



Wastewater Treatment by Using Polyurethane Foams Modified with Bis-[2-ethylhexyl] Phosphoric Acid: Kinetics, Equilibrium and Desorption Studies

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ABSTRACT

Background: Water pollution is an important environmental problem, undoubtedly, the presence of toxic heavy metals forms the main source of water contamination. Sorption characteristics of polyurethane foams modified with bis (2-ethylhexyl) phosphoric acid (DEHPA) for the removal of zinc, lead and cadmium ions from contaminated solutions were investigated.

Methods: Operating variables, such as initial pH of the aqueous solution (1-6), ion concentrations (5-100 mg/l), sorbent dosage (1-8 g) and contact time (0-60 min), were studied.

Results: A value of $98 \pm 3\%$ of initial amount of studied ions (20 mg/l) was eliminated using 5 g of polyurethane sorbent modified with DEHPA (0.01 M in methanol) at pH 5. The selectivity order for metal ions toward the sorbent is $Zn > Pb > Cd$. Analysis of the equilibrium sorption data using Langmuir, Freundlich and Temkin models revealed that the Langmuir model was well suited to describe the zinc, lead and cadmium ions sorption. Power function, simple Elovich, pseudo first-order and pseudo second-order kinetics were applied for kinetic study in batch sorption and it was found that experimental data can be suitably described by pseudo second-order model.

Conclusion: Removal of studied metal ions from real samples shows that the modified polyurethane foam is useful for the treatment of polluted waters.

1. Introduction

Water pollution is an important environmental problem. The world health organization (WHO) announced that an average of 50,000 people die each day from diseases associated with contaminated water; one person about every two seconds [1-5].

Undoubtedly, the presence of toxic heavy metals

forms the main source of water contamination. It is considered as a chemical pollution and resistant against environmental conditions and easily gets into the food chain and accumulates increasingly in living organisms [6-9]. Rapid industrialization like battery manufacturing, metal processing, mining, electroplating, textile, traffic and similar anthropogenic sources increases the emancipation of toxic heavy metals in the water sources [10-11].

Removal of heavy metals from contaminated waters, include prevalent technologies such as ion exchange, evaporation, membrane separation and chemical precipitation and it requires high operational and capital costs [12-13]. On the other hand, these processes are of low selectivity, high reagent, generate secondary wastes and cannot effectively be used for various wastewaters. Among the different removal methods, sorption is economically attractive with major advantages such as reduction of chemicals, low cost and high efficiency. On the other hand, biological sorbent require no extra nutrient and renewal of sorbent [14-22]. Consequently, different types of sorbent in unmodified and modified form were studied for sorption of metal ions from contaminated waters.

The capability of DEHPA (bis(2-ethylhexyl)phosphoric acid, Figure 1) in the extraction of lead ions has been demonstrated [23-24]. Also, polyurethane, a polymer which includes a chain of organic units joined by carbamate links, is applied as a bed for removal agent and is used in the treatment of waste waters [25-27]. In the present study, polyurethane foam modified with DEHPA was used for the removal of heavy metal ions (Zn, Pb and Cd) from contaminated waters. Polyurethane foam is choice because of its plenty availability, ease of disposal without costly renewal and low cost. Several parameters which affect the process such as; the contact time, the initial ion concentration, pH of aqueous solution, mass of sorbent and bed height were studied and debated using a fixed-bed column.

The kinetic studies and isotherms of the sorption process were scrutinized. The research work was carried out in Environmental Science Research Laboratory, Department of Environmental Science, in collaboration with Phase Equilibria Research Laboratory, Department of Chemistry, University of Zanjan, Iran from Aug. 2013 to Jan. 2014.

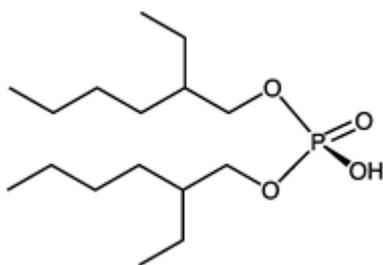


Figure. 1: Structure of bis (2-ethylhexyl) Phosphoric Acid (DEHPA)

2. Materials and Methods

2.1. Chemicals and Reagents

Bis (2-ethylhexyl) phosphoric acid (8141810250, Merck), methanol (8222831000, Merck), nitrate salt of studied metals such as lead (1120671000, Merck) and zinc (1088331000, Merck), cadmium (1020010250, Merck) with purity $\geq 99\%$, sodium hydroxide (106498, Merck) and hydrochloric acid (100317, Merck) were obtained from Merck or Fluka. All chemicals were used throughout the study without further purification.

A stock solution of studied ions (10000 mg/l) was prepared by dissolving a proper quantity of corresponding nitrate salt in distilled water. This solution was standardized complex metrically [28]. All working solutions were prepared by diluting the stock solution. Hydrochloric acid and sodium hydroxide solutions were used for pH adjustments. A pH meter (Metrohm 620) was used for measuring the pH. The pH meter was calibrated before use with three standard buffer solutions 4, 7 and 10. The prepared mixture was stirred with IKA KS 260 BASIC stirrer. The ions concentration in the solution was measured by flame atomic absorption spectroscopy (FAAS) (Varian 220 AA).

2.2. Sorption Procedures

A syringe, 5.0 cm long and 2.0 cm diameter was used as column for the experimental set up. At first, 3 g sorbent was soaked with a DEHPA solution in methanol (0.01 M) for 10 h. Then the excess solvent was removed by filter paper and this modified polyurethane foam was packed in the column (i.e., 2 cm of packing height). Experiments were performed at 28 °C. The temperature of experiment vessel was controlled by circulating thermostated water through the jacket of experiment cell. The effects of the initial pH of solutions, amount of DEHPA on the sorbent and mass of sorbent on uptake of ions were studied in packed-bed column system.

A volume of 100 ml solution containing zinc, lead and cadmium ions (initial concentration 20 mg/l) was passed through the column using a flow rate of 1 ml/min. The flow rate in all experiment was kept constant. To determine the removal efficiency, the concentration of metal ions before and after passing through the column was measured by FAAS.

2.3. Calculations

Sorption capacity (in terms of mg of sorbed species to g of sorbent) and uptake percentage were calculated by the following equations:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

$$\text{Uptake percentage} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Where “ q_t ” is the amount of ion sorbed (mg/g of sorbent) at time “ t ”, “ V ” is the volume of sample solution (l), “ W ” shows the weight of sorbent (g), “ C_0 ” and “ C_t ” are the metal concentrations in aqueous solution (mg/l) at initial and at any time “ t ”, respectively.

In order to investigate the kinetics of sorption, the time dependency of sorption process was studied in batch system. The experiments were performed by mixing 3 g of sorbent with 100 ml of aqueous solutions containing individual zinc, lead and cadmium ions. An efficient mixing of the phases was achieved using a Shaker (IKA-KS260) at 500 rpm. Aliquots were taken at specific time intervals and the metals concentration in the solution was measured by FAAS.

3. Results and Discussion

3.1. The Sorbent Characterization

The FTIR spectra of polyurethane sorbent modified with DEHPA are given in Figure 2. In both spectrums, there are some group of uniform peaks. Stretching vibration of N–H and O–H bonds were observe in the broad absorption band at 3416 cm^{-1} .

The (C–O), (C–N) and (N–H) bands are related to 1530 , 1220 , and 1233 cm^{-1} , respectively. Stretching vibration of hydrogen-bonded carbonyl groups between N–H and C O of polyurethane foam is shown at 1727 cm^{-1} peak. Other peaks of strong absorption were attributed to asymmetrical and symmetrical stretching vibration of $-\text{CH}_2$ at 2928 and 2855 cm^{-1} , respectively. The peak of phosphoryl bond stretching (P = O) vibration is shown at 1233 cm^{-1} and the peak at 1030 cm^{-1} is assigned to P–OH stretching for DEHPA [29].

3.2. Effect of Solution pH Value on the Efficiency of Heavy Metal ions Removal

The removal of zinc, lead and cadmium ions was investigated at a pH of 1.0 to 6.0. Figure 3 shows that the heavy metal sorption increased with pH, this process is determined with cation exchange mechanism. “Sorption edge” called the pH value (often 2 units wide) for any metal ion, is critical as the metal uptake efficiency increases from a very low level to a maximum value [30]. In this work, the pH range of 1–3 was determined for sorption edge and sorption was autonomous for pH alteration and change was negligible at pH range of 3–6. Sorption of the metal ions onto the modified polyurethane surface at a low H^+ concentration in the solution (a high pH) was increased, due to the existence of low competition between the heavy metal and H^+ ions for the sorption sites on the polyurethane. Also, the result shows that at all studied pH values have selective sorption as $\text{Zn} > \text{Pb} > \text{Cd}$. This selectivity was also confirmed in solvent extraction of studied heavy metal ions by DEHPA [23]. Optimum pH at the range of 5–6 was achieved for sorption of studied cations onto sorbent.

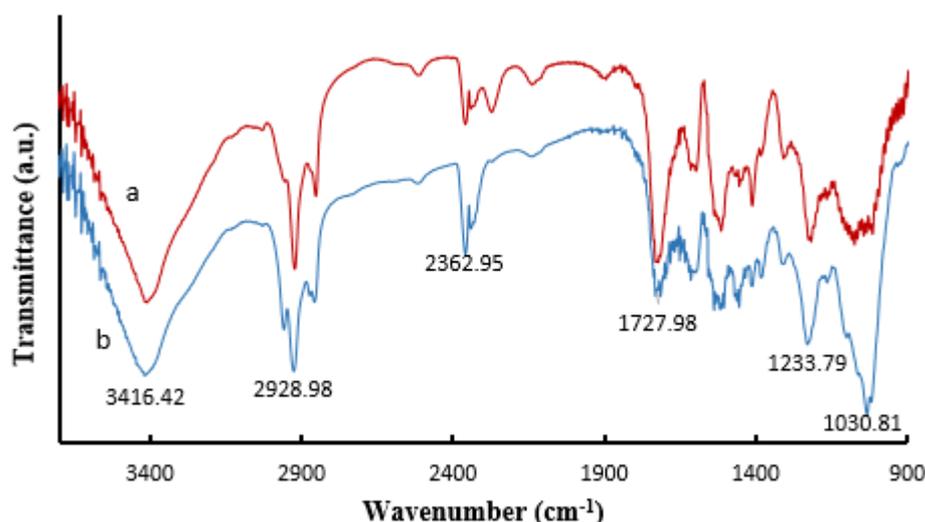


Figure 2: IR Spectra of (a) Polyurethane Foam (b) Polyurethane Modified with DEHPA

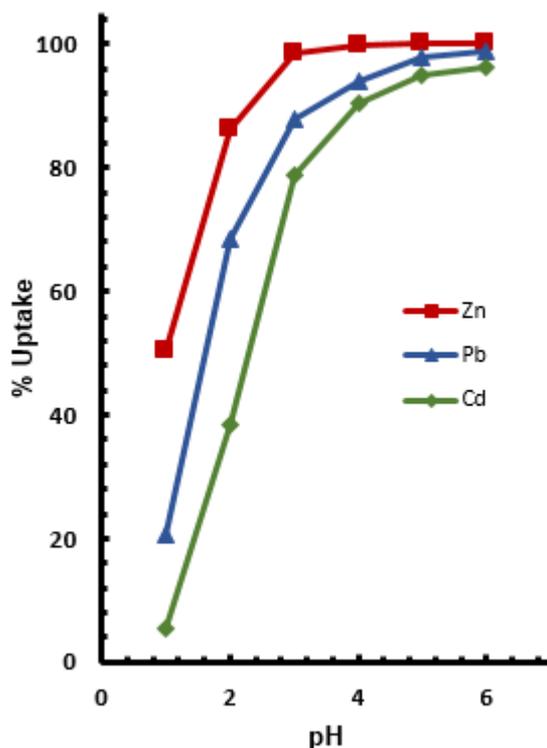


Figure 3: Effect of pH on the Uptake of Zinc (■), Lead (▲) and Cadmium (◆) ions on the Modified Sorbent Surface. Initial ion Concentration: 20 mg/l, Sample Solution Volume: 100 ml, Sorbent: 3 g, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Temperature: 28°C

3.3. Effect of DEHPA Concentration in Socking Solution on the Uptake

The influence of the concentration of DEHPA dissolved in methanol, as the socking solution, on the removal of ions by modified polyurethane was investigated. For example, the removal of lead is shown in Figure 4, higher removal values are obtained by increasing the concentration in the range of 0.00 to 0.01 M of DEHPA in the socking solution after which no remarkable increase in uptake of ions was observed.

Nevertheless, due to the existence of hydroxyl and amide groups on polyurethane surface; almost 48% of lead ions can be removed in the absence of DEHPA.

As a result, 0.01 M of DEHPA is sufficient to attain maximum ions uptake, therefore it was considered for further studies of sorption.

3.4. Effect of Sorbent Weight on the Efficiency of Metal ions Removal

Various masses of sorbent were used for investigating the effect of bed height on sorption of Zn^{2+} , Pb^{2+} and Cd^{2+} .

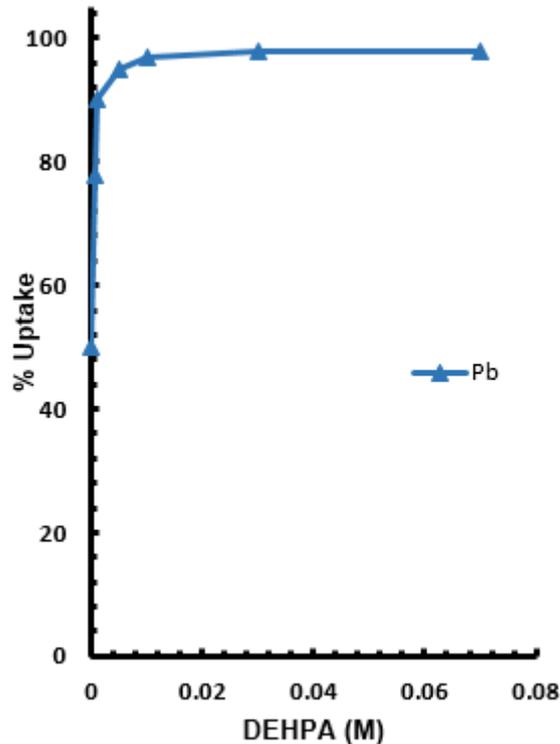


Figure 4: Effect of DEHPA Concentration in Socking Solution on the Uptake of Lead ions on the Modified Sorbent Surface. Initial ion Concentration: 20 mg/l, pH: 5, Sample Solution Volume: 100 ml, Sorbent: 3 g, Socking Time: 10 h, Temperature: 28°C

The uptake of studied ions for different heights of bed was acquired from the fixed concentration of heavy metal ion in the column. Figure 5 shows directly the relevance between the amount of metal ion uptake and the mass of sorbent present in the bed-column. Results indicate that 3 g of modified sorbent can favorably remove heavy metal ions from solution of studied ions (100 ml, 20 mg/l). The amount of modified sorbent in further works has been taken as 3 g. However, uptake of about 95 to 100% of studied ions was achieved with 5 g of the modified sorbent.

3.5. Effect of the Initial Metal Concentration on the Sorption Efficiency of Metal ions Removal

The effect of the initial metal concentration on the sorption efficiency of Zn^{2+} , Pb^{2+} and Cd^{2+} was studied over a range of 5 to 100 mg/l. Results in Figure 6 showed that the initial metal concentration was increased which led to decreasing in the percentage of ion removal from almost 99.80% to 66.97%, 97.40% to 57.20% and 95.42% to 23.31% for Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively.

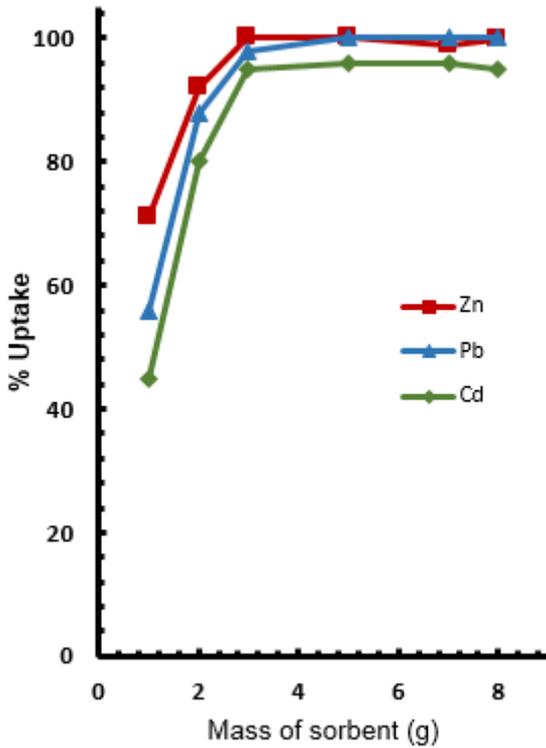


Figure 5: Effect of Mass of Sorbent on the Sorption of Zinc (■), Lead (▲) and Cadmium (◆) ions on the Modified Sorbent Surface. Initial Ion Concentration: 20 mg/l, pH: 5, Sample Solution Volume: 100 ml, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Temperature: 28°C

As removal decreases, the metal concentration increases due to the impregnation of the sorption sites which exist on the sorbent, for its given dosage.

3.6. Sorption Isotherms

Sorption isotherms can come up with some significant information in augmenting the application of sorbent, which is important to describe how solutes interact with sorbents. Isotherm equilibrium models can be used for explaining the interaction between sorbents and sorbate molecules, sorption capacity and procedure energy [31-32]. The Langmuir (Eq. 3), Freundlich (Eq. 5) and Temkin (Eq. 6) isotherm models were used to describe the sorption isotherms:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \tag{3}$$

In this equation, “C_e” denotes the concentration of melamine in solution at equilibrium (mg/l), “q_e” shows amount of analyte that was absorbed at equilibrium time (mg/g) and its maximum is “Q_{max}” which shows the sorption capacity and “b_L” is the constant which indicates the binding energy amount of the sorption procedure.

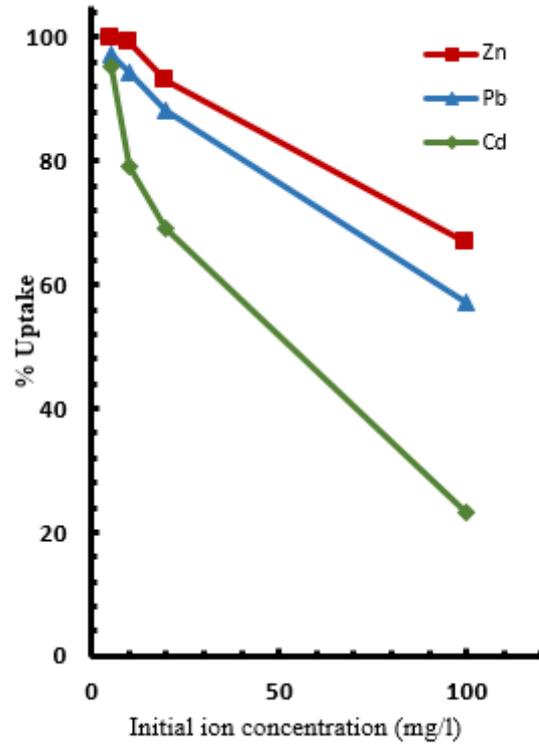


Figure 6: Effect of Initial Concentration on the Sorption of Zinc (■), Lead (▲) and Cadmium (◆) ions on the Modified Sorbent Surface. Sample Solution Volume: 100 ml, pH: 5, Sorbent: 3g, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Temperature: 28°C

Also, the favorability of sorption was evaluated by using a dimensionless constant called separation factor (R_L). The values of R_L which ranges between 0 and 1 confirm feasibility of sorption onto sorbents.

$$R_L = \frac{1}{1 + b_L C_0} \tag{4}$$

Where “C₀” is the initial concentration of melamine in sample solution (mg/l).

Equation 8 describes the Freundlich model in sorption studies:

$$\log q_e = \frac{1}{n} \log C_e + \log K \tag{5}$$

Where “K_F” (related to sorption capacity) and “n_F” (related to sorption intensity) are called Freundlich constants and n_F > 1 shows when a favorable sorption condition is done.

Temkin is another isotherm model (Equation 6):

$$q_e = \frac{RT}{b} \ln(aC_e) \tag{6}$$

Where “a” and “b_T” denote the Temkin isotherm constant (L/g) and heat of sorption (kJ/mol), respectively, R as the gas constant is 0.0083 kJ /K mol and T is temperature of system in Kelvin [33].

Homogeneity of surface, monolayer sorption and absence of interaction between sorbed analytes are the main assumption in the Langmuir model.

Therefore, in the Freundlich model, there are heterogeneity surface and multilayer sorption.

Eventually, Temkin isotherm is based on the linear adsorption of heat versus its logarithmic form in Freundlich equation. Due to the interaction between sorbate and sorbent, the sorption heat of all the molecules in adsorbed layer will linearly decrease.

Table 1 shows the given isotherm constants. It was indicated that determination of R² for Langmuir model of 0.975, 0.994, 0.996 for Zn²⁺, Pb²⁺ and Cd²⁺, respectively among the used model is best fit for the experimental data for studied ions sorption as shown in Figure 7. This designates that modified polyurethane sorbent would provide monolayer and homogeneous sorption for the metal ions. Also, the sorption process is categorized into four classes due to the R_L value; irreversible (R_L =0), linear (R_L =1), unfavorable (R_L >1) and favorable (0<R_L<1) [34]. Accordingly, it can be considered that the presented method as a favorable uptake process for the studied ions. Among the zinc, lead and copper ions value, Freundlich constant, for zinc is higher which indicates that the zinc sorption is better in modified sorbent than other studied ions. The BT and b values for Temkin model which are indication of the heat of sorption illustrate an ion-exchange sorption process.

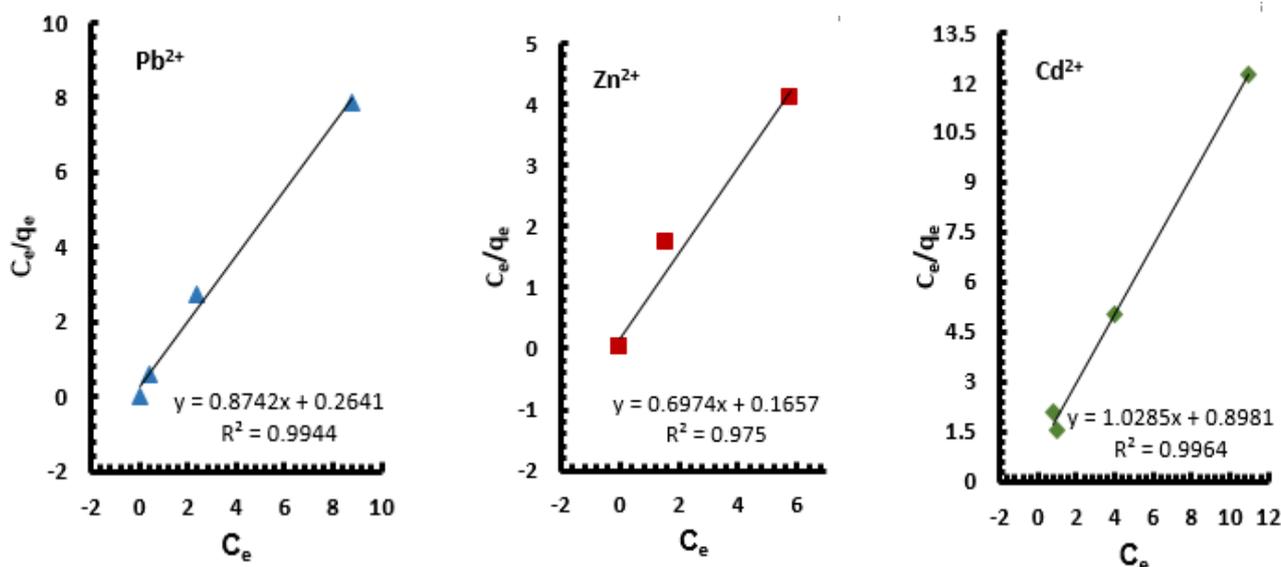


Figure 7: Langmuir Isotherm for Removal of Zinc (■), Lead (▲) and Cadmium (◆) ions by Modified Sorbent. Initial ion Concentration: 20 mg/l, pH: 5, Sample Solution Volume: 100 ml, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Temperature: 28°C

Different contact times were studied separately in a batch system for sorption of zinc, lead and cadmium ions by keeping all other experimental conditions constant (Figure 8). The sorption was increased with additional contact time and beyond 20 min, maximum sorption was achieved. These results can be described by considering a monolayer creation of ions on the sorption surface. Figure 8 shows variation of zinc, lead and cadmium ions uptake as a function of time.

3.7. Kinetic Study of Metal Ion Sorption

In order to investigate the mechanism of sorption, kinetic models, Power function (Eq. 7), simple Elovich (Eq. 8), pseudo-first order (Eq. 9) and pseudo-second-order kinetics (Eq. 10) are abundant useful model in sorption kinetics study:

$$\log q = \log k_p + v_p \log t \quad (7)$$

$$q_t = a_{ac} + 2.303b_{ac} \log t \quad (8)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

Table 1: Sorption isotherm parameters for Zinc, Lead and Cadmium ions sorption on modified polyurethane foam

M ²⁺	Langmuir				Freundlich			Temkin			
	Q _{max}	b _L	R _L	R ²	k _f	n _f	R ²	A	b	B _T	R ²
Zn ²⁺	1.434	0.714	0.065	0.975	1.069	14.705	0.777	37.693	9.958	251.423	0.909
Pb ²⁺	1.144	3.310	0.014	0.994	1.199	14.081	0.910	65.049	14.121	177.298	0.967
Cd ²⁺	0.974	0.001	0.987	0.979	1.945	3.816	0.738	24.651	15.057	166.280	0.831

Q₀ (mg/g), b (l/mg), k_f (mg/g), a (l/g), b (kJ/mol), B_T (J/mol)

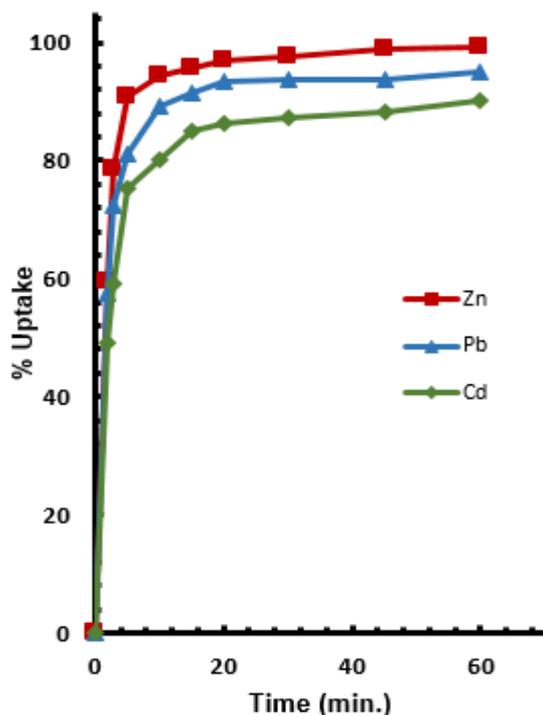


Figure. 8: Variation of Zinc (■), Lead (▲) and Cadmium (◆) ions Uptake as a Function of Time on the Modified Sorbent Surface. Initial Ion Concentration: 100 mg/l, pH: 5, Sample Solution Volume: 500 ml, Sorbent: 15 g, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Shaking Rate: 500rpm, Temperature: 28°C

In these equations, “t” (min.) and “q_t” (mg/g) is the time and quantities of adsorbed analytes on the surface of sorbent at time “t”. Also, “k_p” (mg/g min), “v_p”, “a_{se}” (mg/g min), “b_{se}” (g/mg), “k₁” (l/min) and “k₂” (in g/mg min) are adjustment parameters for studied models [35-37].

In this model, the initial rate (h₀ in mg/g min) of sorption [38] can be evaluated with Equation 11:

$$h_0 = k_2 q_e^2 \tag{11}$$

The results confirm that the pseudo-second order kinetic model conformed to the experimental

sorption data (Figure 9). These results show that the sorption of the metal ions on the modified polyurethane foam was controlled by the chemisorption process. Table 2 includes the evaluated kinetic parameters for the sorption of zinc, lead and cadmium ions onto used sorbent. A consideration of the values of correlation coefficients and the comparison of q_e and q_{exp} can lead to the conclusion that the pseudo second-order kinetic model is an acceptable model for the metal ions sorption in contrast to the other models. Calculated kinetic model parameters of the pseudo second-order model, h₀ and k₂, confirm the selectivity order for metal ions toward the sorbent as Zn> Pb> Cd.

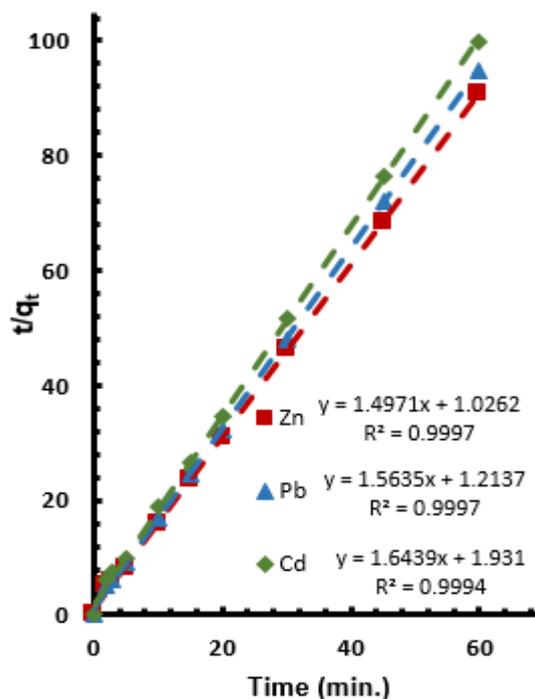


Figure. 9: Pseudo Second Order Models for Removal of Zinc (■), Lead (▲) and Cadmium (◆) ions by Modified Sorbent. Initial Ion Concentration: 100 mg/l, pH: 5, Sample Solution Volume: 500 ml, Sorbent: 15 g, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Shaking Rate: 500rpm, Temperature: 28°C

In recycling standpoint, recovery of sorbed material for reuse metal ions is necessary. Water was not possible for recovery of sorbed metal ions on the sorbent, thus, 20 ml of sulfuric, hydrochloric and nitric acids with concentration 0.5 M were used. All three types of used acid desorb quantitatively the studied ions from the modified polyurethane foam. Under the mentioned conditions, more than 98% of all the heavy metal ions were stripped.

The introduced method was applied for the removal of heavy metal ions from a preliminary treated effluent regarding lead and zinc production industries in Zanjan

Province, Iran. Some characteristics of effluent samples are indicated in Table 3.

Examined real sample included low levels of studied ions, thus the recovery percentage of the optimized removal procedure was investigated by recognizing the amount of added metal ions to each real sample. Table 4 shows the recovery results (4 replicatse) from real sample. As can be seen, the amount of heavy metal ions in the real sample dramatically reduced (more than 96%) with the application of the proposed method.

The studied ions were readily and quantitatively stripped from the modified sorbent using 0.1 M HNO₃ and H₂SO₄.

Table 2: Kinetic model parameters for Zinc, Lead and Cadmium ions sorption on modified polyurethane foam

M ²⁺	Power function			Simple elovich			Pseudo first-order		Pseudo second-order				
	k _p	v _p	R ²	a _{se}	b _{se}	R ²	k ₁	R ²	k ₂	h ₀	q _{exp}	q _e	R ²
Pb ²⁺	1.702	0.006	0.001	0.242	0.118	0.687	0.009	0.013	2.013	0.824	0.639	0.639	0.999
Zn ²⁺	1.629	0.008	0.002	0.121	0.264	0.654	0.007	0.014	2.184	0.974	0.660	0.668	0.999
Cd ²⁺	1.901	0.016	0.005	0.118	0.198	0.758	0.016	0.034	0.214	0.518	0.601	1.555	0.999

k_p(mg/g min), a (mg/g min), b (g/mg), k₁ (min⁻¹), k₂ (g/mg min), h₀ (mg/g min), q_{exp} and q_e (mg/g)

Table 3: Physical and chemical characteristic of the examined real samples

pH	TDS	EC	Pb ²⁺	Cd ²⁺	Zn ²⁺	Ni ²⁺	Cu ²⁺	Co ²⁺
	(mg/l)	(μS/cm)	mg/l					
6.3	158	316	5.5	5	10.1	Nd	Nd	Nd

Nd = Not detected

Table 4: Removal of Zinc, Lead and Cadmium ions from real sample with sorption on modified polyurethane foam

Sample	Metal ion	Concentration of Lead, Zinc and Cadmium ions (mg/l)			Uptake Percent
		Added ion	Before Removal	After Removal	
Zanjan Lead and Zinc Production Industries	Zinc	20.0	30.1	0.71	97.64
	Lead	20.0	25.5	0.90	96.47
	Cadmium	20.0	25.0	1.00	96.00

Nd = Not detected. Experimental Condition: Sample Solution Volume: 100 ml, pH: 5, Modified Sorbent: 3 g, DEHPA in Socking Solution: 0.01 M, Socking Time: 10 h, Temperature: 28°C

4. Conclusion

The present investigation shows that modified polyurethane foam with bis (2-ethylhexyl) phosphoric acid (DEHPA) can be applied as a practicable sorbent for the sorption of heavy metal ions (zinc, lead and cadmium) from contaminated water. Initial ion concentration, contact time and pH considerably affected the sorption capacity of modified polyurethane foam. Increase in pH values caused increased metal uptake. Langmuir isotherm and pseudo-second-order model had the best correlation coefficients for the sorption of Zn²⁺, Pb²⁺ and Cd²⁺ by modified sorbent. The suggested method can be reasonably applied for the optimal removal of heavy metal ions studied in industrial wastewater as real samples. Also, these sorbents could be applied for the removal of relatively higher metal ion concentrations from wastewater.

Conflict of Interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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