# A GREEN APPROACH USING XYLENOL ORANGE ANCHORED AMBERLITE XAD-16-A NEW SORBENT MATERIAL FOR ON-LINE SOLID PHASE EXTRACTION OF CADMIUM IN WATER SAMPLES BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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# ABSTRACT

A simple, sensitive and inexpensive flow injection solid phase extraction (SPE) system is developed for automatic determination of trace level concentrations of Cd(II). The potentials of this novel scheme, coupled to flame atomic absorption spectroscopy (FAAS) is demonstrated for trace Cd(II) in natural water samples. The Xylenol Orange immobilized on Amberlite XAD-16 has been synthesized and is used for on-line preconcentration of Cd(II) with a flow injection–flame atomic absorption spectroscopy (FL-FAAS). All main chemical and hydrodynamic parameters affecting the complex formation, sorption and elution of the analyte were optimized thoroughly. The results demonstrated that Cd(II)can be determined using sample pH of 4.5 – 5.0, elution with 0.5 mol L<sup>-1</sup> nitric acid and a sample flow rate of 5.0 mL min<sup>-1</sup>. Moreover, the effect of potential interfering species occurring in natural water samples were also explored. Enrichment factor of 171 was achieved by using the time-based technique with preconcentration period of 180s. Detection limit (3s) was  $0.13\mu g L^{-1}$  when used preconcentration time of 180s. A good precision (relative standard deviation) of 3.36% at  $20\mu g L^{-1}$  for Cd(II) was obtained. The method was applied to natural water samples, and accuracy was assessed through recovery experiment. The spiked recovery studies in water samples was performed by certified Cd(II) nitrate solution traceable to NIST. Accuracy of proposed preconcentration procedure was confirmed by Cd(II) determination in standard reference material(SRM-1643e) supplied by NIST Gaithersburg, MD, USA.

Keywords - Atomic Absorption Spectroscopy, Online Flow Injection, Preconcentration, Amberlite XAD-16, Xylenol Orange, Cd(II).

# **I INTRODUCTION**

Determination of metal ions in different samples such as water, food, soil and biological material is a very important part of environmental studies. Contamination of the aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain. Cd(II) is a heavy metal with the greatest potential hazard to humans and the environment due to its acute toxicity. Cd(II) is absorbed more efficiently by the lungs than by the gastrointestinal tract, It is transported in the blood and widely distributed in the body but accumulates primarily in the liver and kidneys. It can also cause bone demineralization. Environmental Protection Agency (EPA) established the maximum permissible limit 5  $\mu$ g L<sup>-1</sup> for Cd(II) in drinking water[1]. Cd(II) metabolism and toxicology are of great concern and it can undergo biomagnifications besides its high toxic potential. Therefore it is important to determine this element in food, water and biological materials. However, the direct determination of metal ions at trace levels is limited, due to their low level of concentration and matrix interferences. Flame atomic absorption spectrometry (FAAS), which has been continuously used for the determination of trace metal ions, suffers from insufficient sensitivity for

direct determination of metal ions in environmental samples. Therefore, a preconcentration step is necessary to improve the limit of detection and sensitivity. Among the various methods, solid-phase extraction has gained more importance due to its simplicity, rapidity, and a large preconcentration factor. The methods widely used for preconcentration are based on coprecipitation[2], electrodeposition[3], liquid-liquid extraction[4], membrane filtration[5], cloud point extraction[6], ion exchange or solid phase extraction (SPE)[7]. The ion exchange resins have shown better metal ion separation but with conventional resins the selectivity factor and preconcentration factor is relatively low, this problem can be overcome by chemical bonding of a suitable moiety to the solid substrate. So chemically bonded chelating agents on suitable solid supports would be appropriate medium for ion separation and preconcentration. Chelating resins obtained by immobilization of organic reagents on solid polymeric support have wide spread application in preconcentration of trace metals from a variety of matrices. Development of chelating materials for solid-phase extraction has gained special attention due the advantages in the use of these substances in metal ion enrichment. These advantages include high degree of selectivity by controlling the pH, versatility, durability and good metal loading capacity and enhanced hydrophilicity[8]. Chelating ligands have been functionalized in several materials, such as silicagel[9], polyurethane foam[10], cellulose[11] and styrene-divinylbenzene copolymer, commercially available as Amberlite XAD resin series[12,13]. The use of Amberlite XAD resins with large surface area and macroporous structure convenient for preconcentration, isolation and chromatographic separation of various compounds is an improvement over activated carbon because they are more suitable for elution and are free from contamination risks. In addition Amberlite XAD resins present greater adsorption capacities and easier elution than alumina, silica gel etc. Many ligands, such as nitrosonaphthol[14], salicylic acid[15], o-aminobenzoic acid[16] and 3,4dihydroxybenzoic acid[17], 1-(2-pyridylazo)-2-naphthol[18], Xylenol Orange[19] were covalently coupled with a polymer backbone through an azo group (-N= N-). Automation of sorption separation procedure is very opportune for determination of trace metals due to its flexibility, simplicity, high sampling rate and versatility which allow the method to be used in conjunction with different spectrometric detectors. The combination of on-line systems with flame atomic absorption spectroscopy(FAAS) show good effects, such as strong tolerance to high concentrations of dissolved solids, use of organic solvents can enhance sensitivity and high selectivity of the detection technique[20,21]. Generally, two simple steps, loading and elution, are used in most procedures. Online column packing found on literature include activated carbon[22], silica[23], Cellex-P[24], alumina[25], polymeric resins like Amberlite XAD-4[26] and Amberlite XAD-2 loaded Xylenol Orange[27].

This paper proposes an analytical procedure for determination of trace Cd(II) by FAAS after preconcentration and separation of Cd(II) in natural water samples using a minicolumn packed with sorbent Amberlite XAD-16 resin loaded with Xylenol Orange. In the present paper we also described the synthesis and characterization of a Xylenol Orange grafted XAD-16 resin which is highly effective towards the removal of Cd(II).

#### **II EXPERIMENTAL**

#### **2.1 Instrumentations**

A PerkinElmer (Shelton, CT, USA) Model AAnalyst<sup>™</sup> 400 flame atomic absorption spectrometer, coupled with the FIAS<sup>™</sup> 400 flow injection system, was used for the automatic processing of the method and operated in the preconcentration mode. The whole system was controlled by a personal computer and Winlab32<sup>™</sup> (Version 6.5.0.0266) application software. The on-line flow injection preconcentration system coupled with FAAS. The

FIAS 400 preconcentration system comprises two peristaltic pumps, two positional valves, and a preconcentration column[28]. Two Tygon® R3607 red-red pump tubes (i.d.1.14 mm) were applied for both pumps in most of the experiments. The pH measurements were made with a Model LI614 pH meter (Elico Ltd., India). An IR spectrum was recorded on a PerkinElmer Model Spectrum RX-1. CHNS was carried out on a Model Varo EL-III Elementor. Thermal analysis was performed with a PerkinElmer Model Diamond DSC. SEM was carried out using Scanning Electron Microscope model FEI Quanta 200F.

## 2.2 Materials and reagents

A 1000 mg  $L^{-1}$  stock solution of Cd(II) was prepared from analytical reagent-grade Cd(II) nitrate in doubly distilled water obtained from a double distillation unit and standardized titrimetically with EDTA before use. Standard solutions were prepared by dilution of the stock solutions with doubly distilled water. The pH adjustments were made with 0.1 mol  $L^{-1}$  HCl, 0.1 mol  $L^{-1}$  NaOH, 0.1 mol  $L^{-1}$  acetic acid-acetate buffer (pH 4 and 5), 0.1 mol  $L^{-1}$  phosphate buffer (pH 6 and 7), and 0.1 mol  $L^{-1}$  ammonia-ammonium chloride buffer (pH 8 and 9). All laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution and washed before use with doubly distilled water. The Amberlite XAD-16 resin (Sigma–Aldrich) has a surface area of approximately 800 m<sup>2</sup>/g, moisture holding capacity of 62–70%, particle size of 20–60 mesh, pore diameter of 100 Å (mean pore size), and a pore volume of 1.82 mLg<sup>-1</sup>. Xylenol Orange used was of analytical reagent grade. All analytical reagents were procured form either E. Merck (Darmstadt, Germany) or Thomas Baker (India). Certified Pb(II) nitrate solution, traceable to NIST, was procured from E. Merck. Water samples were collected from Mayapuri area, Naraina, Delhi and Noida, U.P. in Delhi, India. Certified reference material (SRM-1643e), Trace elements in water was supplied by NIST Gaithersburg, MD, USA.

# 2.3 Synthesis of Amberlite XAD-16 loaded with Xylenol Orange-AXAD16-XO (Solid phase extractor)

The styrene-divinylbenzene copolymer was modified according to the procedure reported in the literature[29]. The synthesis involves nitration of XAD-16, followed by the reduction to form an aromatic amine. This amine facilitates the formation of a stable diazonium salt. The diazotized resin was treated with Xylenol Orange at 0-3 °C. The diazotized AmberliteXAD-16 was filtered at -5 to 0°c to avoid its disintegration at higher temperature and treated with Xylenol Orange for 24 h. The resulting dark brown coloured beads were filtered, washed with 4M HCl and doubly distilled water successively and finally air-dried. The proposed structure of Amberlite XAD16-Xylenol Orange(AXAD16-XO) shown in Fig. 1



# Fig.1 Proposed structure of Amberlite XAD-16 functionalized with Xylenol Orange resin 2.4 Preparation of minicolumn

Amberlite XAD-16 loaded with Xylenol Orange resin(130 mg) was packed in a mini glass column (30 x 3.0mm i.d.). The two ends of the column were sealed with cotton. It was treated with 2.0 mol  $L^{-1}$  HNO<sub>3</sub> and was washed with double-distilled water until the resin was free from acid. A suitable aliquot of the solution containing Cd(II)

in the concentration range 20-50  $\mu$ g L<sup>-1</sup> was passed through this column after adjusting its pH to an optimum value The column had a constant performance during all experiments and there was no need for any regeneration or repacking.

#### 2.5 The design of flow injection system for online preconcentration of Cd(II)

The flow injection manifolds used were connected directly to the nebulizer inlet tubing which is two line FImanifold system [28] and a two step procedure. It is used both for preconcentration and determination of Cd(II). Acid resistant tubes (tygon) were used to pump the sample through the minicolumn with peristaltic pump P1, peristaltic pump P2 used for elution of enriched Cd(II) on Amberlite XAD16 – Xylenol Orange resin complex with HNO<sub>3</sub> at an optimum flow rate of 5.0mL min<sup>-1</sup> and then subjected to flame atomic absorption spectrometric determination. Calibrations were linear in the range 1.6-60  $\mu$ g L<sup>-1</sup> of Cd(II). In a similar manner, unknown sample solutions were also carried out for Cd(II) analysis and the amount was determined with reference to the calibration graph. Three series of measurements were carried out for every standards and sample solution. Each measurement was followed by a blank check. FI-FAAS set was controlled by a computer program[28, 30] which includes pre-filling, filling, loading and elution step. Each preconcentration cycle starts with a short loading and elution step performed to filled the tubes. Loading time was 60 s for experiment. Elution includes 30s reading time. During the sample loading step, 10 s before the valve was moved to the elution position , the signal readings were stabilized with the eluent solutions. The flow rate in the elution step was set at 5mL min<sup>-1</sup> to ensure recovery of maximum metal. Absorbance peak was recorded and its height was the analytical signal.

# **III RESULTS AND DISCUSSION**

# 3.1Characterization of the Amberlite XAD-16 functionalized with Xylenol Orange (AXAD16 – XO) chelating resin

#### 3.1.1 FT-IR spectrum of AXAD-16-XO resin

FT-IR spectrum of AXAD-16-XO resin(Fig. 2) has additional bands at 3424 cm<sup>-1</sup> (O-H stretching), 2924 cm<sup>-1</sup> (C-H), 1630cm<sup>-1</sup> (COO<sup>-</sup>), 1536cm<sup>-1</sup> (N=N), 1350 cm<sup>-1</sup> (C-N) and 1265 cm<sup>-1</sup> (C-OH aromatic). This supports the loading of Xylenol Orange onto Amberlite XAD-16 with diazotized (N=N) coupling.



Fig. 2 FT-IR spectra of (a)Amberlite XAD-16 functionalized with Xylenol Orange (b) Xylenol Orange and (c) Amberlite XAD-16

### 3.1.2 Thermogravimetric analysis (TGA)

The thermogram of freshly prepared AXAD16–XO resin showed a very slow but steady weight loss up to  $600^{\circ}$ C. Up to  $130^{\circ}$ C the observed weight loss is 15.3%, this is due to the removal of physisorbed water on the

resin, which supports the presence of eight water molecules per repeat unit of chelating resin. This may be due to very big size of Xylenol Orange. It is reasonable to assume that with each ring one dye molecule is covalently bonded through an azo group. Most probably it occupies a position para to the –CH-CH<sub>2</sub>–group, owing to electronic effect and steric reasons.

# 3.1.3 CHN elemental analysis

Elemental analysis provides a means for the rapid determination of carbon, hydrogen, and nitrogen in organic matrices and other types of materials. The C H N % in AXAD16 – XO resin was found to be Carbon, 47.35%; Hydrogen, 5.07%; Nitrogen, 5.37%; Sulfur, 3.20; while calculated for  $C_{39}H_{51}N_2O_{21}SNa_4N_2$  shows Carbon , 45.22%; Hydrogen, 4.93%; Nitrogen, 5.41%; Sulfur, 3.09. This further confirmed that eight water molecules were present per repeat unit of chelating resin.

#### 3.1.4 Scanning electron microscopy (SEM)

Micrographs (Fig.3) reveals that the resin AXAD16 – XO has a rougher surface than Amberlite XAD-16 implying that the substrate surface was changed after the functionalization with Xylenol Orange. Also, the SEM image of XAD-16- Xylenol Orange shows dense microstructures and granular grains. They are agglomerated polymeric materials with irregular shapes and size varies from 130 µm to 200µm



Fig. 3 SEM images (a) Amberlite XAD-16 (b) Amberlite XAD 16-Xylenol orange resin

# 3.2 Optimization of reaction and concentrating condition

The FL on-line preconcentration system was optimized in order to obtain the best chemical and flow conditions for Cd(II) determination with good sensitivity and precision. These variables include sample pH, sample loading flow rate and time. In order to examine the influence of concentration of Cd(II) solution, a series of different concentration of Cd(II) solution in range of 1.6-60  $\mu$ g L<sup>-1</sup> were tested. The absorbance increased with increasing the concentration of Cd(II) solution. Cd(II) concentration of 20  $\mu$ g L<sup>-1</sup> was chosen for further experiments. **3.2.1 Effect of pH** 

The effect of pH plays a major role in the preconcentration studies, due to this the influence of pH was investigated at the pH ranges 2-11 with  $20\mu g L^{-1}$  of Cd(II) solutions keeping other parameters were constant. The result is presented in Fig.4. The results of this study showed that metal ions were completely adsorbed on the adsorbent over the pH range of 4.5-5.0. Therefore, pH 5.0 was selected as the optimum pH for further studies. As can be seen from the figure, increasing pH led to an increase in the amount of metal ion adsorbed. This indicates that the adsorption process involved the release of H<sup>+</sup> ions to allow the firm complexation of metal ions to AXAD16-XO.

Reaction scheme is as follows :

 $M^{2+}$  + 2 Xylenol Orange  $\rightarrow M$  (Xylenol Orange )  $_2$  + 2 $H^+$ 

#### 3.2.2 Effect of sample flow rate

As the retention of analytes on the adsorbent depends upon the flow rate of the sample solution. The effect of flow rate was examined under pH 4.5 by the sample solution through the mini column with the flow rate carrying in the range of 2-7 mL min<sup>-1</sup>. The quantitative recoveries of metal ions were obtained with a flow rate of 5mL min<sup>-1</sup> (Fig. 5) was observed in sample. At higher flow rates, backpressure is produced by the mini column. Besides, the analytical signal decreased owing to short residence time of ions, which resulted in an incomplete retention. Otherwise, low flow rates decreases sample throughput resulting in a long time of analysis. In order to improve analytical efficiency, 5.0 mL min<sup>-1</sup> was chosen as the loading rate for Cd(II). Studies on the influence of preconcentration time for Cd(II) show that analytical signal increased almost linearly up to 180 s. This indicates that the transfer phase factor is constant within this time interval. Higher preconcentration times could be beneficial to the determination of the samples with lower Cd concentrations. However, long periods are not interesting for FI preconcentration systems. Preconcentration times of 60 s was used for the determination of Cd(II) in water samples.



# Fig. 4 Effect of pH

Fig. 5 Effect of sample flow rate

# 3.3 Optimization of Eluting condition

## 3.3.1 Effect of Eluent Concentration

The effect of nitric acid concentration was studied in the range of  $0.1-1.5 \text{ mol } L^{-1}$ . The results show (Fig. 6) that with increase in the nitric acid concentration up to  $0.5 \text{ mol } L^{-1}$ , absorbance increases and then decreases at higher concentrations. Therefore, nitric acid  $0.5 \text{ mol } L^{-1}$  was chosen as eluent, while the elution time was fixed at 30 s in order to ensure the complete elution of adsorbed Cd(II) ions even at high concentrations.

## **3.3.2 Effect of Eluent flow rate**

The influence of eluent flow rate in the elution step was also studied within the range 2.0-7.0 mL min<sup>-1</sup>, because it establishes the velocity of acid solution through the minicolumn. Results obtained shown that the analytical signal is maximum at eluent flow rate of 5.0 mL min<sup>-1</sup> (Fig. 7) Considering that the total time of elution was 30s, the volume of eluent is 2.5 mL.





Fig. 4 Effect of eluent concentration

Fig. 6 Effect of Eluent flow rate

#### 3.4 Analytical performance of the Flow Injection on-line method for Cd(II)determination

The proposed method provided a calibration graph which gave good linearity over the concentration range of  $1.6-60 \ \mu g \ L^{-1}$  of Cd(II), with linear equation of  $A_{60}$ = 0.04799 + 0.02297[Cd(II)] and correlation coefficient(r) = 0.995964. The limits of detection for 60,120 and 180 s were found to be 0.48, 0.38 and 0.13 respectively. The limit of quantification is defined as concentration that gives a response equivalent to ten times the standard deviation of the blank and it is 0.43  $\mu g \ L^{-1}$  for 180 s preconcentration time. The precision of the method was evaluated in terms of repeatability by determining Cd(II) concentrations of 20 and 50  $\mu g \ L^{-1}$ , where relative standard deviations of 3.36 and 2.79% were obtained respectively. As the preconcentration time increases the detection limits and enrichment factors will increase. The method provided an outstanding improvement on detectability based on high enrichment factor (EF) of 59,123 and 171 at 60,120 and 180s loading time, which was calculated by the ratio between the slopes of the calibration curve with and without preconcentration method. A sample frequency of  $30h^{-1}$  was obtained at 60s preconcentration time. Higher sensitivities can be obtained by modifying the method i.e. using longer preconcentration time of 180s at the expense of lower sample throughput  $15h^{-1}$ . Table 1 summarized the optimum experimental conditions for preconcentration of Cd(II) ion and analytical characteristics of the optimized method, including regression equation determining before and after preconcentration method.

## 3.5 Effect of foreign ions in the flow solid-sorbent method

The effects of representative potential interfering species were tested. To check these effects, a standard solution containing Cd(II) and other ions was prepared and Cd(II) was determined using the procedure proposed. The chloride, nitrate, sulfate and phosphate ions commonly found in natural water samples have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the chelating resins to bind metal ions may be hampered resulting in the reduction of overall enrichment.

•	Parameter	Optimum Conditi	on			
	pH Range Sample Flow rate (mL min <sup>-1</sup> ) Eluent Flow rate (mL min <sup>-1</sup> ) Acid conc. for desorption Preconcentration Time (PT, s) Linear range (µg L <sup>-1</sup> ) Limit of detection (µg L <sup>-1</sup> )	$\begin{array}{cccc} 4.5\text{-}5.0 \\ 5.0 \\ 5.0 \\ 0.5 \text{ mol } \text{L}^{-1} \text{ HNO}_3 \\ 60 \\ 1.6\text{-}60 \\ 1.3\text{-}30 \\ 0.43\text{-}20 \\ 0.48 \\ 0.13 \end{array}$	180			
	Sample Throughput ( h <sup>-1</sup> ) Enhancement factor	30         20           59         123	15 171			
	Regression equation (6 standards, n=3; Cd(II) / $\mu$ gL <sup>-1</sup> ) (with preconcentration)	$\begin{array}{l} A_{60} = 0.04799 + 0.02297 [Cd(II)] \\ A_{120} = -0.03931 + 0.04818 [Cd(II)] \\ A_{180} = 0.03822 + 0.06705 [Cd(II)] \end{array}$				
	Regression equation (6 standards, n=3; Cd(II) / µgL <sup>-1</sup> ) (without preconcentration) Correlation coefficient, r Precision (RSD %)	$\begin{split} A &= -0.00066 + 0.000392 [Cd(II)] \\ 0.995964 & 0.994977 & 0.995761 \\ 3.36, [Cd(II)] &= 20 \ \mu g \ L^{-1} \\ 2.79, [Cd(II)] &= 50 \ \mu g \ L^{-1} \end{split}$				

Table 1. Analytic	al perfo	ormance of the	Flow Injection	on on-line metho	d for Cd(II)	determination
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#### Table 2. Effects of matrix ions on the recoveries of Cd(II) ions using AXAD 16-XO resin

Thus, the effect of NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, NaBr, MgCl<sub>2</sub>, citric acid, tartaric acid & ascorbic acid on the sorption efficiency of AXAD16 - XO resin for  $20\mu g L^{-1}$  Cd(II) were studied using the recommended flowinjection column method under the optimum conditions given in Table 2. The tolerance limits for electrolytes are given in Table 2. A species is considered to interfere when it lowers the recovery of metal ions by more than ±5% compared to the value observed in its absence. In general, the tolerance limits suggest that common ions & organic acids like citric acid, tartaric acid & ascorbic acid ions do not adversely affect sorption on the present resin when present in moderate amounts. The results obtained demonstrate that the proposed method is very tolerant to high concentration of foreign ions and helpful for the Cd(II) determination in industrial water sample samples.

Foreign species	Tolerance limit	Foreign species	Tolerance limit	
NaCl <sup>a</sup>	0.3	$Cu(II)^{b}, Zn(II)^{b}$	15	
Na <sub>2</sub> SO <sub>4</sub> <sup>a</sup> , NaBr <sup>a</sup>	0.03	Al(III) <sup>b</sup>	5	
NaNO <sub>3</sub> <sup>a</sup>	0.01	EDTA <sup>c</sup>	0.5	
$Na_3PO_4^a$	0.05	Citric acid <sup>a</sup>	0.2	
$MgCl_2^{a}$	0.02	Tartaric acid <sup>a</sup>	0.2	
NaI <sup>a</sup>	0.1	Ascorbic acid <sup>a</sup>	0.3	
$K(I)^{b}$ , $Pb(II)^{b}$ , $Fe(III)^{b}$ , $Ca(II)^{b}$	10			

<sup>a</sup>mol L<sup>-1</sup>, <sup>b</sup>mg L<sup>-1</sup>, <sup>c</sup>mmol L<sup>-1</sup>

# 3.6 Accuracy of the method

The accuracy of the proposed method was tested by determining the Cd(II) concentration of a certified reference material NIST CRM 1643e (National Institute of Standard and Technology, Trace elements in water). The results are described in Table 3. Confidence intervals are at 95% level. It was found that there is no significant difference between achieved results by proposed method and certified results.

# Table 3. Cd(II) determination in Standard reference material, Trace elements in water

Sample	Cd(II) amount (µg L <sup>-1</sup> ) Recover			
	Certified value	alue Proposed methodology		
SRM1643e, Trace elements in water	6.568 ± 0.073	$6.42\pm0.46$	97.7%	

# **3.7** Application to Cd(II) determination in water samples

The proposed method was applied to the analysis of natural water samples. The samples were collected from Mayapuri, Naraina and Noida. All the water samples were filtered through a 0.45 µm pore-size membrane filter to remove suspended particulate matter and were stored at 4°C. Standard addition method was used in all instances and the results were obtained by extrapolation. The analytical results along with the recovery are summarised in Table 4 and indicated excellent recoveries in all instances.

#### Table 4. Results for the determination of Cd(II) in water sample using AXAD16-XO resin

Sample	Conc. determined <sup>a</sup> $(\mu g L^{-1})$	Conc. determined <sup>a</sup> by 10 μg L <sup>-1</sup> spiked Cd(II) (μg L <sup>-1</sup> )	Recovery (%)
Noida, U.P, India	$9.47 \pm 0.17$	$18.94\pm0.21$	97.2
Mayapuri, Delhi, India	$12.75 \pm 0.14$	$22.62 \pm 0.17$	99.4
Naraina, Delhi, India	$6.98 \pm 0.25$	$16.57\pm0.19$	98.6

<sup>a</sup>Confidence interval 95%

For comparative purposes, the performance characteristics of the proposed method and other selected on-line SPE preconcentration FAAS methods reported in the literature are given in Table 5. The proposed method shows good sensitivity (detection limit), better precision (RSD) and high sample throughput with very high enhancement factor over other on-line preconcentration methods.

# Table 6. Comparison of the performance characteristics among selected on-line SPE methods and the developed

Support	Chelating Agent	PT(s)	Eluent	EF		RSD	Ref.
					(µgL *)	(%)	
Amberlite XAD-2	Pyrocatechol	180	HCl	44	0.27	6.1	31
Amberlite XAD-2	2-aminothiophenol	180	HNO <sub>3</sub>	74	0.14	5.8	32
Amberlite XAD-2	2-(2-thiazolylazo)-5-	60	HC1	108	1.2	9	33
	dimethylaminophenol (TAM)						
Amberlite XAD-2	Xylenol Orange	120	HNO <sub>3</sub>	32	1.038	1.68	34
Amberlite XAD-4	2-aminothiophenol	180	HCl	99	0.3	3.1	35
Amberlite XAD-4	2,6-dihydroxyphenyl-	60	HCl	42	0.1	2.4	36
	diazoaminoazobenzene						
Polyurethane foam	2-(6'-methyl-2'-	180		37	0.80	3.1	37
-	benzothiazolylazo) chromotropic acid						
Polyurethane foam	2-(2-benzothiazolylazo)-2- <i>p</i> -cresol (BTAC)	60	HCl	41	0.27	1-5	38
Chloromethylated	N,N- bis(naphthylideneimino)	120	-	50	0.25	5.1	20
polystyrene	Diethylenetriamine						
Bamboo Charcoal	-	80	HCI	63	0.36	3.2	39
AmberliteXAD-16	Xylenol Orange	180	HNO <sub>3</sub>	171	0.13	3.36	This
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#### One for Cd(II) determination with FAAS.

#### **IV CONCLUSION**

The work described in this paper has shown that adequate sensitivity and accuracy can be attained using an online preconcentration system with a FI-FAAS method. The coupling of an on-line preconcentration system with FI-FAAS increases the speed of the preconcentration and analysis process, and reduces sample consumption and contamination risks. The Amberlite XAD16-Xylenol Orange resin has high sorption capacities and large preconcentration factors for Cd (II) compared with many other analogous resins reported in the literature. The sorbed ions can readily be desorbed with common mineral acids with the percentage recovery of ~99%. The resin could be recycled many times without affecting its sorption capacity and the procedure show high tolerance to interference ions in different water samples. The proposed system of preconcentration associated with FAAS allowed for Cd(II) determination in natural water sample at concentrations as low as  $\mu g L^{-1}$ . The determination procedure shows good reproducibility and accuracy.

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