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INTRODUCTION

The removal of toxic metal ions from the environmental water samples has gained considerable attention because of their adverse effect on the public health and environment. In field of analytical chemistry determination of toxic elements in environmental samples has become a challenge. The toxicity of an element depends on the oxidation state it is present in. Thus chemical speciation has become an important part of analytical studies. The widespread use of chromium in tanning, pigments, electroplating industries has resulted in release of chromium to the water system. The most stable forms of chromium are Cr(III) and Cr(VI). These two oxidation states of chromium exhibits different toxicity to the environment, plants, animals and humans.

Cr(III) is an essential micronutrient for humans as it is involved with the enzymes responsible for maintenance of glucose and metabolism of lipids and proteins, whereas Cr(VI) is considered to be toxic in nature. The toxicity of Cr(VI) arises from its ability to oxidize biological components as it can easily penetrate through biological membranes. Cr(VI) is a known carcinogen owing to its oxidizing properties thus is responsible for diseases like lung and gastrointestinal cancer [1]. The standardized analytical methods for Cr(VI) determination in soils, waste materials, work place atmospheres in industries, etc. have been published by several environmental regulatory authorities such as EPA, OSHA, WHO etc.[2] The permissible limit for chromium in water sample as decided by WHO[3] is 0.05 mg L^{-1}. Various analytical techniques like electro thermal atomic absorption spectrometry (ET-AAS)[4] and flame atomic absorption spectrometry (FAAS)[5], inductive coupled plasma-optical emission spectrometry[6] (ICP-OES), inductive coupled plasma–mass spectrometry (ICP-MS)[7] can be used directly for the determination of total chromium. Out of these techniques FAAS has proven to be an effective technique for determination of chromium species because of its good analytical performance and low cost. The direct determination using these techniques fails to differentiate between Cr(III) and Cr(VI) species. Thus a preconcentration step before the determination is required to separate Cr(III) and Cr(VI). The determination of chromium species is generally done by speciation analysis[8]. Various chromatographic[9] and non-chromatographic[10] methods can also be used for the speciation of chromium species in different systems. Other separation techniques which have been used are electrochemical separation[11] and ion-exchange[12]. Solid phase extraction has been widely used for the preconcentration and speciation of metal ions as this method offers advantages over others like high enrichment factor, simplicity, high recovery, low cost and ability to combine with various detection techniques[13].

Chelating resins as a solid phase extractant have been used widely for preconcentration of metal ions. Separation of analyte of interest using chelating resins is more selective than other separation techniques as the analyte is separated by more than one interaction such as ion exchange, chelate formation and physical adsorption[14]. The formation of chelate is favored in polymeric materials. The offline method of SPE combined with FAAS has been widely used for chromium determination using Amberlite XAD series[15], nanomaterials[16], alumina[17], chitosan[18], etc. as sorbent material. However this offline method of preconcentration has few disadvantages like loss of analyte during analysis, contamination of analyte, large reagent consumption and needs more time. To overcome these disadvantages, online flow injection methods have found application in determination of trace metal ions in water samples. The coupling of flow-injection system to SPE is used to rectify the problems caused by offline system. This system offers advantages like high sampling frequency, low reagent consumption and lower risk of contamination. Also reproducible results with high preconcentration factor can be achieved using Flow injection coupled to Flame Atomic Absorption Spectrometry (FI -FAAS) system. The determination of chromium in various online systems has been proposed involving different supports like polystyrene[19], alumina[20], silica[21]. The use of polymeric support has advantages like hydrophobic character and high surface area. The surface of commercially available polymeric supports like Amberlite[22] and Dowex[23] can be chemically modified by loading them with chelating agents. The modification of the surface of such polymeric supports by chemical immobilization of a chelating agent can increase the selectivity of the resin towards the analyte of interest. In the present work, the solid support used is Dowex Optipore L493, a commercially available polystyrenic resin which offers a surface area higher than most of the other available polymeric resins. Dithizone is an organic chelating agent and is both selective and sensitive for the preparation of sorbent materials for preconcentration of metal ions. Under optimized chemical and flow conditions it can form complex with metal ions [24,25]. Therefore the aim of the present work is to synthesize Dithizone functionalized Dowex Optipore L493 resin as SPE to be used for online preconcentration and speciation of chromium in industrial water samples and determination by FAAS.

EXPERIMENTAL

Instrumentation

AAnalyst400 (PerkinElmer) flame atomic absorption spectrometer (FAAS) with a 10 cm burner head slot was used as detector. The flow rates of acetylene and air used were 3.46 and 9.56 mL min^{-1}, respectively. A chromium hollow cathode lamp (PerkinElmer Lumina HCL) operated at 10mA was used as the light source with wavelength set at 357.9 nm. The flow injection system (FIAS 400, PerkinElmer) consisting of two peristaltic pumps (P1 and P2), a 5-port 2-positional injection valve and a mini-column for preconcentration, was coupled with the FAAS. All fittings and unions were made up of plastic and polyether ether ketone (PEEK) was used for connections of the flow system. The entire online system was controlled by Winlab32^{TM} (version 6.5.0.0266) application software through a personal computer. pH adjustments were done by a pH meter Model LI-614 (ELICO Ltd., India). Infrared spectra were recorded on a PerkinElmer FT-IR spectrometer Model Spectrum RX-1 (resolution 4 cm^{-1}, number of scans 16 and range 400–4000 cm^{-1} SEM images were recorded using Scanning Electron Microscope model FEI Quanta 200F.

Reagents and materials

The polymeric support Dowex Optipore L493 was obtained from Sigma-Aldrich, which has surface area of approximately 1100 m^2 g^{-1} and moisture holding capacity of 50–65%. Dithizone used was of analytical reagent grade. All other analytical reagents were obtained either from E. Merck or Thomas Baker. The standard solution of chromium (III) was freshly prepared by appropriate dilution of 1000 mg L^{-1} $Cr(NO_3)_3.9H_2O$. All solutions were prepared with 18.2 MΩ water from DirectQ3 purification system (Merck Millipore). For pH adjustments, 0.1 M HCl, phosphate buffer (pH 6-8) and trisodium phosphate buffer (pH 11.7) were used. The polypropylene apparatus (POLYLAB) used were washed with 10 % (v/v) nitric acid, rinsed thoroughly with 18.2 MΩ water and dried before use. The method validation was done using Standard reference material NIST 1643e, Trace elements in water, supplied by National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA was used.

Synthesis of Dowex Optipore L493 functionalized with Dithizone (Dz-493)

The synthesis process of SPE, Dowex Optipore L493 was modified according to the procedure already described earlier[26]. The first step of the synthesis involves nitration of styrene–divinylbenzene copolymer, followed by reduction to form an aromatic amine. This amine was then diazotized to form a stable diazonium salt. The diazotized polymer formed was filtered, washed with cold water and then reacted at 0–5 °C for 24 h with 2 g of dithizone, dissolved in 400 mL of water and 200 mL of glacial acetic acid. The brown beads obtained were filtered, washed with double distilled water and stored in desiccator until use. The reaction scheme for the synthesis of Dz-493 is given in Fig. 1.

Packing of minicolumn

The synthesized Dz-493 resin (~ 80 mg) was packed in a mini glass column (3.0 cm length and 3.0 mm internal diameter). With the help of a syringe, the resin was injected into the minicolumn. To close the ends of the column, cotton was used. After that, the column was washed with 2.0 mol L^{-1} HNO_3, and followed by washing with ultrapure water. The column showed constant performance during all experiments, so no regeneration or repacking was required.

On-line preconcentration procedure for determination of Cr(III)

Flow injection-Flame atomic absorption spectrometry (FI-FAAS) manifold is operated by a computer controlled program, which involves the pre-filling, filling, loading and elution steps[27]. The schematic diagram of the on-line preconcentration system using flow injection analysis system (FIAS) is as described in Fig. 2. A program controlled by a computer is operated in a time based mode which provides operational steps optimized for chromium retention. The first step of every preconcentration cycle involves a prefill step to fill the tubes. The filling steps ensure that both the sample and eluent tubes are filled with respective solutions. Then, for loading step of 60 s, 50 μg L^{-1} Cr(III) solution maintained at pH 5 is passed through the Pump 1. The next step involves elution of the retained Cr(III) using 0.1 mol L^{-1} HNO_3, pumped by Pump 2 for elution time of 30 s. The last 10 s of the elution step trigger the reading step in the program. The desorbed Cr(III) is directly carried to the nebulizer of the FAAS during the elution step. The height of the peak (absorbance) was recorded as the analytical signal. Before every measurement, a blank check was done. Three replicates of measurements were taken for both standard and sample solutions.

Total chromium determination

The determination of Cr(VI) was carried out by first reducing it to Cr(III)[28]. 0.1 mL of 5% hydroxylamine hydrochloride was added to 25 mL solution of 50 μg L^{-1} Cr(VI) . After keeping this solution at room temperature for 45 min it was studied according to the procedure optimized for Cr(III). Cr(VI) was then calculated by subtracting the concentration of Cr(III) from total chromium concentration.

General procedure for analysis of industrial water samples

Water samples were collected from three different Industrial places – Anand Parbat, Wazirpur and Seelampur, Delhi, India. The samples were acidified and stored in clean polypropylene bottles. Before preconcentration, the samples were filtered through a 0.45 μm pore size filter paper (Miilipore) to remove any particulate matter, if present. It was then analysed using the proposed preconcentration method. The recovery studies were done by spiking the water samples with certified Cr(III) and Cr(VI) solutions traceable to NIST.

3. Results and Discussion

Characterization of the Dowex Optipore L493 functionalized with Dithizone (Dz-493) chelating resin

FT-IR spectra

The FT-IR spectrum of chelating resin Dz-493 shows bands of Dowex Optipore L493 and dithizone which shows that chelating agent has been loaded onto the resin. The resin has bands at 3375 cm^{-1} (N-H stretching), 2900 cm^{-1} (C–H stretching), 1638 cm^{-1} (C=N), 1530 cm^{-1} (–N=N–), 1430 cm^{-1} (-N=N- dithizone), 1325 cm^{-1} (-C-N-), 1213 cm^{-1} (C=S). This supports the loading of dithizone onto Dowex Optipore L493 through diazotized (N=N) coupling as shown in Fig. 3.

The comparison of FT-IR spectra of Dz-493 resin before and after Cr(III) sorption is shown in Fig. 4. The spectra shows shifting in the peaks of N-H and C=S vibrations of functionalized resin by 5-10 cm^{-1} and is observed at 3368 and 1201 cm^{-1} respectively. In addition to these bands, the FT-IR spectra of Cr(III) metal complex has shown bands at 495 and 385 cm^{-1} which are assigned to Cr–N and Cr–S respectively. This supports complexation of Cr(III) with dithizone.

Scanning electron microscopy (SEM)

SEM uses a beam of highly focused energetic electrons which generate various signals at the surface of solid specimen. The signals arising from the electron-sample interactions give information about the sample which includes texture, crystalline structure, chemical composition etc. The SEM image of pure Dowex Optipore L493 (Fig. 5a) reveals that the unmodified resin has a smooth and flat surface, whereas the SEM image of the synthesized Dz-493 resin (Fig. 5b) shows a dense and rougher surface. This supports the modification of polymeric surface with the chelating agent, viz. dithizone.

Optimization of Chemical and Flow Variables

Chemical Variables

The optimization of chemical variables is an important step, as both pH and eluent concentration plays a crucial role in metal binding. The sorption of a metal ion is dependent on the acidic/basic conditions of the system. The eluent concentration decides the ability to remove the bonded metal ion from the support. Thus, both factors were studied to ensure maximum recovery of Cr(III) ions.

Effect of pH: Sample acidity plays an important role in controlling complexation of Cr(III) and its adsorption on the sorbent. To improve the performance of on-line preconcentration system, absorption of Cr(III) species on the minicolumn was studied over the pH range of 2-10 with 50 $\mu g\ L^{-1}$ of Cr(III) solution, while the other parameters were kept constant. As shown in Fig. 6a, maximum retention of Cr(III) on the minicolumn was achieved at pH 5. Thus, all successive studies were carried out at pH 5.

Effect of eluent concentration: The desorption of sorbed Cr(III) ions was studied using both HNO_3 and HCl. The signals achieved with HNO_3 were better and sharper and so it was used as the eluent. Then effect of the concentration of HNO_3 on desorption of Cr(III) ions was studied in the range of 0.01-2.0 mol L^{-1}. It was observed that initially desorption increased with increase in HNO_3 concentration up to 0.1 mol L^{-1} and then it decreased with further increase in concentration (Fig. 6b). Thus, 0.1 mol L^{-1} HNO_3 was chosen as the eluent for maximum recovery of Cr(III).

Flow variables

The analytical performance of a system is dependent on flow variables like sample and eluent flow rate. The fast sample flow rates results in reduction of contact time between the solid phase and the liquid phase. Thus for better results both eluent and sample flow rates were optimized.

Effect of sample flow rate**:** Sample flow rate is an important factor influencing the retention of Cr(III) species on the sorbent. At higher sample flow rate, the contact time between the solid stationary phase and mobile phase (liquid sample) gets reduced affecting the optimum sorption of Cr(III), whereas low flow rates can result in increase the time of analysis. Thus, for optimum retention of Cr(III) the effect of sample flow rate was studied in the range of 2.0-7.0 mL min^{-1}. It was observed that at flow rate of 5.0 mL min^{-1} maximum absorbance was obtained at, beyond which the absorbance followed a decreasing trend as shown in Fig. 6c. Thus, sample flow rate of 5.0 mL min^{-1} was chosen for all subsequent studies.

Effect of eluent flow rate: The effect of eluent flow rate is an important factor as it governs the recovery of sorbed metal ion. Thus, on the recovery of Cr(III) it was investigated in the range of 2.0-7.0 mL min^{-1}. As shown in Fig. 6d absorbance increased till 5.0 mL min^{-1} and after that it decreases at higher flow rates. Thus for better analytical performance, eluent flow rate was kept at 5.0 mL min^{-1}.

Effect of common interfering ions

The selectivity of proposed preconcentration system towards Cr(III) was examined by studying the effect of common interfering ions in water. Generally, ions such as nitrate, sulphate, chloride, etc. are usually present in natural water. These ions have the ability to complex various metal ions. Thus, their existence can result in decreased efficiency of the chelating resin towards analyte of interest, thereby lowering effective preconcentration. Hence, preconcentration of 100 µg L^{-1} Cr(III) in the presence of different interfering ions was carried out. If the presence of any species deviates the analytical signal by more than ± 5 %, it is considered to cause interference. The results suggest that the presence of high concentration of reported ions have negligible effect on the absorbance of Cr(III). The tolerance limits of these ions for the preconcentration of Cr(III) is given in Table 1.

Table 1 Effect of interfering ions on the recovery of Cr(III) using Dz-493 resin

Interfering Ion	**Tolerance Limit (mg L^{-1})**
NO_3^-	12150
Cl^-	7500
Na^+	6700
CH_3COO^-	2000
I^-	1800
Br^-	1000
NH_4^+	920
K^+	600
Pb^{2+}	250
Ca^{2+}	150
SO_4^{2-}	140
Zn^{2+}	100

Cd^{2+}	85
Mg^{2+}	60
Cu^{2+}	50
Al^{3+}	45

Analytical Performance

Under the optimum conditions, the analytical performance of the proposed FI-FAAS system for Cr(III) preconcentration with Dz-493 resin was carried out and is reported in Table 2. Preconcentration factor, which is calculated as the ratio of the slopes of the calibration curves with and without preconcentration, was found to be 39 and 82, for preconcentration time of 60 and 120 s. The detection limit, which is calculated as three times of standard deviation of the blank was 0.32 and 0.13 ng mL^{-1}. The limit of quantification, calculated as ten times the standard deviation of the blank was 1.06 and 0.43 ng mL^{-1} at 60 and 120 s as sample loading time respectively. The relative standard deviation (reproducibility, $n = 6$) was found to be 1.15% and 1.13% for 50 and 100 µg L^{-1} of Cr(III) solution, respectively.

Table 2 Analytical performance of FI-SPE-FAAS system for Cr(III) determination using Dz-493 resin

Parameter	**Figures of merit**	
Preconcentration Time (PT, s)	60	120
Sample Consumption (mL)	5.0	10.0
Linear range (µg L^{-1})	1.1 – 530	0.4 – 260
Limit of detection (ng mL^{-1})	0.32	0.13
Limit of quantification (µg L^{-1})	1.06	0.43
Sample Throughput (h^{-1})	30	20

Preconcentration factor	39	82
Concentration Efficiency (h^{-1})	1170	1640
Correlation coefficient	0.9999	0.9996
Regression equation (6 standards, Cr(III)/µg L^{-1})	A_{60} = 0.00270[Cr(III)] - 0.00142	A_{120} = 0.00576[Cr(III)] - 0.00377
Regression equation (6 standards, Cr(III)/ µg L^{-1}) (without preconcentration)	A = 0.00007[Cr(III)] - 0.00023	A = 0.00007[Cr(III)] + 0.00025
Precision (% R.S.D.)	1.15, [Cr(III)] = 50 µg L^{-1} 1.13, [Cr(III)] = 100 µg L^{-1}	

Sorption Capacity

The adsorption capacity of Dz-493 resin was studied by shaking 50 mg of the resin with 50 mL of 100 mg L^{-1} of Cr(III) solution at pH 5, for 5 hours. Then, the resin was filtered and the retained Cr(III) was desorbed by shaking the resin with 30 mL of 2 mol L^{-1} HNO_3. The filtrate was suitably diluted and analyzed using pre-calibrated FAAS. The results show that Dz-493 offers a sorption capacity of 31.8 mg g^{-1}, which is much higher in comparison to other systems as shown in Table 3.

Table 3 Comparison of sorption capacities for Cr(III) using different adsorbent

Adsorbent	**Chelating Agent**	**Sorption capacity (mg g^{-1})**	**Ref.**
Activated carbon	Zincon	26.7	29

Amberlite XAD-16	Quercetin	10.14	30
Chromosorb 108	Dithizone	4.5	31
Chitosan-FeC nanoparticles	-	10.5	32
Multi-walled carbon nanotubes (MWCNTs)	Di-(2-ethyl hexyl)-phosphoric acid (D2EHPA)	0.96	33
poly N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene	-	21.8	34
poly(*N*,*N*'-dipropionitrile methacrylamide-*co*-divinylbenzene-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid)	-	12.1	35
Silica gel	Nanometer titanium dioxide	7.04	36
Surfactant coated alumina	8-hydroxyquinoline	1.23	28
Dowex Optipore L493	***Dithizone***	***31.8***	***This work***

Application to Industrial water samples

The developed preconcentration method was applied to three different industrial water samples according to the procedure described in Experimental section. The suggested method was successfully applied for spike recovery studies in industrial water samples using certified Cr(III) and Cr(VI) solution traceable to NIST as shown in Table 4 .

Table 4 Speciation of Cr(III), Cr(VI) and total chromium in various water samples

Sample	Added (ng mL^{-1})		Found (ng mL^{-1}) [c]			Recovery (%)	
	Cr(III)[a]	Cr(VI)[b]	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)
Anand Parbat Industrial Area, Delhi, India	-	-	22.9 ± 1.0	8.4 ± 2.3	31.3 ± 2.2	100.6	97.2
	20	20	43.2 ± 1.3	27.6 ± 1.4			
Seelampur Industrial Area, Delhi, India	-	-	19.2 ± 2.3	5.6 ± 1.7	24.8 ± 1.1	100.0	96.9
	20	20	39.2 ± 2.6	24.8 ± 1.9			
Wazirpur Industrial Area, Delhi, India	-	-	22.5 ± 3.6	8.3 ± 3.7	30.9 ± 0.6	97.1	98.8
	20	20	40.8 ± 2.0	28.0 ± 3.0			

[a] Spiking with Cr(III) solution traceable to NIST

[b] Spiking with Cr(VI) solution traceable to NIST

[c] Confidence Interval 95%

Accuracy of the on-line preconcentration method

To evaluate the accuracy of the proposed method, total chromium concentration of standard reference material NIST SRM 1643e (National Institute of Standard and Technology, Trace elements in water) was tested. The results are given in Table 5 at confidence interval of 95%. No significant difference was found between achieved results by proposed method and standard results.

Table 5 Cr(III) determination in NIST Standard Reference Material 1643e

Sample	Cr(III) amount (μg L^{-1}) [a]		Recovery (%)
	Certified Value	Proposed Methodology	
SRM 1643e, Trace Elements in Water	20.40 ± 0.24	19.63 ± 1.55	96.22

[a] Confidence Interval 95%

Comparison of performance of proposed method with other on-line SPE methods for chromium determination using FAAS

The analytical performance of the suggested method was compared with other selected on-line SPE preconcentration FAAS methods reported in the literature. The comparison with other systems was done in terms of sensitivity (detection limit), precision (RSD) and preconcentration factor. The suggested method was found be better in terms of all. Table 6 gives a comparison of the figures of merit of some reported on-line SPE methods for chromium speciation with the proposed method.

Table 6 A comparative study for online preconcentration and determination of Cr(III) by FAAS

Support	Chelating agent	Eluent	PT(s)	Sample volume (mL)	RSD (%)	DL (ng mL^{-1})	PF	CE (h^{-1})	Ref.
Divinyl benzene	Poly 2-(5-methylisoxazol) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid	HNO_3	210	5.8	2.3	0.05	48	816	37
FeC nanoparticles	Chitosan	HCl	4000	100	2.5	0.0524	100	--	32
Llama Fibers	--	NaOH	750	25	4.3	0.3	32	--	38

MWCNTs	--	HNO_3	180	6	1.7	1.15	22	352	39
Silica	Al_2O_3/TiO_2	HCl	--	20	2.4	0.66	17.62	372	40
Silica gel	Niobium(V) oxide	HNO_3	120	15	4.6	0.34	23	345	41
Silica gel	Zirconium oxide	HNO_3	225	15	3	1.9	20.8	--	42
Dowex Optipore L493	***Dithizone***	***HNO_3***	***120***	***10***	***1.13***	***0.13***	***82***	***1640***	***This work***

PT: Preconcentration Time; RSD: Relative Standard Deviation; DL: Detection Limit; PF: Preconcentration factor; CE: Concentration Efficiency

Conclusion

In the present work, the performance of the online preconcentration system involving the use of a minicolumn packed with Dowex Optipore L493 modified with dithizone has been described. The synthesized resin allows the determination of chromium species in various industrial water samples. The use of flow injection system with FAAS leads to reduction in analysis time and also less reagent consumption takes place. The developed system has shown selectivity towards Cr(III) ions even in the presence of high concentration of commonly occurring interfering ions. The chelating resin once synthesized can be used for ~ 300 cycles of sorption and desorption. The sorption capacity of synthesized resin was found to be better than its contemporaries (Table 3). The determination of Cr(VI) was done after reducing it to Cr(III) and this method of reduction was also found suitable for unknown water samples. The suggested method was found better in terms of selectivity, preconcentration factor and detection limits as compared to other previously reported on-line SPE based methods (Table 6). The described method has been successfully applied to industrial water samples and spike recovery studies show that good recoveries have been achieved within the confidence interval of 95%. For method validation, the suggested method was applied to NIST Standard Reference Material 1643e and the certified and observed results were found to be in good agreement with each other.

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Figure Captions

Fig. 1 Schematic diagram of the FIA-FAAS system

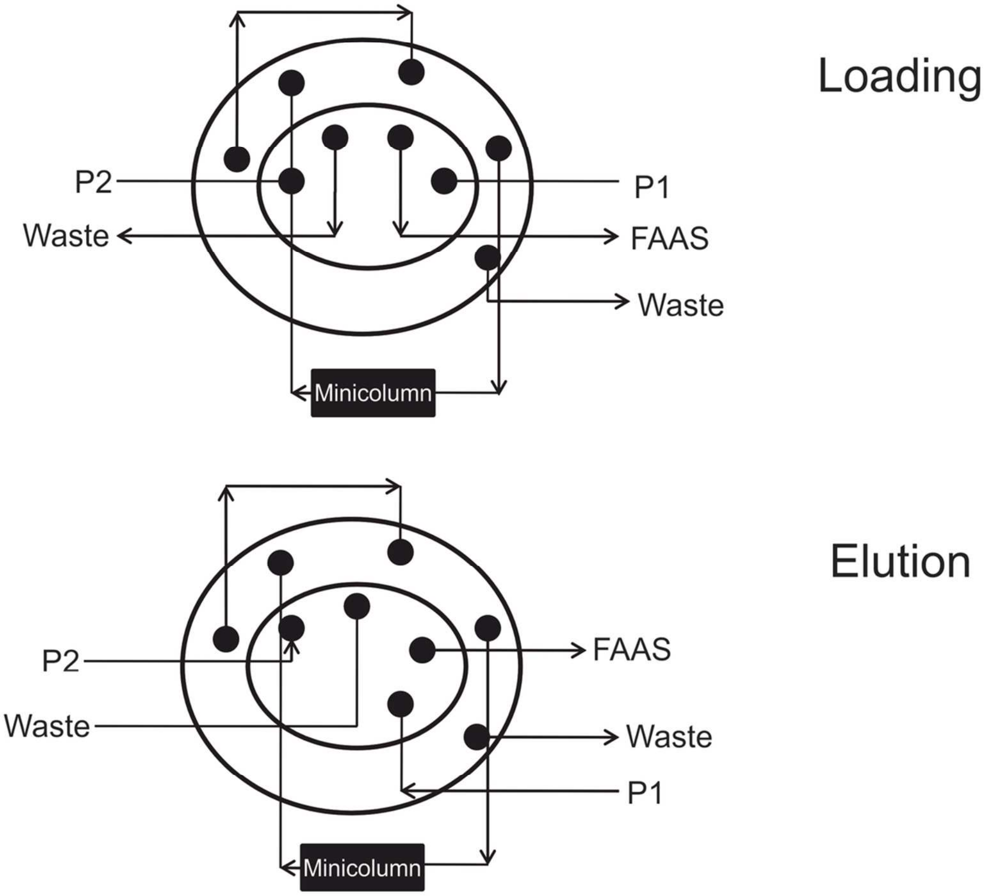
Fig. 2 Synthesis of Dowex Optipore L493 functionalized with Dithizone

Fig. 3 Infrared spectrum of a. Dowex Optipore L493 functionalized with dithizone, b. Dithizone, c. Dowex Optipore L493.

Fig. 4 Infrared spectra of Dowex Optipore L493 functionalized with Dithizone after sorption of Cr(III)

Fig. 5 SEM images of a. Dowex Optipore L493, b. Dz-493 chelating resin

Fig. 6 Optimization of chemical and flow variables for Cr(III) preconcentration a. effect of pH, b. effect of eluent concentration, c. effect of sample flow rate, d. effect of eluent flow rate



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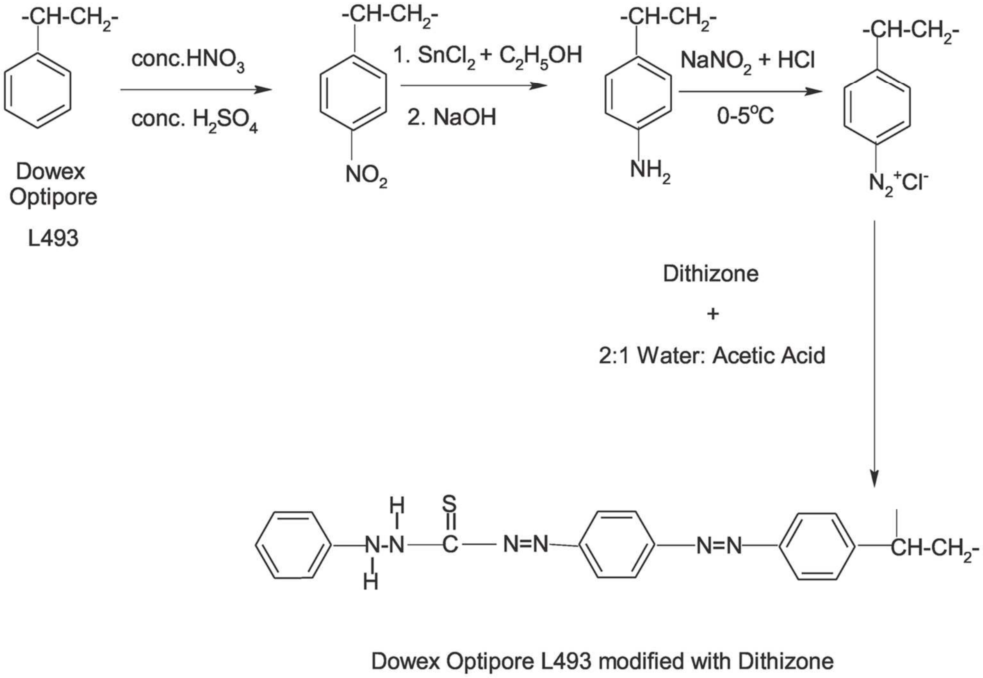

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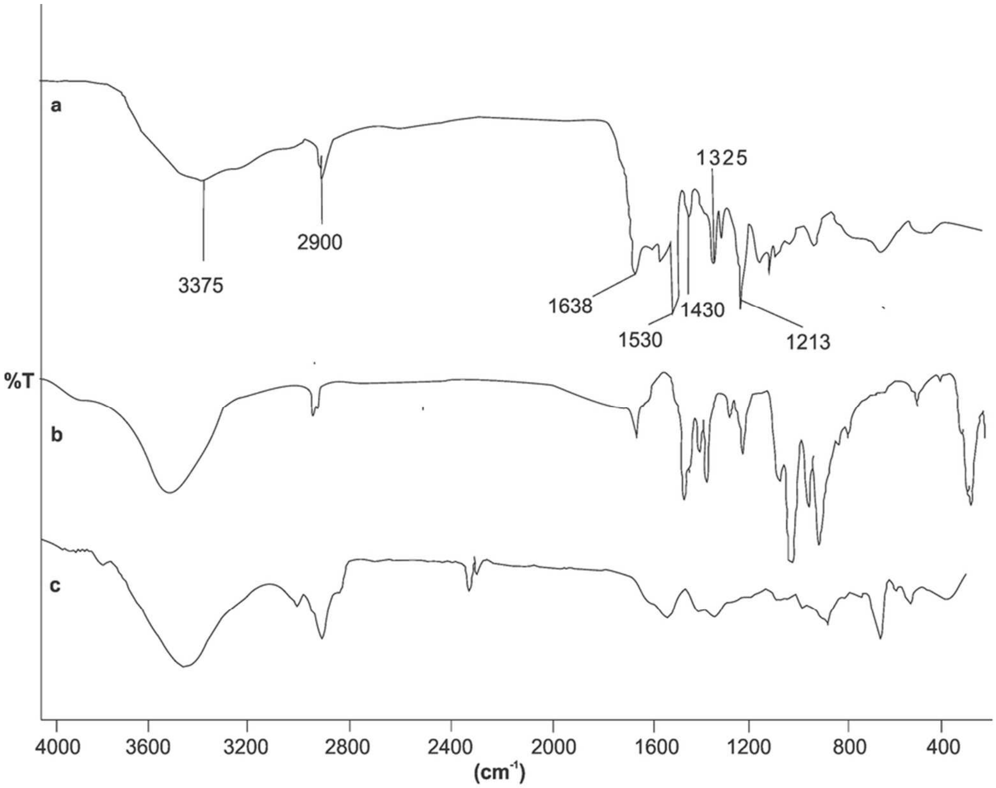

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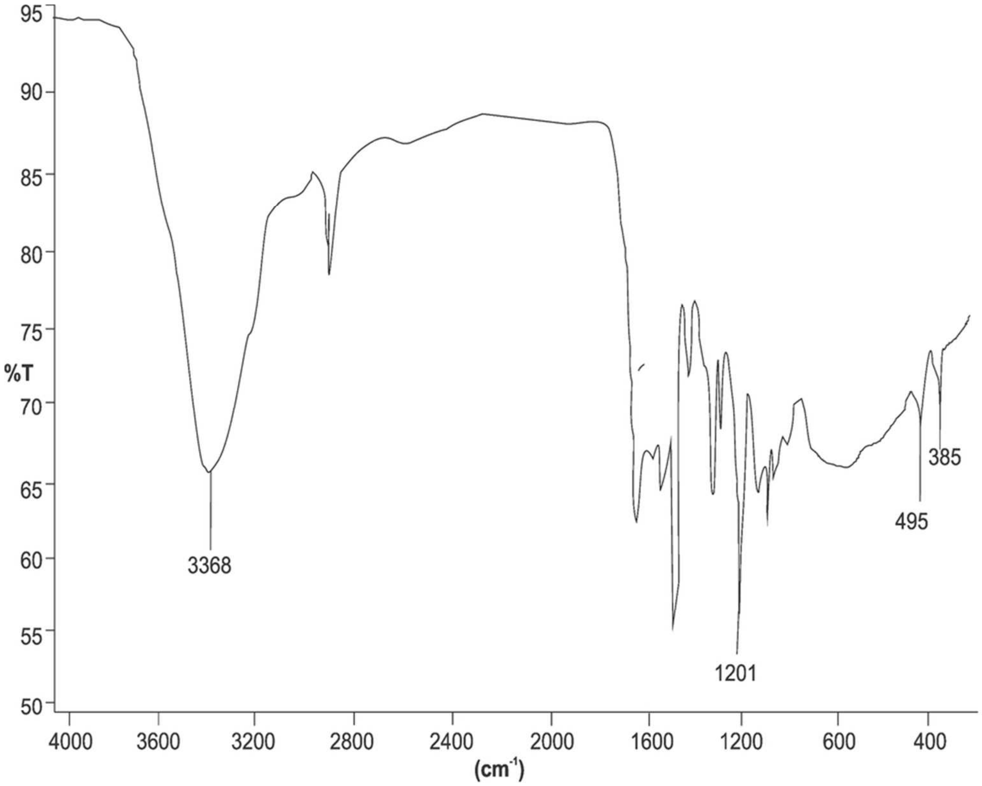

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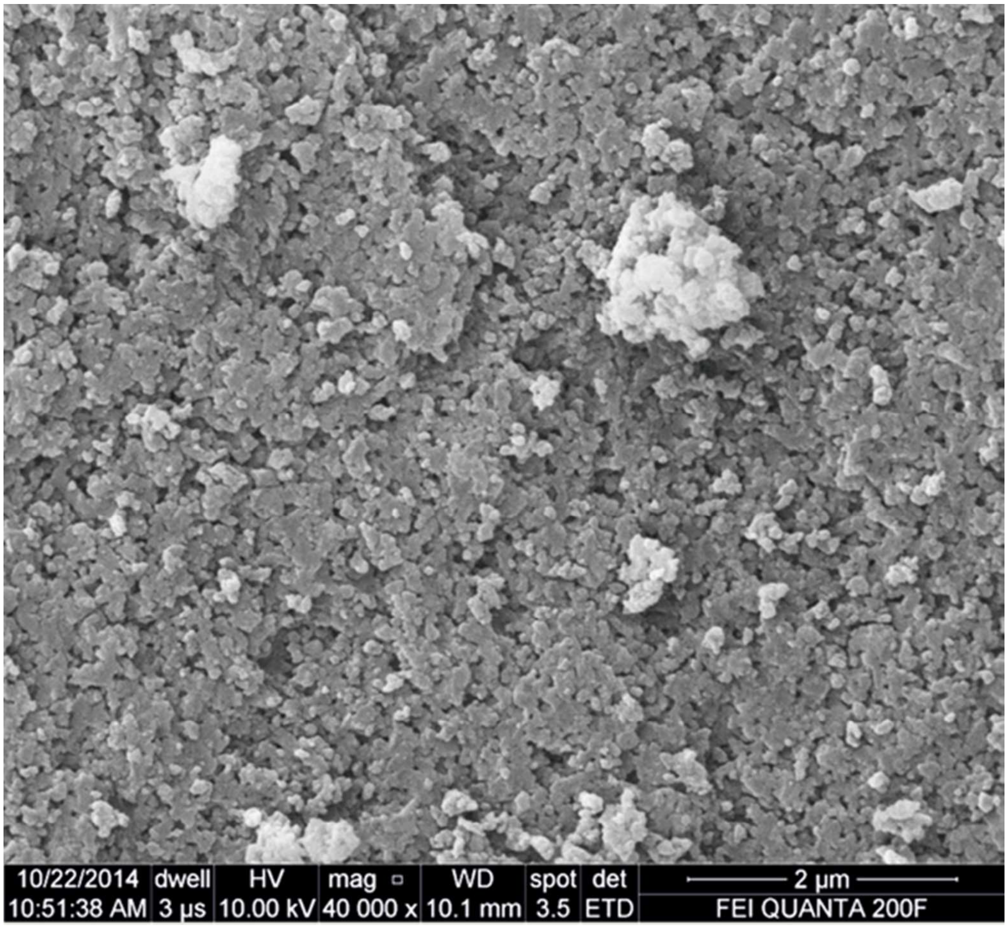

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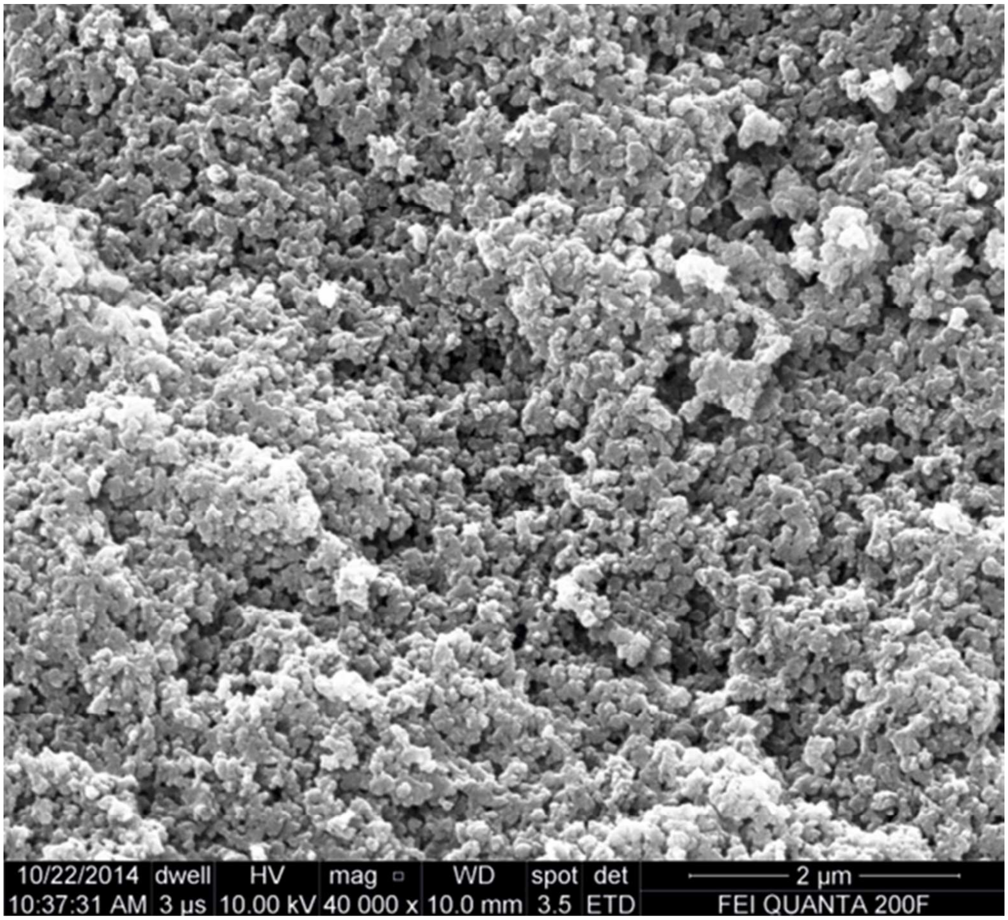

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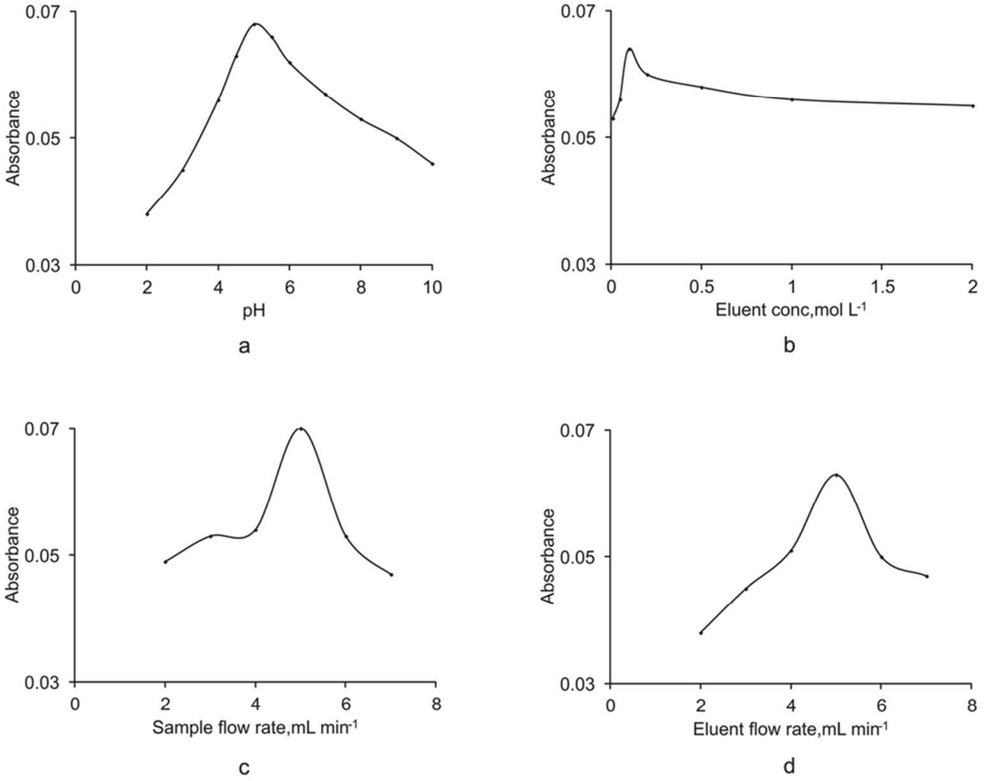

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