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Preparation of ECH-PCCB for the Pre-concentration and Determination of Cadmium (II) Ions Prior to FAAS by FIA

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Abstract

In this study, epichlorohydrin pumice-chitosan composite beads structures were used for the first time as mini-column filling material in a flow injection analyses added to the atomic absorption spectroscopy for the pre-concentration of cadmium ions. This method is simple, accurate and highly selective for pre-concentration of Cd(II) in water samples. Surface analysis of epichlorohydrin pumice-chitosan composite was performed by scanning electron microscopy. Elution of Cd(II) ions from the column was achieved with 0.1 mol L^{-1} EDTA. Some parameters affecting the pre-concentration of Cd(II) ions, such as sample loading time, sample flow rate, eluent type and concentration, pH, and interference ions were investigated. Under the optimized parameters, the enrichment factor was 23 and the detection limit of the method was 16 µg L^{-1} as a result of pre-concentration studies with epichlorohydrin pumice-chitosan composite.

Keywords: Cd (II), Flow injection analyses, Pumice-chitosan composite beads, Online pre-concentration.

1. Introduction

Due to the highly toxic effect of cadmium ions even at trace levels, pre-concentration and determination studies have gained increasing importance worldwide. The WHO and EPA limit for cadmium ions in drinking water is 0.003 mgL^{-1}-0.005 mg L^{-1} [1], as a result, detection of low amounts of cadmium ions is very important. Rapid progress in industry, irregular urbanization, and traffic cause water pollution with heavy and toxic metals.

Cadmium and its compounds are pollutants that cause diseases such as kidney dysfunction, lung cancer, hypertension, and prostate cancer. [2-5]. Detection of metal ions in water is very difficult without preconcentration due to low concentrations and matrix interactions. It is advantageous to use a pre-concentration step to detect low cadmium levels in water samples. The pre-concentration technique is fast, reproducible, can be worked in small volumes, and since it is a closed system, it is a method without contamination from external factors [6-8].

Connecting the flow injection system (FIA) to the flame atomic absorption spectroscopy (FAAS) online is an important technique for the pre-concentration of cadmium ions in water. Thus, while the specification limits are improved, the interference from the matrix is also reduced. The analytical efficiency of the method increases [9]. FIA online pre-concentration techniques have some advantages for trace determination of Cd(II) ions, such as low substance consumption, high efficiency, convenience, no contamination [10-12]. Therefore, prepared new adsorbent in (flow injection) FI pre-concentration techniques are very important.

The limit of detection can be lowered using simple pre-concentration FAAS such as Pumice-chitosan composite beads (PCCB). Applications of chitosan (CTS) composites for the removal of heavy metal ions aqueous solutions were reviewed [13-18]. However, no pre-concentration study of Cd (II) PCCB has been reported in the literature so far. PCCB as a novel and great adsorbent in on-line pre-concentration technique.

Chitosan (CTS) is a natural polysaccharide containing high levels of amino and hydroxyl groups and is formed by deacetylation of chitin. CTS is a suitable adsorbent in wastewater treatment due to its low toxicity, biocompatibility, and biodegradability.

Pumice is a volcanic material that has a rough surface and a porous structure, providing multiple bonding sites with metal ions. Therefore, it has a good efficiency for the removal of cadmium ions. Pumice stone is a porous igneous volcanic rock, with significant accessibility, which it is abundantly found in nature and considered as an inexpensive adsorbent [19-20].

In this paper, epichlorohydrin pumice-chitosan composite beads (ECH-PCCB) was prepared and tested as column packing for FAAS determination of cadmium ions in water samples by pre-concentration method. All analytical features such as sample loading time, pH, eluent type, concentration of eluent, sample, and eluent flow rates, and the effect of matrix components were studied and are described.

2. Materials and Methods

2. 1. Instrumentation

A Varian Spectra FAAS containing a deuterium background correction system was used for cadmium determination. Heidolph brand peristaltic pump (four-channel) and Tygon tubes were used for the flow of solutions. Rheodyne six-way rotary injection valve was used in the FIA. Hanna P211model pH-meter with combined glass electrode was used for pH measurements. Philips (FEI) XL30-SFEG scanning electron microscope (SEM) was used in the surface characterization studies of ECH-PCCB.

2.2. Reagents and Chemicals

All reagents used in the experiments were of analytical purity. (Sigma and Merck). Double deionized water used in the whole study was purified with 18 MΩ cm Millipore brand distilled water device. Stock solutions of Cd (II) was prepared by dissolving of $Cd(NO_3)_2.4H_2O$ (Merck) into deionized water. All solutions were prepared by dilution daily from stock solutions. Buffer solutions of 0.1 M HCl, $CH_3COOH/NaCH_3COO$, and NaH_2PO_4/Na_2HPO_4 were used to adjust the pH to acidic, weakly acidic and neutral, respectively. EDTA (ex. Merck) HCl and HNO_3 (ex. Merck) were used as eluting solutions.

2.3. FIA System Descriptions

The FIA system consisted of four-line peristaltic pump. Mini-column packed with an ECH-PCCB and injection valve (six-way) were employed. A mini-column with a length of 5 cm and a diameter of 3 mm and connecting hoses with a diameter of 1.5 mm were used. Figure 1a shows the peristaltic pump, six-way valve, mini-column, and sample transport to the FAAS system.

Preparation of ECH-PCCB

CTS powder (2g) was dissolved in CH_3COOH (100 mL) (2% v/v) solution. This mixture was stirred for 2 hours until homogeneous. Pumice stone was crushed to fine size in agate mortar. It was sieved to 100 mesh size. 20 g of pumice stone was soaked overnight in 30 mL of distilled water. The pumice chitosan mixture was dropped into Tri-Polyphosphate (TPP) with a pH adjusted to 8.2 using a syringe needle. The beads were mixed for 4 hours to harden. The filtered and washed beads were dried at 40°C for 12 hours and placed in a desiccator. 50 mL 2.0 M NaOH, 0.266 g $NaBH_4$ and 5 mL of ECH were added and the beads were crosslinked for 15 hours at 37°C. After the cross-linking process was completed, the PCCB, washed and filtered, were dried in an oven set at 50 degrees. The ECH-PCCB particle size were 100-150 µm.

2.4. Preparation of ECH-PCCB Column

The pre-concentration mini-column for retaining cadmium was prepared by polytetrafluoroethylene(PTFE) with ECH-PCCB. A tygon tube with a radius of 5.0 mm and a size of 6.0 cm was used. Before placing the pumice CTS adsorbent into the tube, glass wool was placed at the bottom, and glass wool was placed on the top to prevent spillage after the ECH-PCCB was placed. The amount of ECH-PCCB in the tube was 0.020 grams.

Pre-concentration Methods:

FIA pre-concentration consists of three steps: enrichment step, washing step and elution step. First step (Pre-concentration): 50 µg of L^{-1} cadmium solution or sample solution was carried out the system for 2 minutes. Second step (Washing): Pure water was passed through the system for 30 seconds for washing. (Figure 1 a). Since this stage is the loading stage to the column, the solution passing through the mini-column goes to waste. Meanwhile, the FAAS signal was not measured.

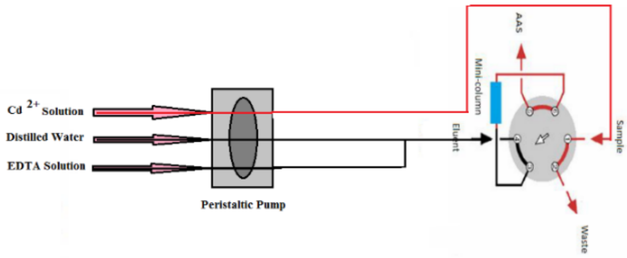

Figure 1. a. Sample Load Position

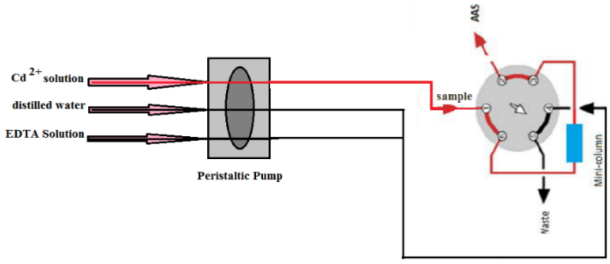

Figure 1. b. Eluting Position

Third step (Elution): starts after 2.5 minute of pre-concentration. The valve was moved to the third position and the eluent was directed to the mini-column.

At this stage, the solutions carry to the FAAS system, and the signal was read. After measuring, the valves were returned to their starting position so that the next sample could be enriched (Figure 1 b).

3. Results and Discussion

3.1. Characterization of ECH-PCCB

In the studies, ECH-PCCB synthesized to be used as mini-column filling material were taken under scanning electron microscope. In Figure 2 a show the SEM image of natural pumice stone [20], b) ECH-PCCB(x1000) c) ECH-PCCB(x250) d) ECH-PCCB(x100). While the surface of the natural pumice stone appears flat in figure 2 a, the surface of the ECH-PCCB is recessed and porous as shown in figure 2 b. Increasing the pore size of the surface also increases the adsorption ability of pumice and enables the evaluation of pumice material, which is abundant and cheap in nature.

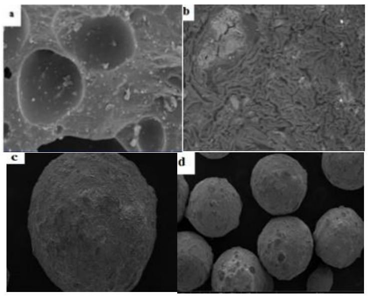

Figure 2. a. SEM image of natural pumice stone [20] **b)** ECH-PCCB (x1000) **c)** ECH-PCCB (x250) **d)** ECH-PCCB (x100).

3.2. Batch Studies

3.2.1. Adsorption and Desorption Studies

In batch experiments, 25 mL of 20 mg L^{-1} Cd (II) solution was transferred into a 50 mL beaker and 0.1 ± 0.0002 g of natural pumice powder, chitosan beads and ECH-PCCB were added. ECH-PCCB and Cd (II) solution was shaken for 10 minutes to ensure the adsorption of metal ions to the sorbent. It was filtered by decantation. The filtrate was measured at FAAS. Adsorbed natural pumice powder, CTS beads and ECH-PCCB were washed with distilled water. Since the most used desorbents in our previous studies and literature are EDTA, HNO_3 and HCl, the performance of these three solutions as elution solutions has been investigated. The washed adsorbents were added to the beaker containing 25 mL of 0.1 M EDTA and 0.1 M HNO_3 and stirred in a magnetic stirrer for 10 minutes. Decanted filtrate was measured at FAAS. For adsorption and desorption processes, two parallel beads were studied from each bead species. % Adsorption and % Desorption values for the best adsorbent selected in the preliminary experiments the calculations were carried out with the following equations;

$$\%\,A = \frac{Ci-Ce}{Ci}x100 \qquad \textbf{(3.1)}$$

where Ci and Ce are the initial and equilibrium concentrations of Cd (II) ion, respectively.

$$\%D = \frac{amount\ of\ desorbed\ metal\ ion}{amount\ of\ adsorbed\ metal\ ion}x100 \qquad \textbf{(3.2)}$$

The results were given in Table 1. As a result, adsorbent was chosen to be used as mini-column filler material in flow injection analysis for the best results ECH-PCCB. Since it can be desorbed 90% of Cd (II) ions, EDTA has been chosen as eluent in FIA.

Table 1. Comparison of adsorption and desorption % of column fillers.

Epichlorohydrin cross linked pumice-chitosan composite beads	Adsorption (%)	Desorption (%) EDTA
1	89.40	90.00
2	89.36	88.95
3	89.30	88.93
4	89.30	88.89

To measure the repeatability of the adsorbent, the best adsorbent was determined by repeating the adsorption and desorption processes and the results were given in Table 2.

Table 2. Reusability of adsorbent

	Adsorption (%)	**Desorption (%) HNO_3**	**Desorption (%) EDTA**
Natural pumice stone powder	48.6	50.0	51.1
Chitosan beads	60.6	70.6	63.0
Epichlorohydrin cross linked pumice-chitosan composite beads	89.4	87.6	90.0

3.3. FIA Studies:

3.3.1. Optimizing Sample and Eluent Flow Rate

The effect of Cd (II) ions on the pre-concentration of the column was investigated by experiments with sample and eluent flow rates set to 1.5, 3.0, 4.0 and 6.0 mL min^{-1}. Recovery values for ECH-PCCB decreased after 1.5 mL min^{-1} (Figure 3). 1.5 ml min^{-1} was chosen as the sample and eluent flow rate, since the highest recovery value.

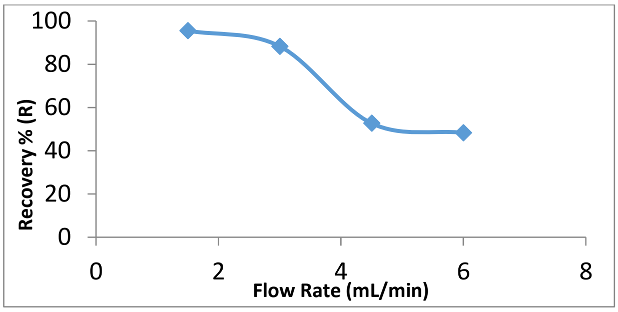

Figure 3. Effect of Sample and Eluent Flow Rate.

3.3.2. Optimizing Sample Load Time

In the studies carried out for ECH-PCCB filled mini-column, the system was first passed through distilled water for 30 seconds. Then 50 µg L^{-1} Cd (II) solution was sent to the system for 0.5-1-2-3 minutes and passed through the mini-column. Then, the eluent was passed and the FAAS signals were read. Experimental results for optimization of sample loading time are given in Figure 4. The optimum time for loading ECH-PCCB filled mini-column for Cd (II) was determined as 2 minutes.

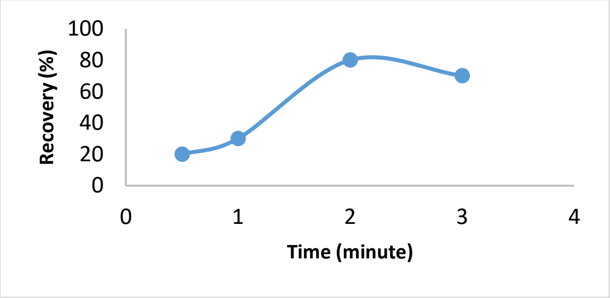

Figure 4. Effect of Sample Loading Time.

3.3.3. Determining of Eluent Type

The Cd (II) solution prepared at the appropriate concentration was carried out the column at the determined optimum minute (2 minutes).

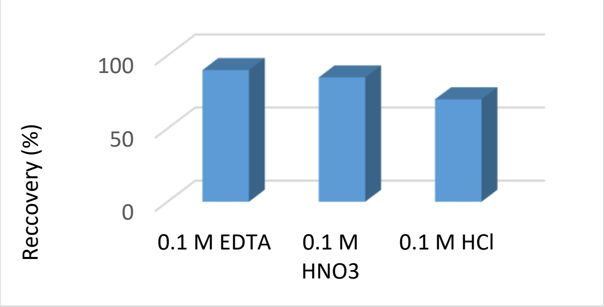

Figure 5. Effect of Eluent Type.

Then, 0.1M EDTA, 0.1M HNO$_3$ and 0.1 M HCl solutions were passed through the mini-column to select the appropriate eluent and the signal value at FAAS was read. Results obtained from the studies to determine the eluent type are given in Figure 5.

90% recovery was found by using EDTA for eluting. For cadmium (II), EDTA was chosen as the most suitable eluent for loading into ECH-PCCB filled mini-column.

3.3.4. Optimizing of Solution pH

The effect of pH on recovery value were investigated. Buffer solutions in the range of pH 3.0 to pH 8.0 were prepared. Signals were determined by FAAS for each pH. The results are given in Figure 6. At pH <6 the free ion Cd^{2+} is the predominating species. The main species at pH 9.5 are Cd(OH)$^{+}$ and at pH =8.0 Cd(OH)$_2$ thus the removal of Cd^{2+} is possibly accomplished by simultaneous precipitation of Cd(OH)$_2$ and sorption of Cd(OH)$_2$. For cadmium (II), the optimum pH for loading into ECH-PCCB filled column was determined as 5.0. At this pH value the adsorption of Cd (II) ions was not masked by precipitation.

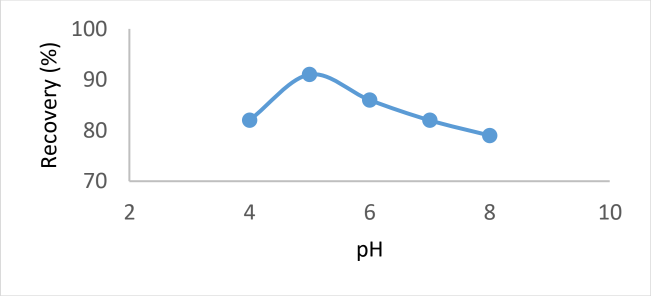

Figure 6. Effect of pH.

3.3.5. Effect of Interfering Ions

The effect of trace metals such as Na^{+}, Ca^{2+}, Mn^{2+}, Pb $^{2+,}$ NH$_4^{+}$, Al^{3+}, Zn^{2+}, which are thought to interfere in the pre-concentration of Cd (II) ions, was investigated. These species were added to the Cd (II) solutions in a 100-fold excess and the pH was adjusted to 5.0. The results are given in Table 3.

$$LOD = \frac{3xS_{blank}}{m} \quad \textbf{(3.3)}$$

$$LOQ = \frac{10xS_{blank}}{m} \quad \textbf{(3.4)}$$

LOD: Limit of Detection
LOQ: Limit of Quantification
The LOD of the analyte determined was calculated. The LOD of Cd (II) ion was found to be 16 µg L^{-1} and the LOQ measurement was 31 µg L^{-1}.

Table 3. Effect of Interfering Ions.

Ions	Concentration (µg/L)	Recovery (%)
		Cd^{2+}
Na^{+}	200.0	35± 1
Ca^{2+}	200.0	45 ± 1
Mn^{2+}	200.0	65 ± 1
Pb^{2+}	200.0	21 ± 1
NH_4^{+}	200.0	35± 1
Al^{3+}	200.0	41± 1
Zn^{2+}	200.0	64± 1

The equation of the obtained calibration curve was found as $y = 0,0396x + 0.0104$. R^2 was found as 0.9109. The RSD was found 3% for five replicate separate mini-column measurements. Table 4 shows general performance values for reported literatures for Cd (II) ion analysis.

3.3.6. Determination of Cadmium, in Water Samples

The application of this method developed for the pre-concentration of cadmium ions has been tested in tap water samples. The recovery results obtained were given in Table 5. According to the results repeated 3 times, the recovery was in the range of 96.8–99.4% as shown in Table 5. It demonstrated the suitability of the ECH-PCCB for the pre-concentration of Cd (II) from water samples prior to FAAS analysis.

Table 4. Analytical Performance Values for online Pre-concentration Analysis for Cd (II).

Adsorbent	Working range	Limit of detection	Pre-concentration factor	Ref.
Sulphoxine Chitosan	5–25 µg L^{-1}	0.2 µg L^{-1}	13.9	[21]
Chitosan with complexing agent 8-hydroxyquinoline:	10–40 µg L^{-1}	0.1 µg L^{-1}		[22]
Functionalization of chitosan with 2-aminopyridine-3-carboxylic acid		0.021 µg L^{-1}		[16]
XAD-4-2,6-dihydroxy phenyldiazoaminoazobenzene	0.3–100 µg L^{-1}	0.1 µg L^{-1}	42	[10]
Modified silica gel-chitosan	0.45 mg L^{-1} to 2.5 mg L^{-}	20 ngL^{-1}	166.7	[17]
Cross-linked chitosan functionalized with 2-amino-5-hydroxy benzoic acid moiety (CCTS-AHBA resin)	0.01–5 ppb	0.006 ppb	21.6	[23]
Epichlorohydrin cross linked pumic stone	50-250 µg L^{-1}	16 µg L^{-1}	23	This Study

Table 5. Recovery of Cd(II) in water samples.

Sample Water	**Cd (II) added (µg L^{-1})**	**Cd (II) found (µg L^{-1})**	**Recovery (%)**
Tap Water	50.00	49.68 ±0.14	99.36
Tap Water	70.00	67.75 ±0.20	96.78

Conclusion

The newly synthesized ECH-PCCB were found to be effective for the adsorption of Cd (II) ions prior to its atomic absorption spectrophotometric determination. The ECH-PCCB were characterized using SEM images. The developed method provided good accuracy to determine Cd (II) in samples of tap water, according to the results of recovery tests. The LOD was found to be 16 µg L^{-1}. This method is recommended as an inexpensive analytical pre-concentration technique for the determination of trace Cd (II) ions in water samples.

Author's Contributions

Vedia Nüket Tirtom: She did the planning, analytical evaluation and interpretation of the trials and ensured that the results were reported.
Fatma Özkafalı: Performed the experiment and result analysis.

Ethics

There are no ethical issues after the publication of this manuscript

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