

Modification and Application of Amberlite XAD-4- 1-Amino-2-Naphthole for Cobalt Removal from Environmental Samples

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Abstract: A new chelating resin is prepared by coupling Amberlite XAD-4 with 1-amino-2-naphthole through an azo spacer. The resulting sorbent has been characterized by FT-IR, elemental analysis and thermogravimetric analysis (TGA) and studied for preconcentrating of Co(II) using flame atomic absorption spectrometry (FAAS) for metal monitoring. The optimum pH value for sorption of the Cobalt ions was 6.5. The resin was subjected to evaluation through batch binding of mentioned metal ion. Quantitative desorption occurs instantaneously with 0.5 M HNO₃. The sorption capacity was found 3.08 mmol.g⁻¹ of resin for Co(II) in the aqueous solution. The chelating resin can be reused for 10 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 100% was obtained the metal ions with 0.5M HNO₃ as eluting agent. The method was applied for metal ions determination from industrial waste water sample.

Key words: Amberlite XAD-4 • Cobalt (II) • Flame atomic absorption • Chelator • 1-amino-2- naphthole

INTRODUCTION

The development of metallurgical industry causes a steady increase of nickel and cobalt contents in natural environment. The excess of these two elements is toxic to plants. That is, it results in leaf chlorosis, inhibits root growth, limits biochemical functions of iron and manganese [1, 2]. Cobalt is known to be an essential element at trace level to humans, animals and plants for metabolic processes. Cobalt helps to repair the myelin sheath, pernicious anemia and building of red blood cells [3]. More attention has been focused on the toxicity of cobalt in large concentrations, since it has been found that cobalt can cause vasodilation, flushing and cardiomyopathy in humans and animals [4, 5]. It was reported that cobalt-mediated free radical generation contributes to interfere with DNA repair processes [6- 8]. The International Agency for Research on Cancer (IARC) has classified this metal as possibly carcinogenic to humans [9].

Except occupational sources, main sources of cobalt are foods and beverages. World Health Organization (WHO) recommends that 0.005-0.010 mg of cobalt might be the daily optimal intake for adults [10]. Therefore, the

determination of Co in water, food and environmental samples is important in the fields of environmental analysis and medicine.

Due to the allowable low levels of cobalt in food and beverages and its very low concentrations in natural waters as described above, reliable and sensitive analytical methods are required for determination of this metal. For this purpose, preconcentration techniques in connection with the analytical methods such as electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) have been used [11-14]. As a result, the use of preconcentration techniques in the determination of Co by flame atomic absorption spectrometry (FAAS) is still important because of the disadvantages such as the interferences from matrix components, the necessity of expert for usage and the high costs of other methods, relatively [15, 16]. Among the preconcentration techniques, solid phase extraction (SPE) has received the most attention due to its simplicity, high concentration factor and more environmentally friendly reagents used. Moreover, SPE and solvent extraction were also used for speciation studies [17, 18].

In this work, Amberlite XAD-4 (1-amino-2-naphthole) was prepared by chemically bonding to be used as an adsorbent. 1-amino-2-naphthole could form chelates with metallic ions on the surface of the resin. Absorption of metal ions from aqueous solution using modified Amberlite XAD-4 was studied under different experimental conditions to assess its affinity towards the chelator.

MATERIALS AND METHODS

Reagents: Amberlite XAD-4 resin (surface area 745 m²/g, pore diameter 5 nm and bead size 20-60 mesh) was obtained from serva (Heidelberg, New York). The metal ion solution was prepared by dissolving following metal salts: CoCl₂·6H₂O. The following buffers were used to control the pH of the solutions: Hydrogen disodium phosphate (pH=7-9), Sodium Hydroxide-Acetic acid (pH=5), Acetic acid (pH=3-4). CH₃COOH, NaH₂PO₄, Na₂HPO₄, CoCl₂·6H₂O, SnCl₂, HCl, H₂SO₄, HNO₃, NaNO₂, NaOH, 1-Naphthole, Aniline and Iodide-Starch Paper were products of Merck (Darmstadt, Germany).

Instruments: A flame atomic absorption spectrometer of the Shimadzu, model AA-680, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L.min⁻¹,

respectively) was used for measuring the concentration of metal ions. The pH measurements were made with Metrohm model 744 (Switzerland). IR spectra were recorded on a FT-IR spectrometer Jasco / FT-IR-410 by KBr pellet method. Elemental analysis was carried out on an elemental analyzer from Thermo-Finnigan (Milan, Italy) model Flash EA. TGA analysis was carried out by using TGA-50H (Shimadzu, Japan).

Synthesis of XAD-4- (1-Amino-2-Naphthole): Amberlite XAD-4 bead (5g) were treated with 10 mL of concentrated HNO₃ and 25 mL of concentrated H₂SO₄ and the mixture stirred at 60°C for 1h on an oil bath. There after, the reaction mixture was poured into an ice water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid and there after treated with a reducing mixture of 40 g of SnCl₂, 45 mL of concentrated HCl and 50 mL of Ethanol. The mixture was refluxed for 12 h at 90°C. The solid precipitate was filtered and washed with water and 2 mol.L⁻¹ NaOH which released amino resin (R-NH₂) from (RNH₃)₂ SnCl₆ (R=resin matrix). The amino was first washed with 2 mol.L⁻¹ HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice-water mixture (350 mL) and treated with 1 mol.L⁻¹ HCl and 1 mol.L⁻¹ NaNO₂

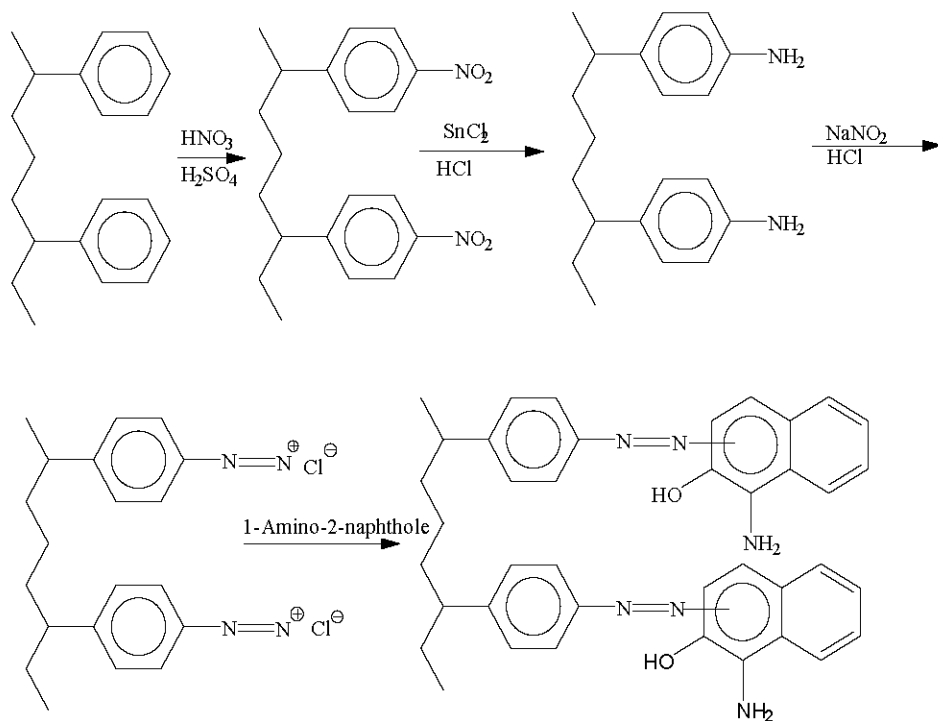


Fig. 1: The methodology of synthesise of 1-amino-2-naphthole - Amberlite XAD-4

(added in small aliquots of 1 mL) until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was filtered, washed with ice-cold water and react with 1-amino-2-naphthole 0.03 mol in 200 mL of 10% NaOH solution. The reaction mixture stirred at 0-3°C for 24 h. The resulting colored beads were filtered, washed with water and dried in air. The methodology used to synthesize modified XAD-4 resins is summarized in Fig. 1.

Batch Method: A sample solution (100 ml) containing 0.1-30 µg.mL of Co(II) was placed in glass stopper bottle after adjusting its pH to the optimum value. The modified Amberlite XAD-4 (0.1 g) was added. The bottle was shaken for 5h. The resin was filtered and the metal ions were desorbed by shaking the resin beads with 10 mL HNO₃ 1M. The resin was filtered off and the filtrate was aspirated in to FAAS.

RESULT AND DISCUSSIN

Characterization of Modified Amberlites

IR Spectrum: The IR spectrum of 1-amino-2-naphthole loaded Amberlite XAD-4 (Fig. 2) is compared with that of free Amberlite XAD-4 (Fig. 2). There are 4 additional bands at 1557, 1606, 1279 and 3415 cm⁻¹ which appear to originate due to modification of N-H (bending), N=N, C-N (bending) and O-H, NH₂ vibrations, respectively.

Elemental Analysis: The instruction used in this study is reported in ThermoFinnigan elemental analyzer manual. Elements of C, H and N in the sample and standards in a column containing oxidant at 900°C were converted to CO₂, H₂O and N₂, respectively. They separated in a GC column containing molecular sieve and detected by a Thermal conductivity detector (TCD).

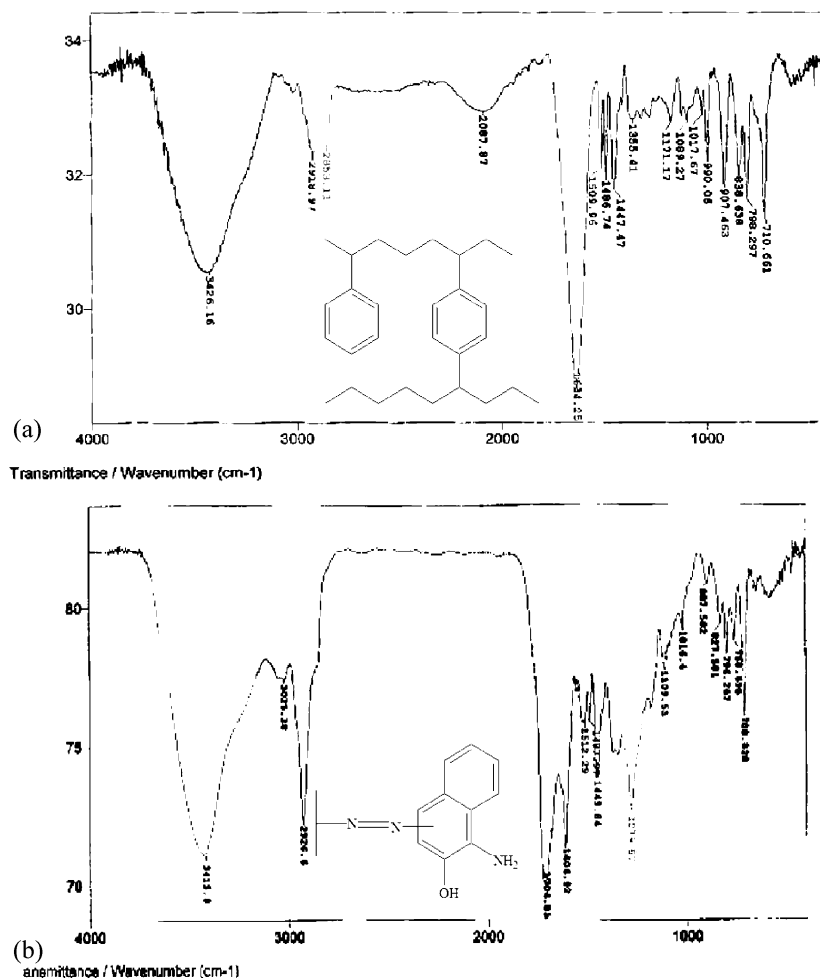


Fig. 2: IR spectrum of a) Amberlite XAD-4 b) 1-amino-2-naphthole - Amberlite XAD-4

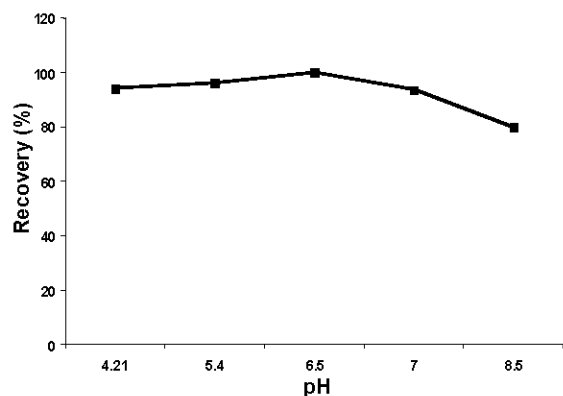


Fig. 3: Effect of pH sorption of Co(II) onto 1-amino-2-naphthole - Amberlite XAD-4

Table 1: Results obtained for metal determination in plating waste water sample

Analyte	Ni (II)	Zn (II)	Co (II)
Before preconcentration (mg.L ⁻¹)	759.00	0.46	0.26
After preconcentration (mg.L ⁻¹)	6986.00	4.30	2.50
Preconcentration factor	10.00	10.00	10.00
Recovery %	92.00	94.00	96.00
Standard deviation ^a	3.14	0.18	0.09
Relative standard deviation (%) ^a	0.45	4.19	3.60

a: For three determinations

The percentages of C, H and N in the sample were ascertained after drawing the calibration curve for standards and data processing for the sample.

The elemental analysis for Amberlite XAD-4 (1-Amino-2-Naphtole) (found: C, 75.85; H, 9.02; N, 4.11%; calculated for $(C_8H_7)_6 C_{10}N_3H_8O(H_2O)_6$: C, 77.67; H, 6.91; N, 4.68%) show that on an average one (1-amino-2-Naphtol) molecule is present in each 6 repeat unit of the polymer.

Thermal Analysis: TGA of the Amberlite XAD-4 shows two-step weight loss up to 510°C. The weight loss up to 100°C was due to the water molecules in the polymer. The major weight loss after 400°C is due to decomposition of the polymer. Amberlite XAD-4- (1-Amino-2-Naphtole) shows completely different thermal behavior. The weight loss up to 100°C was due to the water molecules in the polymer and the weight loss 290-600 was due to the dissociation of chemically immobilized moiety and the polymeric matrix.

Metal Sorption as a Function of pH: The degree metal sorption at different pH values was determined by batch equilibration technique. A set of solutions

(volume of each 50 mL) containing $0.3 \mu\text{g.mL}^{-1}$ Co(II) was taken. Their pH values were adjusted in range 3-9 with 0.01 M acetate and/or phosphate buffer solutions. The 0.1 g of 1-amino-2-naphthole loaded Amberlite XAD-4 was added to each solution and the mixture was shaken for 5 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the metal ions content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from resin with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption Co(II) is shown in Figure 3. The maximum recovery was 100% at pH 6.5.

Stability and Reusability of the Resin:

The mentioned metal ion was sorbed and desorbed on 1g of the resin several times. It was found that sorption capacity of resin after 10 cycles of its equilibration with the metal ions, changes less than 5%. Therefore, repeated use of the resin is feasible. The resin cartridge after loading it with samples can be readily regenerated with 0.5 M HNO_3 . The sorption capacity of the resin stored for more than 6 month under ambient conditions has been found to be practically unchanged.

Total Sorption Capacity: The 0.01 g of resin beads were stirred for 5 h with 100 mL solution containing $30 \mu\text{g.mL}^{-1}$ of Co(II), at optimum pH. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the resin for each metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The saturated adsorption capacity of the resin for Co(II) is 3.08 mmol.g^{-1} of resin.

Application of Method: Solid phase extraction with 1-amino-2-naphthole loaded Amberlite XAD-4 coupled with FAAS determination was supplied to determine the Ni(II), Zn(II) and Co(II) in plating waste water sample. The sample solution (100 mL) was taken in a glass stoppered bottle (250 mL), after adjusting its pH to the optimum value. The 0.5 g of 1-amino-2-naphthole - Amberlite XAD-4 was added to the bottle and the mixture was shaken for 30 min. The resin was filtered and sorbed metal ion was eluted with 0.5 M HNO_3 (10 mL). The concentrations of metal ions in the eluate were determined by a pre-standardized FAAS. The results are shown in Table 1. These results demonstrate the applicability of the procedure for Ni, Zn and Co determination in waste water samples.

CONCLUSION

New resin was synthesized by coupling of Amberlite XAD-4 with 1-amino-2-naphthol. Amberlite XAD-4-1-amino-2-naphthole has a good potential for enrichment of trace amounts of Co from large sample volumes. The synthesis of the resin is simple and economical. The resin can be applied over a wide pH range (3-9) for collection of trace metals. The resin also present the advantage of high adsorption capacity, good reusability and high chemical stability. Preconcentration by this resin combine with FAAS can be applied to the determination of trace Co(II), Zn(II) and Ni(II) ions in water and mineral reference sample with satisfactory results.

REFERENCES

1. Kabata-Pendias, A. and H. Pendias, 1993. The Biogeochemistry of Trace Elements. PWN, Warsaw.
2. Opydo, J., 2001. Cathodic Adsorptive Stripping Voltammetry for Estimation of the Forest Area Pollution with Nickel and Cobalt, *Mikrochim. Acta*, 137: 157-162.
3. Korolczuk, M., A. Moroziewicz and M. Grabarczyk, 2005. Determination of subnanomolar concentrations of cobalt by adsorptive stripping voltammetry at a bismuth film electrode. *Anal. Bioanal. Chem.*, 382: 1678-1682.
4. Sigel, H., (Ed.), 1988. Metal ions in biological systems, 24, Dekker, New York.
5. Wardak, C., 2008. Cobalt (II) ion-selective electrode with solid Contact. *Cent. Eur. J. Chem.*, 6(4): 607-612.
6. Valko, M., C.J. Rhodes and J. Moncol, 2006. Free radicals, metals and antioxidants in oxidative stress-induced cancer. *Chem. Biol. Interact.*, 160(1): 1-7.
7. Lison, D., M. De Boeck and V. Verougstraete, 2001. Update on the genotoxicity and carcinogenicity of cobalt compounds. *Occup. Environ. Med.*, 58(10): 619-624.
8. Yaman, M., 2006. Comprehensive comparison of trace metal concentrations in cancerous and non-cancerous human tissues. *Curr. Med. Chem.*, 13(21): 2513-2520.
9. International Agency for Research on Cancer (IARC), 1991. Monographs on the Evaluation of Carcinogenic Risks to Humans., pp: 52.
10. Jiang, Z., J.C. Yu and H. Liu, 2005. Simultaneous determination of cobalt, copper and zinc by energy dispersive X-ray fluorescence spectrometry after preconcentration on PAR-loaded ion-exchange Resin. *Anal. Sci.*, 21: 851-860.
11. Sawula, G.M., 2004. On-site preconcentration and trace metal ions determination in the Okavango Delta water system, Botswana. *Talanta*, 64: 80-86.
12. Guo, Y., B. Din and Y. Liu, 2004. Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized amberlite XAD-2 by inductively coupled plasma-atomic emission spectrometry. *Talanta*, 62: 209-215.
13. Tanaka, T., Y. Ando, T. Saitoh and M. Hiraide, 2002. Preconcentration of traces of cobalt, nickel, copper and lead in water by thermoresponsive polymer-mediated extraction for tungsten filament electrothermal vaporization-inductively coupled plasma mass spectrometry. *J. Anal. At Spectrom.*, 17: 1556-1563.
14. Zhang, Y., W.H. Luo and H. Li, 2005. Determination of trace cobalt in water samples by graphite furnace atomic absorption spectrometry after cloud point. *Spectrosc. Spect. Anal.*, 25: 576-582.
15. Tuzen, M., M. Soylak and L. Elci, 2005. Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108. *Anal. Chim. Acta*, 548(1-2): 101-108.
16. FeizBakhsh, A.R., H. Ahmad Panahi, M. Nikpour Nezhati, M. Amrollahi and F. Mahmoudi, 2009. Synthesis, Characterization and Application of m-Phenylendiamine-Modified Amberlite XAD-4 Resin for Preconcentration and Determination of Metal Ions in Water Samples. *Water Environ. Res.*, 81(5): 532-538.
17. Ahmad Panahi, H., H. Sid Kalal, E. Moniri, M. Nikpour Nezhati, M. Taheri Menderjani, S. Ranjbar Kelahrodi and F. Mahmoudi, 2009. Amberlite XAD-4 functionalized with m-phenylendiamine: Synthesis, characterization and applications as extractant for preconcentration and determination of rhodium (III) in water samples by Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES). *Microchem. J.*, 93: 49-55.
18. Hashemi-Moghaddam, H., H. Ahmad Panahi and M. Nikpour Nezhati, 2009. Synthesis and Application of New Resin Functionalized by Brilliant Green for Spectrophotometric Determination of Mercury in Environmental Samples. *Anal. Lett.*, 42: 1-8.