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Preconcentration and determination of chromium in water with flame atomic absorption spectrometry by thiourea-formaldehyde as chelating resin

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Abstract−Thiourea-formaldehyde chelating resin is synthesized simply and rapidly from thiourea and formaldehyde by condensation polymerization and characterized by IR spectra and studied for the preconcentration and determination of trace Cr(III) ion from solution samples. The optimum pH value for sorption of the metal ion was 6.5. The sorption capacity of resin for Cr(III) was determined. The chelating resin can be reused for 20 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 96% was obtained for the metal ion with 0.5 M HNO_3 as eluting agent. The equilibrium adsorption data of Cr(III) on modified resin were analyzed by Langmuir, Freundlich and Temkin models. Based on equilibrium adsorption data the Langmuir, Freundlich and Temkin constants were determined as 0.016, 0.040 and 0.074 at pH 6.5 and 20 °C. The method was applied for chromium ion determination from river water sample.

Key words: Solid Phase Extraction, Thiourea-formaldehyde, Chromium, Preconcentration, Isotherm Study

INTRODUCTION

As a result of industrial development, many chemical substances have generated air, water, and soil pollution. At least 20 metals including chromium are classified as toxic and half of these are emitted into the environment in higher quantities that pose risks to human health [1]. Chromium has both beneficial and detrimental properties. In the environment, chromium usually exists in its compounds in the forms of hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)], which have different toxicities, mobilities and bioavailabilities [2]. Cr(III) is essential in human nutrition (especially in glucose metabolism) as well as for plants and animals at trace concentrations. 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 [3]. It is relatively innocuous and immobile in most environmental systems [4]. In contrast, Cr(VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [5]. It is known to be toxic to human, animals and plants and classified as a carcinogen associated with the risk of respiratory tract cancer [6-9]. Unfortunately, in recent years, due to the extensive use of chromium in industrial processes (such as electroplating, leather tanning, paints and pigments, textile, steel fabrication and production of chromium chemicals), large quantities of Cr containing wastes that lead to serious problems and hazardous risks for human health are discharged into the environment. Therefore, recently, a number of methods exist for removal of chromium pollutants from liquid waste [10-19].

Solid phase extraction (SPE) has been increasingly used for preconcentration/separation of trace and ultra trace amounts inorganic and organic species from complex matrices as seen from recent reviews [20-23]. Various researchers [22-25] have highlighted the advantages of SPE over other preconcentration techniques and in particular over liquid-liquid extraction.

The purpose of the present study is to indicate the feasibility of using thiourea - formaldehyde as a solid-phase extractant for preconcentration of trace chromium in environmental water samples. It is also examined the Cr(III) ions adsorption behavior on synthesized thiourea - formaldehyde by batch method as a function of contact time, initial pH solution, initial metal ion concentration and temperature.

EXPERIMENTAL

1. Instruments

A flame atomic absorption spectrometer of the GBC Awanta, 932 plus, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 $L\cdot min^{-1}$, respectively) and inductively coupled plasma (ICP), Varian, model Vista were used for measuring the concentration of metal ions. The pH measurements were made with Metrohm model 744 (Switzerland). IR spectra and NMR spectra were recorded on a FT-IR spectrometer Perkin Elmer Spectrum GX by KBr pellet method and Brucher 500, respectively.

2. Reagents and Solutions

CH_3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4, HCl, H_2SO_4, HNO_3, NaOH, thiourea, formaldehyde were products of Merck (Darmstadt, Germany). $CrCl_3\cdot 6H_2O$ was obtained from Fluka, Switzerland.

All the solutions were prepared in deionized water using analyt-

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ical grade reagents. A stock solution (1,000 mg·L^{-1}) of Cr (III) was prepared by dissolving appropriate amounts of $CrCl_3·6H_2O$, in deionized water. 10 mL, 0.01 M acetic acid - acetate buffer (pH 3-6.5), 0.01 M phosphate buffer (pH 6.5-9) were used to adjust the pH of the solutions, wherever suitable.

3. Method

3-1. Synthesis of Thiourea-formaldehyde as Chelating Agent

Thiourea-formaldehyde was synthesized by reacting formaldehyde (HCHO) with thiourea (CON_2H_4). In a 20 mL reaction vessel, pH of 6 mL of 37% formaldehyde was adjusted to 8 with 20% NaOH solution. 3 g Thiourea was added to the mixture and kept in the water bath at 50 °C for 25 min with intermittent stirring. Then it was acidified with HCl 1 M to pH 2-3. Thereafter, it was kept at room temperature for 24 h, and then the precipitated polymer washed for three to four times with warm water to remove unreacted thiourea and formaldehyde and dried by applying vacuum in a vacuum desiccator. Thiourea-formaldehyde synthesized was of white color resinous material. The reaction scheme is shown in Fig. 1.

3-2. Batch Method

A sample solution (50 mL) containing (0.3 μg·mL^{-1}) of Cr(III) was taken in a glass stoppered bottle, after adjusting its pH to the optimum value. Then 0.1-0.3 g of thiourea-formaldehyde was added to the bottle and the mixture was shaken for optimum time. The resin was filtered and sorbed metal ion was eluted with 0.5 M HNO_3 (10 mL). The concentration of metal ion in the eluate was determined by FAAS.

3-3. Isotherm Studies

Isotherm studies were done by adding a fixed amount of adsorbent (0.3 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 and shaken at 200 rpm with the required adsorbent time (4 h) at 20, 30 and 40 °C and optimum pH (6.5). pH adjustments were done by 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 thiourea-formaldehyde was calculated from the following equation:

$$q_e=(C_0-C_e)\ V/W \tag{1}$$

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

RESULT AND DISCUSSION

1. Characterization of Resin

Structure of thiourea-formaldehyde was elucidated by IR (Fig. 2). IR (NaCl, cm^{-1}) 1532 (C=S), 3312 (N-H), 3000 (C-H).

2. Metal Sorption as a Function of pH

The degree of metal sorption at different pH values was determined by batch equilibration technique. A set of solutions (volume of each 50 mL) containing 0.3 μg·mL^{-1} of Cr(III) was taken. Their

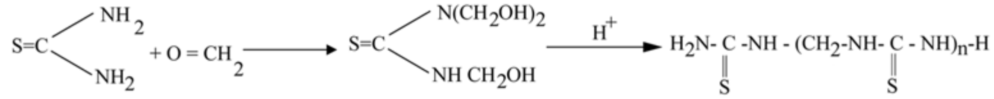

Fig. 1. The methodology of synthesize of thiourea-formaldehyde.

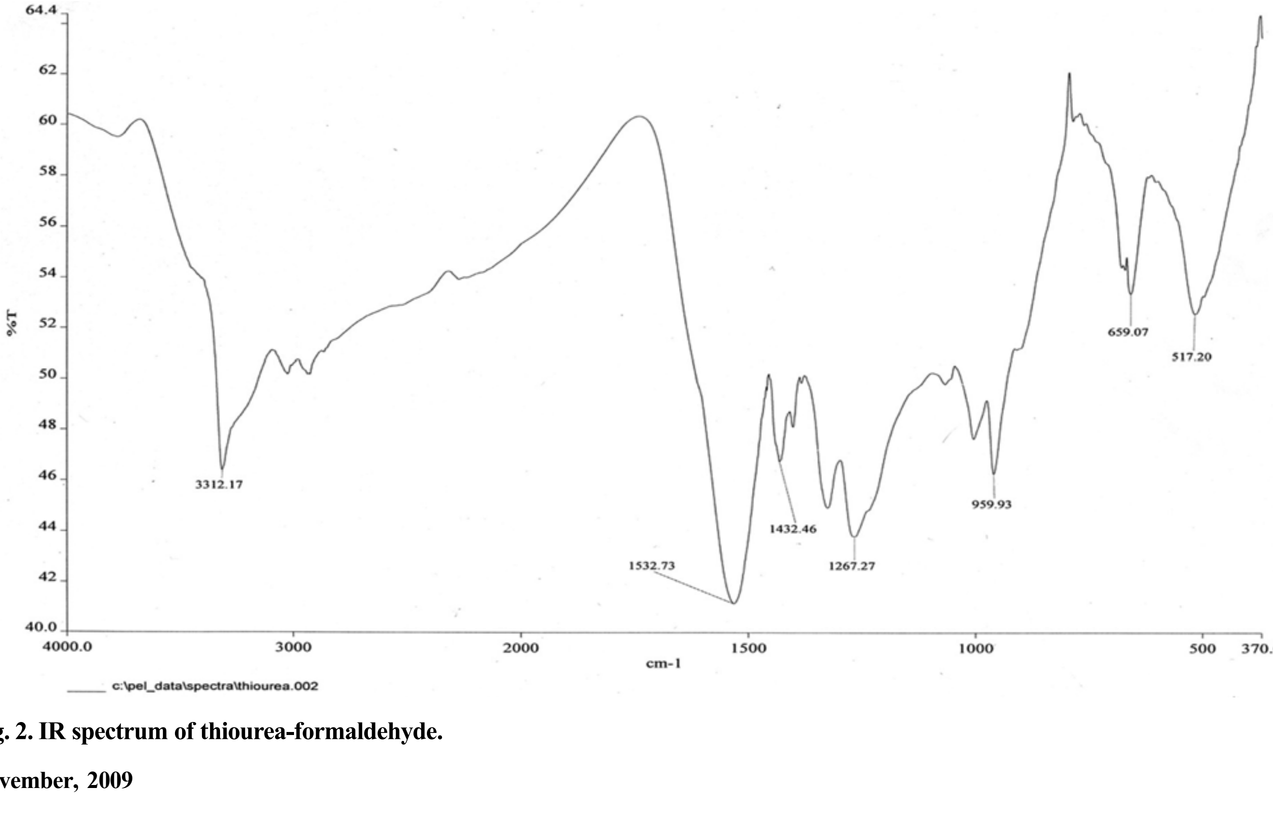

Fig. 2. IR spectrum of thiourea-formaldehyde.

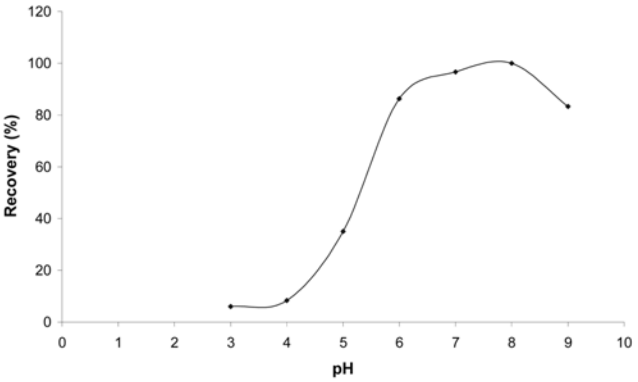

Fig. 3. Effect of pH sorption of Cr(III) onto thiourea-formaldehyde.

pH values were adjusted in range 3-9 with 0.01 M acetate and/or phosphate buffer solutions. The 0.3 g of thiourea-formaldehyde was added to each solution and the mixture was shaken for 4 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Cr(III) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from resin with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Fig. 3. The maximum recoveries were 86-100% at pH 6.5-8.5.

3. Total Sorption Capacity

The 0.3 g of resin beads were stirred for 5 h. with 50 mL solution containing 10-100 μg·mL^{-1} of Cr(III), at optimum pH and 20 °C. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the resin for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The saturated adsorption capacity of the resin is shown in Fig. 4. This figure indicates the effect of initial concentration of the Cr in the solution on capacity sorption of Cr(III) by thiourea-formaldehyde. The capacity goes up with initial concentration of the Cr in the solution.

4. Optimization of Sorption Time of Metal Ions

Thiourea-formaldehyde (0.2 g) was shaken with 100 mL of solution containing 0.3 μg·mL^{-1} of Cr(III) at different time (5, 15, 30, 45, 60, 90, 120 and 180 min) under optimum pH. After filtration the concentration of the chromium ions in supernatant was determined with FAAS by using the recommended batch method. The sorption as a function of contact time for all the metal ions is shown in Fig. 5. Less than 5 min shaking was required for 83% sorption. The profile of chromium uptake on this resin reflects good accessibility of the chelating sites in the resin.

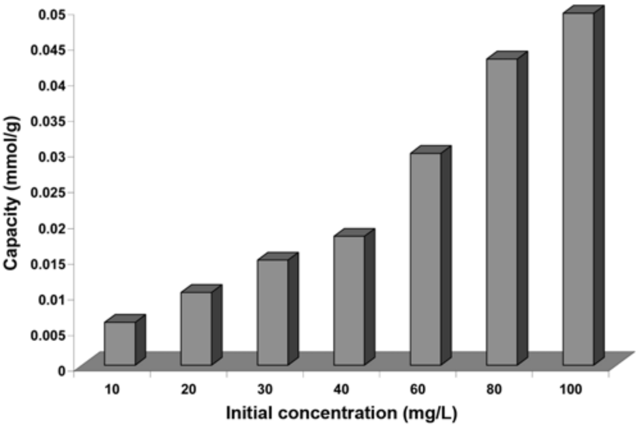

Fig. 4. Effect of initial concentration of the Cr(III) in the solution on capacity sorption of Cr(III) onto thiourea-formaldehyde at 20 °C.

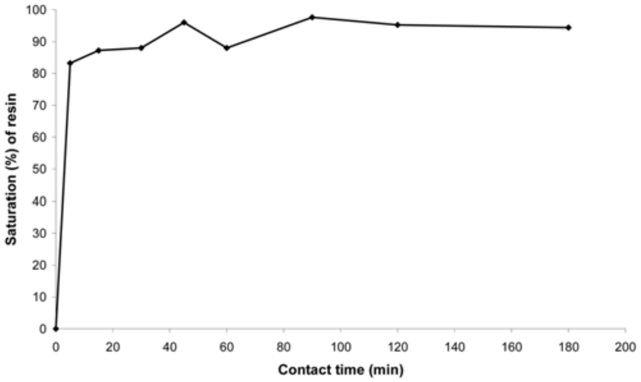

Fig. 5. Kinetics of chromium sorption on chelating resins.

5. Stability and Reusability of the Resin

The Cr(III) was sorbed and desorbed on 1 g of the resin several times. It was found that sorption capacity of resin after 20 cycles of its equilibration with Cr(III), changes less than 5%. Therefore, repeated use of the resin is feasible. The resin cartridge after loading it with samples can be readily regenerated with 0.5 M HNO_3. The sorption capacity of the resin stored for more than 6 months under ambient conditions has been found to be practically unchanged.

6. Effect of Temperature

The adsorption studies were performed at three different temperatures, 20, 30 and 40 °C, and the results of these experiments are shown in Fig. 6. The adsorption capacity increases with the increasing temperature, indicating that the adsorption is an endothermic process (Table 1). This may be a result of the increase in the mobility of the Cr(III) with increasing temperature [26]. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Table 1 also shows the maximum adsorption capacity of thiourea-formaldehyde

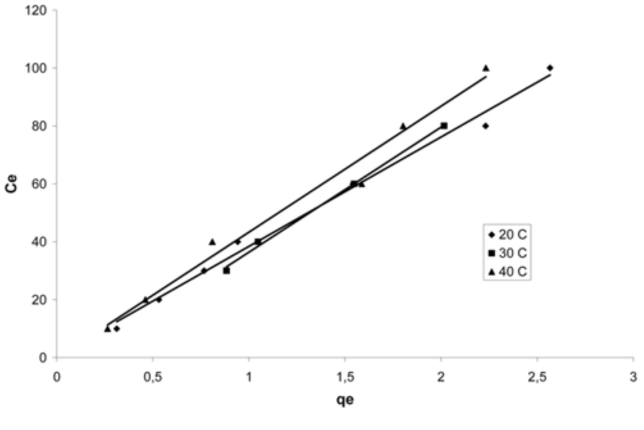

Fig. 6. Adsorption isotherms for Cr(III) on thiourea-formaldehyde at different temperatures [q_e (mg·g^{-1}) and C_e (mg·L^{-1})].

Table 1. Langmuir, Freundlich and Temkin isotherm and separation factors (R_L) for adsorption of Cr(III)

T (°C)	Langmuir isotherm model				Freundlich isotherm model			Temkin isotherm model			
	q_{max}	K_L	R^2	R_L	K_F	n	R^2	A	B	b	R^2
20	2.64	0.016	0.945	0.384	0.040	1.077	0.986	0.074	1.3129	856.4	0.934
30	4.96	0.004	0.701	0.704	0.041	1.079	0.995	0.082	1.1316	2180.7	0.965
40	2.37	0.031	0.992	0.242	0.041	1.060	0.983	0.124	0.8474	3072.4	0.928

q_{max} (mg/g), K_L (L/mg), K_F (mg/g) $(L/mg)^{1/n}$, A (L/g), b (J/mol)

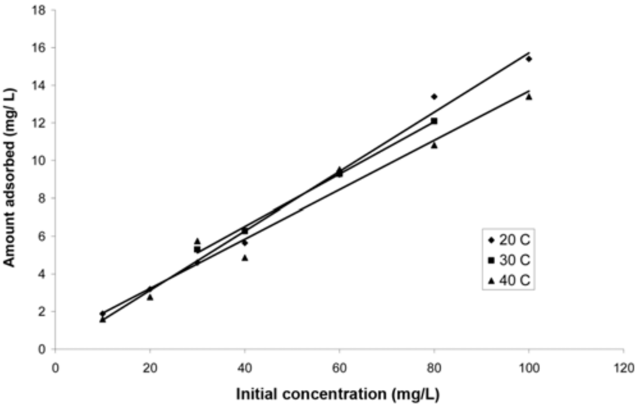

Fig. 7. Effect of concentration for the uptake of Cr(III) on thiourea-formaldehyde at different temperatures.

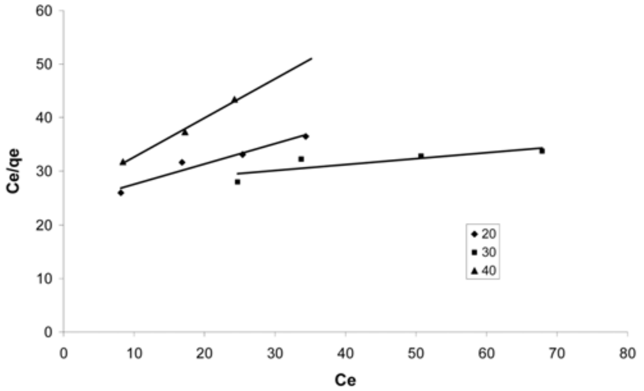

Fig. 8. Langmuir isotherm for Cr(III) adsorption onto thiourea-formaldehyde at different temperatures [q_e ($mg \cdot g^{-1}$) and C_e ($mg \cdot L^{-1}$)].

Table 2. The parameter R_L indicating the shape of the isotherm

Value of R_L	Type of isotherm
$R_L>1$	Unfavorable
$R_L=1$	Linear
$0<R_L<1$	Favorable
$R_L=0$	Irreversible

was determined as 2.64, 4.96 and 2.37 mg/g at 20, 30 and 40 °C, respectively.

The adsorption of Cr(III) was also recorded in the concentration range from 10-100 $mg \cdot L^{-1}$, at optimum pH and temperatures 20, 30 and 40 °C (Fig. 7). Fig. 7 indicates that the adsorption of Cr(III) by thiourea-formaldehyde increases with the increase in temperature, indicating thereby the process to be endothermic in nature.

7. Adsorption Isotherms

The Langmuir equation is given in the following equation [27].

$$q_e=q_{max} \cdot K_L \cdot C_e/(1+K_L \cdot C_e) \tag{2}$$

Where q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g) and K_L is the Langmuir constant (L/mg). Eq. (2) can be rearranged to a linear form:

$$C_e/q_e=(1/q_{max} \cdot K_L)+(C_e/q_{max}) \tag{3}$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Fig. 8).

Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of thiourea-formaldehyde surface. Langmuir parameters calculated from Eq. (3) are listed in Table 1.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as [28]:

$$R_L=1/(1+K_L \cdot C_0) \tag{4}$$

Table 1 shows the values of R_L (0.30-0.36) were in the range of 0-1 at pH studied which confirms the favorable uptake the Cr(III) (Table 2).

The Freundlich equation is an empirical equation employed for the described heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written [29]:

$$q_e=K_F \cdot C_e^{1/n} \tag{5}$$

Where K_F is the Freundlich constant (mg/g) $(L/mg)^{1/n}$ and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (5):

$$\text{Ln } q_e=\text{Ln } K_F+1/n \text{ Ln } C_e \tag{6}$$

Therefore, a plot of Ln q_e versus Ln C_e (Fig. 9) enables the constant K_F and exponent 1/n to be determined. The Freundlich equation predicts that the Cr(III) concentration on the adsorbent will increase so long as there is an increased in the Cr(III) concentration in the liquid.

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

The Temkin isotherm has been generally applied in the flowing form:

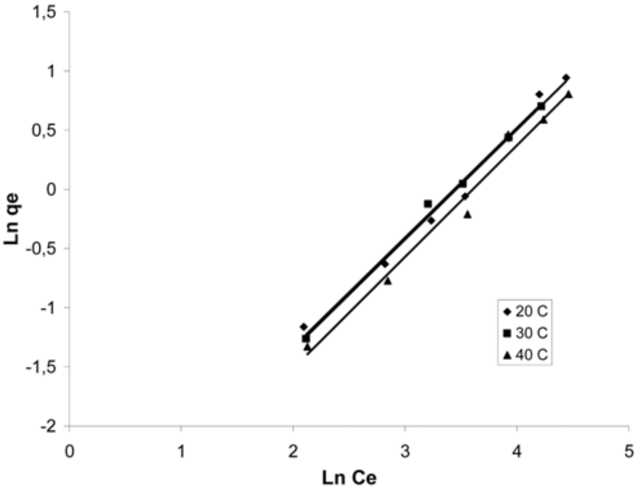

Fig. 9. Freundlich isotherm for Cr(III) adsorption onto thiourea-formaldehyde at different temperatures [q_e (mg·g^{-1}) and C_e (mg·L^{-1})].

$$q_e = \frac{RT}{b}\ln(AC_e) \tag{7}$$

and can be linearized:

$$q_e = B \ln A + B \ln C_e \tag{8}$$

Where B=RT/b and b is the Temkin constant related to heat of sorption (J/mol). A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol·K) and T is the absolute temperature (K). Therefore, plotting q_e versus ln C_e (Fig. 10) enables one to determine the constants A and B. Temkin parameters calculated from Eq. (7) and (8) are listed in Table 1.

8. Application of Method

Thiourea-formaldehyde was used to preconcentrate and determine Cr(III) ions in thte Kan river (Tehran, Iran). The pH of water sample (acidified with 0.1 M HNO_3) was adjusted to the optimum pH. Solid phase extraction with thiourea-formaldehyde coupled with ICP determination was supplied to determine the Cr(III) in water sample. The results, shown in Table 3, demonstrate the applicability of the procedure for Cr determination in samples.

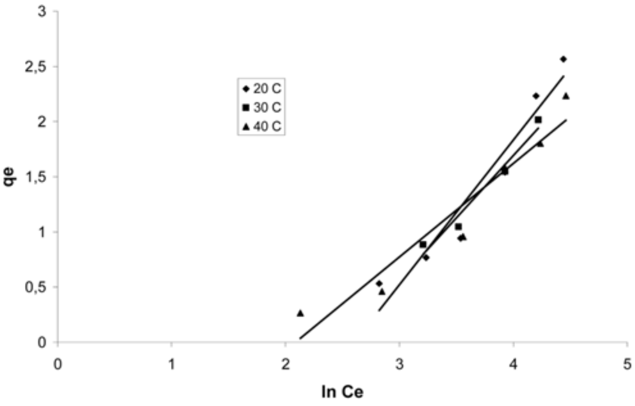

Fig. 10. Temkin isotherm for Cr(III) adsorption onto thiourea-formaldehyde at different temperatures [q_e (mg·g^{-1}) and C_e (mg·L^{-1})].

Table 3. Results obtained for chromium determination in water sample

Analyte	Cr(III)
Sample (without spiking of Cr (III))	N.D.
Before preconcentration (after spiking Cr(III)) (ppm)	4
After preconcentration (ppm)	13.8
Preconcentration factor	5
Recovery %	69
Standard deviation	0.19
Relative standard deviation (%)[a]	2.2
Before preconcentration (after spiking Cr(III)) (ppm)	6
After preconcentration (ppm)	17.6
Preconcentration factor	5
Recovery %	58.7
Standard deviation	0.18
Relative standard deviation (%)[a]	1.7
Before preconcentration (after spiking Cr(III)) (ppm)	8
After preconcentration (ppm)	22.3
Preconcentration factor	5
Recovery %	55.7
Standard deviation	0.17
Relative standard deviation (%)[a]	1.2

[a] For three determinations

CONCLUSION

A new resin was synthesized with 2-nitroanilin and 3-nitrophenol. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Cr(III) from large sample volumes. The Cr(III) adsorption was due to thiourea-formaldehyde - metal ion interactions. The resins also present the advantage of high adsorption capacity, good reusability and high chemical stability. The sorption of the investigated metal ion increases by increasing the contact time. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 2.64, 4.96 and 2.37 (mg/g) at 20, 30, and 40 °C, respectively. The R_L values showed that the thiourea-formaldehyde was favorable for the adsorption of Cr(III). Preconcentration by this resin combined with FAAS and ICP- AES can be applied to the determination of trace chromium (III) ions in water and the mineral reference sample with satisfactory results.

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