



ISSN (E): 2277- 7695
 ISSN (P): 2349-8242
 NAAS Rating: 5.23
 TPI 2022; 11(3): 1133-1136
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www.thepharmajournal.com

Received: 15-12-2021

Accepted: 20-02-2022

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Solid-phase extraction of trace nickel in soil sample using dithioamide-loaded activated carbon prior to determination by flame atomic absorption spectrometer

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Abstract

A solid-phase extraction method was carried out to concentrate and separate very trace amounts of nickel from the soil sample for the estimation by flame atomic absorption spectrometry. Nickel ions were adsorbed when aqueous samples of soil were passed through activated carbon. More than 90% recoveries were obtained at pH 5.5. The limits of detection, the limit of quantitation, linear range, and percent relative standard deviation was $0.021 \mu\text{g g}^{-1}$, $0.065 \mu\text{g g}^{-1}$, $0.5\text{-}6.0 \mu\text{g g}^{-1}$, and 1.5% respectively. The optimized method was validated and yielded an accuracy greater than 90% and precision $<1.5\%$.

Keywords: Activated carbon, Flame atomic absorption spectrometer, Nickel, Solid –phase extraction

1. Introduction

The effect of trace elements on environment has stimulated the development of analytical techniques and instrumentation that are capable of measuring lower concentrations (Rojas *et al.*, 2013) [18]. Nickel is present in large quantities in the earth's crust (0.01 to 0.02% of the Earth's crust). It ranks about 22nd among the chemical elements in terms of availability in the Earth's crust (Diagomanolin *et al.*, 2004) [8]. Nickel is pervasive in the environment and is present in natural waters, soils and foods. It is found in atmospheric air at very low levels as a result of emissions from oil and coal combustion, metal refining, sewage sludge burning, manufacturing, and other sources (Cempel and Nikel. 2006) [7].

Direct determination of nickel in soil samples by atomic absorption, inductively coupled plasma mass or inductively coupled plasma emission spectrometry is not always feasible due to matrix interference and trace concentrations of metal ions (Komjarova and Blust. 2006) [13]. Most of these methods are expensive or require complex instruments and some of them are time-consuming. Therefore, a pre concentration / separation step is needed in order to obtain low detection limits in the determination of many trace elements by several analytical techniques (Hirata *et al.*, 2001) [10]. Some techniques have been widely used for this purpose, such as solid-phase extraction (SPE) (Camel 2003; Lima *et al.* 2012; Poole 2003; Płotka-Wasyłka *et al.* 2016) [3, 14, 17, 16], liquid-phase extraction (LPE) (Amorim and Ferreira 2005) [1], cloud point extraction (CPE) (Bezerra *et al.* 2005) [2], and co-precipitation (Soylak and Aydin 2011). SPE has several advantages, such as speed, high enrichment factors, lesser utilization of samples, reagents, and solvents, and the possibility of automation (Camel 2003) [3]. This technique has been increasingly used for the pre-concentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices (Camel 2003; Cassella *et al.* 1999; Karve and Pandey 2012) [3, 4, 11].

The solid phase extraction method is based on the segregation between a liquid containing a sample matrix and a solid phase (sorbent). It is based on the contact of a homogeneous liquid sample passed through a column (a flask, a cartridge, a tube) or a disc containing a selective absorber that holds metal ions (Moghimi and Yari. 2019) [15]. After this step, recovered metal is eluted by a proper solution with a suitable solvent (Su *et al.*, 2003) [20]. Sorbents used for pre-concentrate and determining metal can be loaded with complex reactions by suitable reagents such as activated carbon, natural adsorbents, Amberlite XAD resins (Tokalioglu *et al.*, 2002; Fernandes *et al.*, 2003; Tuzen *et al.*, 2004; Ceccarini *et al.*, 2005 and Kim *et al.*, 2005) [21, 9, 22, 6, 12], polyethylene (Castillo *et al.*, 2005) [5] and others.

The aim of this work is pre-concentration of Ni^{2+} on activated carbon loaded with dithioamide (DTO) and study of the impact of various parameters such as pH and sample volume on the quantitative recoveries of the ions.

2. Experimental

2.1. Instruments

The measurement of Nickel ions was performed with the Agilent 240FS AA atomic absorption spectrometer, capable of handling multi-element suites with ease, automatic lamp selection, programmable gas box, and D2 background correction. An Agilent 3200P pH meter was used for pH adjustments.

2.2. Reagents

All the chemicals used were of analytical grade and purchased from Sigma Aldrich. Nitrate salt of nickel (Nickel nitrate hexahydrate- $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$) and dithioamide (DTO) were purchased from Sigma Aldrich. The pH adjustments were done by addition of phosphate buffer. Doubly distilled deionized water was used throughout the experiment. Activated carbon (AC) purchased from Sigma Aldrich was soaked in hydrochloric acid for 2 days, followed by washing with distilled water and drying at 110°C .

2.3 Soil digestion

4 Gram of soil sample was put in a beaker. 20 ml of distilled deionized water, 24 ml concentrated Nitric acid (HNO_3) and 6 ml of 30% hydrogen peroxide (H_2O_2) were added to it. The solution was covered with a watch glass and evaporated on a hot plate till volume reduced to half. The mixture was then cooled, filtered and diluted to 200 ml.

2.4 Preconcentration procedure

Activated carbon was loaded with Dithioamide. 25 mg of dithioamide was dissolved in 15 ml of 0.005 mol L^{-1} NaOH. This solution was added to 500 mg of activated carbon and left for 18 hours. Then the mixture was washed several times with distilled water till activated carbon is no longer alkaline. Then the residue was dried at 70°C overnight. The pH of solutions containing analyte ions was adjusted to pH 6 by adding phosphate buffer solution. The buffered solutions were passed through the column of DTO coated activated carbon at a flow rate of 5 mL min^{-1} . The adsorbed ions were then eluted with 5 mL of 3.0 mol L^{-1} nitric acid in acetone at a flow rate of 1 mL min^{-1} .

3. Results and Discussion

3.1 Effect of activated carbon

The study revealed that ligand (DTO) loaded activated carbon quantitatively traps the nickel ions. The effect of amount of the activated carbon on the adsorption of nickel ions at a pH value 6 was studied in the range of 200-800 mg. Fig.1 shows that recoveries greater than 95% were obtained at a 500 mg activated carbon. Above and below 500 mg recoveries were less than 95%.

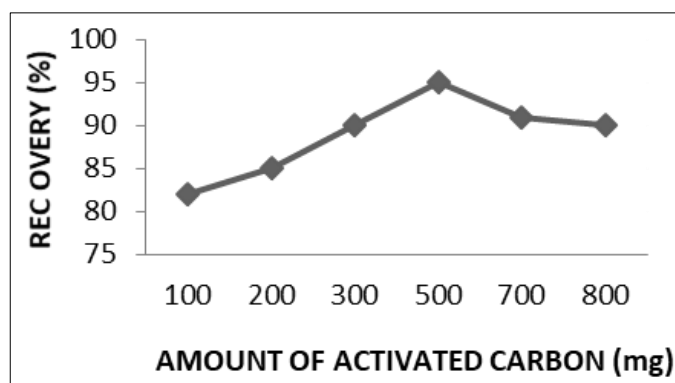


Fig 1: Effect of amount of activated carbon on recovery of nickel ions.

3.2 Effect of pH on recovery

pH plays a very important role in the adsorption and quantitative recoveries of the nickel ions. The effect of pH was investigated at the pH ranges of 3-10. Ion sorption varied with the pH of the sample as shown in Fig. 2. A relatively higher sorption was observed at a pH 6. The decrease in retention of the metal ions may be attributed to the competition of the metal ions and hydrogen ions at low pH values for binding with the ligand (DTO). An increase in pH above 6 lead to a reduced retention of the metal ions. The reduction may be attributed to the instability of the metal chelates at higher pH.

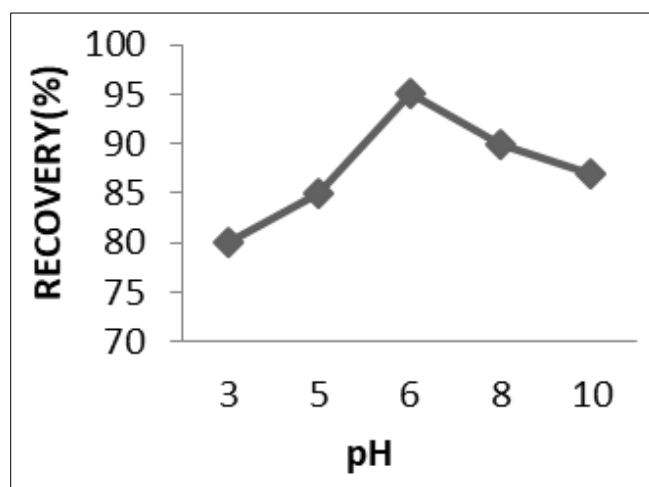


Fig 2: Effect of pH on recovery of nickel ions.

3.3 Effect of the amount of DTO

The impact of the amount of ligand on the sorption of the nickel ion was examined. The results are shown in Fig. 3. The recoveries of analytes were studied in the range of 5 to 50 mg. The recoveries were quantitative till use of 25 mg ligand. Above 25mg ligand, the recovery values considerably reduced probably due to the formation of charged complexes that could not be completely adsorbed on the sorbent (activated carbon).

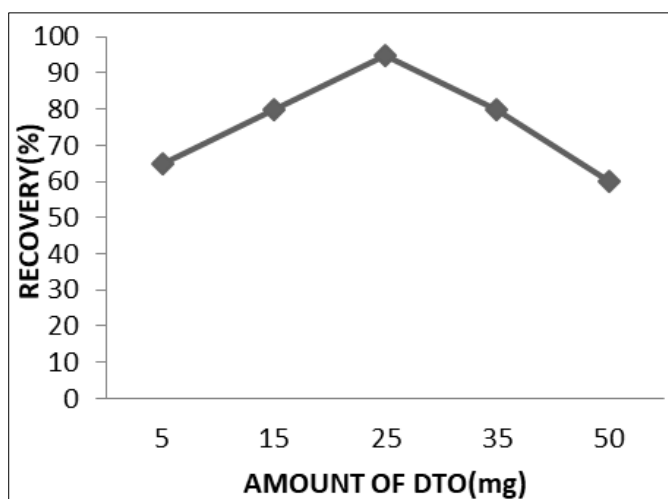


Fig 3: Effect of amounts of DTO on recovery of nickel ions.

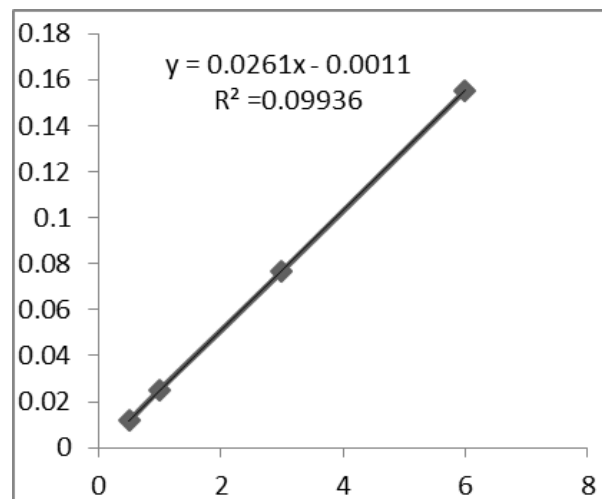


Fig 5: Analytical performance

3.3 Effect of volume of sample

The effect of the sample volume was studied at various volumes (between 100 and 1000 mL). According to the results depicted in Fig. 4 quantitative recoveries were obtained up to volumes of 500 mL, and then, the recoveries decreased. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 500 mL. Hence, maximum applicable sample volume of the method was 500 mL.

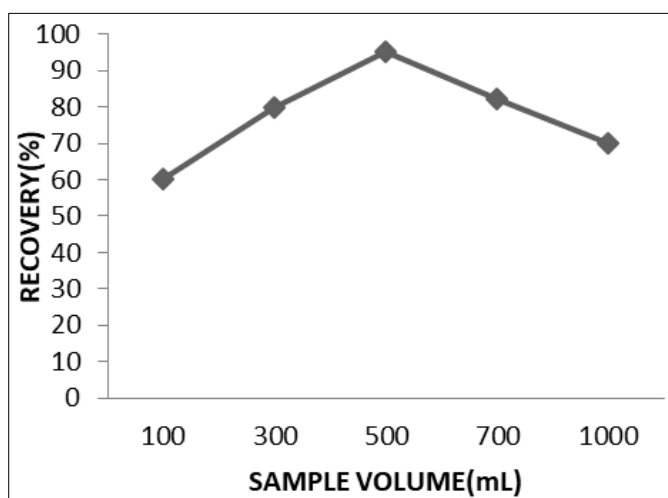


Fig 4: Effect of sample volume on recovery of nickel ions

3.4 Analytical performance

Table 1 reveals the analytical performance of the optimized method, including the limits of detection (LOD), limits of quantification (LOQ), relative standard deviations (RSD, %), preconcentration factors (PF), calibration curves and correlation coefficients (R^2). The detection limits of the analytes were defined as 3 times the signal/slope (slope of calibration curve), whereas the quantification limits were defined as 10 times the signal/slope (slope of calibration curve). The relative standard deviations (RSD, %) for the analytes were evaluated using the results of the analysis of seven replicates containing 100 mg L^{-1} of Ni (II). The preconcentration factors were calculated as the ratio of the highest sample volume to the eluent volume.

Table 1: Analytical performance

Parameters	Analytical features
Linear range ($\mu\text{g g}^{-1}$)	0.5-6.0
Coefficient of determination (R^2)	0.9936
Limit of detection (LOD) ($\mu\text{g g}^{-1}$)	0.021
Limit of quantitation (LOQ) ($\mu\text{g g}^{-1}$)	0.065
Accuracy	>90%
Precision	<1.5%
Relative standard deviation (%RSD)	1.5
Pre-concentration factor	100

4. Conclusion

The present study illustrates the use of a sorbent based on the modification of activated carbon with Di-thioxamide reagent. The modification of activated carbon is simple, and the reagent remains in the column, which allows its multiple usage. The procedure offers a useful, rapid and reliable enrichment technique for preconcentration of Ni(II) ions in soil sample with acceptable accuracy and precision. The results depicted in this paper have established the applicability of the separation and preconcentration of metals. The proposed method has a low detection limit. Also the preconcentration factor is higher and the method is economical due to the possibility of multiple uses of the sorbent.

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