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KARADENIZ CHEMICAL SCIENCE AND TECHNOLOGY

Journal web page: www.kcstjournal.org

Research Article

Investigation of bonding properties of Pb(II), Cd(II) and Co(II) ions in some cation exchanger resins

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Keywords:
Cation exchanger resins, atomic absorption spectrophotometry, adsorption capacity, heavy metal ions

ABSTRACT

This study deals with the properties of ion exchange by Pb(II), Cd(II), and Co(II) on six different polystyrene cation exchanger resins (R) containing poly(ethylene glycol-dimethyl methacrylate) (PEG-DM) units as cross linkers. Micro beads of resins are 150-200 μm in diameter. Swelling ratios, ion exchanger capacities, initial metal ion concentrations, competitive ion exchange properties and regeneration ratios of resins were investigated. Ion exchangers' capacity shows a decrease with the increase of the degree of cross-linking. The maximum and minimum capacities were 3.29±0.22 and 2.28±0.18 meq/g, respectively. There were complex effects of pH on the ion exchange orders and capacities. Effects of initial concentration of metals were Pb(II) > Cd(II) > Co(II) for the R-PEG-DM-(400, 600, 1000, 1500, 10000, 35000) resins. Molar masses of PEG were in the range of 400-35000. The regeneration ratios were minimum 88.13±1.48% for Cd(II) on R-PEG-DM-600 and maximum 92.12±2.85% for Cd(II) on R-PEG-DM-1500.

TR

Bazı katyon değiştirici reçinelerin Pb(II), Cd(II) ve Co(II) iyonlarını bağlama özelliklerinin incelenmesi

Anahtar Kelimeler:
Katyon değiştirici reçine, atomik absorpsiyon spektrofotometri, adsorbsiyon kapasitesi, ağır metal iyonları

ÖZET

Bu çalışma, poli(etilenglikol-dimetil metakrilat) (PEG-DM) birimlerini çapraz olarak içeren altı çeşit polistiren katyon bağlayıcı reçinenin (R) Pb(II), Cd(II) ve Co(II) iyon bağlama özellikleri ele alındı. Reçinelerin mikro boncukları 150-200 μm çapındadır. Şişme oranları, iyon değiştirici kapasiteleri, başlangıç metal iyonu konsantrasyonları, yarışmalı iyon değişimi özellikleri ve reçinelerin rejenerasyon oranları araştırıldı. İyon değiştiricilerin çapraz bağlanma derecesi arttıkça iyon değiştirme kapasiteleri azalır. Katyon bağlama kapasiteler 3,29±0,22 ile 2,28±0,18 meq/g arasında bulundu. pH'nın iyon değişim sıraları ve kapasiteleri üzerinde karmaşık etkileri vardı. PEG-DM reçineleri R-PEG-DM- (400, 600, 1000, 1500, 10000, 35000) için metallerin başlangıç konsantrasyonunun etkisi Pb(II) > Cd(II) > Co(II) olarak bulundu. 400-35000 değerleri PEG'ün mol kütleleridir. Rejenerasyon oranları, R-PEG-DM-600'de Cd(II) için en az %88,13±1,48, R-PEG-DM-1500'de Cd(II) için maksimum % 92,12±2,85 bulundu.

1. Introduction

Ion exchange method has evolved as a technique for the separation and enrichment of metal ions at plentiful and trace levels. Investigations into the synthesis [1-6] and application of new cation exchangers have been actively pursued by a number of workers [7-11]. The recovery and concentration of metal ions from aqueous solutions have been the subject of much effort for metals such as copper from solutions derived from leaching of ores, which is well established commercially [12].

Heavy metal pollution is an important environmental problem today, and few studies have been reported about the use of polymeric ion exchange resins to identify and remove it [13,14]. The environmental pollution caused by heavy metals reaches the soil in various ways. The end result of agricultural pollution in contaminated soil reaches the food chain. As a result, all living things suffer from this situation [15,16].

Heavy metal determinations have been reported with some ion-exchange resins [17,18]. Ion exchange resins are also used in the treatment of wastewater [19,20]. Copper, chromium, cadmium ions were detected by atomic absorption spectroscopy in environmental samples using ion exchange resins [21].

We planned this study to identify some polymeric ion exchange resins for certain heavy metal ions. Ion-exchange resins used in this work were prepared from styrene and divinyl benzene crosslinked copolymers starting from styrene copolymerization by poly (ethylene glycol dimethyl methacrylate) [22].

This paper deals with the properties of ion-exchange by Pb(II), Cd(II) and Co(II) on six kinds of polystyrene cation exchanger resins containing poly(ethylene glycol dimethyl methacrylate) units as crosslinkers. The equilibrium of heavy metal uptake was measured under various pH and metal ion concentrations for cations mentioned above.

In the scope of this work, determination of swelling ratios of the resins, measurement of ion-exchange capacities, effect of initial metal ion concentrations, competition of ion-exchange on the exchanger resins, the regeneration ratios of the resins were studied.

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Citation: Ocak M., Özdemir, M., Savaşkan Yılmaz, S., Investigation of bonding properties of Pb(II), Cd(II) and Co(II) ions in some cation exchanger resins, *Karadeniz Chem. Sci. Tech.* 2017, 1, 43-48.

DOI:
ISSN:

2. Experimental

2.1. Apparatus

In this study, Unicam 929 model atomic absorption spectrophotometer was used for determination of metal ion concentrations. Grant Model SS 30 Type Shaker with Thermostat was used for obtaining equilibrium. pH measurements were accomplished by Jenway 3040 pH meter. Perkin-Elmer 1600 FTIR spectrophotometer was used for structure elucidation of polymers and ion-exchangers used in the experiments of present work.

2.2. Preparation of the ion-exchange resins

Ion-exchange resins were prepared according to the procedure reported previously [23,24]. Polystyrene-PEG crosslinked block copolymers were prepared from styrene copolymerization with poly(ethylene glycol dimethyl metacrylate) (PEG-DM). MW values of PEG of PEG-DM were 400, 600, 1000, 1500, 10000 and 35000 [22].

2.3. Chemicals and reagents

All of the chemicals used were of analytical reagent grade. All of the solutions were prepared with distilled deionized water. The chemicals hydrochloric acid, nitric acid, ammonia, sodium hydroxide, potassium hydroxide, disodiumhydrogen phosphate, sodium dihydrogenphosphate, stock Pb(II), Co(II), Cd(II) solutions, sulfuric acid solutions and phosphorus pentoxide were obtained from Merck. Preparation of stock and standardized solutions were explained in the corresponding text.

2.4. Procedure

In this study, six ion-exchanger resins containing poly(ethylene glycol dimethyl methacrylate) units were used. The resin materials were dried in vacuum oven at 30±0.5 ºC. Then they were placed in desiccator for avoiding moisture.

2.4.1. Determination of swelling ratios of the ion-exchange resins

The swelling ratios of polymers in water, chloroform and toluen were detected by using the polymer in 100 mL of these solvents at 20±0.5 ºC for 24 hours. The swelling ratio was estimated by the following equation [25]:

$$q_v = \frac{V_{dry\ polymer} + V_{solvent}}{V_{dry\ polymer}} = \frac{V_{swollen\ polymer}}{V_{dry\ polymer}} \qquad (1)$$

where, $V_{dry\ polymer}$ and $V_{solvent}$ are volume of dried polymer and solvent, respectively. The swelling ratios of the ion exchanger resins in water, chloroform and toluene are shown in Fig. 1.

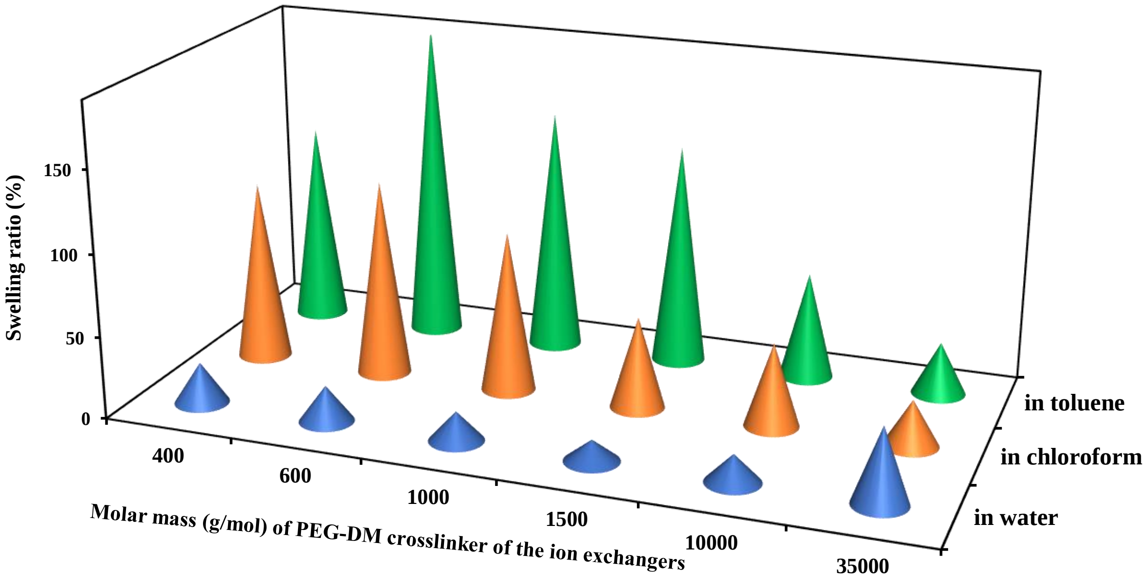

Fig. 1. The swelling ratios of R-PEG-DM-cation exchange resins

2.4.2. Determination of ion exchange capacities of the resins

The capacity of ion exchange resins was determent volumetrically. 200 mL of a 5% (w/v) NaCl solutions containing 0.8 g of NaOH and 0.5 g of the ion exchange resin prepared were kept overnight. Then 25 mL of the solution from mixture was taken by a pipette and titrated by 0.1021 M HCl. The capacity of ion exchanger was calculated using the acid consumption. The results are calculated as meq/g.

2.4.3. Effects of pH on ion uptake of the resins

To study the effect of pH on ion exchange, 25 mL of aqueous solutions containing 20 ppm of metal ions were equilibrated with R-PEG-DM-(400-35000) at different pHs of 2, 3, 4, 5, 6 and 7. The pH of solutions was adjusted with universal buffer solutions at 20±0.5 ºC in the flasks, and agitated magnetically at an agitation speed of 1600 rpm. After ion exchange, the cation exchanger was separated from the polymer medium by filtration. The concentrations of metal ions in the aqueous phases after 8 hour treatment were measured by using an ATI Unicam 929 model atomic absorption spectrophotometer.

Many investigations have been conducted about alkaline metal ion [26-28], alkaline earth metal ion [29, 30] and heavy metal ion [31-35] absorption properties of ion exchange resins at different pH values. The amount of exchange per unit mass of ion exchanger was calculated by using the following equation [36]:

$$Q = \frac{C_0 - C}{m} x V \qquad (2)$$

where, Q is the amount of metal ions exchanged by H^+ ions on to unit mass of the ion exchanger (mg/g). C_0 and C are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively, V is the volume of the aqueous phase as mL, and m is the amount of R-PEG-DM-(400-35000) ion exchanger in g. Results are given in Table 1.

Table 1. The effect of pH on the ion exchange (in aqueous media)

pH	Pb(II)	Cd(II)	Co(II)
	Metal ion uptake (mg/g) with R-PEG-DM-400[a] (X±SD)		
2	56.64±2.77	25.91±1.22	19.46±0.93
3	95.62±6.41	55.52±2.47	32.98±1.79
4	193.05±11.77	79.17±2.44	36.86±2.41
5	275.41±10.17	107.32±2.24	60.14±3.66
6	441.45±10.14	192.40±8.83	98.94±4.21
7	657.48±19.05	273.84±12.28	145.21±8.84
	Metal ion uptake (mg/g) with R- PEG-DM-600[a] (X±SD)		
2	33.04±1.41	23.04±0.89	12.06±0.46
3	70.80±2.59	40.96±2.04	21.44±0.59
4	136.35±4.21	56.32±1.92	32.16±1.21
5	197.13±4.72	79.36±1.58	41.54±1.51
6	311.85±5.91	125.44±4.62	65.66±2.53
7	470.51±17.86	199.68±5.77	108.54±3.02
	Metal ion uptake (mg/g) with R- PEG-DM-1000[a] (X±SD)		
2	44.73±1.54	25.47±0.85	12.69±0.41
3	74.55±2.88	43.04±1.33	22.56±0.71
4	147.28±2.64	59.18±1.47	31.01±0.82
5	201.15±2.61	83.39±2.57	47.94±1.64
6	321.35±9.95	131.81±3.53	78.96±3.17
7	489.13±6.84	212.51±4.66	117.03±1.49
	Metal ion uptake (mg/g) with R- PEG-DM-1500[a] (X±SD)		
2	36.26±1.12	25.21±0.57	16.23±0.49
3	77.71±1.92	44.80±0.92	23.60±0.48
4	195.69±5.07	58.83±1.21	35.41±0.73
5	273.17±5.73	103.61±3.19	60.47±1.86
6	456.84±14.51	131.64±4.45	75.23±2.85
7	503.21±10.56	221.25±6.85	116.52±2.43
	Metal ion uptake (mg/g) with R-PEG-DM-10000[a] (X±SD)		
2	54.65±1.67	24.12±0.74	14.16±0.43
3	79.48±2.68	42.88±1.63	22.65±0.55
4	191.23±4.01	64.32±1.34	33.98±1.05
5	285.69±5.98	109.88±2.72	60.88±1.26
6	387.34±9.67	139.36±4.31	75.05±1.87
7	496.38±10.41	211.72±4.43	111.86±3.77
	Metal ion uptake (mg/g) with R-PEG-DM-35000[a] (X±SD)		
2	86.38±2.15	43.14±1.21	22.72±0.81
3	112.96±3.92	57.52±1.82	37.39±1.44
4	252.76±9.57	82.69±2.29	43.56±1.21
5	379.08±13.64	147.40±3.82	77.65±2.01
6	575.17±16.17	194.14±6.59	96.59±2.44
7	659.22±13.83	278.40±8.06	137.19±4.24

[a] Average of six determinations

2.4.4. Effect of initial concentration of metals on ion uptake of the resins

The study was focused on the effect of the initial concentration of metal ions on the ion exchange. Aqueous solutions of 25 mL with different amounts of heavy metal ions in the range of 2-12x10^{-3} mol/L were separately treated with R-PEG-DM-(400-35000) ion exchangers at pH=7 for 8 hours. The extent of ion exchange was calculated according to Eq. 2. The results are given in Table 2.

2.4.5. Competetive ion exchange on the ion exchanger resins

Competetive ion exchange of Pb(II), Cd(II) and Co(II) from their mixture was also tested in the same study. 25 mL of solution containing 30 ppm from each metal ion was equilibrated with 100 mg of R-PEG-DM-(400-35000) ion exchangers at a pH of 7.0 at 25±0.5 ºC. The results are given in Fig. 2.

Table 2. Effect of initial concentration of metal ions on the ion exchange (in aqueous media)

Metal ion concentration (mol/L)	Pb(II)	Cd(II)	Co(II)
	Metal ion uptake (mg/g) with R-PEG-DM-400[a] (X±SD)		
2x10^{-3}	101.18±3.13	53.44±0.63	28.29±0.86
4x10^{-3}	201.34±4.22	110.15±1.43	56.58±1.45
6x10^{-3}	309.14±3.39	159.27±2.97	85.87±2.04
8x10^{-3}	410.35±4.12	215.14±6.66	115.16±2.76
10x10^{-3}	485.18±6.79	269.14±7.53	144.45±4.46
12x10^{-3}	487.12±8.76	270.05±2.97	145.14±1.74
	Metal ion uptake (mg/g) with R-PEG-DM-600[a] (X±SD)		
2x10^{-3}	100.83±2.14	52.45±2.13	27.24±0.83
4x10^{-3}	200.15±2.98	108.71±2.26	54.91±1.29
6x10^{-3}	304.82±4.56	157.13±2.51	83.46±1.74
8x10^{-3}	348.18±4.17	205.21±6.35	103.72±3.19
10x10^{-3}	349.12±5.58	206.74±4.32	105.14±2.24
12x10^{-3}	349.15±9.12	206.93±3.91	105.87±1.99
	Metal ion uptake (mg/g) with R- PEG-DM-1000[a] (X±SD)		
2x10^{-3}	100.21±2.16	50.89±1.73	26.17±0.81
4x10^{-3}	199.17±5.17	101.42±1.91	51.45±1.37
6x10^{-3}	297.82±3.56	148.73±2.66	74.87±2.24
8x10^{-3}	371.35±7.04	199.17±4.77	91.39±2.51
10x10^{-3}	375.84±9.08	210.83±7.77	115.43±2.18
12x10^{-3}	376.14±6.76	211.35±6.54	116.13±1.73
	Metal ion uptake (mg/g) with R- PEG-DM-1500[a] (X±SD)		
2x10^{-3}	99.27±2.07	48.28±1.01	25.71±0.69
4x10^{-3}	197.34±6.10	97.35±3.12	49.27±1.51
6x10^{-3}	295.79±9.14	143.14±3.43	76.18±2.32
8x10^{-3}	378.17±11.71	189.73±3.59	99.14±2.67
10x10^{-3}	381.47±11.81	220.81±3.74	115.88±2.18
12x10^{-3}	381.95±8.01	221.28±2.43	116.63±3.13
	Metal ion uptake (mg/g) with R- PEG-DM-10000[a] (X±SD)		
2x10^{-3}	98.83±6.27	47.93±1.12	25.13±0.77
4x10^{-3}	191.76±4.58	95.28±1.99	50.05±1.27
6x10^{-3}	293.32±12.59	142.36±2.98	74.28±1.77
8x10^{-3}	389.91±9.33	188.17±5.24	99.81±2.37
10x10^{-3}	406.28±6.09	210.24±4.83	110.21±2.32
12x10^{-3}	406.39±5.27	210.51±6.51	110.96±4.61
	Metal ion uptake (mg/g) with R- PEG-DM-35000[a] (X±SD)		
2x10^{-3}	97.89±2.71	47.19±1.59	25.03±0.52
4x10^{-3}	193.15±6.56	93.71±2.97	49.81±1.12
6x10^{-3}	290.71±0.34	140.05±3.78	74.68±2.28
8x10^{-3}	387.29±8.12	178.33±3.75	99.13±3.95
10x10^{-3}	453.21±4.98	234.81±7.25	124.48±3.84
12x10^{-3}	453.84±4.57	235.18±3.76	125.13±2.87

[a] Average of six determinations

2.4.6. Determination of regeneration ratios of the ion exchanger resins

Regeneration of metalic cations was studied with HNO_3, HCl, CH_3COOH (0.01-0.2 M). The volumes of the acid solutions were varied from 5 to 50 mL. The optimum regeneration condition was 20 mL 0.1 M nitric acid. The ion exchanger resins carrying metal ions were placed in this desorption medium and stirred for 24 h at 20±0.5 ºC. The resulting metal ion concentration in the aqueous phase was determined by using AAS. The amount of metal ions absorbed on the ion exchanger resins and the final metal ions in the desorption medium were calculated by using Eq.3. Fig. 3 shows recovery percentage of metal ions on the ion exchanger resins.

$$\text{Regeneration\%} = \frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on the ion exchanger resins}} \text{ x } 100 \qquad (3)$$

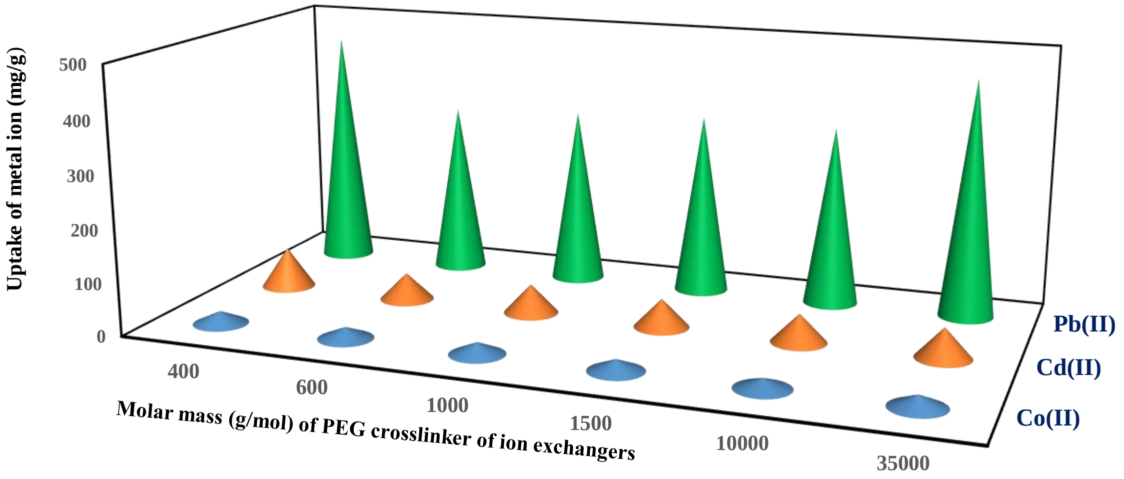

Fig. 2. Competitive ion exchange of Pb(II), Cd(II), Co(II) metal ions on R-PEG-DM cation exchange resins (in aqueous media)

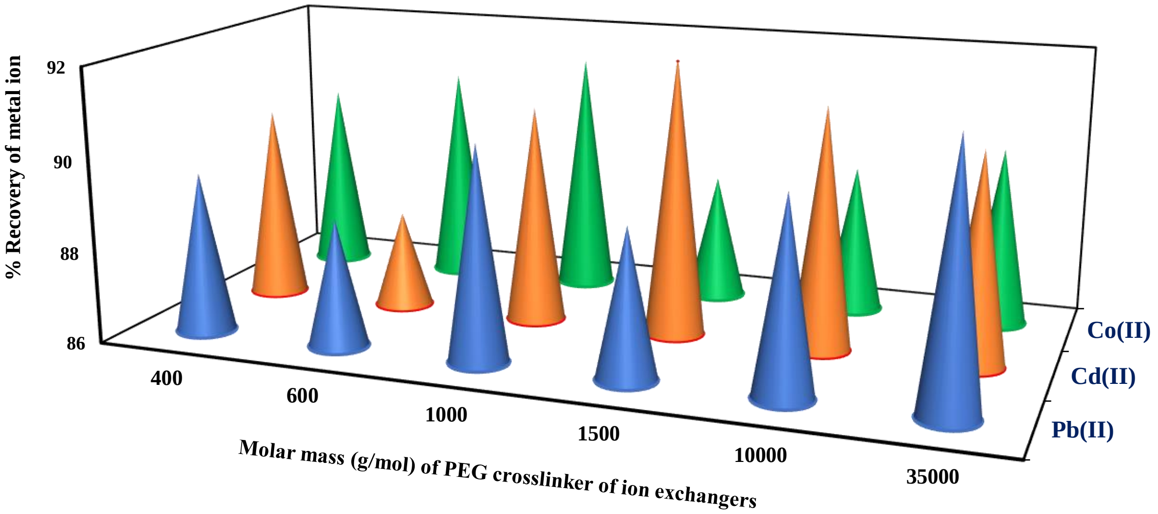

Fig. 3. Recovery of metal ions (in aqueous media)

3. Results and discussion

The primary objective of this study was to explore the cation exchange properties of R-PEG-DM-(400, 600, 1000, 1500, 10000, 35000) resins.

3.1. Swelling ratios of the ion exchanger resins

The swelling ratios of water, chloroform and toluene of unsulphonated crosslinked, and sulphonated crosslinked polymers were considerable. Results are given in Fig. 1. This situation is suitable for the conclusion that increasing the crosslinkage degree decreases the capacity of solvent uptake and shows decrease of porosity of ion exchanger [37, 38].

The swelling ratios of the ion exchanger resins in toluene and chloroform are greater than in water. Because the skeleton of ion exchanger has hydrocarbon chain, the solvent of low polarity has more uptake tendency. The manner of ionic character of functional groups causes electrostatic solvation. This ensures the affinity of solvent for carboxylic groups in the resins [39]. The swelling is more in nonaqueous solvents than in pure water [40].

3.2. Capacities of ion exchanger resins

Resulting ion-exchange resin capacity shows a dependency on the crosslinkage degree. The ion exchange capacities of R-PEG-DM-(400-35000) are 3.29±0.22; 2.28±0.18; 2.43±0.19; 2.51±0.21; 2.43±0.16 and 3.21±0.14 meq/g, respectively. The results show that the ion exchange capacity decreases while increasing the amount of crosslinker monomer PEG-DM. These results are in line with the literature values that the capacity is decreased with increasing the amount of crosslinker [41].

3.3. Effect of pH on ion exchange with the resins

The effects of pH and metal ion concentration on the absorption of Pb(II), Cd(II) and Co(II) with these six resins were investigated at different pHs and different metal ion concentrations. The optimum pH value was found to be seven. The absorption capacities of these resins for metal ions were roughly proportional to the total ion exchange capacity and metal ion concentration.

The order of metal ion uptake capacities on R-PEG-DM-(400-35000) ion exchanger are Pb(II) > Cd(II) > Co(II).

The comparison of six lists in Table 1 of pH values vs. metal ion uptake shows that metal ions are more strongly taken up by these resins, in particular, in the high pH region of pH > 4. Table 1 demonstrates pH profiles of capacities for the uptake of diverse metal ions; these data indicate that Pb(II), Cd(II), Co(II) metal ions exhibit decreasing affinity toward acidic region of pH=2. Among tested divalent heavy metal ions, the highest affinity with R-PEG DM-(400-35000) resins was detected for Pb(II) and the lowest one for Co(II) order. This manner is suitable for the amount of metal ion uptake of ion exchanger which increases with increasing radius of ion [42].

Table 3. Conditions for the spectrophotometric determination of metal ions (in aqueous media)

	Pb(II)	Cd(II)	Co(II)
Wavelength of maximum absorbance (nm)	217.0	228.8	240.7
Exit-slit (nm)	0.5	0.5	0.2
Lamb current (mA)	6.0	3.0	12
Species of flame	Air-acetylene	Air- acetylene	Air- acetylene
Air flow pressure (bar)	2.1	2.1	2.1
Rate of acetylene flow (L/min.)	1.0	1.2	0.9
Limit of detection (LOD) (µg/L)	38	11	24
Limit of quantification (LOQ) (µg/L)	130	40	80
LOD/LOQ	0.29	0.27	0.30
Range of linearity (mg/L)	0.13-10	0.04-1.25	0.08-8
Optimum pH	7	7	7
Calibration graph			
Slope	0.0183	0.118	0.0936
Intercept	-0.0008	0.1431	0.0022
Correlation coefficient (r)	0.999	0.903	0.999
Relative standard deviation (%)	0.97	1.05	1.12

The selectivity order of the ions in certain pH ranges can be investigated for hydration tendencies. The effects of hydration tendencies of metal ions on ion-trapping capacities of ion-exchange resins have been reported [43].

3.4. Effect of initial concentration of metals

The experimental results show that the order of metal ion uptake of ion exchanger resins changes at different initial metal ion concentrations. The optimum starting concentration is taken as $1{,}0x10^{-2}$ mol/L. The total solution concentration has an intricate effect on ion exchange [44-47]. The specific effects are observed in the ion exchange at very high solution concentrations. Exceptional problems which are not encountered in dilute aqueous solutions are brought out due to the measurement of the metal ion between the resin and bulk electrolyte. As the invasion to the resin becomes especially detectable, nonexchange electrolyte concentrations may become higher than the concentration of exchange sites. When the external solutions become very concentrated, the water activities decline in the resin, and the resin is swollen. Thus, the pressure-volume term becomes insignificant. The results are given in Table 2.

3.5. Competitive ion exchange

Competitive adsorption of the heavy metal ions are evaluated in this study. Fig. 2 shows the amount of exchange which is decreased with increasing the crosslinking degree of ion exchanger resins. The order of competitive ion exchange on R-PEG-DM-(400-35000) is Pb(II) > Cd(II) > Co(II). It is almost impossible to generalize the order of ion exchange or to define the amount of heavy metal ion uptake when the ions compete.

3.6. Regeneration ratios of the ion exchanger resins

In order to recurrently use these resins for recovery of metal ions, it is necessary for metal ions adsorbed to be eluted effortlessly. The elution of Pb(II), Cd(II), Co(II) on R-PEG-DM-(400-35000) was examined by the batch method. Fig. 3 indicates the elution of Pb (II), Cd(II) and Co(II) ions with 0.1 mol/L HNO_3 solution. Regenerations ratio was calculated by the expression given in Eq. 3. Regeneration were very high (up to 88.13±1.48%) with the eluant system and conditions used for all heavy metal ions. As seen here, the ion exchangers were used with regeneration repeatedly.

3.7. Beer's law and sensitivity

Calibration graphs for the determination of every metal cations were prepared under optimum experimental conditions. Beer's law is obeyed within a range of 0.13-10 µg/L, 0.04-1.25 µg/L, 0.08-8 µg/L of lead, cadmium, cobalt, respectively. Experimental conditions are listed in Table 3.

In this work, it has been demonstrated that a new knowledge can be given to the literature for the selective determination and removal of heavy metal ions by using polymeric ion exchange resins. Polymeric resins have also been found to be significantly altered by pH in relation to heavy metal ions. In addition, the results of the recovery studies show that these resins can be used repeatedly and analytically.

Acknowledgements

This work was supported by The Research Fund (Project No: 94.111.002.2) of Karadeniz Technical University (Trabzon, Türkiye). Authors thank Prof. Celal Duran for the assistance about AAS experiments.

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