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Chemically modified activated carbon with tris(hydroxymethyl)aminomethane for selective adsorption and determination of gold in water samples

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Abstract In the current study, a sensitive and simple method for selective separation of gold, Au(III), from water samples prior to its determination by inductively coupled plasma-optical emission spectrometry (ICP-OES), was investigated. The method utilized activated carbon modified with tris(hydroxymethyl)aminomethane (AC–TRIS) as a solid-phase extractant. Surface properties of the AC–TRIS phase were characterized by Fourier transform infrared (FT-IR) spectroscopy. The separation parameters for effective adsorption of Au(III), including effects of pH, Au(III) concentration, shaking time, and common coexisting ions were examined using batch method. The optimum pH value for the separation of Au(III) on the new sorbent was 1.0, and the maximum static adsorption capacity of Au(III) onto the AC–TRIS was 33.57 mg g^{-1} at this pH and after 1 h contact time. The Au(III) adsorption data were modeled using both Langmuir and Freundlich classical adsorption isotherms. Results demonstrated that the adsorption of Au(III) onto activated carbon followed second-order kinetic model. In addition, the efficiency of this methodology was confirmed by applying it to real environmental samples.

1. Introduction

The release of several harmful heavy metal ions into the environment has become one of the major economic and environmental problems due to their toxicity and widespread use (Li et al., 2009; Rao et al., 2009). Therefore, the development of simple, rapid, and efficient methods has continued to be of interest for monitoring heavy metal ions in the environment, in particular aqueous media. Several approaches have been implemented for analyses of heavy metal ions in aqueous solutions. For instance, the most frequently used techniques for

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determination of heavy metal ions are spectrophotometry (Raimundo and Narayanaswamy, 2003), atomic absorption spectrometry (AAS) (Ajtony et al., 2007), inductively coupled plasma-mass spectrometry (ICP-MS) (Montes-Bayon et al., 2006), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Li et al., 2009; Gao et al., 2009), anodic stripping voltammetry (Bonfil and Kirowa-Eisner, 2002), ion chromatography (Tanikkul et al., 2004), and fluorescence spectroscopy (García-Reyes et al., 2006). However, heavy metal ions at ultra-trace concentration cannot be directly measured in aqueous systems using above methods. The sensitivity and selectivity of these methods are usually insufficient for direct determination of heavy metal ions at a very low concentration level in complex matrix environmental samples. These problems can be overcome by the combination of an effective preconcentration and/or separation techniques with subsequent determination.

Separation and preconcentration methods involve several procedures, including liquid–liquid extraction (Nasu et al., 1997), ion exchange (Tao and Fang, 1998), and chemical precipitation (Soylak and Erdogan, 2006). These traditional separation and/or preconcentration methods for heavy metal ions, however, are usually time consuming and require relatively large volumes of high purity solvents. The most powerful and widely used method for pretreatment of environmental samples is solid phase extraction (SPE). This is due to its advantages of high recovery, rapid extraction time and phase separation, high enrichment factor, low cost, and low consumption of organic solvents over liquid–liquid extraction (Ahmed, 2008; Alvarez et al., 2007).

In addition, a large variety of adsorbents have been used as solid phase extractors for preconcentration of metal ions, such as alumina (Soliman and Ahmed, 2009), C18 (Pei and Fang, 1994), XAD resins (Guo et al., 2004), cellulose (Gustavo Rocha de et al., 2004), and silica gel (Mahmoud et al., 2008). Activated carbon (AC) is the most widely used adsorbent in the environmental pollution control among all of adsorbents because of its simple handing, large surface area, high adsorption capacity, porous structure, selective adsorption, and high purity standards (Sanchez-polo and Rivera-utrilla, 2002; Sato et al., 2007). However, adsorption of heavy metal ions at trace and ultra-trace levels can not be quantitatively accomplished by AC alone (Starvin and Rao, 2004). The nature and concentration of AC functional groups may be modified by various surface treatments (Yin et al., 2007).

There are various methods of surface treatments of AC such as oxidative (Santiago et al., 2005) and non-oxidative (Sato et al., 2007) methods. They have been used for the modification of its interfacial region by increasing surface functional groups. Generally, adsorption of heavy metal ions on AC has been intensively investigated (Dabrowski et al., 2005). In previous studies, the presence of protonable complexing groups in AC surface, such as carboxylic, lactonic, and phenolic groups have been extensively investigated (Snoeyink and Weber Jr., 1967; Üçer et al., 2006). However, studies reported to modified AC are relatively fewer (Villacañas et al., 2006; László, 2005). The chemical modification of AC with organic chelating agents improves its interfacial region, enhancing its selectivity and capability for monitoring heavy metal ions in the environment.

Over the past years, the effect of surface functional groups modification of AC on the adsorption behavior with heavy metal ions has been of a continual concern. For example, AC functionalized with complexing agents, such as pyrocatechol violet (Narin et al., 2000), ammonium pyrrolidine dithiocarbamate (Soylak et al., 1996), and 5,5-diphenylimidazolidine-2,4-dione (phenytoin) (Ghaedi et al., 2008) has been reported as a chelating collector for heavy metal ions, such as Cu, Co, Cd, Mn, Ni, and Pb. In addition, several heavy metal ions enrichment is achieved after modification of AC with chelating agents, such as pyrocatechol violet for Cu, Mn, Co, Cd, Pb, Ni, and Cr (Narin et al., 2000), 8-hydroxyquinoline for Cd (Cerutti et al., 2003), Co, Hg, and Ni (Shiowatana et al., 2000), pyridyl azo resorcinol for Cu, Co, Cd, Cr, Ni, Pb, and, V (Chakrapani et al., 1998) and 1,10-phenanthroline for Cd, Co, Ni, Cu, and Pb (Mikula and Puzio, 2007; Ali et al., 1999). Thus, there is an increasing interest for preparation of modified AC with specific surface functional groups in order to selectively bind the analyte of interest.

Accordingly, this study aimed to explore the effect of modified AC on the selectivity and metal ion adsorption capacity. Surface properties of the chemically modified activated carbon with tris(hydroxymethyl)aminomethane (AC–TRIS) were characterized by FT-IR spectroscopy. The preparation of the adsorbent involves a chemical modification of oxidized AC with tris(hydroxymethyl)aminomethane (AC–TRIS), allowing it to bind Au(III) prior to its determination using ICP-OES under the optimum conditions. Several parameters controlling the maximum uptake of the target heavy metal ion under batch conditions, including effects of pH, Au(III) concentration, shaking time, and common coexisting ions were investigated. The Au(III) adsorption data were also modeled using both Langmuir and Freundlich classical adsorption isotherms. Results of the kinetic study showed that this adsorption obeyed the pseudo-second order. Finally, the efficiency of this methodology was also supported by applying it to real environmental samples.

2. Materials and methods

2.1. Chemicals and reagents

Tris(hydroxymethyl)aminomethane (TRIS), N,N′-Dicyclohexylcarbodiimide (DCC), activated carbon (AC), stock standard solution (1000 mg L^{-1}) of gold, and dimethyl formamide (DMF) were obtained from Sigma-Aldrich (Milwaukee, WI). All reagents used were of high purity and of analytical reagent grade, and doubly distilled deionized water was used throughout.

2.2. Preparation of the new solid phase extractor based on activated carbon

2.2.1. Purification of activated carbon

Activated carbon powder was first purified with 10% (v/v) hydrochloric acid solution for 24 h to remove adsorbed impurities and metal ions. Then, it was filtered, washed with 18.2 MΩ cm distilled deionized water, and oven dried at 80 °C for 5 h.

2.2.2. Preparation of carboxylic acid derivative of activated carbon (AC–COOH)

Ten grams of purified activated carbon was suspended in 300 mL of 32.5% (v/v) nitric acid solution under stirring and heating for 5 h at 60 °C. The mixture was filtered, thoroughly rinsed with 18.2 MΩ cm distilled deionized water to neutral, and oven dried at 80 °C for 8 h.

2.2.3. *Synthesis of activated carbon covalently bonded tris(hydroxymethyl)aminomethane (AC–TRIS)*

Five grams of AC–COOH was mixed with 5 g DCC dissolved in 100 mL DMF and 6 g of TRIS dissolved in 350 mL of warmed ethanol. The mixture was kept under stirring for 48 h (Gao et al., 2009). The resulting solid phase was filtered, washed with DMF, ethanol, and dichloromethane, and then dried at 80 °C for 8 h. The synthetic route of AC–TRIS is illustrated in Scheme 1.

2.3. *Samples preparation and procedure*

A stock solution of Au(III) was prepared in 18.2 MΩ cm distilled deionized water and stored in the dark at 4 °C. For pH study, standard solutions of 1 mg L^{-1} Au(III) were prepared by adding the appropriate amount of Au(III) stock solution and adjusted to pH values from 1.0 to 8.0 with the appropriate buffer solutions, HCl/KCl buffer for pH (1 and 2), acetate buffer for pH (3–6), and Na_2HPO_4/H_3PO_4 buffer for pH (7–8). An amount of 25 mg AC–TRIS was also mixed with each standard solution. For the Au(III) uptake capacity study, Au(III) standard solutions of (1, 2.5, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 mg L^{-1}) were prepared as above, adjusted to the optimum pH value of 1.0 with the buffered aqueous solutions (0.2 M HCl and 0.2 M KCl) and mixed with 25 mg AC–TRIS. These mixtures were mechanically shaken for 1 h at room temperature. Moreover, the effect of shaking time on the metal uptake capacity was determined under the same batch conditions but at different equilibrium periods (2.5, 5, 10, 20, 30, 40, 50, and 60 min) and at the pH of the highest metal ion uptake.

2.4. *Apparatus*

Fourier transform infrared (FT-IR) spectra were acquired before and after modification of the activated carbon phase on a Shimadzu IR 470 spectrophotometer in the range 4000–600 cm^{-1}. A pH meter (inoLab® pH 7200, IL, USA) was employed for the pH measurements with absolute accuracy limits at the pH measurements being defined by NIST buffers. A Perkin Elmer inductively coupled plasma-optical emission spectrometer (ICP-OES) model Optima 4100 DV, USA was used for the determination of Au(III). The ICP-OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP-OES spectrometer was used with following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min^{-1}; auxiliary gas (Ar) flow, 0.2 L min^{-1}; nebulizer gas (Ar) flow, 0.8 L min^{-1}; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min^{-1}; integration time, 3 s; replicates, 3; wavelength range of monochromator 165–460 nm. The selected wavelength for Au(III) was 242.80 nm.

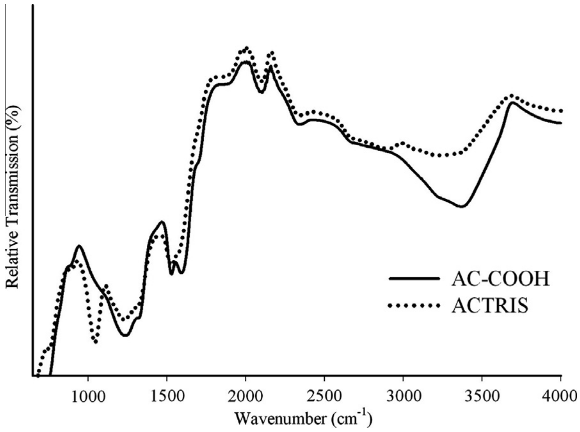


Figure 1 FT-IR spectra of AC–COOH and ACTRIS.

3. Results and discussion

3.1. *FT-IR characterization of AC–TRIS and surface coverage*

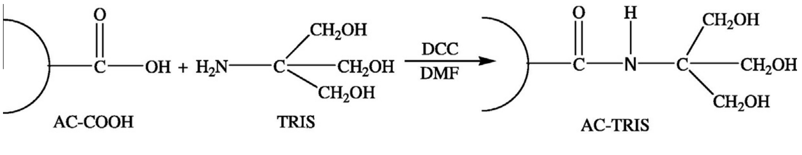
The carboxylic acid derivatives of activated carbon (AC–COOH) surfaces were confirmed by FT-IR analysis (Fig. 1). In the FT-IR spectrum of AC–COOH, the bands of oxidized activated carbon were three ranges of spectra: 4000–2000 (dehydration and aliphatic units), 2000–1300 (oxygen function groups) and 1300–800 cm^{-1} (various C–O single bond). For the oxidized activated carbon, the characteristic vibration of unionized and uncoordinated carboxyl is shown as a strong peak of COO^{-}, stretching at 1710 cm^{-1} and a shoulder of OH deformation vibration at 1460 cm^{-1}, which indicated the carboxylic derivative of activated carbon was successfully prepared. In addition, the FT-IR spectrum of AC–TRIS was collected (Fig. 1). Several new peaks appeared in the FT-IR spectrum of AC–TRIS. According to the literature (Tang, 1992), molecular species are identified by their characteristic absorbance ν (cm^{-1}): 1661.16 (CO); 1550.56 (C–N and N–H); 3385.73 (N–H); 3620 (OH).

The concentration of TRIS on the surface of activated carbon was determined to be 1.65 mmol g^{-1} based on thermal desorption method (Soliman and Ahmed, 2009).

3.2. *Batch method*

3.2.1. *Effect of pH*

The pH value plays an important role with respect to the adsorption of different ions on AC–TRIS. The oxidation of activated carbon with conc. HNO_3 leads to the surface functionalization with oxygen containing groups that increase



Scheme 1 Synthetic route of AC–TRIS phase.

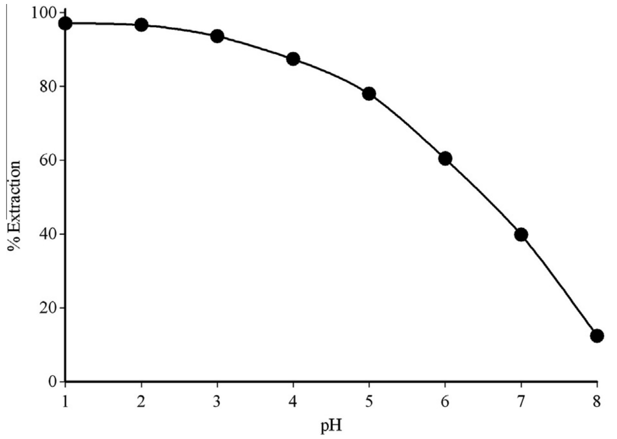


Figure 2 Effect of pH on the adsorption of 1 mg L^{-1} Au(III) on AC–TRIS phase at 25 °C.

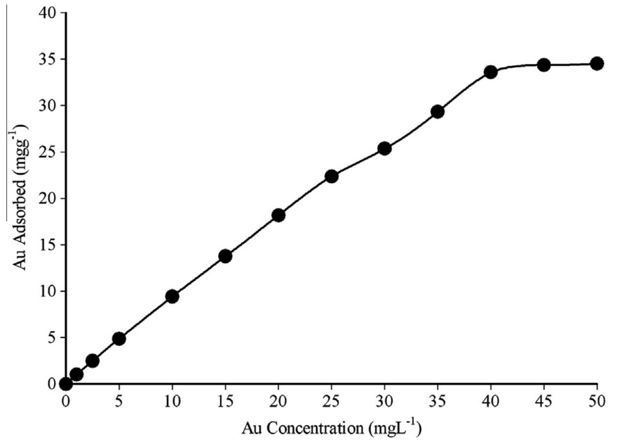


Figure 3 Breakthrough curve of Au(III) on 25 mg AC–TRIS phase at pH 1.0 and 25 °C.

proton acceptor centers. Thus, the positive charge on the surface of AC–COOH provides electrostatic attraction that is favorable for the adsorption of $AuCl_4^-$ species, the primary form of Au(III) in HCl solution. In order to evaluate the effect of pH, the pH values of 1 mg L^{-1} Au(III) standard solutions individually mixed with 25 mg AC–TRIS were adjusted to a range of 1 up to 8 and processed according to the recommended procedure. The adsorption percentage was calculated based on a difference between the amounts of Au(III) in the starting sample and the solution after filtration with AC–TRIS. The results of the effect of pH on the adsorption of Au(III) to the AC–TRIS phase are shown in Fig. 2. A close inspection of Fig. 2 shows that almost all Au(III) was extracted (97%) in the pH range of 1–3, Thus, it makes possible to selectively separate Au(III) from the matrix. Therefore, the optimum pH selected for this study was 1.0.

3.2.2. Adsorption capacity

For determination of the Au(III) uptake capacity, 25 mL sample of standard solutions having different Au(III) concentrations (in the range from 0 to 50 mg L^{-1}) were adjusted to pH 1.0 with buffered aqueous solutions (0.2 M HCl and 0.2 M KCl) and mixed with 25 mg AC–TRIS, these mixtures were mechanically shaken for 1 h at room temperature. The

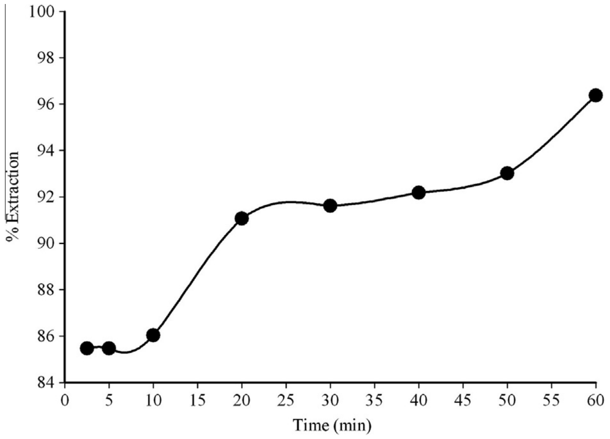


Figure 4 Effect of shaking time on the adsorption of Au(III) on AC–TRIS phase at pH 1.0 and 25 °C.

proposed separation procedures described above were applied. The amount of Au(III) at each concentration level was determined. The breakthrough curve for Au(III) was obtained by plotting the Au(III) concentration (mg L^{-1}) versus the Au(III) adsorbed on AC–TRIS (mg g^{-1}), as displayed in Fig. 3. From the adsorption isotherm study, the adsorption capacity of AC–TRIS for Au(III) was found to be 33.57 mg g^{-1}, which is comparable to those previously reported in other studies (12.3, 14.8, and 35.88 mg g^{-1}) (Senturk et al., 2007; Liang et al., 2008; Nakbanpotea et al., 2002). In fact, the high value of adsorption capacity of Au(III) reported in this study (33.57 mg g^{-1}) using AC–TRIS is attributed to the additional four new proton acceptor centers created via the reaction of AC–COOH with TRIS. These newly positively charged centers are able to easily bind with $AuCl_4^{-1}$ species through electrostatic attraction at pH 1.

3.2.3. Effect of shaking time

The effect of shaking time is an important factor for determining the possibility of applications of AC–TRIS to selectively bind metal ions of interest. Thus, in this study, different shaking times ranging from 2.5 to 60 min were studied for the percentage extraction of Au(III) by AC–TRIS. Fig. 2 indicates the maximum extraction (97%) of Au(III) when 1 mg L^{-1} concentration is used. However, the effect of shaking time study was performed as a function maximum uptake of Au(III) when its concentration was 50 mg L^{-1} concentration. The results in Fig. 4 displays that equilibrium kinetics of the adsorption of Au(III) by the newly modified AC–TRIS are very fast. It was found that the percentage of extraction was above 85% after 10 min and raised up to more than 90% after 20 min until the maximum extraction was reached to 98% after 60 min. It can also be noticed that the optimization of shaking time is not linear (Fig. 4). This behavior is in agreement with the saturation of binding sites of the phase with $AuCl_4^{-1}$ species at the specified shaking time. Consequently, no effect of time was observed on maximum uptake after this saturation process.

3.3. Sorption isotherms and kinetic studies

The results obtained on the sorption of Au(III) were examined by well-known models given by Langmuir and Freundlich. The Langmuir equation, which is valid for monolayer sorption

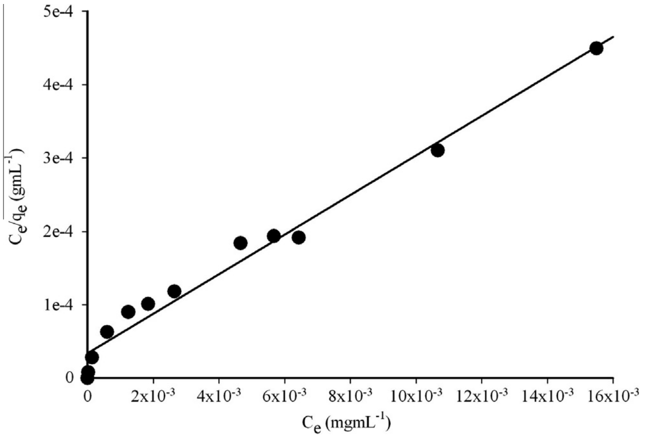


Figure 5 Langmuir sorption isotherm model of Au(III) adsorption on AC–TRIS phase. Adsorption experiments were obtained in a batch mode using different concentrations of Au(III) ranging from 1 to 50 mg L^{-1}, 25 mg AC–TRIS, and at pH 1.0 and 25 °C.

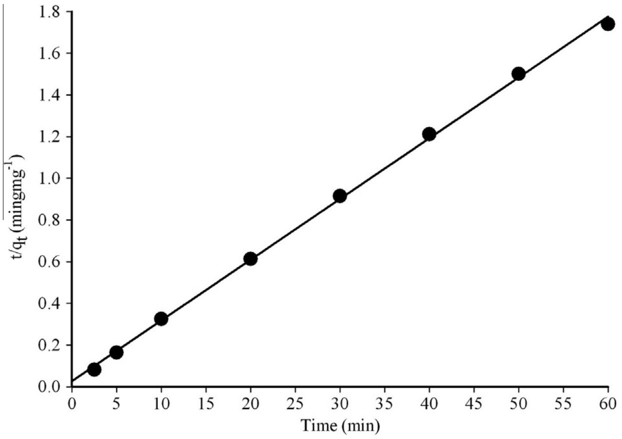


Figure 6 Pseudo second-order sorption kinetic of Au(III) uptake by adsorption on AC–TRIS phase at 25 °C.

onto a completely homogeneous surface with a finite number of identical sites and with a negligible interaction between the adsorbed molecules, is given by the following equation:

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b$$

where C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phase in mg mL^{-1} and mg g^{-1}, respectively (Rao et al., 2009). The symbols Q_o and b refer Langmuir constants for AC–TRIS, which are related to the maximum Au(III) sorption capacity (mg g^{-1}) and affinity parameter (L mg^{-1}), respectively, and can be calculated from the slope ($1/Q_o$) and intercept ($1/Q_o b$) of the linear plot, C_e/q_e versus C_e (Fig. 5). Calculated Langmuir constants Q_o and b are found to be 37.04 mg g^{-1} and 0.9 L mg^{-1}, respectively. The correlation coefficient obtained with the Langmuir model is found to be r^2 = 0.98 for adsorption of Au(III) on AC–TRIS, indicating that this model fitted the results better as compared to the Freundlich model. Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as $R_L = 1/(1 + bC_o)$, where b is the Langmuir constant (indicates the nature of sorption and the shape of the isotherm); C_o the initial concentration of the analyte (Rao et al., 2009). The R_L for Au(III) sorption (0.03) supports a highly favorable sorption process based on the Langmuir model. The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption (Pehlivan et al., 2008). This model is the earliest known empirical equation, and is shown to be consistent with the exponential distribution of active centers, characteristic of heterogeneous surfaces,

$$\log q_e = \log K_f + 1/n \log C_e$$

where K_f and n are the characteristic Freundlich constants that are related to the adsorption capacity and intensity, respectively. These parameters can be obtained from the linear plot of log q_e versus log C_e, which has a slope of *1*/*n*, and an intercept of log K_f. It was, however, observed from the isotherm and regression coefficient (Rao et al., 2009) that the data were better fitted with the Langmuir model in comparison to those with the Freundlich model.

The adsorption kinetic study is quite significant in a water treatment, since it describes the solute uptake rate, which in turn controls the residence time of the adsorbate uptake at the solid–solution interface. The sorption kinetic data of Au(III) measured on AC–TRIS phase were analyzed in terms of pseudo first- and second-order sorption equations (Rao et al., 2009). The pseudo first-order equation is as follows:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

here k_1 (min^{-1}) is the rate constant of the pseudo first-order sorption, q_t (mg g^{-1}) denotes the amount of sorption at time t (min), and q_e (mg g^{-1}) is the amount of sorption at equilibrium. The kinetic plot is drawn for the AC–TRIS phase. The adsorption rate constant k_1 and adsorption capacity q_e for AC–TRIS can be calculated from the slope and intercepts of the plot of $\log(q_e - q_t)$ against t.

The sorption kinetic data of Au(III) measured on AC–TRIS are also examined in terms of a pseudo second-order sorption (Rao et al., 2009). The pseudo second-order equation can be written as follows:

$$t/q_t = 1/\upsilon_0 + (1/q_e)t$$

where $\upsilon_o = k_2 q_e^2$ is the initial sorption rate (mg g^{-1} min^{-1}) and k_2 (g mg^{-1} min^{-1}) corresponds to the rate constant of sorption, q_e (mg g^{-1}) is the amount of metal ion sorbed at equilibrium, and q_t (mg g^{-1}) refers to the amount of meal ion on the surface of the sorbent at any time t (min). The parameters υ_o and q_e can be obtained from the intercept and slope, respectively, of a plot of t/q_t versus t (Fig. 6). They were determined to be υ_o = 61.35 mg g^{-1}min^{-1}, q_e = 33.56 mg g^{-1}, and k_2 = 0.05 g mg^{-1} min^{-1} for AC–TRIS. Since the kinetics of the uptake has to be determined in order to establish the time course of the uptake process, the previous results showed that the adsorption kinetics data were best fitted with the pseudo second-order model, which gives a correlation coefficient factor of r^2 = 0.99 and more appropriately than that (r^2 = 0.92) of the pseudo first-order equation.

3.4. Performance of method in analytical applications

3.4.1. Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Au(III) on AC–TRIS were investigated. In these experiments,

Table 1 Tolerance limits for coexisting ions of the Au(III) adsorption on AC–TRIS phase.

Coexisting ions	Ions tolerance limit (μg L^{-1})
Na(I) and K(I)	9000
Ca(II) and Mg(II)	4000
Cu(II), Cd(II), Mn(II), Ni(II), and Zn(II)	900
Cr(III), Fe(III), and Al(III)	400

Table 2 Determination of Au(III) at different concentrations (0, 10, and 20 mg L^{-1}) in natural water samples using 25 mg AC–TRIS phase at pH 1.0 and 25 °C.

Samples	Added (mg L^{-1})	Founded (mg L^{-1})	Recovery (%)
Lake water	0	ND	ND
	10	0.40 (±0.012)	96.00
	20	1.03 (±0.220)	94.85
Seawater	0	ND	ND
	10	0.02 (±0.003)	99.80
	20	1.09 (±0.250)	94.55

Standard deviation for $N = 3$.

a standard solution of 60 μg L^{-1} of Au(III) containing the added interfering ions was treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Au(III) less than 90%, are given in Table 1. It can be seen that the presence of major cations and anions has no significant influence on the adsorption of Au(III) under the selected conditions.

3.4.2. Application to environmental samples

The validity of the method for Au(III) selective separation and determination was achieved via spiking known mg L^{-1} concentrations of the targeted metal ion onto natural water samples. This procedure is an alternative to the use of a certified reference sample, which is unfortunately not in hand. The chosen environmental water samples were the lake water and seawater, collected from the forty lake and Red sea coast, respectively, at Jeddah in Saudi Arabia. In addition, the recovery experiments of different amounts of Au(III) were carried out, and the results are summarized in Table 2. The results indicated that the recoveries were reasonable for trace analysis, in a range 94.55–99.80%.

4. Conclusions

A proposed selective and sensitive method for the separation and determination of trace levels of Au(III) was developed using tris(hydroxymethyl)aminomethane (AC–TRIS). The synthesized AC–TRIS was relatively simple and convenient in which additional four new positively charged centers were created. The adsorbent showed excellent characteristics adsorption of Au(III), in aqueous solution at pH 1 due to the electrostatic interaction of $AuCl_4^{-1}$ with the positively charged centers. The results presented that the new sorbent has excellent selectivity and short contact time for extraction. The Au(III) adsorption isotherm data were better fit into the Langmuir than Freundlich adsorption isotherm. Results demonstrated that the adsorption of Au(III) onto AC–TRIS followed the second-order kinetic model. In addition, most of common coexisting ions did not interfere with study of Au(III) under the optimum conditions. The proposed method was applied to real environmental samples, providing acceptable results.

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