



Carminic acid modified anion exchanger for the removal and preconcentration of Mo(VI) from wastewater

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ABSTRACT

Removal and preconcentration of Mo(VI) from water and wastewater solutions was investigated using carminic acid modified anion exchanger (IRA743). Various factors influencing the adsorption of Mo(VI), e.g. pH, initial concentration, and coexisting oxyanions were studied. Adsorption reached equilibrium within <10 min and was independent of initial concentration of Mo(VI). Studies were performed at different pH values to find the pH at which maximum adsorption occurred and was determined to be at a pH between 4.0 and 6.0. The Langmuir adsorption capacity (q_{\max}) was found to be 13.5 mg Mo(VI)/g of the adsorbent. The results showed that modification of IRA743 with carminic acid is suitable for the removal of Mo(VI), as molybdate, from water and wastewater samples. The concentration of Mo(VI) was determined spectrophotometrically using bromopyrogallol red as a complexation reagent. This allows the determination of Mo(VI) in the range 1.0–100.0 $\mu\text{g}/\text{mL}$. The obtained material was subjected to efficient regeneration.

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1. Introduction

Molybdenum has long been known as one of the biologically active transition elements [1]. It is intimately involved in the function of enzymes called nitrogenases which cause atmospheric N_2 to be reduced to NH_3 or its derivatives. It also plays a role in enzymes concerned with reduction of nitrate and other biological processes [1]. Molybdenum is considered as an essential trace element for both plants and animals. The provisional recommended dietary intake is 75–250 $\mu\text{g}/\text{day}$ for adults and older children [2]. Molybdenum deficiency has often been reported, but at large concentrations it may be toxic as it leads to secondary copper deficiency [3].

Molybdenum is the most concentrated trace metal in seawater, in part owing to its stability and weak adsorption behavior. Molybdenum and its compounds are used primarily in the production of metal alloys, in thermo-couples for high temperature measurements, standard weights, blue pigments, dying silk, wool, leather, and rubber [2,4]. Subchronic and chronic oral exposures can result in gastrointestinal disturbances, growth retardation, anemia, hypothyroidism, bone and joint deformities, sterility, liver and kidney abnormalities, and death [2]. Therefore, removal of this ion from wastewaters and ground waters is of significant importance from an environmental point of view.

Different methods have been developed to remove metal ions from water samples. These include precipitation, ion exchange, membrane separation, and adsorption. Among these methods adsorption has been shown to be an economical alternative for removing trace metals from water [5–10]. The removal of Mo(VI), as molybdate, from aqueous solutions has been studied using different adsorbents like carbon cloth [5,6], goethite [11], ferric oxide gel [12], $\gamma\text{-Al}_2\text{O}_3$ [13], natrolite [14], and pyrite [11,15].

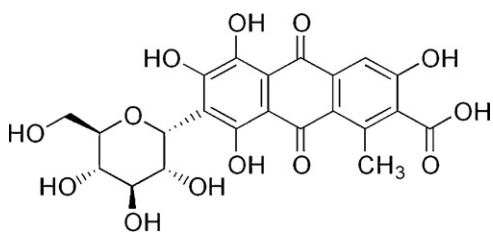
Several reports have also been published on the determination of Mo(VI) after preconcentration in different real samples. These include preconcentration and determination by inductively coupled plasma optical emission spectrometry (ICP-OES) [16], spectrophotometry [17–21] and atomic absorption spectrometry (AAS) [22–25].

Carminic acid was chosen as a model for polyol compounds which have the ability to form surface complexes with oxyanions in the lower pH range. This is due to the large number of hydroxyl groups which are positively charged at low pH and can attract negatively charged oxyanions. When using these hydroxylated compounds there is no chance for the competing effect of other competing oxyanions such as SO_4^{2-} , CrO_4^{2-} , SeO_4^{2-} and AsO_4^{2-} . The chemical structure of carminic acid is shown in Scheme 1.

In this work carminic acid was loaded on IRA743 resin (strong base anion exchanger with N-methylglucamine functional group) and dried at room temperature. The prepared resin was used for the removal of molybdate oxyanions from water wastewater samples. Removal occurs due to the fact that carminic acid has hydroxyl

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Scheme 1. Chemical structure of carminic acid.

groups that are replaceable by metal and oxygen atom which can form stable complexes. The aim of this work was to evaluate the potential applicability of removing Mo(VI) in the form of molybdate from wastewater samples.

2. Materials and methods

2.1. Instrumentation

2.1.1. Determination of oxyanions

Determination of Mo was performed using a UV/VIS spectrometer (Perkin-Elmer, Lambda 2). Total dissolved As and Se analyses of samples were carried out using a PerkinElmer atomic absorption spectrophotometer (AAS) with graphite furnace accessories (Model SIMAA 6000) and an electrodeless discharge lamp (EDL).

2.1.2. Column run

Fixed bed column runs were carried out using a glass column (11 mm in diameter), constant-flow stainless steel pumps, and an ISCO fraction collector.

Exhausted IRA743 loaded with carminic acid was regenerated using 0.5% NaOH.

2.2. Reagents and materials

Deionized water and analytical grade reagents were used for preparing feed solution. The anion exchanger used was Amberlite™ IRA743 Industrial Grade Chelating Resin. Its characteristics are depicted in Table 1.

2.3. Synthesis of adsorbent

20 g of IRA743 was treated with 0.0001 M carminic acid (Fischer scientific 90% C.I. 75470, Natural Red 4) at neutral pH and agitated for 1 h at room temperature using handmade mechanical shaker. The modified resin was washed with deionized water and dried at room temperature.

2.4. Adsorption studies

Adsorption studies were carried out by mixing 0.1 g IRA743 loaded with carminic acid with 100 mL of 100 mg/L Mo(VI) solution. The mixture was shaken for 3 h to reach equilibrium.

Table 1

Physical and chemical characteristics of IRA743 resin.

Functional groups	N-methylglucamine
Moisture holding capacity	48–54%
Mean size	0.500–0.700 mm
Uniformity coefficient	≤1.6
Maximum operating temperature	75 °C (Cl form)

2.5. Determination of Mo(VI) in wastewater samples

0.1 mL of 1×10^{-3} mol/L bromopyrogallol red and 1.5 mL of 1×10^{-3} mol/L cetyltrimethylammonium bromide (CTAB) were added to 2.5 mL of wastewater samples. The pH of solution was adjusted to 1.0 with HCl and diluted to 5 mL with deionized water. The absorbance of the solution was measured at 635 nm using a spectrophotometer.

3. Results and discussion

3.1. Effect of pH

The effect of pH on the Mo(VI) adsorption was investigated in the 2–9 range. 100 mL of solution with an initial concentration of 100 mg/L was passed through a column of carminic acid modified beads at varying pH as depicted in Fig. 1. It should be noted that the removal efficiency decreased with increasing pH and shows a maximum removal value at pH 2. This is due to the fact that the hydrogen atoms in the hydroxyl groups of carminic acid are replaceable by metal or oxygen atoms and form stable complexes with Mo. At higher pH, the negatively charged carminic acid surface sites did not favor the adsorption of Mo oxyanion due to electrostatic repulsion.

3.2. Effect of competitive oxyanions (sulfate, selenate, arsenate and chromate)

The presence of negative ions coexisting with MoO_4^{2-} invariably implies competition for available adsorption sites. Therefore, it is important to investigate the competitive influence of some anions and oxyanions.

The effects of CrO_4^{2-} , SeO_4^{2-} and AsO_4^{2-} on the adsorption of 10 ppm MoO_4^{2-} were studied with 0.1 g resin. The presence of such competing oxyanions showed significant adsorption at lower pH values due to the formation of hydrogenated oxyanions which form complexes with carminic acid hydroxyl groups [26]. Furthermore, upon raising the pH to 5.5 there is no competition between MoO_4^{2-} and the above mentioned oxyanions. For this reason all column runs were carried out at this pH. The absence of other oxy-anions competition with MoO_4^{2-} at pH 5.5 may be due the fact that the measured pK_a of carminic acid was 5.5 (Fig. 2).

Furthermore, the investigation of sulfate effect at higher concentration range (120–10,000 mg/L) does not indicate any effect on the molybdate removal as depicted in Fig. 3.

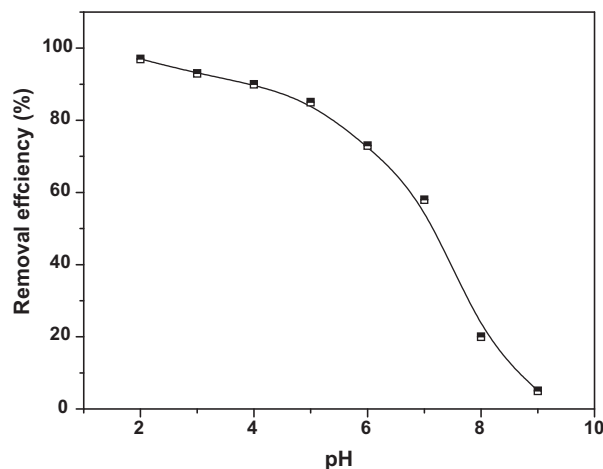


Fig. 1. pH effect on the removal of Mo(VI). Conditions: 0.1 g carminic resin, 200 mL of 50 mg/L Mo(VI).

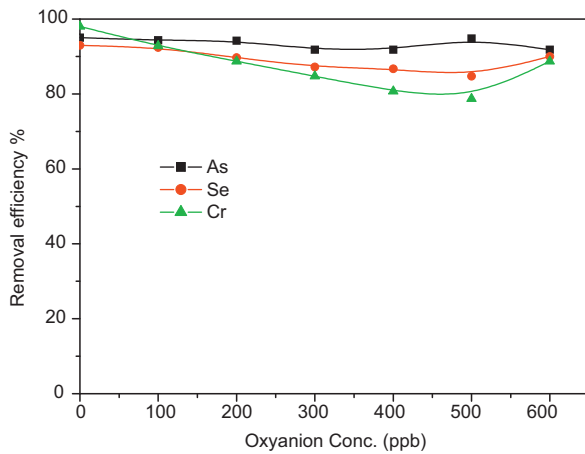


Fig. 2. Effect of oxyanions on the removal of Mo(VI). Conditions: 0.1 g carminic resin, 200 mL of 50 mg/L Mo(VI) and different concentration range 100–600 ppm of As, Se and Cr oxyanion.

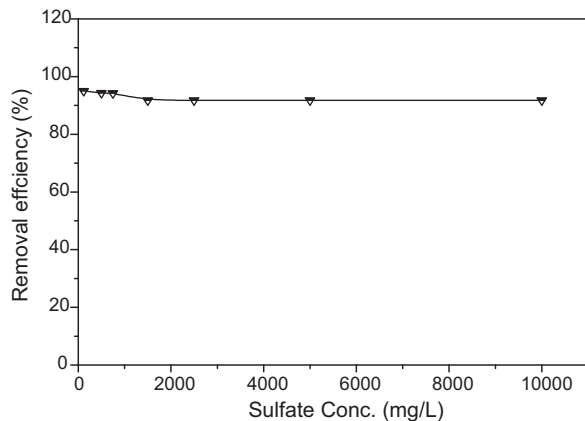


Fig. 3. Effect of sulfate on the removal of Mo(VI).

3.3. Adsorption mechanism

The surface of IRA743 modified with carminic acid is generally covered with a large number of hydroxyl groups which play an important role in the adsorption process. Surface charge of hydroxyl groups in acidic medium is positive and anion adsorption occurs. By increasing pH to 5, uptake of MoO_4^{2-} increases since there is no competition with the other oxyanions at this pH. However, by increasing the pH to 8, uptake of MoO_4^{2-} ions decreases since at higher pH the adsorption surface sites are negatively charged which increases electrostatic repulsion between MoO_4^{2-} and the adsorbent. The adsorption mechanism of molybdate can be explained as shown in Fig. 4.

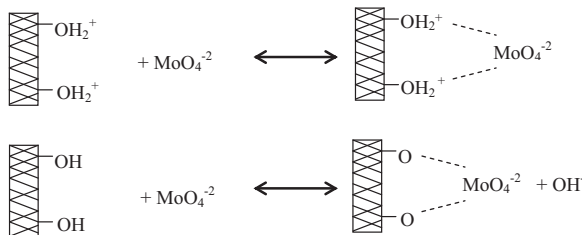


Fig. 4. Proposed mechanism for MoO_4^{2-} adsorption.

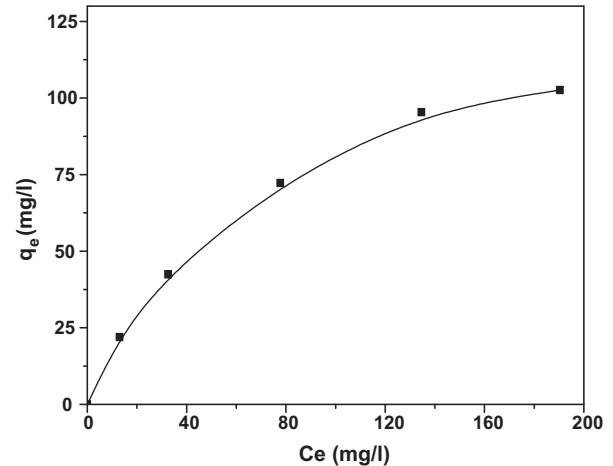


Fig. 5. Langmuir adsorption isotherm for Mo(VI) at 25 °C, pH 5.5 and 0.1 g carminic loaded IRA743 resin.

3.4. Adsorption isotherm

Adsorption isotherms are basic requirements for establishing the adsorption systems and provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. The Langmuir [27] is the most frequently used isotherm model in the literature describing the non-linear equilibrium between adsorbed pollutant and pollutant in the solution at a constant temperature. This model is simple, gives a good description of experimental behavior in a large range of operating conditions, and is characterized by a limited number of adjustable parameters.

The linearized form of Langmuir equation can be represented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mg/g, C_e is the equilibrium concentration in mg/L, q_{\max} is the maximum adsorption at monolayer coverage in mg/g, and b is the equilibrium constant related to the energy of adsorption. Langmuir model assumes uniformity in the heat of adsorption [28]. The amount of molybdate adsorbed at equilibrium per unit mass of resin, q_e , was calculated by:

$$q_e = \frac{V(C_0 - C)}{m}$$

where V is the volume of molybdate solution in L, C_0 and C_e are the initial and equilibrium concentration in mg/L, respectively, and m is the mass of adsorbent in g. The plot of q_e versus C_e is shown in Fig. 5. The linear plot of C_e/q_e versus C_e shows that the adsorption obeys the Langmuir isotherm model (Fig. 6). The Langmuir isotherm shows that the amount of Mo(VI) adsorbed increases as its concentration increases up to saturation point.

3.5. Fixed-bed column run

Fig. 7 shows the effluent history during a fixed-bed column run using IRA743 and carminic acid loaded IRA743 strong base anion exchanger. The data obtained reveals that Mo(VI) broke through almost immediately after the start of the column run with IRA743 while the carminic acid loaded IRA743 broke through after about 2500 bed volumes.

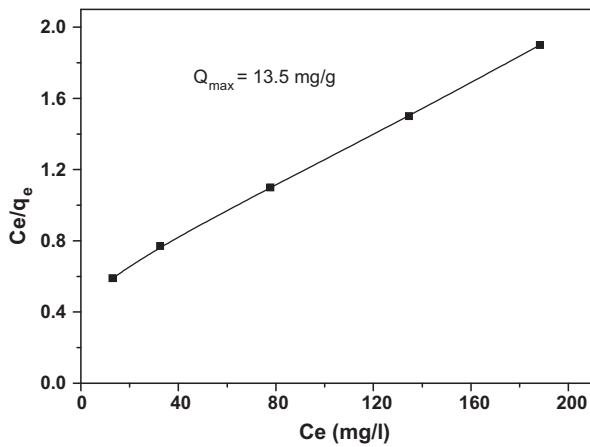


Fig. 6. Linearization of the adsorption isotherm (Langmuir) of Mo(VI).

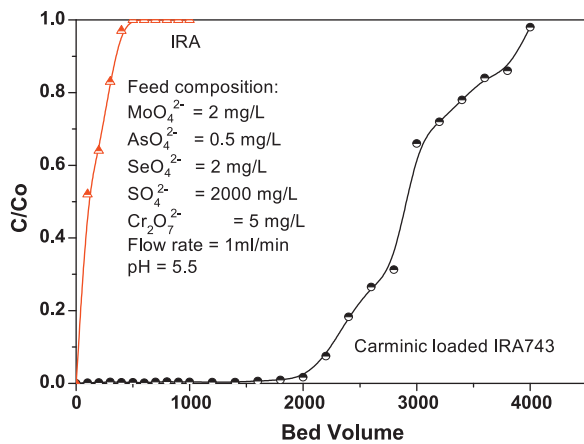


Fig. 7. Effluent history of Mo(VI) during a fixed-bed column run with carminic loaded IRA743 resin.

3.6. Regeneration, rinsing and reuse

A portion of the exhausted carminic acid loaded IRA743 was regenerated using 0.5% NaOH. Concentration profiles of molybdate during the process of desorption is provided in Fig. 8. Note that in less than 20 bed volumes, almost the entire amount of Mo(VI) was completely desorbed from the bed. It is important to mention that during the process of regeneration some of the loaded carminic

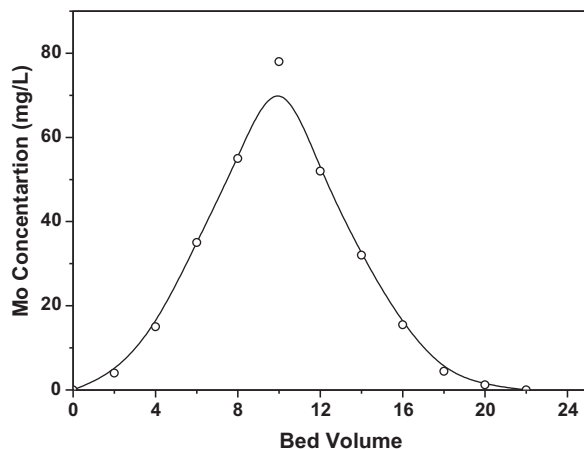


Fig. 8. Dissolved Mo(VI) concentration profile during regeneration with 0.5% NaOH.

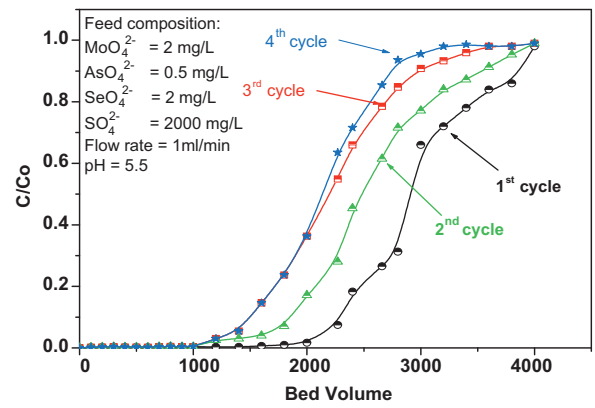


Fig. 9. Comparison of Mo(VI) effluent histories during the fixed-bed column run with regenerated carminic loaded IRA743 resin.

acid leached out with NaOH. By increasing the pH to an alkaline, carminic acid became ionized giving rise to leaching out from the resin matrix.

Following regeneration, the bed was rinsed with 0.01 M HCl to bring down pH from alkaline to near-neutral condition. For resin reuse, the regenerated and rinsed material was subjected to 4 more exhaustion/regeneration cycles to get a full idea about the resin capacity after the process of regeneration. Fig. 9 shows the results of the study; note that Mo(VI) removal capacity markedly decreased among the different cycles due to the leaching of some loaded carminic acid.

4. Conclusion

In this study the removal and preconcentration of Mo(VI) was carried out to evaluate the selective behavior of carminic loaded IRA743. Upon loading of carminic acid, the IRA743 resin possessed a huge number of hydroxyl groups which were dispersed in the gel phase of the beads. This gave rise to the selective removal of Mo(VI) species even in the presence of higher concentrations of other competitive anionic species. Following sorption, carminic acid loaded IRA743 can be efficiently regenerated with 0.5% NaOH in less than 20 bed volumes. Subsequent rinsing with 0.01 M HCl solution for less than 11 bed volumes was enough for the preparation of the column to be ready for another sorption cycle. A noticeable amount of the total carminic content of the resin leached out following the regeneration and Mo(VI) removal capacity dropped by about 15% for the 1st and 2nd cycles whereas for 3rd and 4th cycles removal capacity remains the same.

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