

INVESTIGATION OF MOLYBDATE ION SORPTION  
ON THE SORBENT FROM INDUSTRIAL WASTE*Alisa Vaziyeva<sup>1, \*</sup>, Oksana Pavlenko<sup>2</sup>*<https://doi.org/10.23939/chcht11.03.291>

**Abstract.** The dependence of molybdate ion sorption in co-precipitated iron and manganese hydroxides (CPH) on the value of pH solutions and the salt background has been described. Industrial wastes of manganese sulfate  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  (from hydroquinone production) and iron sulfate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (waste production of titanium dioxide pigment) were used for the obtaining of CPH hydroxides.

**Keywords:** industrial waste, co-precipitated hydroxides, sorbents, iron sulfate, manganese sulfate.

## 1. Introduction

Water is considered as an important and scarce commodity in many countries around the world. Therefore, the contamination of surface and ground water with heavy metals is a source of concern [1].

Industrial waste water from different industries contains heavy metals. Its excessive release into the environment due to rapid industrialization has created a major global concern. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death [2, 3].

The problem of increasing of molybdenum concentration in water objects is being actualized at present time. Participation in specific amounts of this element in biological processes is necessary for the functioning of plants, animals and humans. However, low level exposure of molybdenum leads to accumulate them in ecosystems, and its concentration can achieve dangerous levels. In addition, recently molybdenum has become one of the controlled parameters. The interest of enterprises has increased towards purification of waste water from molybdenum due to high environmental charges for its release.

A large amount of molybdenum is lost at different stages from raw materials during the processing of molybdenum ore.

Working staff poisoning as well as negative impact on nature is possible due to leak of molybdenum into the ground water and their poisoning from dumps after molybdenum ores processing [4].

A lot of treatment processes have been proposed for the removal of heavy metals in the literature. Adsorption is considered to be a particularly competitive and effective process for the removal of the tiniest quantities of heavy metals [5].

Inorganic sorbents have some advantages in comparison with organic ones for extraction and concentration of molybdenum from the solution. As previously found [6], the hydroxides of polyvalent metals (Mn, Fe, Ti, Sn) are widely used as sorbents and ion exchangers.

In the recent years, the production of sorbents is greatly increased due to interest for ocean iron-manganese concretions (IMCs). As is well known, IMCs possess the sorption properties towards various metals, especially the non-ferrous ones [7].

IMC is a major fraction of iron-manganese formations (IMF) of the world's oceans and represents bottom mineral associations of iron (III) oxide and manganese oxide (IV). It is possible to use these formations as natural sorption materials for purification of waste water and recycled water of industrial enterprises in various industries (non-ferrous metallurgy, chemical industry, metal processing, *etc.*), containing metals of different hazard categories [8].

According to results of systematic experimental studies of the sorption properties of the oceans ferromanganese formations it can be affirmed that the sorption complex of ocean ferromanganese formations consists of ore Mn- and Fe-minerals, the first being the main sorption dominant.

The aim of this work is investigation of molybdenum sorption from material which was obtained by Mn and Fe hydroxides co-precipitation. The industrial waste iron sulphate (from  $\text{TiO}_2$  pigment) and

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$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  (from hydroquinone factory) were used for the co-precipitated hydroxides (CPH).

The solution for precipitation was obtained by reductive leaching of Mn-containing tailings with  $\text{H}_2\text{SO}_4$  solution to the formed  $\text{MnSO}_4$ , and necessary quantities of  $\text{FeSO}_4$  were added. Obtaining of sorbent was carried out by oxidative co-precipitation of Fe and Mn hydroxides from 0.1M  $\text{FeSO}_4$  and  $\text{MnSO}_4$  with 1M  $\text{NaOCl}$  and 1M  $\text{NaOH}$  solutions [9]. Addition of oxidative agents promotes formation of amorphous  $\text{Fe}(\text{OH})_3$  precipitate, the oxidation and sorption of Mn takes place at the surface of them and finished at  $\text{pH} = 9-10$ .

The washed hydroxides had air-dried state. The expected amounts of main elements based on X-ray fluorescence analysis are given in Table 1.

The obtained sorbent possesses higher chemical resistance in comparison to pure Fe hydroxides based sorbents. It was expected that obtained material should possess sorption activity towards heavy metals similar to natural IMC. The possibility of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  sorption has been established recently [9]. It should be expected that applying of co-precipitated Fe and Mn hydroxides will be useful for extraction of molybdenum.

## 2. Experimental

Sorption of molybdenum(VI) was carried out under static and dynamic conditions of  $\text{Na}_2\text{MoO}_4$  solutions. Molybdenum content in solution was 48–480 mg/l. The concentration of molybdenum in the initial solutions and in the solutions after adsorption was determined photocolometrically (Unico 2100 spectrophotometer) using rhodanate method [10]; the value of pH solutions was measured with laboratory ionomer I-160M. The definite values of pH were created by the addition of  $\text{NaOH}$  or  $\text{HCl}$  solutions.

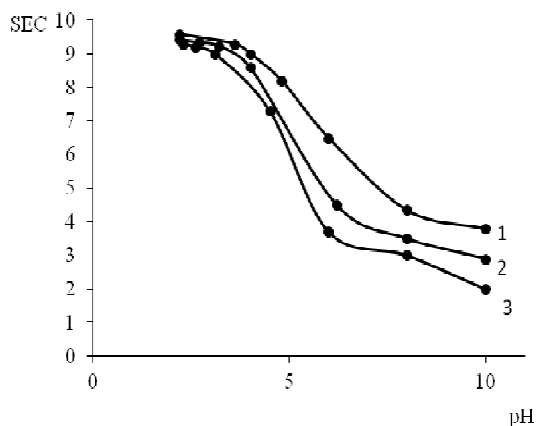
Molybdenum absorption was performed under static conditions with occasional stirring for 24 h. The ratio of solid to liquid was 1:100. The quantity of adsorption (SEC static exchange capacity) CPH was determined from the difference in the content of molybdenum in the initial solution and in the solution after contact with the sorbent. At the same time the pH of the solutions after sorption was being measured.

Experiments on studying of adsorption in dynamic conditions were carried out using columns of 10 mm diameter. A charge of sorbent was 3 g. Solution transmission rate through the sorbent column was 3 ml/min.

All experiments were carried out on a sorbent obtained by co-precipitation of iron and manganese hydroxides from a mixture of 0.1M of  $\text{FeSO}_4$  and  $\text{MnSO}_4$  solution using 1M  $\text{NaOCl}$  and 1M  $\text{NaOH}$  solutions [9].

## 3. Results and Discussion

Sorption of molybdate ions CPH has been studied in a wide range of pH values of  $\text{Na}_2\text{MoO}_4$  solution and initially optimum absorption conditions were chosen based on them (Fig. 1). Curves shown in Fig. 1 indicate high absorbency of CPH relative to molybdenum(VI). Sorption of molybdenum depends on the pH value of the solution strongly, as it is evident from the above data. The decrease of adsorption with increasing pH values is observed for all investigated sorbents.



**Fig. 1.** The dependence of hydroxides SEC (mg  $\text{M}_0/\text{g}$ ) on pH solution. The initial concentration of molybdenum is 96 mg/l. CPH of the Mn:Fe composition: 3:1 (1); 1:1 (2) and 1:3 (3)

Adsorption is insignificantly depending on pH at the range 2–3. Further increase of pH solution causes a sharp decrease of adsorption. From a comparison of the sorption curves (Fig. 1) it can be seen that the sorbent composition has an effect on the sorption of molybdenum. With the increase in the proportion of manganese in the CPH their sorption activity to molybdenum increases. More perceptible differences in activity of sorbents are observed upon absorption of molybdenum from solutions with  $\text{pH} > 4$ .

The study of the sorption of molybdenum (Table 2) has proven that in an acidic environment ( $\text{pH} = 2-6$ ) the process is accompanied by an increase of the value of pH solution.

By the sorption of molybdenum(VI) from alkaline solutions ( $\text{pH} = 8-10$ ) there is a decrease of the value of pH solution. The results obtained show that the sorption of molybdenum in an acidic medium by ion-exchange mechanism takes place through the exchange of surface hydroxyl groups of sorbents on the molybdenum anions. Therefore, the value of sorption must be influenced by both ion-exchange properties of sorbents and the state of molybdenum in the solution.

Table 1

Content of the main elements in the composition of CPH samples Mn:Fe = 1: 1

Element	S	Cl	Ti	Mn	Fe	Zn
Mass fraction, %	2.766±0.091	0.390±0.073	0.619±0.047	48.751±0.183	47.776±0.181	0.021±0.010

Table 2

The change of pH solutions during the sorption of molybdenum(VI) ( $C_{M_0} = 96$  mg/l)

Sorbent	The value of pH solution		$\Delta$ pH
	Before sorption	After sorption	
CPH, Mn:Fe = 3:1	2.10	2.45	0.35
	3.05	4.80	1.75
	6.00	7.45	1.45
	8.00	7.60	-0.40
	10.00	7.80	-2.20
CPH, Mn:Fe = 1:1	2.05	2.80	0.75
	3.05	6.20	3.15
	6.00	7.60	1.60
	8.00	7.70	-0.30
	10.00	7.80	-2.20
CPH, Mn:Fe = 1:3	2.05	2.80	0.75
	3.05	6.20	3.15
	6.00	7.60	1.60
	8.00	7.70	-0.30
	10.00	7.80	-2.20

Table 3

The dependence of molybdenum(VI) sorption on the concentration of NaCl to CPH of the composition of Mn:Fe = 1:1 ( $C_{M_0} = 48$  mg/l)

Concentration NaCl, mol/l	pH Value of the solution		SEC, mg/g
	Before sorption	After sorption	
0.0	2.1	3.95	4.3
0.05		3.95	4.3
0.1		4.05	4.25
0.5		–	4.16
1.0		–	4.15
0.0	6.1	8.2	2.8
0.05		7.65	3.3
0.1		7.35	3.8
0.5		7.0	4.01
1.0		–	4.01
0.0	9.0	7.95	2.4
0.05		7.45	3.8
0.1		7.3	4.3
0.5		7.0	4.4
1.0		6.65	4.4

Table 4

Results of molybdenum(VI) sorption mixed by hydroxides of Mn and Fe in dynamic conditions (pH = 4)

$C_{M_0}$ , mg/g	FDEC, mg/l		
	CPH		
	Mn:Fe = 3:1	Mn:Fe = 1:1	Mn:Fe = 1:3
48	13.9	11.5	9.1
480	66.6	52.1	40.2

Since iron and manganese hydroxides are weakly basic ion-exchangers, with a change in the pH solution the degree of ionization is changed. With the decrease of pH solution the ionization with OH-groups elimination increases, and as a consequence the exchange capacity increases as well. With the increase of pH solution the competing effect of hydroxyl ions is enhanced, thereby the sorption of molybdenum is reduced. In the environment close to neutral, iron and manganese hydroxides exhibit its amphoteric properties: ionization is equally both the acid type and the basic one. As a result of this a simultaneous adsorption of sodium and molybdenum ions is taking place. Low-limit value of pH solution during adsorption of alkaline solutions probably shows the preferential absorption of sodium ions.

The same character of change curves of SEC from the value of pH solution, apparently points at proximity of acid-base properties of CPH with individual manganese and iron hydroxides. And to adsorption value should be influenced by the change of states of molybdenum ions from the pH solution [11]. It is known that in the area of  $\text{pH} < 7$  there are polymeric forms of molybdenum which must be absorbed better than simple anions  $\text{MoO}_4^{2-}$ . Therefore, in the absorption of solutions at  $\text{pH} < 7$  in each sorption exchanger center more molybdenum is sorbed.

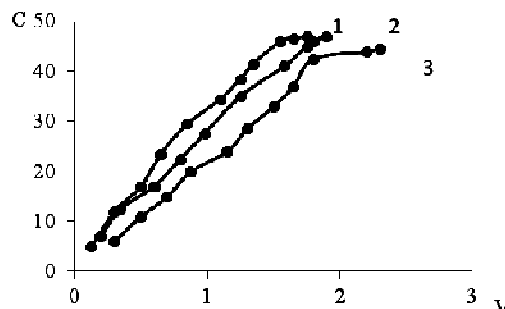
The data on the background electrolyte effect on the capacity point at the complex mechanism of sorption of molybdenum(VI) are presented in (Table 3).

The obtained results indicate that the presence of NaCl differently affects sorption depending on the value of pH solutions. Thus, the content of NaCl has virtually no effect in acidic solutions ( $\text{pH} = 2.1$ ) and increases the sorption by absorption from solutions close to neutral ( $\text{pH} = 6.1$ ) or with  $\text{pH} > 7$ . In these conditions the sorption of molybdenum increases with increasing NaCl concentration. Small additions of NaCl (0.1 mol/l) have the greatest influence on the sorption. Since the absorption of chloride ions on the metal hydroxides takes place preferably in an acidic environment, it can be assumed that the effect of NaCl on the sorption of molybdenum is due to the absorption of sodium ions.

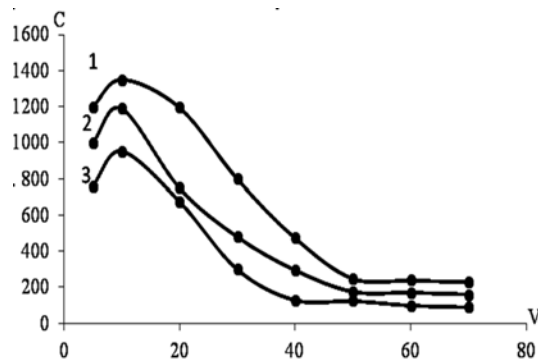
The study of the molybdenum(VI) sorption under dynamic conditions (Fig. 2, Table 4) showed that the order of the sorption activity of sorbents set under static conditions is stored in dynamics. It is interesting to note that although the full dynamic exchange capacity (FDEC) should not depend on the initial concentration of molybdenum ions in the solution, from the given data indicate its increase with increasing molybdenum content in the solution. Apparently FDEC increase in this case is due to the formation of polymerized molybdenum ions not only in the solution but in the phase of sorbent. Types of output sorption curves are the same for all the studied sorbents and shows a high rate of establishment of equilibrium.

Desorption of absorbed molybdenum is carried out easily by 0.1 M sodium hydroxide solution (Fig. 3).

In the sorption process molybdenum concentration (for Mn:Fe = 3:(1–26); 1:(1–20); 1:(3–16.6)) is achieved in the first portions of discharging solution (20 ml).



**Fig. 2.** Output sorption curves of molybdenum(VI) hydroxides, where  $C$  – the concentration of molybdenum(VI) in the solution after passing through the column, mg/l;  $V$  – volume of solution passed through a column, l.  
CPH of the Mn:Fe composition: 3:1 (1); 1:1 (2) and 1:3 (3)



**Fig. 3.** Output curves of molybdenum(VI) desorption 0.1 M with solution of sodium hydroxide.  
CPH of the Mn:Fe composition: 3:1 (1); 1:1 (2) and 1:3 (3)

## 4. Conclusions

The possibility to use industrial waste – iron sulphate and manganese containing tailings as components in the preparation of the material from CPH of iron and manganese possessing absorption properties to molybdenum ions, has been shown. As a result of the study of molybdenum(VI) adsorption in static and dynamic conditions in the co-precipitated hydroxides of manganese and iron it was revealed that the greatest activity takes place in an acid medium ( $\text{pH} = 2-4$ ). The influence of the composition of the co-precipitated hydroxides on their sorption activity has been studied. It has been found that with the increase in the proportion of manganese in the CPH their sorption activity increases.

The possibility of molybdenum(VI) concentrating from dilute solutions to co-precipitated iron and manganese hydroxides has been shown.

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## ДОСЛІДЖЕННЯ СОРБЦІЇ ЙОНІВ МОЛІБДЕНУ СОРБЕНТОМ З ПРОМИСЛОВИХ ВІДПАДКІВ

**Анотація.** Описано результати дослідження залежності сорбції молибдену(VI) від складу спільно висаджених гідроксидів (СОГ) заліза і марганцю, значення рН розчинів і сольового фону. Для отримання гідроксидів використовувалися промислові відпадки – залізний купорос  $FeSO_4 \cdot 7H_2O$  (відпадки виробництва пігментного діоксиду титану) і марганцевий купорос  $MnSO_4 \cdot 5H_2O$ , отриманий з відпадків виробництва гідроксиду.

**Ключові слова:** промислові відпадки, спільно висаджені гідроксиди, сорбенти, залізний купорос, марганцевий купорос.