

High capacity polymer for nickel determination in environmental samples

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Abstract. A new high capacity sorbent for preconcentration and determination of nickel in environmental samples was synthesized. The sorbent was synthesized by copolymerization of allyl glycidyl ether / iminodiacetic acid with N,N-dimethylacrylamide as functional monomers in the presence of N,N-bismethylenacryl amid as cross linker and characterized by Fourier transform infra red spectroscopy, elemental analysis, thermogravimetric analysis and scanning electron microscopy. A recovery of 93.6% was obtained for the metal ion with 0.1 M, sulfuric acid as the eluting agent. The sorption capacity of the functionalized sorbent was 55.9 mg g⁻¹. The equilibrium sorption data of Ni(II) on polymeric sorbent were analyzed using Langmuir, Freundlich, Temkin and Redlich–Peterson models. Based on equilibrium adsorption data the Langmuir, Freundlich and Temkin constants were determined 0.87 (L mg⁻¹), 25.87 (mg g⁻¹) (L mg⁻¹)^{1/n} and 171.4 (J mol⁻¹) respectively at pH 4.5 and 20°C.

Keywords: High capacity sorbent; Nickel; Preconcentration; Isotherm study

1. Introduction

Nickel is harmful to health, carcinogenic and creates environmental problems. Nickel can also cause a skin disorder and famous as nickel-eczema. This is a considerable health problem especially among women (Kristiansen *et al.* 2000). So, removal of nickel from the body should be investigated and the purification of this metal ion containing process liquids needs much more attention. The traditional separation and/or preconcentration methods for heavy metals are co-precipitation (Tsai *et al.* 1994, Atanassova *et al.* 1998, Kagaya *et al.* 2001), ion exchange (Cuesta *et al.* 1996, Cespon-Romero *et al.* 1996), solvent extraction (Holynska *et al.* 1996, Kojima and Katsuzaki 1997, Kara and Alkan 2001, Carasek 2000) and solid phase extraction (Ahmad Panahi *et al.* 2012, Persson *et al.* 2011, Ahmad Panahi *et al.* 2010). These methods often require large amounts of inorganic and organic solvents, some of which are toxic and cause environmental pollution. The need of more system with high capacity for uptaking of nickel has increased the development of the synthesis of new adsorbents and extractants.

The aim of this research is to present a novel method for free-radical co-polymerization of N,

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N-dimethylacrylamide (DMAA) and allyl glycidyl ether-iminodiacetic acid (AGE/IDA) as functional monomer containing metal chelating group in presence of N,N-bismethylenacrylamid as cross-linker. This network co-polymer shows grate sorbent capacity for removal trace Ni(II) from environmental samples. The merits of this co-polymer supports except the capacity are good chemical and physical properties such as high surface area available for chelating heavy metals and durability. The effects of some analytical conditions such as sample pH, stirring rate, contact time and matrix interferences were examined. The reasonable recoveries were obtained with sulfuric acid as eluting agent prior to determination by flame atomic absorption spectroscopy (FAAS).

2. Experimental

2.1 Instrument

A flame atomic absorption spectrometer AA670/g (shimadzu) equipped with an air acetylene flame (air and acetylene flow rate 8 and 1.7 L/min respectively) was used for concentration measurement of metal ion. The pH measurement was made with a Mettler Toledo model MP250 pH meter. IR spectra were recorded on Jasco FT-IR 410 (Easton.md) by sodium chloride pellet method. Thermogravimetric analysis (TGA) was carried out using a TGA-50H (shimadzu corp, kyoto Japan). The scanning electron micrographs of the dried polymer were obtained using a Philips model XL30 scanning electron microscope.

2.2 Reagent and solutions

N, N-bismethylenacrylamid and N,N-dimethylacrylamide were products of Aldrich (Steinheim, Germany). Allyl glycidyl ether was purchased from Fluka Chemicals (Buchs, Switzerland). Iminodiacetic acid, 2, 2'- Azoisobutironitrile and all inorganic salts and reagent were purchased from Merck (Darmstadt, Germany). All the reagents were of analytical grade and used without any further purification. A stock solution (1000 mg L^{-1}) of Ni(II) was prepared by dissolving appropriate amounts of $\text{Ni}(\text{NO}_3)_2$ in deionized water. To adjust the pH of the solution, 0.01 mol L^{-1} acetic acid - acetate buffer and phosphate buffer were used wherever suitable.

2.3 Preparation of AGE/IDA

Details of the preparation and characterization of the functional monomer (AGE/IDA) was reported in the previous work (Ahmad Panahi *et al.* 2010). Briefly, 6.93 g of IDA was dissolved in KOH solution at pH 8.5. Then 20 mL of AGE was added drop wise in 20 min. The solution was kept in 65°C by water bath and stirred for 1h. At the end, the functional monomer was extracted with acetone. The product obtained was confirmed as the monomer by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

2.4 Synthesis of polymer

The high capacity polymer for nickel ion was synthesized by adopting tow steps procedure based on free radical polymerization technique. In the first step solution of ethanol (20 mL) containing AGE/IDA as functional monomers and 1 mL N,N-dimetylacrylamid as co-monomer was prepared. Then, the nitrogen gas was purged to the above solution for 10 min to create inert

atmosphere and then 2,2'-Azobisisobutyronitrile as initiator was added and the solution was refluxed for 2 h at 60°C in water bath. In second step, N,N-dimethylene acrylamid as cross-linker and again 2,2' Azoisobutyronitrile were added to the solution. The solution was refluxed at 75°C until the polymer was formed. All the mentioned reactions were performed in inert nitrogen atmosphere. Finally, the synthesized polymer was washed with bidistilled water, ethanol and again bidistilled water to removal of unreacted monomers from the polymer. The polymer was dried in vaccume oven and then characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA). The methodology used to synthesize of high capacity Poly(AGE/IDA-DMAA) for Ni(II) (HC- Polymer) is summarized in Fig. 1.

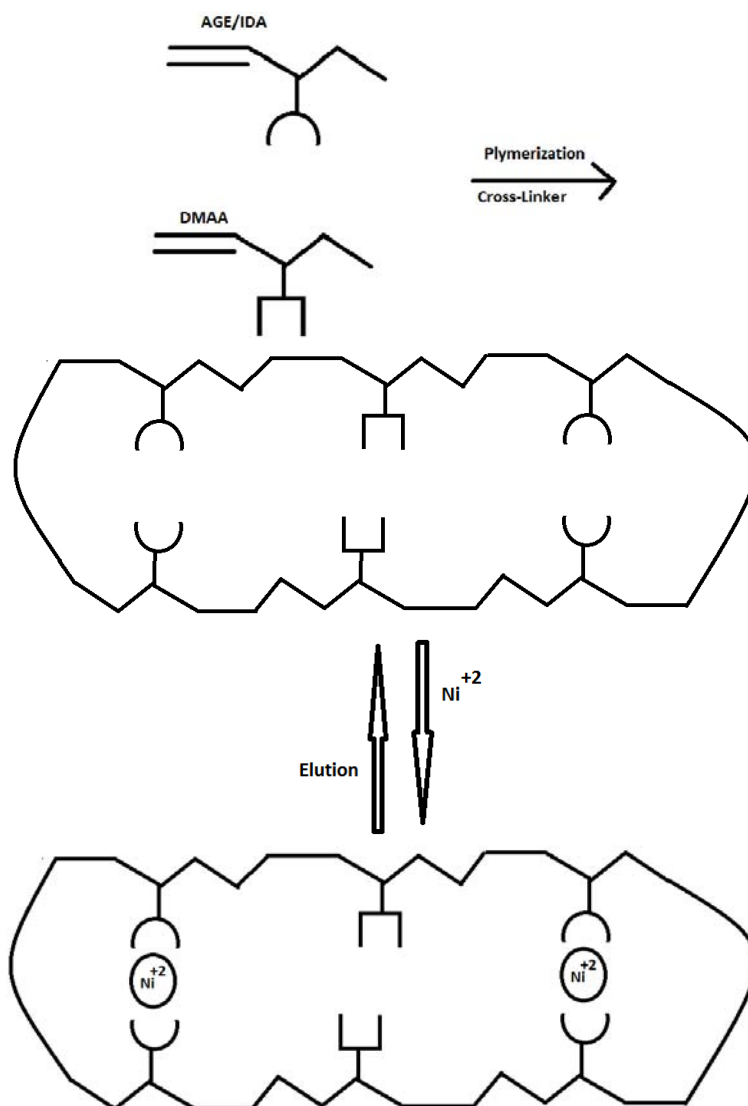


Fig. 1 Schematic presentation of synthesis process of HC- Polymer

2.5 Batch method

The degree of metal sorption at different pH values was determined by a batch equilibration technique. A set of solutions (each 100 mL) containing $0.5 \mu\text{g mL}^{-1}$ Ni(II) were taken. Their pH values were adjusted in the 3-9 range. HC- Polymer (0.1 g) was added to each solution, and the mixture was shaken for 3 h. The optimum pH values for quantitative uptake of nickel ions were ascertained by measurement the Ni(II) content in the supernatant liquid and in the eluent with flame atomic absorption spectroscopy. The 0.1 M H_2SO_4 (10 mL) was used as elution agent.

2.6 Isotherm studies

Isotherm studies were carried out by adding 0.1 g HC- Polymer each to a series of beakers filled with 100 mL dilute solutions of Ni(II) ($10\text{-}100 \mu\text{g mL}^{-1}$) in acetate buffer, pH 4.5. The beakers were then sealed and placed in a water bath stirrer and stirred at 350 rpm for 4 h at 20°C . The beakers were then removed from the stirrer, and the final concentration of Ni(II) in the solution was measured. The amount of Ni(II) at equilibrium q_e (mg/g) on HC- Polymer was calculated from the following equation

$$q_e = (C_0 - C_e) V / W \quad (1)$$

where C_0 and C_e (mg. L^{-1}) are initial and equilibrium concentration of the Ni(II), respectively, V (L) is the volume of the solution and W (g) is the mass of the HC- Polymer used.

3. Results and discussion

3.1 Polymer characterization

FTIR (NaCl, cm^{-1}) 3390 (OH), 1633 (C=O), 2938 bending (CH_2), 1114 (C-O), 1401 stretching (CH_2), 1391 stretching (CH_3). FT-IR confirmed the presence of hydroxyl and carbonyl groups in the polymer which is due to carboxylic group in the polymer. The elemental analysis of HC- Polymer (C, 47.09; H, 8.14; N, 12.20%) demonstrates the formation of the HC- Polymer. The presence of nitrogen in HC- Polymer by elemental analysis indicates that DMAA or AGE/IDA monomers are present in the repeated unit of the polymer. The TGA of the HC- Polymer showed a weight loss up to 150°C due to the desorption of water molecules from the surface, and the weight loss at $350\text{-}700^\circ\text{C}$ was attributed to the decomposition of the polymeric matrix. TGA clearly revealed that the HC- Polymer is stable in temperature up to 350°C (Fig. 2). SEM was used to observe the external surface of the polymer. The SEM micrographs for studding of external surface of HC- Polymer are presented in Fig. 3. The surface of the HC- Polymer has a smooth and highly homogeneous appearance. The size of polymer particles is about $200 \mu\text{m}$ in an average. The specific surface area of HC- Polymer was calculated by Brunauer, Emmett and Teller method using nitrogen isotherm adsorption data. The surface area of the HC- Polymer was $8.78 \text{ m}^2 \text{ g}^{-1}$.

3.2 Ni(II) Sorption conditions

The pH of the medium is the first and most important parameters that should be optimized. So the HC- Polymers subjected to Ni(II) sorption in different pH levels. The maximum adsorption of Ni(II) was achieved at pH 4.5. Desorption was carried out by the various eluents including EDTA,

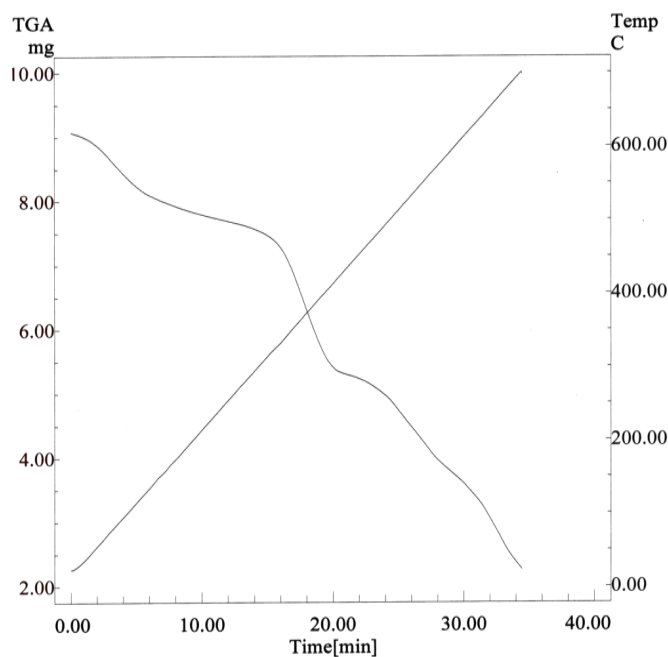


Fig. 2 Thermogravimetric analysis of HC- Polymer

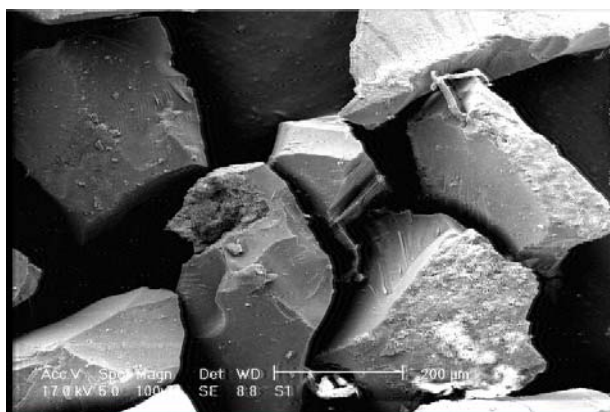


Fig. 3 Scanning electron microscopy photograph of HC- Polymer

0.1 M nitric acid, hydrochloric acid and sulfuric acid. Sulfuric acid (0.1 M) appeared to be the most effective of the above-mentioned solutions. The optimum pH range for the sorption of the metal ions is shown in Fig. 4. The maximum recovery was 93.6% at pH 4.5. The extraction recovery was defined as the percentage of the total Ni(II) which was extracted into the solid phase and subsequently into eluent. The sorption, as a function of contact time for Ni(II), was investigated in different time and shown in Fig. 5. Just 5 minute was required for more than 90% of maximal sorption. The profile of Ni(II) uptake by the HC- Polymer reflects good accessibility of the active sites in the synthesized polymeric sorbent. Also the Ni(II) sorption, as a function of

string rate, was studied. The result was shown in Fig. 6. This Figure demonstrates string rate of 150 rpm is enough for Ni(II) sorption. The sorption capacity of the HC- Polymer for Ni(II) was ascertained from the difference between concentrations in solution before and after the sorption. The sorption capacity was around 55 mg g^{-1} at pH 4.5 and 20°C (Fig. 7). The Ni(II) was sorbed and desorbed on 0.1 g of the HC- Polymers several times. It was found that sorption capacity of HC- Polymers after 5 cycles of its equilibration with Ni(II), changes less than 10%. Therefore, repeated use of the HC- Polymers is feasible. The HC- Polymers cartridge after loaded with samples can be readily regenerated with 0.5 M sulfuric acid. The sorption capacity of the HC- Polymers stored for more than 4 month under ambient conditions has been found to be practically unchanged.

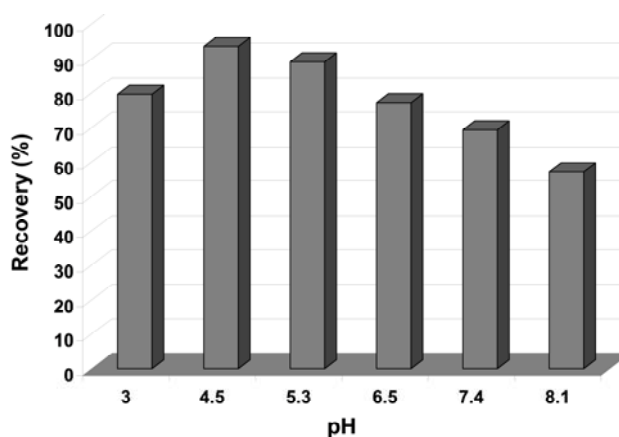


Fig. 4 Effect of pH on sorption of Ni(II) onto HC- Polymer. Volume of each 100 mL containing $0.5 \mu\text{g mL}^{-1}$ of Ni(II) ions. Their pH values were adjusted with buffer solutions. The 0.1 g of HC- Polymer was added to each solution and the mixture was shaken for 1 h

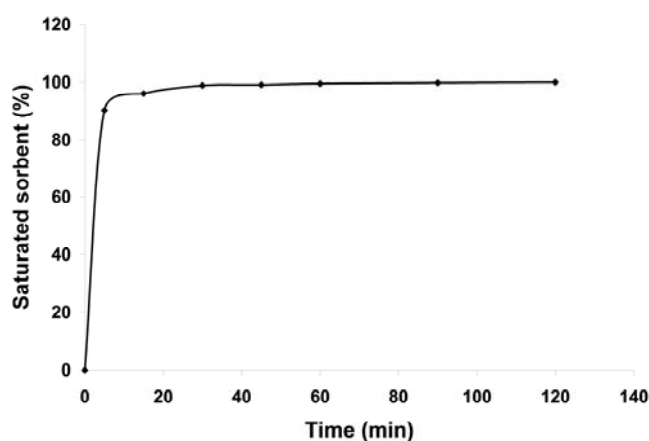


Fig. 5 Kinetics of Ni(II) sorption on HC- Polymer. Volume of each 50 mL containing $40 \mu\text{g mL}^{-1}$ of Ni(II) ions. The 0.05 g of HC- Polymer was added to each solution and the mixture was shaken for different length of time under pH 4.5

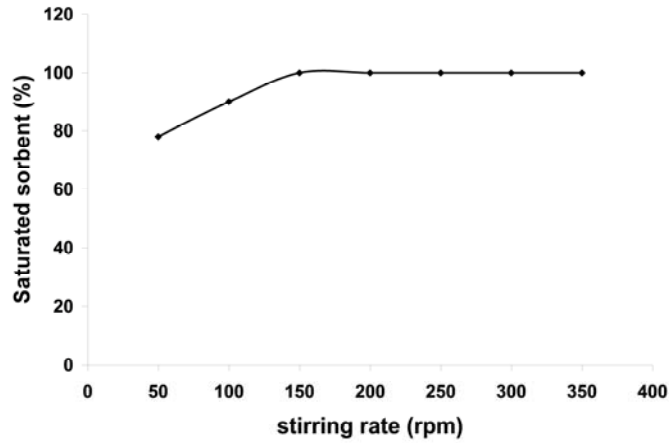


Fig. 6 Effect of stirring rate on sorption of Ni(II) onto HC- Polymer

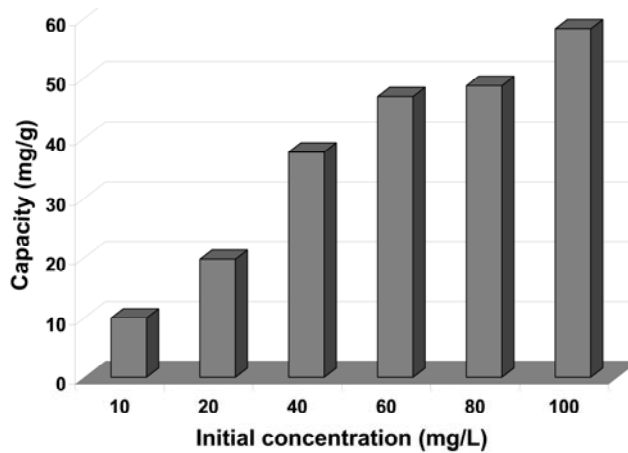


Fig. 7 Effect of initial concentration of the Ni(II) in the solution on sorption capacity

3.3 Isotherms studies

The experimental results obtained for the adsorption of nickel ion on HC- Polymer at 20°C was found to obey Langmuir, Freundlich, Temkin and Redlich–Peterson sorption isotherm. Isotherm factors calculated from following equations (Langmuir 1918, Hall *et al.* 1966, Freundlich 1906, Ho and Ofomaja 2006) are listed in Table 1.

$$\text{Langmuir equation : } C_e / q_e = (1/q_{\max} \cdot K_L) + (C_e / q_{\max}) \tag{2}$$

$$\text{Freundlich equation : } \ln q_e = (\ln K_L) + 1/n \ln C_e \tag{3}$$

$$\text{Temkin equation : } q_e = U_T \ln K_T + U_T \ln C_e \tag{4}$$

where q_{\max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}), K_L is the Langmuir constant (L mg^{-1}), R_L is the essential characteristic of the Langmuir equation, K_F is the Freundlich constant (mg g^{-1}) (L mg^{-1})^{1/n}, $1/n$ is the heterogeneity factor, $U_T = RT/u$ and u is the Temkin constant related to heat of sorption (J mol^{-1}), K_T is the Temkin isotherm constant (L g^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (293 K).

Langmuir isotherm is one of the best models in adsorption isotherms. Langmuir isotherms were used for the determination of maximum sorbent capacity defined as the amount of nickel ion adsorbed by one gram of HC- Polymer. A plot of C_e/q_e versus C_e indicates a linear relationship (Fig. 8), and q_{\max} and K_L can be calculated from the slope and intercept of the plot (Table 1). The q_{\max} (55.9 mg L^{-1}) for sorption of Ni(II) by the HC- Polymer was superb. The value of R_L (0.01) is in the range of 0-1 at optimum pH which confirms the favorable uptake of the Ni(II).

Table 1 Isotherm parameters obtained by using linear method

Langmuir isotherm model				
Temperature ($^{\circ}\text{C}$)	q_{\max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
20	55.86	0.87	0.01	0.9853
Freundlich isotherm model				
Temperature ($^{\circ}\text{C}$)	K_F (mg g^{-1}) (L mg^{-1}) ^{1/n}	n		R^2
20	25.84	4.48		0.9712
Temkin isotherm model				
Temperature ($^{\circ}\text{C}$)	K_T (L g^{-1})	U_T (J mol^{-1})	U	R^2
20	171.40	6.11	399.16	0.9737
Redlich–Peterson isotherm model				
g	P_r ($\text{dm}^3 \text{ mg}^{-1}$) ^g	R_p ($\text{dm}^3 \text{ g}^{-1}$)		R^2
0.9994	160	3.83		0.9984

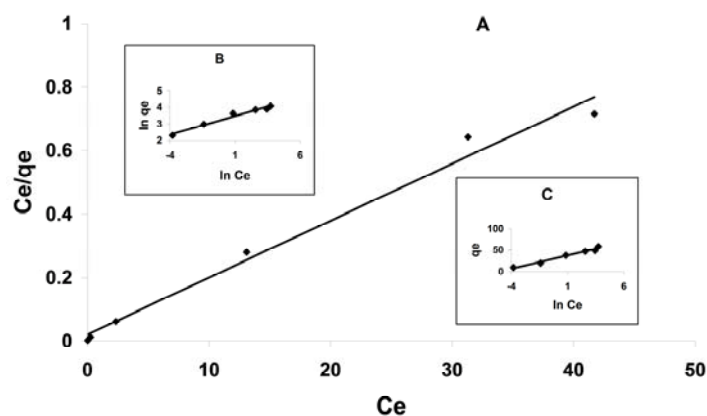


Fig. 8 Langmuir, Freundlich and Temkin isotherm for Ni(II) adsorption onto HC- Polymer at 20°C

The Freundlich adsorption isotherm represents the relationship between the amount of nickel ion adsorbed per unit mass of HC- Polymer (q_e) and the concentration of the Ni(II) in solution at equilibrium (C_e). Fig. 8 shows the plot of $\ln q_e$ (mg g^{-1}) versus $\ln C_e$ (mg L^{-1}), the linear form of the plot indicating the applicability of the classical adsorption isotherm to this system. The Freundlich equation predicts that the Ni(II) concentration on the HC- Polymer will increase as long as there is an increase in the Ni(II) concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the adsorptional centers of HC- Polymer is increased. Plotting q_e versus $\ln C_e$ enables one to determine the constants K_T and U_T (Fig. 8).

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows

$$\ln\left(R_p \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(P_r) \quad (5)$$

It has three isotherm constants, namely, R_p , P_r , and g ($0 < g < 1$), which characterize the isotherm. Three isotherm constants, R_p , P_r , and g can be evaluated from the linear plot represented by Eq. (5) using a trial and error procedure, which is applicable to computer operation. Table 1 shows that the values of g were close to unity, which means that the isotherms are approaching the Langmuir form for HC- Polymer.

3.4 Effect of foreign ions

In order to evaluate the selectivity of the preconcentration system the effect of 10 mg L^{-1} interfering on the sorption behavior of Ni(II) ion (10 mg L^{-1}) was investigated. The extraction percentage (E %) and the distribution ratio (D) was calculated from the following equations

$$Q = (C_0 - C_e) V / W \quad (6)$$

$$E = (C_0 - C_e) / C_0 \quad (7)$$

$$D = Q / C_e \quad (8)$$

where Q represents the adsorption capacity (mg.g^{-1}), C_0 and C_e represent the initial and equilibrium concentration of Ni(II) ($\mu\text{g.mL}^{-1}$), V is the volume of sample solution (L), W is the mass of HC- Polymer (g), E (%) is the extraction percentage and D is the distribution ratio (mL g^{-1}). Table 2 indicates the Ni(II) adsorption by HC- Polymer is mostly affected by Pb(II) whereas the effects of other mentioned ions at given concentration is negligible allowing for quantitative Ni(II) determination in environmental samples.

3.5 Comparison with other methods

Comparative information from a number of researches on preconcentration of Ni(II) by various methods for the figure of merits is given in Table 3. The sorption capacity of the HC- Polymer is superior in comparison to all the sorbents shown in Table 3. This new developed method has been successfully applied to the analysis of trace nickel ions in natural water sample.

Table 2 Effect of other ions on sorption

Interfering ion	Amount of adsorbed Ni(II) (mg L ⁻¹)	Loss of adsorption (%)	Extraction percentage (%)	Distribution ratio
—	8.81	0	88.1	7.40
Cd(II)	8.56	2.84	85.6	5.94
Ca(II)	8.38	4.88	83.8	5.17
Mg(II)	8.42	74.43	84.2	5.33
Zn(II)	8.38	4.88	83.8	5.17
Cu(III)	7.26	17.59	72.6	2.65
Pb(II)	8.44	4.20	84.4	5.41
Na(I)	8.81	0	88.1	7.40
K(I)	8.81	0	88.1	7.40

Table 3 Comparison of recovery, preconcentration factor and capacities with other works

Sorbent used	Recovery (%)	Preconcentration factor	Capacity (mg g ⁻¹)	Ref.
Tungsten Foil	93-103	—	—	(Ohta <i>et al.</i> 1998)
[1-(2-Pyridylazo)-2-Naphthol] -Naphthalene	—	—	8.9	(Taher <i>et al.</i> 2000)
Pyrrolidinedithiocarbamate on Cellulose Filters	100	—	—	(Gordeeva <i>et al.</i> 2002)
Poly(Vinyl Pyrrolidinone)	95	10	11.9	(Tokman <i>et al.</i> 2004)
Thiacalix[4]arenetetrasulfonate- loaded Sephadex A-25	97	200	—	(Matsumiya <i>et al.</i> 2004)
1-(2-Pyridylazo)-2-Naphtol(PAN) Immobilized on Surfactant -Coated Alumina	97	5-300	0.93	(Shemirani and Abkenar 2004)
Chitosan functionalized with 3,4-dihydroxy benzoic acid	—	10	0.09	(Sabarudin <i>et al.</i> 2007)
DMAA-AGE/IDA- grafted silica gel	92.6	10	12.51	(Ahmad Panahi <i>et al.</i> 2012)
Ionic imprinted polymer	100	40	1.98	(Otero-Romani <i>et al.</i> 2009)
Methacrylate (HEMA) with nickel vinylbenzoate complex in the presence of ethylene glycol dimethacrylate	97.8	—	38	(Singh and Shradha 2010)
Poly (thioure-formaldehyde)	96	10	0.295	(Ahmad Panahi <i>et al.</i> 2010)
Poly(AGE/IDA-DMAA)	93.	10	55.9	Our work

Table 4 Ni(II) determination in environmental water and biological fluid samples

Kosar aqueduct water				Plasma			
Added (mg L ⁻¹)	Found (mg L ⁻¹)	Rrccovery (%)	Preconcentration factor	Added (mg L ⁻¹)	Found (mg L ⁻¹)	Rrccovery (%)	Preconcentration factor
0	—	—	10	0	—	—	5
0.20	1.87 ± 0.08	93.7	10				
0.40	3.65 ± 0.06	91.2	10	0.40	1.01 ± 0.21	50.6	5
0.60	5.32 ± 0.05	88.7	10				

*Average of three determinations

Table 5 Analytical performance of Ni(II) determination by HC- Polymer

Analytical calibration curve	R ²	Linear range (μg mL ⁻¹)	RSD*	Enhancement factor	LOD (ng mL ⁻¹)	LOQ (ng mL ⁻¹)
Y = 0.016X + 0.002	0.9980	0.1-10	3.4	4	6.9	23.0

* For four experiments

3.6 Determination of Ni(II) in real water and biological samples

HC- Polymer was used to preconcentrate and determine Ni(II) ion in Kosar aqueduct samples collected from Omid shahrak, Tehran, Iran. The solid phase extractions at optimum conditions were performed for spiked aqueduct water as extractant sample without any pretreatments. The estimation of the metal ion was made with 50 mL of water sample (spiked with different amount of Ni(II)) and determining the Ni(II) by FAAS after elution as described in the recommended procedure. The results are presented in Table 4. The closeness of results to expected concentration indicates the reliability of present results of Ni(II) analyses in environmental water samples. Adsorption of Ni(II) by HC- Polymer from human plasma was also studied in batch-wise method. The moderate recovery (Table 4) indicates a rather strong competition of plasma components for Ni(II) binding or a blockage of binding sites on the HC- Polymer by human plasma components.

3.7 Analytical performance of the proposed method

The figure of merits of the developed method was presented in Table 5. The calibration curve was plotted after preconcentration at different concentrations. Limits of detection (LOD) and quantification (LOQ) for the target drug were calculated based on the equations $LOD = 3 \sigma/f$, $LOQ = 10 \sigma/f$, respectively, where σ is the standard deviation (SD, $n = 4$) of the intercept of the regression lines and f is the preconcentration factor. Table 5 shows that the proposed method had good analytical performance for HC- Polymer: the RSD was less than 4% and the R^2 value of the proposed method was over 0.9980. The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 4. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10. The LOD and LOQ values of the proposed method are rather good.

4. Conclusions

The solid phase extraction procedure developed in this research using HC- Polymer facilitates a 10-fold concentration of Ni(II) from dilute aqueous solutions. The HC- Polymer allows for sorption of Ni(II) in the presence of interfering metal ions. The proposed method is simple and the sorption capacity of the sorbent is superb comparing to other sorbent. Equilibration is fast as 96% of Ni(II) is sorbed within 15 min. HC- Polymer has high mechanical strength and good chemical stability. In addition, the new synthesized HC- Polymer offers reliable analysis of Ni(II) in environmental samples using instrument like FAAS. The recoveries of Ni(II) are nearly quantitative.

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