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Recovery of vanadium element from wastewater of petroleum refineries using effective adsorbent: Mathematical approach via isothermal, kinetics and thermodynamic simulation

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ABSTRACT

Adsorption behavior can be determined using different essential studies such as adsorption isotherm, kinetics, and thermodynamics. In this study, adsorption isotherm models, and kinetic, and thermodynamics studies are used to describe the use of alumina as an effective adsorbent and a remover of vanadium (V^{+5}) ions from aqueous solutions contaminated by this metal. The aqueous solutions used simulate the wastewater of most traditional oil refineries. Efficiency can be determined by comparing the correlation coefficients of the linear relationships used with each model. Using alumina, the perfect removal of vanadium ions was achieved. Vanadium removal increases with an increase in the operating conditions, which are time temperature, agitation speed, pH, and adsorbent's media dose. However, it also increases with the elimination of the initial concentration. This study shows that the vanadium's adsorption based on the Langmuir isotherm model gives a correlation coefficient of 0.9999, while when it is based on the Temkin and Freundlich isotherms the correlation coefficient is less. Hence, adsorption on the surface of alumina takes place in monolayer surfaces with a regular distribution of particle's binding energy and a narrow quantity of identical sites on the surface of alumina. Subsequently, the kinetic study shows that the adsorption behavior matched the pseudo-second-order kinetic model with R^2 equaling 0.9999. Also, thermodynamics studies approves that the adsorption is a spontaneous endothermic process of enthalpy change.

1. Introduction

Crude oil, the lifeblood of the modern industry, contains a myriad of compounds, and among them, heavy metals such as chromium, cadmium, nickel, vanadium, zinc, iron… etc., from the stage of its extraction to its conversion into usable petroleum products [1]. As soon as crude oil reaches the surface of the earth, pollution to the environment begins with these metals, similar to other types of pollutants resulting from oil, such as exploration, extraction, transportation, shipping, unloading, refining, and others [2]. Crude oil, extracted with various heavy metals, necessitates a preliminary washing in the desalination unit before refining to mitigate its detrimental impact on refinery equipment. During this process, a portion of the associated minerals, predominantly in the form of dissolved salts, is eliminated. These salts are parts of residues from the desalination unit [1].

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Nomenclature:

b	Temkin isotherm constant related to adsorption heat (J mol^{-1})	
B	Constant in Temkin Isotherm Model (dimensionless)	
C_e	Equilibrium adsorbed concentration (mg g^{-1})	
G	Gibbs free energy of adsorption (kJ mol^{-1})	
H	Enthalpy of adsorption (kJ mol^{-1})	
I	Thickness of boundary layer (mg g$^-$)	
k_1	First order rate constant (min^{-1})	
k_2	Second order rate constant (g mg^{-1} min^{-1})	
k_{ad}	Thermodynamic equilibrium coefficient of adsorption (dimensionless)	
K_F	Constant of Freundlich adsorption isotherm model (mg g^{-1}).(l.mg^{-1})$^{1/n}$	
K_L	Constant of Langmuir adsorption isotherm model, expressed the binding sites (l mg^{-1})	
k_p	Rate constant in intra-particle diffusion model (mg g min$^{-0.5}$)	
K_T	Temkin isotherm equilibrium binding constant (l mg^{-1})	
n	Intensity of the adsorption in Freundlich model (dimensionless)	
q_e	Adsorption capacity at equilibrium state (mg. g^{-1})	
q_{max}	Maximum adsorption capacity of Langmuir model (mg. g^{-1})	
q_t	Adsorption capacity at any time (mg. g^{-1})	
$\mathbb{R}$	Universal gas constant (8.3144 J mol^{-1} K^{-1})	
R^2	Correlation coefficient (dimensionless)	
R_L	Separation factor in Langmuir model (dimensionless)	
S	Entropy adsorption (kJ mole^{-1} K^{-1})	
t	Contact time (min)	
T	Absolute temperature (K)	

Greek symbols

α	Initial adsorption rate in Elovich model (mg g^{-1} min^{-1})	
β	Desorption constant in Elovich model (g mg^{-1})	
Δ	Change	

Subscripts

ad	Adsorption
e	Equilibrium
F	Freundlich
L	Langmuir
max	Maximum
p	Intra-particle diffusion
t	Time
T	Temkin
1	First order
2	Second order

In contrast, the segment existing in a complex form as organometallic compounds resists the desalination process, persisting in the crude oil outside the desalination unit [3]. This liquid wastewater, recognized as the primary source of liquid waste generation in oil refineries, is not only highly saline but also contains hazardous elements with considerable toxicity, notably heavy metals [2]. These minerals, characterized by their high toxicity, serve as potent pollutants and indicators of environmental contamination [1]. The discharge of such elements by industrial facilities into water sources or their proximity poses a significant risk as they can enter the food chain, eventually settling in the human body [4]. One of the most important and well-known metals found in crude oil is vanadium of chemical symbol V, and atomic weight of 23, is located in the periodic table within the elements of the fifth group and the fourth cycle, and it is a toxic and harmful metal for organisms and ecological system [5]. Vanadium, in particular, is an emerging concern due to the negative impacts it poses on ecosystems and human health. In crude oil waste, the concentration of vanadium can vary, but it typically ranges from a few parts per million (ppm) to several hundred ppm [6]. The toxicity of this element comes through its effect on biological systems and its danger is equal to that of cadmium and lead. The toxic action of vanadium is mainly concentrated on the respiratory and digestive systems [5]. Generally, vanadium compounds are not considered a serious risk to human health if the exposure concentration is low. Water contains between 1-6 ppb of vanadium, but in urban areas it may contain 30 ng/m^3, due to the use of petroleum products. The normal level of this metal in the serum contains between 35-48 µg/100 ml [7]. The presence of vanadium and some other heavy metals in crude oil and its derivatives causes a lot of technical problems for refinery equipment. Elevated vanadium concentrations have the potential to hasten corrosion rates in refinery equipment, resulting in higher maintenance expenses and a reduced lifespan for infrastructure [3]. The environmental impact is equally concerning, as vanadium emissions during refining contribute to air pollution, posing risks to air quality and human health [5]. Thus, researchers have been interested in determining the vanadium concentration as an introduction to avoid its problems or to achieve a high

economic income for using petroleum products that contain vanadium, as Venezuela's oil is required to extract vanadium from it because it contains the highest percentage of vanadium among the various types of petroleum in the world [8]. There are many ways to remove heavy metals from wastewater such as biological methods, chemical precipitation, dissolved air flotation, coagulation-flocculation, ion exchange, ozonation, reverse osmosis, and others [5]. However, these methods have several obstacles, including required specific conditions to grow the microorganisms, or accumulate the toxic residues, or high cost of infra-structure and energy, or need for special equipment or materials, or producing the sludge that needs treatment because it is toxic material, or requires large areas [9]. From another side, the adsorption technique shows many advantages against the aforementioned methods. It is a simple method and does not require primary treatment, chemicals or energy consumption, and it can treat wide range of concentrations and have a very appropriate cost [10]. Adsorption, in precise terms, is a surface phenomenon that delineates the capacity of solids or liquids to attract and bind molecules from gases or liquid solutions, bringing them into direct contact with their surface [7]. The terminology distinguishes between adsorbents, representing the solids or liquids responsible for adsorbing gases or dissolved substances, and adsorbate, referring to the particles that undergo this adsorption process [5]. An illustrative example is the application of charcoal in gas masks, where its capability to eliminate toxic substances and air-borne impurities showcases the practical manifestation of adsorption [11]. A number of commercially available materials possess characteristics that qualify them for use as good adsorbents, such as: activated carbon, silica gel, zeolite and porous clays [9]. But due to the high cost of these media, the researchers seek for an alternative materials that achieve suitable efficiency and in the same time available and low-cost [12]. Agricultural and industrial wastes is emerging as a very good choice, where it is non-valuable substance, cheap, and must be dispose in suitable way to save the environment [13]. Various kinds of these materials are tested such as rice husk [14], banana peels [15], watermelon rinds [16], eggshells [17], pomegranate peels [18], orange peels [19], lemon peels [20], buckthorn leaves [4], used tea leaves [21], alga [22],

water hyacinth [23], date pits [24] etc. These waste prove their ability to purified polluted water from hardness [25], non-organic toxic [26], dyes [27], drugs [28], 2,4-D [29], and deltamethrin [30] pesticides, thallium [31], also the heavy metals [32] and phenols from soil [33], flowing river [34], and building materials [35] of different contaminations. Due to its ability, the residues of these material can be used in different applications, such as enhancing materials for concrete [36], preparation of valuable chemical [37], producing fertilizer [38], rodenticides [39], nanoparticles [40], or composite materials [41] after adsorption ending via concept of zero residues level. Although of these high advantages, but there are materials can give better efficiency using small amount comparing with agricultural and industrial wastes, like alumina [11]. Alumina is considered as one of most materials used for adsorbed the heavy metals from different types of wastewaters and has wide used in petroleum industries due its workable ability, unique properties and high surface area [42]. Furthermore, the efficiency of removal processes is a critical consideration. Alumina, widely material used in petroleum industry, has demonstrated effectiveness in removing heavy metals generally and vanadium especially from crude oil waste [25]. Experiments conducted with varying doses of alumina (as example), typically in the range of 0.1 to 0.5 g per 100 ml of refinery wastewater, reveal the intricate relationship between adsorbent dosage and removal efficiency [30]. Achieving optimal removal often involves a delicate balance, considering factors such as contact time, temperature, agitation speed, and pH [5]. The importance of adsorption is still lake unless the determination of its behaviour is detected [40]. Thus, this paper aims to study the adsorption behaviour of vanadium heavy metal using alumina prepared from aluminium foil as non-valuable source. The studying includes isothermal, kinetic and thermodynamic using famous model [43]. However, in this study the modelling of adsorption process, isothermally, kinetically and thermodynamically is tested carefully. The isothermal modelling performs via three types of mathematical models, while the adsorption kinetics conducted through four models. The thermodynamic study achieves by calculating the values of enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) functions to give adequate explanation for removing of vanadium metal from refinery wastewater by alumina.

2. Methodology

2.1. Adsorption experimental procedure

This process including the preparation of alumina from aluminum foil wastes according to [44] and the concentrations of vanadium ions in stock solution and treated solutions can be detected by atomic absorption spectrophotometer and plotted graphically using the procedure described by [45]. The adsorption process conducted using multi-operating parameters. The operating parameters used were pH, dose of alumina, temperature, contact time, concentration of antimony (V^{+5}) ions and finally the shaking speed of the samples in shaker water bath unit. The aforementioned design factors were changed in range between 1-8, 0.01-1.0 g/100 ml, 20-50 °C, 10-180 min, 1-400 ppm and 100-500 rpm, respectively.

3. Mathematical analysis of adsorption results

3.1. Adsorption isotherm

The adsorption isotherm pertains to the connection between the quantity of the adsorbent substance (q_e) and the residual concentration (C_e) at a stable equilibrium state and a consistent temperature [15]. The study of the

adsorption isotherm is important for understanding the pattern that the dissolved substance relates to the adsorbent media. It provides important information describing the adsorption nature and determining the optimal conditions for adsorption involves assessing the concentration of the adsorbed substance in solution or the pressure in the case of gases [17]. Moreover, the adsorption isotherm provides insights into the distribution of molecules between the liquid and solid phases at the point of equilibrium. As adsorption transpires, a correlation materializes between the quantity of the adsorbate and the surface of the adsorbent material, specific to a given temperature. However, with the establishment of a new equilibrium, a distinct concentration at equilibrium emerges [18]. The partitioning of metal ions between the liquid phase (solution) and the solid phase (adsorbent substance) is elucidated through theoretical models applied post-equilibrium establishment. Numerous models elucidate these surface phenomena, with notable mentions being the Langmuir isotherm model, Freundlich isotherm model, and Temkin isotherm model—each employed in our current investigation. Evaluating the suitability of these models in characterizing the system based on the experimental results involves a comparative analysis of the correlation coefficients derived from the linear relationships associated with each model.

3.1.1. Langmuir isotherm model

In 1916, the pioneering chemist and physicist Irving Langmuir introduced this model. According to Langmuir's model, the adsorption process unfolds exclusively on a monolayer surface. It posits that the adsorption sites are uniform and possess a finite capacity, with maximum adsorption transpiring by saturating the primary layer with solute ions. Furthermore, the model conjectures that the adsorption layer is singularly one unit in thickness and that the energy distribution across the adsorption surface is homogeneous [45]. Equation (1) represents the mathematical form of the Langmuir isotherm model [18], while Equation (2) represents the linear form of this model [45]. An essential feature of this model lies in its capacity to discern the nature of adsorption, gauging whether it is favorable or unfavorable. This determination is facilitated by calculating the separation factor (R_L), an important parameter derived from Equation (3) [19]:

$$q_e = \frac{q_{max} \cdot K_L C_e}{1 + K_L C_e} \tag{1}$$

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L} \frac{1}{C_e} + \frac{1}{q_{max}} \tag{2}$$

$$R_L = \frac{1}{1 + K_L C_e} \tag{3}$$

The separation factor holds significant importance in delineating the nature of adsorption. When $R_L > 1$, it signals unfavorable adsorption, while a value of R_L equal to 1 indicates linear adsorption. The adsorption is a favorable type if R_L greater than one and when $R_L = 0$ the adsorption becomes irreversible. Plotting a graph of $(1/q_e)$ vs $(1/C_e)$ gives a linear relationship of $(1/q_{max} K_L)$ slope and $(1/q_{max})$ intercept.

3.1.2. Freundlich isotherm model

It is the oldest and most important isotherm models used to describe the nature of adsorption. It was accomplished by the German chemist Herbert Max Finlay Freundlich in 1909 and can be used for imperfect systems. In this model, the presumption is that the adsorbent surface is comprised of diverse and heterogeneous layers. Additionally, it posits that the adsorption

sites are unsaturated and are situated at different energy levels, introducing non-uniform changes in underlying energy. The isotherm equation for Freundlich is expressed in Equation (4) [46], with its linear representation articulated in Equation (5).

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (5)$$

The intensity of adsorption in the Freundlich model, which represented by the constant (n), shows the degree of linearity between the concentration of the adsorbent material in the adsorption surface and solution. It also indicates the homogeneity degree of adsorption sites and the relative distribution of system energy. Also, its value determines the type of adsorption. If the value of $n > 1$, the adsorption is of a physical type, and the adsorption is chemical if the value of $n < 1$, while the adsorption is linear in the case of $n = 1$. The determination of Freundlich isotherm coefficients involves extracting information from the graph depicting the correlation between $(\ln q_e)$ and $(\ln C_e)$. In this graphical representation, the slope of the straight line corresponds to $(1/n)$, while the intercept corresponds to $\ln K_F$. The coefficients of Freundlich isotherm can be inferred from the graph of the relationship between $(\ln q_e)$ and $(\ln C_e)$ where $(1/n)$ represents the slope of the straight line while the intercept represents $(\ln K_F)$.

3.1.3. Temkin isotherm model

This model was brought up by the Russian scientist Mikhail Issak Temkin in 1940. It is usually used for systems in which the adsorption temperature is distributed unevenly. This model posits that the adsorption temperature of all molecules decreases in a linear fashion, rather than exponentially, as the surface of adsorption increases. It further assumes that the binding energies are uniformly distributed over the adsorbent media's surface, specifically above the maximum binding energy. The interference between the adsorbate and adsorbent material is taking into account the interfacial layer between them. The overarching formula for the isotherm is expressed in Equation (6), whereas the linear representation of the Temkin isotherm model is delineated in Equation (7) [18].

$$q_e = \frac{RT}{b} \ln K_T C_e \qquad (6)$$

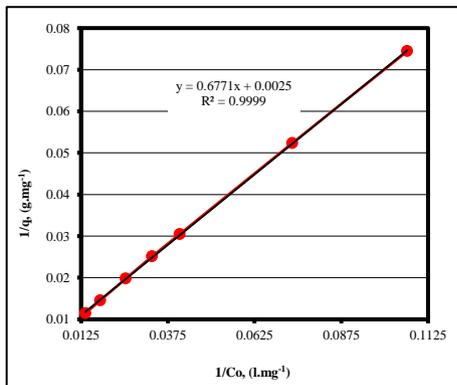$$q_e = B \ln K_T + B \ln C_e \qquad (7)$$

Figure 1. Langmuir isotherm of alumina for vanadium adsorption

$$B = \frac{RT}{b} \qquad (8)$$

The coefficients of this model are ascertainable by constructing a linear correlation between $(\ln C_e)$ and (q_e). In this graphical representation, the slope and intercept of the line correspond to (B) and $(\ln K_T)$, respectively. The figures 1-3 show the Langmuir, Freundlich and Temkin adsorption, respectively, while Table 1 shows the constant values of these isotherms.
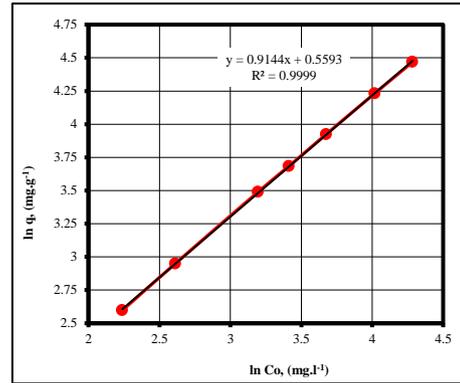

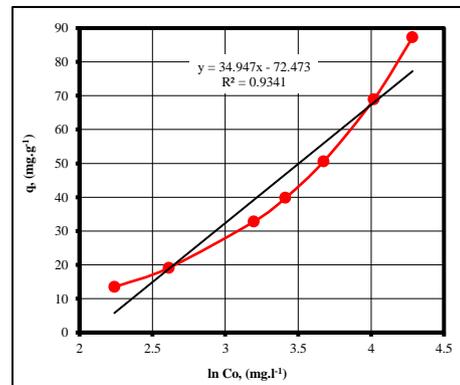**Figure 2.** Freundlich isotherm of Alumina for vanadium adsorption

Figure 3. Temkin isotherm of alumina for vanadium adsorption

Table 1. Constant values of Langmuir, Freundlich and Temkin isotherms for vanadium ions adsorption using alumina.

Model	Parameter	Value
Langmuir	q_{max}, (mg.g^{-1})	400
	K_L, (l.mg^{-1})	0.00369
	R_L, (−)	0.0093
	R^2, (−)	0.9999
Freundlich	K_F, (mg.g^{-1}).(l.mg^{-1})$^{1/n}$	1.74945
	n, (−)	1.094
	R^2, (−)	0.9999
Temkin	B	34.947
	K_T, (l.g^{-1})	0.1257
	R^2, (−)	0.9341

Figures 1-3 show the Langmuir, Freundlich, and Temkin isotherms for the adsorption of the vanadium by alumina as an adsorbent, respectively, while Table 1 shows the constant values of these isotherms. The adsorption

process of vanadium using alumina as adsorbents is subject to the Langmuir and Freundlich isotherms better than the Temkin model due to their high correlation coefficients (R^2) value. This implies that the adsorption takes place on a monolayer surface featuring a defined number of identical sites. The favorability of the adsorption process is contingent upon the value of the separation factor. On the other hand, the Freundlich model was also the best model for vanadium adsorption, according to the correlation coefficient (R^2) value. As per this model, adsorption transpires on a surface that is not uniform in its composition (which can be consistent with the results to some extent) and the adsorption is of the physical type (and this contradicts some of the results of the kinetic and thermodynamic models of the current study results), which will be detailed later. While the Temkin model exhibited the least efficiency in representing the outcomes, the results also aligned with this model, displaying the lowest correlation coefficient (R^2) value. This suggests that the obtained results do not conform well to this particular model.

3.2. Adsorption kinetics

It constitutes a mathematical depiction, either by a curve or a straight line, elucidating the pace at which adsorbate ions are either released from the aqueous medium or captured by the solid phase, represented by the adsorbent surface, under specific operating conditions. Hence, the kinetic study holds paramount significance in comprehending the efficiency and dynamics of the adsorption process [18]. Numerous kinetic models exist to portray the adsorption process, with notable examples being the Pseudo first-order model, pseudo-second order model, the Elovich model, and the Intra-particle diffusion model — the latter being employed in analyzing the experimental data in this study.

3.2.1. Pseudo first order model

Also known as the Lagergren model, named after its proposer, the Swedish physicist Sten Yngve Dennis Lagergren in 1898, this model posits that adsorption takes place in a monolayer between the liquid and solid phases at the adsorption surface [45]. This model can be represented mathematically as shown in Equation (9)

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{9}$$

By integrating Equation (9) under boundary conditions ranging from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the linear representation for this model is derived, as articulated in Equation (10) [27], which can represents by linear relationship by plotting $[\ln(q_e - q_t)]$ against (t). The slop and intercept are equilibrium constant (k_1) and ($\ln q_e$) respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

3.2.2. Pseudo second order model

In instances where the adsorption of dissolved ions from an aqueous solution stems from physicochemical reactions between the adsorbate (liquid phase) and the adsorbent (solid phase), the most suitable model for depicting this condition is the pseudo second-order model. This model posits that the rate of adsorption is directly proportional to the number of active sites accessible on the surface of the adsorbent media. The mathematical expression for this model is depicted in Equation (11) [22]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{11}$$

By integrating Equation (11) under boundary conditions spanning from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, and subsequent rearrangement of terms, the linear representation for this model is obtained, as elucidated in Equation (12) [22]. This can be depicted through a linear relationship by plotting (t/q_t) against (t). The slope and intercept of this linear representation are $(1/q_e)$ and $(1/k_2 q_e{}^2)$, respectively.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e} t \tag{12}$$

3.2.3. Elovich model

Formulated in 1934 by the Belarusian physicist J. B. Zeldowitsch and the Russian scientist S. Z. Roginsky, later acknowledged as the Elovich model, this conceptual framework posits that the rate of adsorption experiences an exponential decline with an increment in the quantity of adsorbate adhered to the adsorption surface [25]. Therefore, this model can be represented mathematically as shown in Equation (13):

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{13}$$

By integrating Equation (13) within the boundary conditions, extending from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, and subsequent arrangement of terms, the linear representation for this model is derived, as presented in Equation (14) [25].

$$q_t = \frac{1}{\beta}\ln\left(\frac{1}{\alpha\beta} + t\right) + \frac{1}{\beta}\ln(\alpha\beta) \tag{14}$$

As the system approaches the state of equilibrium, $t \gg (1/\alpha\beta)$. So, Equation (14) [25] can be represented as in the following form:

$$q_t = \frac{1}{\beta}\ln t + \frac{1}{\beta}\ln \alpha\beta \tag{15}$$

Which can represents by linear relationship by plotting (q_t) against (t). The slop and intercept are $(1/\beta)$ and $[1/\beta\,(\ln\alpha\beta)]$ respectively.
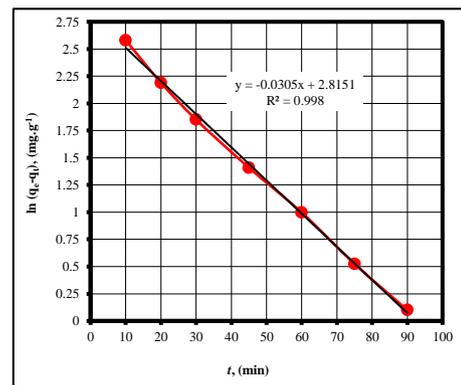

Figure 4. Pseudo first order kinetic model of vanadium adsorption by alumina

3.2.4. Intra-particle diffusion model

In 1963, W.J. Weber and J.C. Morris introduced a model aimed at discerning the rate-limiting step. According to this model's hypothesis, the process of transferring solute from the solution to the adsorption surface involves four distinct steps. The initial step is mass transfer, characterized

by the swift movement of solute molecules when the adsorbent substance is present in the solution [46]. Following this, there is film diffusion, where the solute moves within the boundary layer of the adsorbent material. Another step involves the diffusion of solute particles toward the pores of the adsorption surface, termed surface diffusion. The ultimate step is the adsorptive attachment of solute molecules to the active sites on the adsorption surface, referred to as pore diffusion. The mathematical equation describing the intra-particle diffusion model is explained by Equation (16) [32].
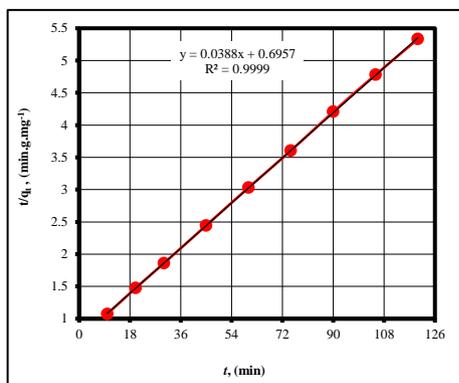
$$q_e = k_P t^{0.5} + I \tag{16}$$

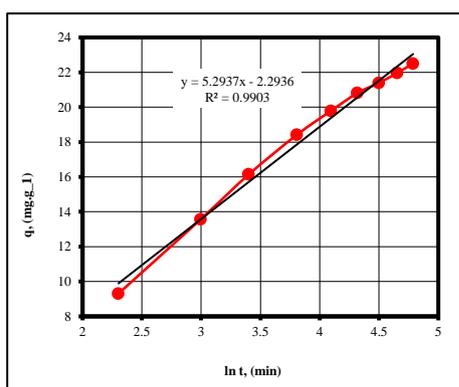**Figure 5.** Pseudo second order kinetic model of vanadium adsorption by alumina

Figure 6. Elovich kinetic model of vanadium adsorption by alumina

The presented equation exhibits linearity. By plotting (q_e) against $(t^{0.5})$, the slope of the resulting straight line corresponds to the time constant (k_P), while the intercept facilitates the calculation of the constant (I). The experimental data acquired from the kinetic study on the removal of vanadium ions utilizing alumina has been graphically presented, Figs 4-7. Simultaneously, Table 2 compiles the parameter values for the four applied kinetic models—Pseudo First Order, Pseudo Second Order, Elovich, and Intra-Particle Diffusion models—employed to scrutinize the study results. Notably, according to the data of Table 2, the pseudo-second-order model emerges as the most fitting for representing this dataset, closely followed by the pseudo-first-order model, then Elovich and intra-particle diffusion models. This determination is based on the value of experimental adsorption capacity observed for both of these models compared to the other kinetic models.
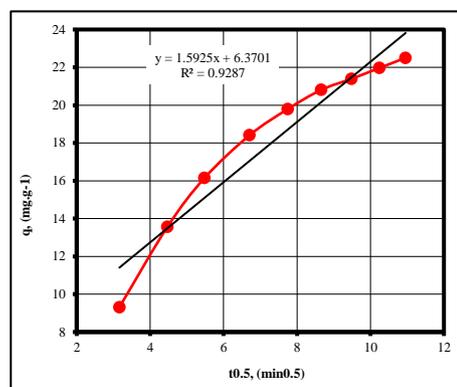

Figure 7. Intra-particle diffusion kinetic model of vanadium adsorption by alumina

This finding can be elucidated by the correlation between the quantity of adsorbed metal ions and the available active sites on the alumina surface, as per the pseudo-second-order model. Additionally, the pseudo-first-order model suggests that the adsorption is achieved in a single layer. What confirms this interpretation is that the results of the isothermal study closely matched the Langmuir isotherm model, which assumes that the adsorption occurs in a single layer. While for the Elovich model, the results of the kinetic study matched with it with a lower correlation coefficient than the previous two models, which confirms the practical results obtained.

Table 2. Constant values of Pseudo First Order, Pseudo Second Order, Elovich, and intra-particle diffusion kinetic models for adsorption of vanadium ions using alumina.

Model	Parameter	Value
Pseudo first order model	q_e, (mg.g^{-1})	16.695
	k_1, (min^{-1})	00.031
	R^2, (−)	0.9980
Pseudo second order model	q_e, (mg.g^{-1})	25.773
	k_2, (g.mg^{-1}.min^{-1})	0.0021
	R^2, (−)	0.9999
Elovich model	q_t, (mg.g^{-1})	22.500
	α, (mg.g^{-1}.min^{-1})	03.432
	β, (g.mg^{-1})	00.189
	R^2, (−)	0.9903
Intra-particle diffusion model	q, (mg.g^{-1})	22.500
	k_P, (mg.g^{-1}.min$^{-0.5}$)	01.593
	I, (mg.g^{-1})	06.370
	R^2, (−)	0.9287

As the percentage adsorption of vanadium ions gradually decreases with increasing concentration and this is precisely the hypothesis of the Elovich model. On the other hand, the model of intra-particle diffusion model corresponded to less value according to the correlation coefficients shown in Table 2, because the hypotheses of this model contradict the practical results obtained under optimal conditions. The reason for this effect may be due to the boundary layer on the surface of the adsorbent material is little and the ions may reach the active sites easily and with less resistance due to the high mixing speed. Based on the values of the experimental adsorption capacity, the degree of conformity of the kinetic models used with the results of this study takes the following form:

Pseudo second-order model > Elovich model > Intra-particle diffusion model > Pseudo first-Order model

3.3. Adsorption thermodynamic study

The significance of thermodynamic functions is pronounced in elucidating various reactions, particularly the adsorption process. These values enable an understanding of the prevailing forces' nature and the reaction's direction. Moreover, they offer a comprehensive depiction of the molecular uniformity across diverse systems resulting from varied molecular interactions. Enthalpy (ΔH) serves as a direct measure of the interference forces between the adsorbed particle and the adsorbent surface. Simultaneously, entropy (ΔS) gauges the disorder and randomness of molecules on the adsorption surface, while Gibbs free energy (ΔG) distinguishes the spontaneity of a reaction or change. These thermodynamic variables can be computed through the van't Hoff relation, as formulated by the Dutch chemist Jacobus Henricus van't Hoff in 1884 (Equation 17) [26].

$$\ln k_{ad} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \tag{17}$$

The thermodynamic equilibrium coefficient of adsorption can be calculated by Equation (18) [26]

$$k_{ad} = \frac{q_e}{C_e} \tag{18}$$

Graphing the correlation between ($\ln k_{ad}$) and ($1/T$) results in a linear representation, where the slope denotes (ΔH), and (ΔS) can be computed from the intercept. The system's Gibbs free energy (ΔG) is ascertainable through Equation (19) [26] as follows:

$$k_{ad} = \frac{q_e}{C_e} \tag{19}$$

Figure 8 illustrates the outcomes of the thermodynamic investigation, and the values for the three thermodynamic functions are detailed in Table 3. As widely acknowledged, thermodynamic functions (ΔH), (ΔS), and (ΔG) serve as crucial indicators in gauging the spontaneity of a process and explicating the adsorption mechanism of metal ions onto the adsorbent media's surface. Concurrently, they provide a precise method for characterizing the interference state between the solid and liquid phase surfaces. The derived data from the aforementioned figures and tables, pertaining to the adsorption of vanadium onto the alumina surface, suggest that the thermodynamic equilibrium coefficient k_{ad} diminishes with an increase in time (t). This may be attributed to elevated temperatures causing a breakdown in the bonding bonds between the ions of the adsorbent metals and their associated active sites on the adsorption surface, subsequently resulting in the ions being released and returning to the solution [46]. The alteration in the enthalpy function, represented by (ΔH), consistently yielded negative values. This observation signifies that the studied adsorption process of heavy metal ions on the surfaces of adsorption materials is an exothermic phenomenon.

Additionally, it's noteworthy that the adsorption, particularly for vanadium using alumina, was of a chemical nature, specifically chemisorption [47]. This phenomenon can be attributed to the enthalpy value exceeding 40 kJ/mol, indicating heightened interaction between the adsorbed metal ions and the adsorption surface.
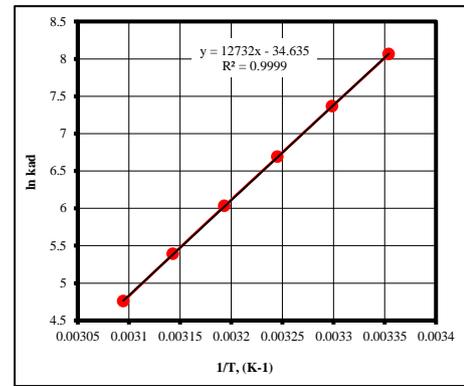

Figure 8. Thermodynamic behaviour of vanadium adsorption using alumina

Table 3. Thermodynamic Functions of vanadium adsorption using alumina

Temp., (°C)	ΔH, (kJ/mol)	ΔS, (J/mol. K)	ΔG, (kJ/mol)
20			-21.4409
25			-20.0011
30			-18.5612
35	-105.86	-287.9714	-17.1213
40			-15.6815
45			-14.2416
50			-12.8018

This heightened interaction arises from a chemical reaction, leading to the formation of new types of electronic bonds with the functional groups on the surface of adsorbent material [48]. The consistently negative values of the entropy function change, (ΔS), in all adsorption experiments using alumina suggest a reduction in the state of randomness at the surface interface between the solid and liquid phases during the adsorption process. Furthermore, it reflects the surface affinity for the adsorption of vanadium heavy metal ions from the solution [49]. The negativity of the entropy function implies that the adsorbed molecules attain a greater uniformity compared to their state in solution during the adsorption process. This phenomenon can be ascribed to the exchange between heavy metal ions and less mobile ions on the material's surface, resulting in a reduction in entropy throughout the adsorption process. Furthermore, the adsorption of heavy metal ions, as studied using the adsorption material, is determined to be spontaneous under the experimental conditions investigated, given the negative values of the Gibbs free energy change, (ΔG) [44]. This signifies that the adsorption of vanadium ions onto the adsorption sites in alumina is a spontaneous process, necessitating no external energy input for its completion. Moreover, the reduction in the negative value of the Gibbs free energy, corresponding to an increase in system temperature, implies a decrease in spontaneity. This indicates a preference for lower temperatures in the adsorption process.

4. Conclusions

The adsorption of vanadium metal onto alumina conforms to the Langmuir and Freundlich isotherm models, displaying a high correlation coefficient of 0.9999. Whereas it aligns less effectively with the Temkin isotherm, reflected in the lower correlation coefficient. This indicates that vanadium

adsorption on alumina occurs in a monolayer surface with a restricted number of identical sites and a uniform distribution of particle binding energy on the adsorbent surface. In terms of kinetics, the adsorption is best represented by the pseudo-second-order kinetic model with an impressive correlation coefficient of R²=0.9999. Conversely, other models rank as follows based on their correlation coefficients: *Pseudo First Order model > Elovich model > Intra-particle diffusion model*. Thermodynamically, the adsorption is a spontaneous endothermic process, evident in the negative enthalpy change $(\Delta H = -105.86 \, kJ/mol)$. The system's randomness increases, as indicated by the positive entropy change $(\Delta S = -287.9714 \, J/mol.K)$, while the Gibbs free energy change values remain negative across all temperatures. Many kinds of wastes can be disposed of using this economical and environment-friendly method with zero residue level (ZRL).

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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