



## Synthesis and adsorption characteristics of ionic imprinted polymers IIPs for removal and preconcentration of Nickel from aqueous solution

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### Abstract

A novel Nickel(II) ion-imprinted polymers (IIPs) was prepared by bulk polymerization using different types of monomers such as Styrene and 1-vinyl imidazole, respectively. Molar ratios of template, monomer and cross-linking agent for polymerization, solvents, and several monomers were studied to obtain the largest adsorption capacity. The prepared Nickel-IIPs were characterized using fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The three-dimensional network structure surfaces are unaffected by the elution process of Nickel-IIPs. Nickel(II) ions could be eluted from IIPs successfully by mixture solution from ethanol and acetic acid. The highest capacity for adsorption of Nickel-IIPs was is 457.3 $\mu\text{mol/g}$  for Nickel-IIP1 (using styrene as a monomer) and 355 $\mu\text{mol/g}$  for Nickel-IIP2(using 1-vinyl imidazole as a monomer). The adsorption by Nickel-IIPs followed a Langmuir isotherm models. Solid-phase extraction (SPE) syringe packed with ionic imprinted polymers (IIPs) were used to selective separation and preconcentration for Nickel (II) ion from aqueous solutions and digest the polymer to determination the Nickel by flame atomic absorption spectroscopy (FAAS) Abbreviation IIP-SPE-FAAS.

*Keyword : Nickel-Ionic imprinted polymer, adsorption, SPE-FAAS, preconcentration*

### 1. Introduction

Nickel (Ni) is silver-white metal was found in many oxidation states. Humans are exposed to Ni via water, food and air produced from different sources, such as mining, smelting, refining, electroplating, welding, food processing and Nickel waste disposal [1]. Ni is an environmental pollutant, causes cytotoxicity and causes oxidative stress [2]. Diseases, such as liver cirrhosis, diabetes, and uremia are caused by lack of Nickel. However, Nickel at high concentrations is toxic to humans, especially the skin. When humans are exposed to Nickel for an extended period of time, they develop neurological disorders. In addition, Nickel will lead to lung cancer and nose cancer. Nickel is now widely employed in a variety of applications such as mechanical, electrical, chemical and building industries. Moreover, Heavy metal contamination in water and soil is caused by the smelting process, mining, and steel manufacturing and processing sectors. [3].

Nickel ion has been removed from wastewaters using a variety of common processes, including membrane filtering and chemical precipitation. [4,5], activated carbon adsorption [6,7], ion exchange and electrolysis [8,9]. However, these ordinary technologies show lots of disadvantages, such as just

suitable for simply system, secondary pollution, short service life, low processing capacity, low selectivity high cost and highly energy consuming. Therefore, a pollution-free technique, low-cost and economic with both selectivity and high adsorption capacity is badly in need of development.

Continuous advances in analytical chemistry have recently resulted in the creation of novel chemical separation methods that are critical. The development of novel extractants and adsorbents has been fueled by the demand for a more selective system for metal ion separation. [10,11,12].

Currently, the researchers are interested in developing the selective preconcentration of the sorbents used in solid-phase extraction (SPE). This equitable is particularly important when analyzing complex matrices such as waste water or river water samples.

SPE is more simple, rapid, economical and environmental-friendly than the traditional liquid-liquid extraction. The essential problem associated with SPE columns packed with ordinary stationary phases is the low selectivity of the retention mechanism. A desired grade of selectivity may be reach using columns packed with materials based on

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Receive Date: 05 June 2021, Revise Date: 16 June 2021, Accept Date: 21 June 2021

DOI: 10.21608/EJCHEM.2021.79231.3892

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molecularly imprinted polymers (MIPs) as selective sorbents [13-15].

Molecular imprinting as a type of special technology is realized by the specific identification. A molecularly imprinted polymer is prepared by mixing the template molecules with functional monomers first. Then the crosslinking agents and initiators are added for polymerization. Later, the template molecules are removed with a chemical or physical method. Certainly, a molecularly imprinted polymer with full of space cavities which match well with the destination molecules is completely prepared [16-19]. For metal ions, the synthesized sorbent is called ion-imprinted polymer (IIP) which is related to MIPs but it recognizes inorganic ions after imprinting [20]. Various methods, such as bulk polymerization [21], suspension polymerization [22] precipitation polymerization [23], sol-gel polymerization [24,25], and surface imprinted technique [26,27] have been used for the preparation of ion imprinted polymers.

In this work, Nickel(II)-IIP was synthesized by bulk polymerization using Nickel nitrate as a template with styrene and 1-vinyl imidazole as monomer to prepare two types of Nickel(II)-IIPs with ethylene glycol dimethacrylate (EGDMA) as crosslinker and benzyl peroxide as initiator for removal of Ni(II) ions from aqueous solution. Effects of monomer and EGDMA dosages on adsorption performance were studied. Adsorption behaviours with various functional monomers, cross-linking agents and solvents were also investigated. SEM, FTIR, and EDX were used to characterize the prepared IIPs. In addition, effects of adsorption conditions, such as adsorption time, flow rate of solution pass-through solid phase extraction syringe and initial Ni(II) concentration, on adsorption capacity were studied.

## 2. Experimental

### 2.1 Reagents and Chemicals

Styrene, 1-vinyl imidazole, ethylene glycol dimethacrylate (EGDMA) and benzyl peroxide were purchased from Sigma–Aldrich (St. Louis, MO, USA, [www.sigma-aldrich.com](http://www.sigma-aldrich.com)), methanol, chloroform, acetonitrile, acetic acid, and Nickel nitrate hexahydrate  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were purchased from Merck (Darmstadt, Germany, [www.merck.com](http://www.merck.com)). nitrogen gas (99.99%) from Arab gulf factory Baghdad.

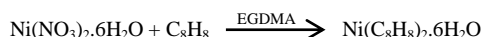
### 2.2 Instrument

The control was performed using atomic absorption spectrophotometer pginstrument (England), the use of UV 1800pc spectrophotometer (Shimadzu, japan), scanning electron microscopy SEM and EDX MIRA3 TESCAN (Czechoslovakia)

FTIR FTIR 8000 (Shimadzu, Japan) and ultrasonic (W.GERMANY) was used to stir up the copolymer solution.

### 2.3 Preparation ionic imprinted polymer

For preparation number one Nickel molecularly imprinted polymer (Nickel-MIP1), 1mmol (0.291 g) from Nickel nitrate hexahydrate dissolved in little amount of methanol then mixed with 20 mmol (2.08 g) styrene as the monomer, after that added 40 mmol (7.92 g) ethylene glycol dimethacrylate (EGDMA) to the solution as the crosslinker, followed that added 0.32 mmol (0.07 g) benzoyl peroxide as the initiator. All these materials were dissolved in 5 mL methanol ( $\text{CH}_3\text{OH}$ ). While the second Nickel-MIP2 were achieved by mixed the same amount of Nickel nitrate hexahydrate as the template with 20 mmol (1.88g) 1-vinyl imidazole as the monomer after that added 40 mmol (7.92 g) ethylene glycol dimethacrylate (EGDMA) to the solution as the crosslinker and 0.36 mmol (0.08 g) benzoyl peroxide as the initiator which dissolved in 5 mL of methanol ( $\text{CH}_3\text{OH}$ ). For obtaining a homogeneous solution, the mixture was shake for 5 minutes.  $\text{N}_2$  passes for 30 minutes on the mixture to extract oxygen from the solution. then, the solution was placed in a water bath at  $60^\circ\text{C}$  overnight. when the reaction completes the molecularly imprinted polymer became hardened, after the polymerization process, the polymer was drying and crashed to obtain a polymer particle and the reactions equation show in the following



The template extract from MIP by soxhlate in  $\text{CH}_3\text{OH}/\text{CH}_3\text{COOH}$  (30:3 v/v) 100 ml for 8 hour. Non-molecularly imprinted polymers were created utilizing the same materials and circumstances as Nickel-MIP1 and Nickel-MIP2, but without the Nickel nitrate hexahydrate (template). Non-imprinted polymers (NIPs) were made using the same distribution, but without the template.

### 2.4 sampling procedure

Prepare a stock solution at concentration (1,10,20, 30,40,50,60,70,80 ppm) of Nickel nitrate hexahydrate and 1 ppm solution diluted to prepare (0.1, 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 25 ng) for preconcentration method to determination the little amount note detect

direct in flame atomic absorption spectrophotometer. Also, several samples before and after treatment were brought from industrial water to refineries for washing crude oil to rid it of salts before the refining process.

### 2.5 The Sampling Device

A 3 ml solid phase extraction syringe was used and each syringe was filled with different weights (0.1 and 0.2gm) from MIP.

### 2.6 Extraction and digestion procedure

Nickel ion was extracted from synthetic solution, diluted synthetic solution and industrial water to refineries using Nickel-IIP1 (styrene as a monomer) and Nickel-IIP2 (1-vniyl imidazole as a monomer) by solid phase extraction (SPE) syringe. This syringe was prepared by packing it with a IIP, 0.2mg, the size of its container 5ml. The solution containing Nickel pass through SPE syringe by vacuum process using peristaltic pump in different rate.

IIP was collected from column in the small beaker, dried for 60 minutes, than a 1mL of concentrated sulfuric acid is added to it and left for a 8 minute, the next step concentrated nitric acid 1ml is added to it and heated at a 60 temperature after that added deionized water to the mixture, later estimated directly by flame atomic absorption spectrophotometer.

## 3. Result and dissection

### 3.1. Characterizations

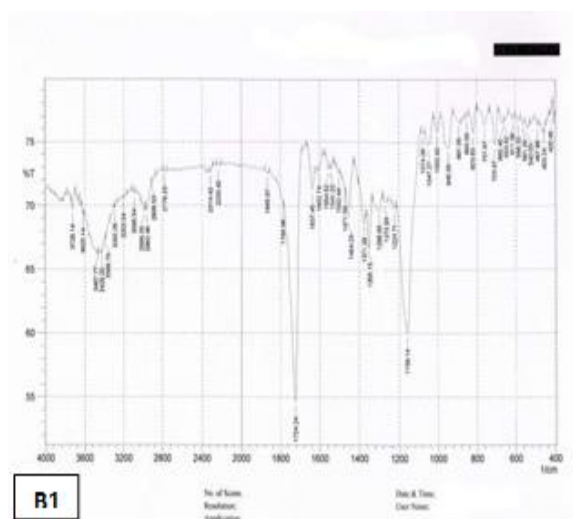
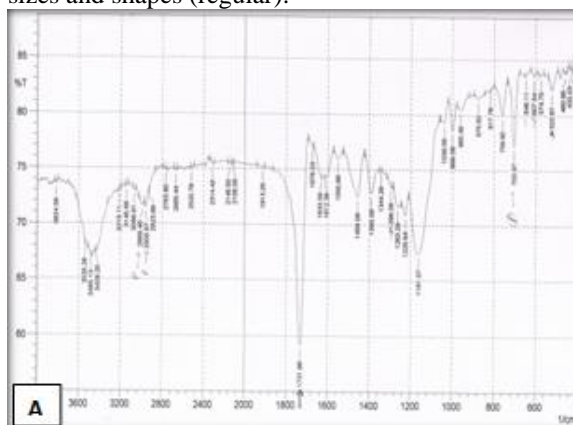
#### 3.1.1. FT-IR

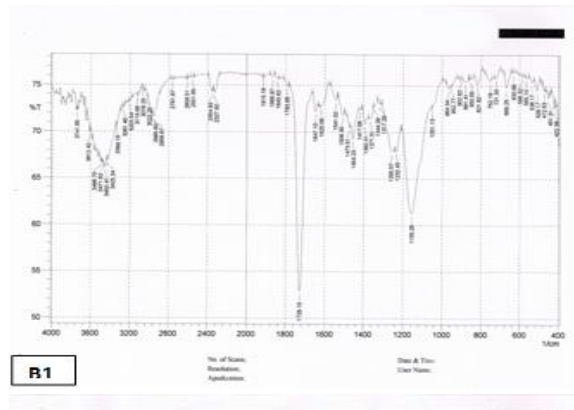
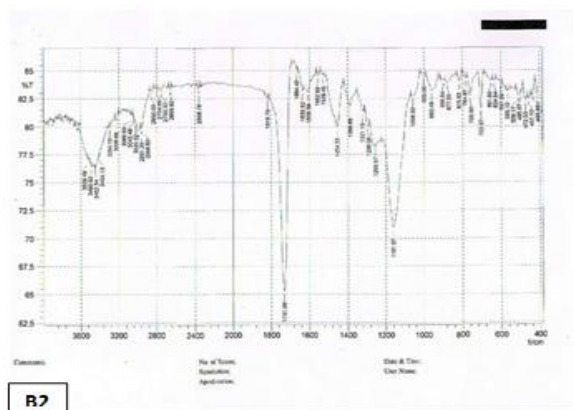
Spectral analysis was used to determine the interaction between Nickel (II) ion and monomer. The Cesium Iodide (CsI) pellet technique registered the FT-IR spectrum in the range of 250–4000  $\text{cm}^{-1}$ . The FT-IR spectra of NIP1 (polymer without using templet), Nickel-IIP1 before and after elution are shown in Fig.(1). It can be seen that both spectra (B1,B2) have similar backbones, mean that the elution process has nearly no influence on the primary polymer network structure. The spectrum of Nickel-IIP1 before elution has strong bands at 823.55, 1376.0 and 1620  $\text{cm}^{-1}$ , corresponding to Ni-N, N-O and N=O groups, which indicates that Nickel nitrate hexahydrate had participated in the synthesis of Nickel-IIP1. However, these three peaks disappear after eluting Ni(II) ions due to destruction of original interaction between styrene and  $\text{Ni}^{2+}$ , indicating that  $\text{Ni}^{2+}$  had been removed successfully. The FT-IR spectra of for NIP2 (polymer without using templet) Nickel-IIP2 are shown in Fig.(2) where a appears band at 821.62, 1371.51, 1620.09  $\text{cm}^{-1}$  corresponding to Ni-N, N-O and N=O groups. these three peaks

disappear after eluting Ni(II) ions due to the destruction of original interaction between 1-vniyl imidazole and  $\text{Ni}^{2+}$ . The main peaks obtained from figures list in the table (1) and table (2).

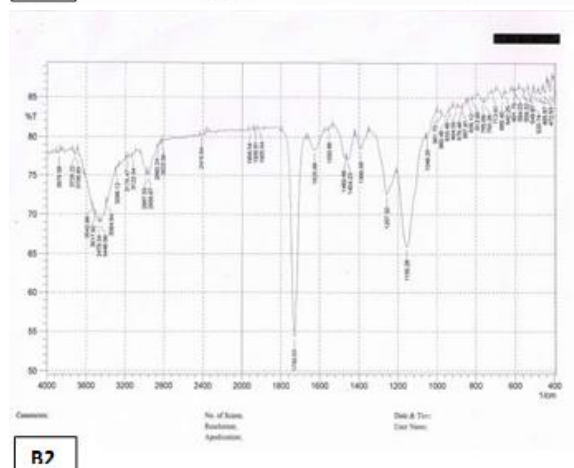
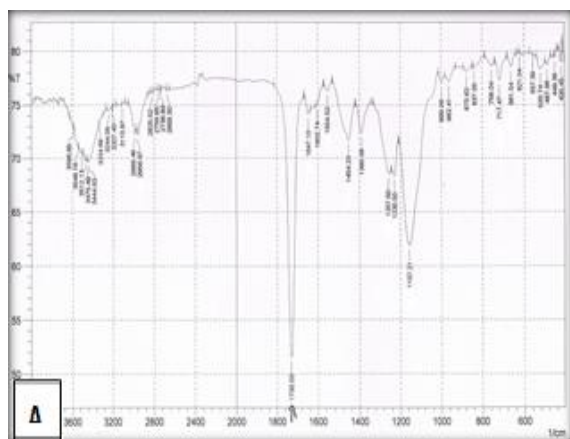
#### 3.1.2. SEM

Morphological analysis is an important characteristic for understanding the size and arrangement of areas where Nickel ion was removed. The morphology of the Ni(II)-IIPs was evaluated by SEM images. For Nickel-IIP1 Fig.3(A,B) shows the surface morphologies of the particles before and after elution. It can be seen that the surface of eluted Nickel-IIP1 is containing pores and rougher than that of non-eluted one as a result of the removing of Ni(II) ions. surface morphologies of Nickel-IIP2 before and after elution shown in Fig.4(A,B). for two kind of prepare IIPs shows numerous pores on the surface which made it a suitable sorbent because of the well-defined binding sites on the imprinted polymer. In addition, the images shows that the diameters of pores ranging between (100-150 nm) for Nickel-IIP1 and (50-100 nm) for Nickel-IIP2 are uniform in sizes and shapes (regular).





**FIG. 1. A.** FTIR spectrum of NIP1 (without using templet)  
**B.** FTIR spectrum of Nickel-IIP1 (Using styrene as a monomer).  
**B1.** before the removal of Ni(II) **B2.** after the removal of Ni(II)



**FIG.2. A.** FTIR spectrum of NIP2 (without using templet)  
**B.** FTIR spectrum of Nickel-IIP2 (Using 1-vinyl imidazole as a monomer). **B1.** before the removal of Ni(II) **B2.** after the removal of Ni(II)

**Table (1):** The most identified peaks of FTIR spectrum Nickel-IIP1 using (styrene) as a functional monomer

NO	Functional Group	Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	Nickel-IIP1 before templet removal	Nickel-IIP1 after templet removal
1	C-H aliphatic	-----	2995.25 2962.46	2991.39 2958.60
2	C=O ester	-----	1724.24	1731.96
3	C-H aromatic	-----	3095.54	3020.32
4	C=C aliphatic	-----	1554.52	1552.59
5	CH <sub>2</sub> =CH <sub>2</sub> aromatic	-----	1604.66	1610.45
6	C-O	-----	1298	1298.08
7	Ni-N	823.55	823.83	-----
8	N-O	1376.0	1371.29	-----
9	N=O	1620	1637.45	-----

**Table (2):** The most identified peaks of FTIR spectrum Nickel-IIP2 using (1-vinyl imidazole) as monomer

NO	Functional Group	Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O (cm-1)	Nickel-IIP1 before templet removal (cm-1)	Nickel-IIP1 after templet removal (cm-1)
1	C-H aliphatic	-----	2995.25 2962.46	2991.39 2958.60
2	C=O ester	-----	1724.24	1731.96
3	C-H aromatic	-----	3095.54	3020.32
4	C=C aliphatic	-----	1554.52	1552.59
5	CH <sub>2</sub> =CH <sub>2</sub> aromatic	-----	1604.66	1610.45
6	C-O	-----	1298	1298.08
7	Ni-N	823.55	823.83	-----
8	N-O	1376.0	1371.29	-----
9	N=O	1620	1637.45	-----



### 3.1.3. EDX

The EDX teste was used to determine the composition of Nickel-IIPs and approve that the Ni(II) ion was eluted successfully. The EDX spectra of Nickel-IIPs before and after elution are shows Fig.(5,6). The results in Fig. 5A and 6A confirm the presence Ni(II) in the structure. As shown in Fig 5B and 6B , Ni(II) ion is not present in the structure of Nickel-IIPs after elution, indicating that the elution of Ni(II) ion with porogen solvent CH<sub>3</sub>OH/CH<sub>3</sub>COOH (30:3 v/v) is succeeded.

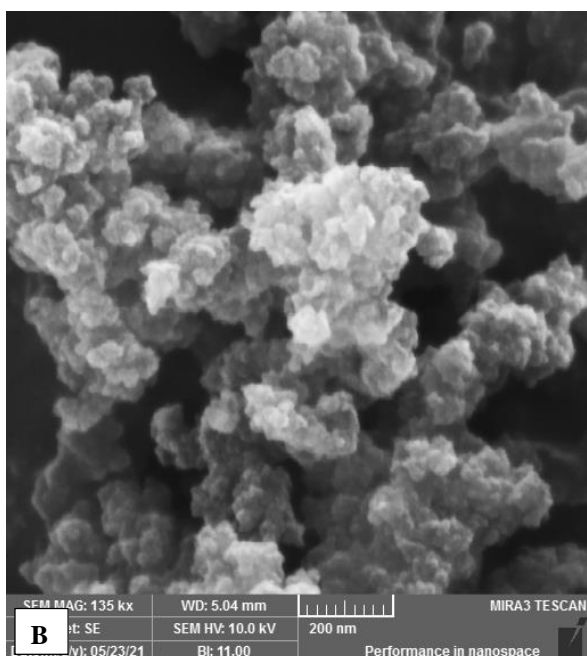
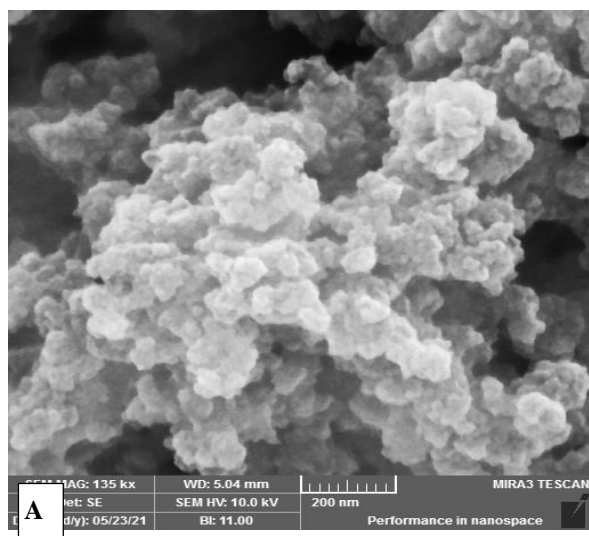


FIG. 3. SEM of Nickel-IIP1(Using styrene as a monomer).

A .before the removal of Ni(II) B. after the removal of Ni(II)

### 3.2. The optimum ratio of materials

Several experiments were conducted to determine o the optimal ratios of Nickel(II) ion: monomer: cross linker for preparing molecularly imprinted polymers and non-imprinted polymers. Table (3) shows the ideal ratios for creating MIPs and NIPs with the best performance characteristics

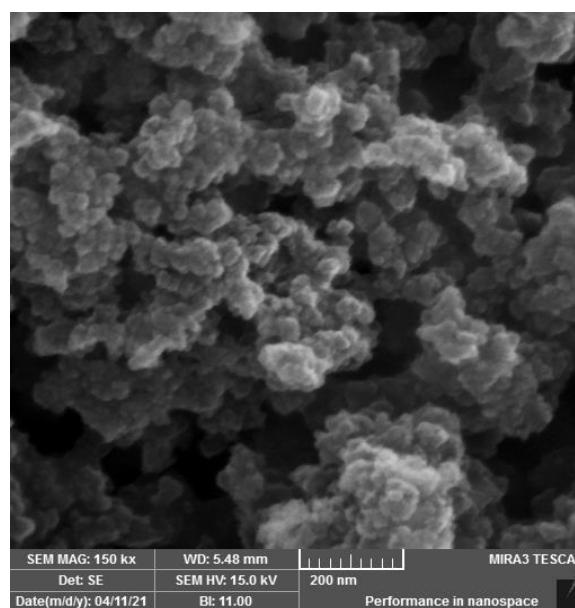
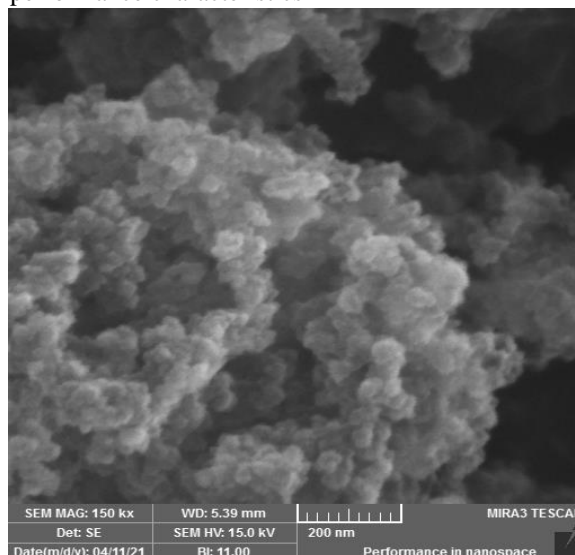
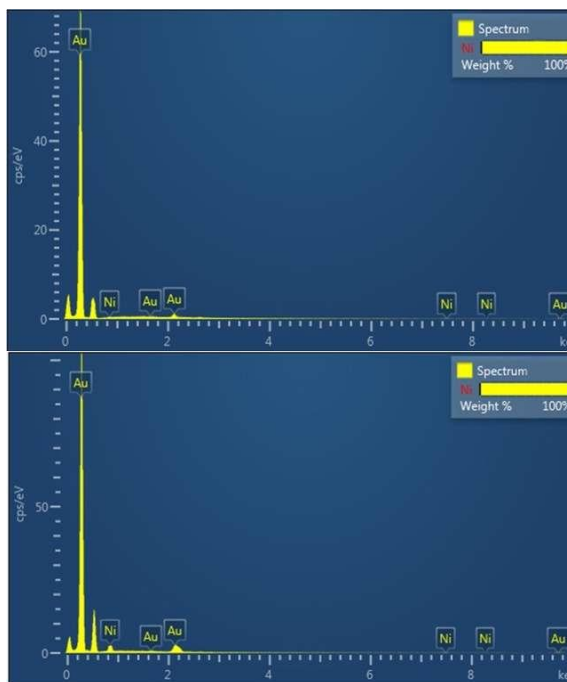
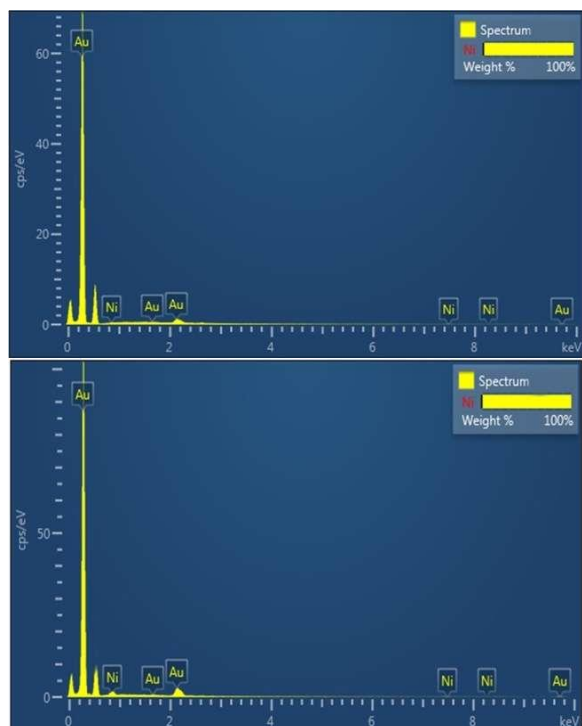


FIG.4. SEM of Nickel-IIP2 (Using 1-vinyl imidazole as a monomer). A. before the removal of Ni(II) B. after the removal of Ni(II)



**FIG. 5.** EDX spectrum of Nickel-IIP1(Using styrene as a monomer). **A.** before the removal of Ni(II) **B.** after the removal of Ni(II)



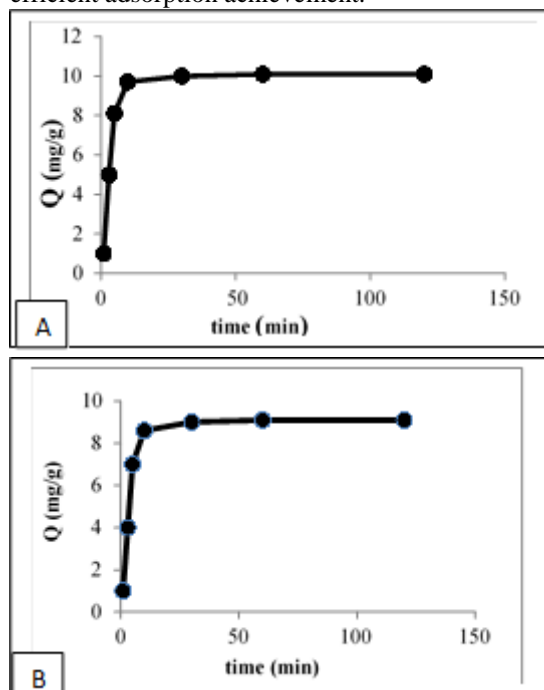
**FIG.6.** EDX spectrum of Nickel-IIP2(Using 1-vinyl imidazole as a monomer).

**A.** before the removal of Ni(II) **B.** after the removal of Ni(II)

### 3.3. Adsorption condition

#### 3.3.1. Adsorption time

Adsorption rate is an important parameter in the industrial application of prepared IIPs. Variations in adsorption capacity with respect to adsorption time (1, 3, 5, 10, 30, 60, and 120 min) were studied and the results for two IIPs are shown in **Fig.(7)**. The adsorption capacity increases sharply in the first 5 minutes, indicating that the adsorption process of Ni(II) ion in aqueous solution with prepared Ni(II)-IIPs is very fast at the beginning. Then the adsorption capacity increases lightly with increasing adsorption time from 5 min to 10 min and remains unchanged after 10 min. very Fast adsorption kinetics establish that the binding sites in prepared Nickel-IIPs have excellent affinity to Ni(II) ions, leading to high efficient adsorption achievement.



**FIG.7.** Time-dependent changes in adsorption capacity (20 mL 50 mg.L<sup>-1</sup> Nickel(II) solution, 100 mg IIPs, 25°C).

**A.** Nickel-IIP1(Using styrene as monomer)

**B.** Nickel-IIP2(Using 1-vinyl imidazole as monomer)

#### 3.3.2. Adsorption capacity

Appraise the adsorption achievement of Nickel-IIPs, the effect of initial Nickel(II) ion concentration ranging from 0.172 to 12.06  $\mu\text{mol/ml}$  on adsorption capacity was studied using the following equation.

$$Q = \frac{(C_1 - C_f)V_s \times 1000}{M_{\text{MIP}}} \quad \text{----- (1)}$$

where  $Q$  is the binding capacity of MIPs ( $\mu\text{mol/g}$ ),  $C_f$  is the final Nickel(II) concentration ( $\mu\text{mol/ml}$ ),  $C_i$  is the initial Nickel(II) concentration ( $\mu\text{mol/ml}$ ),  $V_s$  is the volume of solution tested (ml) and  $MMIP$  is the mass of dried polymer (mg).

As shown in **Fig(8)**, the adsorption capacity increases sharply at first and gradually increasing with rise the concentration of Nickel(II) ion. Mass transfer driving force acts by the difference between the concentration of Nickel(II) ion in bulk solution and around surface of IIPs increases with the increase of initial Nickel(II) ion concentration, which significantly increases the equilibrium adsorption capacity. However, when the Nickel(II) concentration is higher than  $8 \mu\text{mol/ml}$ , the amount of adsorbed metal constant

**Tables (4,5)** and shows the adsorption capacity if Nickel-IIP1 and Nickel-IIP2 respectively. Langmuir isotherm models may be used to calculate Nickel-IIPs' maximal adsorption capacity. shown in **Fig(9)**. The maximum adsorption capacity is  $457.3 \mu\text{mol/g}$  for Nickel-IIP1 and  $355 \mu\text{mol/g}$  for Nickel-IIP2. The Nickel-IIPs prepared in this work has the high adsorption capacity. The uniform and attainable imprinted binding sites greatly enhance the adsorption execution of Nickel(II) ions by the prepared Ni(II)-IIPs. Moreover, the binding between monomers and Nickel(II) is very stable, allowing for simpler chelation formation. The Langmuir adsorption isotherm equation shown in the following

$$\frac{Q}{C_{\text{free}}} = \frac{Q_{\text{max}} - Q}{K_d} \text{----- (2)}$$

where  $Q$  is the binding capacity,  $Q_{\text{max}}$  is the maximum apparent binding capacity,  $C_{\text{free}}$  is the free analytical concentration at equilibrium ( $\mu\text{mol/L}$ ), and  $K_d$  is the dissociation constant at binding site. In a linear plot of  $Q/C_{\text{free}}$  vs.  $Q$ , the equilibrium dissociation constant was estimated from the slopes (slop =  $-1/K_d$ ), and the apparent maximum number of binding sites was derived from the y-intercepts (intercept =  $Q_{\text{max}}/K_d$ ) [28].

### 3.4. Application

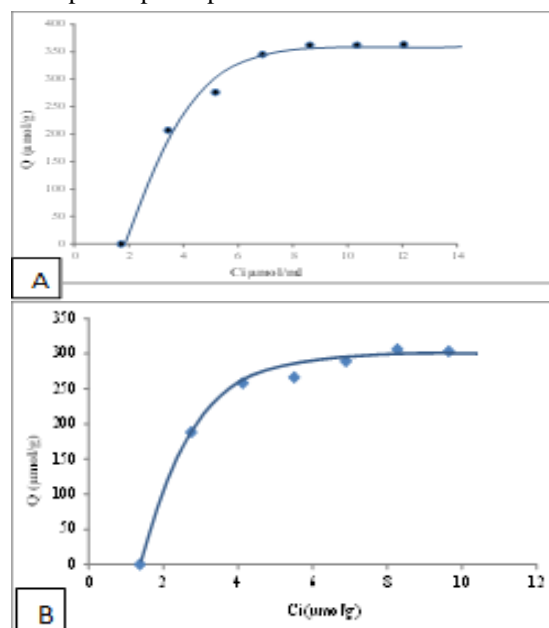
#### 3.4.1. Determination of V(II) ion in synthetic solution

Series of synthetic solution was prepared to studied the recovery of SPE-FAAS by using Vanadium -IIPs shows in table (6)

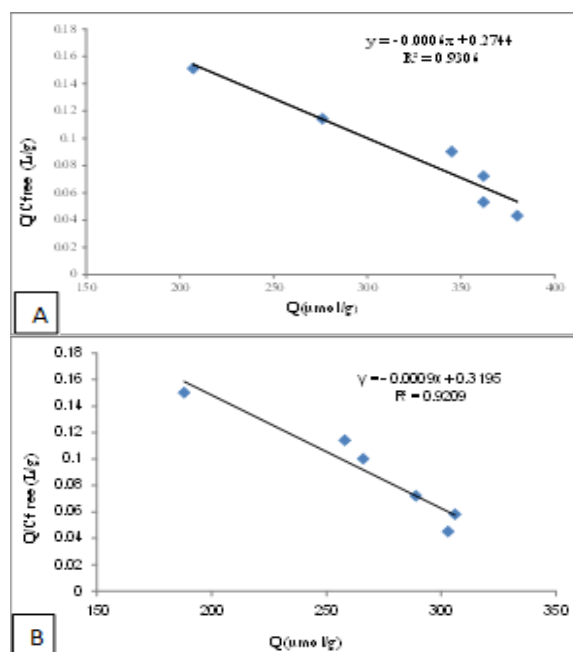
#### 3.4.2 preconcentration in aqueous solution

Preparation of 100 ml of sample containing 5.0 ng/ml of Nickel (II) ion by using deionized water were loaded into the Nickel-IIPs SPE syringe at 1.0

ml/min. After the sample loading, For 5 minutes, air was circulated through the column. Then, Nickel-IIP was collected from column in the small beaker and add 1mL of concentrated sulfuric acid left for a 8minute. After that concentrated nitric acid 1ml is added to it and heated at a 60 temperatures and added distilled water to the mixture to complete volume to 5ml, later estimated directly by flame atomic absorption spectrophotometer.



**Fig.(8)** the relationship between adsorption capacity and initial Ni(II) ion . **A.** for Nickel-IIP1 **B.** for Nickel-IIP2



**Fig.(9)** the relationship between  $Q/C_{\text{free}}$  (L/g) and adsorption capacity to calculate maximum adsorption capacity **A.** for Nickel-IIP1 **B.** for Nickel-IIP2

**Table (3)** The variation ratios of templet, monomer, crooslinker and solvent in the preparation of Nickel- IIPs and NIPs

NO. of IIP	Ratio	salt Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Monomer Styrene	Cross linker EGDMA	Initiator	Solvent	Result
IIP1	%	1.777	10.529	87.749	0.3	6ml CH <sub>3</sub> OH	Salt Precipitate at the bottom
	mmole	0.078	0.31	3.9	0.3		
IIP1	%	0.689	5.517	93.793	0.3	6ml CH <sub>3</sub> OH	Pile white gel
	mmole	0.025	0.2	3.4	0.3		
IIP1	%	1.63	32.62	65.25	0.3	6ml CH <sub>3</sub> OH	White rigid
	mmole	1	20.0	40.0	0.3		
NIP1	%	-----	7.010	92.63	0.3	6ml CH <sub>3</sub> OH	White rigid
	mmole	-----	0.3	3.964	0.3		
		salt Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Monomer 1-vinyl imidazole	Cross linker EGDMA	Initiator	Solvent	Result
IIP2	%	1.66	9.85	82.15	0.3	6ml CH <sub>3</sub> OH	Salt Precipitate at the bottom
	mmole	0.079	0.468	3.9	0.3		
IIP2	%	0.689	5.517	93.793	0.3	6ml CH <sub>3</sub> OH	Pile white gel
	mmole	0.025	0.2	3.4	0.3		
IIP2	%	1.63	32.62	65.25	0.3	6ml CH <sub>3</sub> OH	White rigid
	mmole	1	20.0	40.0	0.3		
NIP2	%	-----	7.010	92.63	0.3	6ml CH <sub>3</sub> OH	White rigid
	mmole	-----	0.3	3.964	0.3		

**Table (4)** show the results of the adsorption capacity experiments for Nickel-IIP1 and their relationship with the initial

C <sub>i</sub> (μmol/ml)	C <sub>f</sub> (μmol/ml)	C <sub>i</sub> -C <sub>f</sub> (μmol/ml)	Q (μmol/g)	Q/C <sub>f</sub> (L/g)
0.172	0	0	0	0
0.862	0	0	0	0
1.72	0	0	0	0
3.44	1.37	2.07	207	0.151
5.17	2.41	2.76	276	0.114
6.89	3.44	3.45	345	0.1
8.62	5	3.62	362	0.072
10.34	6.72	3.62	362	0.053
12.06	8.43	3.63	363	0.043

**Table (5)** show the results of the adsorption capacity experiments for Nickel-IIP1 and their relationship with the initial

C <sub>i</sub> (μmol/ml)	C <sub>f</sub> (μmol/ml)	C <sub>i</sub> -C <sub>f</sub> (μmol/ml)	Q (μmol/g)	Q/C <sub>f</sub> (L/g)
0.172	0	0	0	0
0.862	0	0	0	0
1.72	0	0	0	0
2.75	0.862	1.88	188	0.15
4.13	1.55	2.58	258	0.114
5.51	2.844	2.66	266	0.093
6.89	4.00	2.89	289	0.072
8.27	5.206	3.064	306	0.058
9.65	6.62	3.03	303	0.045

**Table (6)** the results of the determination of nickel (II) ion in synthetic solutions

NO.	Concentration Ni(II) ion (μg/ml)	Ni(II) ion found (μg/ml)	Recovery
1	1	0.99	99
2	3	2.98	99.3
3	5	4.98	99.6
4	8	7.95	99.3
5	10	9.85	98.5

The loading of 100 ml water sample with an digest volume 5ml results in a potential 20-fold concentration increase in the analytes for each extraction technique taken into account. Assuming we have a quantitative recovery, it is a concentration of 2–25 ng/ml, a value that is easily quantifiable by GFAAS but not by FAAS.

The characteristic performance information for the Nickel-IIP2 SPE and preconcentration procedure as shown in table(7). The precision of the method for a standard, evaluated as the relative standard deviation ( $n = 8$ ) was 5.0 ng/ml of Ni(II) ions. The limit of detection, defined as the concentration of analyte that generates signals that are three times the blank's standard deviation plus the net blank's standard deviation ferocity for 100 ml of sample volume, were 2 ng/ml

**Table (7)** Preconcentration procedure performance characteristics

Specification	Ni
Detection limit	2 ng/ml
precision	3.9
Linear rang	2 - 25 ng/ml
Equation of regression	AA = 6.659 C <sub>Ni</sub> - 0.0001

### 3.4.3. Determination of Ni(II) ion in refineries industrial water .

Industrial water is sampling from refineries before and after treatment to remove chemical component from water and filtered with filter of 0.5 μm. Then, these solutions were introduced into the Nickel-IIP-SPE packed column system in in the same manner as described previously. The obtained results as well as the recovery tests shown in table(8)



**Table (8)** determination of nickel (II) ion in industrial water

Samples	Nickel (II) ion add (ppm)	Nickel (II) ion found (ppm)	Recovery (%)
Industrial water before treatment	0.0	19.7 ± 0.15	-
	1.00	20.4 ± 0.21	98.5
	5.00	24.3 ± 0.18	98.3
	10.0	29.4 ± 0.26	98.9
Samples	Nickel (II) ion add (ng/ml)	Nickel (II) ion found (ng/ml)	Recovery (%)
Industrial water after treatment	0.0	4.18 ± 0.21	-
	5.0	9.00 ± 0.29	98
	10.0	14.1 ± 2.1	99.4
	15.0	20.0 ± 1.5	100.4

#### 4. Conclusion

Novel Nickel-IIPs was prepared by bulk polymerization. Styrene and 1-vinyl imidazole selected as functional monomer and EGDMA as crosslinker. Besides, benzyl peroxide was used as an initiator in the presence of chloroform solvent. The optimal molar ratios of Nickel (II) ion to monomer and crosslinker dosage were studied. The irregular shapes and three-dimension network structure of polymers it was possible to notice by SEM. The results of FT-IR and EDX proved the successful elution of Ni(II) ions by  $\text{CH}_3\text{OH}/\text{CH}_3\text{COOH}$  (30:3 v/v) solution. Effects of operating time and initial Nickel(II) ion concentration on adsorption performance were investigated. Adsorption by IIPs was fast (adsorption equilibrium was reached within 10 min) and followed Langmuir isotherm models. The maximum adsorption capacity of the IIPs is  $457.3 \mu\text{mol/g}$  for Nickel-IIP1 and  $355 \mu\text{mol/g}$  for Nickel-IIP2, which is higher than other sorbents reported in literatures. The elution process has nearly no influence on cavity structure and chemical property of the polymers, indicating that Nickel -IIPs have excellent stability and regeneration capabilities.

#### Acknowledgements

This work was supported by Petroleum research and development center / ministry of oil and Service laboratories of College of Sciences, University of Baghdad .

#### References

1. Pari L, Prasath A. Efficacy of caffeic acid in preventing nickel induced oxidative damage in liver of rats, *Chem Biol Interact* 173. (2008).77–83.
2. Amudha K, Pari L.. Beneficial role of naringin, a flavanoid on nickel induced nephrotoxicity in rats, *Chem Biol Interact.*193.(2011).57–64.
3. K.S.Kasprzak,F.W.Sunderman,K.Salnikow. Nickel carcinogenesis, *Mutat.Res.* 533 (2003) 67 97.
4. R.S.Juang,R.C. Shiau, Metal removal from aqueous solutions using chitosan enhanced membrane filtration. *J. Membr. Sci.* 165 (2000) 159–167
5. J.J.Qin, M.N.Wai, M.H., F.S.Wong, A feasibility study on the treatment and recycling of a waste water from metal Plating, *J. Membr. Sci.* 208 (2002)213–221
6. T.A. Kumiawan, S. Babel, A research study on Cr (VI) removal from contaminated wastewater using chemical modified low cost adsorbents and commercial activated carbon, in: *The Proceeding of the 2nd International Conference on Energy Technology Towards a Clean Environment, Phuket, Thailand, (2003)*, 1110–1117
7. T.A.Kumiawan, G.Y.S. Chan, W.H. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metal, *Sci. Total Environ.* 336 (2006) 409–426.
8. S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, *J. Hazard. Mater.* 87 (2001) 273–287.
9. N. Sapari, A. Idris, N. Hisham, Total removal of heavy metal from mixed plating rinse waste water, *Desalination* 106 (1996) 419–422.
10. J. Scancar, R. Milacic, A novel approach for speciation of airborne chromium by convective-interaction media fast-monomolithic chromatography with electro thermal atomic-absorption spectrometric detection, *Analyst* 127 (2002) 629.
11. V.M. Biju, J.M. Gladis, T.P. Rao, Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications *Anal. Chim. Acta* 478 (2003) 43.
12. R. Say, E. Birlik, A. Ersöz, F. Yılmaz, T. Gedikbey, A. Denizli, Preconcentration of copper on ion-selective imprinted polymer microbeads *Anal. Chim. Acta* 480 (2003) 251.
13. L.I. Andersson, Efficient sample pre-concentration of bupivacaine from human plasma by solid-phase extraction on molecularly imprinted polymers *Analyst* 125 (2000) 1515.
14. Lars I. Andersson, Efficient sample pre-concentration of bupivacaine from human plasma by solid-phase extraction on molecularly imprinted polymers *Analyst*, 125,(2000), 1515–1517.
15. O. Vigneau, C. Pinel, M. Lemaire, Ionic imprinted resins based on EDTA and DTPA derivatives for lanthanides (III) separation, *Anal. Chim. Acta* 435 (2001) 75.
16. Xue Zhanga, Jian Yanga, Chao Wanga, Yakun Suna, Zhaosheng Liua, Yanping Huangaa, Haji Akber Aisaa, Improving imprinting effect by reducing sites

- embedding: Selective extraction of 1,2,3,4,6-penta-O-galloyl- $\beta$ -D-glucose from *Paeonia lactiflora* Pall by hydrophilic molecularly imprinted polymers based on macromonomer and metal ion pivot, *Microchemical Journal*, 158 (2020) 105140.
17. Fatma N. Abd, Baker A. Joda, Yehya Kamal Al-Bayati, Synthesis of molecularly imprinted polymers for estimation of anticoagulation drugs by using different functional monomers. *AIP Conference Proceedings*, 2290, (2020), 030042.
  18. Adnan R Mahdi, Suham T Ameen, Yehya K Al-Bayati, Preparation of New Molecularly Imprinted Polymers and its Use in the Selective Extraction For Determination Phenylephrine Hydrochloride at Pharmaceuticals, *International Journal of Drug Delivery Technology*, 10.25258, (2019), 651-659
  19. Zahraa Mahdi, Yehya Kamal Al-Bayati, Synthesis New Liquid Electrodes for Determination Lansoprazole Based on a Molecularly Imprinted Polymer. *International Journal of Pharmaceutical Quality Assurance*, 10.25258, (2020), 175-182.
  20. Mohammad Behbahani, Mohsen Taghizadeh, Akbar Bagheri, Hadi Hosseini, Mani Salarian, Atieh Tootoonchi, A nanostructured ion-imprinted polymer for the selective extraction and preconcentration of ultra-trace quantities of nickel ions, *Microchim Acta* 178 (2012) 429-437.
  21. M. Behbahani, A. Bagheri, M. Taghizadeh, M. Salarian, O. Sadeghi, L. Adlnasab, K. Jalali, Synthesis and characterisation of nano structure lead (II) ion-imprinted polymer as a new sorbent for selective extraction and preconcentration of ultra trace amounts of lead ions from vegetables, rice, and fish samples, *Food Chem.* 138 (2013) 2050–2056.
  22. M. Gawin, J. Konefał, B. Trzewik, S. Walas, A. Tobiasz, H. Mrowiec, E. Witek, Preparation of a new Cd(II)-imprinted polymer and its application to determination of cadmium(II) via flow-injection-flame atomic absorption spectrometry, *Talanta* 80 (2010) 1305–1310.
  23. J. Otero-Romani, A. Moreda-Pineiro, P. Bermejo-Barrera, A. Martin-Esteban, Inductively coupled plasma-optical emission spectrometry/mass spectrometry for the determination of Cu, Ni, Pb and Zn in seawater after ionic imprinted polymer based solid phase extraction, *Talanta* 79 (2009) 723–729.
  24. C.A. Quirarte-Escalante, V. Soto, W.D.L. Cruz, G.R. Porras, R. Manriquez, S. Gomez-salazar, Synthesis of hybrid adsorbents combining sol-gel processing and molecular imprinting applied to lead removal from aqueous streams, *Chem. Mater.* 21 (2009) 1439–1450.
  25. G.Z. Fang, J. Tan, X.P. Yan, An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol-gel process for selective solid-phase extraction of cadmium(II), *Anal. Chem.* 77 (2005) 1734–1739.
  26. Y.C. Zhan, X.B. Luo, S.S. Nie, Y.N. Huang, X.M. Tu, S.L. Luo, Selective separation of Cu(II) from aqueous solution with a novel Cu(II) surface magnetic ion-imprinted polymer, *Ind. Eng. Chem. Res.* 50 (2011) 6355–6361.
  27. Z.C. Li, H.T. Fan, Y. Zhang, M.X. Chen, Z.Y. Yu, X.Q. Cao, T. Sun, Cd(II)-imprinted polymer sorbents prepared by combination of surface imprinting technique with hydrothermal assisted sol-gel process for selective removal of cadmium from aqueous solution, *Chem. Eng. J.* 171 (2011) 703–710.
  28. Helena M.V. Oliveira, Felismina T.C. Moreira, M. Goretí F. Sales, Ciprofloxacin-imprinted polymeric receptors as ionophores for potentiometric transduction. *Electrochimica Acta* 56, (2011), 2017–2023.