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The application of acetylacetone for the separation of heavy metals in roadside soil belts by extraction methods

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ABSTRACT

The content of heavy metals in the vicinity of roads with high traffic intensity was determined. The possibility of recovery and separation of these metals from sulfate model solutions was also investigated using three methods: liquid–liquid system solvent extraction, transport through polymer inclusion membranes and by measuring sorption on polymeric sorbents based on polyvinyl chloride. Acetylacetone was the active substance in all processes. The parameters characteristic for these separation processes were determined. Excessive amounts of Zn, Cu, Cr, and Ni were found in soil samples. Even though all applied methods of metal separation are comparably effective, the sorption process is the cheapest. With sorption at pH = 7.8, the reduction of Zn, Cu, Cr, and Ni concentrations was 91%, 99%, 43%, and 11%, respectively, and the Zn/M separation coefficients for Cu, Cr and Ni were 1.15, 2.60 and 8.72, respectively.

Keywords: Heavy metals removal; Soil; Solvent extraction; PIM; Sorption

1. Introduction

Vehicle traffic and road operations are the sources of emissions of toxic gases, dust, and aerosols containing heavy metals [1]. According to the data from the Central Statistical Office of Poland (GUS) statistical yearbook, the emission of heavy metals resulting from road exploitation in Poland in 2015 amounted to 14.5 mg of lead, 5.96 mg of nickel, 3.58 mg of copper, 1.73 mg of chromium and 0.43 mg of cadmium, which, in total, constitutes 2.3% of the total emission of these metals [2]. Heavy metals are mainly generated by fuel combustion processes (Pb, Cu, Zn, Ni, Cd, Cr), wear and tear of vehicle parts (mainly structural elements and brake blocks for Cu, and tires for Zn), by fuel, lubricants and oils leaks (Cd, Cu, Ni) as well as by damaged road surface, corrosion of vehicles and road infrastructure (traffic barriers and road signs are particularly responsible for Zn generation), or by all waste material left behind by road users [3]. Despite the standards in force, the petrol used in the European Union member states has a high content of Cd (0.0038–1.5 μg/kg), Cr (0.14–28 μg/kg), Cu (0.14–23 μg/kg), Ni (0.02–6.1 μg/kg), Pb (0.035–9.7 μg/kg), Zn (0.19–240 μg/kg) [4]. With the rapid industrialization and urbanization trend, the increment of traffic activities substantially contributes to the accumulations of heavy metals discharged by vehicles in roadside environments. Heavy-metal pollution in agricultural areas owing to traffic emissions may contaminate the crops growing near the roadways [5]. In agricultural areas, uptake of heavy metals through the soil-crop system could play a predominant role in human exposure to heavy metals [6].

Heavy metals are found in all types of soil. They are very harmful if they exceed the permissible standards, even

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though their natural level does not pose a threat [6]. Metals in the soil environment can occur in various chemical forms with varying bioavailability to plant and animal organisms [7]. They are present in the soil solution in the form of cations and anions. Moreover, they have the ability to form sparingly soluble oxides and salts, are adsorbed on the surface of minerals components and may bind to organic acids and humus substances [8].

Metals and their compounds are not biodegradable. They can not only accumulate but also migrate to other compartments of the environment [9,10].

High concentrations of heavy metals may affect the ecosystem and human health. Heavy metals present in the roadside soils and grasses may be transported through the food chain to the human body and have significant toxicity to people. The environmental issues related to heavy-metal contamination are becoming serious in developing countries [11–19].

For several decades, a handful of technologies for the separation of heavy metal ions from aqueous solutions have been developed.

Over decades, several technologies have been developed to separate or remove heavy metal ions from aqueous solutions, such as chemical precipitation (including hydroxide precipitation [20] sulfide precipitation [21] and chelating precipitation [22], ion exchange [23], membrane techniques [24], solvent extraction [25–27], sorption [28]. Sorption methods draw more attention because they are simple to pursue without additional consumption, high performing and cost-effective [29–31].

Chelating compounds are used to effectively bind metals [32]. The 5- or 6-part membered chelate complexes are characterized by exceptional resistance.

The objective of the study was to determine the degree of heavy metal contamination of the upper layers of soils located along heavily trafficked roads. The possibility of recovery and separation of the metals occurring in the soil in the largest amounts was also investigated. To have a known and stable composition of the water phase, it was decided to investigate the separation processes from model solutions The investigations were carried out on model solutions using three methods: liquid–liquid system solvent extraction, transport through polymer inclusion membranes (PIM) and by measuring sorption on polymeric sorbents based on polyvinyl chloride (PVC). Acetylacetone was an active substance in all processes (Fig. 1). The parameters characteristic for these separation processes, such as the percentage reduction of metal concentration and separation coefficients, were determined.

2. Experimental section

The study was carried out on 6 samples (1–6) of soils collected at a distance of approx. 20 m from heavily trafficked roads and a layer of the depth of up to 30 cm. 3 samples (a, b, c) were taken from each portion of soil and then, for each sample the content of heavy metals was determined. For this purpose, each soil sample was weighed on an analytical balance with a precision of 1 g +/– 0.0001 g. Before leaching, the soil samples were dried to remove water. Thus, a sample of the sludge was placed in a laboratory dryer (WTC Binder 78532 Tuttlingen/Germany) and dried at 105°C to a constant weight. They were then ground in an agate mortar.

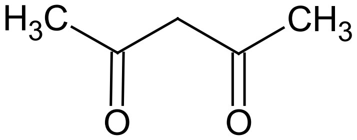


Fig. 1. Structure of acetylacetone (acac).

The content of metals in soil samples was determined by:

- Mineralization in a mixture (5:1 v/v) of concentrated HNO_3 (65%) and $HClO_4$ (65%) acids.
- Leaching with concentrated ammonia at ambient temperature.

Heavy metal content (Cd, Pb, Cr, Zn, Cu, Ni) was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) technique in a cyclone separator chamber at the following apparatus setup: 1 kW output power, argon plasma flow 15 dm^3/min, argon shielding flow - 1.5 L/min and argon nebulizing flow - 0.75 L/min, sample administration - 30 s, pump speed 15 rpm, number of reruns - 3. The wavelengths at which metals were determined were 226.502, 220.353, 267.716, 202.548, 327.395 and 231.604 nm for Cd, Pb, Cr, Zn, Cu, and Ni, respectively.

The possibility of separation of metals occurring in the largest quantities (Zn, Cr, Cu, and Ni) was studied in model solutions. The model solutions were prepared using zinc, copper, chromium and nickel sulfates ($ZnSO_4\cdot 7H_2O$, $CuSO_4\cdot 5H_2O$, $Cr_2(SO_4)_3\cdot 12H_2O$, and $NiSO_4\cdot 7H_2O$, POCh, Gliwice, Poland). The prepared standard solutions of zinc and cadmium salts contained the average content of these metals resulting from their original amount in soil samples.

Model solutions of each metal ion were prepared by dissolving appropriate amounts of sulfates in deionized water. All aqueous solutions were prepared using analytical reagent grade chemicals and deionized water (conductivity - 0.10 μS/cm).

2.1. Extraction procedure

The potassium sulfate of analytical reagent grade (POCh, Gliwice, Poland) was recrystallized from distilled water and its concentration was determined gravimetrically. Ammonia buffer was prepared from ammonia and ammonium sulfate (both analytical reagent grade, POCh, Poland). Sulphuric acid (analytical reagent grade, POCh, Poland) was standardized with anhydrous sodium carbonate. Kerosene (pure for analysis, Chempur Company, Piekary Śląskie, Poland) was used as received. The pH-meter (PHM 250, Radiometer, equipped with a glass-calomel combination electrode C 2401-8 (Radiometer)) was calibrated using commercial buffer solutions (Radiometer) having a pH of 7.00 ± 0.01 and 9.21 ± 0.01. The pH was also checked against hydrochloric acid according to the International Union of Pure and Applied Chemistry (IUPAC) recommendations [33].

The measurements were carried out at 20°C and a fixed ionic strength (0.5 mol/L) maintained in the aqueous phase with K_2SO_4. Whereas constant pH was maintained with ammonia buffer ($NH_3 + NH_4NO_3$, 1:1). Before extraction, the concentrations of Zn(II), Cr(III), Cu(II), and Ni(II) ions in the aqueous phase were kept constant (0.01 mol/L) and the ligand (acac) concentration in the organic phase (methylene chloride) was varied (from 0.01 to 0.04 mol/L). A volume of 5 ml of the aqueous phase was placed in a graduated test tube and an equal volume of acac (Sigma Aldrich, Poland) solution was added to the organic solvent. The test tubes were then shaken for 30 min. The equilibrium was established after a few minutes; however, no longer than 30 min. Afterward, it was checked if any changes had occurred in the phase volumes, then the phases were separated and the pH of the aqueous phase was measured. The Zn(II), Cu(II), Cr(III), and Ni(II) concentrations in the aqueous phase were determined using the ICP-OES technique.

2.2. Preparation and characteristics of PIMs

The concentration of the ion carrier in the membrane was 60% since earlier studies [34] indicate that the concentration is optimum for that group of carriers. The polymer membranes were prepared according to the procedure reported in our previous papers [34,35]. Organic solutions with 35% of support (PVC, Anvil, Wloclawek, Poland), 60% of the ion carrier, and 5% of the plasticizer (DAO – di(2-ethylhexyl) adipate, Boryszew, Sochaczew, Poland) were prepared in tetrahydrofuran (THF - Avantor, Gliwice, Poland). A portion of such a solution was poured into a membrane mold comprised of a 6.0 cm glass ring attached to a glass plate with PVC – THF. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water.

The thickness of the PIM was measured using a digital micrometer (Panametrics® Magna-Mike® 8500, San Diego, CA, USA) with an accuracy of 0.1 μm. The thickness of a membrane was measured 10 times for each case and shown as the average value of these measurements, with the standard deviation below 1%. The thickness of membranes before and after transport was found to be the same. The average PIMs thickness varied in the range 26–31 μm.

Each experiential point was repeated 4 times, that is, the membrane formed by immobilization, thickness measured and transport parameters calculated. Experimental reproducibility was high with a standard deviation below 1% of the measured values.

Transport experiments were carried out in a permeation cell described in earlier papers [35]. The membrane film (surface area of 4.9 cm^2) was tightly clamped between two cell compartments. Both the feed phase and the receiving aqueous phase (45 cm^3 each) were mechanically stirred at 600 rpm. Metal sulfates were used in the source phase, whereas the receiving phase was a 0.5 mol/L solution of sulphuric acid. The PIM transport experiments were carried out at 20°C ± 0.2°C. Small samples of the aqueous receiving phase were taken periodically from the sampling port equipped with a syringe and analyzed by the ICP-OES technique to determine zinc(II), copper(II), chromium (III), and nickel(II) concentrations. The pH of the source phase equal to 7.8 was kept constant using tetramethylammonium hydroxide.

2.3. Sorption process

Acac—previously adsorbed on the surface of PVC—was used as the sorbent for the study of Zn(II), Cu(II), Cr(III), and Ni(II) ions sorption from model source solutions. For impregnation, PVC was mixed with 0.05 mol/L acac solution in kerosene for 12 h and then dried for 24 h. The amount of sorbent adsorbed on PVC was determined by gravimetric analysis.

To study the sorption process of heavy metals, each time 1 g +/– 0.0001 g of the obtained composite materials was weighed. Heavy metal solutions were prepared from Zn(II) and Cd(II) sulfates. For each metal ion, it is (initial concentration) analytical concentration was 0.01 mol/L. Stock metal ion solutions were adjusted with ammonia (Avantor Performance Materials Poland S.A., Gliwice, Poland) to a pH of 7.8 (pH-meter MeterLab PHM240, Radiometer, Copenhagen, Denmark). For sorption testing, 50 ml of the prepared stock solutions were used. The mixing time for PVC-acac sorbent with metal salt solutions was: 0.5, 1, 2, 4, and 8 h. Tests were performed at a temperature of 20°C and the atmospheric pressure.

For the study, a thermostatic laboratory shaker 357 Elpan, Poland, was used. Concentrations of Zn(II), Cu(II), Cr(III), and Ni(II) ions in the solution after a specified sorption time were analyzed by ICP-OES technique.

The process of metal ion desorption was studied using 0.5 mol/L H_2SO_4.

3. Results and discussion

The content of heavy metals in the tested soil samples located along national expressways is presented in Tables 1 and 2, after the process of acid mineralization and ammonia leaching, respectively. Average values are also indicated in the tables.

As can be seen from the data are shown in Table 1, Cd, Pb, Cr, Zn, Cu, and Ni are found in soils around expressways. Their average contents range from 0.80 to 75 mg/kg and increase in the following manner: Cd < Cr < Pb < Cu < Ni < Zn. They do not exceed the permissible toxic metal concentrations in soils in transport areas at the depth of up to 30 cm [36].

The ions of these metals which may form ammine complexes (Eq. (1)) are transferred to the solution as a result of leaching of soil samples with ammonia (Table 2). These are Cd, Cr, Zn, Cu, and Ni.

$$M^{n+} + 4\,NH_3 = [M(NH_3)_4]^{n+}$$

or

$$M^{n+} + 6\,NH_3 = [M(NH_3)_6]^{n+} \tag{1}$$

where $n = 2$ or 3.

No lead was determined in the solutions after leaching with ammonia. The content of other heavy metals (Cd, Cr, Zn, Cu, Ni) increases in the following manner:

Table 1
Heavy metal content in soil samples 1–6 after mineralization of HNO_3:$HClO_4$ mixture (5:1 v/v) and their average content in samples, mg/kg

Sample No.	Heavy metal content, mg/kg					
	Cd	Pb	Cr	Zn	Cu	Ni
1	2.14	10.9	13.6	106	12.3	9.46
	2.09	10.8	13.4	104	12.1	9.71
	2.16	10.9	13.6	106	12.5	9.50
Average value	2.13	10.9	13.5	105	12.3	9.56
2	0.38	37.2	0.12	57.2	4.08	21.6
	0.32	37.2	0.09	57.4	4.12	21.5
	0.34	37.4	0.11	57.3	4.06	21.5
Average value	0.35	37.3	0.11	57.3	4.09	21.5
3	1.13	2.59	9.64	78.1	24.9	10.8
	1.18	2.56	9.67	78.1	24.9	10.8
	1.11	2.54	9.66	78.1	24.9	10.8
Average value	1.14	2.56	9.66	78.1	24.9	10.8
4	0.72	3.55	7.68	112	10.4	59.2
	0.70	3.61	7.66	111	10.2	60.1
	0.74	3.57	7.71	111	10.3	59.3
Average value	0.72	3.58	7.68	111	10.3	59.5
5	0.18	6.87	2.11	40.6	4.19	70.2
	0.19	6.85	2.09	40.6	4.21	70.4
	0.17	6.85	2.14	40.5	4.23	70.3
Average value	0.18	6.86	2.11	40.6	4.21	70.3
6	0.25	3.66	0.00	55.8	124	3.26
	0.23	3.67	0.01	55.8	124	3.24
	0.26	3.70	0.03	55.8	124	3.25
Average value	0.25	3.68	0.01	55.8	124	3.25
Min.	0.17	2.54	0.00	40.5	4.06	3.24
Max.	2.16	37.4	13.6	112	124	70.4
Average value	0.80	10.8	5.52	74.8	21.4	29.2

Table 2
Heavy metal content in 1–6 soil samples after ammonia leaching and their average content, mg/kg

Sample No.	Heavy metal content, mg/kg				
	Cd	Cr	Zn	Cu	Ni
1	1.84	13.0	95.9	12.0	8.15
	1.79	12.9	96.0	12.0	8.17
	1.83	13.0	95.9	12.0	8.14
Average value	1.82	13.0	95.9	12.0	8.15
2	0.30	0.08	57.0	3.97	20.4
	0.28	0.09	57.0	3.99	20.4
	0.28	0.08	56.9	3.96	20.4
Average value	0.29	0.08	57.0	3.97	20.4
3	1.01	9.45	76.6	22.8	9.16
	0.99	9.47	76.7	22.8	9.15
	0.98	9.43	76.7	22.8	9.17
Average value	0.99	9.45	76.7	22.8	9.16
4	0.65	7.37	108	9.76	57.5
	0.63	7.41	108	9.68	57.5
	0.66	7.39	108	9.71	57.5
Average value	0.65	7.39	108	9.72	57.5
5	0.14	1.89	37.8	3.92	68.5
	0.11	1.86	37.8	3.97	68.6
	0.13	1.88	37.9	3.95	68.5
Average value	0.13	1.88	37.87	3.95	68.6
6	0.22	0.01	53.3	120	3.09
	0.21	0.00	53.3	120	3.04
	0.23	0.00	53.3	120	3.11
Average value	0.22	0.00	53.28	120	3.05
Min.	0.21	0.00	37.9	3.92	3.04
Max.	1.84	13.0	108	120	68.6
Average value	0.68	10.6	71.5	28.8	27.8

Cd < Cr < Cu < Ni < Ni < Zn. Their average contents from ca. 0.70 to ca. 71.5 mg/kg.

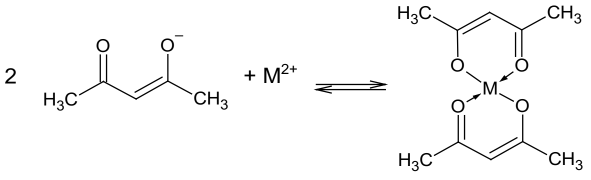
The average metal content of soils for Zn and Ni after acid mineralization and ammonia leaching is almost the same. As for Cd and Cu, the content falls within the same limits. However, a stark difference was detected for Cr: its average content is twice as high after leaching with ammonia.

3.1. Separation of Zn, Cr, Cu, and Ni

The possibility of separation of metals occurring in the largest amounts (Zn, Cr, Cu, and Ni) was studied in sulfate model solutions containing 0.01 mol/L of each metal ion. For this purpose, 3 methods commonly used in the separation of metal ions were used, namely: solvent extraction, membrane techniques, and sorption.

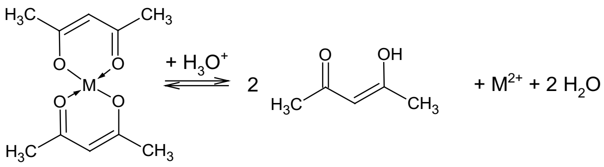
Acac was chosen as a metal ion binding agent. As has been shown by previous studies, acac is effective not only as an extractant [37–39] or a medium in PIMs [40] but also as a sorbent [41,42].

The process of binding metal ions by acac can be described by formula (2).



(2)

Chelate complexes that are being formed as the pH of the aqueous phase increases are dissociated under the influence of the decreasing pH value, as shown in formula (3).



(3)

3.1.1. Solvent extraction

The process of extraction of metal complexes using acac was carried out at different acac concentrations (0.01–0.04 mol/L) and thus at different aqueous phase pH values.

The efficiency of the process was determined by the percentage of extraction of a given metal depending on the pH of the aqueous phase, as can be calculated using Eq. (4).

$$\%E = \frac{C_0 - C_E}{C_0} \times 100 \quad (4)$$

where C_0 is the initial concentration of metal ions (mol/L), C_E is the concentration of metal ions in the aqueous phase after the extraction equilibrium was achieved (mol/L).

The results are presented in Fig. 2.

Fig. 2 shows that the complexes of the ions of the tested metals and acac are extracted in the pH ranging from 7.2 to 7.8. At higher pH levels, the percentage of extraction remains constant because, under these conditions, hydroxycomplexes—which do not enter the organic phase in the extraction process—are formed. The extraction is most efficient with complexes of acac and Zn or Cu. The Ni(II) complexes are the least likely to enter the organic phase. It may be that tetrahedral complexes are formed by acac and the ions of Zn and Cu: they are less hydrated than the Ni(II)-acac octahedral complexes and thus easier to extract.

Using the extraction method at pH = 8.2, 99% of Zn, ca. 97% of Cu, 65% of Cr and only 14% of Ni were extracted.

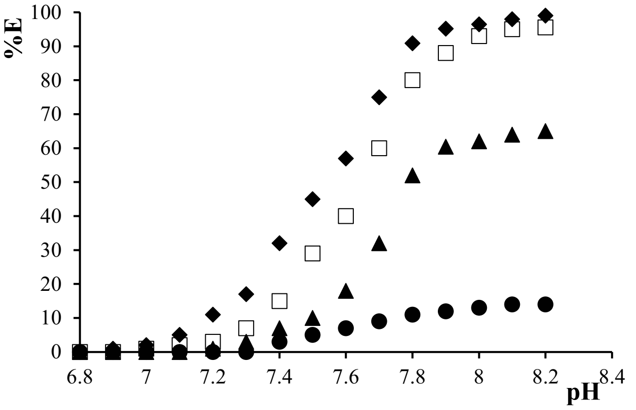


Fig. 2. Percentage of the extracts of (◆) Zn(II), (□) Cu(II), (▲) Cr(III) and (●) Ni(II) complexes from acac depend on the pH of the aqueous phase.

3.1.2. Transport across PIMs

The studies of the transport process were carried out at pH = 7.8. This pH value was adjusted based on extraction tests, which showed that the above pH value enables an optimal separation process.

The results of the transport of Zn(II), Cu(II), Cr(III) and Ni(II) ions across PIMs containing acac as a carrier are presented in Fig. 3 in the form of graphs showing the changes in the concentration of metal ions in the feed and receiving phases during the process.

Generally, as a consequence of metal ion transport across the membrane, the content of metal ions in the feed phase decreases, while it increases in the receiving phase.

As shown in Fig. 4, the transport across PIMs decreases in the following order: Zn(II) > Cr(III) > Ni(II). The concentration of Zn(II) and Cr(III) ions in the feed phase decreases faster and finally reaches lower values compared to Ni(II).

The percentage of metal ion removal recovery factors (RF) from the model solution was calculated using Eq. (5).

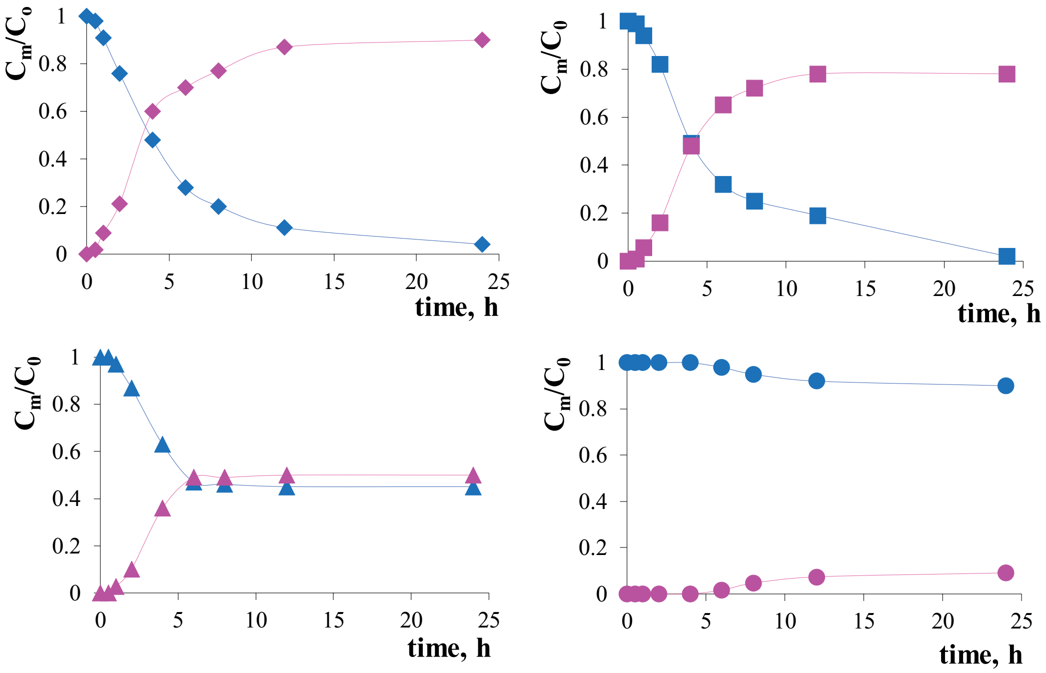


Fig. 3. Changes in the concentration of (◆) Zn(II), (■) Cu(II), (▲) Cr(III), and (●) Ni(II) ions over time in the feed phase (blue line) and receiving phase (pink line) through PIMs with acac as a carrier.

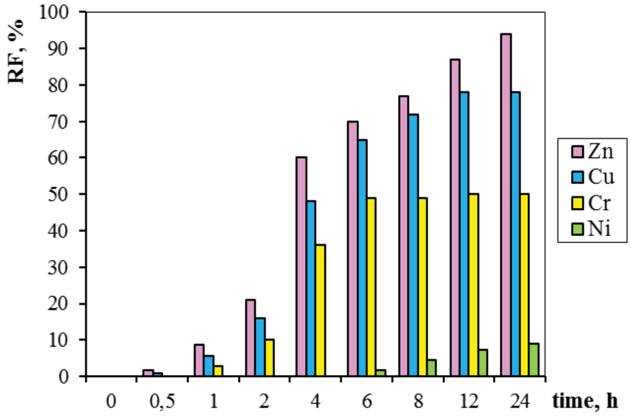


Fig. 4. Recovery factors (RF) of Zn(II), Cu(II), Cr(III), and Ni(II) ions during transport across PIMs doped acac.

$$\mathrm{RF} = \frac{C_0 - C_m}{C_0} \times 100 \quad (5)$$

where C_0 is the initial concentration of metal ions (mol/L), C_m is the concentration of metal ions in the aqueous phase after a given time (mol/L).

Fig. 4 shows the values of metal RF calculated from Eq. (5).

Metal RF increases with the duration of the transport process. These coefficients depend on the type of metal ion transferred and increase in the following manner: Ni(II) > Cr(III) > Cu(II) > Zn(II). The highest values were obtained after 24 h transport process: 94%, 78%, 50% and 9% for Zn(II), Cu(II), Cr(III) and Ni(II), respectively. Ni(II) ions are scarcely transported across this type of membrane.

3.1.3. Sorption on PVC-acac granules

Fig. 5 shows the results of zinc, copper, chromium, and nickel sorption on acac-modified sorbent over a specified period.

As demonstrated in Fig. 5, the balance is determined after 4 h. Sorption is a fast separation process. The sorption increases in the following manner: Ni(II) > Cr(III) > Cu(II) > Zn(II). Ni(II) ions practically do not undergo sorption, enriching the aqueous phase.

Fig. 6 shows the percentage reduction of the concentration of metals in the solution after sorption (R_S) as calculated from Eq. (6).

$$R_S = \frac{C_0 - C_S}{C_0} \times 100 \quad (6)$$

where C_0 is the initial concentration of metal ions (mol/L), C_S is the concentration of metal ions in water solution after sorption (mol/L).

The most significant reduction of Zn and Cu concentration was achieved after 4 h of sorption: 91% and 79%, respectively. Both Zn and Cu forms stable complexes with acac (Eq. (2)). They are not easily dissociated. The sorption of Zn and Cu on the PVC-acac is the best. We have also observed this phenomenon in our previous studies on the separation Zn or Cu from the Zn–Cu–Co–Ni mixture [35,39,41,43].

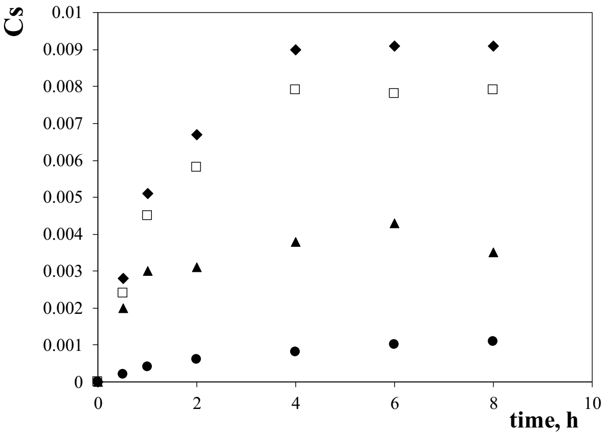


Fig. 5. Concentration of (◆) Zn(II), (□) Cu(II), (▲) Cr(III), and (●) Ni(II) in water solution over time after sorption on the PVC-acac sorbent.

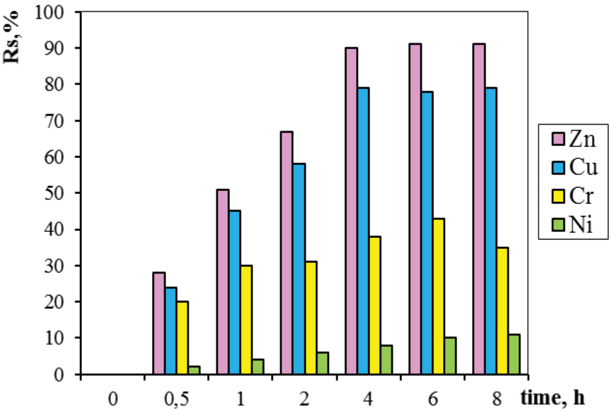


Fig. 6. Reduction of Zn(II), Cu(II), Cr(III), and Ni(II) concentrations in the solution after sorption on the PVC-acac sorbent.

Table 3
Comparison of the efficiency of the applied methods of Zn(II), Cu(II), Cr(III) and Ni(II) ions separation at pH = 7.8

Metal ions	Removal of metal ions, %		
	Solvent extraction	PIM	Sorption
Zn(II)	91	94	91
Cu(II)	80	78	79
Cr(III)	52	50	43
Ni(II)	11	9	11

The results (Figs. 5 and 6) show that for Cr(III) ions the lowest concentration was obtained in the solution where the sorption was conducted for 6 h. The equilibrium concentration was 0.0057 mol/L and the percentage of the extraction of metal from the solution was 43%. Subsequently, an increase in Cr concentration in the solution was observed. After 8 h of sorption, the equilibrium concentration was 0.0065 mol/L. and the percentage of the extraction of metal from the solution decreased to 35%. Changes in the concentration of

Table 4
Comparison of values of zinc separation coefficients ($S_{Zn/M}$) in relation to Cu(II), Cr(III), and Ni(II) ions during solvent extraction, transport across polymer inclusion membranes and sorption for pH = 7.8

Separation method	$S_{Zn/M}$		
	Cu(II)	Cr(III)	Ni(II)
Solvent extraction	1.14	1.75	8.26
Transport across PIMs	1.21	1.88	10.4
Sorption	1.15	2.60	8.27

chromium in the solution may indicate alternating processes of metal sorption from the solution and its leaching from the sorption material to the solution: in other terms, a dynamic process of sorption and desorption. A similar phenomenon was observed by Bao et al. [44]. It is also worth noting that after 8 h of sorption the extraction of nickel from the solution was at its lowest and decreased to 11%.

In Table 3, the effectiveness rates of the separation methods used have been compared.

As shown in Table 3, in the three applied methods of separation at pH 7.8, comparable results of percentage reduction of ion concentration of individual heavy metals were obtained.

The coefficients of $S_{Zn/M}$ separation with regard to other metal ions were calculated for pH = 7.8 and using Eq. (7).

$$S_{Zn/M} = \frac{C_{Zn}}{C_M} \tag{7}$$

The results are shown in Table 4.

As can be observed from the data in Table 4, the coefficients of zinc separation from Cu, Cr, and Ni ions are mostly comparable, except for the transport process (where Zn/Cr and Zn/Ni separation coefficients are higher) and the sorption (where Zn–Cr separation is most effective). It is worth noting that the coefficient of Zn/Ni separation is very high in case of the transport across acac-doped PIMs.

4. Conclusion

Cd, Pb, Cr, Zn, Cu, and Ni are located in the soils near the express roads. Their average contents range from 0.80 to 75 mg/kg and increase in the following manner: Cd < Cr < Pb < Cu < Ni < Zn.

Using acac as an extractant in the extraction method and for pH = 8.2%, 99% of Zn, ca. 97% of Cu, 65% of Cr and only 14% of Ni was extracted.

After 24 h transport across acac-doped PIMs, the extraction coefficients of Zn(II), Cu(II), Cr(III) and Ni(II) were 94%, 78%, 50%, and 9%, respectively. Ni(II) ions are scarcely transported across this type of membrane.

The greatest concentration reduction of Zn and Cu was achieved after 4 h sorption time on PVC acac-immobilized granules: 91% and 79%, respectively.

In every separation process, Ni(II) ions remain in solution.

These techniques can be used to remove heavy metals from small amounts of soils, once the latter has been leached with ammonia.

From an economic point of view, sorption is the most convenient process for extraction and separating metals.

The removal of heavy metals from the soils located along expressways may become a necessity as the sources of pollution are unlikely to disappear shortly and the content of toxic metals in soils is bound to increase proportionally to road traffic.

It is advisable to consider placing cheap materials along expressways to prevent the spreading of heavy metals in the environment.

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