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Alternative extraction for separation of trace Chromium (VI) by 2-Aminopyridine/Graphene oxide nano-plates in water samples

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ABSTRACT: A simple method has been developed for the preconcentration of chromium (VI) based on the adsorption of its modified by2-aminopyridine/graphene oxide nano-plates.A novel and selective method has been developed for the fast determination of trace amounts of chromium (VI) ions in water samples .The procedure is based on the selective formation of chromium (VI) ions using modified 2-aminopyridine/graphene oxide nano-plates at different pH values followed by elution with organic eluents and determination by atomic absorption spectrometry The preconcentration factor was 20. The limit of detection of the proposed method is 9.7 ng mL^{-1}. The maximum sorption capacity of the sorbent under the optimum conditions has been found to be 5mg of chromium (VI) per gram of sorbent. The relative standard deviation under the optimum conditions was 2.5% (n = 10). Accuracy and application of the method was estimated by using the test samples of natural and synthetic water spiked with different amounts of chromium (VI) ion.

Keywords: *Chromium (VI) ion; Graphene oxide nano-plates; Preconcentration of heavy metals; SPE.*

INTRODUCTION

Metals find many useful applications in our daily lives but as pollutants, metals pose harm to plants, animals and humans. Increase in use of metal for anthropogenic activities such as industrial, agricultural and domestic activities in turn leads to generation of more metal pollutants stemming from the resulting wastes [1, 2], which could be in liquid form (mine waters, wastewaters from metal surface treatment processes like electroplating and pickling, wastewaters from tanning, wood processing, inorganic pigment production) or solid form (solid residues from mineral processing, electrical and electronic waste, spent catalysts and batteries) [3, 4]. However, it is not feasible to do away with usage of metals. More metals are continued to be mined and produced to meet demand.Depletion of high-grade metal ores and the need for managing metal pollution call for processes that can recover metals from low-grade ores and secondary sources through waste recycling [3, 6]. chromium (VI) used 0.25 mol/L hydrochloric acid to scrub away coextracted zinc before stripping chromium

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(VI) [20]. In another study on separating copper and nickel by solvent extraction, nickel could be stripped first from the loaded solvent containing both metals by more dilute sulfuric acid was later stripped from the nickel-free solvent using more concentrated sulfuric acid [1]. Similarly, a solvent extraction study intended for separative recovery of cadmium, nickel, zinc and copper from smelting wastewater first extracted all the mentioned metals and subsequently selectivelys-tripped one metal at a time using progressively more acidic stripping solution after each metal removal [21-33]. Consequently, in the current investigation, the researchers focused on the first application of 2-aminopyridine/graphene oxide nano-plates as a novel adsorbent for dispersive solid-phase and extraction of chromium (VI) wastewater samples before the flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation

The determination of chromium (VI) by PG-990 flame atomic absorption spectrometer is equipped with HI-HCl which was done according to the recommendations of the manufacturers. Accordingly, the pH measurements were used by Sartorius model PB-11.

Materials

In the current investigation, the following materials have been applied for the experiments; graphene oxide nano-plates, hexahydrate chromium (VI), thio-semi-carbazide ligand, buffer, and nitric acid. Additionally, ethylenediamine, thio-semi-carbazide ligand (CH_5N_3S) was prepared from Darmstadt, Germany of Merck.

Synthesis GrO

To prepare GrO, a certain amount of graphite oxide powder (0.1 g) was placed in 100 mL of water and ethanol solution (50/50%, v/v) under ultrasonic power of 140 W for 2 h. The resulted powder was dried in a vacuum desiccator [31].

GrO functionalized with 2-aminopyridine

The 0.1 g of GrO powder was poured in 200 mL of deionized water, then 0.2 g of 2Ap was poured and the mixture was placed in a homogenizer for 30 min

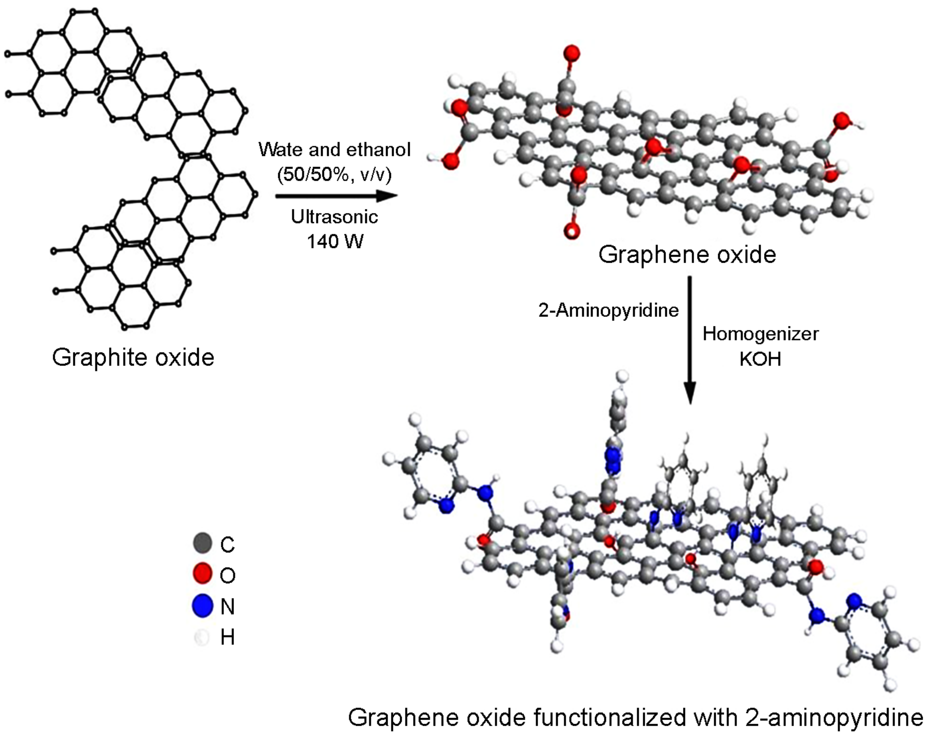

Fig. 1. Preparation of graphene oxide functionalized with 2-aminopyridine.

at 13000 rpm. Then, the 0.2 g KOH was added to the homogeneous mixture and was subjected to ultrasonic power of 140 W for 30 min. The precipitate was refluxed at 80 °C and then washed with water and ethanol and dried at 25 °C (Fig. 1) [32].

The initial experiment of chromium (VI) extraction for determining the suitable adsorbent

The procedure for extraction and recovery of chromium (VI) ions by 2-aminopyridine/graphene oxide nano-plates is as follows; in the first step, 0.2 g of thiosemicarbazone ligand and 0.3 g of 2-aminopyridine/graphene oxide nano-plates and were dissolved in the little amount of acetone, and then it dried. Four 50-mL ballons were adopted, and then 0.05 g of 2-aminopyridine/graphene oxide nano-plates was poured into one of the balloons. Thereupon, a 1 ml buffer solution with a pH of 6.0 was added to balloons and a 2 ppm solution was prepared with an analyte. Four solutions were shaken at 25°C for 20 min, then these solutions for 15 min were centrifuged and the supernatant injected into an atomic absorption apparatus.

The effect of adsorbent amount for chromium $(VI)^+$ extraction

Seven 2.0 ppm solutions with 50 mL of chromium (VI) were provided and poured into seven flasks. Seven solutions were adjusted at pH=6.0 (optimum pH) and different amounts of the adsorbent (0.005, 0.01, 0.03, 0.05, 0.07, 0.12, and 0.15) added to flasks. The mixtures were shaken for 20 min, and then the mixtures were centrifuged and the top solution of the examine tube injected in flame atomic absorption spectrophotometry.

Application on real samples

Once the extraction method was performed by the adsorbent, optimal conditions were achieved for it, and Multiple real aqueous samples were investigated. The real samples were as follows; well and drinking water in Pishva Town were collected with temperatures of 20 and 22°C, pH=7.1, 7.3 in 23.8.95 at 9:45, 10:00, respectively. Finally, a fish farming sample was collected at, pH=6.20 in 23.8.95 at 11:20. First, these suitable bottles were provided for the sampling of samples. The bottles were washed first with ordinary and distilled water. The bottles dried completely, and the 'suitable' label was attached to each bottle. To collecting of water samples, the used containers sample dried and cleaned and they had already been washed. For the analysis of the samples in the first stage, colloidal and suspended particles were removed. To this aim, the water samples passed through 0.22 µm filters. Next, the volume of 100 mL of samples was poured into the sample container. The pH of samples was adjusted at 10 and then, graphene oxide nano-plates and ligand were added to samples. They stirred for 20 min and the mixture was then centrifuged. Then, they were washed with HNO_3 0.1 M and were shaken again for 20 min. Finally, following the centrifugation of the mixture, absorption of chromium (VI) ion was identified from the filtered solution by flame atomic absorption spectrophotometry. In the first step, the sample itself was injected into the apparatus without any chromium (VI) ion, wherein water samples, the device displayed no absorption. To identify certain amounts of chromium (VI) of the samples, the method of standard elevation was used. This stage was accomplished like the first step, the only discrepancy was that 0.5 mL of 200 ppm solution with chromium (VI) added to the water samples. Finally, the absorption of chromium (VI) ion was identified from the filtered solution by flame atomic absorption spectrophotometry.

RESULT AND DISCUSSION

This section deals with the results of the research experiments. The results achieved in the experimental chapter, calibration curve, and the factors influencing the extraction (e.g. pH, temperature effect, time, etc.) of chromium (VI) ion by the 2-aminopyridine/graphene oxide nano-plates are discussed which are followed in the presentation of scientific justification and overall conclusion of the study.

Investigation of the influential factors on chromium (VI) extraction

Study the effect of pH on chromium (VI) extraction

As the results in Fig. 2 indicate, at pH=4, chromium (VI) adsorption was maximized, while at lowest and

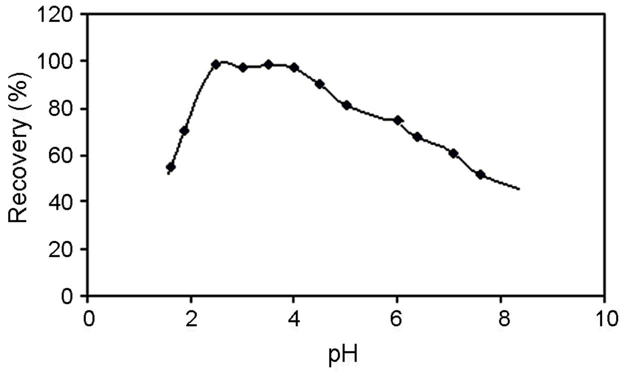

Fig. 1. Preparation of graphene oxide functionalized with 2-aminopyridine.

highest pHs, the extent of adsorption declines, inferring that at pH<4 adsorptions of chromium (VI) ions cannot occur completely. To determine the amount of 2-aminopyridine/graphene oxide nano-plates required for effective removal of chromium (VI), different amounts of the 2-aminopyridine/graphene oxide nano-plates (50 mg) for modification of 2-aminopyridine/graphene oxide nano-plates with fixes amount (3 mg) and its effect for the removal of chromium (VI) from 20 mL solutions of chromium (VI) (50 µg/L) were investigated.

Investigation of the effect of time on chromium (VI) extraction

Based on the results, the extent of absorption increases, and the chromium (VI) ions present in the solution find more chance to be adsorbed in the adsorbent's sites. Therefore, the quantitative extraction of chromium (VI) ion is possible for a period of longer than 20 min, and within durations longer than 20 min and more, the reaction happens completely.

Table 1. Selection of the appropriate desorption for recovery of chromium (VI).

Solvent	Recovery (%)
HNO_3 0.1M	90.20(2.4) [a]
HNO_3 1M	80.32(2.4)
HNO_3 3M	70.05(2.4)
H_2SO_4 0.1M	70.64(2.0)
H_2SO_4 1M	66.70(2.0)
NaOH 0.1M	50.46(2.0)

a) Measurement RSD after three replications

Survey of the effect of type of various desorption solvent for recovery of chromium (VI)

Based on the results (Table 1), NaOH cannot be used as appropriate desorption and these bases do not possess a complete detergence power. Therefore, mineral acids with determined concentrations, H_2SO_4, and HNO_3 were applied. As shown in Table 1, the results of this table offer that all acids contain a good detergence power for chromium (VI), but the recovery percentage of HNO_3 is higher than that of other acids. In an acidic environment, the possible deposits dissolved and recovery of these ions increased. However, the results obtained from nitric acid were better than H_2SO_4, in that 0.1 M of solution washed 92.54% of the chromium (VI) ion adsorbent. So, for the rest of the experiments, nitric acid 0.10 M was used as the desorption solution.

Survey of optimization of the volume effect of desorption solvent for chromium (VI) recovery

After the investigation and choice of optimal desorption, the volume of solvent was investigated, with the results which are shown in Table 2. The volume of 12 mL for HNO_3 was selected as the optimal volume for washing.

Investigation the effect of breakthrough volume

Following the optimization of the pH of the desorption solvent and sample solution, etc., to elute the chromium (VI) in the adsorbents, the maximum volume of the aqueous solution containing chromium (VI) should be measured. If the volume of the test solution to be less than the breakthrough volume, and passaging of that volume, all analytes are kept in the solid phase. The results in (Table 3) verify that up to 250 mL of ions are adsorbed by the nano adsorbents and if the

Table 2. The optimum volume of the desorption solvent

Solvent volume (mL)	Recovery (%)
5	41.20(2.4) [a]
7	55.67(2.3)
9	76.66(2.4)
12	90.05(2.1)
14	89.02.1)

a) Measurement RSD following three replications

Table 3. Investigations of the effect of solution volume in the sample

V (mL)	Recovery (%)
50	85.2(2.5) [a]
100	79.2(2.1)
150	69.7(2.2)
250	65.5(2.3)
350	58.4(2.4)
500	31.9(2.4)

a) Measurement RSD following three replications

sample volume is greater than this value, some of the chromium (VI) is not kept on the adsorbent and pass over the adsorbent with no inhibition. Also with definition by the concept of breakthrough volume, it can be reported that the breakthrough volume in the current study is 250 mL and if the sample solution volumes which includes chromium (VI) is over 250 mL, adsorption does not occur completely and hence if 250 mL of sample volume is passed over the adsorbent and then with 12 ml of the desorption solvent washed, the concentration factor could not be achieved as 30. This concept that the concentration of chromium (VI) in 7 mL of desorption solvent which was passed over the adsorbent grows by 20 times. Based on the related results (Table 3), the breakthrough volume calculations are as follows:

Concentration factor = breakthrough volume/the desorption solvent volume= 250/12=20

Determination of the blank standard deviation (S_b)

The accuracy or replicability of any method is the main factor to recognize its validity and reliability. To inquire about the method's replicability, the results data of the study of four blank solutions (deionized water) deposited in Table 4.

Based on the results achieved in Table 4, the blank standard deviation was obtained as follows; S_b=0.0005

Table 4. measurement RSD following three replications

Sample	Device response
1	0.026(2.5) [a]
2	0.025(2.7)
3	0.024(2.8)
4	0.023(2.4)

a) Measurement RSD following three replications

Determination of the accuracy and RSD% of the method

This parameter was used to investigate the accuracy and proximity of the examined data. As shown in 2.5% standard deviation has been calculated for three tests and the relative standard deviation (RSD) achieved for three replications.

The linear range and a calibration curve of the method

To assess the linear range in the analysis method, a calibration curve should be plotted. This curve is not linear across all concentrations and different factors cause the calibration curve to the situation in the linear range and follow from Beyer Law. the calibration curve of the method is as conform and the line equation is y= 0.003x+0.021 and R^2= 0.99924.

Study of the effect of disturbances on the measurement of chromium (VI)

A disturbing ion is an ion that causes a certain variation of over ±5% in the adsorption and recovery of chromium (VI). To study the effect of disturbance of other ions on chromium (VI) extraction, a certain quantity of interfering factors added to the initial solution, and the experiment was performed at breakthrough volume. Absorption of the recovered solution is analyzed with flame atomic absorption and then compared versus the solution absorption resulting from the sample recovery which lacks the interfering ion. As can be shown in Table 5, in the presence of external ions, chromium (VI) recovery occurred with ±5% variations and the external ions had no particular effects on the analysis and cause no disturbance.

Determining the method's limit of detection

The lowest chromium (VI) concentration or weight in a sample that could be determined with a certain confidence level is called the limit of detection (LOD), which is defined as follows. The LOD of a method is a concentration of an analysis sample where the device response to concentration (which is significantly different from the response of the control sample) is defined as follows; the limit of detection is the low-

Table 5. The effect of interfering ions on the recovery of chromium (VI).

Ions	Added value (ppm)	Recovery percentage chromium (VI)
Na^+	200	88.92(2.5)[a]
Zn^{2+}	5.0	89.34(2.4)
K^+	200	89.88(2.4)
Mg^{2+}	100	88.68(2.0)
Cu^{2+}	6.0	89.75(2.2)
Cl^-	400	88.77(2.5)
NO_3^-	317	89.27(2.5)
SO_4^{2-}	400	89.94(2.3)

a) Measurement RSD after three replications

est amount of chromium (VI), where the presented method can detect it. Based on the presented definition, LOD can be calculated by the following relation;

$$LOD = \frac{3S_b}{m} \quad (1)$$

Where S_b and m are the standard deviations of the blank signal and the slope of the calibration curve, respectively. Based on the experimented, S_b=0.0006 and the slope of the calibration curve is 0.0003. Therefore, LOD can be calculated at 9.7 ppb.

Investigation of the obtained results on real sample

The proposed method has been successfully applied to the determination of chromium (VI) in three real drinking water samples (tap water of tehran, pure water and industrial wastewater sample of Charmshar Varamin. The results were shown in Table 6, together with results of a recovery test by added known amounts of silver in water sample. The results of this analysis are shown in Table 6. The level of chromium (VI) ions was measured across different water and biological samples at 250 mL. As can be seen, in the water samples, in the Tap water sample of Tehran, on 30 march 2022, and industrial wastewater sample of Charmshar Varamin on 30 march 2022, there is a larger amount of chromium (VI) than in the experimented water samples. Although, in other samples, there is less chromium (VI) ions. Based on this, the performance and power of preconcentration and chromium (VI) ions measurement could be deduced.

A comparison between the current method and other methods

A comparison of this method with other methods verified that the current method is more accurate, easiest, and faster as it had smaller relative standard deviation values in comparison with other methods [36-50]. The current method is one of the foremost systems for determining the very trace amounts of heavy metal ions including chromium (VI) in aqueous samples. Another point in the usage of graphene oxide nano-plates adsorbent is that instead of using the proposed ligand, one can put other ligands on the adsorbent which to adsorb mineral ions, thereby measuring trace amounts of metal ions. A wide variety of ligands can be used given their properties, which act selective towards one or several ions and applying this set, preconcentration, and determination of cations can be carried out. Using flame atomic absorption and solid drop microextraction, single-drop liquid-liquid extraction, and homogeneous liquid-liquid extraction with other devices,

Table 6. Determination of chromium (VI) in the real sample.

Recovery	R.S.D.% (n=5)	This method ($\mu g.g^{-1}$)*	Reference method ($\mu g.l^{-1}$) *	Samples
88.4	2.5	48	52	Tap water
89.6	2.4	545	538	Pure water
85.6	2.3	346	351	Industrial wastewater

*Average of five determinations.

one can determine trace amounts of chromium (VI) by this adsorbent and achieve a smaller limit of detection value.

CONCLUSIONS

In comparison with other procedures reported for measurement of chromium (VI), this method has considerable advantages that are easy and inexpensive and can be applied quickly for environmental aqueous samples. Furthermore, it minimizes the utilization of organic, toxic, and costly solvents. Moreover, the design and development of this procedure for separation, measurement, and preconcentration of chromium (VI) are essential considering its importance in various industries and the little concentration of chromium (VI) ion in most samples. Therefore, this research aims to present an effective, selective, cost-effective, and simple method for measurement of the level of chromium (VI) across different environmental aqueous samples (in this research, the limit of detection, the value of breakthrough volume, and RSD has been obtained). This research indicated that the measurement of chromium (VI) occurs at an appropriate level without the interference of any other interfering factor and thus the current method can be applied easily in the measurement of the quantity of chromium (VI) in aqueous samples.

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