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ORIGINAL ARTICLE

Application of Modified Nanocellulose with 2-aminopyrimidine as a New Sorbent for Separation and Determination of Trace Amounts of Nickel Ions in Human Blood and Urine

Ali Mirabi

Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

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KEYWORDS

Determination of nickel;
Modified nanocellulose;
2-Aminopyrimidine

ABSTRACT: In the present study, trace amount of nickel (II) ions in real samples has been separated, preconcentrated and determined by a synthesized nanocomposite. Our suggested nanocomposite was prepared by immobilization of 2-aminopyrimidine on nanocellulose. The properties of nanocomposite were characterized by TEM, TGA, elementalanalysis CHNS, EDS, and BET techniques. The effective factors such as pH, nanocomposite amount, extraction time, eluent type, ionic strength and sample volume were optimized for quantitative determination of nickel (II) ions. The linear range of the calibration graph was between 5 and 500 ng mL^{-1} with limit of detection (LOD) 2.33 ng mL^{-1}. Relative standard deviations (RSD) were 2.33%. Modified nanocellulose was used for measurement of the trace amounts of Ni (II) ions in the real samples such as human blood and urine with suitable fallouts.

INTRODUCTION

The trace amount of nickel is indicated to be either essential or toxic depending on its concentration range. For instance, due to studies on chicks and rats (the latter of which are relatively close to human genetically) nickel is apparently essential for proper liver function. On the other side, some of nickel compounds are carcinogenic [1–3]. Ni is a somewhat toxic element compared with other metals. It is known that inhalation of Ni and its compounds can lead to serious problems, including respiratory system cancer [4, 5]. Moreover, Ni can cause a skin disorder known as nickel eczema [6] and allergic reaction, and certain Ni compounds may be carcinogenic [7]. Thus it is clear that determination of nickel, at trace level, in human blood and urine samples is of great significance from the public health and environmental point of view [8].

Currently, the most common analytical methods for trace determination, of Ni (II) ions are; flame atomic absorption spectrometry (FAAS) [9, 10]; electrothermal atomic absorption spectrometry (ET-AAS) [11, 12]; inductively coupled plasma emission spectrometry (ICP-AES) [13]; and inductively coupled plasma-mass spectrometry (ICP-MS) [14]. However, all aforementioned methods (except FAAS) require relatively high-cost apparatus, and high instrumentation complexity; limiting their widespread application to routine analytical works. FAAS is widely employed, in the determination of Ni (II) ions, because of its low cost, friendly operation, high sample throughput and good selectivity [15]. There are many difficulties in determining trace amounts of Ni (II) ions in human blood and urine samples by FAAS due to insufficient sensitivity of instrument and/or matrix interferences. In order to achieve detection limits within the range of FAAS. An

*Corresponding author: mirabi2012@yahoo.com, a.mirabi@qaemiau.ac.ir (A. Mirabi)
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initial preconcentration step allows lower limits of detection for analytes, as well as the separation of the analytes from its matrix, which may interfere in atomic absorption spectrometric determinations. Preconcentration procedure is required for the determination of low contents of trace elements in real samples. Of all preconcentration and separation procedures sorption possesses several advantages: large preconcentration factors that can be obtained in a short time, simplicity of phase separation and suitability for automation [16, 17].

The most widely used techniques, for the separation and preconcentration of trace metals, include solid phase extraction (SPE), coprecipitation, ion-exchange, liquid–liquid extraction, membrane filtration, floatation and cloud point extraction (CPE) [18–26]. Numerous substances have been proposed, and applied as SPE sorbents, such as Diaion HP-20 [27], cellulose [28], activated carbon [29], Lewatit S 100 [30], SDS coated alumina [31] polyurethane foam [32], Chelex 100 [33], microcrystalline naphthalene [34], modified silica [35] and diaion HP-2MG [36]. Modified nanocellulose can offer several advantages over traditional SPE sorbents, such as having very large surface areas, thermal stability and selectivity, which result in high extraction capacity and efficiency.

In this work, we explore the possibility of 2-aminopyrimidine coated nanocellulose to act as SPE sorbent for the separation and preconcentration of trace amounts of Ni (II) ions from human blood and urine samples.

MATERIALS AND METHODS

Reagents and apparatus

Pyridine, 2-aminopyrimidine ligand, nickel (II) nitrate, tosyl chloride, hydrobromic acid, ethanol, acetone and sodium hydroxide have been purchased from Merck Corporation and α-cellulose were purchased from sigma Aldrich. Analytical grade nitrate salts of elements (all from Merck) were of the highest purity available and used without any further purification. pH meter model Metrohm 744 from Switzerland was used to measuring pH. Kokusan model H-11n centrifuge was used to precipitating nanocomposite. Measuring nickel ions was done by a Thermo M series (Model: M5) FAAS with a Ni hollow cathode lamp. The following conditions were used: λ_{max}=232.0 nm; monochromator spectral bandpass=0.1 nm; lamp current=15 mA; burner head=50 mm; acetylene and air-flow rates were 0.8 and 10.0 L min^{-1} respectively. Transmission electron microscope (TEM) HF2000, Hitachi high-technologies Europe GmbH, Krefeld model was used to measuring porous size. Detecting surface area was done by BET technic (Quanta chrome, Chem BET 300 TPR/TPD). For elemental analysis of nanosorbent from energy-dispersive X-ray spectroscopy (EDS) with specifica-tion Mira 3-XMU was used. To consolidation of 2-aminopyrimidine on surface of sorbent elemental analysis CHNS of Costech ECS4010 Italy and TGA of Bahr thermo analyse were done. The as-synthesized sample was heated from 25°C to 400°C at a rate of 20°C/min in a nitrogen atmosphere.

Synthesis of nanocellulose

The cellulose nanocrystals employed in this study were formed by acidic hydrolysis as reported in the literature with only minor modification [37]. Briefly, 2.0 g of cellulose pulp were obtained from Whatman filter paper (98% α-cellulose, 80% crystallinity) and blended in a 10 Speed Osterizer Blender. Hydrolysis of the resulting pulp was achieved after 3 h at 100 ˚C using 100 mL of 2.5 M HBr and intermittent ultrasonication (5 min per hour, 50% power, Omni Ruptor 250 w ultrasonic homogenizer. After dilution with deionized water, the mixture was subjected to five washing/centrifugation cycles (5000 rpm, 10 min, IEC Centra-CL3 Series) to remove excess acid and water-soluble fragments. Once pH 4-5 was reached, the fine cellulose particles started to disperse into the aqueous supernatant. The polydisperse cellulose contained in the turbid supernatant was collected and subjected to centrifugation at 10000 rpm for 60 min in a Sorvall Superspeed centrifuge to remove ultrafine particles. The sediment containing the cellulose nanocrystals with an average length of 100-400 nm was dried using a lyophilizing system, yielding 0.9 g CNC (1; 47% yield).

Modification of the nanocellulose/2-aminopyrimidine

First, 3.0 g of nano-cellulose, 5.4 g of tosyl chloride were added to 60 mL of pyridine and this solution were placed in ice bath at 10℃ to mix up and then it was stirred at 25℃ for 48 hours by a magnetic stirrer. After mixing, 100 mL of ethanol was added to the reaction mixture to precipitate, then stripped off with filter paper and washed several times with ethanol and distilled water and dried at 60 ℃ for one week. In the next step, for the preparation of modified nanocellulose, 0.8 g of tosylate nanocellulose, 0.8 g of 2-aminopyrimidine and 50 mL of ethanol were placed under reflux conditions using an oil bath at 80 ℃ for 24 hours. Then, the precipitate was removed with filter paper, and dried at 50 ℃ for two weeks (Figure 1).

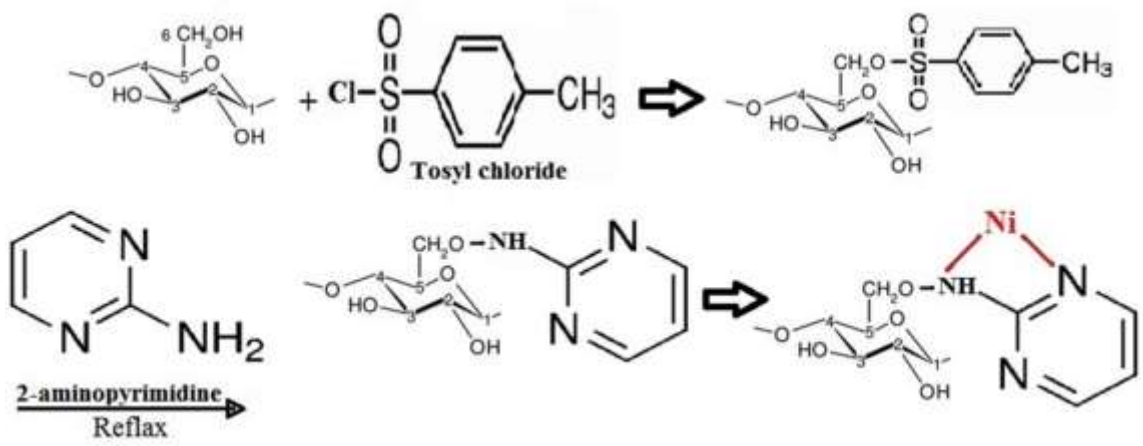

Figure 1. A suggested binding mode of 2-aminopyrimidine to nanocellulose toward adsorption of Ni (II) ions

General Procedure of Extraction

100 mL of Ni (II) ions solution (50 ng mL^{-1}) was prepared and pH value was adjusted to 8 using ammonium buffer solutions, then 0.05 g of modified nanocellulose was added to 100 mL of solution. The mixture was stirred for 10 min at room tempretuer, after centrifugation of the mixture (at 5000 rpm for 5 min) Ni (II) ions retained on nanosorbent were eluted with 1.0 mL HCl (0.2 mol L^{-1}). Finally, after stirring and centrifuge (at 5000 rpm for 10 min) the mixture acidic, Ni (II) ions determined by FAAS.

RESULTS AND DISCUSSION

Characterization of the nanocellulose and nanocellulose/2-aminopyrimidine

Figures 2 (a, b) shows the TEM image of synthesized nanocellulose. As can be seen, the size of the fibers or cellulose veins is reported to be less than 50 nm in this study, and its lengths are about a few microns.

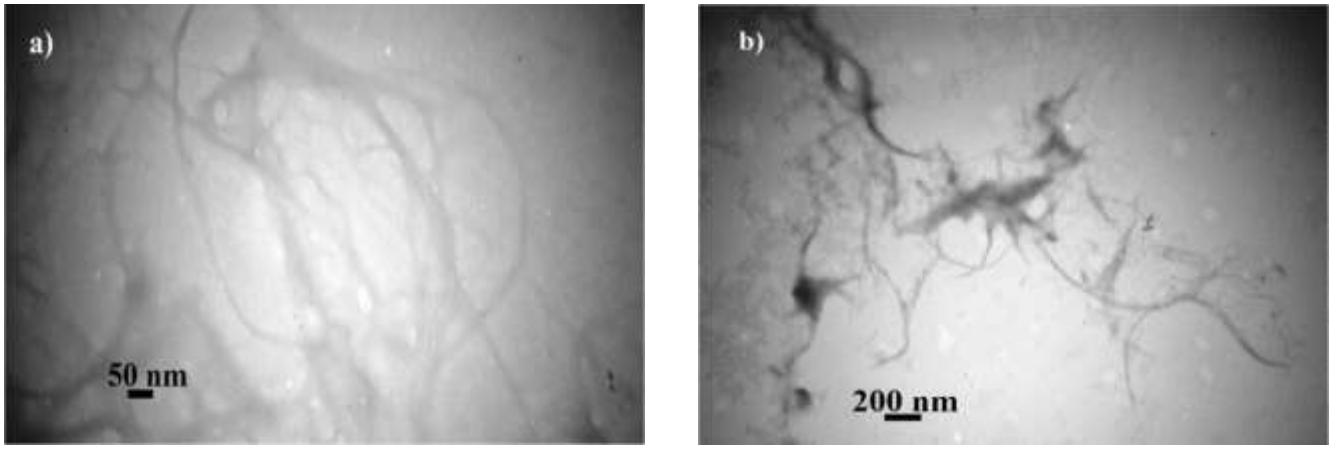

Figure 2. TEM image of the nanocellulose

BET analysis for nanocellulose was performed before and after surface modification. Due to the high surface of nanocellulose, one gram of nanocellulose shows a surface area of about 258.37 m²/g before the placement of 2-aminopyrimidine and about 224.91 m²/g after the placement of 2-aminopyrimidine (see Table 1). This lowering on the surface is anticipated because of covering the surface by ligand. In fact, both of these wide surfaces provide good places to absorb Ni (II) ions.

Table 1. Analyzer placement

Test	m^2/g
Surface area of nanocellulose before the placement of the ligand	258.37
Surface area of nanocellulose after the placement of the ligand	224.91

Elemental CHNS analysis (that shows the percent of C, H, N, and S atoms) was used to characterization of 2-aminopyrimidine absorption. Table 2 confirms that the nitrogen resource attributes to the 2-aminopyrimidine in nanocomposite. As we know, nanocellulose contains C, O, and H atoms. It can be concluded from Table 2 that 2-aminopyrimidine is stabilized on the surface of nanocellulose

Table 2. Multi-elemental CHNS analysis results from nano-cellulose / 2-aminopyrimidine

Reten. Time (min)	Response	Weight (mg)	Weight (%)	Element Name	Carbon Response Ratio
1.294	3105.5	1.612	17.09	Nitrogen	0.361
1.986	8610.9	4.467	47.36	Carbon	1.000
6.417	1110.9	0.576	6.11	Hydrogen	0.129
17.285	8.7	-	-	sulphur	-
Weight of sample for analysis: 9.432 mg					

To show the stability of the nanocellulose and nanocomposite and the presence of the ligand on the sorbent surface, the TGA analysis of the nanocellulose and nanocomposite is shown in Figure 3. Approximately, 50 mg of the sample was heated to 20°C/min in the argon atmosphere. Lower weight loss up to 305°C is due to water withdrawal in the nanocellulose. we can conclude that nanocellulose has good thermal stability because the nanocellulose was not degraded and no specific weight loss was observed up to 305 ˚C and weight loss (about 17.5%)

between 305 °C and 390 °C is due to the withdrawal of nanocellulose (Figure 3a), and in the temperature range of 196-240°C corresponds to the evaporation of 2-aminopyrimidine (Figure 3b). This result confirms 2-aminopyrimidine existence within nano-composite backbone.

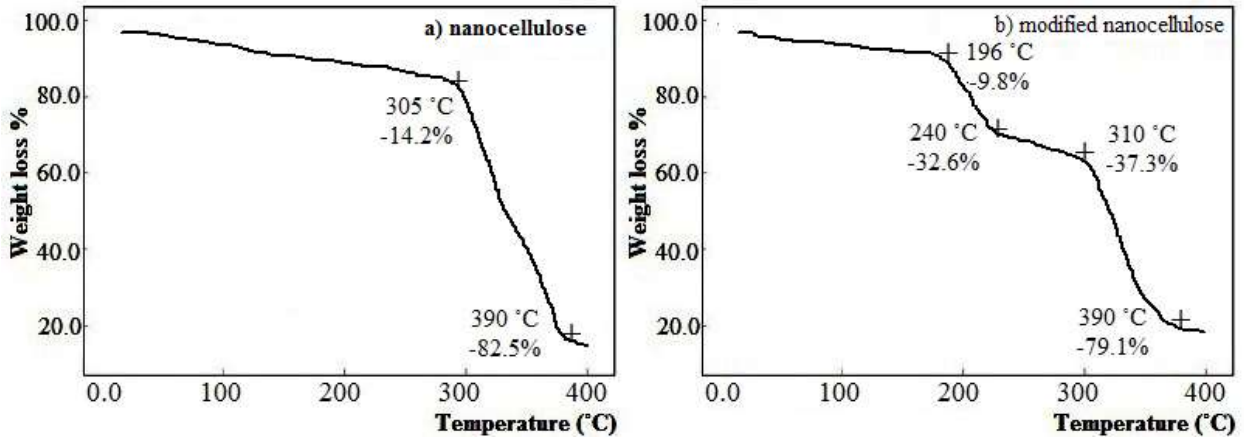

Figure 3. TGA analysis curve for nanocellulose (a) and nanocellulose/2-aminopyrimidine (b).

Figure 4 shows EDS analysis of nanocomposites. The elements C and O of nanocellulose, and the elements O and N of 2-aminopyrimidine can be seen in Figure 4. The present of above-mentioned elements is a sign for the purity of sample (nanocomposite). Figure 4a represents the EDS of nanocomposite before nickel adsorption while Figure. 4b reveals that after nickel adsorption. It can be concluded that after Ni adsorption the peak associated with Lα, Kα and K_β that attributes to the nickel element is appeared.

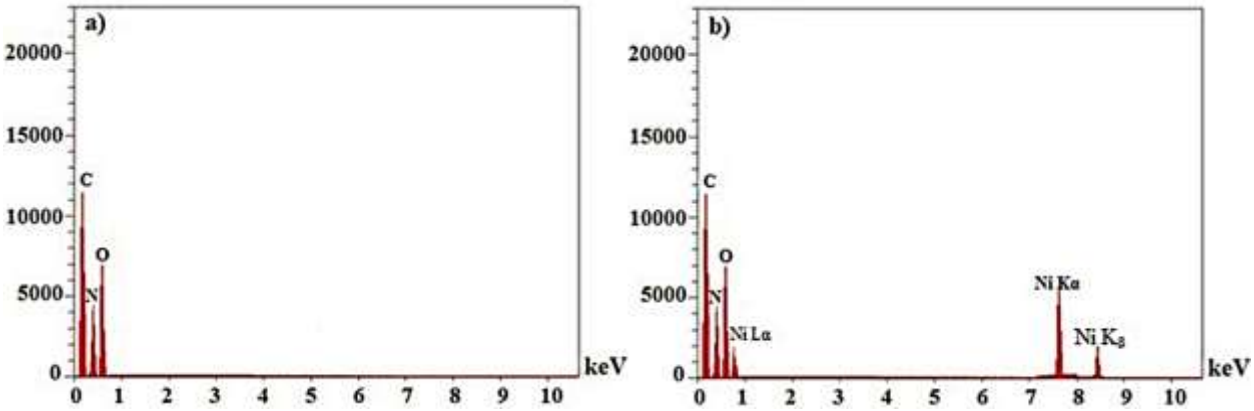

Figure 4. EDS spectra analysis for nanocomposite befor of adsorption (a), and after adsorption (b).

Optimization of the extraction stage

In order to obtain quantitative recoveries of Ni (II) ions on nanocomposite, the impact of each effective parameter on the extraction and preconcentration of Ni (II) ions was investigated. In all of the optimization steps, concentration of Ni (II) ions was adjusted to 50 ng mL^{-1}.

Effect of pH on the extraction efficiency

To find the best pH for maximum extraction of Ni (II) ions, different values of pH (in the range of 3-10) were analyzed. As shown in Figure 5, the maximum extraction can be found at pH=8. At low pH values, owing to the electrostatic repulsion between positively charge of nanocomposite surface and positive charge of Ni (II) ions, the adsorption

of Ni (II) ions will decrease. On the other hand, at the high pH values, the charge of nanocomposite surface is negative owing to existing hydroxide ions; so, one can conclude increase in the adsorption of Ni (II) ions because of electrostatic attraction between them.

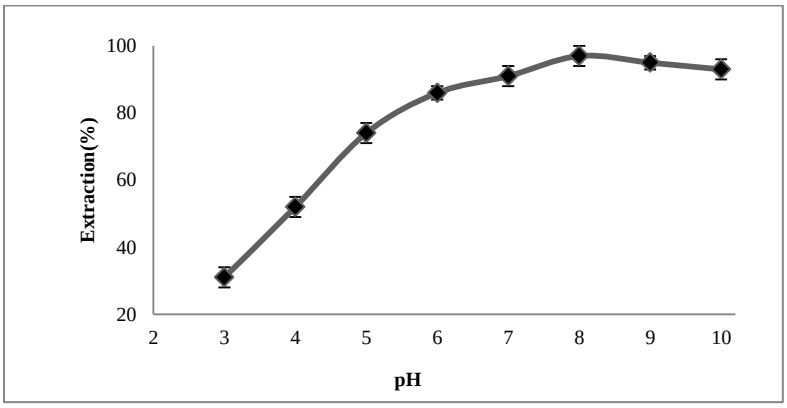

Figure 5. Effect of pH on extraction of Ni (II) ions. Extraction conditions: sample volume, 100 mL; recovery solvent, 1.0 mL 0.2 mol L^{-1} HCl; amount of nanocomposites, 50 mg; and concentration of Ni (II) ions, 50 ng mL^{-1}.

The effect of the amount of nanocellulose and nanocomposite

Figure 6 shows the effect of different amounts of nanocomposite and nanocellulose in extraction of Ni (II) ions. As can be seen in Figure 6, for each amount of nanosorbents, the recovery of nanocomposite is much higher compared to nanocellulose, confirming the good performance of nanocomposite toward Ni (II) ions extraction. However, we can conclude from Figure 6 that by increasing the amount of adsorbent up to 0.05 g, the extraction of Ni (II) ions increases owing to increase in the surface of interaction. The amount of 0.05 g of nanocomposite gives the highest recovery percent and there is no significant increase in Ni (II) ions extraction by increasing the amount of adsorbent to 0.07 g. So, 0.05 g of nanocomposite was selected for further studies.

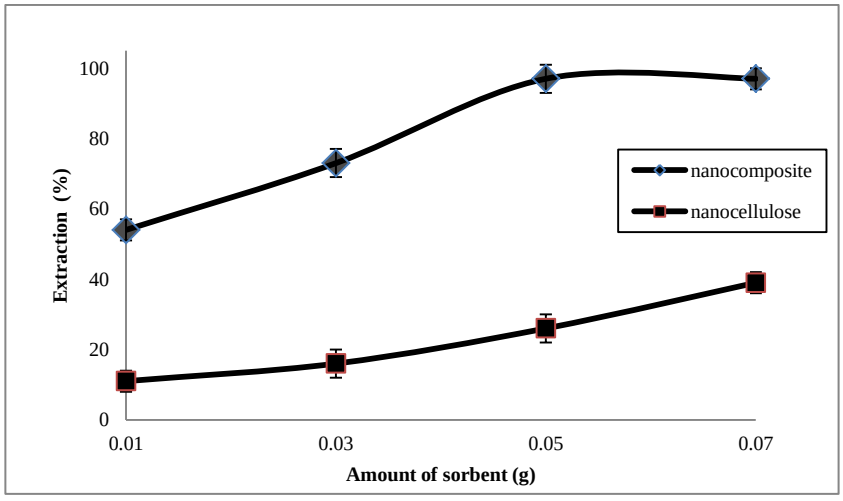

Figure 6. Effect of different doses of nanocomposite and nanocellulose for extraction of Ni (II) ions. Extraction conditions: sample volume, 100 mL; recovery solvent, 1.0 mL 0.2 mol L^{-1} HCl; pH value, 8.0; and concentration of Ni (II) ions, 50 ng mL^{-1}.

Effect of shaking time

The rate of adsorption of Ni (II) ions by modified nanocellulose was studied with 0.005 g of the sorbent over a series of varying shaking times (5-20 min). It was observed (Figure 7) that after 10 min, absorbance of the Ni (II) ions had no significant variation thus the extraction time of 10 min was selected for further studies.

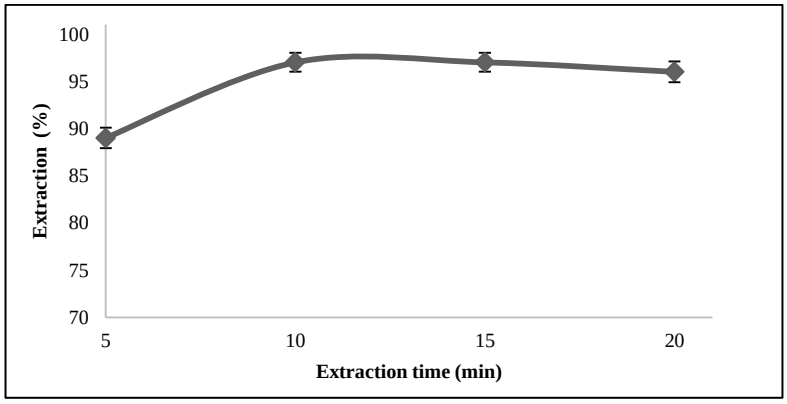

Figure 7. Effect of extraction time on extraction of Ni (II) ions. Extraction conditions: sample volume, 100 mL; amount of nanocomposites, 50 mg; recovery solvent, 1.0 mL 0.2 mol L^{-1} HCl; pH value, 8.0; and concentration of Ni (II) ions, 50 ng mL^{-1}.

Effect of type and concentration of eluent on recovery

To obtain a high enrichment factor, a suitable eluent should be used. Thus, the recovery of Ni (II) ions was studied in applying different type (acetic acid, nitric acid, hydrochloric acid and sulphuric acid) of eluents. The results showed that HCl 0.2 M accomplished the quantitative elution of target analyte in SPE (Table 3), hence HCl 0.2 M was selected for the further experiment.

Table 3. Effect of eluent type and concentration on extraction of Ni (II) ions. Extraction conditions: sample volume, 100 mL; amount of nanocomposites, 50 mg; pH value, 8.0; and concentration of Ni (II) ions, 50 ng mL^{-1}.

Eluent	Concentration (mol L^{-1})	Recovery (%)
CH_3COOH	0.2	63.5 ± 1.3
	0.5	68.1 ± 1.8
	1	72.4 ± 1.5
HNO_3	0.2	93.8 ± 2.1
	0.5	95.2 ± 2.6
	1	96.3 ± 2.0
HCl	0.2	98.7 ± 1.7
	0.5	98.1 ± 2.1
	1	98.2 ± 1.9
H_2SO_4	0.2	85.2 ± 2.2
	0.5	89.4 ± 2.5
	1	91.6 ± 2.6

The effect of ionic strength

To search on the impact of ionic asset on performance of SPE, various experiments have been done by addition of various amount of $NaNO_3$ (0.1-1.0 mol L^{-1}). Further experimental circumstances were retained constant. The results showed, ionic strength has no noticeable impact upon extraction efficiency up to 0.7 mol L^{-1} of $NaNO_3$ (Figure 8). These observations showed the possibility of using this method to separation of Ni (II) ions from highly saline solutions.

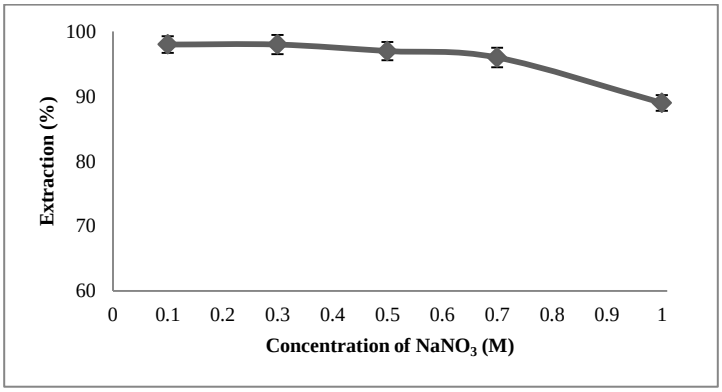

Figure 8. Effect of ionic strength on extraction of Ni (II) ions. Extraction conditions: sample volume, 100 mL; amount of nanocomposites, 50 mg; recovery solvent, 1.0 mL 0.2 mol L^{-1} HCl; pH value, 8.0; and concentration of Ni (II) ions, 50 ng mL^{-1}.

Maximum sample volume and enrichment factor

The sample volume is one of the important parameters to obtain high preconcentration factors. For this purpose, 10-150 mL of sample solutions containing of Ni (II) ions was used at optimum conditions. The results showed (Figure 9), increase the volume to 100 mL had no effect on the efficiency of extraction of Ni (II) ions by nanosorbent. Therefore, enrichment factor of the method was calcluted as 100.

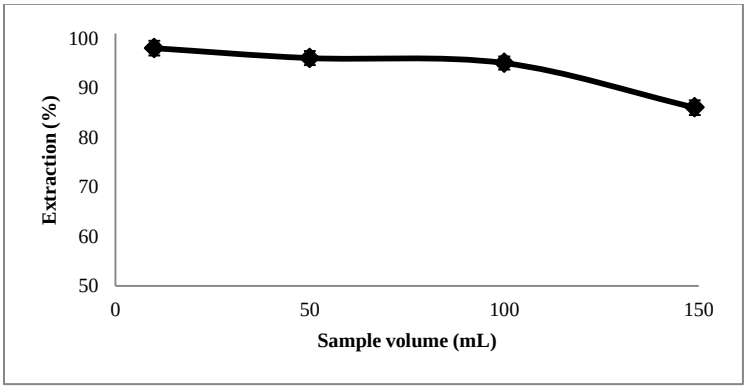

Figure 9. Effect of sample volume on extraction of Ni (II) ions. Extraction conditions: sample volume, 100 mL; amount of nanocomposites, 50 mg; recovery solvent, 1.0 mL 0.2 mol L^{-1} HCl; pH value, 8.0; and concentration of Ni (II) ions, 50 ng mL^{-1}.

Effect of foreign ions

In order to assess the applications of the recommended procedure, the effect of potentially interfering some foreing ionss on the extraction recovery of Ni (II) ions was examined. For this purpose, by spiking appropriate amounts of potentially interfering ions in the range of 1-25 µg mL^{-1} to 100.0 mL of solution containing 50 ng mL^{-1} of

Ni (II) ions evaluation was done. The tolerance level was defined as the maximum concentration of the interfering ions causing a change in the analytical signal not higher than 5% when it was compared with the signal of Ni (II) ions lonely. The attained outcomes are abridged in Table 4.

Table 4. Effect of the interfering ions on the determination of Ni (II) ions

Interfering ions	Added as	Interference/Ni (II) (weight ratio)	Extraction (%)
Na^+	$NaNO_3$	500	99.5 ± 0.9
Ca^{2+}	$Ca(NO_3)_2$	500	102.2 ± 1.7
Cu^{2+}	$CuCl_2$	100	96.2 ± 1.5
Ag^+	$AgNO_3$	100	96.2 ± 2.1
Mn^{2+}	$MnCl_2$	50	101.1 ± 1.9
Zn^{2+}	$ZnSO_4$	40	104.9 ± 2.4
Fe^{2+}	$FeSO_4$	30	95.6 ± 1.8
Co^{3+}	$Co(NO_3)_3$	30	102.7 ± 2.6
Pb^{2+}	$Pb(NO_3)_2$	30	97.8 ± 1.9
Hg^{2+}	$Hg(NO_3)_2$	30	99.5 ± 2.6
Al^{3+}	$Al_2(SO_4)_3$	20	103.3 ± 2.1
Cr^{3+}	$Cr(NO_3)_3$	20	96.2 ± 1.4
NO_3^-	$NaNO_3$	500	99.5 ± 0.8
Cl^-	NaCl	200	98.4 ± 1.1
SO_4^{2-}	Na_2SO_4	200	100.5 ± 1.5

Validation of the method

Analytical characteristics of the method

Under the optimal experimental conditions, a series of experiments were designed for obtaining linear range, limit of detection, preconcentration factor, enrichment factor and other characteristics of the proposed method (Table 5).

Table 5. Analytical characteristics of proposed method

Parameter	Analytical feature
Linear range (ng mL^{-1})	5-500
Regression equqtion	y= 0.0018X+ 0.0013
Correlation coefficient (R^2)	0.9992
Detection limit (ng mL^{-1})	2.33
Repeatability (RSD %)	2.33
Preconcentration factor	100
Enrichment factor	100

The calibration graph (Figure 10) is linear in the range of 5-500 ng mL^{-1} of Ni (II) ions in aqueous solution. The limit of detection (LOD) was found to be 2.33 ng mL^{-1}. The relative standard devation (RSD) for 8 replicate measurements of 50 ng mL^{-1} Ni (II) ions was calculated to be 2.33%. The preconcentration factor (PF=100) was obtained from the ratio of sample valume (100 mL) to eluent volume (1.0 mL), and enrichment factor (EF=100) was obtained from the ratio between the analyte concentration after and before preconcentration.

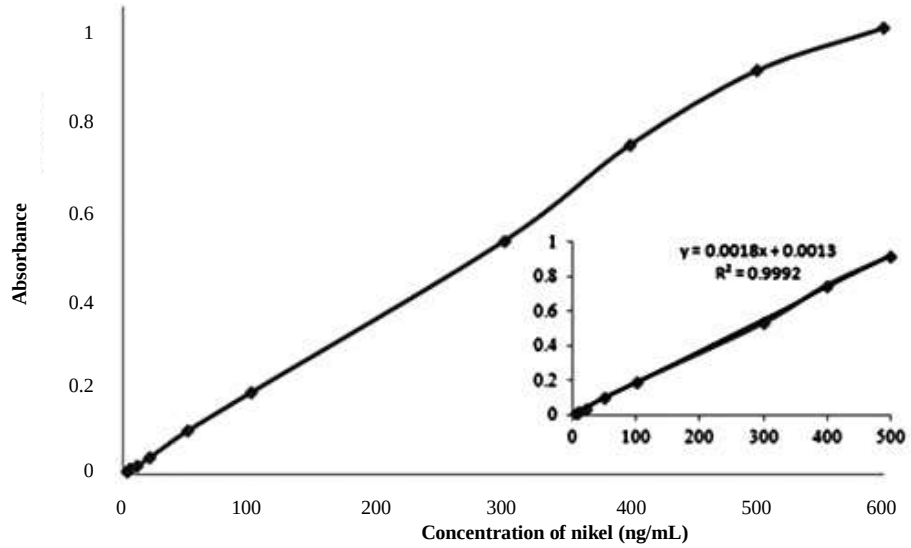

Figure 10. The calibration curve for Ni (II) ions

Application of the proposed method to real samples

In order to investigate the reliability of proposed method, it was employed to determine the amounts of Ni (II) ions in real samples (human blood and human urine). As can be seen from Table 6, the concentration of Ni (II) ions in human blood and human urine was below the LOD of the method. In all cases, the spike recoveries confirmed the reliability of the proposed method.

Table 6. Determination of Ni (II) ions in real and spiked samples. Extraction conditions: sample volume, 100 mL; amount of nanocomposites, 50 mg; recovery solvent, 1.0 mL 0.2 mol L^{-1} HCl; pH value, 8.0.

Sample	Ni (II) spiked (ng mL^{-1})	Ni (II) detected (ng mL^{-1})	Extraction (%)
	—	BDL[a]	—
Human blood	50	47.8 (2.9)[b]	95.6
	100	101.9 (3.6)	101.9
	—	BDL	—
Human urine	50	48.5 (2.1)	97.0
	100	99.8 (2.4)	99.8

a. Below the detection limit
b. RSD of three replicate experiments

A comparison of analytical performance data with literatures

To compare the proposed method with other methods of measuring the concentration of Ni (II) ions, the physical properties of the proposed method are summarized in Table 7. Although a direct comparison between methods is very difficult due to the different experimental conditions, it is clear that the present work has a comparable relatively good LOD and enrichment factor.

Table 7. Comparison of the proposed method with other methods reported

Method	LOD (ng mL^{-1})	Enrichment factor	Ref.
Emulsion-ETFAAS	10	100	38
DLPME–GFAAS	33	200	39
CPE–FAAS	1220	29	40
SPE–FAAS	800	43	41
SPE–FAAS	25	100	42
SPE–FAAS	28.7	63	43
SPE–FAAS	2.33	100	This work

DLPME: dispersive liquid phase microextraction

CONCLUSIONS

The results of this study show that nanocellulose was modified by the use of ligand 2-aminopyrimidine for determination of trace amount of Ni (II) ions. The ligand used in this work was distinct in terms of sensitivity and selectivity towards Ni (II) ions. SPE method was used due to the vast surface, high thermal and chemical stability and good performance of the nanocomposite. SPE is a powerful technique for sample preparation. The advantage of such a method is its reproducible results, the need of less technical skills, low consumption of organic solvents and extraction cleaner, and its high speed and low cost. The proposed method gave low detection limits, high enrichment factor and good standard deviations. The method significantly improved the performance of the FAAS detection of nickel. The method was verified with real samples and it was proven satisfactory for the determination of trace levels of Ni (II) ions in a variety of real samples (human blood and human urine).

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