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Sorption of Cr(VI) by Amberlite XAD-7 resin impregnated with brilliant green and its determination by quercetin as a selective spectrophotometric reagent

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ABSTRACT

A new chelating polymeric sorbent as an extractant-impregnated resin (EIR) has been developed using brilliant green (BG) and Amberlite XAD-7 resin. The BG-impregnated resin showed superior binding affinity for Cr(VI) in the presence of many co-existing ions and no considerable interference was observed. The influence of various physicochemical parameters on the recovery of Cr(VI) were optimized by both static and dynamic methods. The Langmuir adsorption isotherm gave a satisfactory fit of the equilibrium data. The kinetic studies performed for Cr(VI) sorption revealed that <45 min was sufficient for reaching equilibrium metal ion sorption. A preconcentration factor of 100 was found for the column-mode extraction. The spectrophotometric determination of eluted Cr(VI) was carried out using quercetin as a selective reagent. The calibration graphs were linear in the range 5.0×10^{-8} to 4.0×10^{-7} M with a detection limit of 8×10^{-9} M. The proposed method has been successfully employed for the analysis of natural water. The recoveries for the Cr(VI) amounts spiked to the samples were >93%, which confirmed accuracy of the measurements.

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1. Introduction

The determination of low level of Cr(VI) in environmental samples and its removal from the water by using an inexpensive processing are very important. Several methods have been described for the separation and determination of Cr(VI) ions including, solvent extraction [1], coprecipitation [2], and solid phase extraction [3-6]. Solid phase extraction is one of the wellknown preconcentration/separation techniques for this purpose [7–10]. In this technique, various reagents used as chelating agents are grafted onto appropriate solid supports, such as Amberlite XAD series, which have been successfully used in most studies in our working group [11-13]. Among the various methods of solid sorbent preparation, impregnating methods have been more developed in the last decade [12-16]. The impregnation method is free from difficulties encountered in chemically linking a chelating reagent to a support matrix. In addition, there is a wide choice of reagents for desired selectivity [17-20].

Brilliant green (BG) is one of the commonly known cationic dye (structure is shown in Fig. 1(a)) used for various purposes,

e.g. biological stain [21], veterinary medicine [22], an additive to poultry feed to inhibit propagation of mold [23], intestinal parasites and fungus [24]. It is also extensively used in textile dying and paper printing [25]. Recently, adsorption of BG on a series of organic/inorganic substances was characterized for various purposes, e.g. removal of BG from aqueous solution [26–28], preparation of optical pH sensor [29], separation/preconcentration of uranyl ions [30].

In the light of the requirements for the search of a simple and inexpensive method for separation/preconcentration of Cr(VI) followed by their individual elution and determination, this work has been designed to prepare a selective anion-exchange resin containing BG via the impregnation in/on Amberlite XAD-7, a copolymer backbone for the selective uptake of Cr(VI) from weakly acidic solutions. Subsequently, enabling to determine Cr(VI) eluted from the resin by a simple spectrophotometric method has targeted to use quercetin, a natural antioxidant reagent, which was used previously as a selective agent for the determination of Cr(VI) in natural water samples [31].

2. Experimental

2.1. Reagents

All the chemical reagents were of analytical reagent grade and supplied by Merck (Darmstadt, Germany). Amberlite XAD-7

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Fig. 1. Chemical structure of brilliant green (BG).

 $(20-50 \text{ mesh}, \text{ surface area: } 450 \text{ m}^2 \text{ g}^{-1}, \text{ pore diameter: } 90 \text{ Å}) \text{ was}$ obtained from Fluka (Switzerland). Double distilled and deionized fresh water was used in all the experiments. BG solutions were prepared by dissolving the appropriate amounts in 100 mL of methanol. Quercetin solution (1.0×10^{-3} M) was prepared by dissolving the appropriate amount in 100 mL of n-amyl alcohol. All of these solutions were stored in refrigerator at 4°C. Cr(VI) solution $(1 \times 10^{-2} \,\mathrm{M})$ was prepared by dissolving appropriate amounts of K₂Cr₂O₇ in distilled water and the prepared solution was standardized by iodometric titration. Working solutions were papered by diluting the stock solution. A solution with concentration of 0.1 M respect to NH₃ and NaCl was prepared as the eluent. The following solutions with equal concentrations of 1 M were used for buffering the experimental solutions at the pH of interest: HCl/KCl for pH 1-2; formic acid/sodium formate for pH 2-4; acetic acid/sodium acetate for pH 4-6.

2.2. Apparatus

Spectrophotometric Cr(VI) determinations with quercetin were performed by use of a Shimadzu model UV-1601PC spectrophotometer equipped with quartz cuvettes of 1 cm thickness. A Corning model 130 pH-meter was used for pH measurement. The flow of liquids through the short column was controlled with an Eyela SMP-23 peristaltic pump and a 6-port valve (V-451, Upchurch). Nitrogen analysis of the prepared impregnated resin was carried out using a Gerhardt micro Kjeldahl apparatus. A Sartorius membrane filter of pore size 0.45 μm was used for filtration of the natural water samples.

2.3. Preparation of the EIR

In order to remove each type of impurity, which may be found with the fabricated beads, before the impregnation, the Amberlite XAD-7 resin was treated with 1:1 methanol-water solution containing 6 M HCl for 12 h. Then, the resin was thoroughly rinsed with doubly distilled water and placed into a drying oven at 50°C for 30 min. To prepare the impregnated resin, portions of Amberlite XAD-7 (1 g of dry resin) was transferred into a series of glassstoppered bottles containing 200 mL of BG solutions with different concentrations. The mixtures were slowly shaken for 6h to complete the impregnation process. After that, they were placed into a drying oven to remove the solvents at the ambient temperature. Each type of the resin beads was then transferred to a porous filter and washed successively with HCl and large amounts of distilled water until none amount of BG was detected in the filtrate, spectrophotometrically. Finally, the impregnated resins were dried at 50 °C and weighed. The amount of BG impregnated on/in the resin bead was determined from the amount of weight change in resin. To protect the prepared EIR from damage, it was kept in a stoppered dark glass bottle under the distilled water content.

2.4. Sorption equilibrium procedure

The sorption isotherms of Cr(VI) ions on/in the EIR were obtained using the batch technique at the pH of maximum uptake. For this purpose, aliquots of 100-mL of the buffered solutions (pH 3.0) containing Cr(VI) with the concentration range of 1.0×10^{-4} to $5.0\times10^{-4}\,\mathrm{M}$ were placed in a series of conical flasks and $0.05\,\mathrm{g}$ of the EIR was added to each of them. The mixtures were placed in a constant temperature shaker and were shaken at $298\pm1\,\mathrm{K}$ for 45 min. After that, portions of 5-mL of the supernatants were withdrawn and subjected to the determination process of Cr(VI) as discussed at the following.

2.5. Sorption rate procedure

A series of fixed weighed portions (0.0500 g) of the EIRs were immersed into aliquots of 100-mL of Cr(VI) buffered solutions (pH 3.0) with concentration of 2.0×10^{-5} M at $25\,^{\circ}\text{C}$. The mixtures were stirred mechanically for a pre-determined time interval at a fixed speed (220 rpm). The EIR amount, contact time and temperature of sorption were carefully controlled. At the appointed time, each one of the mixtures was rapidly filtrated using a porous filter and the SIR was treated with 4.5 mL of the eluent solution. After that, the filtrate eluent was acidified with 0.5 mL 1 M HCl and subjected to the determination process of Cr(VI) as discussed at the following. The optimum contact period was taken as the time at which maximum Cr(VI) sorption took place.

2.6. Metal extraction procedure

0.5 g of EIR was packed into a column with an internal diameter of 0.4 cm. The ends were fitted with glass wool to keep the EIRs inside of the column. The bed length of resin in the column was about 75 mm. Working solutions containing Cr(VI) with the concentration exceeding the detection limit prepared in which the pH and ionic strength were respectively adjusted to 3.0 and 0.01 M using the formic acid and ammonium formate solutions. Periodically, aliquot of 500-mL of the prepared solutions was passed through the column at a flow rate of $6 \, \text{mL} \, \text{min}^{-1}$. After washing the column with $10\,mL$ of distilled water to remove free matrix substances, the Cr(VI)content sorbed on the EIR was desorbed using 4.5 mL of the eluent solution at a flow rate of 1 mL min⁻¹. The eluent was transferred to a 10-mL screw cap test tube, then 0.5 mL of 1 M HCl and 5 mL of the quercetin solution were added to it. The tube was capped and shaken for 20 min. After centrifugating the tube contents and separating the aqueous and organic phases, aliquot of the aqueous phase was withdrawn and subjected to the spectrophotometric measurement at the maximum wavelengths of 292 nm against a reagent blank prepared by the same manner.

3. Results and discussion

3.1. Preparation and characterization of the EIR

As pointed out above, there is no report referring to use BG as an extractant for Cr(VI) ion recovery. In the current study, BG was impregnated on/in Amberlite XAD-7, which is an inert polymeric substance based on acrylic ester, hydrophobic, continuous pore phase with a weak dipole moment of 1.8. It is used for removal of organic pollutants form aqueous wastes, ground water and vapor streams. It has been also used in the impregnation procedures for preparation of various impregnated resin employed for selective separation of certain metal ions [17,20,31–34].

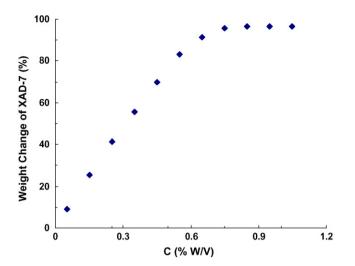


Fig. 2. Effect of BG concentration on the EIR preparation at the condition that portions of 1-g of the dry polymer beads of Amberlite XAD-7 was subjected to the impregnation process.

To prepare the appropriate form of the EIR, the impregnation process was carried out at various impregnation ratios (g eosin B/g dry polymer adsorbent). Fig. 2 depicts the weight change obtained against the BG concentration. As it is shown, a maximum weight change (96%) was found at the concentrations more than 0.85% BG, which was used for the EIR preparation.

The chemical stability of the EIR was examined by sequentially suspending a portion of 0.5-g of the EIR in 50-mL aliquots of 6 M HCl and 4 M $_{\rm 12}{\rm SO_4}$ and shaking for 2 h. After filtering the solution and rinsing the EIR with distilled water, the released amount of BG in the acidic rinsed solutions was examined by absorbance measuring at $\lambda_{\rm max}$ of BG (625 nm). It was found that the EIR benefited from a high stability since no considerable quantity of BG was observed in the solutions.

In another experiment, the nitrogen content of 0.5 g of the EIR used continuously for 150 runs of column sorption/desorption processes was determined by Kjeldahl method. The result obtained was 3.48 mmol N/g-dry EIR, which was in agreement with that obtained from the nitrogen analysis of 0.5 g fresh EIR (3.62 mmol N/g-dry EIR). This observation confirmed reuse stability of the EIR, satisfactorily.

3.2. Characterization of the spectrophotometric determination

Quercetin (3,3',4',5,7-pentahydroxy-flavone) is a flavonoid of widespread occurrence in nature whose medicinal properties have been extensively demonstrated in the literature, especially the antioxidant capacity [35,36]. It is weakly soluble in water and its solubility increases in lipids and proteins. Quercetin acts as a free radicals scavenger in treatment with different bioorganic materials [37–39]. The mechanism of such oxidation reactions has been studied in organic solvents using the electrochemical techniques [40]. In our previous work [41], the reaction between quercetin and Cr(VI) has been investigated and spectrofluorometric determination of Cr(VI) was carried out using this reaction. In the present work, due to arise a high selectivity and sensitivity from the reaction between quercetin and Cr(VI), it was used for the spectrophotometric determination of Cr(VI) in the eluent solution.

3.3. Effect of pH and ionic strength on Cr(VI) sorption

The initial pH of the Cr(VI) solution is an important parameter, which controls the sorption process particularly the sorption capacity. This parameter causes to change of the surface charge of

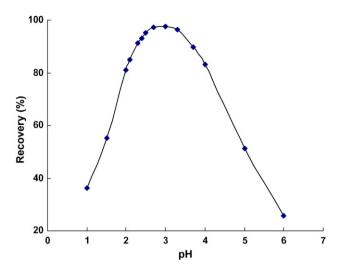


Fig. 3. Effect of sample pH on the sorption process using 500 mL of model solutions of 5×10^{-7} M Cr(VI) containing 0.5 g of the EIR.

the sorbent, convert of the chromium species and the other ions present in the solution, and extent of dissociation of functional groups on the active sites of the adsorbent. To observe the effect of pH on sorption of Cr(VI) on/in the EIR, 0.5 g of the EIR was added to a solutions in which the concentration of Cr(VI) was fixed to 2×10^{-7} M, whereas the pH was varied at each step from 1 to 6 using the appropriate buffering system. The results are depicted in Fig. 3. As it is shown, maximum sorption was achieved at pH range of 2.5–3.3. The low efficiency of the sorption at the pHs less than 2.5 and more than 3.3 may be related to the structural change of BG and chromium species, respectively. Therefore, the buffering pH of 3.0 was selected for subsequent investigations.

The effect of ionic strength on the sorption process was also studied at the presence of sodium nitrate within the concentration range 0.001–0.5 M. It was found that the sorption efficiencies were diminished at the ionic strength values greater than 0.1 M. Hence, the ionic strength was not exceeded from this value at subsequent investigations.

3.4. Sorption equilibrium study

In order to optimize the design of an adsorption system to remove Cr(VI) from solutions, it is essential to establish the most appropriate correlation for the equilibrium curve. The most common type of isotherms is the Langmuir model. The Langmuir isotherm is based on the assumption that there is a finite number of binding sites, which are homogeneously distributed over the adsorbent surface. These binding sites have the same affinity for adsorption of a single molecular layer so that there is no interaction between adsorbed molecules. The Langmuir isotherm given in Eq. (1) gave the best fit of the experimental data:

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{1}{Q_{\rm m}K_{\rm L}} + \frac{C_{\rm e}}{Q_{\rm m}} \tag{1}$$

where $Q_{\rm m}$ is the amount adsorbed per unit mass of the adsorbent corresponding to formation of a complete monolayer (mmol ${\rm g}^{-1}$), and $K_{\rm L}$ is the Langmuir constant related to energy of adsorption (Lmmol $^{-1}$). $C_{\rm e}$ and $Q_{\rm e}$ are the equilibrium liquid phase concentration (mM) and amount of solute adsorbed at equilibrium (mmol ${\rm g}^{-1}$), respectively. The linear regression equation obtained is $C_{\rm e}/Q_{\rm e} = 9.3110C_{\rm e} + 0.2298$ with regression coefficient (r^2) equal to 0.9996. Isotherm parameters of $Q_{\rm max}$ and $K_{\rm L}$ calculated from this equation are 0.1074 mmol ${\rm g}^{-1}$ and 40.52 L mmol $^{-1}$, respectively.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , known as the separation factor [42], which is given by Eq. (2):

$$R_{\rm L} = \frac{1}{1 + K_{\rm L}C_0} \tag{2}$$

where C_0 (mg/L) is the initial Cr(VI) concentration. The value of $R_{\rm L}$ indicates the shape of the isotherms to be either unfavorable ($R_{\rm L} > 1$), linear ($R_{\rm L} = 1$), favorable ($0 < R_{\rm L} < 1$) or irreversible ($R_{\rm L} = 0$). Considering the energy of sorption calculated as the Langmuir constant ($34.17\,{\rm L\,mmol^{-1}}$), the prepared EIR appears to be a favorable sorbent for Cr(VI) since the $R_{\rm L}$ value is in the range of $0 < R_{\rm L} < 1$. The dependence of sorption of Cr(VI) on the EIR with temperature have been evaluated using the classic Van't Hoff equation:

$$\Delta G = -RT \ln K_C \tag{3}$$

where ΔG and T are Gibbs free energy and absolute temperature, respectively. R is the gas constant (8.314 J mol $^{-1}$ K $^{-1}$) and $K_{\rm C}$ is the sorption equilibrium constant. The value of ΔG at room temperatures for the sorption of Cr(VI) was found to be -8.57 kJ mol $^{-1}$, which is denoted on the spontaneous chemisorption nature of the sorption process.

3.5. Sorption rate study

The sorption rate of Cr(VI) was studied via a separate batch of experiments at constant temperature with a fixed amount of the EIR and a fixed adsorptive concentration. As illustrated in Fig. 4, the equilibrium half-time for sorption of Cr(VI) was estimated to be 20 min and total equilibrium was established in about 45 min. The maximum sorption capacity was found to be 0.105 mmol g $^{-1}$, which is in agreement with that value obtained from the Langmuir equation.

3.6. Desorption studies

For desorption of Cr(VI) ions from the EIR, various types of basic reagents were examined including sodium hydroxide, sodium carbonate and ammonia. Among them, ammonia was preferred owing to protect EIR from damage. Consequently, a number of experiments with the eluent flow rate of 1 mL min⁻¹ were carried out in which the recovery of Cr(VI) was investigated against the change in volume and concentration of ammonia solution as the eluent. The results showed that achievement to quantitative recoveries

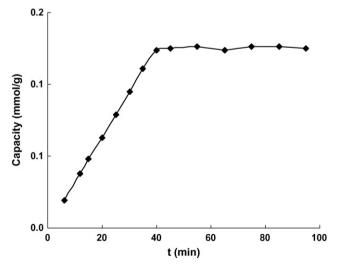


Fig. 4. Effect of the contact time on the sorption rate using 100 mL of model solutions of 2×10^{-5} M Cr(VI) containing 0.05 g of the EIR.

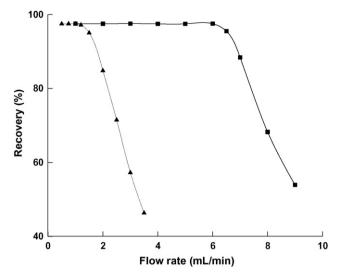


Fig. 5. Effect of sample (–) and eluent (----) flow rates on the recovery of Cr(VI) using 500 mL of model solutions of 2×10^{-7} M Cr(VI) containing 0.5 g of the EIR.

is not possible even using ammonias with high concentration as the eluent. After that, the ionic strength of the eluent solution was enhanced by addition of NaCl to the ammonia solutions and finally it was observed that elution with 4.5 mL of solution containing ammonia and sodium chloride with both concentrations of 0.1 M is sufficient to obtain quantitative recoveries (>95%) for the Cr(VI) analysis.

3.7. Sample and eluent flow rates

The sample and eluent flow rates are important parameters to obtain quantitative retention and elution, respectively. The influences of the sample and eluent flow rates on the recovery of Cr(VI) ions were respectively examined in the flow rates range of 1–9 and 0.5–4 mL min $^{-1}$ using 500 mL of model solutions of 2×10^{-7} M Cr(VI). When the influences of flow rates of sample examined, the eluent flow rate was kept constant as $1\,\mathrm{mL\,min}^{-1}$ and also the flow rate of sample was kept as $5\,\mathrm{mL\,min}^{-1}$, when the effects of flow rates of the eluent examined. As shown in Fig. 5, the sorption of Cr(VI) was quantitative up to the sample flow rate of $6\,\mathrm{mL\,min}^{-1}$ and the desorption could be carried out, properly, at the flow rate of 0.5–1.5 mL min $^{-1}$. All further studies were performed at the sample and eluent flow rates of 6 and $1\,\mathrm{mL\,min}^{-1}$, respectively.

3.8. Effect of sample volume on the recoveries

In order to explore the possibility of enriching low concentrations of Cr(VI) ions from the large sample volume, the influence of the sample volume on the recovery of Cr(VI) was also investigated. The amount of Cr(VI) was 0.5 µmol in the model solutions and this amount was hold constant while increasing the sample volume up to 1400 mL. It was found that the recoveries were constant up to 850 mL of the sample solutions. At the volumes more than 850 mL, the recoveries were decreased. Considering the results obtained, the preconcentration factor was found to be 170, which is calculated as the ratio of the highest sample volume (850 mL) to volume of the solution prepared for the absorbance measurements (5 mL). In spite of this feasibility, it was preferred to use aliquots of 500-mL of the samples because of the sorption process was taken a long time when more excessive volume was passing through the column in lieu of obtaining a greater preconcentration factor.

3.9. Analytical figures of merit

Under the optimum conditions described above, the calibration curve was linear over the concentration range of 5.0×10^{-8} to $4.0 \times 10^{-7} \, \text{M}$ (2.6–20.6 µg/L) of Cr(VI) present in 500 mL of solution. The linear regression equation is as follows: $A = 1.0968 \times 10^6 C + 0.0120$; $R^2 = 0.9991$; where A is the absorbance, C is the molar concentration of Cr(VI), and R^2 is the correlation coefficient. All of the statistical calculations were based on the average of three determinations. The detection limit corresponding to three times the standard deviation of the blank (n=7) was found to be 8×10^{-9} M. The R.S.D. obtained in the replicate treatments (n=7) with 2×10^{-7} M Cr(VI) was 2.15%, which is denoted on appropriate reproducibility of the process. The experiments also exhibit a linear calibration curve as: $A = 1.1169 \times 10^4 C + 0.0075$ over the range of 5.0×10^{-6} to 4.0×10^{-5} M with the correlation coefficient of 0.9997 for the direct spectrophotometric determination of Cr(VI). By considering that the experimental preconcentration factor defined as the ratio of the slopes of the calibration graphs with and without preconcentration [43], the calculated ratio is 98.2, which is in agreement with those obtained under the optimum conditions.

3.10. Interference effect

Under the optimum conditions, the effects of various co-existing ions, which may be found in natural water samples were studied by introducing each one to 500-mL aliquots of the solutions containing Cr(VI) with the concentration of 1.0×10^{-7} M. Each ion was considered as interfering agent, when the absorbance value exhibited a deviation more than $\pm 5\%$. Hence, the tolerance limit was taken as the interfering ion's amounts that cause an error less than $\pm 5\%$ in the absence of interference. The results obtained are shown in Table 1 from which it is clear that none of the co-existing ions tested were found to have deleterious effect on the determination of Cr(VI) with this method. The blank resin, i.e., Amberlite XAD-7 without BG, retained neither Cr(VI) nor any metal ions, suggesting that the selective sorption process was caused by selective ion-association with the BG impregnated on the resin. This performance emphasized on selective sorption behavior of Cr(VI) on/in the EIR so that it could be used for separation/preconcentration of ultra trace amount of Cr(VI) at the presence of many co-existing ions.

3.11. Application

The proposed method was applied to determination of Cr(VI) in spring, well and river water samples collected from areas of Kashmar, a city in Iran, Khorasan Rasavi province. The water samples were filtered through a membrane filter with a pore size of 0.45 mm before the determination. The accuracy of the determinations was investigated by spiking water samples with Cr(VI) ions at various concentrations. The results obtained are summarized in Table 2. As can be seen from the results, the recoveries for the spiked amounts of Cr(VI) were found to be >95%, which confirmed the accuracy at the 95% confidence level for application of the proposed method

Table 1 Tolerance ratio of co-existing ions on the determination of 2×10^{-7} M of Cr(VI) in 500 mL of model solutions.

Co-existing ions	Tolerance ratio (mol/mol)	
NH ₄ ⁺ , Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , NO ₃ ⁻	10,000	
Cd ²⁺ , Cu ²⁺ , Co ²⁺ , Mn ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺ , Al ³⁺ , I ⁻ , Cl ⁻	5,000	
Cr ³⁺ , Fe ³⁺ , F ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻	1,000	

Table 2 Determination of Cr(VI) in water samples. The results are mean of three measurements \pm standard deviation.

Water sample ^a	Spiked amount (μg) to 1000 mL	Found value $(\mu g L^{-1})$	Recovery (%)
Spring	-	-	-
water	5.2	5.32 ± 0.35	102.4
	20.80	9.93 ± 0.31	95.5
Well	-	_	_
water	5.20	5.60 ± 0.42	107.7
	10.40	10.86 ± 0.27	104.4
River	-	1.75 ± 0.31	_
water	5.20	6.73 ± 0.45	95.8
	10.40	11.49 ± 0.36	93.7

^a All of the water samples were collected from areas of Kashmar, a city in Iran, Khorasan Rasavi province.

for ultra trace determination of Cr(VI) in contaminated water samples.

4. Conclusion

Column-mode solid phase extraction of Cr(VI) with an impregnated resin containing BG provides an effective preconcentration and separation of Cr(VI). The newly impregnated resin exhibited a good affinity and selectivity to extract Cr(VI) ions as an ion-exchange ligand. This EIR seems promising for removal of Cr(VI) ions as apparent from the column studies. Enhanced detection limit, relatively simple sample preparation, and cost effective analysis of trace amount of Cr(VI) are feasible with this method. The prepared EIR can be successfully regenerated for 150 cycles of operation in the column. The results obtained from the analysis of natural water samples proved the reliability of the proposed method.

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