

## Development of 2-acetylpyridine-4-phenyl-3-thiosemicarbazone functionalized polymeric resin for the preconcentration of metal ions prior to their ultratrace determinations by MIS-FAAS

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**Abstract:** 2-Acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT) ligand was incorporated onto Amberlite XAD-2 resin through an azo spacer and characterized by FTIR spectroscopy, elemental analysis, TGA, and SEM analysis. The synthesized resin was used for the preconcentration of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions. The sorbed metal ions were eluted with 10 mL of 2.0 mol L<sup>-1</sup> HCl and determined by microsample injection coupled flame atomic spectrometry (MIS-FAAS). The recoveries of studied metal ions were  $\geq 95.1\%$  with RSD  $\geq 4.0\%$  at optimum pH 8; resin amount, 300 mg; flow rates, 2.0 mL min<sup>-1</sup> (of eluent) and 3.0 mL min<sup>-1</sup> (sample solution). The limits of detection (LOD) and limits of quantifications (LOQ) of the studied metal ions were 0.11, 0.05, 0.07, 0.08, 0.09, and 0.03; and 0.37, 0.17, 0.21, 0.13, 0.31, and 0.10  $\mu\text{g L}^{-1}$ , respectively, with a preconcentration factor of 500 for the 6 studied metal ions. The total saturation capacity of the resin was 0.36, 1.20, 1.50, 1.61, 1.07, and 0.71 mmol g<sup>-1</sup>, respectively.

**Key words:** Amberlite XAD-2, chelating resin, 2-acetylpyridine-4-phenyl-3-thiosemicarbazone, preconcentration, MIS-FAAS

### 1. Introduction

Some heavy metals are essential for life functioning at trace level but most of them are recognized as potentially toxic beyond their permissible limits.<sup>1</sup> The toxicity of heavy metal ions may be caused by the inhibition and reduction of various enzymes by substitution of essential metal ions from enzymes and complexation with certain ligands of amino acids.<sup>2</sup> Thus, accurate and precise determination of trace heavy metal ions in air, water, soil, plant, food, and geological samples has become a major interest of chemists.<sup>3,4</sup> Flame atomic absorption spectrometry (FAAS) has been extensively employed for the determination of metal ions because of its low cost, high selectivity, and ease of operation.<sup>5</sup> However, direct determination of trace heavy metal ions by FAAS is limited because of matrix interferences and insufficient sensitivity of instruments.<sup>6,7</sup> To solve this problem, a preconcentration procedure is often recommended prior to the trace determination of heavy metal ions.<sup>8</sup> Several preconcentration based onco-precipitation,<sup>9,10</sup> ion exchange,<sup>11,12</sup> solvent extraction,<sup>13,14</sup> and solid phase extraction (SPE)<sup>15,16</sup> methods have been developed. Among these methods, SPE is the most

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attractive because of its advantages such as ease of operation, recycling of solid phase, higher preconcentration factor, higher selectivity, lower cost and operation time, and low solvent consumption.<sup>17</sup> For SPE, various materials such as activated carbon, silica gel, polyurethane foam, microcrystalline naphthalene, C18 cartridges, Chelex-100, fullerene, alumina, and Amberlite XAD resins have been widely used as solid phases.<sup>18</sup> Interest has been increasing in the synthesis of chelating resins for SPE due to their high degree of selectivity, versatility, durability, and high metal loading capacity.<sup>19</sup> For the synthesis of chelating resins, chelating ligands are coupled with a polymeric matrix through an azo or methylene spacer.<sup>20</sup> The chelating resins prepared by these methods exhibit excellent resistance to ligand leaching as compared to the impregnation method in which ligands are physically incorporated on the polymer matrix.<sup>21</sup> Effective chelating resins can be designed by choosing a cross-linked polymer matrix and small sized ligand, populated with functional groups of interest.<sup>20</sup> Amberlite XAD-2 has been widely used as a polymeric matrix for the synthesis of chelating resins due to its good physical and chemical properties such as porosity and surface area.<sup>22</sup> Various chelating ligands such as Tiron,<sup>23</sup> *o*-vanillin thiosemicarbazone,<sup>24</sup> 1-(2-pyridylazo)-2-naphthol (PAN),<sup>25</sup> thiosalicylic acid,<sup>26</sup> pyrocatechol,<sup>27</sup> 3,4-dihydroxybenzoic acid,<sup>28</sup> 2-aminothiophenol,<sup>29</sup> quinalizarin,<sup>30</sup> 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione,<sup>31</sup> 2-(2-benzothiazolylazo)-*p*-cresol (BTAC),<sup>32</sup> pyrocatechol violet,<sup>33</sup> and *o*-aminophenol<sup>34</sup> have been reported for the synthesis of Amberlite XAD-2 based chelating resins for SPE. Various thiosemicarbazones and phenyl-3-thiosemicarbazones have been widely used as spectrophotometric and spectrofluorimetric reagents for metal ions.<sup>35</sup> Among these, 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT) ligand is more suitable for metal chelation.<sup>36</sup> APPT has been used as a spectrophotometric reagent for the determination of Cu(II) ions<sup>37</sup> but APPT functionalized solid phase has not been screened for solid phase extractive preconcentration of metal ions.

In the present study, we focused on the synthesis and characterization of APPT functionalized Amberlite XAD-2 resin for solid phase extractive preconcentration and ultratrace determination of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions in water samples by MIS-FAAS using 100  $\mu$ L of sample solution per element determination (for a single run).

## 2. Results and discussion

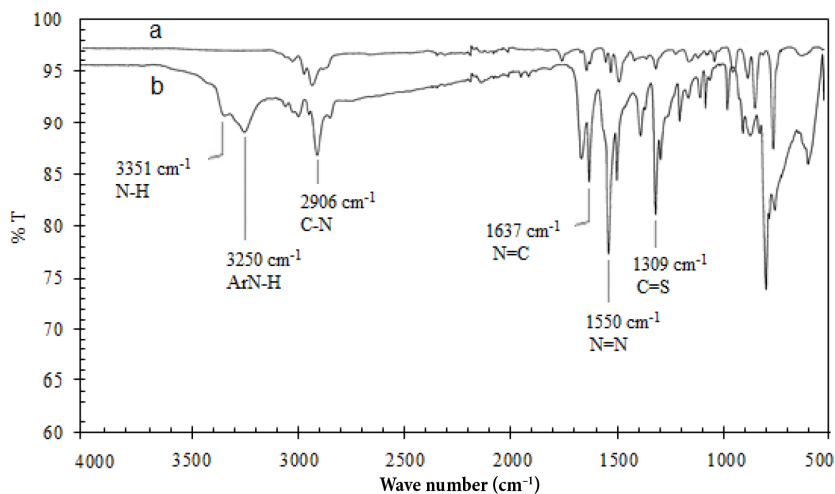
### 2.1. Characterization

#### 2.1.1. FTIR spectroscopy

Figure 1 shows the FTIR spectrum of plain Amberlite XAD-2 (a) and Amberlite XAD-2-N=N-APPT resin (b). The characteristic bands in spectrum b at 3351, 3250, 2906, 1637, 1550, and 1309  $\text{cm}^{-1}$  can be attributed to the stretching vibrations of N-H, ArN-H, C-H, C=N, N=N, and C=S, respectively, indicating the successful coupling of APPT with Amberlite XAD-2 through an azo spacer.

#### 2.1.2. Elemental analysis

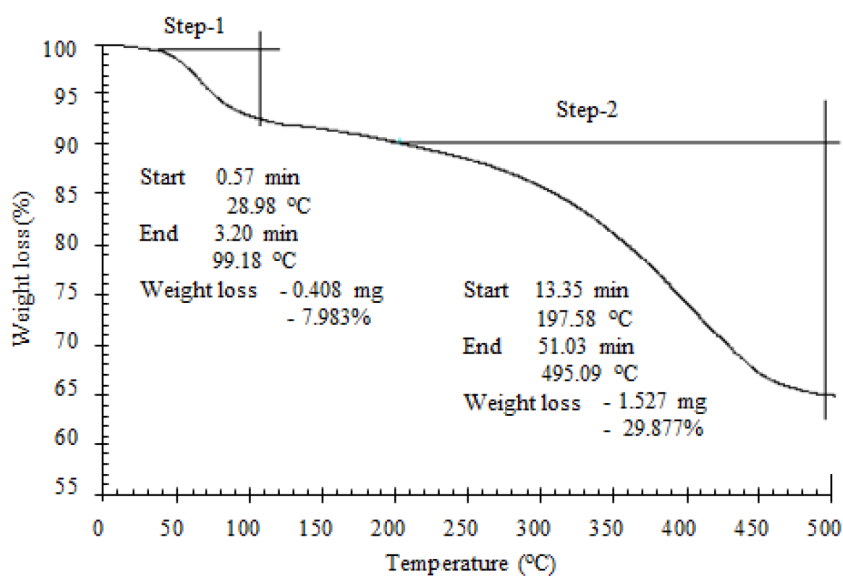
The synthesized resin was characterized by elemental analysis. Experimental values were C, 61.29%; H, 5.79%; N, 18.55%; S, 7.14%; O, 7.23% and theoretical values of elements calculated for a single repeating unit ( $\text{C}_{23}\text{H}_{22}\text{N}_6\text{S}_2\text{H}_2\text{O}$ ) of polymeric chelating resin were C, 61.31%; H, 5.82%; N, 18.65%; S, 7.12%; O, 7.10%. The results showed good correlation between experimental and theoretical values, which indicated the successful coupling of APPT ligand with each of the repeating units of Amberlite XAD-2 through an azo spacer.



**Figure 1.** FTIR spectrum of Amberlite XAD-2 (a) and Amberlite XAD-2-N=N-2-APPT resin (b).

### 2.1.3. Thermal gravimetric analysis (TGA)

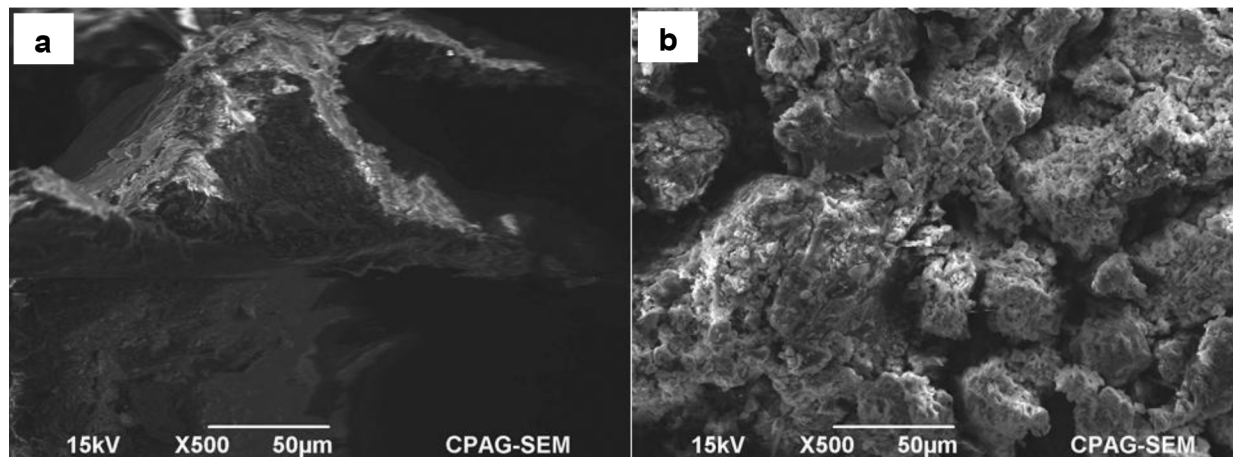
Figure 2 shows a thermogram of Amberlite XAD-2-N=N-APPT resin with 2 distinct mass loss steps. Step 1 shows mass loss of 7.98% up to the temperature of 99.0 °C, which corresponds to the loss of 2 water molecules per repeating unit of polymeric chelating resin. The theoretical value calculated for mass loss of 2 water molecules is 7.99%. Step 2 shows mass loss of 29.87% at the temperature range of 197.58–495.09 °C (start–end), which is attributed to the mass loss of the fragment, 1-(1-(pyridin-2-yl)ethylidene)-hydrazinyl per repeating unit of the polymeric chelating resin. The theoretical value calculated for loss of the fragment is 29.78%. The good correlation between experimental and theoretical mass loss values confirmed the successful coupling of APPT with each of the repeating units of Amberlite XAD-2 through an azo spacer.



**Figure 2.** Thermogram of Amberlite XAD-2-N=N-2-APPT resin.

### 2.1.4. Scanning electron microscopy (SEM) analysis

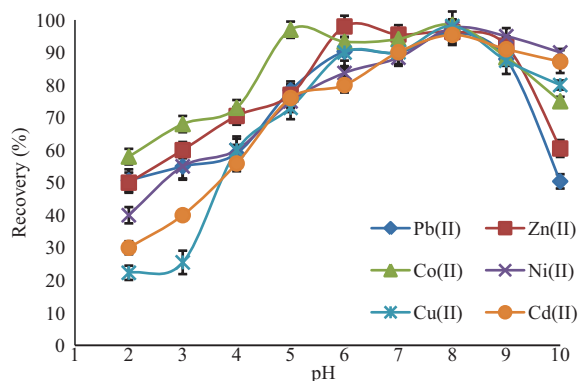
Morphological studies of the modified Amberlite XAD-2 surface were carried out by SEM analysis. Figure 3 shows the SEM images of ground Amberlite XAD-2 resin (a) and Amberlite XAD-2-N=N-APPT resin (b). A clear difference in morphology between the ground Amberlite XAD-2 resin and the resin can be seen in the images, which confirmed the surface modification of Amberlite XAD-2.



**Figure 3.** SEM images of ground Amberlite XAD-2 (a) and Amberlite XAD-2N=N-2-APPT resin (b).

### 2.2. Effect of pH

The surface activity of the resin for metal ions is strongly pH dependent. Thus, the effect of pH on the retention of studied metal ions was investigated. For this purpose, 50 mL of model solution containing 2.5–20  $\mu\text{g}$  of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions was adjusted to pH 2–10 using desired buffer solutions and passed through the column. The metal ions were eluted with 10 mL of 2.0 mol L<sup>-1</sup> HCl. The recoveries of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions were 96.1  $\pm$  3.1%, 96.3  $\pm$  3.5%, 95.0  $\pm$  2.1%, 95.0  $\pm$  3.5%, and 95.6  $\pm$  3.0%, respectively, at pH 8 as shown in Figure 4. Therefore, pH 8 was chosen as the optimum pH for further experiments.



**Figure 4.** Effect of pH on the recoveries of studied metal ions ( $V = 50$  mL,  $n = 3$ ).

### 2.3. Effect of type and concentration of eluent

The effect of type, concentration, and volume of eluents on the recoveries of the studied metal ions was investigated. For this, 5–20 mL of 1.0–3.0 mol L<sup>-1</sup> HCl and HNO<sub>3</sub> were tested as eluent solvents. The

recoveries of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions were  $96.7 \pm 3.2\%$ ,  $97.9 \pm 3.6\%$ ,  $97.9 \pm 2.9\%$ ,  $97.3 \pm 2.9\%$ ,  $96.6 \pm 3.5\%$ , and  $98.1 \pm 2.9\%$ , respectively, with 10 mL of  $2.0 \text{ mol L}^{-1}$  HCl as shown in Table 1. Therefore, 10 mL of  $2.0 \text{ mol L}^{-1}$  HCl was chosen as the best eluent for further experiments.

**Table 1.** Effect of type, concentration, and volume of the eluent on the recoveries of metal ions ( $V = 50 \text{ mL}$ ,  $n = 3$ ).

Eluent			R $\pm$ RSD (%)					
Type	Conc.	V	Pb(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Cd(II)
HNO <sub>3</sub>	1.0	10	51.0 $\pm$ 1.5	46.7 $\pm$ 1.6	54.6 $\pm$ 2.7	48.0 $\pm$ 1.5	55.5 $\pm$ 3.1	65.5 $\pm$ 1.4
HNO <sub>3</sub>	1.0	20	53.0 $\pm$ 3.4	55.5 $\pm$ 3.1	60.0 $\pm$ 2.5	56.5 $\pm$ 3.8	67.0 $\pm$ 3.0	76.6 $\pm$ 2.7
HNO <sub>3</sub>	2.0	10	47.8 $\pm$ 3.6	65.1 $\pm$ 2.5	65.2 $\pm$ 3.4	60.5 $\pm$ 2.9	76.0 $\pm$ 2.4	74.3 $\pm$ 1.8
HNO <sub>3</sub>	2.0	20	67.7 $\pm$ 4.1	70.5 $\pm$ 2.5	71.1 $\pm$ 1.3	76.3 $\pm$ 1.7	85.4 $\pm$ 2.3	80.8 $\pm$ 2.6
HNO <sub>3</sub>	3.0	10	51.7 $\pm$ 2.3	76.9 $\pm$ 3.0	78.2 $\pm$ 3.2	80.5 $\pm$ 3.1	88.9 $\pm$ 2.5	84.9 $\pm$ 1.6
HNO <sub>3</sub>	3.0	20	74.8 $\pm$ 2.5	88.9 $\pm$ 1.7	85.9 $\pm$ 4.1	85.9 $\pm$ 2.5	90.5 $\pm$ 1.7	89.2 $\pm$ 3.1
HCl	1.0	10	71.5 $\pm$ 4.1	60.3 $\pm$ 3.1	70.9 $\pm$ 3.7	80.5 $\pm$ 2.9	75.2 $\pm$ 3.6	71.8 $\pm$ 2.5
HCl	1.0	20	80.5 $\pm$ 3.7	73.7 $\pm$ 3.7	83.1 $\pm$ 1.9	88.3 $\pm$ 1.5	87.1 $\pm$ 2.9	88.9 $\pm$ 3.1
HCl	2.0	5.0	90.7 $\pm$ 3.2	87.9 $\pm$ 3.6	91.9 $\pm$ 2.9	86.3 $\pm$ 2.9	90.6 $\pm$ 3.5	82.1 $\pm$ 2.9
HCl	2.0	10	96.7 $\pm$ 3.2	97.9 $\pm$ 3.6	97.9 $\pm$ 2.9	97.3 $\pm$ 2.9	96.6 $\pm$ 3.5	98.1 $\pm$ 2.9
HCl	3.0	5.0	85.4 $\pm$ 2.2	88.7 $\pm$ 1.7	83.2 $\pm$ 1.5	90.1 $\pm$ 1.6	92.1 $\pm$ 2.7	90.5 $\pm$ 2.1
HCl	3.0	10	96.8 $\pm$ 2.4	97.1 $\pm$ 2.5	97.8 $\pm$ 2.3	97.9 $\pm$ 2.3	97.2 $\pm$ 3.1	98.4 $\pm$ 3.2
HCl	3.0	20	96.8 $\pm$ 1.3	97.3 $\pm$ 3.1	97.6 $\pm$ 2.2	92.5 $\pm$ 2.5	97.1 $\pm$ 2.3	98.8 $\pm$ 3.4

Conc.: Concentration of eluent ( $\text{mol L}^{-1}$ ), V: Volume of eluent (mL), R: Recoveries (%), RSD: Relative standard deviation.

#### 2.4. Effect of flow rate

The effect of flow rate of eluent and sample solution on the recoveries of the studied metal ions was investigated. For this, 25 mL of model solution was passed through the column at a flow rate of  $1.0\text{--}5.0 \text{ mL min}^{-1}$ , and the retained metal ions were eluted with 10 mL of  $2.0 \text{ mol L}^{-1}$  HCl at a flow rate of  $1.0\text{--}5.0 \text{ mL min}^{-1}$ . The recoveries of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions were  $96.5 \pm 3.2\%$ ,  $97.4 \pm 2.1\%$ ,  $97.3 \pm 1.9\%$ ,  $96.0 \pm 2.0\%$ ,  $98.1 \pm 1.1\%$ , and  $97.4 \pm 2.1\%$ ; and  $95.0 \pm 2.4\%$ ,  $98.5 \pm 2.1\%$ ,  $95.0 \pm 2.2\%$ ,  $96.0 \pm 2.0\%$ ,  $97.5 \pm 3.9\%$ , and  $96.8 \pm 4.1\%$  at flow rates of  $2.0 \text{ mL min}^{-1}$  (of eluent) and  $3.0 \text{ mL min}^{-1}$  (of sample solution) as shown in Table 2. Therefore,  $2.0$  and  $3.0 \text{ mL min}^{-1}$  were chosen as the optimum flow rates of eluent and sample solution, respectively.

**Table 2.** Effect of flow rates of eluent and sample solutions on the recoveries of metal ions ( $V = 50 \text{ mL}$ ,  $n = 3$ ).

Solution	FR	R $\pm$ RSD (%)					
		Pb(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Cd(II)
Sample	2	98.8 $\pm$ 1.1	100.0 $\pm$ 1.1	97.0 $\pm$ 2.1	97.1 $\pm$ 2.0	98.0 $\pm$ 3.9	98.1 $\pm$ 3.2
	3	95.0 $\pm$ 2.4	98.5 $\pm$ 2.1	95.0 $\pm$ 2.2	96.0 $\pm$ 2.0	97.5 $\pm$ 3.9	96.8 $\pm$ 4.1
	4	88.1 $\pm$ 2.9	98.7 $\pm$ 1.9	82.6 $\pm$ 3.5	92.1 $\pm$ 3.1	87.3 $\pm$ 2.1	88.1 $\pm$ 1.2
	5	85.1 $\pm$ 2.1	98.9 $\pm$ 3.1	70.1 $\pm$ 3.5	90.1 $\pm$ 3.1	81.4 $\pm$ 2.2	80.0 $\pm$ 2.8
Eluent	1	97.0 $\pm$ 2.4	98.0 $\pm$ 2.1	98.4 $\pm$ 3.1	97.0 $\pm$ 2.1	99.0 $\pm$ 2.1	98.9 $\pm$ 1.3
	2	96.5 $\pm$ 3.2	97.4 $\pm$ 2.1	97.3 $\pm$ 1.9	96.0 $\pm$ 2.0	98.1 $\pm$ 1.1	97.4 $\pm$ 2.1
	3	91.5 $\pm$ 2.2	88.5 $\pm$ 3.5	92.1 $\pm$ 2.5	90.9 $\pm$ 3.2	87.8 $\pm$ 3.6	90.0 $\pm$ 1.3
	4	89.9 $\pm$ 2.2	81.4 $\pm$ 3.0	84.6 $\pm$ 2.0	85.6 $\pm$ 2.5	77.4 $\pm$ 3.8	86.1 $\pm$ 2.5
	5	80.3 $\pm$ 3.5	73.0 $\pm$ 2.5	72.5 $\pm$ 3.5	70.3 $\pm$ 3.0	63.7 $\pm$ 2.0	81.3 $\pm$ 3.3

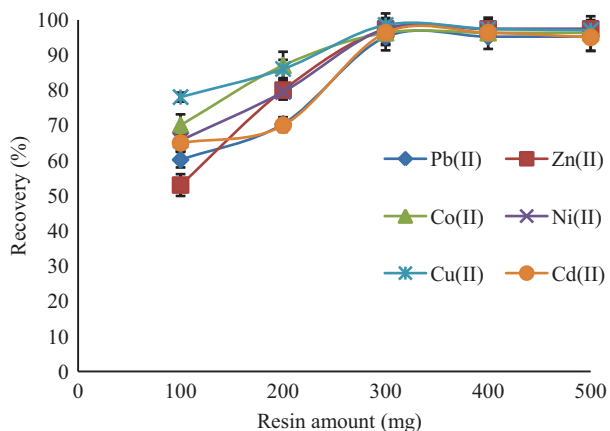
FR: Flow rate ( $\text{mL min}^{-1}$ ), R: Recoveries (%), RSD: Relative standard deviation.

## 2.5. Effect of resin amount

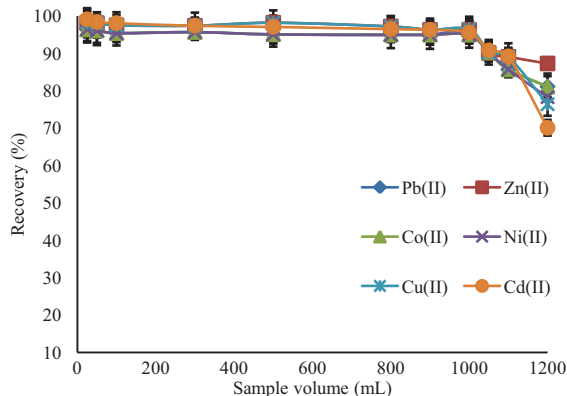
The effect of resin amount on the recoveries of the studied metal ions was investigated. For this, 50 mL of model solution was adjusted to pH 8 and passed through the column packed with 100–500 mg of the chelating resin at a flow rate of 3.0 mL min<sup>-1</sup>. The retained metal ions were eluted with 10 mL of 2.0 mol L<sup>-1</sup> HCl at a flow rate of 2.0 mL min<sup>-1</sup>. The quantitative recoveries ( $\geq 95.1\%$ ) of the studied metal ions were achieved with 300–500 mg of the resin as shown in Figure 5. Therefore, 300 mg was chosen as the optimum resin amount for further experiments.

## 2.6. Effect of sample volume

The effect of sample volume on the recoveries of the studied metal ions was investigated. For this, model solution containing 50, 10, 40, 25, 15, and 5.0  $\mu\text{g}$  of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions, respectively, was diluted to 25–1200 mL and passed through the column at optimum conditions. The retained metal ions were eluted with 10 mL of 2.0 mol L<sup>-1</sup> HCl. The recoveries of the studied metal ions from diluted solutions were achieved quantitatively ( $\geq 95.0\%$ ) until 1000 mL of sample solution as shown in Figure 6. Therefore, the preconcentration factor calculated was 500 for all 6 studied metal ions as 2.0 mL of final solution was subjected to MIS-FAAS.



**Figure 5.** Effect of resin amount on recoveries of studied metal ions ( $V = 50$  mL,  $n = 3$ ).



**Figure 6.** Effect of sample volume on the recoveries of studied metal ions ( $n = 3$ ).

## 2.7. Effect of matrix ions

The effect of possible matrix ions present in natural water samples on the recoveries of the studied metal ions was investigated. For this, 50 mL of model solution containing matrix ions was passed through the column at optimum conditions. The recoveries of studied metal ions were  $\geq 95.0\%$  with  $RSD \geq 3.5\%$ , which reflected high tolerance limits of the chelating resin for the studied matrix ions as shown in Table 3.

## 2.8. Sorption capacity

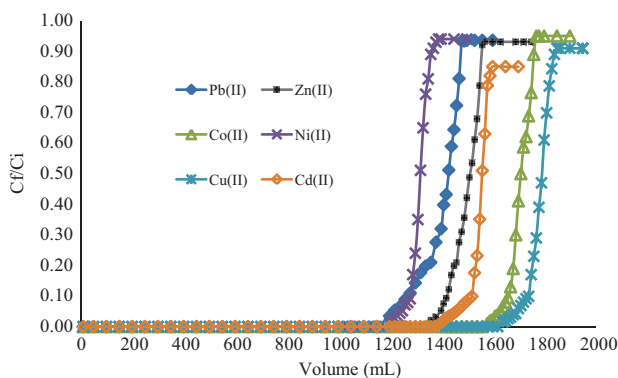
The capacity of Amberlite XAD-2-N=N-APPT resin for the studied metal ions was examined by determining by plotting a breakthrough curve (Figure 7). The break point occurs when the effluent concentration ( $C_f$ ) becomes 5.0% of the initial concentration ( $C_i$ ) and the column attains complete saturation when  $C_f$  approaches  $C_i$ .<sup>38</sup> The resin amount, initial concentration of studied metal ions, and flow rate of sample solution were fixed as 500

mg, 10 mg L<sup>-1</sup>, and 3.0 mL min<sup>-1</sup>, respectively, for the column experiment. Therefore, the total saturation and breakthrough capacities of chelating resin for Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions were 0.36, 1.20, 1.50, 1.61, 1.07, and 0.71; and 0.29, 1.07, 1.38, 1.44, 0.98, and 0.65 mmol g<sup>-1</sup>, respectively.

**Table 3.** Tolerance limits of the resin for the matrix ions ( $V = 50$  mL,  $n = 3$ ).

Ions	TLC	R $\pm$ RSD (%)					
		Pb (II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Cd(II)
K <sup>+</sup>	3000	98.0 $\pm$ 1.3	97.2 $\pm$ 2.3	98.6 $\pm$ 2.1	97.5 $\pm$ 3.0	95.5 $\pm$ 3.0	97.3 $\pm$ 2.4
Na <sup>+</sup>	22,000	96.2 $\pm$ 3.5	96.0 $\pm$ 3.3	95.9 $\pm$ 2.1	98.0 $\pm$ 1.9	96.1 $\pm$ 2.1	96.6 $\pm$ 2.1
Ca <sup>2+</sup>	5000	97.6 $\pm$ 3.5	95.0 $\pm$ 2.9	96.0 $\pm$ 3.0	96.1 $\pm$ 2.9	95.5 $\pm$ 2.5	95.5 $\pm$ 3.1
Mg <sup>2+</sup>	5000	98.0 $\pm$ 1.3	96.0 $\pm$ 3.7	96.2 $\pm$ 2.1	97.4 $\pm$ 2.3	97.0 $\pm$ 2.2	96.9 $\pm$ 2.5
Ba <sup>2+</sup>	1100	97.9 $\pm$ 3.5	95.2 $\pm$ 1.9	97.8 $\pm$ 1.9	96.0 $\pm$ 3.1	96.5 $\pm$ 1.9	95.3 $\pm$ 3.1
SO <sub>4</sub> <sup>2-</sup>	1000	95.4 $\pm$ 2.7	95.6 $\pm$ 3.5	95.5 $\pm$ 2.1	96.5 $\pm$ 1.8	95.0 $\pm$ 2.9	97.9 $\pm$ 2.4
PO <sub>4</sub> <sup>3-</sup>	4000	98.1 $\pm$ 2.2	96.0 $\pm$ 2.9	97.1 $\pm$ 1.3	95.9 $\pm$ 2.4	95.0 $\pm$ 3.1	95.9 $\pm$ 3.0
CH <sub>3</sub> COO <sup>-</sup>	3000	95.7 $\pm$ 2.7	97.6 $\pm$ 1.3	96.0 $\pm$ 2.5	96.5 $\pm$ 3.0	96.1 $\pm$ 2.4	95.4 $\pm$ 2.1
CO <sub>3</sub> <sup>2-</sup>	2700	96.3 $\pm$ 3.5	95.0 $\pm$ 3.5	97.3 $\pm$ 2.0	96.0 $\pm$ 2.6	94.5 $\pm$ 3.1	95.9 $\pm$ 2.9
HCO <sub>3</sub> <sup>-</sup>	3000	97.2 $\pm$ 3.5	98.0 $\pm$ 2.1	97.7 $\pm$ 1.1	95.7 $\pm$ 1.9	95.0 $\pm$ 2.6	96.0 $\pm$ 3.5
NO <sub>3</sub> <sup>-</sup>	8000	96.1 $\pm$ 1.4	94.6 $\pm$ 2.1	96.4 $\pm$ 2.9	95.7 $\pm$ 2.0	95.2 $\pm$ 3.6	96.1 $\pm$ 2.0
Cl <sup>-</sup>	2200	97.5 $\pm$ 2.3	96.0 $\pm$ 3.9	97.1 $\pm$ 2.1	96.0 $\pm$ 3.5	96.9 $\pm$ 3.1	95.1 $\pm$ 3.1
F <sup>-</sup>	3500	95.3 $\pm$ 1.9	97.5 $\pm$ 3.0	95.6 $\pm$ 3.0	97.0 $\pm$ 2.6	95.6 $\pm$ 3.0	97.0 $\pm$ 2.6

TLC: Tolerance limits concentration ( $\mu\text{g mL}^{-1}$ ) of matrix ions, R: Recoveries (%), RSD: Relative standard deviation.



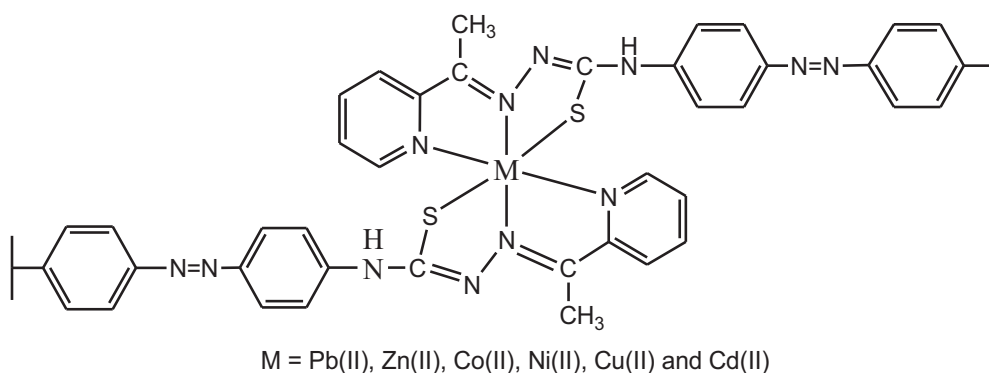
**Figure 7.** Breakthrough curve for capacity of the resin for the studied metals ions.

## 2.9. Sorption mechanism

Incorporation of the polydentate ligand APPT onto Amberlite XAD-2 resin played a vital role in metal ion adsorption. The N and S of Amberlite XAD-2-N=N-APPT resin participated in the metal chelate formation. The formation of APPT-metal (II) complex increased to its maximum at pH 8.0 due to the formation of enolate-like ions. These 2 enolate-like ions interacted with divalent metal ions through S and N to form 5-membered chelate rings (Figure 8).

## 2.10. Analytical performance of the method

Validation and accuracy of the proposed method were evaluated by analysis of CRMs. The recoveries of studied metal ions were achieved in good agreement with certified values as shown in Table 4. The validation and



**Figure 8.** The sorption mechanism for the retention of metal ions onto Amberlite XAD-2-N=N-2-APPT resin.

high accuracy of the proposed method were confirmed by t-test at a confidence level of 95.0%. The linear concentration ranges of the studied metal ions before preconcentration were 0.5–20 mg L<sup>-1</sup> with the regression equations  $y = 0.0144x + 0.0067$  with  $R^2 = 0.998$ ,  $y = 0.0200x + 0.0022$  with  $R^2 = 0.999$ ,  $y = 0.0142x + 0.0091$  with  $R^2 = 0.998$ ,  $y = 0.0147x + 0.0003$  with  $R^2 = 0.999$ ,  $y = 0.0157x + 0.0006$  with  $R^2 = 0.998$ , and  $y = 0.016x + 0.0016$  with  $R^2 = 0.998$  for Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions, respectively. The linear concentration ranges of the studied metal ions after preconcentration were 0.001–0.04 L<sup>-1</sup> with the regression equations  $y = 7.1831x + 0.011$  with  $R^2 = 0.999$ ,  $y = 9.2416x + 0.0056$  with  $R^2 = 0.998$ ,  $y = 7.0618x + 0.0078$  with  $R^2 = 0.999$ ,  $y = 7.3373x + 0.0027$  with  $R^2 = 0.998$ ,  $y = 7.8169x + 0.0022$  with  $R^2 = 0.999$ , and  $y = 7.8937x + 0.0047$  with  $R^2 = 0.999$  for Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions, respectively. The experimental enhancement factors (EFs) and theoretical preconcentration factors (PFs) were calculated from the ratio of the slopes of the calibration equations and from the ratio of the sample solution volumes (1000 mL) to 2.0 mL of final effluent volume, respectively. The relative errors of the experimental enhancement factors were smaller than 7.6%. The limits of detection (LOD) (blank + 3 $\sigma$ , where  $\sigma$  is the standard deviation of blank analysis,  $n = 15$ ) were calculated according to IUPAC.<sup>39</sup> The analytical performance data and optimum parameters of the method are summarized in Table 5. The resin was recycled more than 100 times ( $n = 3$ ) in different intervals of time without significant loss in recoveries and capacities for the studied metal ions.

**Table 4.** Determination of the studied metal ions in CRMs ( $V = 100$  mL,  $n = 3$ ).

Metals	Tibet soil (NCS DC-78302)			Wastewater (BCR-715)		
	CV ( $\mu\text{g g}^{-1}$ )	FV ( $\mu\text{g g}^{-1}$ )	R $\pm$ RSD (%)	CV ( $\mu\text{g mL}^{-1}$ )	FV ( $\mu\text{g mL}^{-1}$ )	R $\pm$ RSD (%)
Pb(II)	14.4	14.1	97.9 $\pm$ 3.1	490	470	95.9 $\pm$ 3.5
Ni(II)	31.1	30.5	98.1 $\pm$ 2.5	1200	1180	98.3 $\pm$ 2.5
Cu(II)	24.6	24.0	97.6 $\pm$ 2.5	900	888	98.6 $\pm$ 2.0
Co(II)	13.1	12.7	96.9 $\pm$ 2.1	-	-	-
Zn(II)	58.0	57.7	99.5 $\pm$ 1.5	4000	4000	100.0 $\pm$ 1.0
Cd(II)	0.081	0.077	95.1 $\pm$ 3.5	40.0	39.0	97.5 $\pm$ 2.5

CV: Certified value, FV: Found value, R: Recoveries (%), RSD: Relative standard deviation.

### 2.11. Applications of the method

The optimized method was successfully applied for preconcentration and ultratrace determination of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions in wastewater, river water, canal water, and lake water samples.



The samples were analyzed with and without the standard addition method. The recoveries of the studied metal ions were  $\geq 95.1\%$  with  $RSD \leq 4.0\%$  as shown in Table 6.

**Table 5.** Method's parameters for the preconcentration of metal ions.

Method's parameters	Pb(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Cd(II)
Recovery (%)	95.1	97.4	96.3	97.4	98.5	96.3
pH	8	8	8	8	8	8
Concentration (mol L <sup>-1</sup> ) of HCl (eluent)	2	2	2	2	2	2
Flow rate of eluent (mL min <sup>-1</sup> )	2	2	2	2	2	2
Flow rate of sample solution (mL min <sup>-1</sup> )	3	3	3	3	3	3
Resin amount (mg)	300	300	300	300	300	300
PF	500	500	500	500	500	500
EF	499	462	497	499	498	493
Breakthrough capacity (mmol g <sup>-1</sup> )	0.29	1.07	1.38	1.44	0.98	0.65
Saturation capacity (mmol g <sup>-1</sup> )	0.36	1.2	1.5	1.61	1.07	0.71
LOD ( $\mu\text{g L}^{-1}$ )	0.11	0.05	0.07	0.08	0.09	0.03
LOQ ( $\mu\text{g L}^{-1}$ )	0.37	0.17	0.21	0.13	0.31	0.10

LOD: Limit of detection, LOQ: Limit of quantification, PF: Preconcentration factor, EF: Enhancement factor.

**Table 6.** Determination of the studied metal ions in spiked water samples ( $V = 100 \text{ mL}$ ,  $n = 3$ ).

Metals	Added ( $\mu\text{g}$ )	Wastewater		River water		Canal water		Lake water	
		FV ( $\mu\text{g}$ )	R $\pm$ RSD (%)	FV ( $\mu\text{g}$ )	R $\pm$ RSD (%)	FV ( $\mu\text{g}$ )	R $\pm$ RSD (%)	FV ( $\mu\text{g}$ )	R $\pm$ RSD (%)
Pb(II)	0.0	3.5	-	nd	-	nd	-	nd	-
	5.0	8.6	102.0 $\pm$ 1.2	4.9	98.0 $\pm$ 1.2	5.0	100.0 $\pm$ 1.5	5.0	100.0 $\pm$ 2.5
	10	13.6	101.0 $\pm$ 2.6	10.0	100.0 $\pm$ 2.5	9.9	99.0 $\pm$ 2.5	10.0	100.0 $\pm$ 2.5
	20	23.5	100.0 $\pm$ 1.5	19.9	99.5 $\pm$ 1.5	19.9	99.5 $\pm$ 1.5	19.8	99.0 $\pm$ 2.5
Zn(II)	0.0	nd	-	nd	-	nd	-	nd	-
	5.0	5.1	102.0 $\pm$ 3.1	4.8	96.0 $\pm$ 3.5	5.0	100.0 $\pm$ 2.5	5.0	100.0 $\pm$ 1.5
	10	10.1	101.0 $\pm$ 2.8	10.0	100.0 $\pm$ 2.0	9.9	99.0 $\pm$ 1.5	9.8	98.0 $\pm$ 2.5
	20	20.0	100.0 $\pm$ 1.7	19.5	97.5 $\pm$ 2.5	19.8	99.0 $\pm$ 1.8	19.8	99.0 $\pm$ 2.5
Co(II)	0.0	nd	-	nd	-	nd	-	nd	-
	5.0	5.0	100.0 $\pm$ 1.5	5.0	100.0 $\pm$ 2.0	4.9	98.0 $\pm$ 4.0	5.0	100.0 $\pm$ 2.5
	10	10.0	100.0 $\pm$ 2.0	10.0	100.0 $\pm$ 2.5	9.9	99.0 $\pm$ 3.5	10.0	100.0 $\pm$ 1.5
	20	20.0	100.0 $\pm$ 2.5	19.9	99.5 $\pm$ 2.8	19.8	99.0 $\pm$ 2.9	19.9	99.5 $\pm$ 2.0
Ni(II)	0.0	nd	-	nd	-	nd	-	nd	-
	5.0	5.1	102.0 $\pm$ 3.0	4.9	98.0 $\pm$ 3.1	5.0	100.0 $\pm$ 2.0	5.0	100.0 $\pm$ 2.5
	10	10.1	101.0 $\pm$ 2.0	9.7	97.0 $\pm$ 2.2	9.9	99.0 $\pm$ 1.5	10.0	100.0 $\pm$ 1.8
	20	20.0	100.0 $\pm$ 2.9	19.5	97.5 $\pm$ 4.0	20.0	100.0 $\pm$ 1.5	19.0	95.0 $\pm$ 2.5
Cu(II)	0.0	nd	-	nd	-	nd	-	nd	-
	5.0	5.2	104.0 $\pm$ 3.9	5.0	100.0 $\pm$ 2.5	5.0	100.0 $\pm$ 2.5	5.0	100.0 $\pm$ 2.0
	10	10.0	100.0 $\pm$ 2.9	9.5	95.0 $\pm$ 2.0	10.0	100.0 $\pm$ 3.0	9.9	99.0 $\pm$ 2.9
	20	19.9	99.5 $\pm$ 3.1	19.7	98.5 $\pm$ 3.5	19.5	97.5 $\pm$ 3.5	19.8	99.0 $\pm$ 3.0
Cd(II)	0.0	nd	-	nd	-	nd	-	nd	-
	5.0	5.0	100.0 $\pm$ 3.3	4.8	96.0 $\pm$ 2.1	5.0	100.0 $\pm$ 2.0	5.0	100.0 $\pm$ 2.6
	10	10.0	100.0 $\pm$ 2.7	9.6	96.0 $\pm$ 2.7	9.8	98.0 $\pm$ 3.5	10.0	100.0 $\pm$ 1.5
	20	20.4	102.0 $\pm$ 2.0	19.5	97.5 $\pm$ 4.0	19.9	99.5 $\pm$ 2.5	20.0	100.0 $\pm$ 2.7

FV: Found value ( $\mu\text{g}$ ), R: Recoveries (%), RSD: Relative standard deviation, nd: Not detected.

**Table 7.** Comparison of analytical parameters for the trace determination studied metal ions by FAAS using different chelating resins.

Resins	Matrix	Analytes	CP	PF	LOD	RSD (%)	Ref.
X-2-N <sub>2</sub> -DHP	water, milk & mvt	Pb(II) Zn(II)	0.15 0.18	300 250	13.9 3.88	≤ 2.6	40
		Co(II) Ni(II)	0.09 0.12	150 250	0.30 8.72		
		Cu(II) Cd(II)	0.41 0.07	250 200	1.24 4.71		
X-16-N <sub>2</sub> -DMABA	water, milk & mvt	Pb(II) Zn(II)	0.13 0.20	250 300	0.67 1.12	≤ 8.0	41
		Co(II) Ni(II)	0.22 0.27	167 100	1.08 1.76		
		Cu(II) Cd(II)	0.47 0.10	300 250	2.52 0.77		
X-16-N <sub>2</sub> -HIMB	water & mvt	Pb(II) Zn(II)	0.11 0.17	200 200	2.10 1.72	≤ 4.9	42
		Co(II) Ni(II)	0.24 0.22	250 300	3.23 2.56		
		Cu(II) Cd(II)	0.42 0.56	250 150	2.93 0.44		
X-2-N <sub>2</sub> -oAP	water	Pb(II) Zn(II)	0.02 0.04	40 40	25.0 2.50	≤ 8.0	34
		Co(II) Ni(II)	0.06 0.06	100 65	5.00 7.50		
		Cu(II) Cd(II)	0.05 0.03	50 50	4.00 2.00		
X-1180-N <sub>2</sub> -oAP	water	Pb(II) Co(II)	0.23 0.12	50 50	4.30 1.20	≤ 5.5	43
		Ni(II) Cu(II)	0.12 0.50	50 60	1.10 0.90		
		Cd(II) -	0.14 -	40 -	1.00 -		
X-2-N <sub>2</sub> -PC	water	Zn(II) Co(II)	0.03 0.02	200 200	2.85 0.06	≤ 7.3	27
		Ni(II) Cu(II)	0.05 0.09	200 100	0.24 3.76		
		Cd(II) -	0.04 -	200 -	0.39 -		
X-16-N <sub>2</sub> -PAN	water	Pb(II) Co(II)	0.02 0.08	200 200	0.12 0.07	≤ 4.0	44
		Ni(II) Cu(II)	0.08 0.08	200 200	0.16 0.08		
		Cd(II) -	0.04 -	200 -	0.06 -		
X-4-N <sub>2</sub> -SA	water	Zn(II) Co(II)	0.15 0.07	320 200	0.63 1.41	≤ 4.6	2
		Ni(II) Cu(II)	0.12 0.24	280 360	0.96 0.42		
		Cd(II) -	0.14 -	300 -	0.77 -		
X-4-N <sub>2</sub> -SAS	water	Pb(II) Zn(II)	0.38 1.13	50 50	0.15 0.19	≤ 1.4	5
		Co(II) Ni(II)	1.24 1.24	50 50	0.21 0.18		
		Cu(II) -	1.16 -	50 -	0.18 -		
X-4-N <sub>2</sub> -oABA		Pb(II) Zn(II)	0.06 0.12	400 400	2.50 2.50	≤ 3.5	20
		Co(II) Ni(II)	0.08 0.12	150 200	6.50 5.00		
		Cd(II) -	0.08 -	400 -	2.50 -		
X-4-N <sub>2</sub> -PTA	water	Zn(II) Co(II)	0.15 0.06	180 160	0.75 0.85	≤ 10.1	45
		Ni(II) Cu(II)	0.22 0.18	190 190	0.62 0.65		
		Cd(II) -	0.12 -	180 -	0.72 -		
X-4-N <sub>2</sub> -APPT	water	Pb(II) Zn(II)	0.36 1.20	500 500	0.11 0.05	≤ 4.0	This work
		Co(II) Ni(II)	1.50 1.61	500 500	0.07 0.08		
		Cu(II) Cd(II)	1.07 0.71	500 500	0.09 0.03		

X: Amberlite XAD resin, CP: Capacity (mmol g<sup>-1</sup>), LOD: PF: Preconcentration factor Limit of detection ( $\mu\text{g L}^{-1}$ ), mvt: Multivitamin tablet, mvc: Multivitamin capsule, DHP: 2,3-Dihydroxypyridine, San: Salicylanilide, HIMB: 4-[[[2-Hydroxyphenyl] imino] methyl] -1,2-benzenediol, DMABA: 2-[[1-(3,4-Dihydroxyphenyl)methylidene]amino] benzoic acid, oAP: o-Aminophenol, PC: Pyrocatechol, PAN: 1-(2-pyridylazo)-2-naphthol, SA: salicylic acid, SAS: Salicyl aspartide, oABA: o-Aminobenzoic acid, PTA: Phthalic acid, APPT: 2-Acetylpyridine-4-phenyl-3-thiosemicarbazone

## 2.12. Comparison with other methods

Various methods have been reported for preconcentration of metal ions on different chelating resins as an adsorbent. In our method, Amberlite XAD-2-N=N-APPT resin was used for preconcentration of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions in water samples. The analytical parameters such as preconcentration

factor and sorption capacities are better and LODs are lower than those of the methods reported previously (Table 7). The RSD values of the proposed method are comparable<sup>2,5,20,41–44</sup> or better than the reported methods.<sup>27,34,41,45</sup>

In conclusion, the chelating ligand, APPT, was successfully immobilized on the polymer backbone of Amberlite XAD-2 resin through an azo spacer. The synthesized chelating resin, i.e. Amberlite XAD-2-N=N-APPT, was successfully characterized by FTIR spectroscopy, elemental analysis, TGA, and SEM analysis. The resin was used for the development of an effective preconcentration method for the simultaneous ultratrace determinations of the studied metal ions in different water samples by innovative MIS-FAAS using 100  $\mu\text{L}$  of sample solution. The analytical performance of the method was evaluated by analysis of wastewater (BCR-715) and Tibet soil (NCS DC-78302) as CRMs for the determination of the studied metal ions. The chelating resin was recycled ( $n = 3$ ) more than 100 times in different intervals of time without significant loss in recoveries or capacity values for the studied metal ions. The innovative MIS-FAAS offers 100  $\mu\text{L}$  of sample for single element determination.

### 3. Experimental

#### 3.1. Apparatus

The determinations of the studied metals were performed by PerkinElmer FAAS (Analyst 800, USA) equipped with a hollow cathode lamp. The operating parameters for the studied elements were set as recommended by the manufacturer. A PerkinElmer FTIR spectrometer (SN-92417, USA) was used to record the FTIR spectra. A PerkinElmer (Series II, USA) CHNSO Analyzer 2400 was used for elemental analysis. The thermogram was recorded on a PerkinElmer Thermogravimetric Analyzer (Pyris, Diamond, TG-DTA, 115V, USA) using an aluminum pan with a heating rate of 10  $^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere. A scanning electron microscope (JSM-6490LV, JEOL, Japan) was used to record SEM images. A digital pH meter (Hanna 211, Germany) was used for pH measurements. A reverse osmosis system (Human Corp., Seoul, Korea) was used to obtain ultrapure quality water.

#### 3.2. Reagents and solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Ultrapure quality water was used throughout the experiments. The working and reference solutions were prepared daily by dilution of commercial stock solutions ( $1000 \pm 4.0 \text{ mg L}^{-1}$ ) of the studied metal ions purchased from Fluka, Germany. The buffer solutions, phosphoric acid/dihydrogen phosphate, sodium acetate/acetic acid, disodium hydrogen phosphate/sodium dihydrogen orthophosphate, and ammonium hydroxide/ammonium chloride were used for adjusting pH to 2, 4–6, 7, and 8–10, respectively. All chemicals used for the preparation of buffer solutions were purchased from Sigma-Aldrich, USA. Amberlite XAD-2 (bead size 20–60 mesh, pore diameter 90 nm, and surface area  $330 \text{ m}^2 \text{ g}^{-1}$ ) was purchased from Sigma-Aldrich, Germany. As certified reference materials (CRMs), wastewater (BCR-715) was furnished by the European Commission, Joint Research Center, Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, Belgium; and Tibet soil (NCS DC-78302) was furnished by the China National Analysis Center for Iron and Steel.

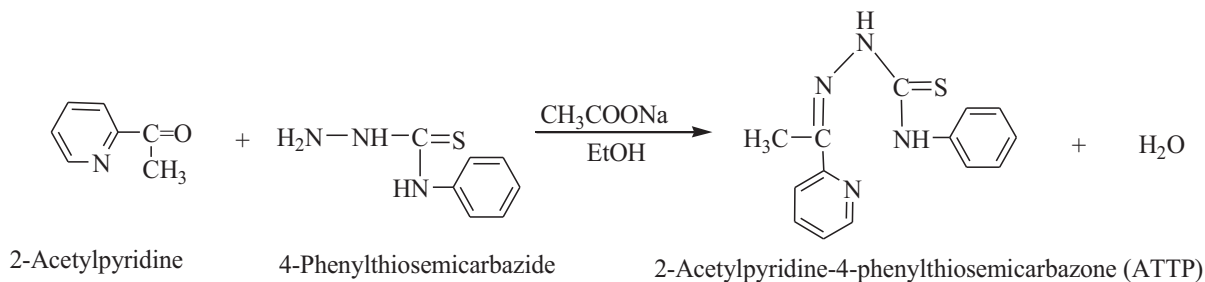
### 3.3. Sample collection

Polyethylene bottles were used for storage of water samples. The bottles were successively washed with water, detergent, dilute nitric acid, and water. The wastewater sample was collected from an industrial area in Kotri, Sindh, Pakistan, on 1 June 2012. The river water sample was collected from the River Indus, Sindh, Pakistan, on 1 June 2012. The canal water sample was collected from the Phuleli Canal, Sindh, Pakistan, on 15 June 2012. The lake water sample was collected from Lake Keenjhar, Thatta, Sindh, Pakistan, on 20 July 2012. All the samples were filtered through a Millipore cellulose nitrate membrane filter (pore size 45.0  $\mu\text{m}$ ), acidified with 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> (1.0 mL of acid in 1000 mL of sample solution), and stored at 4.0 °C for analysis. All the samples were analyzed within 1 week of collection.

### 3.4. Synthesis

#### 3.4.1. Synthesis of 2-acetylpyridien-4-phenyl-3-thiosemicarbazone (APPT)

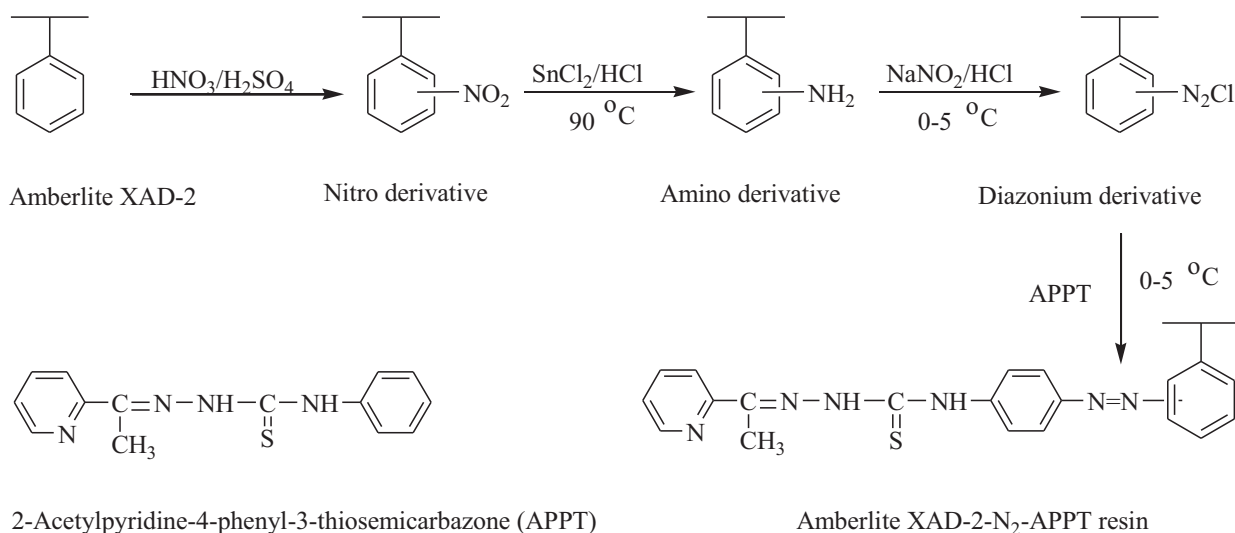
Figure 9 illustrates the reaction scheme for the synthesis of APPT ligand. The APPT was synthesized by the reported procedure; 2 solutions were prepared separately by dissolving 1.0 g of 2-acetylpyridine in 15 mL of water and 0.8 g of 4-phenyl-3-thiosemicarbazide in 50 mL of ethanol. Both solutions were mixed together, neutralized with sodium acetate, and refluxed for 30 min at 80 °C. Thereafter, the reaction mixture was cooled at room temperature until yellow crystals of APPT were formed. The crystalline product was filtered, recrystallized from ethanol, and air dried.<sup>46</sup>



**Figure 9.** Reaction scheme for the synthesis of APPT ligand.

#### 3.4.2. Synthesis of APPT functionalized Amberlite XAD-2 resin

Figure 10 illustrates the reaction scheme for the synthesis of Amberlite XAD-2-N<sub>2</sub>-APPT resin. Amberlite XAD-2 was modified to diazonium resin by the reported procedure: a mixture of 10 mL of concentrated HNO<sub>3</sub> and 25 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was poured into a 250-mL round bottom flask containing 5.0 g of Amberlite XAD-2 resin and stirred for 1.0 h at 60 °C. The reaction mixture was poured into an ice-water mixture and filtered off. The nitro derivative was washed repeatedly with water until free from acid and was refluxed with 40 g of SnCl<sub>2</sub>, 45 mL of 2.0 mol L<sup>-1</sup> HCl, and 50 mL of ethanol for 12 h at 90 °C. The precipitate was filtered off and washed with water and 2.0 mol L<sup>-1</sup> NaOH, which released amino resin (R-NH<sub>2</sub>) from (RNH<sub>3</sub>)<sub>2</sub> SnCl<sub>6</sub> (R = resin matrix). The amino resin was washed with 2.0 mol L<sup>-1</sup> HCl and finally with an excess of water until free from acid. The amino resin was diazotized by suspending in 350 mL of an ice-water mixture and treated with 1.0-mL portions of 1.0 mol L<sup>-1</sup> HCl and 1.0 mol L<sup>-1</sup> NaNO<sub>2</sub> solutions with continuous stirring until the reaction mixture began to turn starch-iodide paper a permanent dark blue.<sup>35</sup> The diazonium resin was filtered off, washed with ice-cold water, and reacted with 11.4 g of APPT (dissolved in 250 mL of methanol) at 0–5 °C for 24 h. Amberlite XAD-2-N=N-APPT resin was filtered off, washed, and air dried.



**Figure 10.** Reaction scheme for the synthesis of Amberlite XAD-2N=N-2-APPT resin.

### 3.5. Column preparation

The synthesized chelating resin (ground and sieved to 150–200  $\mu\text{m}$ ) was packed in a glass column (10 cm  $\times$  1.0 cm) with a porous disk and stopcock. A small amount of glass wool was placed on the disk at both ends of the column to prevent loss of resin during elution. The resin packed in the column was decontaminated by successive washing with water, 1.0 mol L<sup>-1</sup> HCl, water, 1.0 mol L<sup>-1</sup> NaOH, water, 2.0 mol L<sup>-1</sup> HNO<sub>3</sub>, and finally with water. The column was preconditioned at the desired pH. After the experiments, the resin packed in the column was washed thoroughly with water and then stored in water for reuse on the next day.

### 3.6. Preconcentration procedure

The proposed method was optimized with model solution prior to the ultratrace determination of metal ions in real samples. For this, 50 mL of model solution containing 2–10  $\mu\text{g}$  of Pb(II), Zn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions was adjusted to pH 2–10 by addition of a suitable buffer solution and then passed through the column gravitationally (manually) at a flow rate of 3.0 mL min<sup>-1</sup>. The retained metal ions were eluted with 10 mL of 2.0 mol L<sup>-1</sup> HCl. The eluate was evaporated to dryness on a hot plate at  $\sim 40$  °C and quantitatively completed to 2.0 mL using 2.0 mol L<sup>-1</sup> HCl. Finally, 100  $\mu\text{L}$  of sample solution was injected into the MIS-FAAS for the determination of the studied metal ions.

### 3.7. Microsample injection system coupled flame atomic absorption spectrometry (MIS-FAAS)

Routinely, 2.0–4.0 mL of sample solution is required for single element determination by FAAS. Multielement determination requires a larger volume, which leads to a lower preconcentration factor. To solve this problem, MIS-FAAS was employed in the present study.<sup>47</sup> For this, the nebulizer needle of the FAAS was coupled with the disposable tip of a micropipette (capacity 20–200  $\mu\text{L}$ ) using a PTFE capillary tube 10.0 cm in length. The micropipette was used to inject the sample solution and absorbance was recorded as peak area. The absorbance increased with increases in injection volume (sample volume) until 100  $\mu\text{L}$  and then remained constant. The absorbance measured using the injection of 100  $\mu\text{L}$  was found to be almost equal to the absorbance measured

with continuous aspiration under the same instrumental conditions. Therefore, 100  $\mu\text{L}$  of sample solution was chosen for single analysis.

### 3.8. Analysis of certified reference materials (CRMs)

The proposed method was applied for ultratrace determination of the studied metal ions in CRMs. For this, 2.0 g of Tibet soil (NCS DC-78302) was digested with 20 mL of 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> and filtered. The filtrate and wastewater (BCR-715) (3.0 mL) were diluted to 1000 mL with water. The sample solutions were preconcentrated and then subjected to MIS-FAAS according to the proposed method.

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