



## Tea-industry waste activated carbon, as a novel adsorbent, for separation, preconcentration and speciation of chromium

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### ABSTRACT

Activated carbon was produced from tea-industry wastes (TIWAC) and employed as a low cost and effective solid phase material for the separation, preconcentration and speciation of chromium species without using a complexing agent, prior to determination by flame atomic absorption spectrometry (FAAS). The characterization of TIWAC was performed by utilizing several techniques such as Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM), and elemental analysis. The adsorption experiments were conducted in a batch adsorption technique. Under the experimental conditions, Cr(VI) adsorption amount was nearly equal to zero, however the adsorption percentage of Cr(III) was in the range of 95–100%. Therefore total chromium was determined after the reduction of Cr(VI) to Cr(III) and Cr(VI) was calculated by subtracting Cr(III) concentration from total chromium concentration. The suitable conditions for adsorption and speciation processes were evaluated in terms of pH, eluent type and volume, TIWAC concentration, adsorption and desorption contact time, etc. Adsorption capacity of TIWAC was found to be  $61.0 \text{ mg g}^{-1}$ . The detection limit for Cr(III) was found to be  $0.27 \text{ } \mu\text{g L}^{-1}$  and the preconcentration factor was 50 for 200 mL of sample volume. The procedure was applied to the determination and speciation of chromium in stream, tap and sea water. Also, the proposed method was applied to total chromium preconcentration in microwave digested tobacco and dried eggplant samples with satisfactory results. The method was validated by analyzing certified reference materials (CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C) and the results were in good agreement with the certified values.

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### 1. Introduction

Chromium is a prevalent and highly reactive pollutant which dissipates into the ecosystems from a variety of industrial activities such as electroplating, leather tanning, mining, textile dyeing, wood preserving, chromate preparation, and metal finishing [1]. The most stable and common forms of chromium in the environment are trivalent and hexavalent species. The hexavalent chromium, which is primarily present in the form of chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), is more toxic to living organisms than trivalent chromium due to its high oxidation potential and diffusibility through cell membranes [2]. Hexavalent chromium is considered as a powerful carcinogenic agent that modifies DNA transcription process causing important chromosomal aberrations. Furthermore, it causes cancer in the digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [3,4]. However, trivalent chromium often forms soluble hydroxides

thus it is relatively immobile and less toxic for biological systems. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is  $5.0 \text{ } \mu\text{g L}^{-1}$  [5].

The accurate and sensitive determination of the chromium species is very important in analytical chemistry because the change of the oxidation state affects the toxicity of heavy metals. Various spectrometric techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) have been widely used for the determination of chromium. But these techniques can only yield total amount of chromium. And also due to insufficient sensitivity and matrix interferences, the direct determination of chromium species in real samples may not be possible using these techniques [6]. Hence the chromium speciation procedures are based on the separation and preconcentration of one of the chromium species (Cr(III) or Cr(VI)) using several techniques such as coprecipitation [7], solid phase extraction [8], ion-exchange [9], and cloud point extraction [10] and the total chromium is determined after the reduction of Cr(VI) or by the oxidation of Cr(III) [11,12].

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Solid phase extraction (SPE) is one of the widely utilized techniques for the separation and preconcentration of metal ions due to its simplicity, selectivity, flexibility, low cost, safety, ease of automation and high preconcentration factor [13]. The adsorption materials (sorbents) play an important role in SPE process hence the current researches in SPE are mainly focused on the development of new sorbents. Although there are many chromium sorbents such as zeolite, calcite, organo-modified clay minerals, and titanium oxides in literature, activated carbon (AC) is considered as one of the most promising sorbents for SPE of metal ions from aqueous solutions because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity [14]. AC can be prepared from a wide variety of raw materials such as rice husks, fruit stones, nuts, nutshells, soybean, and maize, which should be abundant and cheap, with high carbon content and low inorganic content [15]. There are two different processes for the preparation of AC; physical and chemical activation. The physical activation method involves the carbonization of raw material followed by activation at high temperature in carbon dioxide, steam or water vapor atmosphere [16]. Chemical activation can be carried out in a single step by the thermal decomposition of raw materials with acidic reagents such as  $\text{ZnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  or with basic reagents such as  $\text{K}_2\text{CO}_3$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  [17].

The present work aims to evaluate the usage of tea-industry waste as a potential feedstock for AC preparation and then utilize the produced and characterized TIWAC for the separation, preconcentration and speciation of chromium species. According to our literature knowledge, there is no information related to the utilization of TIWAC for the speciation of metal ions. The tea waste used in the experiments was provided from tea-processing plants located in Black Sea Region (Trabzon/Turkey). Approximately 150,000 t per year (dry basis) of tea is manufactured and 30,000 t per year of tea waste is produced in Turkey [18]. Thus, the production of AC from these abundant wastes and investigation of the potential usage of them for metal speciation analysis is an important application from the view point of economic and environmental aspects.

In present study, after production of TIWAC by  $\text{H}_2\text{SO}_4$  activation, the characterization of it was performed by FTIR; for chemical structure and SEM; for surface morphology. And also pore texture, available surface functional groups, iodine and methylene blue numbers, pH of point zero charge ( $\text{pH}_{\text{PZC}}$ ), elemental compositions were obtained to characterize the TIWAC. Then a novel batch adsorption system for the separation, preconcentration and speciation of chromium species, based on the adsorption of Cr(III) on the TIWAC and desorption of adsorbed Cr(III) species from the TIWAC, has been investigated. There is no need to use a complexing agent for the preconcentration of chromium species so contamination risk from a complexing agent is eliminated. The total chromium level was determined after converting all the Cr(VI) to Cr(III). For separation, preconcentration and speciation experiments, the influences of the various analytical parameters such as effects of pH, amount of TIWAC, eluent type and volume, contact time of Cr(III) adsorption and desorption, and sample volume were investigated. The adsorption kinetics of Cr(III) was also described in terms of pseudo-first-order, pseudo-second-order, intraparticle diffusion models and Elovich models. The proposed method was applied to the speciation of chromium in several environmental samples.

## 2. Materials and methods

### 2.1. Apparatus

The specific surface area of TIWAC was determined from the  $\text{N}_2$  gas adsorption isotherm at 77 K using a Quantachrome Cor-

poration, Autosorb-1-C/MS model specific surface area analyzer. The FTIR spectrum of the TIWAC was recorded between 400 and  $4000\text{ cm}^{-1}$  in a Perkin Elmer 1600 FTIR spectrometer. SEM analyses were applied using JEOL/JSM-6335F apparatus. Elemental analysis of TIWAC was performed on a LECO, CHNS-932 apparatus. A Unicam model AA-929 Flame Atomic Absorption Spectrometer (FAAS) (Solar System ATI, Unicam Analytical Technology Inc., England) was used for the chromium determination in solutions. All measurements were carried out in a  $\text{N}_2\text{O}$ /acetylene flame with 5 cm burner head, and chromium hollow cathode lamp was used. The instrumental parameters were those recommended by the manufacturer. The wavelength, selected for determination of chromium, was 357.9 nm. For batch adsorption experiments Edmund Bühler GmbH model mechanical shaker was used. The pH measurements were made on Hanna pH-211 (HANNA instruments/Romania) digital pH meter with glass electrode. pH meter was calibrated with standard buffer solutions. A centrifuge Sigma 3-16P was employed for the centrifugation of solutions. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature  $300^\circ\text{C}$ ) was operated for the digestion of the solid samples. Distilled/deionized water was obtained from Sartorius Milli-Q system (arium® 611UV).

### 2.2. Reagents and solutions

All the chemicals used were analytical grade of Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), unless otherwise. Distilled/deionized water was used for all experiments. All glassware and plastic materials used were soaked in 10% (v/v) nitric acid solution for 1 day before use then cleaned repeatedly with distilled/deionized water. For storage of water samples prior to analysis, polypropylene bottles (5L) were used. The working solutions of Cr(III) and Cr(VI) were prepared by diluting stock solutions of  $1000\text{ mg L}^{-1}$  of them. Standard reference materials, CRM-TMDW-500 Drinking Water and Sandy Soil standard (CRM-SA-C), were obtained from High-Purity Standard Inc.

### 2.3. Preparation of TIWAC

In present study only one type of tea (*Camelia sinensis*) was used for the production of activated carbon and it was provided from tea factories in Blacksea Region of Turkey (Of/Trabzon) in summer, 2007. Then it was cut in to small pieces of 2–3 cm and dried in sunlight. The dried tea-industry waste was used for AC preparation by mixing with concentrated  $\text{H}_2\text{SO}_4$  (tea-industry waste: $\text{H}_2\text{SO}_4$  ratio; 1:1.5, w/v) and keeping it at  $200^\circ\text{C}$  for 24 h. This carbonized material was washed with distilled water for several times to remove the free acid and soaked in 1% sodium bicarbonate solution overnight to remove any residual acid. This material was then again washed with distilled water and dried at  $105^\circ\text{C}$  in a hot air oven for 24 h. It was ground and sieved to obtain a particle size of  $150\text{ }\mu\text{m}$  [19].

### 2.4. Determination of Cr(III)

The batch adsorption method was tested firstly for the separation, preconcentration and speciation of chromium species using model solutions, prior to application to the speciation procedure to environmental real samples. For that purpose, 50 mL of an aqueous solution containing  $10\text{ }\mu\text{g}$  of Cr(III) and  $2.0\text{ g L}^{-1}$  of TIWAC suspension was placed in a centrifuge tube. The pH of the solution was adjusted to 6.0 using either 0.1 M of  $\text{HNO}_3$  or  $\text{NaOH}$  solutions. Then the mixture was agitated on a mechanical shaker at 400 rpm for 30 min. After reaching equilibrium, the suspension was centrifuged at 3000 rpm for 5 min. The aqueous solution was removed by decantation and the solid accumulated at the bottom of the tube was desorbed with 4 mL of 3.0 M  $\text{HNO}_3$  solution by agitating on a

mechanical shaker for 2.0 h. Then the suspension was again centrifuged at 3000 rpm for 5 min and the concentration of dilute phase was measured for Cr(III) concentration using FAAS.

### 2.5. Determination of total chromium

Total chromium was determined as Cr(III) after reducing Cr(VI) to Cr(III) by the addition of concentrated  $\text{H}_2\text{SO}_4$  and ethanol [20]. For this, 0.5 mL of concentrated  $\text{H}_2\text{SO}_4$  and 0.5 mL of ethanol were added into a 50 mL of an aqueous solution containing 10  $\mu\text{g}$  of Cr(III) and 10  $\mu\text{g}$  of Cr(VI). After cooling to room temperature, the pH of the solution was adjusted to 6.0. Then the procedure described in Section 2.4 was applied to this solution for determination of total chromium. The concentration of Cr(VI) was calculated by subtracting the amount of Cr(III) from the total chromium content.

### 2.6. Application to real samples

The present speciation procedure for Cr(III) and Cr(VI) based on batch adsorption technique was applied to various environmental real samples. The stream water, sea water, and tap water were used as liquid real samples for speciation of chromium, tobacco and dried eggplant were used as solid real samples for determination of total chromium. The method was applied to CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C as standard reference materials. Various amounts of chromium species were also spiked to liquid real samples.

Twenty-five milliliters of CRM-TMDW-500 Drinking Water were taken to determine the level of total chromium. From the other real water samples, 200 mL of sea water (Blacksea, Trabzon/Turkey), stream water (Şana Stream, Trabzon/Turkey) and tap water (Karadeniz Technical University, Trabzon/Turkey) were collected in polyethylene bottles. Before the analysis, the water samples were filtered through 0.45  $\mu\text{m}$  cellulose nitrate membrane then the pH values of the liquid samples were adjusted to 6.0. The appropriate amount of TIWAC was added and the procedure given above was applied. The levels of Cr(III) in the samples were determined by FAAS. After the reduction of Cr(VI) to Cr(III) by the addition of concentrated  $\text{H}_2\text{SO}_4$  and ethanol, total chromium levels in these liquid samples were determined as Cr(III).

The solid samples were digested with a closed microwave digestion system prior to the application of the present method. For that purpose, 1 g of tobacco, 0.5 g of dried eggplant samples and 0.1 g of CRM-SA-C Sandy Soil C were weighed into the Teflon vessels, separately, with a balance which has uncertainty of 0.1 mg. 6 mL of  $\text{HNO}_3$ , and 2 mL of  $\text{H}_2\text{O}_2$  for tobacco and dried eggplant samples, 4.5 mL of  $\text{HCl}$ , 1.5 mL of  $\text{HNO}_3$ , 2 mL of  $\text{H}_2\text{O}_2$  and 1 mL of  $\text{HF}$  for CRM-SA-C Sandy Soil C standard were added into the vessels. Digestion conditions for the microwave system for the samples were applied as (45 bar) 6 min for 250 W, 6 min for 400 W, 6 min for 650 W, 6 min for 250 W, vent: 3 min. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the digested samples.

## 3. Results and discussion

### 3.1. Characterization of TIWAC

The FTIR Spectroscopy was used to obtain idea about the chemical structure and functional groups of the TIWAC. The FTIR spectrum of TIWAC is depicted in Fig. 1. The broad bands observed at 3390, 1708, 1610 and 1048  $\text{cm}^{-1}$  are due to stretching vibrations of the bonded hydroxyl group ( $-\text{OH}$ ),  $\text{C}=\text{O}$  group (due to carboxyl group),  $\text{C}-\text{O}$  group (due to  $-\text{OCH}_3$ ) and  $\text{R}-\text{OH}$  (alcohol) groups, respectively [19].

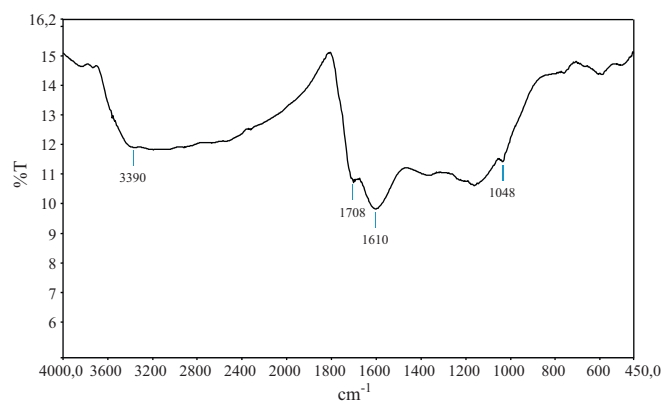


Fig. 1. FTIR spectra of TIWAC.

SEM analyses were applied on the  $\text{H}_2\text{SO}_4$  activated TIWAC in order to disclose the surface texture and morphology of the adsorbent. The TIWAC surface exhibits porous structure and a predominately microporous character which is responsible of the high surface area and adsorption capacity of this material (Fig. 2).

The BET surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_t$ ) and average pore diameter ( $D_p$ ) results obtained by applying the BET equation to  $\text{N}_2$  adsorption at 77 K and DR equation to  $\text{N}_2$  adsorption at 77 K are listed in Table 1. The elemental analysis of TIWAC was performed and the percentage amount of C, H, N, S and O contents is given in Table 1. The surface acidic functional groups and all other characterization parameters were determined using standard methods [21,22] and listed in Table 1. Because of the  $\text{H}_2\text{SO}_4$  treatment increased the quantity of acidic functional groups on TIWAC surface, a high amount of total acidic groups value has been obtained. The number of acidic functional groups is closely related to the capacity of TIWAC to adsorb metallic compounds so it can be concluded that TIWAC should have a great affinity for Cr(III) ions [23]. Methylene blue and iodine numbers of TIWAC have been evaluated because methylene blue is the most recognized probe molecule for assessing the ability of the sorbent to remove large molecules via its macroporosity (pore diameter greater than 1.5 nm) and iodine number gives an indication on microporosity (pore diameter less than 1 nm) [24]. The  $\text{pH}_{\text{PZC}}$  of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality [25]. At  $\text{pH} > \text{pH}_{\text{PZC}}$ , the surface charge of TIWAC is negative, whereas  $\text{pH} < \text{pH}_{\text{PZC}}$  the surface charge of TIWAC is pos-

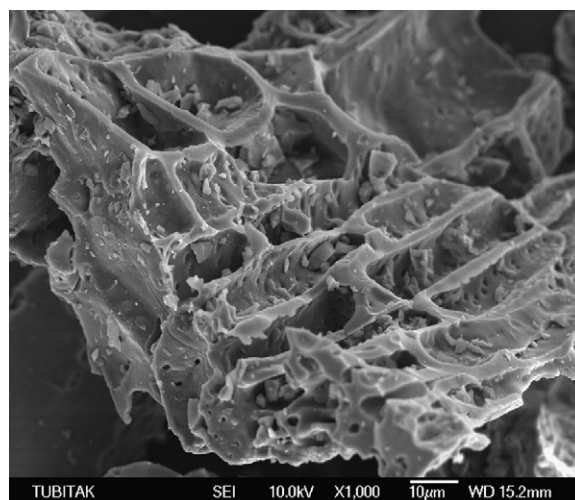


Fig. 2. SEM of TIWAC (magnification: 1000 folds).

**Table 1**  
Characteristics of TIWAC.

Pore structure of TIWAC	
$S_{BET}$ ( $m^2 g^{-1}$ )	45.5
$V_t$ ( $cm^3 g^{-1}$ )	0.136
$D_p$ (nm)	2.25
Elemental analysis (wt%)	
C	56.27
H	3.12
N	3.70
S	1.93
O <sup>a</sup>	34.98
Surface functional groups ( $mmol g^{-1}$ )	
Carboxylic	2.58
Phenolic	1.93
Lactonic	1.42
Total acidic value	5.93
Proximate analyses (wt%)	
Moisture	9.13
Volatile matter	51.68
Fixed carbon	33.75
Ashes	5.44
AC yield	84.2
Iodine number ( $mg g^{-1}$ )	167.9
Methylene Blue number ( $mg g^{-1}$ )	39.1
$pH_{PZC}$	5.25

<sup>a</sup> By difference.

itive. Because of the  $pH_{PZC}$  value of TIWAC was found to be 5.25, the cationic Cr(III) ions can bind easily to the surface of TIWAC, at a pH value of higher than 5.25.

### 3.2. Effect of pH

The pH value of the aqueous solution is an important factor affecting the speciation studies based on the batch adsorption method so the influence of pH on the adsorption of Cr(III) and Cr(VI) onto TIWAC was investigated in the pH range of 1–8 using 50 mL of model solutions containing  $2.0 g L^{-1}$  of TIWAC suspension and  $100 \mu g$  of Cr(III) and Cr(VI), separately. The pH of the solutions was adjusted using 0.1 M of  $HNO_3$  and NaOH solutions then the mixtures were agitated on a mechanical shaker at 400 rpm for 30 min. After reaching equilibrium, the suspensions were centrifuged at 3000 rpm for 5 min and the filtrates were analyzed for the Cr(III) and Cr(VI) levels by FAAS. The amount of adsorption percentage of Cr(III) and Cr(VI) was calculated using following equation;

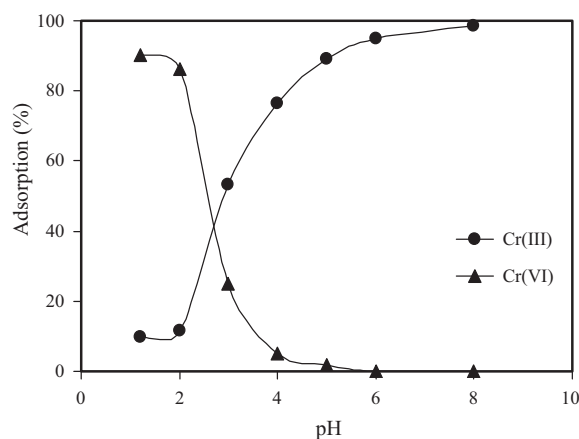
$$\text{Adsorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C_e$  ( $mg L^{-1}$ ) are the initial and equilibrium concentrations of chromium species in aqueous solution, respectively.

At low pH values Cr(VI) could be adsorbed onto TIWAC but its adsorption amount was not quantitative. On the other hand the adsorption percentages of Cr(III) in the pH range of 6–8 were quantitative (>95%), while the adsorption percentages of Cr(VI) were below 1% (Fig. 3). The results showed that the separation and speciation of Cr(III) and Cr(VI) are possible by the present procedure in the pH range of 6–8 so all subsequent experiments were performed at pH 6.0.

### 3.3. Eluent type and volume

An appropriate eluent for effective desorption of metal ions from an adsorbent should be cheap, effective, non-polluting and non-damaging to the adsorbent. For that purpose, dilute solutions of some mineral acids such as hydrochloric, sulphuric, acetic and nitric acids are widely used. Under acidic conditions the adsorbent surface is protonated by  $H_3O^+$  ions to make possible desorption of positively charged metal ions from the adsorbent surface [26].



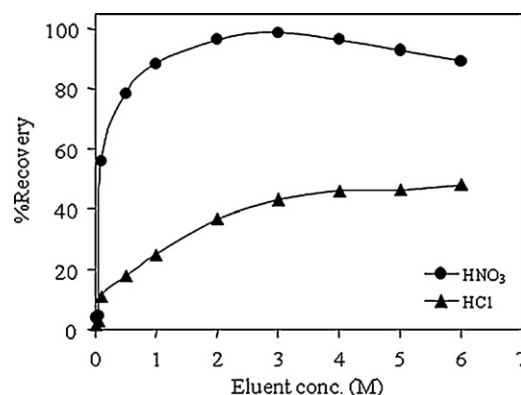
**Fig. 3.** Effect of pH on the adsorption of chromium species on TIWAC (TIWAC conc.:  $2.0 g L^{-1}$ , quantity of each chromium species:  $100 \mu g$ , sample volume: 50 mL, contact time: 30 min).

For that purpose different concentrations of HCl and  $HNO_3$  solutions were used to identify the best eluent for the adsorbed Cr(III) on TIWAC. The results indicated that the  $HNO_3$  solutions provided higher recovery efficiency compared to the HCl solutions (Fig. 4). Thus 3.0 M of  $HNO_3$  solution was specified as the eluent for the desorption of Cr(III) from TIWAC.

The effects of volume of 3 M  $HNO_3$  as eluent were also evaluated in the volume range of 2–10 mL and quantitative recoveries were obtained after 4.0 mL of the eluent volume hence the eluent volume was specified as 4.0 mL for the subsequent studies.

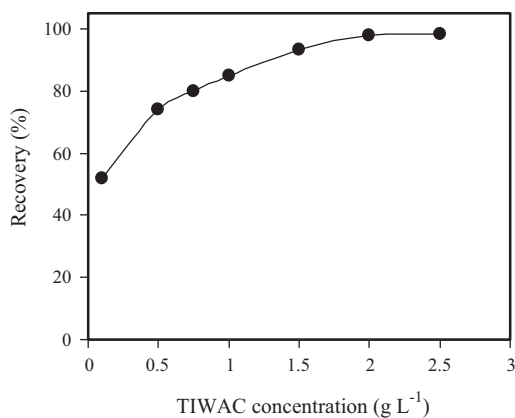
### 3.4. Effect of TIWAC concentration

The effects of TIWAC concentration on Cr(III) recovery were studied using 50 mL of an aqueous solution containing  $10 \mu g$  of Cr(III) at pH 6.0 by varying the concentration of TIWAC over the range of  $0.1$ – $2.5 g L^{-1}$ . As the TIWAC concentration was increased from  $0.1$  to  $2.5 g L^{-1}$ , the recovery of Cr(III) increased from 52.0 to 98.2% (Fig. 5). The increase in recovery percentage of Cr(III) was probably due to the increased more availability of active adsorption sites with the increase in TIWAC concentration thereby more Cr(III) can be adsorbed on TIWAC surface and can be eluted with 3.0 M of  $HNO_3$  solution. Thus,  $2.0 g L^{-1}$  of TIWAC concentration was used for subsequent experiments.



**Fig. 4.** Effect of eluent type on the recovery of Cr(III) (Cr(III) amount:  $10 \mu g$ , pH: 6.0, TIWAC conc.:  $2.0 g L^{-1}$ ).





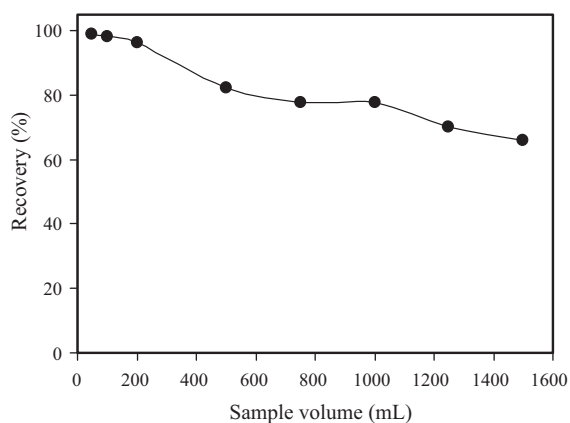
**Fig. 5.** Effect of TIWAC amount on the recovery of Cr(III) (Cr(III) amount: 10  $\mu\text{g}$ , pH: 6.0, sample volume: 50 mL, eluent type and volume: 4 mL of 3.0 M  $\text{HNO}_3$ ).

### 3.5. Effect of sample volume

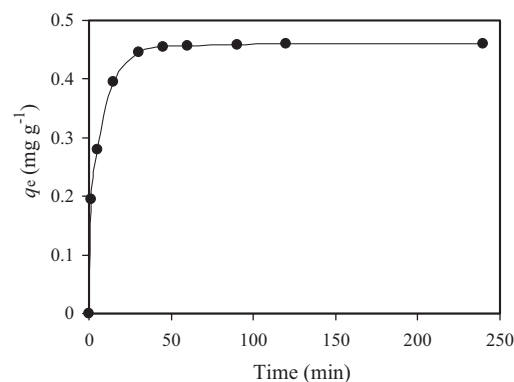
In order to obtain a high preconcentration factor in the analysis of real samples, the effect of sample volume on the recoveries of Cr(III) was investigated in the sample volume range of 50–1500 mL containing 20  $\mu\text{g}$  of Cr(III) using model solutions. For the sample volumes above 50 mL, the TIWAC particles were separated from the solutions by filtration through 0.45  $\mu\text{m}$  cellulose nitrate membrane. The results showed that the recovery of Cr(III) was quantitative up to 200 mL of sample volume (Fig. 6). Above 200 mL, the recovery values of Cr(III) decreased with increasing sample volume. The preconcentration factor, calculated as the ratio of the highest sample volume for Cr(III) and lowest final volume, was found 50 for Cr(III) when the final volume was 4 mL.

### 3.6. Effect of diverse ions

The influence of matrix components is one of the most significant problems in determination of chromium and other heavy metals in real samples using FAAS. In order to assess possible analytical applications of the present separation, preconcentration and speciation procedure, the effects of some common foreign ions on the recovery of Cr(III) were evaluated under the optimal conditions. In these experiments, different amounts of salts and heavy metal ions were added in 50 mL of aqueous solution containing 10  $\mu\text{g}$  of Cr(III) and then the present procedure was applied (Table 2). The results showed that the presence of major interfering anions and cations and also some transition metals at  $\text{mg L}^{-1}$  level had



**Fig. 6.** Effect of sample volume on the recovery of Cr(III) (Cr(III) amount: 20  $\mu\text{g}$ , pH: 6.0, TIWAC amount: 50 mg for each sample volume, eluent type and volume: 4 mL of 3.0 M  $\text{HNO}_3$ ).



**Fig. 7.** Effect of contact time on Cr(III) adsorption (Cr(III) amount: 20  $\mu\text{g}$ , pH: 6.0, TIWAC conc.: 2.0  $\text{g L}^{-1}$ ).

no obvious influences on the determination of Cr(III) under optimal conditions indicating that the TIWAC has a good selectivity for Cr(III) and the proposed separation, preconcentration and speciation procedure can be applied for the analyses of samples with complicated matrix [27].

### 3.7. Effect of adsorption and desorption contact time

The adsorption of Cr(III) onto TIWAC was studied as a function of contact time in order to decide whether the equilibrium was reached. For this, 50 mL of an aqueous solution containing 10  $\mu\text{g}$  of Cr(III) at pH 6.0 was contacted with 2  $\text{g L}^{-1}$  of TIWAC suspensions. The samples were taken at different periods of time and analyzed for their Cr(III) concentrations. The Cr(III) adsorption rate is high at the beginning of the experiments because initially the adsorption sites are more available and Cr(III) ions are easily adsorbed on these sites (Fig. 7). The equilibrium can be reached within 30 min and thus, further adsorption experiments were carried out for a contact time of 30 min.

The elution of the adsorbed Cr(III) ions from TIWAC was also studied in a batch system. To determine the contact time of elution firstly, 2.0  $\text{g L}^{-1}$  of TIWAC suspensions was equilibrated with a series of 50 mL of aqueous solutions containing 10  $\mu\text{g}$  of Cr(III) at pH 6.0. After reaching the equilibrium the TIWAC was separated by centrifugation at 3000 rpm for 5 min. Secondly, TIWAC, loaded with Cr(III) ions, was treated with 4 mL of 3 M  $\text{HNO}_3$  solutions for different time intervals from 1 to 240 min by agitating at 400 rpm on a mechanical shaker. The quantitative recovery was obtained for the elution contact time of 120 min so all the subsequent elution studies were performed for a contact time of 120 min.

### 3.8. Adsorption kinetics

The adsorption kinetics is one the most important data in order to understand the mechanism of the adsorption and to assess the performance of the adsorbents. Different kinetic models including the pseudo-first-order, pseudo-second-order, intraparticle diffusion models and Elovich model were applied for the experimental data to predict the adsorption kinetics of Cr(III) on TIWAC.

The pseudo-first-order kinetic model was described by Lagergren [28];

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the amounts of the Cr(III) adsorbed on TIWAC at equilibrium and at any time  $t$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the first order model. After integration and applying boundary conditions  $q_t = 0$  at  $t = 0$  and

**Table 2**  
Influences of some foreign ions on the recoveries of Cr(III) (Cr(III) quantity: 10 µg, N: 3, sample pH: 6, TIWAC concentration: 2.0 g L<sup>-1</sup>, sample volume: 50 mL).

Ions	Added as	Conc. (mg L <sup>-1</sup> )	Cr(III) recovery (%)
Na <sup>+</sup>	NaCl	5000	97.0 ± 3.1
K <sup>+</sup>	KCl	1000	94.3 ± 3.4
Ca <sup>2+</sup>	CaCl <sub>2</sub>	500	99.6 ± 1.1
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	250	95.3 ± 0.8
CO <sub>3</sub> <sup>2-</sup>	Na <sub>2</sub> CO <sub>3</sub>	250	97.0 ± 4.9
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	1000	100.1 ± 0.9
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	100	100.2 ± 0.5
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1000	94.2 ± 5.1
NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> NO <sub>3</sub>	1000	98.0 ± 1.1
F <sup>-</sup>	NaF	500	99.9 ± 0.9
CH <sub>3</sub> COO <sup>-</sup>	NaCH <sub>3</sub> COO	250	101.7 ± 1.2
Al <sup>3+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> , Fe <sup>3+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup> , V <sup>4+</sup> , Ni <sup>2+</sup>	a	25	97.3 ± 2.4
Mixed <sup>b</sup>			92.1 ± 2.6

<sup>a</sup> V<sup>4+</sup> added as VOSO<sub>4</sub>, other ions added as their nitrate salts.

<sup>b</sup> 6025 mg L<sup>-1</sup> Na<sup>+</sup>, 8390 mg L<sup>-1</sup> Cl<sup>-</sup>, 2560 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 250 mg L<sup>-1</sup> K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, F<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>, 10 mg L<sup>-1</sup> Al<sup>3+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, V<sup>4+</sup> and Ni<sup>2+</sup>.

$q_t = q_t$  at  $t = t$  the integrated form of Eq. (2) becomes;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

A straight line of  $\ln(q_e - q_t)$  versus  $t$  suggests the applicability of this kinetic model and  $q_e$  and  $k_1$  can be determined from the intercept and slope of the plot, respectively. The calculated  $q_{e\text{cal}}$  value was not in a good agreement with the experimental value of  $q_{e\text{exp}}$  and the correlation coefficient was found a relatively low value (Table 3). These observations suggested that the pseudo-first-order model is not suitable for modeling the adsorption of Cr(III) onto TIWAC.

The pseudo-second-order model has the following form [29];

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

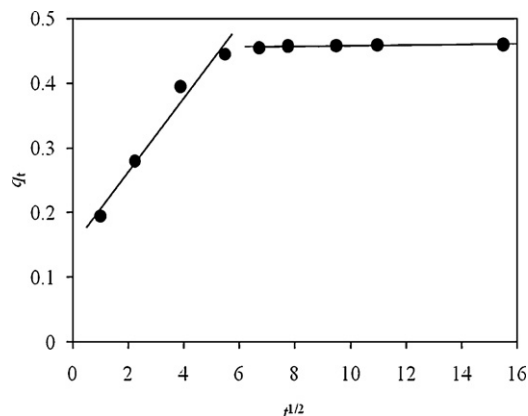
where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the second-order equation;  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the amounts of the Cr(III) adsorbed on TIWAC at equilibrium and at any time  $t$ . After definite integration by applying the conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$  Eq. (4) becomes the following;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

If second-order kinetics is applicable, the plot of  $t/q_t$  against  $t$  gives a straight line and  $q_e$  and  $k_2$  can be obtained from the slope and intercept of the plot, respectively. The pseudo-second-order kinetic model constants,  $k_2$  and  $q_{e\text{cal}}$  values along with the corresponding correlation coefficient were presented in Table 3. The correlation coefficient was nearly equal to unity and calculated  $q_{e\text{cal}}$  value was much close to the experimental value of  $q_{e\text{exp}}$ . The results indicated that the pseudo-second-order adsorption mechanism is predominant for the adsorption of Cr(III) onto TIWAC, and it is considered that the rate of the Cr(III) adsorption process is controlled by the chemisorption process.

**Table 3**  
Kinetic parameters of Cr(III) adsorption onto TIWAC.

C <sub>0</sub> (µg)	Pseudo-first-order model				Pseudo-second-order model			
	$q_{e\text{exp}}$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$q_{e\text{cal}}$ (mg g <sup>-1</sup> )	R <sup>2</sup>	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_{e\text{cal}}$ (mg g <sup>-1</sup> )	R <sup>2</sup>	
10.0	0.460	-0.056	0.174	0.908	1.520	0.464	0.999	
C <sub>0</sub> (µg)	Intraparticle diffusion model				Elovich model			
	$k_{id,1}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	R <sup>2</sup>	$k_{id,2}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	R <sup>2</sup>	C	$\beta$ (g mg <sup>-1</sup> )	$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>
10.0	0.057	0.973	0.0005	0.721	0.204	0.054	58.556	0.887



**Fig. 8.** Intraparticle diffusion plots for adsorption of Cr(III) on TIWAC.

In order to predict the rate controlling step of the Cr(III) adsorption, intraparticle diffusion model has been used. Generally any sorption process involves three main successive transport steps which are (i) film diffusion, (ii) intraparticle or pore diffusion and (iii) sorption onto interior sites. The last step is considered negligible since it occurs rapidly and hence sorption should be controlled by either film diffusion or pore diffusion depending on which step is slower [30]. The intraparticle diffusion model equation is expressed as [31];

$$q_t = k_{id} t^{1/2} + c \quad (6)$$

where  $q_t$  (mg g<sup>-1</sup>) is the amount of sorption at time  $t$  (min) and  $k_{id}$  (mg g<sup>-1</sup> min<sup>-1/2</sup>) is the rate constant of intraparticle diffusion model. By evaluating the intraparticle mass transfer curve (Fig. 8), it was observed that the Cr(III) adsorption process tends to be followed by two distinct phases. The first phase is attributed to the diffusion of Cr(III) through the solution to the external sur-

**Table 4**Total chromium determination in spiked test solutions (mean  $\pm$  standard deviation,  $N=3$ , sample volume: 50 mL, sample pH: 6.0, TIWAC concentration: 2.0 g L<sup>-1</sup>).

Added ( $\mu\text{g}$ )			Found ( $\mu\text{g}$ )			Recovery for total chromium (%)
Cr(III)	Cr(VI)	Total chromium	Cr(III)	Cr(VI)	Total chromium	
0	25	25	BDL <sup>a</sup>	24.1 $\pm$ 0.7	24.1 $\pm$ 0.7	96
5	20	25	4.8 $\pm$ 0.1	18.9 $\pm$ 0.9	23.7 $\pm$ 0.9	95
10	15	25	9.8 $\pm$ 0.4	14.9 $\pm$ 0.9	24.7 $\pm$ 0.8	99
15	10	25	14.5 $\pm$ 0.8	9.6 $\pm$ 1.3	24.1 $\pm$ 1.0	96
20	5	25	19.6 $\pm$ 0.7	5.2 $\pm$ 1.1	24.8 $\pm$ 0.9	99
25	0	25	24.5 $\pm$ 0.8	BDL	24.5 $\pm$ 0.8	98

<sup>a</sup> Below detection limit.**Table 5**Speciation of Cr(III), Cr(VI) and total chromium in environmental water samples (mean  $\pm$  standard deviation,  $N=3$ , sample volume: 50 mL, sample pH: 6.0, TIWAC concentration: 2.0 g L<sup>-1</sup>).

Samples	Added ( $\mu\text{g}$ )		Found ( $\mu\text{g}$ )			Recovery (%)		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total chromium	Cr(III)	Cr(VI)	Total chromium
Stream water	–	–	BDL	BDL	–	–	–	–
	5	5	4.8 $\pm$ 0.3	4.9 $\pm$ 0.6	9.7 $\pm$ 0.5	96	98	97
Sea water	10	10	9.4 $\pm$ 0.5	9.8 $\pm$ 1.2	19.2 $\pm$ 1.1	94	98	96
	–	–	BDL	BDL	–	–	–	–
Tap water	5	5	5.1 $\pm$ 0.2	4.7 $\pm$ 0.4	9.8 $\pm$ 0.4	102	94	98
	10	10	9.8 $\pm$ 0.4	10.4 $\pm$ 0.9	20.2 $\pm$ 0.8	98	104	101
Tap water	–	–	BDL	BDL	–	–	–	–
	5	5	4.7 $\pm$ 0.4	4.9 $\pm$ 0.6	9.6 $\pm$ 0.5	94	98	96
	10	10	9.9 $\pm$ 0.5	10.2 $\pm$ 0.9	20.1 $\pm$ 0.8	99	102	101

**Table 6**

Application of the present method to real water samples for chromium speciation and to solid samples for total chromium determination.

	Cr(III)	Cr(VI)	Total chromium
Water samples ( $\mu\text{g L}^{-1}$ )			
Tap water <sup>a</sup>	3.1 $\pm$ 0.2	1.8 $\pm$ 0.4	4.9 $\pm$ 0.4
Sea water <sup>a</sup>	7.2 $\pm$ 0.4	BDL	7.2 $\pm$ 0.4
Stream water <sup>a</sup>	6.8 $\pm$ 0.2	BDL	6.8 $\pm$ 0.2
Solid samples ( $\mu\text{g g}^{-1}$ )			
Dried eggplant <sup>b</sup>	–	–	3.8 $\pm$ 0.4
Tobacco <sup>c</sup>	–	–	2.7 $\pm$ 0.5

<sup>a</sup> Sample volume: 200 mL.<sup>b</sup> Sample quantity: 0.5 g.<sup>c</sup> Sample quantity: 1.0 g.

face of TIWAC and the second phase indicates the intraparticle diffusion of Cr(III) into the pores of TIWAC. The intraparticle rate constants  $k_{id,1}$  (for the first phase),  $k_{id,2}$  (for the second phase) and  $c$  parameters were obtained from the plot of  $q_t$  versus  $t^{1/2}$  and the results were given in Table 3. The values of  $k_{id,1}$  were higher than  $k_{id,2}$  so it can be concluded that the rate limiting step in present adsorption process is intraparticle diffusion. However the line did not pass through the origin indicating that the intraparticle diffusion model is not the only rate limiting mechanism. Therefore it can be concluded that Cr(III) adsorption onto TIWAC is a complex process and both intraparticle diffusion and surface sorption contributes to the rate-limiting step [32,33].

**Table 7**

Application of the present method to standard reference materials for total chromium determination.

Samples	Total chromium		
	Obtained value	Certified value	Error (%)
CRM-TMDW-500 ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	20.4 $\pm$ 0.6	20.0 $\pm$ 0.1	+2.0
Sandy Soil C ( $\mu\text{g g}^{-1}$ ) <sup>b</sup>	51.5 $\pm$ 3.5	54.1 $\pm$ 4.2	–4.8

<sup>a</sup> Sample volume: 25 mL.<sup>b</sup> Sample quantity: 0.1 g.

The Elovich equation is given as follows [34];

$$q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta \ln t} \quad (7)$$

where  $\alpha$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) is the initial sorption rate, and the parameter  $\beta$  ( $\text{g mg}^{-1}$ ) is related to the extent of surface coverage and activation energy for chemisorption. If Cr(III) adsorption on TIWAC fits the Elovich model, a plot of  $q_t$  versus  $\ln(t)$  should give a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta)\ln(\alpha\beta)$ . The Elovich model constants,  $\alpha$  and  $\beta$  values along with the corresponding correlation coefficient were presented in Table 3. The correlation coefficient value was relatively small indicating that Elovich model is not suitable for modeling the adsorption of Cr(III) onto TIWAC.

### 3.9. Adsorption capacity and reusability of TIWAC

The maximum adsorption capacity of TIWAC for the sorption of Cr(III) was determined by shaking 1000 mL of aqueous solution containing excess Cr(III) ions (1000  $\mu\text{g}$ ) at pH 6.0 with 10 mg of TIWAC under studied conditions [35]. After reaching equilibrium, the suspension was filtered through 0.45  $\mu\text{m}$  of nitrocellulose membrane and the filtrate was analyzed for residual Cr(III) concentration. The adsorption capacity of TIWAC was found to be 61.0  $\text{mg g}^{-1}$  using following equation;

$$q_e = \frac{C_0 - C_e}{m_s} \quad (8)$$

$C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of Cr(III) solution,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of Cr(III) in aqueous solution, and  $m_s$  ( $\text{g L}^{-1}$ ) is the TIWAC concentration;  $q_e$  ( $\text{mg g}^{-1}$ ) is amount of calculated Cr(III) adsorption onto 1.0 g of TIWAC.

In order to evaluate the reutilization of TIWAC, the adsorption–desorption cycles were repeated for six times using same preparations. In these tests, 50 mL of an aqueous solution containing 10  $\mu\text{g}$  of Cr(III) was treated with 2.0  $\text{g L}^{-1}$  of TIWAC suspension. The concentration of Cr(III) ions was determined after elution with 4.0 mL of 3.0 M  $\text{HNO}_3$  solution. There was no significant change observed for the adsorption performance of TIWAC after sixth adsorption–desorption cycle so it can be concluded that TIWAC can be used effectively at least 6 times with repeated elution.

### 3.10. Analytical performance of the method

The precision of the method was evaluated as the relative standard deviations (RSD). In order to evaluate the precision of the determination of Cr(III) (10  $\mu\text{g}$  of Cr(III) in 50 mL aqueous solution), the procedure was repeated 10 times under studied conditions mentioned above. RSD and the recovery of Cr(III), were found 3.9% and  $98 \pm 3.9$  at 95% confidence level, respectively. The detection limit, defined as the concentration that gives a signal equivalent to three times the standard deviation of 10 replicate measurements of the blank samples, for Cr(III) was 0.27  $\mu\text{g L}^{-1}$  for 50 mL of sample volume and 4.0 mL of final volume. The limit of detection was calculated by dividing the instrumental detection limit by the pre-concentration factor (50).

The method was also compared with other separation, preconcentration and speciation procedures for chromium by utilizing the SPE technique in terms of adsorption capacity of sorbents, detection limit and relative standard deviation of the methods, and preconcentration factors. The comparative data from some recent studies on chromium speciation were given in Table 8. As could be seen, the adsorption capacity of TIWAC has a relatively high value when compared the other sorbents. Also the proposed method is superior to those reported chromium preconcentration and speciation methods in terms of low detection limit, relative standard deviation and high preconcentration factor.

### 3.11. Determination of total chromium

A series of model solutions containing different concentrations of Cr(III) and Cr(VI) were prepared in order to determine the total chromium using present batch adsorption technique. Because of the quantitative recoveries for Cr(III) were obtained at pH 6.0, after reduction of Cr(VI) to Cr(III) in the model solutions using 0.5 mL of concentrated  $\text{H}_2\text{SO}_4$  and 0.5 mL of ethanol, the pH values of these solutions were adjusted to 6.0. Quantitative recovery values were obtained by applying the presented procedure to these solutions and a good agreement was found between the added and measured Cr(III) and Cr(VI) amount (Table 4). The recoveries of Cr(III) were higher than 95%. It can be concluded that the proposed batch adsorption technique for the separation, preconcentration and speciation of chromium can be successfully applied for the determination of total chromium.

### 3.12. Application to real samples and method accuracy

The feasibility of the proposed speciation method was investigated in terms of the determination of Cr(III), Cr(VI) and total chromium in various environmental water samples including sea water (Blacksea, Trabzon/Turkey), stream water (Şana Stream, Trabzon/Turkey) and tap water (Karadeniz Technical University, Trabzon/Turkey). Different amounts of chromium species were also

**Table 8**  
Comparison of the method some recent SPE studies reported in literature.

SPE Material	Medium pH		Adsorption capacity		LOD		RSD (%)		PF		Detection	Ref.
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)		
Cr(III)-imprinted silica gel	7.0	2.0	33.4 $\text{mg g}^{-1}$	11.7 $\text{mg g}^{-1}$	0.004 $\text{ng mL}^{-1}$	0.008 $\text{ng mL}^{-1}$	4.44	4.41	40	40	ICP-MS	[27]
BrPMAAm/AMPS/DWB	2.0	-	21.8 $\text{mg g}^{-1}$	-	1.58 $\mu\text{g L}^{-1}$	-	3	-	100	-	FAAS	[6]
Chromosorb 108 resin	8	-	4.50 $\text{mg g}^{-1}$	-	0.75 $\mu\text{g L}^{-1}$	-	2	-	71	-	FAAS	[8]
Bacillus sphaericus loaded diaion SP-850 resin	5	-	6.95 $\text{mg g}^{-1}$	-	0.5 $\mu\text{g L}^{-1}$	-	1–5	-	50	-	FAAS	[11]
Activated carbon	5	-	-	-	3 $\text{ng L}^{-1}$	-	4	-	35	-	ETAAS	[37]
DAPCH loaded Duolite C20	6	2	41.6 $\text{mg g}^{-1}$	25.05 $\text{mg g}^{-1}$	13.3 ppb	10 ppb	<3	<3	150	200	FAAS	[35]
Acetyl acetone modified XAD-16	>4	<3	15.0 $\text{mmol g}^{-1}$	18.8 $\text{mmol g}^{-1}$	0.02 $\mu\text{g mL}^{-1}$	0.014 $\mu\text{g mL}^{-1}$	2	2	100	140	FAAS	[38]
Sawdust	3	1	-	-	0.05 $\mu\text{g mL}^{-1}$	0.04 $\mu\text{g mL}^{-1}$	2	2	100	80	UV-Vis Spect.	[39]
Amberlite XAD-2000	3	2	-	7.4 $\text{mg g}^{-1}$	-	0.6 $\mu\text{g L}^{-1}$	-	4	-	80	FAAS	[12]
Activated carbon	6	-	61.0 $\text{mg g}^{-1}$	-	0.27 $\mu\text{g L}^{-1}$	-	3.9	-	50	-	FAAS	This work

PF, preconcentration factor; LOD, limit of detection; RSD, relative standard deviation; BrPMAAm/AMPS/DWB, poly N-(4-bromophenyl)-2-methacrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene; DAPCH, 1-(3,4-dihydroxybenzaldehyde)-2-acetylpyridiniumchloride hydrazone.



spiked to these water samples in order to test the accuracy of the method. The results for sample volumes of 50 mL were given in Table 5. A good agreement was obtained between the added and measured analyte amounts. The Cr(III), Cr(VI) and total chromium contents of water samples for sample volumes of 200 mL were given in Table 6. From the results it can be concluded that the proposed method can be successfully applied for separation, preconcentration, and speciation of trace amounts of chromium in tap water, sea water, and stream water.

In order to decide the applicability of the proposed separation and preconcentration method for the environmental solid samples, tobacco and dried eggplant was used for the determination of total chromium contents of them (Table 6). On the other hand the validation of the method was performed by determination of total chromium using certified reference materials, CRM-TMDW-500 Drinking Water and CRM-SA-C-Sandy Soil C (Table 7). The analytical values were in good agreement with the certified values. Statistical evaluation was applied to the results obtained from the accuracy study (Table 7) using Student's *t*-test [36]. The results revealed good agreement between the observed values and certified values such that for CRM TMDW-500 Drinking Water analyses, the difference between the value of standard material ( $X_R$ ) and mean value ( $\bar{X}$ ), obtained by applying the procedure, was found to be 0.4 and  $ts/\sqrt{N}$  value was found to be 1.5 (*t*: 4.30 at 95% confidence intervals, *s*: 0.6 and *N*: 3). For CRM-SA-C Sandy Soil C analyses,  $X_R - \bar{X}$  value was found to be 2.6 and  $ts/\sqrt{N}$  value was found to be 8.7 (*t*: 4.30 at 95% confidence intervals, *s*: 3.5 and *N*: 3). As can be seen for both standard reference materials analyses ( $X_R - \bar{X}$ ), values were lower than ( $ts/\sqrt{N}$ ) values.

#### 4. Conclusions

A new solid phase material, activated carbon, was produced from tea-industry wastes (TIWAC), characterized and applied for the separation, preconcentration and speciation of chromium species by batch adsorption technique. The utilization of tea wastes, which is industrial waste that must be removed, in the determination of one of the highly toxic and carcinogenic heavy metals is the main advantage of present study. There is no need to use a complexing agent for the preconcentration of chromium species so contamination risk from a complexing agent is eliminated in present study. High adsorption capacity of TIWAC for Cr(III) ( $61.0 \text{ mg g}^{-1}$ ), high preconcentration factor (50 for 200 mL of sample volume), low detection limit ( $0.27 \mu\text{g L}^{-1}$ ), low relative standard deviation (%3.9), reusability of TIWAC in repeated cycles (at least six times), low matrix effects and also simplicity, low cost, safety and ease of automation are another advantages of the method.

The results of present study demonstrated that the TIWAC can be successfully applied for the separation, preconcentration and speciation of chromium in environmental water samples (tap water, sea water and stream water) and also preconcentration of chromium in environmental solid samples (tobacco and dried eggplant) by batch adsorption technique.

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