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PAPER

ADSORPTION BEHAVIOR OF MOLYBDENUM IONS ON A CPVC-BASED ANION-EXCHANGE SORBENT: KINETIC, ISOTHERMAL, AND MECHANISTIC ASPECTS

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Abstract

This study examines the adsorption behavior of Mo(VI) ions on a chlorinated polyvinyl chloride (CPVC)-based sorbent under static conditions at various concentrations and temperatures. Kinetic results revealed rapid initial uptake followed by a slower approach to equilibrium, suggesting a two-stage adsorption mechanism. Adsorption capacity increased slightly with increasing temperature, indicating improved ion mobility and diffusion. Equilibrium analysis revealed that the process conforms to the Langmuir isotherm model, confirming monolayer adsorption on a homogeneous surface. Thermodynamic parameters revealed that the adsorption process is spontaneous and endothermic, with increasing disorder at the solid–solution interface.

Key words: CPVC-based sorbent; molybdenum adsorption; adsorption kinetics; chemisorption; water purification.

INTRODUCTION

The increasing pollution of water resources with heavy metals and toxic oxyanions has become a serious environmental problem due to rapid industrialization and anthropogenic activities [1,2]. Among these pollutants, molybdenum, typically present in aquatic systems as molybdate ions (MoO_4^{2-}), is widely emitted by the mining, metallurgy, and petrochemical industries. Although molybdenum is an essential trace element at low concentrations, its excess presence in water can lead to ecological imbalances and adverse health effects, including metabolic disturbances and toxicity to living organisms [3]. Various methods have been developed to remove molybdenum ions from aqueous media, including chemical precipitation, membrane filtration, electrochemical treatment, and ion exchange. However, many of these methods have drawbacks, such as high operating costs,

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low selectivity, and secondary waste generation . In recent years, adsorption has emerged as a promising alternative due to its simplicity, cost-effectiveness, and high efficiency in removing ionic contaminants from water [4,5].

The development of effective adsorbents with high affinity for molybdate ions remains a key research area. Polymeric sorbents, particularly those containing nitrogen-containing functional groups, have attracted considerable attention due to their tunable structure, chemical stability, and strong interactions with anionic species. In this context, CPVC-based materials represent a promising platform due to their availability, low cost, and the presence of reactive C–Cl bonds, which enable further chemical modification [6,7].

Chemical functionalization of CPVC allows the introduction of active sites capable of interacting with molybdenum particles via electrostatic attraction, ion exchange, and complexation mechanisms [8]. The adsorption capacity of such materials is highly dependent on their surface properties, functional group density, and structural characteristics, which in turn influence adsorption kinetics and equilibrium behavior [9,10]. Despite growing interest in polymeric adsorbents, the adsorption behavior of molybdenum ions on CPVC-based sorbents, particularly in terms of kinetic modeling and adsorption isotherms, remains poorly understood. A comprehensive understanding of adsorption kinetics and equilibrium is essential for elucidating the interaction mechanism and developing effective sorbent systems [11].

Therefore, the aim of this study is to investigate the adsorption behavior of molybdenum ions on a CPVC-based sorbent, with a particular emphasis on kinetic and isotherm analysis. The results are expected to provide a deeper understanding of the adsorption mechanism and contribute to the development of effective materials for water treatment.

MATERIALS AND METHODS

Adsorption Kinetics Experiments

The adsorption kinetics of molybdenum ions onto a CPVC-based sorbent were studied under static (batch) conditions. Experiments were conducted to evaluate the effect of different initial molybdenum concentrations (0.013, 0.026, and 0.052 mol/L) and temperatures (298, 308, and 318 K) on their adsorption rate.

A known mass of the sorbent was added to the molybdenum solution, and the mixture was maintained at constant conditions for a predetermined time interval. Aliquots were taken at selected contact times, separated from the solid phase, and analyzed to determine the residual molybdenum concentration.

The concentration of molybdenum ions in the solution was determined spectrophotometrically at a wavelength of 230 nm using a predetermined calibration curve of optical density and concentration.

The specific adsorption capacity (X/m) was calculated using the following expression:

$$\frac{X}{m} = \frac{(C_0 - C_t) \cdot V}{M \cdot m}$$

X — the amount of adsorbed ions (mol)

m — the mass of the sorbent (g)

C_0 and C_t — the concentrations of ions in the solution before and after adsorption (mg/L)

V — the volume of the solution (L)

M — the molar mass of the adsorbed ion (g/mol)

The equilibrium adsorption capacity (X/m) was determined when no other significant change in concentration was observed with increasing contact time.

Kinetic modeling

The experimental kinetic data were analyzed using widely used adsorption kinetic models to determine the mechanism and rate-controlling steps of the process.

The pseudo-first-order model was expressed as:

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

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order model.

The pseudo-second-order model was described as:

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

where k_2 (g/mol min or g/mg min) is the rate constant of the pseudo-second-order model.

In addition, an intraparticle diffusion model was used to estimate the diffusion mechanism:

$$q_t = k_{id}t^{1/2} + C$$

where k_id is the intraparticle diffusion rate constant and C is related to the boundary layer thickness.

The fit of each model was assessed based on the linear correlation coefficient (R^2) and the agreement between the experimental and calculated adsorption capacities.

RESULTS AND DISCUSSION

Mo(VI) Ion Adsorption Kinetics

The adsorption kinetics of molybdenum ions on a CPVC-based sorbent was studied under batch conditions at various initial concentrations and temperatures. The amount of adsorbed molybdenum was determined spectrophotometrically using a calibration curve of optical density versus molybdenum concentration at a wavelength of 230 nm (Fig. 1).

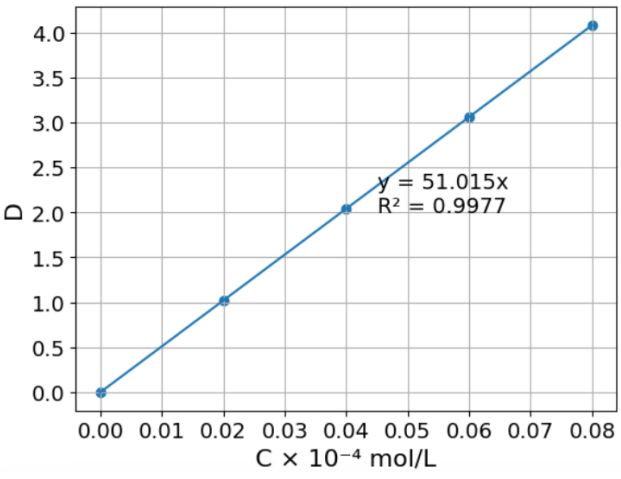

Figure 1. Calibration curve: D vs C

The kinetic curves (Figs. 2, 3, 4) show that the adsorption process is rapid at the initial stage, after which the adsorption rate gradually decreases until equilibrium is reached. This behavior can be explained by the high availability of active sites at the beginning of the process, which facilitates the rapid binding of molybdate ions. As adsorption progresses, the number of available active sites decreases, leading to a decrease in the adsorption rate.

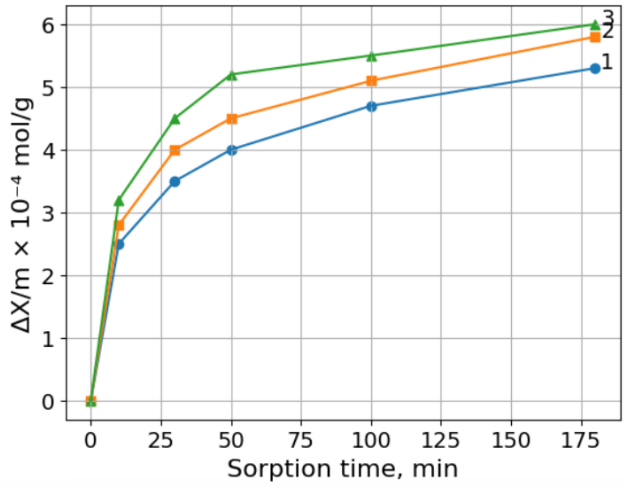

Figure 2. Kinetics of Mo(VI) sorption (C = 0.013 mol/l; T = 298, 308, 318 K)

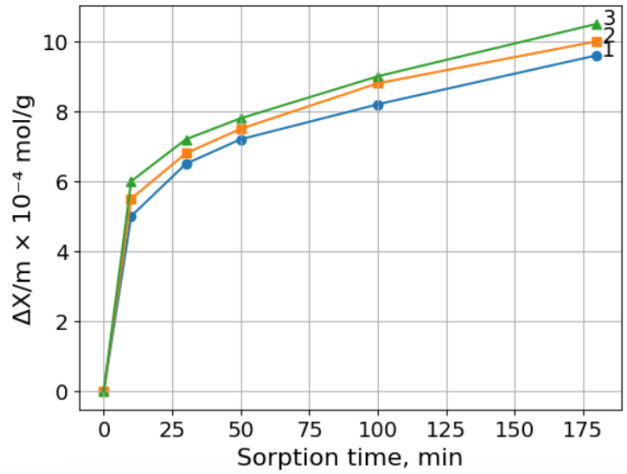

Figure 3. Kinetics of Mo(VI) sorption (C = 0.026 mol/l; T = 298, 308, 318 K)

It is also observed that increasing temperature from 298 to 318 K leads to a slight increase in adsorption capacity. This effect can be explained by the increased mobility of molybdate ions in solution and improved diffusion to the sorbent surface. However, the relatively small change in adsorption capacity suggests that the process is only moderately temperature-dependent.

Furthermore, increasing the initial molybdenum ion concentration leads to a higher adsorption capacity, indicating an increase in the driving force for mass transfer. At the same time, the adsorption rate slows with longer contact times, indicating that

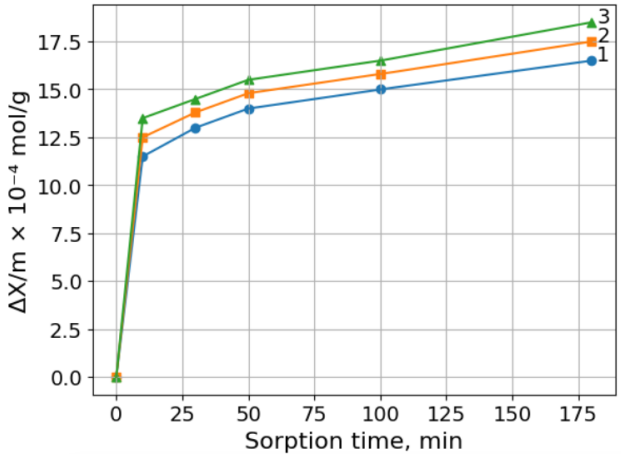

Figure 4. Kinetics of Mo(VI) sorption (C = 0.052 mol/l; T = 298, 308, 318 K)

the system approaches equilibrium and diffusion limitations significantly increase.

Overall, the kinetic behavior indicates a two-stage adsorption mechanism, consisting of a rapid surface adsorption stage followed by a slower intraparticle diffusion stage. Significant uptake at the initial stage and subsequent slowing down of the process indicate that the adsorption of Mo(VI) ions is controlled by chemisorption, which involves strong interactions between molybdate ions and the functional groups of the sorbent.

Adsorption Isotherms

The equilibrium adsorption of molybdenum ions on the CPVC-based sorbent was studied at various temperatures (298, 308, and 318 K). The corresponding isotherms are shown in Fig. 5.

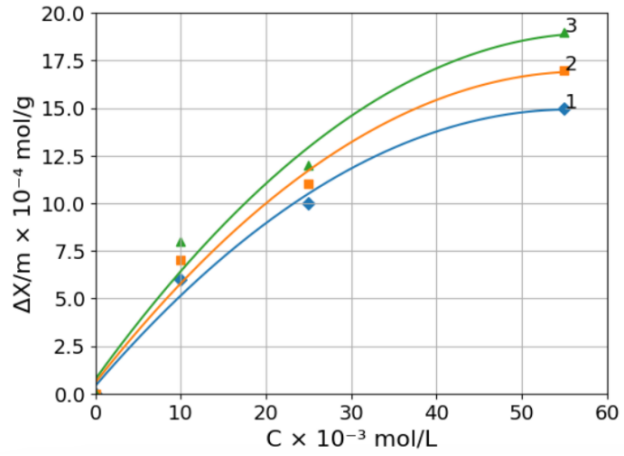

Figure 5. Sorption isotherms of Mo(VI) ions at different temperatures (298, 308, 318 K)

The results show that with increasing molybdenum concentration, the adsorption capacity increases, and the process gradually shifts to a chemisorption-controlled mechanism. This is confirmed by the significant uptake of molybdenum ions at the initial stage and a slower increase in adsorption capacity at higher concentrations.

To further analyze the adsorption mechanism, the experimental data were processed using the linear form of the Langmuir isotherm (Fig. 6). The linear relationship between 1/Γ and 1/C indicates that the adsorption process follows the Langmuir model, assuming monolayer adsorption on a homogeneous surface with a finite number of identical active sites.

c

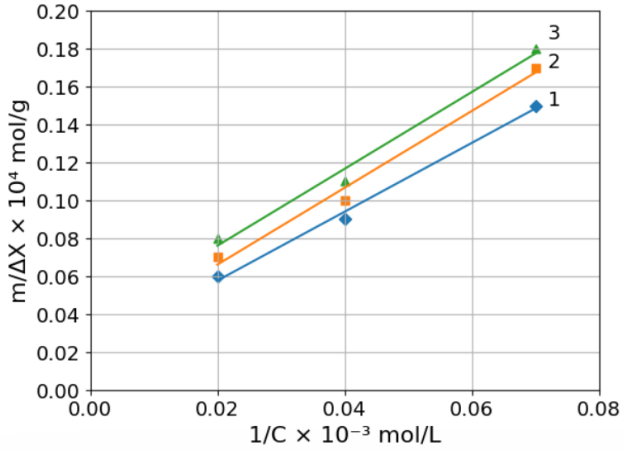

Figure 6. Dependence of 1/⊠ on 1/C for Mo(VI) sorption at 298, 308, and 318 K

These results confirm that the adsorption of Mo(VI) ions on the CPVC-based sorbent occurs primarily through specific interactions between the sorbate and uniformly distributed functional groups.

CONCLUSION

A systematic study of the adsorption behavior of Mo(VI) ions on a CPVC-based sorbent was conducted at various concentrations and temperatures. The results showed rapid initial adsorption followed by a slower equilibrium stage, indicating a two-step mechanism involving surface interaction and intraparticle diffusion. This equilibrium is well described by the Langmuir isotherm model, confirming monolayer adsorption on a

homogeneous surface. Thermodynamic analysis showed that the adsorption process is spontaneous and endothermic, accompanied by an increase in the entropy of the system. Overall, the developed PVC-based sorbent demonstrates promising potential for the efficient removal of molybdenum ions from aqueous solutions and can be considered a promising material for use in water treatment.

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