Asian Journal of Chemistry; Vol. 24, No. 11 (2012), 5279-5282

ASIAN JOURNAL OF CHEMISTRY

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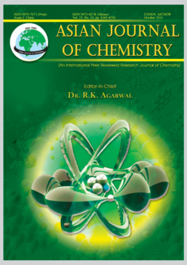

Modified Organobentonite with Dithizone as Adsorbent for Thallium(I) in Water

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(*Received*: 22 October 2011; *Accepted*: 16 June 2012) AJC-11615

Adsorption capability of Tl(I) ions from aqueous solution by modified organobentonite with dithizone(D-O-bentonite) was investigated. The optimum experimental parameters for the adsorption and preconcentration of Tl(I) ions have been investigated. Moreover, the thermodynamics and kinetics of the adsorption were studied. The results showed that the Tl(I) could be quantitatively retained by the D-O-bentonite at pH 9-11. The isothermal data was described by the Langmuir equation. The dynamic data followed the pseudo-second-order kinetic model well. The enthalpy change (ΔH) of the adsorption process was 50.142 kJ/mol. The Gibbs free energy changes (ΔG) were negative, and entropy changes (ΔS) were positive. The activation energy (Ea) was 49.776 kJ/mol for the adsorption. The Tl(I) adsorbed on the D-O-bentonite could be completely eluated by using 0.5 mol/L nitric acid. The method has been applied to the preconcentration for flame atomic absorption spectrometric determinations of trace Tl(I) in water samples with satisfactory results.

Key Words: Dithizone, Bentonite, Thallium(I), Adsorption behaviour, Preconcentration, Flame atomic absorption spectrometric.

INTRODUCTION

Thallium and its compounds are highly toxic. Thallium (Tl) is produced as a by-product in the refining of iron, cadmium and zinc[1,2]. It is used as a catalyst in certain alloys, optical lenses, low-temperature thermometers and semiconductors[2]. At present, the determination of thallium in environment water is accomplished primarily by atomic absorption spectrometry. The flame atomic absorption spectrometry (FAAS) is a simple and well available technique for determination of thallium in real samples. However as the total concentration of thallium in aquatic environment is very low an analytical technique featuring high sensitivity and low detection limit is required. This limitation can be overcome by the use of a preconcentration procedure. For this purpose various preconcentration/separation methods including liquid-liquid extraction[3], hydride generation[4], solid phase extraction[5-8] and flotation[9] had been used. In those techniques, solid phase extraction techniques have become increasingly popular compared with the classical pre-separation and enrichment methods because of their high enrichment factor, rapid phase separation, low cost, and lower organic solvent consumption, as well as the ability to combine with different detection techniques in on-line or off-line mode. The main solid-phase extraction sorbents of thallium in the water are immobilized oxine[10], ion-imprinted polymer[11], sawdust[12], *etc*. In our present study, the modified organobentonite with dithizone (D-O-bentonite) has been used in the adsorption of lead and cadmium with satisfied results[13,14]. But the D-O-bentonite use in solid-phase extraction of thallium in the water has not been studied. In this work, D-O-bentonite was used as an solid phase extraction agent to preconcentration and separation of thallium in water.

EXPERIMENTAL

A modified organobentonite with dithizone (D-O-bentonite) was prepared in our laboratory as previously described elsewhere[13,14]. A stock solution of thallium(I) (1000 mg/L) was prepared by dissolving thallium(I) nitrate (Sinopharm Chemical Reagent Co. Ltd., China) into a 1 L flask and diluting to the mark with 0.2 mol/L HNO_3 solution. Working standard solutions were prepared from the stock solution daily. Sodium citrate solution (0.1 mol/L), borax buffer solution. The water in this study was distilled water. All chemicals and solvents were analytical reagent grade, which were used without further purification.

A WYX-9003A atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co. Ltd.), furnished with thallium hollow-cathode lamps and air-acetylene flame was used for all measurements. The operation conditions of the thallium were as follows: wave length is 276.8 nm, spectral band width is 0.4 nm, lamp current is 3.0 mA, burner height is 5.0 mm, acetylene gas consumption is 1.5 L/min and air flow consumption is 5 L/min. All pH measurements were made with a PHS-3C model digital pH meter (Shanghai REX Instrument Factory, Shanghai, China) equipped with a combined pH electrode. A constant temperature bath shaker (Jintan Experiment Instrument Factory, Jiangsu, China) was used to shaking for adsorption and elution.

A quantity of thallium(I) solution was placed into a 50 mL calibrated Erlenmeyer flask. In 5 mL of sodium citrate solution, 5 mL of borax buffer solution at pH 10 were added. After dilution to the mark with water, 0.1 g of D-O-bentonite was added. Covered with a plug and the Erlenmeyer flasks were shaken for 0.5 h at constant temperature bath shaker. Filtrated using filter, then the concentration of Tl(I) in filtrate was determined by flame atomic absorption spectrometry and absorption capacity was calculated. Then the adsorbed Tl(I) was eluted with 5 mL of 0.5mol/L HNO_3 by shaking for 5 min. The concentrations of the Tl(I) in the eluents was determined by flame atomic absorption spectrometry and the recovery was calculated.

RESULTS AND DISCUSSION

Effect of pH on the adsorption: The pH values of the medium governing the complexation of dithizone with Tl(I). Thus, the influence of pH on adsorption capacity was studied over a range of pH values from 1 to 12. As shown in Fig. 1, it was observed that the D-O-bentonite had strong adsorption capacity to Tl(I) in the range of pH 9-11. In this study, pH 10 was used.

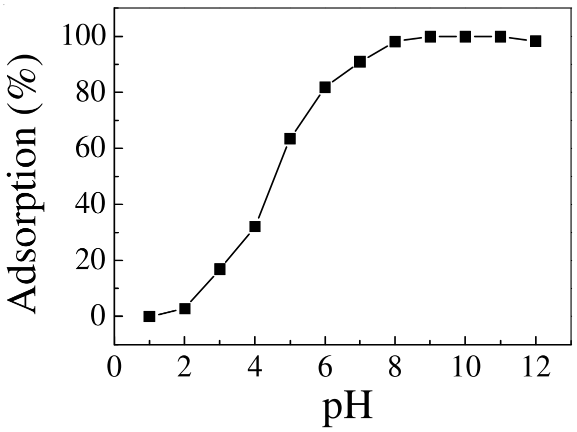

Fig. 1. Effect of pH on the adsorption

Effect of contact time: At different temperature, the effects of contact time on the adsorption of Tl(I) by the D-O-bentonite is shown in Fig. 2. The result showed that temperature and contact time had a great influence on the adsorption. With the increase of shaking time, the adsorption capacities were also increasing with the increase of temperature. At all the temperatures, the equilibrium was achieved when the oscillation time was 0.5 h. The increase of oscillation time had little influence on the adsorption capacities. Therefore, the oscillation time was 0.5 h in this study.

Isotherm analysis: The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. In order to investigate the sorption isotherm, two equilibrium models were analyzed *i.e.*, the Langmuir and the Freundlich isotherm equations. Following the models of Langmuir and Freundlich, thallium adsorption isotherm data starting at different initial concentrations were investigated.

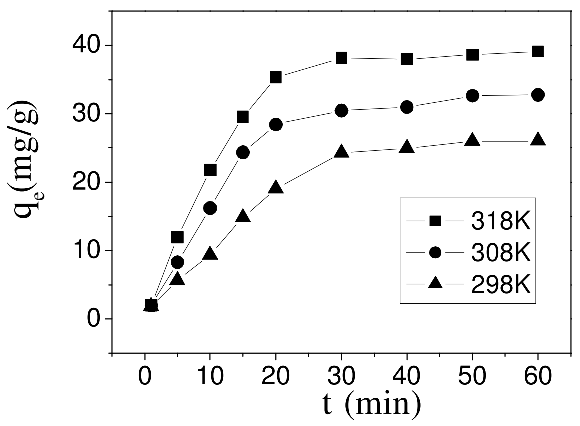

Fig. 2. Effect of contact time on thallium(I) adsorption at various temperatures

The expression of the Langmuir model is[15]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

where, q_e is the equilibrium Tl(I) ion concentration on the adsorbent (mg/g), C_e is the equilibrium Tl(I) ion concentration in solution (mg/L), q_m is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg).

The expression of the Freundlich equation is:[15]

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where, q_e is the equilibrium Tl(I) ion concentration on the adsorbent (mg/g), C_e is the equilibrium for Tl(I) ion concentration in solution (mg/L), and K_F (L/mg) and n are the Freundlich constants.

In order to assess different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been shown with the experimental data for sorption of Tl(I) ions on D-O-bentonite at various temperatures in Fig. 3. The values of q_m, K_L, K_F, and 1/n and the correlation coefficients(r) for Langmuir and Freundlich are given in Table-1.

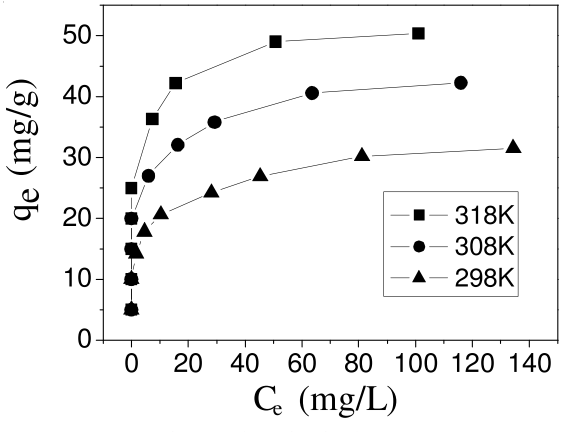

Fig. 3. Adsorption isotherms

TABLE-1
PARAMETER EQUATIONS FOR LANGMUIR AND FREUNDLICH ISOTHERMS

T/K	Langmuir			Freundlich		
	q_m	K_L	r^2	n	K_F	r^2
298	35. 916	1.278	0.997	1.835	71. 461	0.934
308	40.217	3.015	0.999	2.456	161.452	0.937
318	46.080	5.683	0.999	4.173	368.788	0.904

It could be seen that the Langmuir isotherms have best fitted for the sorption of Tl(I) ions on D-O-bentonite at various temperatures ($r^2 > 0.99$). This indicates that the adsorption of Tl(I) ions by the D-O-bentonite was monolayer-type. The values of the Langmuir constant, K_L, increased as temperature increased, indicating that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures[15].

The parameters inclusive adsorption enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) for the adsorption process can be obtained from the van't Hoff equation and Gibbs-Helmholtz equation[15]:

$$\ln C_e = -\ln K_0 + \frac{\Delta H}{RT} \quad (3)$$

$$\Delta G = -RT \ln C_e \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

where, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is temperature (K), K_0 is constant and C_e is the solution concentration at equilibrium. The slope of the plots of ln C_e *versus* 1/T used to determine ΔH, ΔG and ΔS were obtained from eqns. 4 and 5, respectively (Table-2).

TABLE-2
PARAMETERS OF ADSORPTION THERMODYNAMIC

T (K)	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS [J/(mol K)]
298	50.142	-0.810	170.98
308		-3.016	172.59
318		-4.757	172.64

It is easily seen that the positive value of ΔH for the processes further confirms the endothermic nature of the process; Gibbs free energy change, ΔG, is negative, which suggests that the adsorption process is spontaneous at a given temperature. The positive entropy change of adsorption reflects the process is entropy drive.

Kinetics analysis: In order to investigate the kinetics of the present adsorption reactions, two simple kinetic models were tested. First-order rate equation[15] based on solid capacity is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - K_i t \quad (6)$$

where, K_i (min^{-1}) is the equilibrium rate constant of the first-order adsorption and q_e and q_t (mg/g) are the amounts of Tl(I) adsorbed at equilibrium at any time t.

A pseudo-second-order adsorption kinetic rate equation is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where, K_2 [g/(mg min)] is the rate constant of the pseudo-second-order adsorption.

According to the data in Fig. 2, the values of k_1, k_2 and q_e could be obtained from the intercept and slope of the plot of [ln (q_e-q_t)] *versus* t and (t/q_t) *versus* t, respectively. According to coefficients of determination, the results fit the pseudo-second-order plot model better than they fit the first-order rate equation.

The activation energy for Tl(I) adsorption onto the D-O-bentonite was calculated by using the logarithmic expression of the Arrhenius equation:

$$\ln K_2 = \ln K_0 - \frac{E_a}{R}.\frac{1}{T} \quad (8)$$

where, K_2 is the rate constant of the pseudo-second-order adsorption kinetic rate temperature T(K), K_0 is the frequency factor, R is the ideal gas constant [8.314 J (mol K)$^{-1}$] and E_a (kJ mol^{-1}) is the activation energy for the adsorption reaction. The activation energy was obtained from the slope of the plot of ln K_2 values versus 1/T using eqn. (9) and was found to be 49.776 kJ mol^{-1}.

$$\ln K_2 = -5987\ (1/T) + 32.756\ (R^2 = 0.981) \quad (9)$$

For the magnitude of the activation energy can indicate the type of sorption, the adsorption with an activation energy of more than 40 kJ mol^{-1}, the main interaction between the Tl(I) ion and dithizone is probably coordination bond[15].

Elution experiment: The choice of suitable eluent and conditions is very important. After adsorption under optimum adsorption conditions, 5 mL of selected eluent solution such as nitric acid, thiourea and EDTA solution at different concentration were used for elution by shaking 5 min, respectively. The recovery results showed that thiourea (50 % recovery) and EDTA (10 % recovery) were ineffective eluents. While 5 mL of 0.5 mol/L nitric acid was used with shaking eluting time of 5 min, the recovery was up to 95 %. Therefore, 0.5 mol/L nitric acid was chosen. After regeneration, the D-O-bentonite was dried and reused 10 times. Its adsorption performance didn't decrease.

Enrichment factor and detection limit: In order to review the possibility of enrichment low concentrations of Tl(I) from large volume, 1 µg of Tl(I) was dissolved in 50, 100, 250, 500 and 1000 mL volume of water together, respectively. The amounts recovered are listed in Table-3. The results showed when the solution volume was no more than 500 mL, the recovery was above 90 %. The enrichment factor was 100. The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of eleven replicate measurements of blank solution using the preconcentration method, was found to be 0.14 µg/L.

TABLE-3
PRECONCENTRATION AND RECOVERY OF THALLIUM(I)

Volume of the solution (mL)	The quantity in eluent (µg)	Recovery (%)	Enrichment factor
50	0.987	98.7	10
100	0.969	96.9	20
250	0.951	95.1	50
500	0.924	92.4	100
1000	0.892	89.2	200

Static adsorption capacity: According to the Fig. 2, at 298 K, the equilibrium adsorption capacities of D-O-bentonite to Tl(I) was 26.02 mg/g.

Effect of coexisting ions: Different amounts of ions were added into a 50 mL Erlenmeyer flask containing 0.1 mg/L Tl(I). The tolerant amount of coexisting ions was defined as resulting in error of ±5 %, and was listed as follows: 1000 mg L^{-1} for Na^+, K^+, NH_4^+, and NO_3^-; 500 mg L^{-1} for Ca^{2+}, Cl^-, Mg^{2+}, Al^{3+} and PO_4^{3-}; 200 mg L^{-1} for Cr(III), Ag^+, Co^{2+}, In^{3+} and Cu^{2+}; 100 mg L^{-1} for Zn^{2+}, Cr(VI), Te (VI), Se(VI) and 1 mg L^{-1} for Pd^{2+}, Pb^{2+}, Ni^{2+}, $S_2O_3^{2+}$ and Fe^{3+}.

Analytical application: The application of the proposed method was carried out surface water and waste water samples. The surface water samples were collected from the Hunhe river and Nanhu lake (Shenyang china) and the waste water sample was collected from a factory of Shenyang. All the water samples filtered through a 0.45 µm membrane filter. Then, the determinations were conducted according to the experimental method. Meanwhile, the recovery test was conducted. The results of the analyte are summarized in Table-4.

TABLE-4
DETERMINATION OF THALLIUM(I)
IN WATER SAMPLES (*n*=*6*)

Samples	Back ground (µg/L)	RSD (%)	Added (µg/L)	Found (µg/L)	Recovery (%)
River water	0.177	5.75	0.5	0.653	95.20
Lake water	0.298	4.32	0.5	0.807	101.80
Waste water	91.520	3.66	50.0	139.640	96.24

It could be seen that all the recoveries were 95.2-101.8 %, which were excellent for trace analysis of thallium ion in water samples.

Conclusion

With the present results, it is concluded that thallium could be quantitatively retained by the D-O-bentonite in the pH range of 9-11. The capability of adsorption was 26.02 mg/g at 298K. The adsorption behaviour followed a Langmuir adsorption isotherm and a pseudo-second-order kinetic model. The adsorption was an endothermic and spontaneous physical process. The thallium adsorbed on the D-O-bentonite could be completely eluated by using 0.5 mol/L nitric acid. The proposed method has been applied to the determination of trace amounts of thallium in water samples with satisfactory results.

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