ARSENIC AND MOLYBDENUM IONS REMOVAL BY Fe₃O₄ EMBEDDED ACRYLAMIDE – TRIAZINE HYBRID – POLYMER

Can Serkan KESKİN

Sakarya University, Department of Chemistry, Faculty of Arts and Science, Sakarya, Turkey

The synthesized hybrid-polymer was used for the removal of As(V) and Mo(VI) ions from aqueous solution. The treated metal ion solutions were analyzed by inductively coupled plasma-optical emission spectroscopy. The highest removal percentages were obtained at pH 2.5. The effect of time, agitation rate, temperature, initial concentration, and polymer dosage were studied to find optimal removal conditions. The maximum uptake was found to be at 150 min contact time, 150 rpm agitation rate, and 25°C temperature. At the optimal conditions, maximum uptake of As(V) and Mo(VI) ions was found 100% and 98%, respectively by using 0.25 g polymer. The kinetic parameters were calculated by linearized form of pseudo-fist-order and pseudo-second-order models. The results were found to correlate with the pseudo-second-order kinetic model. Also, the results were analyzed by Langmuir and Freundlich isotherms. The equilibrium adsorption data followed the Langmuir isotherm model.

Fabrication of adsorbent

INTRODUCTION

The Fe₃O₄ (magnetite) extensively has been used for biotechnology and environmental studies due to unique magnetic, electrical, and optical properties.[1] One of the disadvantages of these studies is the dissolution of the Fe₃O₄ particles. The magnetite particles can uptake the metal ions efficiently but also pollute the working solution via dissolution of iron especially in the lower pH conditions. The use of capping agents can prevent release of iron, but there is a disadvantage of using capping procedures is that the magnetic power of magnetite can be lost. The co-precipitation is most commonly used method to the synthesis of Fe₃O₄ particles. In this method, Fe³⁺ and Fe²⁺ ions were obtained under the molar ratio of 2 to 1 in alkaline medium. The possible reaction for the formation of Fe₃O₄ particles:[2]

$$Fe^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} + 8NH_3 \cdot H_2O_{(l)} \longrightarrow Fe_3O_{4(s)} + 8NH_4^{+}_{(aq)} + 4H_2O_{(l)} \tag{1}$$

The acrylamide-based polymerization is a well-known method. There are lots of copolymerization agents to produce acrylamide based polymer.[3] 1,3,5-triacryloylhexahydro-1,3,5-triazine is one of the used copolymerization agents. The resulting polymer can be called hydrogel because of the hydrophilic properties. The hydrophilic structure allows the water entry inside of the three-dimensional network of the polymer. These polymers can be used for removal experiments with high efficiency.

Arsenic is a toxic metal and concentration of it in the natural waters is a big problem as causes

---

* Corresponding author: e-mail: ckeskin@sakarya.edu.tr

serious carcinogenic effects on humans. It is mobilized by weather, biological and geochemical activities, volcanic emissions.[4] Arsenic can exist in the natural conditions in different oxidation states such as As^{3-}, As^0, As^{3+}, and As^{5+} and it is mostly found as oxyanion forms of As^{5+} and As^{3+} such as AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$, $H_3AsO_4^0$, AsO_3^{3-}, $HAsO_3^{2-}$, $H_2AsO_3^-$, $H_3AsO_3^0$ depending on the current pH.[5] There are lots of works about the removal of arsenic from waters. Mandal *et al.*[6] studied the adsorption of arsenic(III) from water by zirconium polyacrylamide hybrid material. The polyacrylamide was synthesized by using bisacrylamide as copolymer agent. The reported maximum removal efficiency was 98.22%. Sumathi and Alagumuthu[7] removed arsenic(V) by activated Moringa Oleifera leaves carbon. They reported 71.3% removal percentage. Iron oxide minerals also have been used for removal experiments. Goethite (a-FeOOH), hematite (Fe_2O_3), siderite ($FeCO_3$), magnetite (Fe_3O_4), ferrihydrite minerals are mainly used iron oxide adsorbents.[8] Aredes *et al.*[9] used hematite, magnetite, goethite, and laterite soil for the removal of arsenic(V). The results were 75.2%, 96.4%, 100.0% and 100.0%, respectively. Mostafa *et al.*[10] used nano-sized iron-oxide-coated quartz for the removal of As(V). They found almost 100% removal percentage for 1,000μg-As(V)/L.

The high concentration of molybdenum can be toxic to life forms. In nature, molybdenum can occur in several species (Mo^{2+}, Mo^{3+}, Mo^{4+}, Mo^{5+}, and Mo^{6+}) and in natural waters can predominantly exist in inorganic forms as oxyanions of Mo^{5+} and Mo^{6+} such as MoO_4^{3-}, $HMoO_4^{2-}$, $H_2MoO_4^-$, $H_3MoO_4^0$, MoO_4^{2-}, $HMoO_4^-$, $H_2MoO_4^0$ depending on the pH of the medium.[11] Additionally, molybdenum is an important element in the metallurgical and chemical industry. The presence of molybdenum can affect many industrial operations.[12] In this aspect, the uptake of molybdenum may be more important for the industrial operations. Pennesi *et al.*[13] used Posidonia Oceanica biomass for the removal of molybdenum(V). The reported removal percentage was 40%. Verbinnen *et al.*[14] reported molybdenum oxyanions removal by zeolite supported magnetite and obtained 99% removal efficiency. Budnyak et al.[15] used chitosan–silica composite for Mo(VI) removal. The reported maximum adsorption capacity was 1.5 mmol/g.

The higher iron concentration creates iron toxicity for the humans. In this work, the dissolution of iron was tried to be prevented by polymer network. The triazine compounds can make complexes with the iron ion.[16] The 1,3,5-triacryloylhexahydro-1,3,5-triazine was used as the copolymer agent and complexing ligand for iron. The release of iron was prevented via polymer network properties and complexation. The functional groups of the triazine also provide complexation of the other metals.[17] The removal was carried out with both Fe_3O_4 and acrylamide-triazine polymer. The effect of pH, temperature, contact time, and agitation rate on the removal percentages also investigated. Inductive coupled plasma-optical emission spectroscopy (ICP-OES) was used for the determination of metal concentrations in treated solution. Also, the experimental data were analyzed by the pseudo-fist-order and pseudo-second-order kinetic models and the Langmuir and Freundlich isotherms. The objective of the present work was to find out the As(V) and Mo(VI) ions removal capability of a new adsorbent, Fe_3O_4 embedded 1,3,5-triacryloylhexahydro-1,3,5-triazine – acrylamide hybrid-polymer, without releasing iron ions to the solution. Both the As(V) and Mo(VI) ions are oxyanion-forming elements. They are in the similar oxyanion forms at the same acidic conditions. Thus, these ions can be removed or recovered at the same pH conditions by the same adsorbent.

RESULTS AND DISCUSSION

Synthesis of polymer

The triazine molecules were used as cross-linker and the polymer was synthesized by free radical polymerization. 2,2-diethoxyacetophenone was used as photoinitiator of radical reaction. The synthesized polymer was hydrolyzed after synthesis by 10% N,N,N',N'-tetramethylethylenediamine/NaOH (V/V). The polymer hydrolysis effect on the removal of As(V) and Mo(VI) by Fe_3O_4 embedded acrylamide – triazine hybrid – polymer was investigated. The unhydrolyzed bare polymer, the hydrolyzed bare polymer, the Fe_3O_4 embedded hydrolyzed polymer, the Fe_3O_4 embedded unhydrolyzed polymer and solid Fe_3O_4 were treated with the mixture of the metal ion solution containing 2.5 mg/L of As(V) and Mo(VI). 0.25 g of dried material (polymer etc.) was used in the experiments except for solid Fe_3O_4 (0.1 g). The removal rates of Fe_3O_4 embedded

hydrolyzed and unhydrolyzed polymers were not very different. However, the hydrolysis of Fe_3O_4 embedded polymer was important for the release of iron. The solid Fe_3O_4 was more effective in removal than the polymer because of the surface properties of Fe_3O_4 particles. But, the unmodified Fe_3O_4 could release iron ions to the solution via dissolution of iron depending on the pH. The release concentration reached ~1.2 ppm by using 0.1 g of unmodified Fe_3O_4 at pH 2.5 of the mixture solution (Table 1).

This concentration could be reduced by polymerization. Although the Fe_3O_4 embedded hydrolyzed and unhydrolyzed polymer contained ten times more Fe_3O_4 (1.0 g of Fe_3O_4 – DMSO mixture was used) inside of the polymer, the concentration of released iron was less than the unmodified Fe_3O_4 particles. The hydrolysis of synthesized polymer provided much more prevention for iron release. The amide groups of polymer were converted to the carboxylate groups via hydrolysis. The surface amide groups of polymer were more hydrolyzed than inside amide

groups of the polymer network. Thus, the carboxylate groups were added to the other groups (azine and amide) which could interact with the Fe_3O_4 particles. The ionization of the carboxylate groups caused the immobilization of the counter ion inside of polymer.[18] The polymerization had a disadvantage that the magnetic power of Fe_3O_4 particles was decreased. The embedded particles could not be collected by external magnetic field after polymerization.

Effect of pH

pH was the most important parameter for the removal process. The ionization of polymer groups and the charges of Fe_3O_4 particles were adjusted by pH changes. The removal of negatively charged forms of As(V) and Mo(VI) ($H_2AsO_4^-$ and $HMoO_4^-$ at pH 2.5) probably occurred via protonated groups of the polymer and the positively charged Fe_3O_4 particles in lower pH conditions.

Table 1

Removal percentages and iron release concentrations of different kind of polymers and solid Fe_3O_4

	Removal Percentages (%)		Iron release concentration (mg/L)
	As	Mo	
Unhydrolyzed bare polymer	6.09	26.18	-
Hydrolyzed bare polymer	15.00	87.29	-
Fe_3O_4 embedded hydrolyzed polymer	98.33	96.87	0.22
Fe_3O_4 embedded unhydrolyzed polymer	97.26	96.36	1.08
Solid Fe_3O_4 (0.1 g)	97.47	97.00	1.16

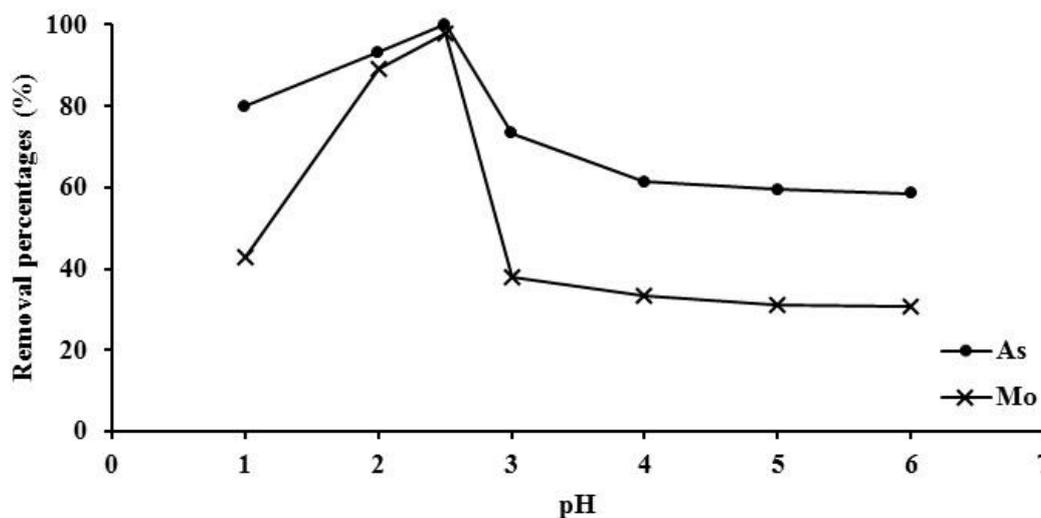Fig. 1 – Effect of initial pH on the removal of As(V) and Mo(VI) ions. t = 120 min; C_0 = 2.5 mg/L; T = 25°C; agitation rate = 150 rpm; polymer dosage = 0.25 g.

In order to investigate the effect of pH, removal studies were carried out in the range of 1.0 – 6.0. According to the Fig. 1. As(V) and Mo(VI) uptake percentages were highest at pH 2.5 of the solution. The As(V) and Mo(VI) ion solutions were prepared using metal standard solutions of As(V) (in diluted nitric acid) and Mo(VI). Because of the nitric acid content of As(V), the pH of the mixed solution, without pH adjustment, was 2.5. The predominate species of As(V) were $H_2AsO_4^-$ (pH 2-6) and H_3AsO_4 (pH 0-2) at working pH range.[19,20] The observed lower removal of As(V) at higher pH than 3 was attributable to increased repulsion between the negatively charged arsenate species and negatively charged groups of polymer and magnetite via starting deprotonation of ferric hydroxides on the surface of the Fe_3O_4 particles.[21] The removal of arsenic decreased at lower than pH 2 due to the non-ionic form of As(V). The similar reason was acceptable for the molybdenum removal. The predominant species of Mo(VI) were $HMoO_4^-$ (pH 2-6) and H_2MoO_4 (pH 0-2) at working pH range.[22] The increased repulsion between negatively charged species decreased the interaction of ions with Fe_3O_4 embedded polymer and determined the rate of the removal.

Effect of the other parameters

In order to see the effect of the contact time, agitation rate, and temperature, the experiments were carried out at different times, speeds and temperatures in the range of 10 – 240 min, 50 – 200 rpm and 20 – 50 °C, respectively. According to results, the equilibrium was obtained at 120 min. contact time for As(V) (Fig. 2). The removal percentages increased from 98.0% to 99.8% by raised time from 120 min to 240 min. for Mo(VI). The selected optimum contact time was 120 min. when considering both of the metals at pH 2.5.

The effect of agitation rate on the uptake of metal ions was shown in Fig. 3. The removal efficiencies increased from 90.3 to 100% and 96.0 to 98.0% for As(V) and Mo(VI), respectively by raised agitation rate from 50 to 150 rpm. The lower agitation rate decreased metal uptake due to liquid film thickness but at higher agitation rate, film resistance was diminished and removal percentages increased.[23]

The interaction between Fe_3O_4 embedded hydrolyzed polymer and metal ions was not affected by raised temperature (Fig. 4). The increased temperature did not destroy the polymer structure. As the temperature was increased from 20 to 25°C (room temperature), the removal efficiencies maintained at ~100% and ~98.0% for As(V) and Mo(VI), respectively.

The metal solutions with different initial concentration were investigated in the range of 0.1 – 10 mg/L. Fig. 5 shows the effect of initial concentrations on metal uptake efficiency. The removal percentages in the range of 0.1 – 5.0 mg/L initial metal concentrations were %100 for As(V). The removal efficiency decreased from 100 to 97.8% by increased concentration from 5 to 10 mg/L for As(V). For Mo(VI), the removal efficiencies were stable (%100) in the range of 0.1 – 1.0 mg/L initial metal concentrations. The uptake percentages decreased to ~97% at higher ion concentrations for Mo(VI) due to the removal capacity of the Fe_3O_4 embedded hydrolyzed polymer.
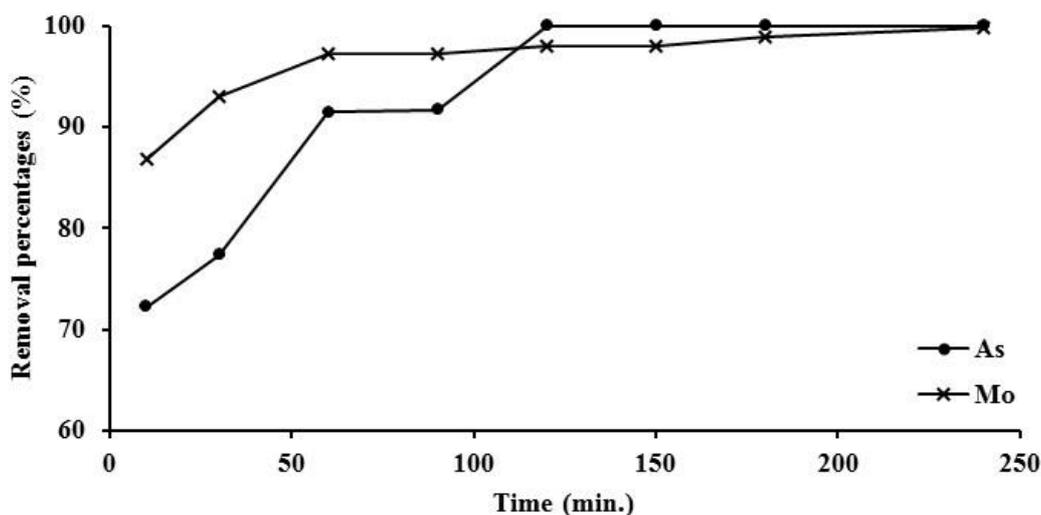

Fig. 2 – Effect of contact time on the removal of As(V) and Mo(VI) ions. pH 2.5; C_0 = 2.5 mg/L; T = 25°C; agitation rate = 150 rpm; polymer dosage = 0.25 g.

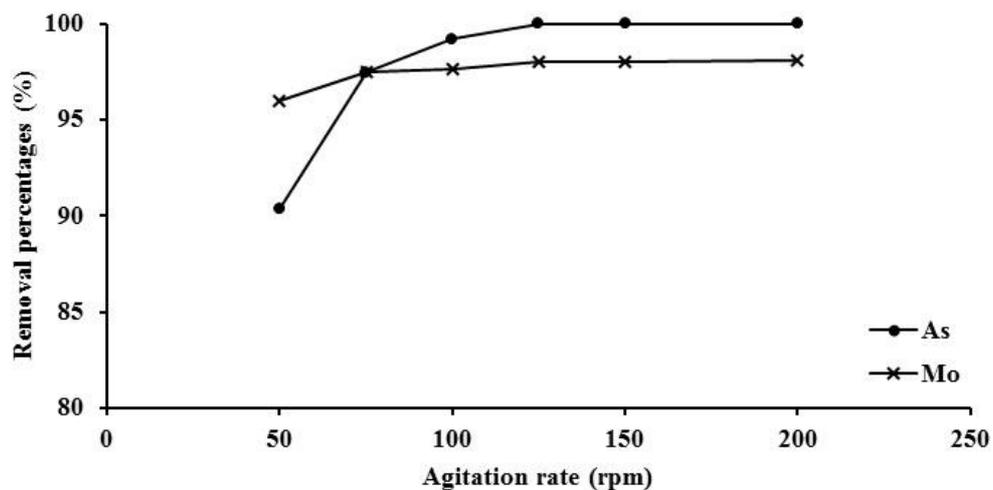Fig. 3 – Effect of contact time on the removal of As(V) and Mo(VI) ions. pH 2.5; t = 120 min; C_0 = 2.5 mg/L; T = 25°C; polymer dosage = 0.25 g.
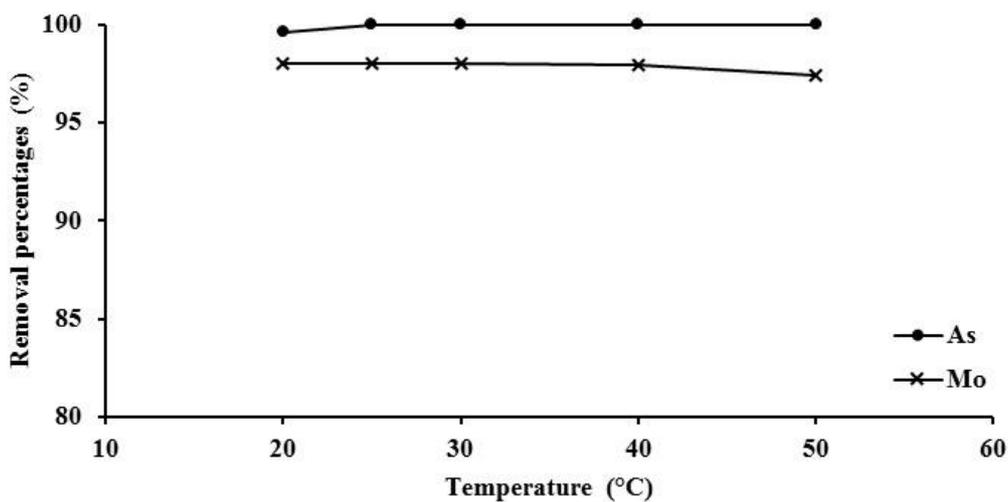

Fig. 4 – Effect of temperature on the removal of As(V) and Mo(VI) ions. pH 2.5; t = 120 min; C_0 = 2.5 mg/L; agitation rate = 150 rpm; polymer dosage = 0.25 g.
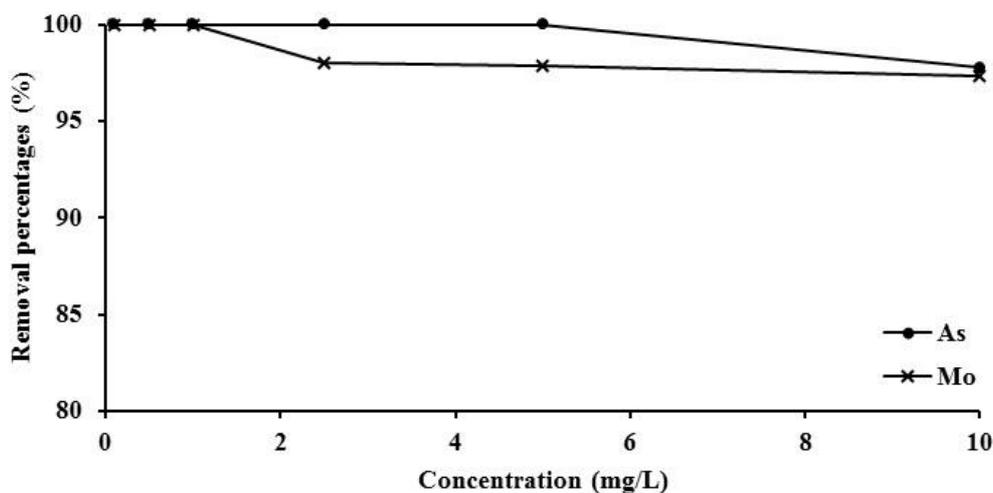

Fig. 5 – Effect of initial concentration on the removal of As(V) and Mo(VI) ions. pH 2.5; t = 120 min; T = 25°C; agitation rate = 150 rpm; polymer dosage = 0.25 g.
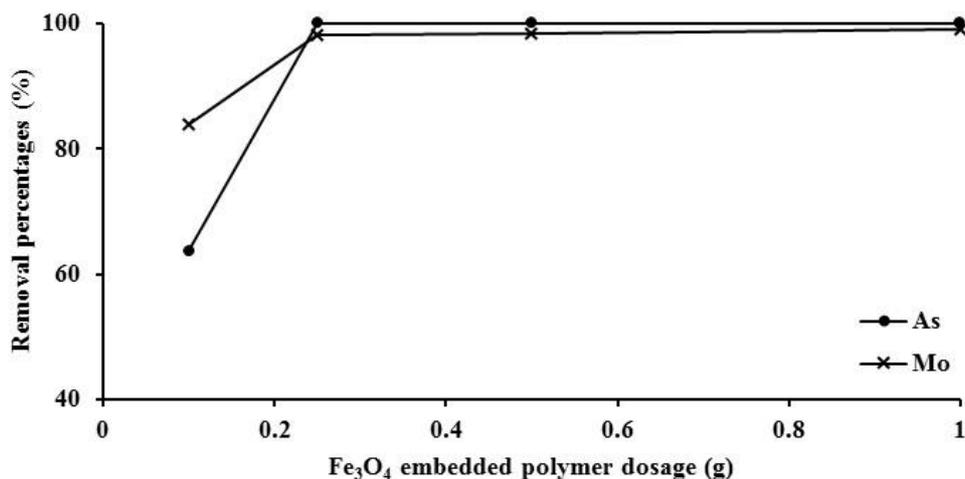
Fig. 6 – Effect of polymer dosage on the removal of As(V) and Mo(VI) ions. pH 2.5; t = 120 min; T = 25°C; C_0 = 2.5 mg/L; agitation rate = 150 rpm.
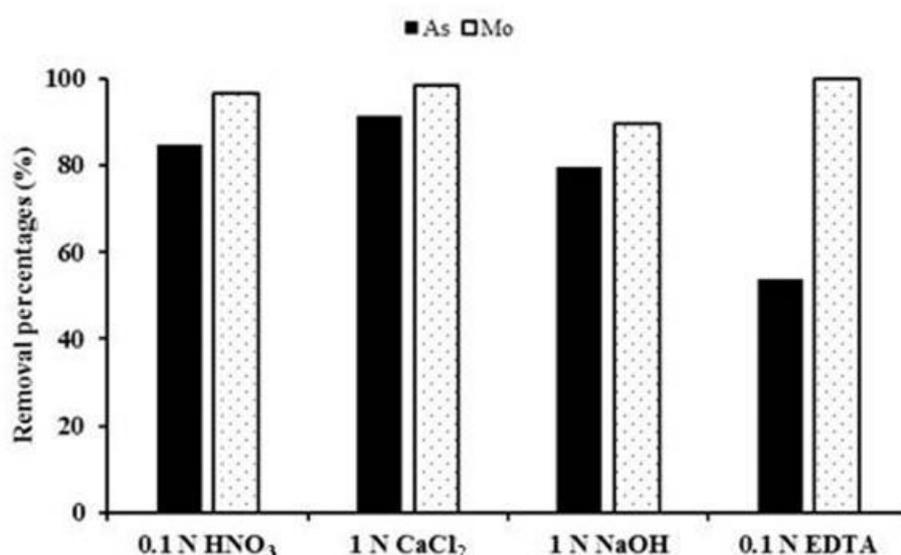

Fig. 7 – Reuse of polymer after treated by regeneration solutions. pH 2.5; t = 120 min; T = 25°C; C_0 = 2.5 mg/L; agitation rate = 150 rpm.

The Fe_3O_4 embedded hydrolyzed polymer dosage was another parameter to be examined (Fig. 6). The uptake efficiencies of heavy metal ions increased from 63.7 to 100% and 83.8 to 98.0% for As(V) and Mo(VI), respectively by raised dosage from 0.1 to 0.25 g. For Mo, the removal percentage reached 99.0% via using 1.0 g of Fe_3O_4 embedded hydrolyzed polymer at pH 2.5.

Additionally, the effect of filter paper was investigated on the removal of As(V) and Mo(VI). In order to see the effect of filter paper, 2.5 mg/L of mixed metal ion solution (control experiment) was shaken for 120 min. contact time at 150 rpm agitation rate, 25°C temperature and pH 2.5 without addition of the Fe_3O_4 embedded hydrolyzed polymer. According to the results, the filter effect was not important for the removal of

As(V) and Mo(VI) at pH 2.5. The calculated percentages were 0.9% and 0.7% for As(V) and Mo(VI), respectively.

Reuse of Fe_3O_4 embedded polymer

HNO_3, $CaCl_2$, NaOH, EDTA, HCl, HCl/HNO_3 solutions were used for the regeneration of Fe_3O_4 embedded hydrolyzed polymer. The Fe_3O_4 particles solubility increased by raised acidity of the solutions. 1.4 mg/L, 2.9 mg/L and 4.8 mg/L iron were released to the solution when 0.1 M HNO_3, 0.1 M HCl, and 0.1 M HCl/HNO_3 mixture were used, respectively. HCl and HCl/HNO_3 solutions were not useful for regeneration experiments because of the raised solubility of

Fe_3O_4 particles in the more acidic pH. 0.1 M HNO_3, 1 M $CaCl_2$, 1 M NaOH and 0.1 M EDTA were selected as regeneration solutions. After regeneration process, the obtained polymers were treated by 2.5 mg/L metal ion solutions at pH 2.5. According to do results, the highest removal percentages were obtained by $CaCl_2$ treated polymer for both of As(V) and Mo(VI) at pH 2.5 (Fig. 7).

The removal efficiencies were 91.50% and 97.00% for As(V) and Mo(VI), respectively. The removal percentages decreased due to loss of polymer weight by regeneration process from 0.25 g to 0.21 g. The polymer weight was lost by $CaCl_2$

treatment due to filtering, transferring and the other human errors. The reason for this decline was not due to the dissolution of Fe_3O_4 particles.

SEM analysis

The SEM images of Fe_3O_4 embedded hydrolyzed polymer and treated Fe_3O_4 embedded hydrolyzed polymer were shown in Fig. 8. It seems that, after removal process, the dispersed materials were aggregated via occurred interactions between metal ions and Fe_3O_4 embedded hydrolyzed polymer.
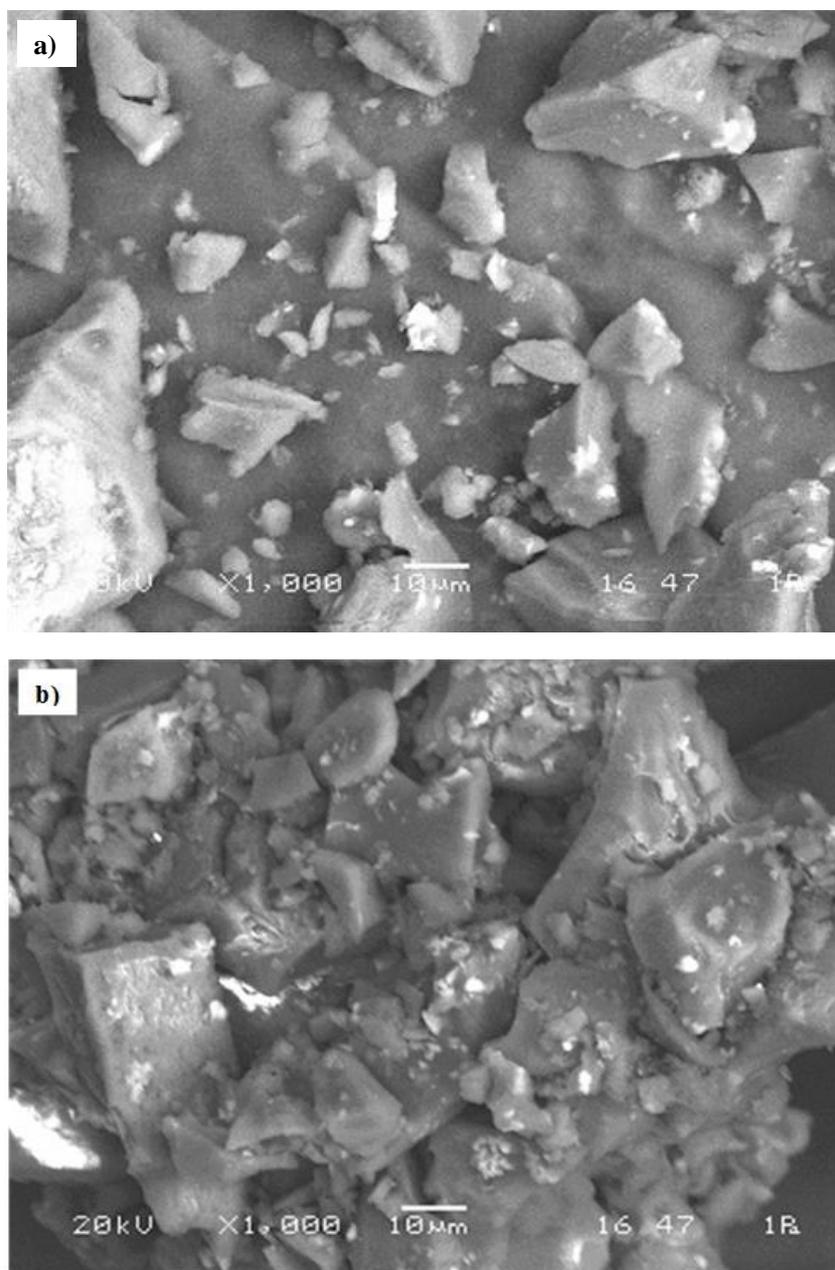

Fig. 8 – SEM images of Fe_3O_4 embedded hydrolyzed polymer (a), treated Fe_3O_4 embedded hydrolyzed polymer (b).

Table 2

Kinetic, Langmuir and Freundlich parameters

	Pseudo-first-order			Pseudo-second-order		
	q_e (mg/g)	k_1 (1/min.)	R^2	q_e (mg/g)	k_2 (g/mg min^{-1})	R^2
As(V)	0.082	0.0170	0.8766	0.259	0.5079	0.9944
Mo(VI)	0.034	0.0358	0.8962	0.248	2.4725	1.0000
	Langmuir			Freundlich		
	Q_0 (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
As(V)	0.1684	1.0004	0.9980	0.1708	-5.2994	0.9893
Mo(VI)	0.2127	1.0001	0.9992	0.2049	-15.873	0.9457

Kinetic models, Langmuir and Freundlich isotherms

In order to investigate the mechanism of sorption, kinetic and equilibrium characteristic parameters of sorption were calculated by Lagergren pseudo-first and second-order models and Langmuir and Freundlich adsorption isotherms, respectively. The integral pseudo-first-order kinetic model equation[24] for sorption analysis can be represented as (2):

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad (2)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of solute adsorbed by an adsorbent at equilibrium and at any time (t), respectively. k_1 (1/min.) is the rate parameter. The integral pseudo-second-order equation[25] can be represented as (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where k_2 (g/mg min^{-1}) is the rate constant.

The calculated pseudo-first and second-order rate parameters, q_e, and coefficient of determination (R^2) were shown in Table 2. k_1 and k_2 parameters depend on the initial concentration and the operating conditions, respectively.[26] The calculated coefficient of determination for pseudo-second-order model is higher than the pseudo-first-order model. Therefore, pseudo-second-order kinetic model is the optimum expression for the sorption of As(V) and Mo(VI) by Fe_3O_4 embedded hydrolyzed polymer.[27] This suggests that the chemical sorption may be the rate-limiting step.[25]

Langmuir (4) and Freundlich (5) adsorption isotherm parameters were calculated by using the following equations:[28]

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (4)$$

$$logq_e = logK_f + \frac{1}{n} logC_e \qquad (5)$$

where C_e (mg/L) is the equilibrium concentration of metal, q_e (mg/g) is the equilibrium amount of metal per unit mass of sorbent, Q_0 (mg/g) is the monolayer adsorption capacity of sorbent, b (L/mg) is parameter related to the energy of adsorption, K_f (mg/g) and n Freundlich parameters related to sorption capacity and intensity, respectively.

The obtained results were shown in Table 2. Langmuir adsorption isotherm is the well-fitted model for As(V) and Mo(VI) ions adsorption onto Fe_3O_4 embedded hydrolyzed polymer. The calculated coefficients of determination were 0.9980 and 0.9992 for As(V) and Mo(VI), respectively. The model followed monolayer adsorption.[26]

EXPERIMENTAL

Chemicals and instruments

The metal solutions were prepared by using ICP standard solutions (Merck) with double distilled water. Acrylamide, 1,3,5-triacryloylhexahydro-1,3,5-triazine, 2,2-diethoxyaceto-phenone (DEAP), dimethyl sulfoxide (DMSO) and 10% N,N,N',N'-tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich. All used glass wares were washed with dilute nitric acid and ethanol to avoid contamination of metal and organic substances, respectively. The pH of the working solutions was adjusted with NaOH (Merck) and HCl (Merck). Heidolph orbital shaker was used for the batch experiments. Spectro Arcos ICP-OES was used for the determination of metal ion concentrations in treated solutions. The SEM images were taken by JEOL (JSM-6060LV) microscope.

Synthesis of Fe_3O_4 particles and Fe_3O_4 embedded polymer

The synthesis of Fe_3O_4 particles was carried out according to the previously described method by Batra et al.[29] with little modification. The ammonium iron(III) sulfate dodecahydrate and ammonium iron(II) sulfate hexahydrate were used as source of Fe^{3+} and Fe^{2+}. The mixture solution was prepared containing 0.25 M of Fe^{3+} and Fe^{2+}. Then, the prepared mixture was added dropwise to the 50 mL of 2 M NaOH. After vigorous mechanical stirring for 35 min. at 80 °C, the particles were washed with double distilled water, ethanol and again distilled water several times. Then, the external magnetic field was applied to the solution for the collection of Fe_3O_4 particles. The collected particles were stored in DMSO.

The polymer synthesis was carried out by free radical photopolymerization procedure.[30,31] The polymerization was performed by adding 0.5 g of acrylamide and 0.5 g of 1,3,5-triacryloylhexahydro-1,3,5-triazine in a baker. Approximately 10 mL of DMSO was added to the beaker and stirred for full dissolution. After that, 1.0 g of Fe_3O_4 particles (in DMSO) and 1.0 mL of DEAP were added to the solution and stirred for a few minutes. Then, the mixture was exposed to UV light from a Black Ray model B-100, UVP Inc. mercury lamp (365 nm maximum wavelength) to initiate polymerization. After 30 min exposure, the resulted polymer was washed with double distilled water, ethanol and again distilled water several times. The solution was filtered and the obtained polymer was hydrolyzed with 0.1 M NaOH containing 10% TEMED in a rotary shaker. The hydrolyzed polymer was washed with double distilled water, ethanol and again distilled water several times. Finally, the obtained Fe_3O_4 embedded hydrolyzed polymer was vacuum oven dried at 25 °C and then grinded in a mortar and stored in a capped glass bottle in the desiccator.

Removal and reuse experiments

The metal solutions were prepared in a mixture of the ICP standard solutions of arsenic and molybdenum. Also, the ICP multi-element solution was used to prepare calibration standards for the ICP measurements. The removal experiments were carried out by adding 0.1 – 1.0 g of Fe_3O_4 embedded hydrolyzed polymer with a rotary shaker at 50 – 200 rpm agitation rate for 10 – 240 min. The effect of initial pH on metal uptake was studied over pH range of 1.0 – 6.0 and natural pH (pH 2.5) of the mixed solution. The effect of temperature on adsorption was investigated in the range of 20 – 50 °C. The metal uptake efficiency with different initial concentrations was investigated in the range of 0.1 – 10.0 mg/L. The metal concentrations in treated solutions were analyzed in ICP-OES after filtration with 0.45 µm pore size cellulose nitrate filter paper (Sartorius). The metal uptake efficiency of removal process was performed using the following formula (2):

$$R(\%) = \frac{C_0 - C}{C_0} x100$$

(6)

where C_0 and C are the concentrations of metals before and after removal in mg/L, respectively.

After the removal experiment, the polymer was washed with double distilled deionized water and centrifuged at 4100 rpm. Before the regeneration process, the polymer was dried in vacuum oven at room temperature. Regeneration of Fe_3O_4 embedded polymer was made by 0.1 M HNO_3, 1 M $CaCl_2$, 1 M NaOH, 0.1 M EDTA and 1 M HNO_3 solutions for 150 min. contact time at 150 rpm agitation rate. After regeneration, the dried polymers were treated with metal ion solutions at pH 2.5.

CONCLUSIONS

In the present study, the Fe_3O_4 embedded acrylamide - 1,3,5-triacryloylhexahydro-1,3,5-triazine polymer was synthesized and hydrolyzed for the evaluation of arsenic(V) and molybdenum(VI) metal ions removal. According

to the results, the highest removal percentages were found for arsenic (100%) and molybdenum (98%) at pH 2.5 of the mixture solution, contact time of 150 min, agitation rate of 150 rpm, temperature of 25°C, initial heavy metal concentration of 2.5 mg/L, and polymer dosage of 0.25 g. The obtained results showed that the Fe_3O_4 embedded acrylamide based hydrolyzed polymer was a powerful material for the removal of As(V) and Mo(VI) with prevention of iron release. The reuse experiments were successfully done by $CaCl_2$ treated polymer for the removal of As(V) and Mo(VI) ions. The pseudo-second-order kinetic model and Langmuir isotherm were fitted on the experimental data.

REFERENCES

1. F. Jiao, J. C. Jumas, M. Womes, A. V. Chadwick, A. Harrison and P. G. Bruce, *J. Am. Chem. Soc.*, **2006**, *128*, 12905-12909.
2. Y. F. Shen, J. Tang, Z. H. Nie, Y. D. Wang, Y. Ren and L. Zuo, *Sep. Purif. Technol.,* **2009**, *68*, 312–319.
3. M. R. Jain, C. Jain and R. C. Jain, *J. Appl. Polym. Sci.,* **2013**, *129*, 2536–2543.
4. D. Mohan and C. U. Jr Pittman, *J. Hazard. Mater.,* **2007**, *142*, 1–53.
5. P. L. Smedley and D. G. Kinniburgh, "United Nations Synthesis Report on Arsenic in Drinking Water: Chapter 1. Source and Behaviour of Arsenic in Natural Waters", World Health Organization (WHO), Switzerland, 2001, p.2-4.
6. S. Mandal, M. Sahu and R. K. Patel, *Water. Resour. Ind.,* **2013**, *4*, 51–67.
7. T. Sumathi and G. Alagumuthu, *Int. J. Chem. Eng.*, **2014**, *2014*, 430417.
8. M. Gallegos-Garcia, K. Ramírez-Muñiz and S. Song, *Miner. Process. Extr. M.*, **2012**, *33*, 301–315.
9. S. Aredes, B. Klein and M. Pawlik, *J. Clean. Prod.,* **2012**, *29-30,* 208-213.
10. M. G. Mostafa, Y. H. Chen, J. S. Jean, C. C. Liu and H. Teng, *Water Sci. Technol.*, **2010**, *62*, 378-386.
11. J. Torres, L. Gonzatto, G. Peinado, C. Kremer and E. Kremer, *J. Solution Chem.*, **2014**, 43, 1687-1700.
12. G. R. LeGendre and D. D. Runnell, *Environ. Sci. Technol.,* **1975**, *9*, 744-749.
13. C. Pennesi, C. Totti and F. Beolchini, *PLoS ONE*, **2013**, *8*, e76870.
14. B. Verbinnen, C. Block, P. Lievens, A. Van Brecht and C. Vandecasteele, *Waste. Biomass. Valor.,* **2013**, *4*, 635–645.
15. T. M. Budnyak, V. A. Tertykh, E. S. Yanovska, D. Kołodyńska and A. Bartyzel, *Adsorpt. Sci. Technol.*, **2015**, *33*, 645-657.
16. J. Gun, I. Ekeltchik, O. Lev, R. Shelkov and A. Melman, *Chem. Commun.,* **2005**, 5319–5321.
17. S. Sivrikaya, E. Cerrahoglu, M. Imamoglu and M. Arslan, *Toxicol. Environ. Chem.*, **2013**, *95*, 899-908.

18. K. Lee and S. A. Asher, *J. Am. Chem. Soc.,* **2000**, *122,* 9534-9537.

19. K. B. Payne and T. M. Abdel-Fattah, *J. Environ. Sci. Heal.,* **2005**, *40*, 723–749.

20. C. H. Liu, Y. H. Chuang, T. Y. Chen, Y. Tian, H. Li, M. K. Wang and W. Zhang*, Environ. Sci. Technol.*, **2015**, *49*, 7726–7734.

21. L. Zeng, *Water. Qual. Res. J. Canada.,* **2004**, *39*, 267–275.

22. M. J. Kim and M. Jang, "Water and Geoscience: Adsorption of Molybdate Onto Hematite: Kinetics and Equilibrium", WSEAS Press, UK, 2010, p.170-173.

23. İ. Şahin, S. Yilmazer Keskin and C. S. Keskin, *Des. Water Treat.,* **2013**, *51*, 4524-4529.

24. S. Lagergren, K. Sven, *Vetenskapsakad. Handl*., **1898**, *24*, 1–39.

25. Y. S. Ho and G. McKay, *Process. Biochem.*, **1999**, *34*, 451–465.

26. Z. Aly, A. Graulet, N. Scales and T. Hanley, *Environ. Sci. Pollut. R.*, **2014**, *21*, 3972–3986.

27. M. Imamoglu, H. Yıldız, H. Altundag and Y. Turhan, *J. Disper. Sci. Technol.*, **2015**, *36*, 284–290.

28. S. Srivastava and P. Goyal, "Novel Biomaterials: Environmental Science and Engineering", C Springer-Verlag Berlin Heidelberg, 2010, p. 87-88.

29. B. Batra, S. Lata and C. S. Pundir, *Bioprocess Biosyst. Eng.,* **2013***, 6,* 1591-1599.

30. A. Özdemir and C. S. Keskin, *J. Anal. Chem+.,* **2011***, 66*, 763–769.

31. S. A. Asher, A. C. Sharma, A. V. Goponenko and M. M. Ward, *Anal. Chem.,* **2003***, 75*, 1676-1683.