Isothermal, Kinetic, and Thermodynamic Studies on the Adsorption of Molybdenum by a Nanostructured Magnetic Material

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Abstract

In this study, the magnetic 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) – poly (4-vinylpyridine) (P4VP) was synthesized and characterized. Removal of Molybdenum (Mo) from aqueous solutions using prepared material as nanosorbet was investigated. The magnetic P4VP was prepared by copolymerization of P4VP with TMSPMA. The prepared adsorbent was characterized by various techniques including the X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR). The batch adsorption was applied and the effect of several important parameters such as pH of the aqueous solution, adsorbent dose, initial Mo(VI) concentration, contact time, and temperature was evaluated. Desorption behavior of Mo(VI) and the effect of foreign ions (Cd²⁺, Ca²⁺, Co²⁺, Fe³⁺, Ba²⁺ and Pt⁴⁺) in real samples were also investigated. Co (II) and Pt (IV) had a greater impact on the adsorption process than other foreign ions. The maximum capacity for Mo(VI) adsorption on the prepared adsorbent was 4.87 mg/g, which was obtained at a temperature of 40°C with an initial concentration of 10 mg/L (of Mo(VI)). The adsorption isotherms were best fitted with the Weber Van Vliet isotherm model. The kinetic data were fitted well with the pseudo-second-order equation with a high correlation coefficient (R² > 0.99). Based on the negative standard Gibbs free energy change (ΔG° < 0) and the positive standard enthalpy change (ΔH° > 0), it was found that the adsorption was an endothermic and a spontaneous process in nature.

Keywords: Molybdenum removal, Batch adsorption, 3-(trimethoxysilyl) propyl methacrylate, Poly (4-vinylpyridine), Magnetic nanosorbet

1. Introduction

Molybdenum (Mo) has important applications for different fields. Mo can be used as an alloying agent in cast iron, steels, reactor vessels, and special batteries due to its various properties. Mo is also applied in solid lubricants, automotive industry, plastics and rubber industry, aircraft engines, glass industry, pigments (for paints, coatings and inks), as well as in electronics industry. There are high concentrations (>5 ppm) of molybdate (MoO₄²⁻) in the environment, which have harmful effects on humans, vegetables, and Animals (1). An examination of the environmental hazards of Mo showed that it is generally a hazardous substance and if swallowed, it can cause severe poisoning. Symptoms of acute poisoning include severe irritation of the gastrointestinal tract with diarrhea, coma, and death from heart failure. It affects the nervous and pulmonary systems in much the same way as it affects the respiratory tract, and it can also cause skin allergies and severe damage to the eyes. This element is flammable in powder form (2). Mo is the most concentrated trace metal in seawater due to its high stability and weak adsorption. Given the above-mentioned reasons, the separation of Mo is mandatory. Molybdenum-99 (⁹⁹Mo) is a radionuclide used in the nuclear fields and medical practices (2-4). Mo belongs to the fission products and is contained in significant concentrations in highly radioactive waste. Due to the complex chemical properties of Mo, soluble and insoluble complexes are formed. In particular, several problems occur in the concentration, storage, and solidification of high-quality waste (5). The proposed methods for removing molybdate (molybdate includes Mo(VI) ion) from aqueous solutions have been described with various adsorbents, namely carbon cloths (6,7), aluminum oxides (8), pyrite (9,10), natrolite (11), goethite (9), and iron oxide gel (12). Nanomaterials are kinds of materials that have a particle size of 100 nm or
less with particular specifications (13). Many researchers have reported the application of different nanosized adsorbents such as nanoparticles (NPs) and nanotubes (14). Recently, the preparation of magnetic nanoparticles (MNPs) has received a lot of attention because of its various technological applications in water purification, photocatalysis and other separation processes (such as extraction bioseparation (15-17), and separation of different ions (17-32). The MNPs are effective adsorbents due to their large specific surface area, low toxicity, and superparamagnetic behavior. Due to their magnetic properties, they can be used for effective separation in a short time using an external magnetic field (33). Chemical modification and surface functionalization of adsorbents make it possible to use them in various physical, chemical, and biological conditions (34). The Fe₃O₄ MNPs have received a great deal of attention in various academic and technological applications because of their inherent properties (35-37). The present study aimed to synthesize the magnetic poly (4-vinylpyridine) (P4VP), which was prepared by copolymerization of P4VP with 3-(trimethoxysilyl) propyl methacrylate (TMSPMA). The physical and chemical characteristics of the synthesized adsorbent were specified. The adsorbent efficiency in removing Mo(VI) ions from aqueous solutions was investigated. Several important parameters were evaluated and optimized. The kinetic, isotherm, thermodynamic, and error investigations were also performed.

2. Materials and Methods
Sodium molybdate dihydrate (Na₂MoO₄·2H₂O) was prepared by diluting a 1000 mg/L Mo(VI) solution. All chemicals and reagents applied in this study were purchased from Merck Company (Merck, Darmstadt, Germany) and met the analytical standard. All solutions were prepared with deionized and double-distilled water. The prepared adsorbent was characterized by several techniques including Fourier-transform infrared spectroscopy (FTIR) (Shimadzu, FT-IR4300 spectrophotometer in the range of 400-4000 cm⁻¹), X-ray powder diffraction (X’pert, Philips, Holland in the 2θ range of 5-100°), and scanning electron microscopy (SEM) (Hitachi S-4160 scanning electron microscope). The concentration of metal ions was determined by inductively coupled plasma (ICP) (Varian liberty 150 XL).

2.1. Synthesis and Functionalization of Fe₃O₄ NPs
First step: FeCl₃·4H₂O (3.32 g, 0.05 mmol) and FeCl₂·6H₂O (5.4 g, 0.06 mmol) were added to a water solution (80 mL). Ammonia solution (25 wt %) was added to the mixture to adjust the pH value to 9. The resultant mixture was kept at room temperature for 12 hours. Then the NPs were disconnected from the solution with a permanent magnetic, and washed several times with water until the pH value reached 7. Finally, the Fe₃O₄ NPs were dried in a vacuum oven at 80°C for 24 hours.

Second step: The purified Fe₃O₄ NPs were added to 45 mL deionized water. Then, 2.0 mL of TMSPMA was added to the Fe₃O₄ NPs solution under mechanical agitation at room temperature. Surface silanization of Fe₃O₄ MNPs was performed for 24 hours. Then, Surface modified Fe₃O₄ MNPs were gathered and rinsed with deionized water several times by a magnet (Fig. 1).

Third step: TMSPMA-functionalized Fe₃O₄ (2.5 g) and 500 mL of Toluene were added to the 1-L flask and then the mixture was subjected to ultrasound for 10 minutes. After dispersing, 7.0 g of 4-vinylpyridine was monomerically dissolved in the mixture. Then 0.07 g of AIBN was added to the piston and the reaction container was warmed to 70°C for initiating solution polymerization under N₂ atmosphere and agitation for 24 hours. After the polymerization step, the resolution was rinsed once with acetone, and the free P4VP was extracted in Soxhlet apparatus with hot methanol for 36 hours. Finally, P4VP-grafted Fe₃O₄ MNPs were prepared. The formation of functionalized NPs is shown in Fig. 2.

2.2. Batch Sorption Studies
Batch sorption experiments were performed by setting the precise quantity of Fe₂O₃/SiO₂/P4VP nanosorbent in 25 mL solution under different situations. The primary pH value of the aqueous solution was set with 0.1 M HNO₃ and 0.1 M NaOH or 0.1 M NH₃. The effect of the most important parameters in different ranges (these ranges were chosen based on similar studies) was investigated as follows:

1. The aqueous solution pH values were varied between 1.5 to 9, at 25°C and time of 210 minutes.
The adsorbent dose values were varied between 0.01 and 0.1 g, at a temperature of 25°C, in 210 minutes contact time, and with optimum pH.

3. The metal concentrations were varied between 0.5–3 mg/L, at a temperature of 25°C, in 210 minutes contact time, and with optimum pH and adsorbent dose.

4. The influence of contact time was examined by changing the time from 5 to 120 minutes, at 25°C and with selected pH value, adsorbent dosage, and initial concentration.

5. The impact of temperature was investigated in the range of 20–40°C, in 210 minutes, and with an optimum pH, adsorbent dose and initial concentration.

The percentage of removal efficiency (1), desorption (2) and the adsorption capacity (3) for Mo(VI) ions were determined based on the following formulas:

\[
\text{removal efficiency} \% = \frac{C_0 - C_e}{C_0} \times 100 \\
\text{desorption} \% = \frac{m_d}{m_a} \times 100 \\
\text{adsorption capacity} (q_e) = (C_0 - C_e) \times \frac{V}{m}
\]

Where \( C_0 \) and \( C_e \) (mg/L) are the initial and equilibrium liquid-phase concentrations of metal ions, respectively. The value \( q_e \) (mg/g) is the sorption capacity. Values \( m_d \) and \( m_a \) are the desorption and adsorption of ions from the adsorbent surface (mg), respectively. \( V \) (L) is the volume of the solution and \( m \) (g) is the weight of dried used adsorbent.

3. Results and Discussion

3.1. Adsorbent Characterization

3.1.2. FT-IR Spectroscopy

To ascertain the presence of SiO\(_2\) and P4VP on Fe3O4 MNPs, FTIR spectra were provided from Fe3O4 MNPs, Fe\(_3\)O\(_4\)/SiO\(_2\), and Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP (Fig. 3). From the FTIR spectra shown in Fig. 3 (curve a), it is evident that the characteristic peak of Fe3O4 MNPs appeared at 588 cm\(^{-1}\). This band was shifted to a high wave number compared to the Fe-O bond peak of bulk magnetite at 570 cm\(^{-1}\) due to nanoparticle size (38). The Si–O–Si bond’s asymmetric stretching vibration at 1100 cm\(^{-1}\) and symmetric stretching vibration at around 800 cm\(^{-1}\) appear in Fe\(_3\)O\(_4\)/SiO\(_2\) and Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP spectra (Fig. 3 (curve b and c)), which indicates that the silica has successfully coated on the surface of Fe3O4 NPs.

Moreover, the peaks around 1583, 1463, and 1367 cm\(^{-1}\) which occurred in Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP spectra, could be...
Fig. 4. (A) Effect of pH, (B) Sorbent Dosage, and (C) Initial Concentration of Mo(VI) on the Sorption of Mo(VI) Ions by Adsorbent, (D) Desorption Results of Mo(VI) from Adsorbent Surface at Different Solvents, (E) Effect of Contact time at Different Temperatures on the Adsorption and Desorption Processes, (F) Effect of Temperature on the Adsorption of Mo(VI) Onto the Adsorbent.

assigned as features of pyridine cycle and amine in the P4VP molecules. The absorption bands at about 3430 and 1650 cm\(^{-1}\) in all the spectra mainly originate from the –OH vibrations in H\(_2\)O. Based on the presence of bands in the range of 2848–2906 cm\(^{-1}\) and 1427 cm\(^{-1}\), which correspond to the -CH\(_2\) stretching vibration in P4VP / Fe\(_3\)O\(_4\) / SiO\(_2\) FTIR spectrum (black line in FTIR spectra), one can deduce that the P4VP molecules are bonded to the surface of Fe\(_3\)O\(_4\) / SiO\(_2\).

3.1.3. XRD Pattern
Fig. 1 shows the X-ray diffraction result of the base magnetite particles. The result revealed diffraction peaks at \(2\theta = 30.13, 35.54, 43.11, 53.73, 57.30\) and 62.77, which are characteristic peaks of magnetite (Fe\(_3\)O\(_4\)) crystals (39). The average diameter which can be evaluated from the Scherrer equation \((D = 0.9\lambda / \beta\cos\theta)\), where \(D\) is the average diameter, \(\lambda\) is the x-ray wavelength, \(\beta\) is the full width at half maximum and \(\theta\) is the x-ray diffraction angle, is 42.4 nm. The XRD pattern of Fe\(_3\)O\(_4\)/SiO\(_2\) NPs (Fig. 3) revealed that the binding and TMSPMA did not cause any measurable change in the phase property of Fe\(_3\)O\(_4\) cores. This could be attributed to the fact that the binding and TMSPMA occurred only on the surface of
the FeO$_4$ cores to form a core-shell structure.

3.1.4. Scanning Electron Microscopy
For obtaining more direct information on particle size and morphology, the SEM micrograph of base magnetite particles, Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$/SiO$_2$/P4VP were provided. SEM photographs showed that the silanized MNPs (Fig. 3b) were roughly spherical in shape, and the average size of these particles was very close to the average size of base magnetite particles (Fig. 3a). The size distribution was 35.1–40.6 nm in base magnetite particles which almost matches the calculated value by the Scherrer equation. Fig. 3b, c represents the SEM images of Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$/SiO$_2$/P4VP. The morphology and size almost maintained the original state (32.8 and 36 nm, respectively).

3.2. Adsorption Investigations
3.2.1. Effect of pH
The pH of the solution is an essential agent that has a great impact on the adsorption of metal ions. This is strikingly due to the difference in chemical characteristics of the sorbent, sorbate, and the ionization of dissolved ions, which can change the kinetic and equilibrium properties of the sorption process (40). Batch sorption experiments of Mo(VI) were performed by putting 0.01 g of Fe$_3$O$_4$/SiO$_2$/P4VP nanosorbent in 25 mL of the metal solutions (2 mg/L) for 210 minutes. The pH value of the solutions was regulated with 0.1 M HNO$_3$ or 0.1 M NaOH. The pH value was evaluated in the range of 1.5 to 9. The adsorption efficiency of Mo(VI) on the adsorbent as the purpose of initial solution pH (1.5–9) is shown in Fig. 4A. At a pH value of 2.5 and minor quantities, there was a powerful condition to develop a chelate complex with the amine combinations of the sorbent between H$^+$ and Mo (VI) ions. This was due to the condition in which by reducing the pH, the protonation percentage of the amine combinations increased and, conversely, the number of active sorption sites for the metal ions adsorption decreased. By increasing the pH from 2.5 to 3.5, the positive charge density of the sorption reduced (due to the decrement in H$^+$ concentration), and the active positions of the sorbent easily absorbed the metal ions. The adsorption efficiency for Mo(VI) was obtained with 89.8% (at pH = 3.5). At pH values above 3.5, the metal ions precipitated out as metal hydroxide due to the high concentration of OH anions. Therefore, the optimal pH range of 3.5 was chosen.

3.2.2. Effect of Adsorbent Dose
The effect of the adsorbent dose on the amount of Mo (VI) sorption is shown in Fig. 4B. The sorption of Mo(VI) by the synthesized material (Fe$_3$O$_4$/SiO$_2$/P4VP) was examined by changing the mass of sorbent in solutions, while keeping other parameters constant. By increasing the sorbent amount from 0.01 to 0.04 g, the adsorption efficiency was increased from 61.5 to 82.3%; but by rising it from 0.04 to 0.1 g, the adsorption efficiency was decreased. By increasing the sorption dose with a uniform metal ion concentration, the sorption sites are not saturated completely. At higher ratios of the mass of the adsorbent to concentration of metal ions, there was a surface sorption causing the metal ion concentration to decrease again when the ratio was reduced. This phenomenon is because of the fact that a specific quantity of sorbate can be separated by a solid enrichment of the adsorbent. The metal ions adsorbed causes a decrease in dose of the sorbent, which is due to a decrease in the concentration gradient between the concentrations of metal ions in the solution and on the surface of the sorbent. In addition, this reduction can be attributed to a partial covering or aggregation of sorption sites, which leads to a reduction in the total accessible sorbent surface for the metal ions and to an extension of the path of propagation (41,42). Finally, the best adsorbent dose was determined to be 0.04 g.

3.2.3. Effect of Initial Concentration
The effect of initial concentration (C$_0$) on the adsorption characteristics was intensively investigated for Fe$_3$O$_4$/SiO$_2$/P4VP by varying C$_0$ of Mo(VI) from 0.5 to 3 mg/L at 25°C. The remaining conditions stayed fixed (no change) over the course of the tests. The results are shown in Fig. 4C. Under optimum conditions, the adsorption efficiency of Mo(VI) increased with the expansion of the initial Mo(VI) concentration from 67% to 83.1%. The phenomenon can be attributed to the fact that the total available adsorption sites are not entirely filled with a fixed adsorbent dose, which leads to an enrichment of the adsorption percentage of adsorbate. Eventually, 2 mg/L was selected as optimum C$_0$ to continue the experiments.

3.2.4. Desorption Study
Four aqueous solutions (each 25 mL) containing Mo(VI) ions (2 mg/L) were magnetically stirred with 0.04 g of the Fe$_3$O$_4$/SiO$_2$/P4VP particles, at 25°C and for 210 minutes. The uptake amount was 84.5% for Mo(VI) ions. The loaded adsorbents were filtered-off and then were contacted with 10 mL of HNO$_3$, HCl, NH$_4$NO$_3$, and a mixture of HNO$_3$ and HCl (1 M), separately. It was observed that the adsorbed ions were desorbed quantitatively using HCl (Fig. 4D). Then, to determine the optimal concentration of HCl, the used adsorbent was transferred to 10 mL of HCl in the concentration area of 0.5–5 M. The concentration of Mo(VI) was evaluated as previously mentioned. The desorption course was also followed to extract Mo(VI) ions from wastewater and adsorbent. According to the results shown in Table 1, HCl 1 M Mo(VI) is suitable for recovery.

3.2.5. Effect of Contact Time and Temperature
The variations of Mo(VI) sorption amount in relation to the contact time in various temperatures (20, 30 and
40°C) were investigated (Fig. 4E). The other parameters stayed constant during the experiments. As it can be stated, the sorption of the Mo(VI) ions occurs in two stages: the first stage involves an external diffusion that follows the introduction of the metal ions into the outer surface of the adsorbent, which is a quick step (rapid phase). The second stage comprises a pore diffusion which follows the sorption of the metal ions on the inner surface of the adsorbent (drag phase). It was evident that the amount of Mo(VI) adsorbed was increased by an increase in the temperature. For Mo ions, the sorption rate was immediate within the first minutes (10 minutes), and this rate gradually decreased as it reached equilibrium. It was concluded that the sorption of Mo(VI) species onto the Fe₃O₄/SiO₂/P4VP sorbent was an endothermic process. Ultimately, sorption is inherently exothermic and diffusion is an endothermic process. With an increase in the amount of adsorption due to rising temperatures, it was concluded that the role of the diffusion process had been more significant than the sorption progress. Under corresponding initial Mo(VI) concentrations from 0.5 to 10 mg/L, the adsorption capacity of Mo(VI) increased with an increase in temperature from 20 to 40°C. The temperature effect on the sorption capacity at the equilibrium state is demonstrated in the Table 2 and Fig. 4F.

### Table 1. Desorption Results of Mo(VI) from Fe₃O₄/SiO₂/P4VP Surface With HCl as Stripping Agent at Different Concentrations

| HCl Concentration (M) | Recovery (%) |
|-----------------------|--------------|
| 0.5                   | 45.65        |
| 1                     | 98.0         |
| 2                     | 53.0         |
| 3                     | 45.45        |
| 4                     | 58.35        |
| 5                     | 47.85        |

### Table 2. Equilibrium Results With Mo(VI) Ions Initial Concentrations From 0.5 to 10 mg/L and Temperatures 293, 303 and 313 k

| C₀ (mg/L) | T (K) | Cₑ (mg/L) | Kd | q (mg/g) | Cₑ (mg/L) | Kd | q (mg/g) | Cₑ (mg/L) | Kd | q (mg/g) |
|-----------|-------|-----------|-----|----------|-----------|-----|----------|-----------|-----|----------|
| 0.5       | 293   | 0.404     | 0.216 | 0.06     | 0.261     | 1.110 | 0.149     | 0.075     | 5.130 | 0.266    |
| 1         | 293   | 0.541     | 0.702 | 0.287    | 0.400     | 2.222 | 0.375     | 0.111     | 6.538 | 0.556    |
| 2         | 293   | 0.853     | 1.075 | 0.717    | 0.783     | 2.467 | 0.760     | 0.256     | 5.366 | 1.090    |
| 4         | 293   | 1.120     | 2.162 | 1.800    | 1.374     | 2.735 | 1.641     | 0.784     | 3.409 | 2.010    |
| 6         | 293   | 1.412     | 2.784 | 2.866    | 1.828     | 3.142 | 2.608     | 1.165     | 3.519 | 3.022    |
| 8         | 293   | 1.701     | 3.114 | 3.937    | 2.520     | 3.111 | 3.425     | 1.688     | 3.108 | 3.945    |
| 10        | 293   | 2.369     | 2.654 | 4.769    | 3.510     | 2.761 | 4.056     | 2.210     | 2.866 | 4.869    |

### 3.2.6. Sorption Kinetics

Kinetics of the adsorption process is extremely important and remarkable for modeling and designing the sorption developed in the industries, as well as for describing the adsorption rate of dissolved substances, and it determines the time required for the adsorption reaction. Therefore, the kinetics of the removal of Mo(VI) ions was determined in this study in order for determining the sorption behavior of Fe₃O₄/SiO₂/P4VP. Various kinetic models were considered to describe the experimental data obtained from the experiments, and to clarify the development of the kinetic sorption (Table 3). The pseudo-first order, pseudo-second order, and intraparticle diffusion types were all analyzed to describe the kinetic data obtained from the experiments. The parameters including rate constants (k₁, k₂) and correlation coefficients were computed; the calculated parameters are shown in Table 4 and Fig. 5. The correlation coefficient values of the pseudo-first-order model were lower than the pseudo-second-order model. As can be seen in Table 4 below, the pseudo-second order model belongs to the kinetic data and describes the data more consistently due to the high value of the correlation coefficient (R² > 0.99). The temperature effect on the adsorption rate constant was determined using the Arrhenius-type relationship (Table 3). The k₀ of Eₐ were 7.9×10¹² g/mg.min and 82.5497 kJ/mol with a C₀ of 2.0 mg/L. The magnitude of activation energy showed a type of adsorption that was physical or chemical. Achieving activation energy of 5–40 kJ/mol coincides with physisorption mechanism, while achieving activation energy of 40-800 kJ/mol coincides with chemisorption mechanism(32). The activation energy (Eₐ) in this study was 82.5497 kJ/mol, which is associated with chemisorption and has a higher potential.

### 3.2.7. Adsorption Isotherms and Thermodynamic Properties

Adsorption isotherm data obtained from the experiments were examined by the Generalized, Fritz
Table 3. Isotherms, Kinetics, and Other Equations Used in This Study

| Models / Equations                  | Parameters                                                                 |
|-------------------------------------|-----------------------------------------------------------------------------|
| Generalized model                   |                                                                              |
|                                     | $q_e = q_m C_e^{ag} / (1 + C_e^{ag})$                                       |
|                                     | $q_e$ (mg/g): equilibrium adsorption capacity                               |
|                                     | $q_m$ (mg/g): maximum adsorption capacity                                   |
|                                     | $C_e$ (mg/L): equilibrium adsorbate concentration in solution               |
|                                     | $ag$: generalized equation exponent                                        |
|                                     | $K_g$ (mg/L): generalized constant                                          |
| Fritz Schlunder model               |                                                                              |
|                                     | $q_e = K_f q_m C_{nf}^{mf} / (1 + K_f C_{nf}^{mf})$.                         |
|                                     | $K_f$ (mg/g/mg/L): fritz schlunder constant                                 |
|                                     | $K_m$ (mg/L): Fritz Schlunder constant                                       |
|                                     | $nf$: fritz schlunder equation exponent                                    |
|                                     | $mf$: fritz schlunder equation exponent                                    |
| Weber Van Vliet model               |                                                                              |
|                                     | $C_e = K_w q_e^{(nm q_e + nw)}$                                              |
|                                     | $K_w$: weber van vliet constant                                             |
|                                     | $nm$: weber van vliet equation exponent                                     |
|                                     | $nw$: weber van vliet equation exponent                                     |
| Pseudo-first-order kinetic model    |                                                                              |
|                                     | $ln((q_e - q_t) / (1 - q_e / q_m)) - ln q_e = k_1 t$.                        |
|                                     | $q_e$ (mg/L): amount of adsorbate adsorbed at time t                         |
|                                     | $k_1$ (min$^{-1}$): pseudo-first-order rate constant                        |
| Pseudo- second order kinetic model  |                                                                              |
|                                     | $t / q_e = 1 / k_2 q_m^2 + t / q_m$                                         |
|                                     | $k_2$ (g mg.min$^{-1}$): pseudo-second-order rate constant                 |
|                                     | $t$ (min): time                                                             |
| Intraparticle diffusion model       |                                                                              |
|                                     | $q_t = k_p t^{1/2} + C_t$                                                   |
|                                     | $k_p$ (mg/g.min$^{1/2}$): intraparticle diffusion rate constant             |
| Arhenius equation                   |                                                                              |
|                                     | $k = k_0 e^{-F_a / RT}$                                                     |
|                                     | $k_0$: Arrhenius constant                                                   |
|                                     | $F_a$ (kJ/mol): activation energy                                           |
| Clausius-Clapeyron equations        |                                                                              |
|                                     | $d(ln C_e) / dt = - \Delta H^\circ / RT$                                    |
|                                     | $\Delta H^\circ$: isosteric heat of adsorption                             |
|                                     | $\Delta H^\circ$ (kJ/mol): activation enthalpy change                      |
|                                     | $\Delta S^\circ$ (kJ/mol): activation entropy change                      |
|                                     | $\Delta G^\circ$ (kJ/mol): activation Gibbs energy change                  |
|                                     | $k_B$: Boltzmann constant                                                   |
|                                     | $C_0$: equilibrium constant                                                 |
|                                     | $\Delta F^\circ$: standard enthalpy change                                 |
|                                     | $\Delta S^\circ$ (kJ/mol): standard entropy change                        |
|                                     | $\Delta G^\circ$ (kJ/mol): standard Gibbs free energy change              |
|                                     | $C_e$ (mg/L): initial adsorbate concentration in solution                   |
| Error equations                     |                                                                              |
|                                     | $RMSE = \sqrt{\frac{\sum_{i=1}^{n}(x_{obs,i} - x_{model,i})^2}{n}}$         |
|                                     | $\chi^2 = \frac{\sum_{i=1}^{n}(x_{obs,i} - x_{model,i})^2}{x_{model,i}}$   |
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Schlunder and Weber Van Vliet isotherm models. The forms can be explained by equations (see Table 3). The three models adsorption isotherms are presented in Table 5 and the curves are presented in Fig. 6.

The adsorption of Mo(IV) onto Fe₃O₄/SiO₂/P₄VP at different temperatures showed (Fig. 4F and Table 4) an ascent in the adsorption amount with rising temperatures. The standard Gibbs free energy change (ΔG°) is the basic principle of spontaneity. Reactions are spontaneous at a certain temperature when ΔG° has a negative value. The standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard Gibbs free energy change (ΔG°), which were associated with the adsorption course, were calculated using the equations (see Table 3). The plot of ln K_d vs. 1/T for the adsorption of Mo (VI) was drawn, which presented the values of ΔH° and ΔS° obtained from the slope and intercept, respectively. The ΔG° was also calculated based on ΔH° and ΔS° (see Table 3). The value of the obtained parameters was shown in Table 6. The ΔH° and ΔS° were found to be 61.30 kJ/mol and 209.84 J/mol K, respectively. The positive results of ΔH° suggested the endothermic nature of adsorption of the Mo(VI) ions on Fe₃O₄/SiO₂/P₄VP.

The positive ΔS° results showed the growing possibility at the interface between solid and solution during the adsorption course. The positive ΔS° of adsorption also represented the affinity of the adsorbent for the Mo(VI)
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Table 4. Parameters for Kinetic Models of Mo (VI) Sorption Onto Fe₃O₄/SiO₂/P₄VP

| T(K) | qₑ,exp (mg/g) | qₑ,cal (mg/g) | k₁(min⁻¹) | R² | Δq% |
|------|---------------|---------------|------------|-----|------|
| 293  | 0.8425        | 0.9265        | 0.0279     | 0.9059 | 9.97 |
| 303  | 1.1187        | 0.4665        | 0.0423     | 0.8724 | 56.51|
| 313  | 0.9575        | 0.7283        | 0.0265     | 0.9602 | 23.93|

Pseudo Second Order Kinetic Model

| T(K) | qₑ,exp (mg/g) | k₂(g/mg.min) | R² | Δq% |
|------|---------------|--------------|----|------|
| 293  | 0.8425        | 1.4883       | 0.9146 | 76.65 |
| 303  | 1.1187        | 1.1608       | 0.9969 | 3.76  |
| 313  | 0.9575        | 1.0352       | 0.9848 | 8.11  |

Intraparticle Diffusion Model

| T(K) | qₑ,exp (mg/g) | kᵣ(g/mg.min) | Cₑ(mg/g) | R² | Δq% |
|------|---------------|--------------|----------|----|------|
| 293  | 0.8425        | 0.8454       | 0.07717  | 0.9516 | 0.34 |
| 303  | 1.1187        | 1.5095       | 0.1378   | 0.1956 | 34.93|
| 313  | 0.9575        | 1.1042       | 1.1042   | 0.8571 | 15.32|

Solution Volume = 25 mL; Initial Mo(VI) concentrations =2 mg/L; Sorbent Dosage=0.04g; pH=3.5.

Table 5. Generalized, Fritz Schlunder, and Weber Van Vliet Isotherm Constants for the Adsorption of Mo(VI) Ions Onto Fe₃O₄/SiO₂/P₄VP

| T(K) | qₑ(mg/g) | k | n   | R² | RMSE | χ² |
|------|----------|---|-----|----|------|----|
| 293  | 5.2856   | 3.1218 | 3.9821 | 0.9979 | 0.0777 | 0.0014 |
| 303  | 5.4652   | 3.7745 | 1.9390 | 0.9956 | 0.0944 | 0.0025 |
| 313  | 2.7503×10¹⁵ | 1.0461×10¹⁵ | 0.7766 | 0.9959 | 0.1046 | 0.0021 |

Fritz Schlunder Model

| K₁ | K₂ | n   | m   | R² | RMSE | χ² |
|----|----|-----|-----|----|------|----|
| 293 | 1.4012 | 0.1013 | 3.1126 | 4.0401 | 0.9988 | 0.0596 | 0.0005 |
| 303 | 1.1307 | 0.0152 | 1.4746 | 3.1363 | 0.9979 | 0.0646 | 0.0014 |
| 313 | 8.0934 | 2.0782 | 0.7766 | 1.8276×10⁴ | 0.9959 | 0.1046 | 0.0021 |

Weber Van Vliet Model

| k | n   | m   | l   | R² | RMSE | χ² |
|----|-----|-----|-----|----|------|----|
| 293 | 0.9343 | 8.3131×10⁻¹ | 5.1146 | 5.3498 | 0.9967 | 0.0370 | 0.0005 |
| 303 | 0.9291 | 1.1208×10⁻¹ | 5.4726 | 0.7112 | 0.9989 | 0.0372 | 0.0004 |
| 313 | 0.3042 | -18.4924 | -0.0013 | 19.7058 | 0.9972 | 0.0446 | 0.0007 |

Table 6. Thermodynamic Results of Mo(VI) Ions Adsorption by Fe₃O₄/SiO₂/P₄VP in Temperatures of 293, 303 and 313

| Temperature (K) | ∆G° (kJ/ mol) | ∆H° (kJ/ mol) | ∆S° (J/ mol.K) |
|-----------------|---------------|---------------|----------------|
| 293             | -0.177        | 61.30         | 209.84         |
| 303             | -2.276        |               |                |
| 313             | -0.374        |               |                |

Table 7. Comparison Between the Results of This Study and Some Similar Studies

| Adsorbent                              | Optimal pH | Capacity (mg/g) | Best Fitted Isotherm Model | Equilibrium Time (min) | Best Fitted Kinetic Model | Reference |
|----------------------------------------|------------|----------------|---------------------------|------------------------|---------------------------|-----------|
| Fe₃O₄/SiO₂/P₄VP                        | 3.5        | 4.87           | Weber Van Vliet           | 210                    | Pseudo-second-order       | Present study |
| Modified resin with aniline formaldehyde | 5          | 3.1            | Freundlich                | 5                      | -                         | (41)      |
| Di-(2-ethylhexyl) phosphoric acid coated silanized magnetite nanoparticles | -          | 25.84          | Langmuir                 | -                      | -                         | (42)      |
| Macroporous resin                      | 7.25       | 228.2          | Freundlich                | 25                     | -                         | (43)      |
| Nanometer-sized titanium dioxide       | 1          | 2.01           |                           |                         |                           | (44)      |
ion. Negative values of \( \Delta G^o \) for Mo(VI) adsorption by Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP indicated that the adsorption process was spontaneous and feasible. Table 7 compares the results of this study with several similar works.

### 3.2.8. Effect of Foreign Ions

To judge the separation of the preconcentration system, the performance of several metal ions (5 mg/L) was investigated for the sorption behavior of Mo(VI) ions (5 mg/L). The results were displayed in Table 8. This table shows that the best competitive ions in adsorption of Mo(VI) ions onto Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP, were Co(II) and Pt(IV). The significance of other foreign ions mentioned at certain concentrations was marginal. The adsorption of Mo(VI) ions on Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP in the presence of all mentioned ions (solution volume=25 mL, adsorbent amount =0.04 g, concentration of each ion=5 mg/L) was evaluated. The Mo(VI) ions in the environmental samples can be made available quantitatively.

### 3.2.9. Application of Method

The Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP was used to preconcentrate and determine Mo(VI) ions in two real samples (Tehran tap water and spring water). The pH of the water samples was adjusted to 3.5. After detecting Mo(VI) ions in the samples, the amounts of 0.2, 0.4 and 0.6 mg/L of Mo(VI) ions were added to 25 mL of these samples and mixed with 0.04 g of adsorbent and stirred for 3.5 hours. The obtained results are presented in Table 9. These results show the practical applicability for the Mo(VI) determination in samples.

### 4. Conclusion

In this study, the adsorption isotherms, kinetic, and thermodynamic properties related to adsorption of Mo(VI) ions on Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP were analyzed using batch-adsorption techniques. The magnetic P4VP was prepared by copolymerization of P4VP with TMSPMA. Several techniques such as FTIR, SEM, and XRD were used for the characterization of the prepared adsorbent. The optimum conditions were determined for Mo(VI) ions adsorption. The values of parameters in tests were: pH (3.5), adsorbent dose (0.04 g), initial Mo(VI) ions concentration (2.0 mg/L), contact time range (0 to 120 minutes), and temperatures (20, 30 and 40°C). In desorption studies, it was found that the 1M HCl was suitable for Mo(IV) ions recovery. The adsorption of Mo(VI) ions on Fe3O4/SiO2/P4VP tends to kinetics of adsorption with high correlation Pseudo-kinetics of second order. The E\(_r\) value of 82.5497 kJ/mol reported in this study indicated that the adsorption had a higher potential in the context of chemisorption and because of the negative \( \Delta G^o \) and the positive \( \Delta H^o \), the total adsorption course was endothermic and spontaneous.

The equilibrium data were analyzed with Generalized, Fritz Schlunder and Weber Van Vliet isotherm models. The information gained from our investigation provided excellent results for the Fritz Schlunder model compared to other models. We determined the influence of other ions including Cd\(^{2+}\), Ca\(^{2+}\), Co\(^{2+}\), Fe\(^{3+}\), Ba\(^{2+}\), and Pt\(^{4+}\) on the uptake of Mo(IV) ions. The results showed that the most effective ions in the uptake of Mo(IV) ions on Fe\(_3\)O\(_4\)/SiO\(_2\)/P4VP were Co(II) and Pt(IV), while the effect of other foreign ions, which were inserted at certain concentrations, was found to be minor. The uptake

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**Table 8. Effect of Interfering Ions on Sorption**

| Interfering Ion | A (mg/L) | %E | %L | D |
|----------------|----------|----|----|---|
| Cd\(^{2+}\)    | 4.47     | 89.4 | 5.89 | 55.88 |
| Ni\(^{2+}\)    | 4.32     | 86.4 | 9.05 | 54.00 |
| Ca\(^{2+}\)    | 4.43     | 88.5 | 6.74 | 55.32 |
| Co\(^{2+}\)    | 4.14     | 84.5 | 12.84 | 52.81 |
| Fe\(^{3+}\)    | 4.46     | 89.4 | 6.10 | 55.88 |
| Ba\(^{2+}\)    | 4.51     | 90.12 | 5.05 | 56.32 |
| Pt\(^{4+}\)    | 4.17     | 83.30 | 12.21 | 52.06 |
| Mixed Above    | 4.15     | 83.00 | 12.63 | 51.88 |

\( A \): Amount of adsorbed Mo(VI), \( L=(C_{C_{Mo(VI)}^A}-C_{C_{Mo(VI)}^A})/C_{C_{Mo(VI)}^A} \): Loss adsorption (%), \( E=(C_{C_{Mo(VI)}^A}-C_{C_{Mo(VI)}^A})/C_{C_{Mo(VI)}^A} \): Extraction percentage (%), and \( D=Q/C_{C_{Mo(VI)}^A} \): distribution ratio

**Table 9. Results Obtained for Mo(VI) Ion Determination in Real Samples**

| Water Samples | Found Mo(VI) (Without Spiking) (mg/L) | Added Mo(VI) Average (After Spiking) (mg/L) | Pre-concentration Factor | Recovery (%) | SD | Relative SD (%) |
|---------------|--------------------------------------|---------------------------------------------|-------------------------|--------------|----|-----------------|
| Tap water     | 0.2                                  | 0.25                                       | 10                      | 123.4        | 0.321 | 13.03           |
|               | 0.6                                  | 0.61                                       | 10                      | 100.8        | 0.153 | 3.79            |
|               | 0.2                                  | 0.27                                       | 10                      | 83.3         | 0.153 | 5.73            |
| Spring water  | 0.12                                 | 0.42                                       | 10                      | 80.1         | 0.153 | 3.67            |
|               | 0.6                                  | 0.72                                       | 10                      | 99.5         | 0.208 | 2.90            |

ND: Not Detected; SD, standard deviation.

\( a \), for three determinations
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of Mo(VI) ions on FeO/SiO2/P4VP in the presence of all above-mentioned ions (solution volume=25 mL, adsorbent amount=0.0 4 g, concentration of each ion=5 mg/L) showed that the amount of Mo(VI) ions is measurable in the environmental samples.

Conflict of Interest Disclosures
The authors declare that they have no competing interests.

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