

Preconcentration and Determination of Chromium (III) from Sea Water Samples Using Ion Imprinted Activated Carbon

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ABSTRACT

A simple ion imprinted amino-functionalized sorbent was synthesized by coupling activated carbon with iminodiacetic acid, a functional compound for metal chelating, through cyanoric chloride spacer. The resulting sorbent has been characterized using Fourier transform infrared spectroscopy (FT-IR), elemental analysis, thermogravimetric analysis (TGA) and evaluated for the preconcentration and determination of trace Cr(III) in environmental water samples. The optimum pH value for sorption of the metal ion was 6. The sorption capacity of functionalized sorbent was 32.36 mg.g⁻¹. The chelating sorbent can be reused for 10 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 104% was obtained for the metal ion with 0.5 M nitric acid as eluting agent. The equilibrium adsorption data of Cr(III) by modified resin were analyzed by Langmuir, Freundlich, Temkin and Redlich-Peterson models. Based on equilibrium adsorption data the Langmuir, Freundlich and Temkin constants were determined as 0.048 (L/mg), 2.849 (mg/g) (L/mg)^{1/n} and 2.124 (L/g), respectively at 25°C.

Keyword: Solid phase extraction; Polymer grafting; Chromium (III); Preconcentration; Isotherm study.

1. INTRODUCTION

Chromium exists in the environment mainly in two states: trivalent Cr(III) and hexavalent Cr(VI). Chromium is a naturally occurring metal, mainly found in natural samples including water, minerals, rocks, soil, plants, volcano dust and gases [1].

Chromium species are major water pollutants, usually as a result of some industrial pollution including tanning factories, industrial electroplating, steelworks, wood preservation, etc. and artificial fertilizers [2-5]. Cr(III) is an essential

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element in humans and is much less toxic than Cr(VI) [6]. It is essential in human nutrition (especially in glucose metabolism) as well as for plants and animals at trace concentrations [7]. It is important in glucose, lipid, and protein metabolism [8-10]. It is recommended that a daily uptake of 50-100 mg is helpful for human beings, without toxic effects observed even at a higher dosage [11]. It is relatively innocuous and immobile in most environmental systems [12]. Chromium (III) ion is mainly used in electrical, electroplating, paper manufacturing, pesticides, herbicides and tannery industries [13]. The effluents of these industries contain Cr(III) ions which cause serious toxicological concerns. Due to these importance of Cr(III), the accurate and sensitive determinations of these ions are the important part of the analytical chemistry [14]. The treatments applied towards the removal of Cr(III) involve physicochemical processes such as coagulation and precipitation [15]. However these techniques proved ineffective in remaining within Cr(III) discharge limits (1-2 mg/dm³) of industrial effluents [16]. As a result, the use of alternative treatments such as ion exchange, carbon adsorption, membrane filtration, electroseparation, and bioaccumulation has been applied in "polishing" these effluents [17-19].

In this work, modification of activated carbon with metal chelating group, for selective sorption of chromium ions in aqueous sample is reported. The purpose of the present study is to indicate the feasibility of using ion imprinted activated carbon (IAC) as a solid-phase extractant for pre-concentration of Cr(III) in environmental water samples. Trace chromium can be retained in the appropriate cavity on the IIP sorbent and then desorbed with 0.5 M nitric acid prior to determination by flame atomic absorption spectroscopy (FAAS).

2. EXPERIMENTAL

2.1. Instruments

Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Thermogravimetric analysis

(TGA) was carried out by using a TGA-50H (Shimadzu Corporation, Kyoto, Japan). Flame atomic absorption spectrometer Varian, (Palo Alto, CA, USA) AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L.min⁻¹, respectively) and was used for concentration measurements of metal ions. Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., and Easton, Maryland). The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). The SEM micrographs were obtained on a SEM-PHILIPS XL30 scanning electron microscopy.

2.2. Reagents and solutions

Anhydrous 1,4-Dioxane, carbon active (particle size < 100 µm), iminodiacetic acid, sodium hydroxide, sulfuric acid, hydrochloric acid, nitric acid, potassium sulfate, sodium chloride, acetic acid, sodium acetate, sodium dihydrogen phosphate, disodium hydrogen phosphate, lead nitrate, fro sulfate, copper sulfate, cobalt nitrate, nickel sulfate, chromium nitrate, mercuric nitrate, aluminum nitrate, silver nitrate, magnesium nitrate, calcium nitrate, barium nitrate and ethanol were products of Merck (Darmstadt, Germany).

All the reagents were of analytical grade and used without any further purification. The stock solution (500 mg.L⁻¹) of Cr(III), was prepared by dissolving appropriate amounts of Cr(NO₃)₃, in deionized water. To adjust the pH of the solution, 10 mL of 0.01 M acetic acid acetate buffer (pH 3-6.5) or 0.01 M phosphate buffer (pH 6.5-9) were used wherever suitable.

2.3. Synthesis

2.3.1. Modification of activated carbon with cyanoric chloride

Before the reaction, the activated carbon particles were cleaned with 20% (v/v) HNO₃, this was followed by immersion in water (for hydrolysis and oxidation of surface) and subsequent filtration. The slurry was then vacuum-filtered and washed with deionized water until the filtrate pH was no longer acidic. The washed activated carbon was dried for 3

h at 100°C and kept at this temperature until the start of the reaction. At this point, 5 g hydroxylated activated carbon particles were modified with 250 mL solution of 2% (w/v) cyanoric chloride in mixture of (1:1) 1,4-dioxane and xylene. The reaction was carried out in room temperature for 10 h. The modified activated carbon particles were washed several times with petroleum ether and dried under vacuum in a desiccator over dry calcium chloride.

2.3.2. Synthesis of IAC

To prepare the IAC sorbent, 18.8 mmol of iminodiacetic acid and 9.4 mmol Chromium(III) nitrate were dissolved in 50 mL of 0.1 M sodium acetate buffer (pH 5) while stirring (15 min), and then 5 g modified activated carbon was added into the mixture. The solution was stirred and refluxed for 12 h at room temperature. The product was filtrated and washed with 250 mL of 0.1 M sodium acetate, 250 mL of 0.1 M sodium chloride and 500 mL water. Second washing step was performed with 250 mL of 0.5 M nitric acid (three times) while stirring for 3 h to remove the Cr(III). The product was recovered by filtration, washed with ultra pure water until the filtrate pH was no longer acidic. Finally, the sorbent was dried under vacuum and stored in 4°C. The IAC was characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA). Elemental analysis was carried out according Thermofinnigan elemental analyzer manual. Elements of C, H and N in the sample and standards in a column containing oxidant at 900°C were converted to CO₂, H₂O and N₂, respectively. They separated in a gas chromatography column containing molecular sieve and detected by a thermal conductivity detector (TCD). The percentages of C, H and N in the sample were ascertained after drawing the calibration curve for standards and data processing for the sample.

2.4. Batch method of Cr(III) adsorption

A set of solutions (the volume of each 100 mL) containing 0.5 µg.mL⁻¹ of Cr(III) was taken. Their pH values were adjusted between the ranges 3-9 with 0.01M acetate and/or phosphate buffer

solutions. The 0.05 g of IAC was added to each solution and the mixture was shaken for 3 h. The sorbent was filtered and the adsorbed metal ions were eluted with 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluate was determined by FAAS.

2.5. Isotherm studies

Isotherm studies were carried out by adding a fixed amount of sorbent (0.05 g) to a series of beakers filled with 50 mL diluted solutions of Cr(III) (10-100 µg.mL⁻¹). The beakers were then sealed and placed in a water bath shaker for 3 h at pH 6 and 20°C. pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Cr(III) in the solution was measured by FAAS. The amount of Cr(III) at equilibrium q_e (mg/g) on IAC was calculated from the following equation:

$$q_e = (C_0 - C_e) V/W \quad (1)$$

Where C_0 and C_e (mg.L⁻¹) are initial and equilibrium concentrations of Cr(III), respectively, V (L) is the volume of the solution and W (g) is the mass of the adsorbent used.

3. RESULTS AND DISCUSSION

3.1. Characterization of IAC

The IAC was characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA). The IR spectrums of activated carbon loaded cyanoric chloride and ion imprinted activated carbon are compared with that of activated carbon. There is an additional band in activated carbon loaded cyanoric chloride at 1704 cm⁻¹ which appear to originate due to C=N and an additional band in ion imprinted activated carbon at 1715 cm⁻¹ which appear to originate due to C=O. The TGA of unmodified activated carbon showed 13% weight loss up to 400°C was due to the desorption of water molecules, acidic and hydroxyl groups from the surface. IAC showed different thermal behavior.

The 33% weight loss up to 400°C was due to the water molecules and decomposition and desorption of chemically immobilized polymeric matrix. The elemental analysis for IAC was demonstrated the percentage of carbon, hydrogen and nitrogen are: C, 83.6; H, 1.53; N: 1.87%. The pH dependence for Cr(III) sorption is shown in Figure 1 with the maximum recovery of 93.56% achieved at pH 6. The binding capacity of IAC at optimum pH increased up to about 32.36 mg.g⁻¹ with increasing initial Cr(III) concentration (Figure 2).

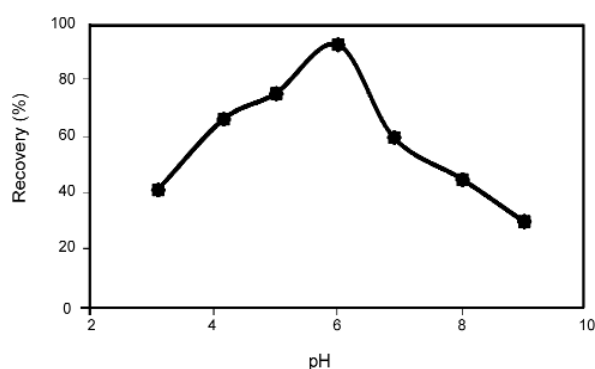


Figure 1: Effect of pH sorption of Cr (III) onto ion imprinted-activated carbon.

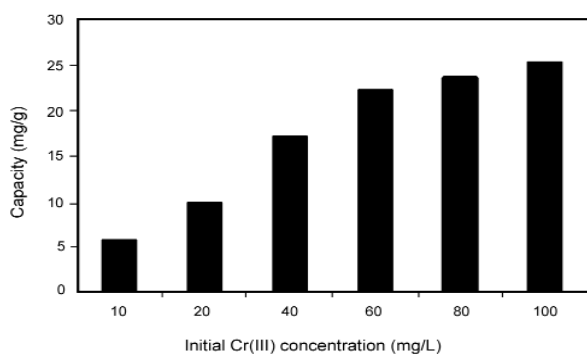


Figure 2: Effect of initial concentration of the chromium (III) in the solution on sorption capacity of Cr (III) onto ion imprinted-activated carbon.

The sorption as a function of contact time for all the metal ions is presented in Figure 3. Less than 15 min shaking was required for about 70% sorption reflecting good accessibility of the chelating sites in the IAC. The sorbent was readily regenerated with

0.5 M HNO₃ and used repeatedly with sorption capacity after 10 cycles changing less than 10%. The sorption capacity of the resin stored for more than 6 month under ambient conditions was unchanged.

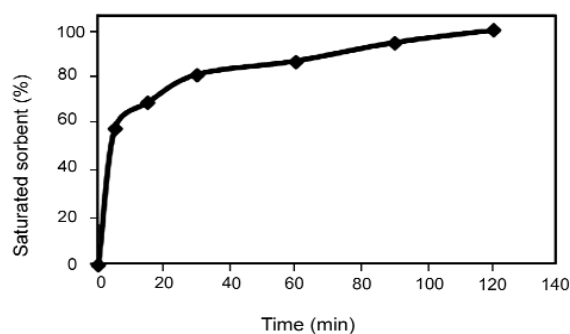


Figure 3: Kinetics of chromium (III) sorption on ion imprinted-activated carbon.

3.2. Adsorption isotherms

Fitting experimental data to the linearized form of Langmuir isotherm $C_e/q_e = (1/q_{max} \cdot K_L) + (C_e/q_{max})$ [20], where q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg.g⁻¹) and K_L is the Langmuir constant (L.mg⁻¹), indicates the homogeneous nature of poly (AGE/IDA-co-DMAA)-grafted surface (Figure 4). Langmuir parameters calculated from mentioned equation are listed in Table 1.

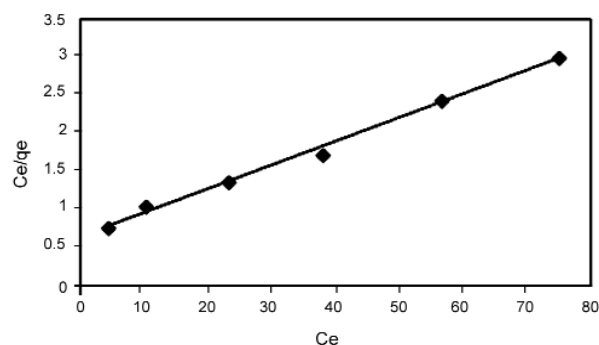


Figure 4: Langmuir isotherm for Cr (III) adsorption onto ion imprinted-activated carbon at 25°C.

The essential characteristics of the Langmuir equation can be expressed in term of a

dimensionless separation factor, R_L , defined as [21]:

$$R_L = 1 / (1 + K_L \cdot C_0) \tag{2}$$

Table 1 shows the values of R_L (0.17) are in the range of 0-1 at optimum pH which confirms the favorable uptake of the Cr(III).

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$ with empirical equation written as [22]:

$$q_e = K_F \cdot C_e^{1/n} \tag{3}$$

Where K_F is the Freundlich constant ($\text{mg} \cdot \text{g}^{-1} (\text{L} \cdot \text{mg}^{-1})^{1/n}$) and $1/n$ is the heterogeneity factor. A plot of $\ln q_e$ versus $\ln C_e$ (Figure 5) enables the constant K_F and exponent $1/n$ to be determined.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

$$q_e = \frac{RT}{b} \ln(AC_e) \tag{4}$$

And can be linearized:

$$q_e = B \ln A + B \ln C_e \tag{5}$$

Where $B=RT/b$ and b is the Temkin constant related to heat of sorption ($\text{J} \cdot \text{mol}^{-1}$). A is the Temkin isotherm constant ($\text{L} \cdot \text{g}^{-1}$), R the gas constant ($8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T is the absolute temperature (K). Therefore plotting q_e versus $\ln C_e$ (Figure 6) enables the constants A and B . Temkin parameters calculated from equation (4 and 5) are listed in Table 1. The Redlich-Peterson isotherm contains three parameters and incorporates the features of both the Langmuir (at $g = 1$) and the Freundlich (at $g = 0$) isotherms [23]:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{6}$$

Three isotherm constants, A , B , and g can be evaluated from the linear form (7) using a best

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B) \tag{7}$$

fitting computer calculations (Table 1). The g

Table 1: Isotherm parameters obtained by using linear method.

Langmuir isotherm model				
Temperature (°C)	q_{\max} (mg/g)	K_L (L/mg)	R_L	R^2
25	32.36	0.048	0.17	0.9954
Freundlich isotherm model				
Temperature (°C)	K_F (mg/g) $(\text{L}/\text{mg})^{1/n}$	n	R^2	
25	2.849	1.876	0.9718	
Temkin isotherm model				
Temperature (°C)	A (L/g)	B (J/mol)	b (J/mol)	R^2
25	2.124	7.197	344.4	0.9853
Redlich-Peterson isotherm model				
g	B (dm^3/mg) ^g	A (dm^3/g)	R^2	
1.10	0.03	1.5	0.9897	

values were close to unity, indicating that the isotherms are approaching the Langmuir form rather than Freundlich isotherm.

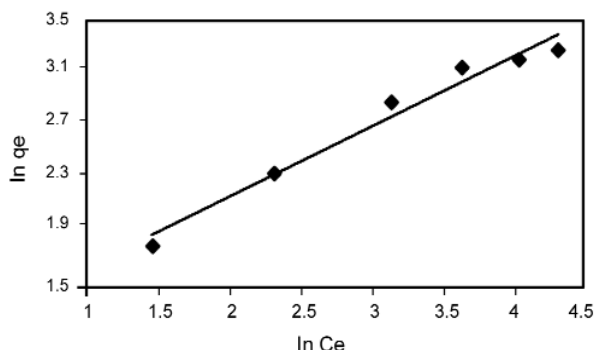


Figure 5: Freundlich isotherm for Cr (III) adsorption onto ion imprinted-activated carbon at 25 °C.

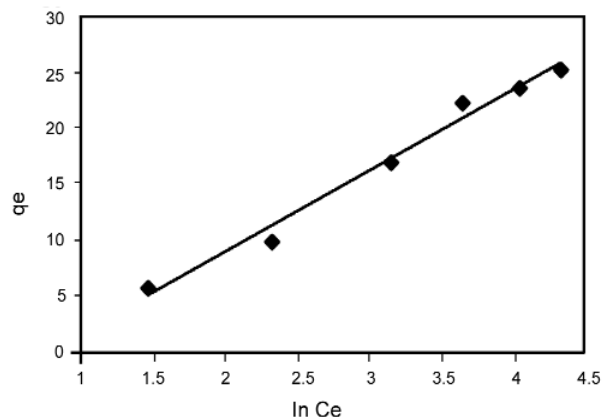


Figure 6: Temkin isotherm for Cr (III) adsorption onto ion imprinted-activated carbon at 25°C.

3.3. Effect of foreign ions

In order to evaluate the selectivity of the preconcentration system, the effect of some metal ions (10 mg.L⁻¹) on the sorption behavior of Cr(III) ion (10 mg.L⁻¹) was investigated. The result was shown in Table 2. This Table indicates the most effective ions on adsorption of Cr(III) on IAC are Co(II), Pb(II) and Cd(II).

The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Cr(III) on the IAC in presence of all mentioned ions (with each ion having the concentration of 10 mg.L⁻¹) shows that the Cr(III) can be determined quantitatively in the environmental samples.

3.4. Application of method

IAC was used to preconcentrate and determine Cr(III) ions in water from, The Caspian sea (Mahmood abad, Mazandaran, Iran). The pH of water sample was adjusted to 6. Solid phase extraction with IAC coupled with FAAS was applied to determine of the Cr(III) in water sample. The results shown in Table 3 demonstrate the applicability of the procedure for Chromium (III) determination with high recovery.

Table 2: Effect of other ions on sorption.

Interfering	amount of adsorbed Cr (III) (mg.L ⁻¹)	Loss adsorption (%)
—	4.32	—
Co(II)	3.12	27.78
Cu(I)	4.32	—
Mn(II)	4.32	—
Cd(II)	3.66	15.28
Pb(II)	3.73	13.65
Zn (II)	4.32	—

Table 3: Results obtained for Cr (III) determination in sea water sample.

Sample (without spiking of Cr (III)) (µg.L ⁻¹)	22
Found (µg.L ⁻¹)	23
Preconcentration factor	10
Recovery %	104
Standard deviation	0.26
Relative standard deviation (%) ^a	4.2

^a For three determinations

4. CONCLUSIONS

A method for the synthesized selective Cr-imprinted sorbent was described. The sorbent has a good potential for enrichment of trace amount of Cr(III) from large sample volumes. The sorbent also present the advantage of high adsorption capacity, good reusability and high chemical stability. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined

to be 32.36 (mg.g⁻¹) at 25°C. Preconcentration by this sorbent combined with FAAS can be applied to the determination of traces of Cr(III) ions in the environmental water samples.

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