suitable adsorbent with a heterogeneous surface. The adsorption heat from Temkin Isotherm model was predicted to be 0.724 $kJ.mol^{-1}$. This result indicates that the adsorbate-adsorbent interaction takes place by physical adsorption. Additionally, the mean free energy from D-R isotherm model was predicted to be 0.013 $kJ.mol^{-1}$, which clearly indicates that the adsorption experiment followed a physical process.

If the R^2 values from the **Table 3** and **Fig. 2-5** are examined again, it can be said that the experimental data fit the four isotherm models. However, when the adsorption capacities of the experimental and isotherm models are compared, it will be seen that the Langmuir (L) and Temkin (T) are best suited to the experimental data. Similar results were reported in the literature [26-28].

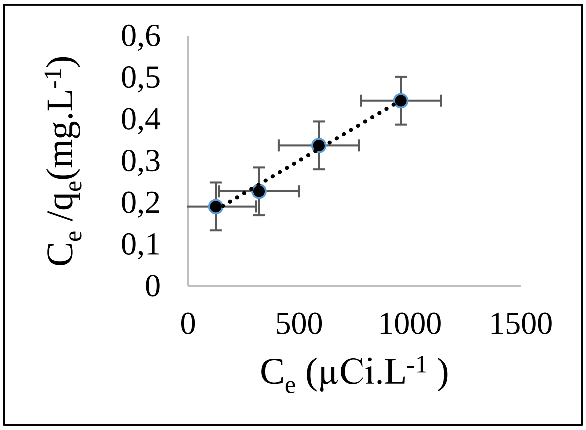

Fig. 2. *Isotherm curves for Langmuir model (25 °C, 700 rpm, +0.15-0.125 mm, 8 pH, 15 min. and 1 g.L⁻¹)*

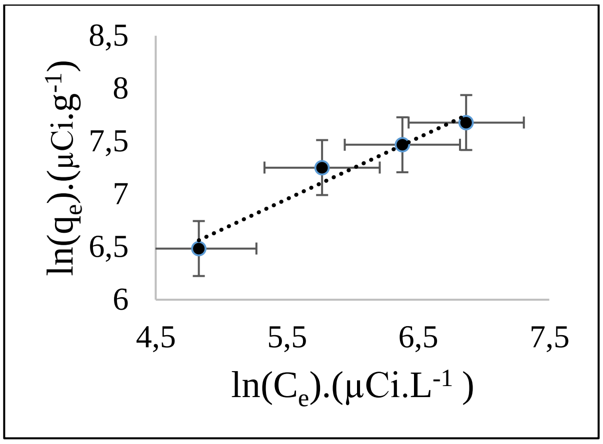

Fig. 3. *Isotherm curves for Freundlich model (25 °C, 700 rpm, +0.15-0.125 mm, 8 pH, 15 min. and 1 $g.L^{-1}$)*

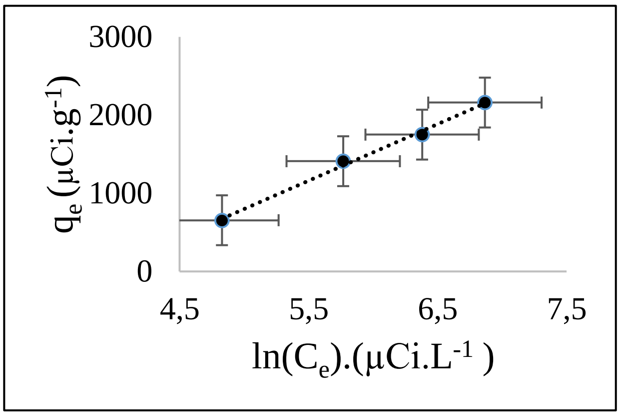

Fig. 4. *Isotherm curves for Temkin model (25 °C, 700 rpm, +0.15-0.125 mm, 8 pH, 15 min. and 1 $g.L^{-1}$)*

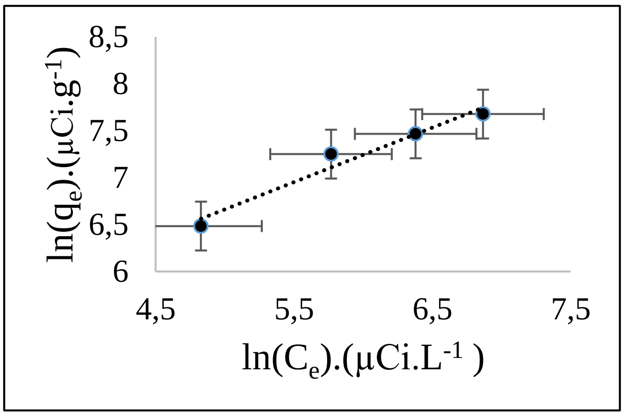

Fig. 5. *Isotherm curves for Dubinin-Radushkevich model (25 °C, 700 rpm, +0.15-0.125 mm, 8 pH,15 min. and 1 $g.L^{-1}$)*

Conclusion

In this paper, investigation of the equilibrium adsorption was carried out at 25ºC for four adsorption isotherm models were studied. The adsorption data fitted into Langmuir, Freundlich, Temkin and Dubunin – Radushkevich isotherms out of which Langmuir and Temkin adsorption isotherm models were found to have the highest correlation coefficients and the best experimental data.

Nikolić et al., used organo-modified bentonite to remove $^{99m}TcO_4^-$. They found that 1536 μCi.g^{-1} is the maximal monolayer adsorption capacity value obtained from Langmuir isotherm model [29]. In this study, this value was found to be 3170 μCi.g^{-1}.

It could be concluded that activated carbon is a potential and active adsorbent for the removal of $^{99m}TcO_4^-$ from aqueous solution.

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