

Determination of Cr (III) and Cr (VI) In Water by Selective Separation and Preconcentration on Hybrid Resin

Nureddin Ben Issa¹, Ali Elmaghrabie², Emhamed Boras³

¹High Institute of Science and Medical Technology-Abo-Saliem

²High Institute of Science and Medical Technology-Algarpooli

³University of Gharyan Faculty of science

ABSTRACT: Simple and rapid method has been developed for separation, preconcentration and determination of Cr(III) and Cr(VI) species in water by using selective hybrid R-Cu-(OH)₂ resin (HCR). The effect of pH value on the adsorbed of Cr(VI) was investigated, Cr(VI) species can be retained on the HCR and eluted by 1.0 M of NaOH solution completely while Cr(III) can not adsorbed on HCR.

Chromium species before and after separation process were measured with 1-5-diphenylcarbazide by using spectrophotometer. The results showed that the capacity of HCR on adsorbed of Cr(VI) was 3.43 mg g⁻¹. The concentration of Cr(VI) determined by different between total Cr and Cr(III). The recovery of the determination of Cr(III) and Cr(VI) were (93.0 % to 101%) and (93.6 % to 105 %) respectively , while the RSD were (0.99% -6.18%) and (1.63%-7.3%) for Cr(III) and Cr(VI) respectively.

KEYWORDS: Chromium species, Separation, Preconcentration, Determination, Hybrid resin.

INTRODUCTION

Chromium contamination of water has been reported in much research as important case due to the health problems. Chromium species exist in two major stable oxidation state, trivalent Cr(III) and Hexavalent Cr(VI). The distribution of Cr depends on the redox and pH value of environmental [1], in the pH range of 3.0-8.0, the Cr(VI) is present as anionic forms of CrO₄²⁻ and HCrO₄⁻ [1], while in the low pH value Cr(III) is present a cationic [2] form as Cr(OH)_n⁽³⁻ⁿ⁾⁺ and it consider trace element. Different species of the chromium have different oxidation state and exhibit different toxicity, Sometimes the high concentration of chromium does not cause significant harm because major chromium in the sample is Cr(III), where the Cr(VI) forms are more toxic than the Cr(III) forms [3, 4].

Cr (VI) cause cancer in bladder tissue [5], and can causes lungs, ephga stricpain nausea, and also causes digestive tract cancer, vomiting, several diarrhea, hemorrhage, brain [6, 7]. Heavy metals generally have an effect on the molecular structure of the organism as chromium leads to the formation of reactive intermediates results from the reduction of chromium (VI) to chromium (III) in the cytoplasm, causing oxidative stress and oxidative tissue damage [7, 8,9].

Chromium exists in environmental from discharge many industries such as metal plating facilitie [10], tanneries [11] and natural in ores, such as ferrochromaite (FeCr₂O₄) [12], pigments, food preservatives , magnetic tapes, photography and others [13].

The methods of analysis of chromium species in trace level are depending on two basic steps; separation and preconcentration of chromium species and then determination.

Several studies have become interested in separation, preconcentration and determination of chromium species due to different toxicity[14]. The methods were varied by using different technique for separation.

The solid phase extraction by using hybride Mesoporous solid for selective retention Cr(VI) [15] was used, the maximum capacity of adsorbed Cr(VI) was 4.35 mmol/g, other authors used sorbent material such as zirconium-loaded activated charcoal [16] while recently combination of dispersive solid phase with liquid-liquid micro extraction [17] and nanoadsorbent extraction[18] which are achieved good recoveries of the separation of Cr(III) and Cr(VI). However Qing[19] applied Mesoporous silica for separation of Cr(VI) basing on the fact that Cr(III) is retained and eluted by nitric acid, while [20] used Octyl modified-silica coated cobalt ferrite nanoparticles for separation chromium species

8-hydroxyquinoline immobilizer fiber as suitable ligand for chelating Cr(III) and eluted with HCl/HNO₃ was used by [21] and recently 1,5-diphenylcarbazide investigated good results for chelating Cr(VI) by using automated spectrophotometric method [22].

1-phenyl-3- methyl-4-benzoylpyrazol-5-one [23] as chelating reagent also used for separation of chromium species.

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The alcohol-soluble quercetin was also used as chromium chelating in acidic media [24], Whereas, [25] used the microextraction technique using 2-thenoyltrifluoroacetone as chelate agent for Cr(III).

While *Saccharomyces cerevisiae* as abiosorbent [26] have been used for preconcentration and determination of Cr(III) and Cr(VI), [27] developed new soft material which formed by nanotubes carbon with 1-butyl-3-methyl imidazolium chloride packed in minicolumn for separation Cr(III).

Several studies have focused on determination of chromium species due to the different toxicity, in the last decade using HPLC for separation technique in combination with various detection methods for speciation analysis [28, 29, 30].

EXPERIMENTAL PROCEDURES

Apparatus

The concentration of oxidized chromium (III) was analyzed with DPC method by using 320 D spectrophotometer with 10 mm quartz cell was used for determination of Cr(VI) at 540 nm.

The pH meter (HANNA, C 211 Multiparameter Ion Specific Meter) was calibrated with buffer solution (HANNA) at (pH 4.0, 7.0 and 10.0).

Reagent

All the solutions were prepared using high purity analytical reagent grade, using deionized water. The chemicals were used: $K_2Cr_2O_7$ p.a. (Merck); $CrCl_3 \cdot 6H_2O$ p.a. (Merck); HCl p.a. (Merck); NaOH p.a. (Sigma-Aldrich); DPC p.a. (Merck).

Chemical compounds and standard solutions

Cr(III) stock solution (100 mg L^{-1}) was prepared by dissolving chromium chloride $CrCl_3 \cdot 6H_2O$ (0.512 g) in deionized water in 1 L volumetric flask.

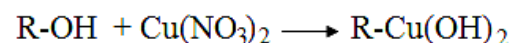
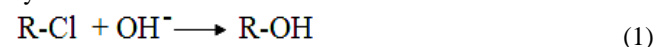
Cr(VI) stock solution was made by dissolving (0.2829 g) potassium dichromate $K_2Cr_2O_7$ in 1 L deionized water (100 mg L^{-1}).

The working solution of Cr(III) and Cr(VI) were prepared daily by dilutions of stock solution.

The different of pH value of solutions were prepared by adjusting with HCl and NaOH.

Sorption preparation

Hybrid resin used in experimental was $HY-Cu(OH)_2$ “HCR” Copper loaded ion exchange resin. The hybrid resin $HY-Cu(OH)_2$ synthesized by treatment of Lewatit MonoPlus M 500, Lanxess with copper nitrate solution in the batch system



(2)

The HCR was filtrated, washed with deionized water to remove OH^- (phenolphthalein test) and dried at room temperature for 48 h, after dried, stored, and the density was 1.15 g mL^{-1} .

The HCR has been prepared for selective separation chromium species

General procedure

pH effect on sorption process

The pH value of solution containing chromium species plays important role on sorption process. The retention of Cr(III) or Cr(VI) by HCR in varied pH value was investigated separately in the batch system at a following condition: mass of HCR ($m = 1.0 \text{ g}$), volume of sample ($V = 100 \text{ mL}$), concentration of Cr(III) = Cr(VI) (1.0 mg L^{-1}), contact time was varied ($30 - 180 \text{ min}$), room temperature constant, shaker speed (150 rpm) and pH value was varied (pH 3.0 – pH 10.0).

RESULTS AND DISCUSSION

The experiments were carried on the separation and preconcentration of Cr(III) and Cr(VI) by use HCR which is specific and selective for inorganic chromium species.

Preliminary investigation

Effect of pH

Many experiments were accomplished in order to know the influence of pH value on separation of inorganic chromium species. The operation condition on separation was conducted in (General procedure).

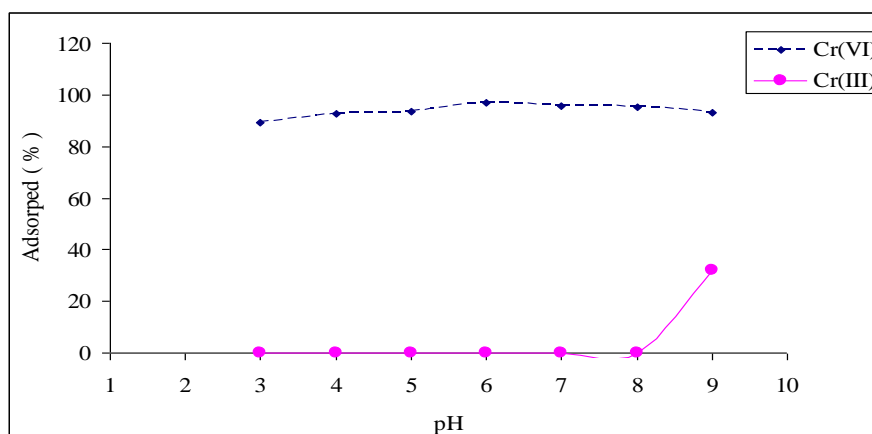


Figure 1: The effect of pH on adsorption of chromium species

The results are presented in fig.1. it showed that the pH of sample has high effect on separation process, the Cr(III) is not bonded to the HCR at pH (3.0 - 8.5) due to in cation forms [31] where the Cr(VI) is highly bonded at the pH (4.0 – 8.0) while the maximum bonded of Cr(VI) was noticed at pH 6.0, with this results the HCR has good affinity to adsorbed only Cr(VI). The HCR can used as selective chemisorption resin for separation of Cr(VI) from Cr(III) due to Cr(VI) in anionic form.

However the results it confirmed that the HCR is high efficient for preconcentration and removal of Cr(VI).

Capacity of HCR for separation and preconcentration in column system in deionized water and tap water

In order to know the capacity of HCR for separation and preconcentration of inorganic chromium species, the experiments were accomplished in fixed flow system.

The operation condition of each chromium species was tested separately in deionized water and tap water: concentration of Cr(III) = Cr(VI) ($C=10 \text{ mg L}^{-1}$), pH value (pH 6.0), mass of HCR ($m=10 \text{ g}$), flow rate ($Q=100 \text{ mL h}^{-1} = 1.66 \text{ mL min}^{-1}$).

The breakthrough point was the maximum level of chromium in water (0.05 mg L^{-1}), the results are presented in fig.2 and fig 3. showed that the HCR in flow system bonds only Cr(VI) while Cr(III) species passed through the column, the retained of Cr(VI) could be ascribed to the chemical reaction between anion Cr(VI) and HCR, while Cr(III) recognized as a cation in acidic medium [32].

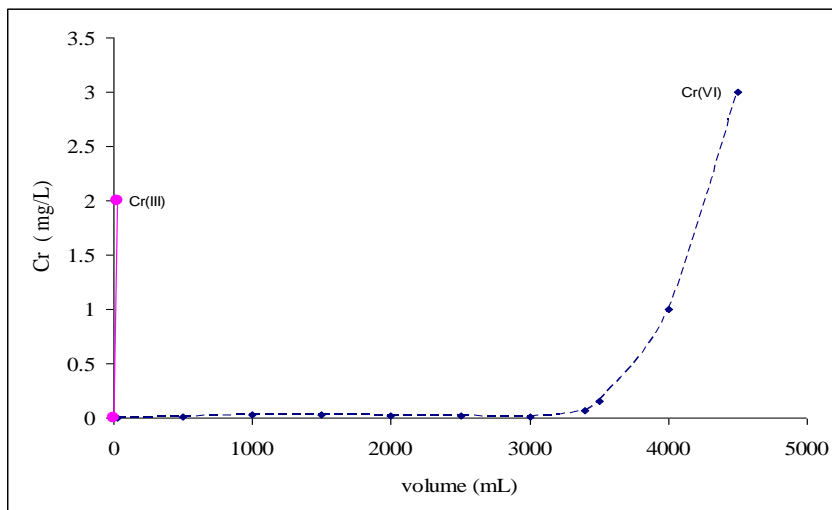


Figure 2: Breakthrough curves for chromium species in deionized water on HCR

At fixed bed flow system HCR bonded more than 3.43 mg g^{-1} and 3.0 mg g^{-1} of Cr(VI) in deionized water and tap water respectively, while all Cr(III) passed through.

The capacity of HCR in flow system lower than in batch system due to contact time.

The results obtained that the HCR was stable and efficient for preconcentration and removal of Cr(VI).

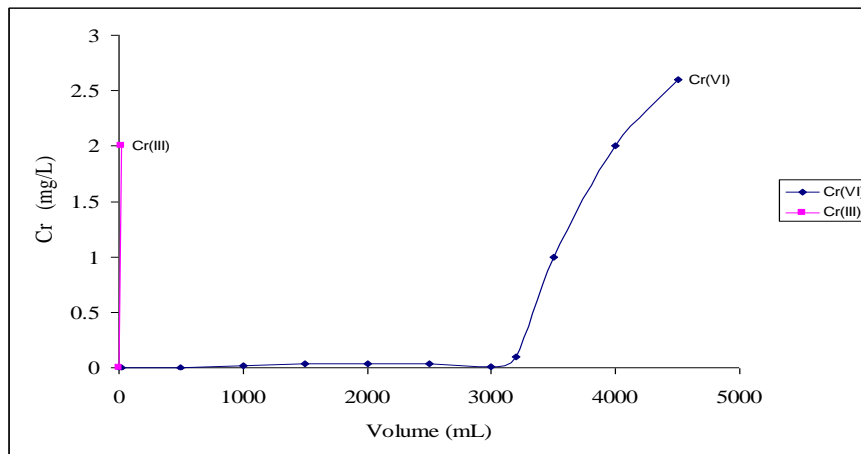


Figure 3: Breakthrough curves for chromium species in tap water on HCR

Evaluation of HCR on separation, preconcentration and determination

The separation process and determination of Chromium species in standard solution by using HCR as a selective resin is based through the following steps:

Step 1. Direct measurement of total content of chromium species without separation process.

Step 2. Procedure of separation, preconcentration (retained Cr(VI)) and determination of Cr(III) species by using flow bed system through the following condition.

- Separation and determination of Cr(III)

A column filled with 10 g of HCR, concentration of Cr(III) and Cr(VI) was varied (0.1 mg L⁻¹ to 5.0 mg L⁻¹), volume of solution (V=100 mL), pH value of standard solution (pH=6.0), contact time (1.66 mL min⁻¹), the concentration of standard solution of Cr(III) to Cr(VI) was (1 : 1), (1 : 2) and (2: 1).

The sample were passed through the column, four portions of 25 mL was taken from effluent. The Cr(VI) species was bonded to the HCR while the Cr(III) species not retained in the column and measured as a total content.

Eluted Cr(VI) by desorption procedure

Desorption of Cr(VI) from HCR was obtained with 50 mL of 2.0M NaOH, the elution was collected in 50 mL of volumetric flask, the total content of Cr species was determined.

The results showed that the Cr(VI) species was retained on the HCR after passing standard sample solution through the column, while Cr(III) was not retained on the HCR due to in cation form (not bonded with copper). The scheme for selective separation, preconcentration and determination of Cr(III) and Cr(VI) is illustrated in fig.4.

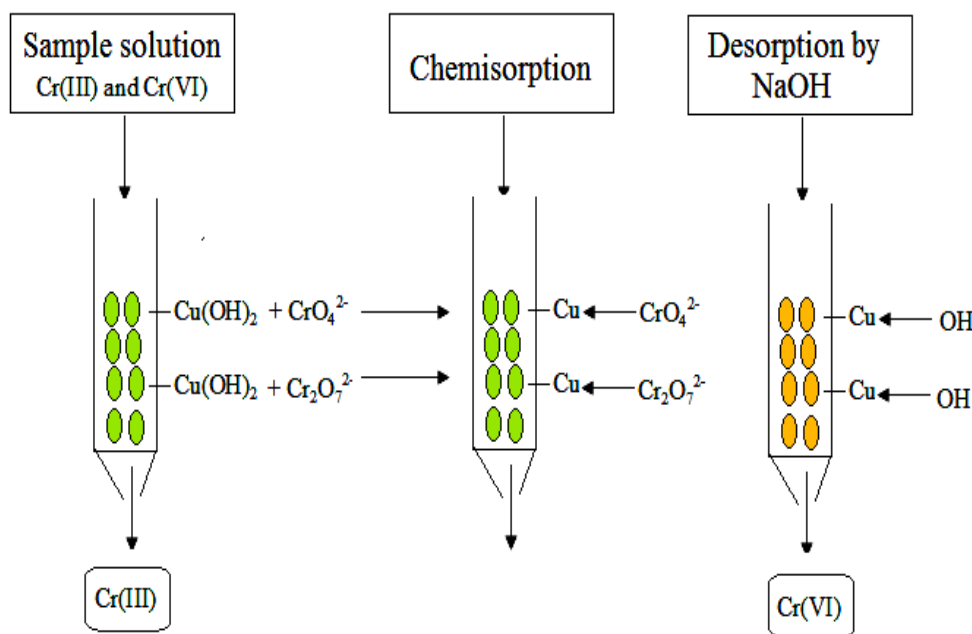


Figure 4: Scheme for selective separation and preconcentration of chromium species using HCR resin.

The analytical data for separation, preconcentration and determination of Chromium species

Standard solutions were prepared with different concentration of Cr(III) and Cr(VI), The standard

concentration of Cr(III) and Cr(VI) species and the results were presented in Table.1,2.

Table1: Determination of Cr(III) in spiked standard solutions by using proposed separation procedure on HCR.

Standard solution	Cr content, standard solution (mg L ⁻¹)			Measured mg L ⁻¹	
	Cr species spiked			Average Cr(III) ±σ	Recovery % Cr(III)
	Cr(III)	Cr(VI)	Total Cr		
1	0.1	0.1	0.2	0.101±0.001	101
2	0.5	0.5	1.0	0.51±0.026	102
3	0.2	0.1	0.3	0.187±0.011	93.5
4	0.1	0.2	0.3	0.093±0.005	93.0
5	5.0	0.1	5.1	4.92±0.029	98.4

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The results confirmed that the good recoveries were found in all five standard sample solutions. The relative standard deviation RSD was between (0.99 % - 6.18%) for Cr (III).

Table 2: Determination of Cr(VI) in spiked standard solution by using preconcentration procedure on HCR.

Standard solution	Cr content, standard solution (mg L ⁻¹)				
	Cr species spiked			determined mg L ⁻¹	
	Cr(III)	Cr(VI)	Total Cr	Average Cr(VI) ±σ	Recovery % Cr(VI)
1	0.1	0.01	0.2	0.010±0.0006	100
2	0.5	0.05	0.55	0.048±.001	96.0
3	0.2	0.1	0.3	0.093±0.001	93.6
4	0.1	0.2	0.3	0.21±0.02	105

The use of 2.0 M of NaOH was benefit in desorption of Cr(VI). The concentrations of Cr(VI) were calculated from difference between the results from total chromium and Cr(III). It is confirmed that the HCR could be used as selective resin for preconcentration, removal of Cr(VI) and it is applicable to use in determination of Cr(III) and Cr(VI).

INTERFERENCE

Common ions in real water sample

The influences of common ions in real water sample on separation and preconcentration of chromium species by using fixed bed flow were investigated.

Mass of HCR (m=10 g), pH value (pH=6.0), flow rate (1.66 mL min⁻¹) and temperature (room temperature).

1- The four real water samples were analyzed and the total Cr content was estimated without spiked with Cr(III) and Cr(VI).

2- The procedure of spiked with different concentration of Cr(III) and Cr(VI) was applied

The results presented in Table.3. It showed that No any influence in the separation, preconcentration and determination of Cr(III) and Cr(VI) species.

Table 3: Results of determination of Cr(III) and Cr(VI) in natural real water sample by use proposed method.

Sample	Cr content, standard solution (mg L ⁻¹)						
	Cr species spiked			Measured (mg L ⁻¹)		Recovery %	
	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	0.1	0.2	0.3	0.11	0.2	36.6	66.6
2	0.05	0.1	0.15	0.06	0.11	40.0	73.3
3	0.25	0.1	0.35	0.25	0.11	71.4	31.4
4	0.1	0.2	0.3	0.1	0.20	33.3	66.6

CONCLUSIONS

The selective HCR resin was used for determination of Cr(III) and Cr(VI) through the bonded Cr(VI) with HCR,. The separation and preconcentration process was conducted in flow bed system.

The pH of solution played important role in preconcentration process. Cr(VI) retained in the pH range (4.0 – 8.0) and eluted by 2.0 M NaOH, while the maximum capacity was 3.43 mg g⁻¹ at pH 6.0. Cr(III) passed through the column then oxidized and determined by using DPC, the influence of common ion in water on separation and preconcentration chromium species was confirmed, the results showed no any interference effect .

The proposed method for determination of Cr(III) and Cr(VI) was applied in spiked samples and the recovery were (93.0 % to 105 %)

The separation, preconcentration, removal and determination of Cr(III) and Cr(VI) can be carried out very effective by using HCR.

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