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Activated carbon immobilized dithizone phase for selective adsorption and determination of gold(III)

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ABSTRACT

A simple method for selective adsorption and determination of gold(III) based on activated carbon immobilized dithizone (AC-DTZ) phase combined with inductively coupled plasma-optical emission spectrometry was developed. Surface properties of the new chemically modified AC-DTZ phase were confirmed by Fourier transform infrared spectroscopy. The effect of pH on the selectivity of AC-DTZ towards eight metal ions, including Au(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II), was investigated. Based on the pH study, it was found that the selectivity of AC-DTZ phase was the most towards Au(III). For a deeper mechanistic understanding of the analytical potential of the AC-DTZ phase towards Au(III), other factors influencing the maximum uptake of Au(III) on AC-DTZ were also investigated. The results showed that the adsorption capacity for Au(III) was improved by 64.07% with the AC-DTZ phase as compared to the carboxylic acid derivative of activated carbon after only 1 h contact time. Adsorption isotherm data confirmed that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. Results displayed that the adsorption of Au(III) onto the AC-DTZ phase obeyed a pseudo second-order kinetic model. In addition, the efficiency of this methodology was supported by applying it to real water samples with satisfactory results.

Keywords: Au(III); Dithizone; Modified activated carbon; Separation; ICP-OES; Batch method

1. Introduction

Gold(III) is one of the precious metals and held an allure for thousands of years. It has a unique combination of properties that have resulted in its use in a wide range of industrial applications. It is also one of non-essential toxic noble elements. However, some studies have reported that Au(III) has allergic eczematous dermatitis and nephrotoxic effects [1]. In general, noble metals have received significant attention because of their extensive applications in fields of petroleum, chemical industry, agriculture and medicine. Additionally, noble metals can be exposed to the environment by various ways such as emitting into the atmosphere with automobile exhaust gases. For sensitive, accurate and interference-free determination of noble metals, an effective separation procedure is usually required prior to the determination of noble metals [2]. There are various separation techniques, including liquid–liquid extraction [3], ion exchange [4], coprecipitation [5], cloud point extraction [6] and solid phase extraction (SPE) [7,8]. Liquid–liquid extraction and coprecipitation often require

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large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems.

However, SPE is one of the most popular techniques because it reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Due to the popularity of SPE, several adsorbents have appeared with the aim of achieving selective separation of analytes, such as alumina [9], C18 [10], molecular imprinted polymers [11], cellulose [12], silica gel [13] and activated carbon [14,15]. Activated carbon (AC) is the most widely used adsorbent due its simple handing, large surface area, high adsorption capacity, porous structure, selective adsorption and high purity standards. However, adsorption of heavy metal ions at trace and/or ultra-trace levels by AC alone cannot be quantitatively accomplished [16]. Therefore, there have been several methods for the modification of the interfacial region of AC by increasing its surface functional groups [17–19].

Generally, a great deal of time was spent on studying adsorption of metal ions based on the presence of protonable complexing groups in AC surface, such as carboxylic, lactonic and phenolic groups [20]. However, the modification of AC with organic chelating agents improves its interfacial region, enhancing its selectivity and capability for monitoring metal ions in the environment. In addition, the selectivity of solid phase extractors are mainly based on the structure of the immobilized organic compound as a whole, the nature of incorporated donor atoms (O, N, P and S), the positioning of functional groups along the surface of the solid support, and steric requirements of the complex formed after uptake of the desired metal ion [21,22]. In recent years, there are a considerable number of several approaches focusing on the modification of AC with organic complexing agents. For example, AC functionalized with dithiophosphoric acid O,O-diethyl ester has been reported as a chelating collector for Au, Ag and Pd [23], pyrocatechol violet for Cu, Mn, Co, Cd, Pb, Ni and Cr [24], 8-hydroxyquinoline for Cd, Co, Hg and Ni [25], and 1,10-phenanthroline for Cd, Co, Ni, Cu and Pb [26].

The development of simple, rapid and efficient methods has become of interest for monitoring metal ions in the environment. Several analytical methods have been applied to analyze metal ions in aqueous solutions, such as atomic absorption spectrometry [27], inductively coupled plasma-optical emission spectrometry (ICP-OES) [28,29], anodic stripping voltammetry [30], and ion chromatography [31]. In spite of great improvements in sensitivity and selectivity of modern instrumental analysis, there is still a crucial need of a selective separation of the analyte prior to its determination in complex matrices because of its frequent low concentrations. In addition, a clean-up step is often required due to high levels of interfering matrix components usually accompany the analyte.

The aim of this investigation, therefore, was to explore the analytical potential of a chemically AC immobilized dithizone phase as adsorbent on the selectivity and adsorption capacity of Au(III) prior to its determination by ICP-OES. Dithizone is well recognized as a nitrogen and sulfur donor atoms containing chelating compound with excellent analytical and spectroscopic applications. Immobilization of dithizone on AC adsorbent can, therefore, afford several advantages owing to chelating properties as well as the acidic and basic characteristics of AC. The preparation of the new adsorbent involved a chemical modification of oxidized AC with dithizone (AC-DTZ) for selective adsorption of Au(III) prior to its determination by use of ICP-OES. Measurements of Fourier transform infrared (FT-IR) spectroscopy confirmed the formation of the new chemically modified adsorbent (AC-DTZ). The effect of pH on the selectivity of AC-DTZ towards different metal ions [Au(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II)] was also investigated in order to study the effectiveness of AC-DTZ on the adsorption of selected metal ions. Based on the pH study, it was found that the selectivity of AC-DTZ towards Au(III) was the most as compared to other metal ions. Furthermore, other parameters controlling the maximum uptake of Au(III) on the AC-DTZ phase were investigated under batch conditions in order to allow for a deeper mechanistic understanding. Adsorption data of Au(III) were modeled using Langmuir classical adsorption isotherm. The kinetic analysis for adsorption process was carried out by a pseudo second-order adsorption model. The efficiency of this methodology was also validated by applying it to real water samples.

2. Experimental

2.1. Chemicals and reagents

Dithizone (DTZ), N,N′-Dicyclohexylcarbodiimide (DCC), AC, dimethyl formamide (DMF), ethyl alcohol (Et-OH) and diethyl ether were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Stock standard solutions of 1000 mg l^{-1} Au(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) were also obtained from Sigma-Aldrich. 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 AC

2.2.1. Purification of AC

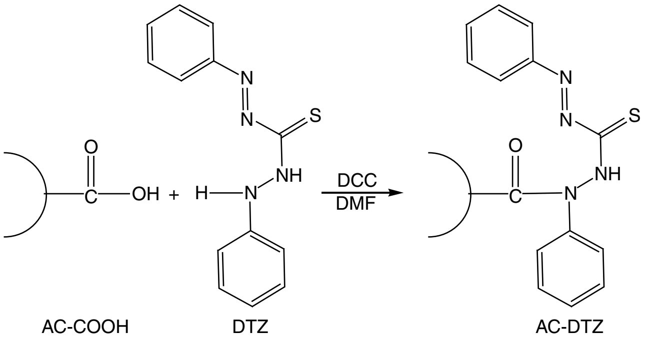
AC powder was first purified with 10% (v/v) hydrochloric acid solution for 24 h to remove adsorbed impurities and metal ions. Then, it was filtered, washed with 18.2 MΩ·cm distilled deionized water, and oven dried at 80°C for 5 h.

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

10 g of purified AC 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 AC-DTZ

2 g dithizone was weighed and completely dissolved by warming in 350 ml Et-OH. To this solution, 5.0 g AC-COOH was mixed with 5 g DCC dissolved in 100 ml DMF. The reaction mixture was stirred at 60°C for 24 h. The newly modified AC-DTZ solid phase was filtered and washed with 50 ml DMF, Et-OH on three portions and diethyl ether. The AC-DTZ adsorbent was then allowed to dry in an oven at 70°C for 8 h. The synthetic route of AC-DTZ is displayed in Scheme 1.



Scheme 1. Synthetic route of AC-DTZ phase.

2.2.4. Determination of the surface coverage value of the AC-DTZ phase by thermal desorption method

100 mg of the newly modified AC-DTZ phase was weighed in a dry porcelain crucible, and this was gradually heated into a furnace from 50°C to 700°C. The ignition was completed in 1 h, and the remaining AC-DTZ phase was left to cool in a desiccator and weighed to determine the mass of desorbed organic compound (dithizone). The concentration of dithizone on the surface of AC was determined to be 1.28 m mol g^{-1} based on thermal desorption method.

2.3. Samples preparation and procedure

Stock solutions of Au(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) were prepared in 18.2 MΩ·cm distilled deionized water and stored in the dark at 4°C. For the effect of pH on the selectivity of AC-DTZ towards selected metal ions, standard solutions of 5 mg l^{-1} of each metal ion were prepared and adjusted to pH values ranging 1.0–8.0, except for Fe(III), with appropriate buffer solutions, HCl/KCl buffer for pH (1.0 and 2.0), acetate buffer for pH (3.0–6.0), and Na_2HPO_4/H_3PO_4 buffer for pH (7.0–8.0). Fe(III) was prepared at the same concentration as above but was only investigated with buffer solutions at pH values ranging 1.0–4.0 in order to avoid any precipitation of $Fe(OH)_3$ with buffer solutions at pH (5.0–8.0). Each standard solution of selected metal ions was individually mixed with 25 mg AC-DTZ. For the study of Au(III) uptake capacity under batch conditions, standard solutions of 0, 5, 10, 25, 40, 60, 75, 100, 125 and 150 mg l^{-1} were prepared as above, adjusted to the optimum pH value of 1.0 with the buffered aqueous solution (HCl/KCl) and individually mixed with 25 mg AC-DTZ. The mixtures were mechanically shaken for 1 h at room temperature. In addition, the effect of shaking time on the Au(III) uptake capacity was studied under the same batch conditions but at different equilibrium periods (1, 5, 10, 20, 30, 40, 50 and 60 min).

2.4. Apparatus

FT-IR experiments were performed before and after modification of the AC 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. ICP-OES measurements were acquired by use of a Perkin Elmer ICP-OES model Optima 4100 DV, USA. 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 metal ions were determined at wavelengths of 242.80 nm for Au(III), 214.44 nm for Cd(II), 228.62 nm for Co(II), 324.75 nm for Cu(II), 259.94 nm for Fe(III), 221.65 nm for Ni(II), 220.35 nm for Pb(II) and 267.72 nm for Zn(II).

3. Results and discussion

3.1. FT-IR characterization of AC-DTZ

FT-IR spectra were taken by using KBr to observe the functional groups of AC-COOH and AC-DTZ (Fig. 1).

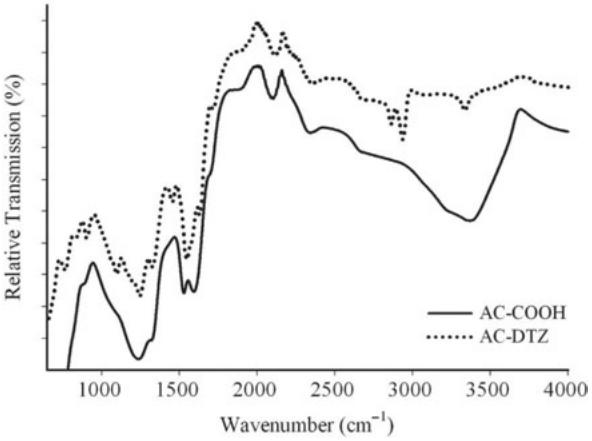


Fig. 1. FT-IR spectra of AC-COOH and AC-DTZ.

For AC-COOH, a characteristic band stretching at 1705.25 cm^{-1} corresponds to the C=O vibration, providing that the carboxylic derivative of AC was successfully prepared. In comparison with the FT-IR of AC-COOH, the FT-IR spectrum of AC-DTZ shows remarkable spectral changes, confirming the formation of the new chemically modified AC-DTZ phase (Fig. 1). As shown in Fig. 1, the new peaks appeared in the FT-IR spectrum of AC-DTZ can be assigned by their characteristic absorbance ν (cm^{-1}) as follows: 1644.11 (C=O); 1461.54 (C–N); 3336.70 (N–H); 2866.03 and 2935.54 (O–H); 1094.71 and 894.55 (C=S).

3.2. Batch method

3.2.1. Effect of pH

The pH value plays a major role in regard to the selectivity of the AC-DTZ phase towards different metal ions. For the effect of pH on the adsorption of selected metal ions [Au(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II)], a concentration of 5 mg l^{-1} of each metal ion was chosen, and pH values of sample solutions were adjusted to a range of 1.0–8.0 with corresponding buffer solution, except for Fe(III) at pH ranges from 1.0 to 4.0 (Fig. 2). Fe(III) was investigated at these specified pH values in order to avoid any precipitation of $Fe(OH)_3$ with buffer solutions at pH 5.0–8.0. All metal ion standard solutions were individually mixed with 25 mg AC-DTZ. The adsorption percentage of each metal ion was calculated based on a difference between the initial and final concentrations before and after filtration with AC-DTZ, respectively. As shown in Fig. 2, it can be noticed that the % extraction is strongly dependent on the pH value of selected metal ions. Fig. 2 displays that there is an increase followed by a subsequent decrease in the % extraction of Au(III), Cd(II), Cu(II), Pb(II) and Zn(II) with an increase of the pH value. It can also be noted that there is an increase in the % extraction with an increase of the pH value for Co(II), Fe(III) and Ni(II). Based on the pH study, it is interesting to notice that the high % extraction was reached for Au(III) at all pH values and for Pb(II) at high pH value as compared to other metal ions. For Au(III), the oxidation of AC with conc. HNO_3 leads to the surface functionalization with oxygen containing groups that increase proton acceptor centers. Moreover, new proton acceptor centers are presented via the AC-DTZ phase. Thus, the positive charge on the surface of AC-COOH and the additional new proton acceptor centers of the AC-DTZ phase are able to selectively bind with anionic species, such as $AuCl_4^-$, through electrostatic interaction at low pH values. In addition, at higher pH values, the negative charge on the surface of AC-COO$^-$ and the nitrogen and sulfur donor atoms containing dithizone produced via the reaction of AC-COOH with dithizone are capable to easily bind with Au(III). Therefore, the association mechanism between the AC-DTZ phase and Au(III) are contributed to both metal species and chelating complexes at all pH values. In comparison of Pb(II) with Au(III), Pb(II) has significant interferences with other metal ions at high pH values even though the maximum % extraction of Pb(II) is achieved. However, a close examination of Fig. 2 indicates that the maximum % extraction (99.92%) of Au(III) is reached, and the selectivity of AC-DTZ phase towards Au(III) is the most among all metal ions at low pH value of 1.0. Based on the above results, Au(III) was selected among other metal ions for the study of other parameters controlling its maximum uptake on AC-DTZ under batch conditions and at the optimum pH value of 1.0.

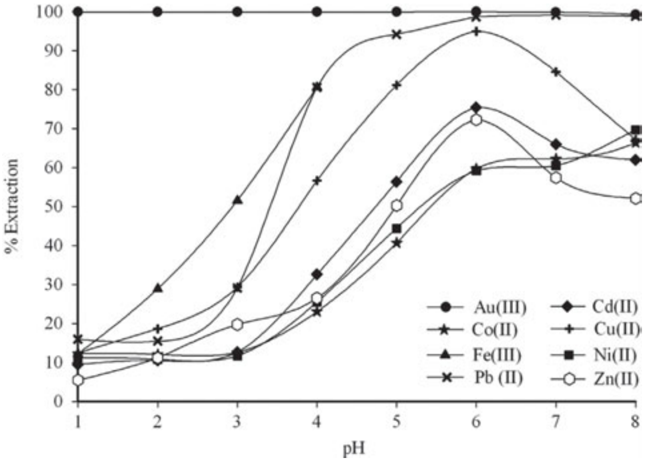


Fig. 2. Effect of pH on the adsorption of 5 mg l^{-1} Au(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) on 25 mg AC-DTZ phase at 25°C.

3.2.2. Adsorption capacity

To determine the adsorption capacity of Au(III) on the AC-DTZ phase, 25 ml Au(III) sample solutions with different concentrations (0–150 mg l^{-1}) were adjusted to pH 1.0 with a buffered aqueous solution and mixed with 25 mg AC-DTZ. These mixtures were mechanically shaken for 1 h at room temperature. The amount of Au(III) adsorbed at each concentration level was determined. The breakthrough curve for the uptake capacity of AC-DTZ for Au(III) was gained by plotting the concentration (mg l^{-1}) of Au(III) solutions versus the milligrams of Au(III) adsorbed per gram AC-DTZ (Fig. 3). From the adsorption isotherm study in Fig. 3, the adsorption capacity of AC-DTZ for Au(III) was found to be 72.01 mg g^{-1}, which is the highest value of adsorption capacity for Au(III) as compared to those previously reported for Au(III) in other studies (12.3, 14.8, 33.57 and 35.88 mg g^{-1}) [1,32–34]. The adsorption capacity of Au(III) on the AC-COOH was also determined to be 43.89 mg g^{-1} under the same batch conditions and at pH 1.0 (Fig. 3). These results indicated that the adsorption capacity for Au(III) was improved by 64.07% with the newly modified AC-DTZ phase as compared to AC-COOH (Fig. 3).

3.2.3. *Effect of shaking time*

The effect of shaking time is one of the most important factors when the static technique is used in the processes of determination of metal adsorption capacity values. In this study, different shaking times ranging from 1.0 to 60.0 min were investigated in order to perform the effect of shaking time on the Au(III) adsorption capacity. The results of the adsorption of Au(III) by AC-DTZ showed that equilibrium kinetics were very fast. It was found that over 70 mg g^{-1} Au(III) was adsorbed on the AC-DTZ phase after only 10 min of the equilibrium periods. The amount of Au(III) adsorbed was also raised up to more than 71 mg g^{-1} after 30 min until the maximum the adsorption of AC-DTZ for Au(III) was reached to 72.01 mgg^{-1} after 60 min.

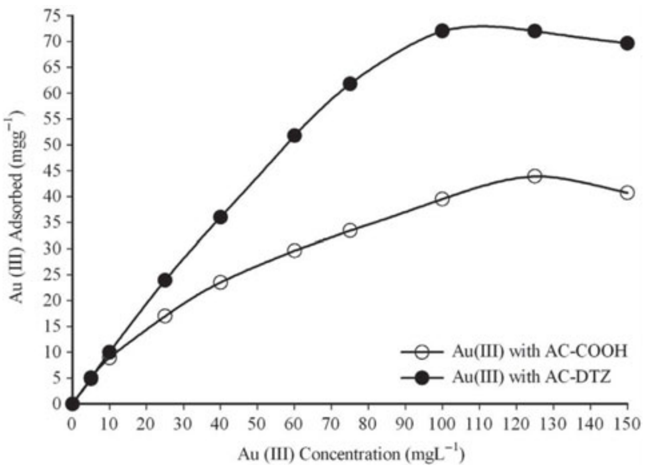


Fig. 3. Adsorption profile of Au(III) on 25 mg AC-COOH and AC-DTZ phases in relation to the concentration at pH 1.0 and 25°C.

3.3. *Adsorption isotherm models*

The analysis of adsorption isotherm data is important for developing an equation that accurately represents the results. Therefore, data obtained from adsorption isotherm study of Au(III) were examined by well known models. Langmuir equation, which is valid for a monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites and a negligible interaction between the adsorbed molecules, is given by the following equation:

$$C_e/q_e = \left(C_e/Q_o\right) + 1/Q_o b$$

where C_e is the unadsorbed metal ion in the filtrate (mg ml^{-1}) when adsorption equilibrium is attained and q_e represents the adsorbed metal ion by the adsorbate (mg g^{-1}) [35]. The symbols Q_o and b refer Langmuir constants for AC-DTZ, which are related to the maximum Au(III) adsorption capacity (mg g^{-1}) and affinity parameter (l mg^{-1}), respectively. These constants can be calculated from a linear plot of C_e/q_e against C_e with a slope and intercept equal to $1/Q_o$ and $1/Q_o b$, respectively. In addition, the essential characteristics of the Langmuir adsorption 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 adsorption and the shape of the isotherm); C_o the initial concentration of the analyte. The R_L value indicates the type of the isotherm, and R_L values between 0 and 1 represent a favorable adsorption [36].

Based on the least square fit, a linear plot was obtained from Langmuir isotherm equation, confirming the validity of Langmuir adsorption isotherm model for the adsorption process (Fig. 4). As a result, adsorption isotherm data indicated that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. Calculated Langmuir constants Q_o and b are determined to be 71.94 mg g^{-1} and 0.695 l mg^{-1}, respectively. The correlation coefficient obtained from the Langmuir model is found to be $R^2 = 0.997$ for adsorption of Au(III) on AC-DTZ, further indicating that the data were well fit with the Langmuir model. The R_L value of Au(III) adsorption on the AC-DTZ is 0.01, supporting a highly favorable adsorption process based on the Langmuir model.

3.4. *Kinetic models*

In order to find intrinsic kinetic adsorption parameters, different kinetic models were investigated. Kinetic models were used for goodness of fit for the experimental

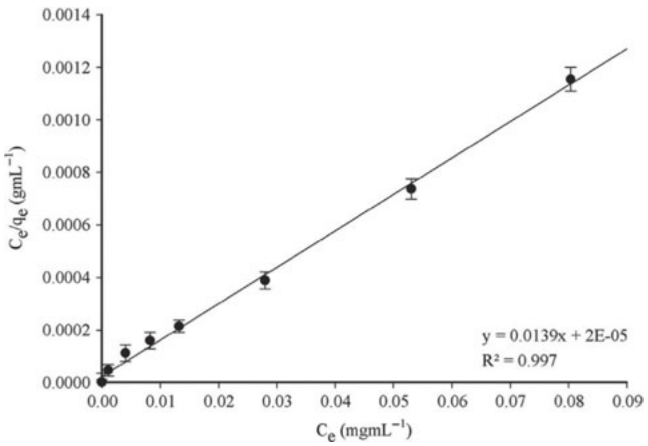


Fig. 4. Langmuir adsorption isotherm model of Au(III) adsorption on 25 mg AC-DTZ phase at pH 1.0 and 25°C. Adsorption experiments were obtained at different concentrations (0–150 mg l^{-1}) of Au(III) under batch conditions.

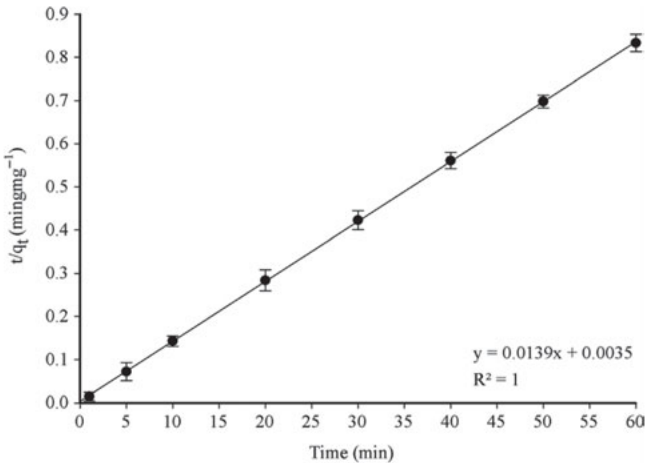


Fig. 5. Pseudo second-order adsorption kinetic model of Au(III) uptake on 25 mg AC-DTZ phase at pH 1.0 and 25°C.

data using the correlation coefficient (R^2) as a measure of agreement between the experimental data. The adsorption kinetic equation of a pseudo second-order adsorption can be written as follows:

$$t/q_t = 1/\upsilon_o + (1/q_e)\,t$$

where $\upsilon_o = k_2\, q_e^2$ is the initial adsorption rate (mg g^{-1} min^{-1}) and k_2 (g mg^{-1} min^{-1}) corresponds to the rate constant of adsorption, q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium, and q_t (mg g^{-1}) refers to the amount of meal ion on the surface of the adsorbent at any time t (min). The parameters υ_o and q_e can be easily deduced from the intercept and slope, respectively, of a plot of t/q_t versus t [37].

Since the kinetics of the uptake has to be determined in order to establish the time course of the uptake process, adsorption kinetics data fitted with the pseudo second-order adsorption proved to be reliable and accurate. The correlation coefficients factor (R^2) was found to be 1.0 (Fig. 5), indicating that the kinetics of Au(III) adsorption onto the AC-DTZ phase obeyed the pseudo second-order kinetic model. The parameters υ_o and q_e were determined to be 285.71 mg g^{-1} min^{-1} and 71.94 mg g^{-1}, and k_2 = 0.06 g mg^{-1} min^{-1} for AC-DTZ. It can be clearly noticed that the value of q_e is in consistency with the results of adsorption isotherms, strongly supporting the validity of Langmuir adsorption isotherm model.

3.5. Performance of method in analytical applications

3.5.1. Effects of coexisting ions

For assessment of the suitability of the developed procedure in analyzing real samples, the effect of several cations and anions was investigated under optimized conditions and pH value of 1.0. Model standard solutions containing fixed amount of 1 µg ml^{-1} Au(III) together with either individual matrix metals or mixed matrix metals were treated according to the recommended procedure. The tolerance limit of coexisting ions is defined as the largest amount making the recovery of analyte less than 90%. The results given in Table 1 showed that the recovery of Au(III) was not affected by the medium composition containing either individual or mixed metals. This may be attributed to the low adsorption capacity or rate for interfering ions towards the AC-DTZ phase.

Table 1
Effect of cations and anions on the recovery of 1 µg ml^{-1} Au(III) adsorption on 25 mg AC-DTZ phase at pH 1.0 and 25°C (N = 3)

Coexisting ions	Concentration (µg ml^{-1})	% Recovery of Au(III)
Na^+, K^+, NH_4^+	2000	99.55
Ca^{2+}, Mg^{2+}, Ba^{2+}	2000	98.98
Mn^{2+}	1000	97.58
Ni^{2+}	1000	97.47
Zn^{2+}	1000	96.64
Pd^{2+}	500	97.89
Cr^{3+}	1000	97.75
Al^{3+}	1000	98.28
Rh^{3+}	1000	97.16
Cl^-, NO_3^-	500	98.78
CO_3^{2-}, SO_4^{2-}	500	96.95
PO_4^{3-}	500	97.97

Pb(II) is also one of common pollutant ions in real water samples. Even though the maximum % extraction of Pb(II) was reached, it can be clearly observed from Fig. 2 that Pb(II) has significant interferences with other metal ions at high pH values. In comparison of Au(III) with Pb(II), the maximum % extraction (99.92%) of Au(III) is reached, and the selectivity of AC-DTZ phase towards Au(III) is the most among all metal ions at low pH value of 1.0 (Fig. 2). Consequently, the effect of several cations and anions was investigated at pH 1.0. In addition, the recovery of Au(III) in presence of Pb(II) is expected to be high because of the low adsorption capacity or rate for Pb(II) towards the AC-DTZ phase at the optimum pH value of 1.0. Thus, the selectivity of the proposed method is high enough to be implemented for determination of Au(III) in real samples.

3.5.2. Application of the proposed method

For confirmation of the applicability of the method to real samples, it was applied to the recovery of Au(III) in different water samples. Four types of water samples were used for evaluation of the method, including ground water, lake water, seawater, and tap water, collected from Jeddah in Saudi Arabia. For the analysis of water samples, the standard addition method was used under the same batch conditions and at the optimum pH (1.0). The % recovery of different amounts of Au(III) was calculated, as reported in Table 2. The results indicated that the recoveries of Au(III) in spiked water samples were satisfactory for trace analysis and apparently demonstrated that the method is reliable, feasible and suitable for analyzing real samples.

Table 2
Determination of Au(III) at different concentrations (0, 10 and 25 mg l^{-1}) in real water samples using 25 mg AC-DTZ phase at pH 1.0 and 25°C (*N* = 3)

Samples	Added (mgl^{-1})	Founded (mgl^{-1})	Recovery (%)
Ground water	0	ND	ND
	10	0.06 (±0.002)	99.36
	25	1.69 (±0.161)	93.22
Lake water	0	ND	ND
	10	0.02 (±0.002)	99.80
	25	0.79 (±0.018)	96.83
Seawater	0	ND	ND
	10	0.45 (±0.030)	95.46
	25	1.92 (±0.182)	92.31
Tap water	0	ND	ND
	10	0.04 (±0.001)	99.56
	25	1.33 (±0.147)	94.68

4. Conclusions

The presented method proved the effectiveness of the synthesized AC-DTZ phase for the adsorption and determination of Au(III) in aqueous solution due to its simplicity and high selectivity and accuracy. The AC-DTZ adsorbent showed excellent characteristics of Au(III) in aqueous solution at pH 1.0 due to the electrostatic attraction of anionic species, such as $AuCl_4^-$, to the positively charged centers. Adsorption data of Au(III) were well fit into the Langmuir adsorption isotherm model, providing that the adsorption process was mainly monolayer onto a homogeneous adsorbent surface. Results also demonstrated that the adsorption of Au(III) on the AC-DTZ phase followed a pseudo second-order kinetic model. The presence of major cations and anions did not interfere on the adsorption of Au(III) on the AC-DTZ phase. Furthermore, the proposed method provided acceptable and reliable results for a selective adsorption and determination of Au(III) in real water samples with complicated and variable matrices. Thus, it can be concluded that the method is an effective approach for a selective separation and determination of Au(III) from complex matrices.

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