

MODIFICATION OF CLINOPTILOLITE BY SURFACTANTS FOR MOLYBDATE (^{99}Mo) ADSORPTION FROM AQUEOUS SOLUTIONS

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Abstract

Experiments were conducted to study the ability of surfactant-modified clinoptilolite for molybdate adsorption from aqueous solutions. Clinoptilolite was treated with some cationic surfactants. Adsorption of surfactants on zeolite surface was confirmed by chemical analysis, IR (Infra-Red Spectroscopy), DTG (Derivative Thermogravimetry) and SEM (Scanning Electron Microscopy) techniques. The modified zeolites were reacted with molybdate solutions having a known activity of radionuclide ^{99}Mo . The results indicated that surfactant modification enhances the ability of zeolite for molybdate adsorption, particularly at pHs lower than 5.5. Adsorption capacity of modified zeolite depends on the surfactant type. The presence of studied anions always reduced the adsorption of molybdate whereas Cs^+ increased it. Desorption studies showed that surfactant-modified clinoptilolite is a good candidate for removal and immobilization of ^{99}Mo .

Keywords: Clinoptilolite; Molybdate adsorption; Modified zeolites; Radionuclides

Introduction

Molybdenum-99 has a 66.7 h half-life and decays to Technetium-99m ($^{99\text{m}}\text{Tc}$). $^{99\text{m}}\text{Tc}$ produces a single 140 keV gamma ray with a 6-h half-life. ^{99}Tc is an ideal isotope for nuclear medicine imaging [1]. Therefore, ^{99}Mo increasingly is used in the preparation of ^{99}Mo - $^{99\text{m}}\text{Tc}$ generator. Its annual world consumption is more than 200,000 Ci. This radionuclide can be produced either by neutron bombardment of MoO_3 according to (n,γ) reaction or as a fission product of nuclear fission of natural or enriched uranium [2]. A significant difference of these two procedures is that ^{99}Mo obtained from fission is "carrier free". This allows production of

^{99}Mo with a specific activity of tens thousands of Ci.g^{-1} . ^{99}Mo produced by activation has the maximum specific activity of several Ci.g^{-1} . To increase the purity of ^{99}Mo , two improved processes have been developed. The first one allows purification of molybdenum of natural isotopic composition from impurities by preferential adsorption before irradiation in nuclear reactor. The second process deals with the separation of pure fission product ^{99}Mo from U-235 irradiated in a reactor. The yield of ^{99}Mo in uranium fission is 6.1%. The main fission products appear as impurity exceeds that of ^{99}Mo by a factor more than 10 and should be thoroughly removed [3]. For recovery and purification of ^{99}Mo from aqueous solutions where molybdenum is present

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as anionic species such as MoO_4^{2-} , the method of precipitation, sorption, extraction and sublimation can be used.

^{99}Mo can be precipitated by use of α -bezoin oxime [4]. The major drawback of the method is addition of a carrier or other components to the solution and also difficult remote control of the procedure.

Liquid extraction is more suitable method for recovery of ^{99}Mo from solution of irradiated uranium than fission products. Trimethyl ammonium chloride diluted with p-xylene was employed as the extracting agent for the recovery of molybdenum from alkaline solution containing an excess of sodium tungstate. The separation was found to be effective only when sulfide ion was added [5]. The sublimation procedure allows very efficient separation of ^{99}Mo from all active and inactive impurities. The procedure is more complex in practical implementation than sorption or extraction.

Different adsorbents have been proposed for separation of molybdenum. Dadachova *et al.* [6] used alumina and anion exchanger resin, AG(R)1-X8 for separation of molybdenum from nitric acid solution. The yield of ^{99}Mo was between 80-89% in both adsorbents. In the course of preparation of $^{99\text{m}}\text{Tc}$ generator, adsorption of ^{99}Mo on manganese (IV) oxide and chromatographic alumina was studied [7]. The use of a cellulose ion-exchanger (Hyphan) for separation of MoO_4^{2-} has also been investigated [8]. Selective separation of molybdenum as molybdate on inorganic gel was studied by Malik [9]. El-Absy [10] studied the adsorption behavior of Mo(IV) on activated and impregnated charcoal. Mo(IV) was found to be strongly adsorbed on activated charcoal but its elution was not easy and suffered from high tailing.

Selective separation of molybdenum by Wofatitt MK51, a synthetic ion exchanger was reported by Schilde [11]. However, high volume activity of solutions being processed limits the use of organic sorbent because of their insufficient radiation stability. Inorganic sorbents are free of this drawback. Natural zeolites, due to their large surface areas, high cation exchange capacities, favorable hydraulic characteristics, and low cost, are a major class of materials being considered for adsorption of different species. Zeolites possess a net negative structural charge resulting from isomorphic substitution of cations in the crystal lattice. This permanent negative charge results in the favorable ion exchange selectivity of zeolites for certain cations, and makes natural zeolites of interest for use in the treatment of nuclear, municipal and industrial wastewaters. This negative charge also causes natural zeolites to have little or no affinity for anions. Recent studies have shown that modification of zeolites with

certain surfactants yield sorbents with strong affinity for many anions [12].

Experimental Section

The sample was collected from a deposit known as Absard Mine placed in Absard region, Damavand in north-east of Iran. The mineral have already been characterized and known to be clinoptilolite [13]. The material were ground and screened to particle size of 224-400 μm . The ground materials were subjected to a purification process. Ultrasonic cleaning and washing were used to remove clays and other fine particles from zeolite surface. Carbonate impurities were dissolved in 1 N sodium acetate buffer solution. Treatment with sodium dithionite-citrate-bicarbonate mixture dissolved iron oxide impurities. Remaining mineral impurities (*e.g.* quartz and feldspar) were separated by density separation method in which zeolite particles were suspended in the solution in a vertical column while the dense impurities were deposited [14].

Surfactant-modified zeolites were prepared by reacting purified zeolite with different reagent-grade surfactant-bromides including hexadecyltrimethylammonium bromide (HDTMA), tetradecyltrimethylammonium bromide(TDTMA), dodecyltrimethyl-ammonium bromide (DDTMA), tetrabutylammonium bromide (TBA) and tetramethyl- ammonium bromide (TMA).

Ten grams of zeolite was treated with surfactant solution with known concentration. The mixture was mechanically shaken for 24 h at 25°C. The mixture was centrifuged, and the supernatant solution was decanted for measurement. The solid was then rinsed with deionized water several times, filtered, air dried, and stored in plastic containers before they were used for molybdate adsorption. The samples were designated as follows;

Treatment	Concentration	Designation
Zeolite treated with HDTMA	0.45 mM	ZHD _{0.45}
Zeolite treated with HDTMA	17 mM	ZHD ₁₇
Zeolite treated with HDTMA	50 mM	ZHD ₅₀
Zeolite treated with HDTMA	67 mM	ZHD ₆₇
Zeolite treated with HDTMA	100 mM	ZHD ₁₀₀
Zeolite treated with TDTMA	50 mM	ZTD ₅₀
Zeolite treated with DDTMA	50 mM	ZDD ₅₀
Zeolite treated with TBA	50 mM	ZTB ₅₀
Zeolite treated with TMA	50 mM	ZTM ₅₀

Surfactant measurement was carried out by turbidimetric method proposed by J.W. Park *et al.* [15]. A Varian Cary-3 UV-Vis spectrophotometer was used at wavelength 500 and 650 nm. Calibration curve was

linear between 0.001 to 0.007 M. (Fig. 1). Batch molybdate adsorption experiments were conducted by reacting of known amount of each sample with 10 mL molybdate-bearing solution having a known concentration of radionuclide. (special activity of the solution was adjusted to 10^{-8} Ci.ml $^{-1}$ by ^{99}Mo). The mixtures were shaken for 48 h to allow sorption equilibrium. The amount of ^{99}Mo retained on the solid was determined from the initial and final radionuclide activity in the experimental solutions. ^{99}Mo activity in initial and equilibrated solution was measured by γ -spectrometric method using an Ortec Gamma pure germanium detector under identical operational conditions. The effect of initial concentration of molybdate on the adsorption capacity of modified zeolite was studied. Adsorption measurement was also investigated at different pH values from 1 to 13. Desorption of molybdate from modified zeolite into distilled water and 0.1 M solutions of HCl, HNO $_3$, NaCl, NaOH, and NH $_4\text{OH}$ was studied at 25°C for different modified zeolites. The effect of some interferences (Cs $^+$, I $^-$, Br $^-$, Cl $^-$, TeO $_4^{2-}$, AsO $_4^{3-}$, SeO $_4^{2-}$) on the molybdate adsorption was studied when their initial concentration was 0.01 M.

Results and Discussion

Adsorption capacity of natural zeolites towards molybdate is very limited. The experiments conducted by Faghihian *et al.* [16] show that clinoptilolite do not uptake considerable amounts of molybdate from solutions (0.48 mg.g $^{-1}$). The uptake of molybdate was sharply increased by modification with surfactants through admicelle formation on zeolite surface. The amount of admicelle can be predicted from adsorption isotherm such as Figure 2. External cation exchange capacity (ECEC) of clinoptilolite, determined by the method suggested by Prikryl *et al.* [14] was 0.17 meq.g $^{-1}$. A previous study suggested that sorption of surfactant is maximized when the ECEC of the zeolite is fully satisfied by surfactant [17]. In this study, maximized adsorption was 0.33 mmol.g $^{-1}$. This capacity is almost twice of ECEC of zeolite, confirming double layer formation of surfactant on zeolite surface [17]. IR Spectrum of modified zeolites shows some new peaks around 3000 cm $^{-1}$. These peaks are related to anti-symmetrical and symmetrical stretching of -CH $_3$ and -(CH $_2$) $^-$, confirming adsorption of surfactant on the zeolite surface (Fig. 3). SEM image of modified zeolite also confirms the surfactant uptake (Fig. 4). On the thermal curve (DTG) of the HDTMA-modified zeolite, a new weight loss peak was observed around 250°C. This peak is attributed to decomposition of HDTMA

from zeolite surface. Depending on the amount of adsorbed surfactant the height of the peak was changed (Fig. 5).

Figure 6 represents molybdate adsorption isotherms of different modified samples. Exchange isotherms were constructed at 298 K. Az and As are defined as:

Az = amount of adsorbed molybdate on zeolite phases at equilibrium (mg.g $^{-1}$ of zeolite)

As = amount of molybdate in solution at equilibrium (mg.ml $^{-1}$ of solution)

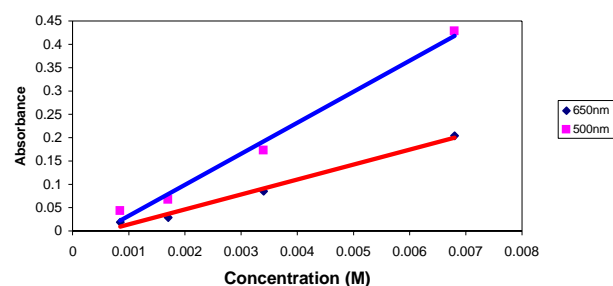


Figure 1. Turbidimetry calibration curve.

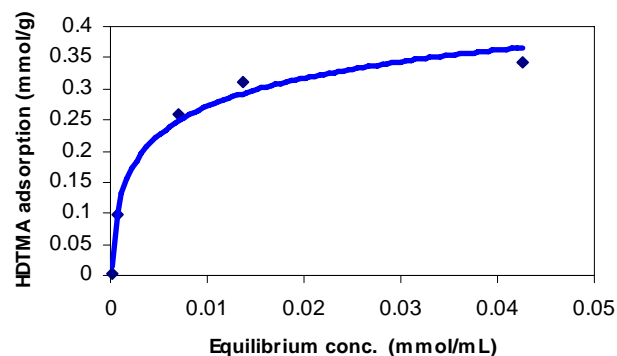


Figure 2. HDTMA adsorption isotherm.

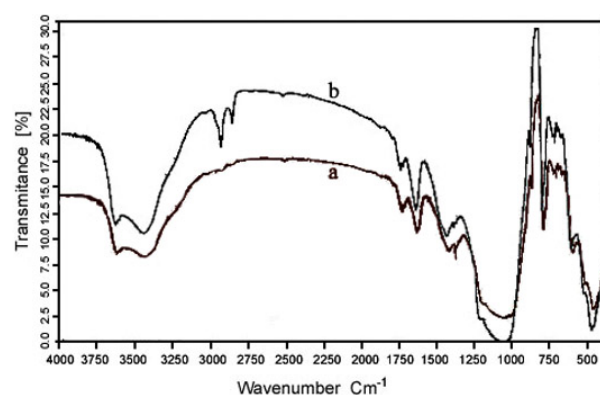


Figure 3. Infrared spectrum of a) natural; and b) modified zeolite.

The maximum capacity of adsorption (S_m) was obtained from these isotherms. The selectivity of zeolites towards a species can also be obtained from the isotherm shape [18]. It was observed that among the studied samples ZHD₁₀₀, ZHD₆₇ and ZHD₅₀ were selective towards molybdate as well as ZTD₅₀ and ZDD₅₀ with about identical amount of molybdate adsorption in comparison with ZHD₅₀. The selectivity and capacity of untreated zeolite, ZHD_{0.45}, ZHD₁₇ and also ZTMA₅₀ and ZTBA₅₀ was very small. It is suggested that in these samples, due to low concentration of surfactant, the two layer adsorption of surfactant has not been formed. A survey of the existing literature on ion exchangers reveals that except of some hydrous oxides metal ions, no other compound has so far been reported to exhibit anion exchange characteristics [9]. Studies suggest that in surfactant-modified zeolites anion exchange process is responsible for anion adsorption [17]. The anion exchange sites are produced when positively charged surfactant head groups which are balanced by counterions are presented to the surrounding solution. The counterions can be replaced by the other anions. Therefore, the capacity of the modified zeolite depends on its ECEC. For mathematical expressions of adsorption it was found that Langmuir model was perfectly fit the results of this research. This model is expressed as:

$$S = K_L S_m C / (1 + K_L C) \quad \text{or} \quad C/S = 1/K_L S_m + C/S_m,$$

Where:

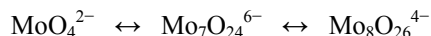
C = equilibrium solute concentration in the solution ($\text{mg} \cdot \text{ml}^{-1}$)

S = solute concentration in the zeolite phase ($\text{mg} \cdot \text{g}^{-1}$)

S_m = maximum capacity towards solute ($\text{mg} \cdot \text{g}^{-1}$)

K_L = isotherm parameter for Langmuir isotherm ($\text{ml} \cdot \text{mg}^{-1}$).

The effect of pH on adsorption process is shown in Figure 7. Highest amount of adsorption was achieved in acidic media. This could be attributed to the formation of polyanionic species such as $\text{Mo}_7\text{O}_{24}^{6-}$ or $\text{Mo}_8\text{O}_{26}^{4-}$ which possess higher molybdenum content per unit charge, according following equilibria [10]:



Furthermore at higher pH, OH^- , as an anion will compete with molybdate adsorption. Figure 8 shows the effect of initial molybdate concentration on the uptake of molybdate. It was observed that due to the saturation of the exchange sites, at initial concentrations above 0.01 M, the uptake was independent of MoO_4^{2-} concentration.

The effect of temperature on the adsorption process was also studied. Due to increasing of diffusion

coefficient at higher temperature, the uptake of molybdate was increased at higher temperature (Fig. 9).

Desorption experiments carried out at 300 K, showed that among modified zeolite, the sample treated with HDTMA had the lowest desorption (Fig. 10). It is believed that as the chain of the surfactant is longer, the anion is held more strongly [19]. On the other hand, desorption phenomena were more serious in NaCl and NaOH solutions. It is firstly attributed to higher ionic strength of the solutions and also the high selectivity of clinoptilolite towards sodium which cause release of surfactant with molybdate together.

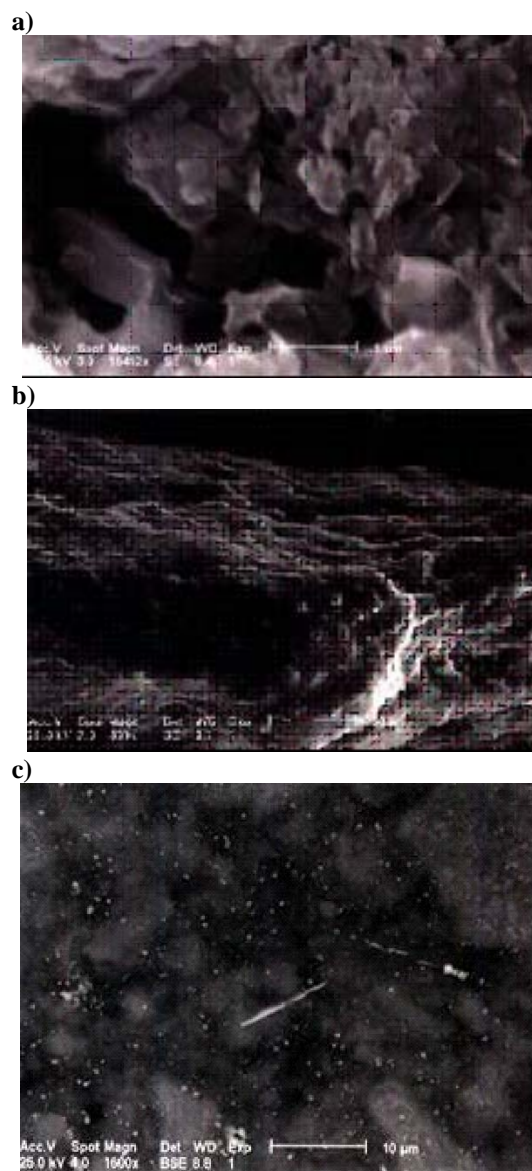


Figure 4. SEM images of a) initial unmodified zeolite; b) modified with HDTMA 50 mM; c) Mo loaded after modification.

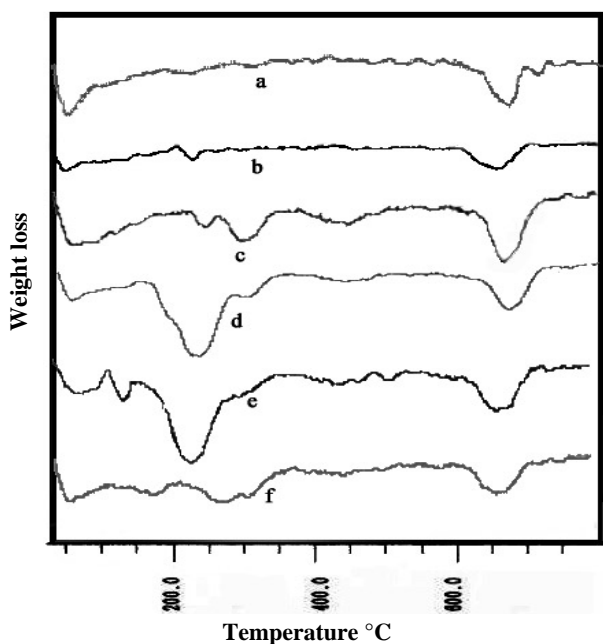


Figure 5. DTG curves of natural and modified samples a) Zeolite in natural form; b) ZHD_{0.45}; c) ZHD₁₇; d) ZHD₅₀; e) ZHD₁₀₀; f) ZHD₅₀ loaded molybdate.

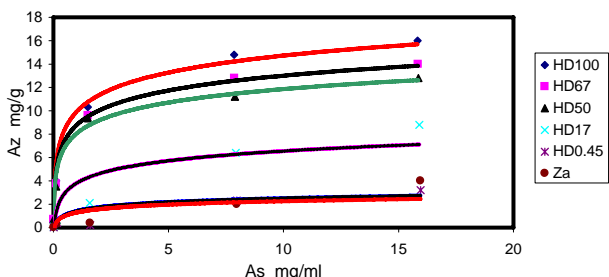


Figure 6. Molybdate adsorption isotherms on modified samples.

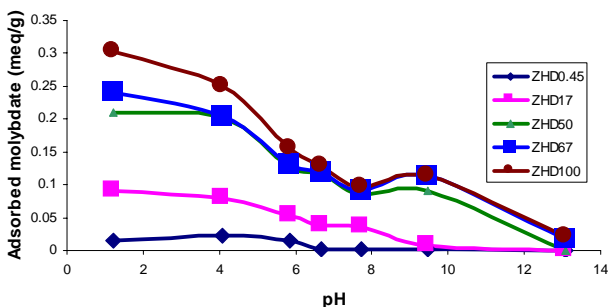


Figure 7. Effect of pH on molybdate adsorption.

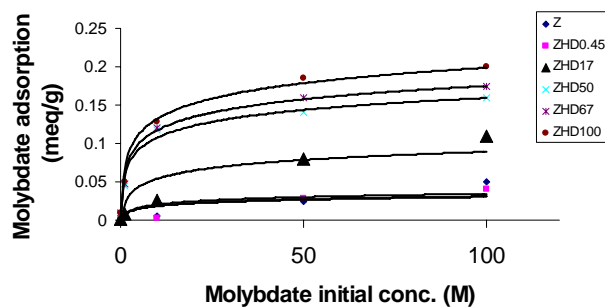


Figure 8. Effect of molybdate initial concentration.

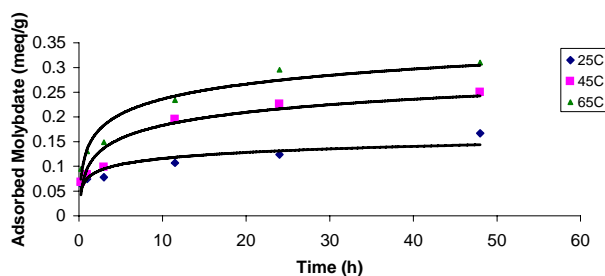


Figure 9. Effect of temperature and contacting time for ZHD₅₀.

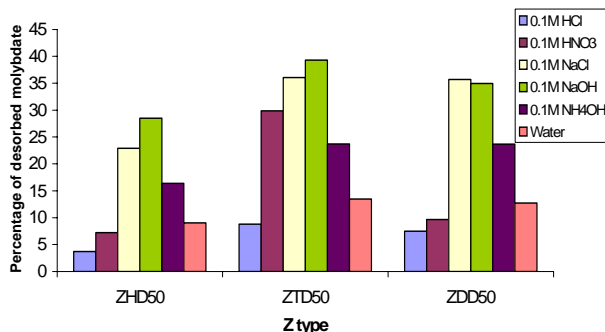


Figure 10. Desorption of molybdate in different solutions.

Effect of some cationic and anionic interference on molybdate adsorption also investigated. The selected ions are the most abundant species produced in the molybdenum production processes. The presence of some cationic species such as Cs⁺ increased the adsorption amount whereas anionic species especially Γ^- , TeO_4^{2-} and CrO_4^{2-} decrease adsorption amount (Fig. 11).

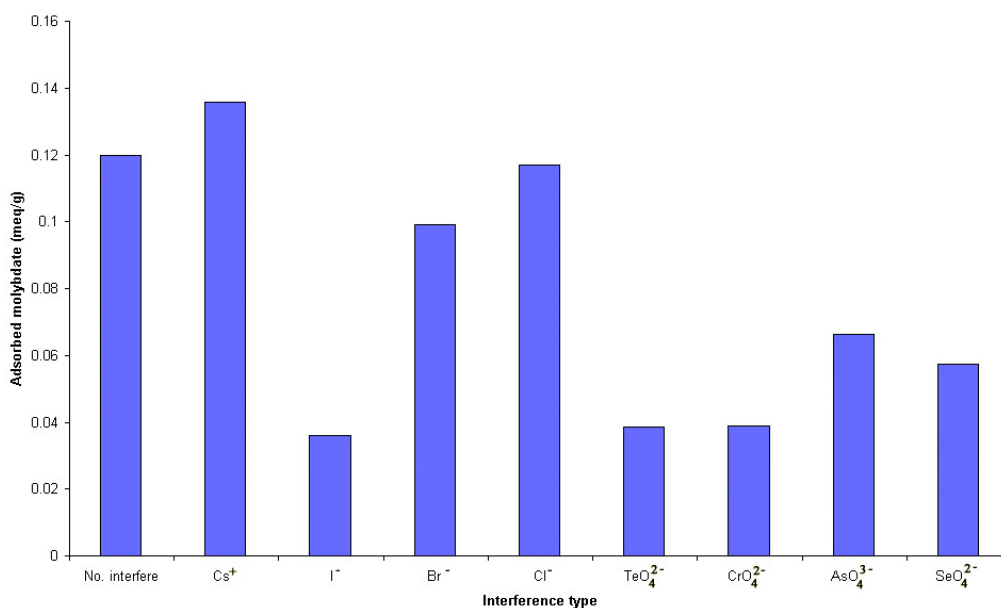


Figure 11. Effect of interference on molybdate adsorption by ZHD₅₀.

Conclusions

The results of this study indicate that surfactant modification enhances the sorption of molybdate on clinoptilolite. At initial molybdenum concentrations of 0.01 M, some of modified samples remove about 0.2 meq.g⁻¹ of molybdate. As desorption studied reveals that molybdate is strongly bonded to the zeolite surface, modified clinoptilolite may be consider as Tc genaertor. ⁹⁹Mo can be chemically bonded to the zeolite structure and cannot be eluted from the matrix. Zeolite structure is sufficiently porous to permit ready diffusion of ^{99m}Tc with a favorite elution solution [20]. Considering both adsorption and desorption processes, it is concluded that ZHD₆₇ is the most promising sample for removal and immobilization of ⁹⁹Mo.

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