Simultaneous preconcentration and removal of iron, chromium, nickel with *N,N′*-etylenebis-(ethane sulfonamide) ligand on activated carbon in aqueous solution and determination by ICP-OES

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Abstract

In this study, Fe, Cr and Ni have been preconcentrated and removed by using *N,N′*-ethylenebis (ethane sulfonamide), (ESEN) ligand on activated carbon (AC) in aqueous solution. For this purpose, complexes between these metals and ligands have been investigated and used in preconcentration and removal studies. Factors which have affected adsorption of metals on activated carbon have been optimized. Adsorbed metals have been preconcentrated 10-fold and determined by ICP-OES. Interferences of Ca, Mg and K to this process have been investigated. The proposed method has been applied to the tap water and Ankara Creek water in order to Fe, Cr, and Ni remediation and preconcentration. Determination of metals by ICP-OES has been checked with standard reference material (NIST 1643e). The proposed method provides the recoveries of 87%, 108% and 106% for Fe, Cr and Ni, respectively, in preconcentration. It also provides the removal of Fe, Cr and Ni by 93%, 100% and 100% removal from waters, respectively.

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1. Introduction

Enrichment may work out the low concentrations problems which are near or below the limit of detection of the instrument and leads to simplified heavy metal determination. There are a lot of enrichment methods such as: co-precipitation, solvent extraction, electrolysis and solid phase extraction, etc. Solid phase extraction has some advantages for enrichment as like lower solvent volume, solvent exposure, disposal costs and time for sample preparation. Recently, solid phase extraction has been used for the separation and preconcentration of metal ions in water samples. Activated carbon (AC) has been also widely used for adsorb metal complexes. It has allowed to very high enrichment factor in various matrix [1].

Industrial activated carbon obtained from different natural sources for sorption and determination of metals has been recently announced [2–6]. Activated carbon widely uses a trace collector for multi-element preconcentration in analysis of water, high-purity substances, vegetable sample, etc. There are general approaches to metal preconcentration using activated carbon, namely from aqueous solution by simply adjusting the pH to an adequate value and by using a chelating agent. A literature survey revealed that enrichment of heavy metals on actived carbon is usually carried out after chelating with; pyrocatechol violet for Cu, Mn, Co, Cd, Pb, Ni, and Cr [7], 8-hydroxyquinoline for Cd [8], Co, Hg, and Ni [9], *O,O*-diethyl-dithiophosphate for Pb [10], pyridyl azo resorcinol for Cu, Co, Cd, Cr, Ni, Pb, and V [11] thiourea and bromide ion for Bi [12], ammonium pyrrolidinedithiocarbamate for Cd, Cu, Ni, Zn [13], cupferron for Ni [14], 1,10-phenanthroline for Cd, Co, Ni, Cu, Pb [15], ammonium salt of dithiophosphoric acid *O,O*-diethyl ester for Mo [16], diethyldithiocarbamate for Zn, Pb, Cd, Cr, Ni, Cu, Co, Bi, Mn [17], ammonium pyrrolidine dithiocarbamate for Cu, Ni, Pb, Fe, Cd, Zn, Co [18], dithiophosphoric acid *O,O*-diethyl ester for Au, Ag and Pd [19], 5,5-diphenylimidazolidine-2,4-dione, 5,5-diphenylimidazolidine-2-thione-4-one and 2-(4-methoxy-benzylidenimine) thiophenole for Pb [20], dithioxamide for Co,

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Table 1
Comparative data from some studies about adsorption of heavy metals on actived carbon with complexation

Elements	Chelating reagent	Detection method	PF	DL (µg/L)	Reference
Cu, Mn, Co, Cd, Pb, Ni, Cr	Pyrocatechol violet	FAAS	100	0.025, 0.021, 0.036, 0.013, 0.048, 0.054, 0.069	[7]
Cd	8-Hydroxyquinoline	ICP-OES	80	0.018	[8]
Cd, Co, Hg, Ni	8-Hydroxyquinoline	GFAAS	20,000	0.0003, 0.007, 0.12, 0.007	[9]
Pb	*O,O*-Diethyl-dithiophosphate	FAAS	23	3	[10]
Cu, Co, Cd, Cr, Ni, Pb, V	Pyridyl azo resorcinol	FAAS	200	9, 14, 3, 10, 24, 4, 14	[11]
Cd, Cu, Ni, Zn	Ammonium pyrrolidinedithiocarbamate	FAAS	10	0.020, 0.019, 0.023, 0.028	[13]
Pb, Cu	5,5-Diphenylimidazolidine-2,4-dione	FAAS	240	0.52, 0.37	[20]
	5,5-Diphenylimidazolidine-2-thione-,4-one			0.65, 0.42	
	2-(4'-Methoxy-benzylidenimine) thiophenole			0.46, 0.31	
Cu, Ni, Co,	Dithioxamide	FAAS	330	0.50, 0.75, 0.80	[21]
Ni, Co, Cu, Pb	4,6-Dihydroxy-2-mercaptopyrimidine	FAAS	260	3.5, 3.4, 2.9, 8.4	[22]
Fe, Cr, Ni	*N,N'*-ethylenebis (ethane sulfonamide	ICP-OES	10	0.38; 0.31; 0.06	This study

DLs were given according to element order, PF: Preconcentration factor.

Ni, Cu [21], 4,6-dihydroxy-2-mercaptopyrimidine for Ni, Co, Cu and Pb [22].

There are a lot of studies interested in complexation with thiocyanate for Mo [23], 1,5-diphenylcarbazone for Cr [24], α-benzoin oxime for Cr, Mn, Fe, Co, Cu, Cd and Pb [25], α-benzoin oxime for Cr [26] and benzyl dioxime for Ni [27] on the other adsorbents. Some comparative studies about heavy metals on activated carbon after chelating with some ligands are summarized in Table 1.

Adsorption with activated carbon has been one of the most useful techniques in water treatment. While in the past, activated carbon was predominantly used to remove odor and color producing, molecules in water [28] recent experimental results have been reported for the removal of inorganic chemicals with it [29]. There are some studies related to remediation of metal by complexation on activated carbon from contaminated water [30,31].

In this work, solid phase extraction was used for preconcentration and removal of Fe, Cr, and Ni by using *N,N'*-ethylenebis(ethane sulfonamide) on activated carbon from aqueous solution. The natural waters used in the remediation studies generally have lower level of Fe, Cr and Ni according to Maximum Contamination Levels in the drinking water (200, 50, 20 µg/L, respectively) [32]. Nevertheless, removal studies were performed in order to demonstrate the activity of ESEN ligand in the remediation of the some metals.

2. Materials and methods

2.1. Apparatus

In this study, PerkinElmer Optima 5300DV ICP-OES has been used for the determination of Fe, Cr, and Ni. The instrumental parameters were given in Table 2. Conductivity, pH and dissolved O_2 of water were measured with Orion 5-Star Bench-top Multimeter (pH electrode: 8102BNU; conductivity cell: 013005; DO probe: 081010MD). Spectrophotometric measurements of metal–ligand complexes were performed with Unicam UV2-100 spectrophotometer.

2.2. Materials and reagents

$K_2Cr_2O_7$, $FeSO_4 \cdot 7H_2O$, $NiCl_2 \cdot 6H_2O$, ethyl alcohol, dimetyl formamide, EDTA and calibration standards for ICP-OES were all analytical reagent grade batches purchased from Merck. Columns were packed with activated carbon (BDH). NIST 1643e (Trace elements in water) was used as Certified Reference Material. Ultra pure water obtained at Innovation Pure Water System (18.3 MΩ cm = 0.055 µS/cm) was used for the preparation of reagent solutions and of the synthetic water sample.

N,N'-ethylenebis(ethane sulfonamide)ligand was synthesized using ethane sulphonyl chloride and ethylene diamine and characterized by Özbek et al. (submitted paper). The *N,N'*-

Table 2
Operational parameters used for the determination of elements by ICP-OES

Apparatus	PerkinElmer Optima 5300 DV
RF generator	40 MHz
RF forward power	1300 W
Plasma gas (Ar) flow	15 L/min
Aux. gas (Ar) flow	0.2 L/min
Nebulizer gas (N_2) flow	0.80 L/min
Replicates	3
Pump rate	2.0 mL/min (peristaltic pump)
Viewing configuration	Axial
Studied wavelength (nm)	Fe: 259.939; Cr: 267.716; Ni: 231.604, Ca: 317.933, Mg: 285.215; K: 766.490

Table 3
Some measured properties of stream and tap water

	pH	Conductivity (μS/cm)	BOD_5 (mgO_2/L)	Ca[a] (mg/L)	Mg[a] (mg/L)	K[a] (mg/L)
Ankara stream water	7.65 ± 0.01	911 ± 0.12	18 ± 1	57.77 ± 0.19	13.68 ± 0.13	16.70 ± 0.14
Tap water	7.24 ± 0.01	321 ± 0.11	<5	23.39 ± 0.09	6.83 ± 0.08	3.30 ± 0.45

Values are mean $\pm$ standard deviation ($n = 5$).

[a] Ca, Mg and K were determined with ICP-OES.

ethylenebis(ethane sulfonamide) was prepared by dissolving 0.496 g of the reagent in 25 mL of ultra pure water.

Tap water was collected from the domestic water line of Ankara. Water samples from Ankara Creek and tap water were used to test the validity of the procedure. Some measured properties of tap water and Ankara Creek water were given in Table 3.

2.3. Preconcentration procedure

The preconcentration procedures of iron, chromium and nickel by adsorption on activated carbon with the use of ESEN were as follows:

Activated carbon powder was kept in nitric acid (1:1) solution for 24 h so as to remove the metal ions and other impurities sorbed on it. Then it was filtered and rinsed with ultra pure water until it was free from acid. It was dried in a drying oven at 110 °C. The 500 mg of activated carbon was packed in a column which a glass tube of 1 cm inner diameter and 30 cm length with a glass wool plug above the valve. 100 mL of solutions containing Fe, Cr, Ni and complexing reagent (ESEN) were passed through the column of 500 mg activated carbon at a flow rate of 0.8 mL min^{-1}. The metals were then desorbed from the column with 10 mL of 0.5 M HCl. So adsorbed metals were preconcentrated 10-fold. The metals concentration was determined with ICP-OES.

2.4. Removal procedure

Removal of metals has been studied by using both column and static methods. In the column method, 100 mL of synthetic water sample containing 1 mg/L Fe(II), 1 mg/L Cr(VI), 1 mg/L Ni(II) and 10^{-3} M ESEN was passed through the column of 500 mg activated carbon at a flow rate of 0.8 mL min^{-1}.

In the static method, 100 mL of synthetic water sample containing 1 mg/L Fe(II), 1 mg/L Cr(VI), 1 mg/L Ni(II) and 10^{-3} M ESEN and 500 mg activated carbon were added to an erlen. The mixture was stirred with a magnetic bar for 2 h at the room temperature. Then the sample was filtered through a filter paper.

Table 4
λ_{max} of metals and their complexes

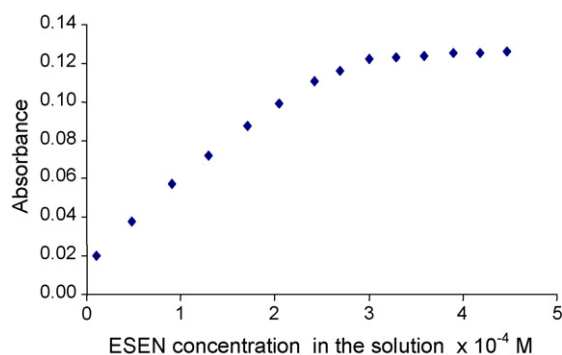| Species	λ_{max} (nm)
Fe^{2+}	254
Cr^{6+}	416
Ni^{2+}	395
Fe(II)–ESEN	307
Cr(VI)–ESEN	579
Ni(II)–ESEN	400

Fig. 1. Spectroscopic determination of mole ratio of Fe(II)–ESEN complex.

The metal concentrations in the filtrate were determined with ICP-OES.

2.5. Optimization studies

ESEN was investigated by UV–vis spectrometry if complexed with Fe^{2+}, Cu^{2+}, Cr^{6+}, Sr^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, Ca^{2+}, and Mg^{2+} in the pH range of 1 and 8. ESEN was formed a complex with Fe, Ni and Cr in the pH range of 6–6.5.

In order to obtain quantitative recoveries of the metal ions on the activated carbon, the preconcentration procedure was optimized for the various analytical parameters such as pH, amount of activated carbon, desorption solution and the stirring time.

The effect of pH on the separation of metal ions was studied in the pH range of 1–8, keeping the other parameters constant. The optimum pH range for complex formation and quantitative recoveries of Fe, Ni and Cr was ranging between 6 and 6.5. The effect of amount of activated carbon was examined in the amount of 300, 500 and 700 mg.
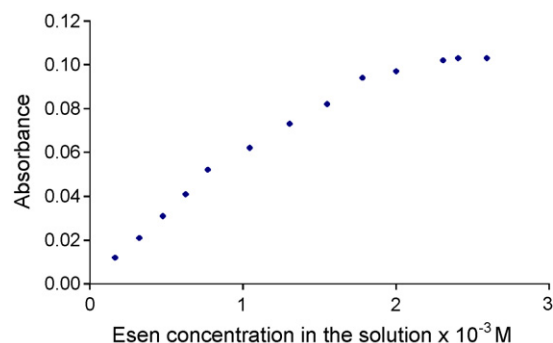

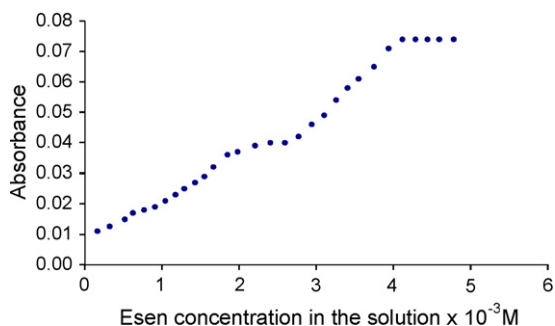Fig. 2. Spectroscopic determination of mole ratio of Cr(VI)–ESEN complex.

Fig. 3. Spectroscopic determination of mole ratio of Ni(II)–ESEN complex.

In order to optimize to desorption solution, HCl (0.1, 0.5 and 1.0 M) EDTA (0.01 M), ethyl alcohol and dimetyl formamide solutions were tried and it was obtained about 95% recovery with 10 mL 0.5 M HCl solution.

The stirring time of the solution was tested in the range of 1–4 h in the remediation studies. The result of the stirring time effect demonstrated that the sorption of the complex was quantitative after 2 h.

3. Results and discussion

λ_{max} of Fe, Cr, Ni and their ESEN complexes were given in Table 4. ESEN does not absorb at these wavelengths.

3.1. Fe(II)–ESEN complex

Fe concentration was kept as 1×10^{-4} M and ESEN concentration was increased gradually. The absorbances of the solutions were measured at 307 nm. As shown in Fig. 1, absorbance was reached a plateau at 3.01×10^{-4} M ESEN concentration. As a result from this, there was a complex as ML_3.

3.2. Cr(VI)–ESEN complex

Cr concentration was constant as 2.3×10^{-3} M and ESEN concentration was increased gradually. The absorbances of the solutions were measured at 579 nm. As shown in Fig. 2, absorbance was reached a plateau at 2.3×10^{-3} M ESEN

Table 5
Percentage of metal sorption of untreated (AC) and complexation on activated carbon

Metal	Sorption (%)	
	Activated carbon	Complexation on activated carbon
Fe	40 ± 3	83 ± 4
Ni	31 ± 3	100 ± 4
Cr	24 ± 2	100 ± 3

Values are means ± standard deviations ($n = 3$).

Table 6
Recovery of Fe, Ni and Cr with various eluents

Eluent	Recovery (%)[a]		
	Fe	Ni	Cr
Ethyl alcohol	45	41	38
Dimetyl formamide	65	62	56
EDTA (0.01 M)	60	55	57
0.1 M HCl	76	67	72
0.5 M HCl	80	98	101
1.0 M HCl	80	98	101

[a] Mean of three measurements.

concentration. As a result from this, there was a complex as ML.

3.3. Ni(II)–ESEN complex

Ni concentration was constant as 2.3×10^{-3} M and ESEN concentration was increased gradually. The absorbances of the solutions were measured at 400 nm. As shown in Fig. 3, absorbance was reached a plateau at 2.2×10^{-3} M and 4.2×10^{-3} ESEN concentrations. As a result from this, there were two complexes as ML and ML_2.

3.4. Effect of complex formation on sorption

Since ESEN ligand were formed complexes with Fe, Cr and Ni in the range of 1:1 and 1:4, 10^{-3} M ESEN concentrations were used for all of preconcentration and removal studies.

Table 7
Concentrations and recoveries of Fe, Cr and Ni in water samples

Sample	Metal	Concentration in sample (μg/L)	Sample dilution factor	Added (μg/L)	Found (μg/L)	Recovery (%)
Tap water	Fe	244 ± 7	200	1	1.9 ± 0.3	86
				5	5.3 ± 0.4	85
	Cr	9.9 ± 0.3	10	1	1.9 ± 0.5	100
				5	6.6 ± 0.7	112
	Ni	12 ± 1	10	1	2.3 ± 0.4	104
				5	6.5 ± 0.4	105
Ankara Creek water	Fe	164 ± 6	100	1	2.3 ± 0.5	88
				5	5.8 ± 0.6	87
	Cr	11.7 ± 0.4	10	1	2.3 ± 0.6	104
				5	7.0 ± 0.7	113
	Ni	10.1 ± 0.6	10	1	2.1 ± 0.4	105
				5	6.5 ± 0.4	108

Values are means ± standard deviations ($n = 3$) (initial concentrations of metals are sum of metal concentrations in the waters and additions).

Table 8
Removal of Fe, Cr and Ni with ESEN ligands in the synthetic sample

Sample (100 mL)	Metal	Column		Static	
		Residual concentration (μg/L)	Removal (%)	Residual concentration (μg/L)	Removal (%)
1 mg/L Cr, Fe, Ni + 10^{-3} M ESEN	Cr	14.9 ± 0.4	98.5	339 ± 6	66.1
	Fe	38.2 ± 0.7	96.2	303 ± 4	69.7
	Ni	8.6 ± 0.5	99.1	864 ± 12	13.6

Values are mean $\pm$ standard deviation ($n = 3$).

The efficiency of the complexation on AC column for the sorption of metals was studied by using 500 mg of AC in comparison with ESEN complexation for preconcentration of metals in a model solution. Starting with 10 μg/L of each metal and 10^{-3} M ESEN in 100 mL of solution, the quantity of unretained metals in the filtrate was determined by ICP-OES. The percentage sorption of the metals retained on the sorbent was calculated from the difference between the starting concentration of each metal (μg/L) (N_s) and the concentration of metal (μg/L) left in the filtrate (N_f) according to Eq. (1):

$$\text{sorption}(\%) = \frac{N_s - N_f}{N_s} \times 100 \tag{1}$$

The results are shown in Table 5. The complexation can retain all the metal ions while the AC cannot quantitatively retain Fe, Ni and Cr. Evidently, the preconcentration of Fe, Ni and Cr with the AC is not suitable.

3.5. Desorption of metals

A suitable eluent for metal desorption was chosen by considering the following evaluations: (a) the eluent should desorb the metals or complexes, (b) the eluent should not damage the sorbent and (c) the eluent should be appropriate for the following determination method [33]. Organic solvents and inorganic acids have been found to meet the requirements. In this study, all metal ions form a complex with ESEN (Figs. 1–3), so the adsorption on AC and desorption mechanisms are possibly similar to each other. In this experiment, the standard solutions for preconcentration were 10 μg/L of each metal in 100 mL of solution. The eluents tested were ethyl alcohol, dimetyl formamide, 0.01 M EDTA, 0.1 M HCl, 0.5 M HCl and 1 M HCl. The effectiveness of metal des-

orption was evaluated from the recoveries (%) of metals (Table 6).

Percent recoveries in this section were calculated from the concentration of metals (μg/L) in the initial solution (N_i) and the concentration of metals (μg/L) eluted from the column (N_l) according to Eq. (2). The results are summarized in Table 6:

$$\text{recovery}(\%) = \frac{N_l}{N_i} \times 100 \tag{2}$$

3.6. Application of preconcentration methods to real sample

The proposed method was applied for the determination of Fe, Cr, and Ni in tap water and natural water samples. The results are given in Table 7. The recoveries of the metal ions were in the order of 85–113%. However, additions of 1 μg/L Fe were revealed 85–88% recoveries; it would be satisfactory for these lower concentrations. In order to perform preconcentration studies of metal ions from water sample, water samples were first diluted.

3.7. Method detection limit

Detection limit of the preconcentration method were calculated by three times the standard deviation ($n = 15$) of the blank. The values were 0.38 μg/L for Fe, 0.31 μg/L for Cr and 0.06 μg/L for Ni. These limits were based on 100 mL of blank undergoing the preconcentration to a final volume of 10 mL.

3.8. Interferences

The effects of representative potential interfering species (at the concentrations levels at which they may occur in the sam-

Table 9
Removal of metals in the tap water and Ankara Creek water

Sample (100 mL)	Metal	Metal concentration in sample (μg/L)	Column		Static	
			Residual concentration (μg/L)	Removal (%)	Residual concentration (μg/L)	Removal (%)
Tap water + 10^{-3} M ESEN	Cr	9.9 ± 0.3	Not detected	100	5.4 ± 0.3	45.5
	Fe	244 ± 7	18.4 ± 0.5	92	121 ± 2	50.0
	Ni	12 ± 1	Not detected	100	6.2 ± 0.6	48.3
Ankara Creek water + 10^{-3} M ESEN	Cr	11.7 ± 0.4	Not detected	100	6.8 ± 0.4	41.8
	Fe	164 ± 6	11.4 ± 0.8	93	23 ± 1	86
	Ni	10.1 ± 0.6	Not detected	100	7.8 ± 0.7	22

Values are mean $\pm$ standard deviation ($n = 3$).

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