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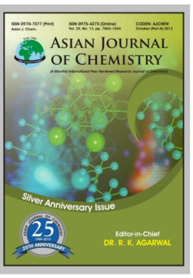

Adsorption Behaviour of Modified Organobentonite with Dithizone for Hg(II) in Water and Its Application for Concentration and Separation of Hg(II) in Surface Water

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In this paper, the adsorption behaviour of modified organobentonite with dithizone (D-O-bentonite) for mercury(II) in water was investigated. Optimal experimental conditions for the adsorption of the mercury, including pH, contact time, eluent concentration and volume and co-existing ions have been studied. Moreover, the thermodynamics and kinetics of the adsorption were completely investigated. The result showed that the Hg(II) could be adsorbed on the D-O-bentonite. The adsorbed quantity was affected by the pH value of medium and contact time. 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 14.20 kJ/mol. Gibbs free energy changes (ΔG) were negative and entropy changes (ΔS) were positive. The activation energy (E_a) was 14.06 kJ/mol for the adsorption. The mercury adsorbed on the D-O-bentonite could be completely eluated by using 3 mol/L HCl. The adsorption agent has been applied to the pre-concentration/ separation of Hg(II) in surface water samples with satisfied results.

Key Words: Organobentonite, Dithizone, Mercury, Adsorption behaviour, Concentration, Separation, Surface water.

INTRODUCTION

In the past several decades, with the development of modern industry, water pollution has received increasing attention because of the requirement for the environment and the health of human beings, which are threatened by the various contaminants, such as organic pollutants and heavy metal in water[1]. Among the heavy metal, mercury is considered as one of the most harmful metal ions to the human being. Mercury may enter a human body by inhalation of mercury vapour; drinking water and by the consumption of fish and fish products in the food[2]. Environmental monitoring, biological and food science always requires determination of mercury in trace levels in various samples.

At present, several analytical techniques such as hydride generation-atomic absorption spectrometry (HG-AAS), cold vapor atomic absorption spectrometry (CV-AAS)[3], cold vapour atomic fluorescence spectrometry (CV-AFS)[4], inductively coupled plasma optical emission spectrometry (ICP)[5]. Mercury cold vapor generation associated to atomic absorption spectrometery (Hg-CV-AAS). In those methods, the hydride generation-atomic absorption spectrometry (HG-AAS) is one of the most powerful analytical methods for the determination of mercury. However, in order to circumvent the limitation of low mercury concentration in environmental samples, different methodologies involving preconcentration procedures are often needed before HG-AAS. In this sense, activated carbon (AC) has been widely used for many purposes both in laboratory and industrial settings. But it has poor selectivity. In order to decrease the cost of treatment process and improve the selectivity, the scientists have been attempted to investigate inexpensive, with functional groups and easily available adsorbents. Dithizone-immobilized organobentonite (D-O-bentonite) as an adsorbent for the removal of lead, cadmium and thallium has been reported earlier[6-8]. The preliminary work of D-O-bentonite use in adsorption and pre-concentration/ separation of mercury has been communicated in international conference[9]. But further mechanism has not been investigated. In this work, the adsorptive potential of D-O-bentonite for the preconcentration of trace mercury was assessed using the batch adsorption method. And the thermodynamics and kinetics of the adsorption were thoroughly examined. A new method using D-O-bentonite as sorbent has been developed for the preconcentration of trace mercury in water analyses by hydride generation-atomic absorption spectrometry. The method has been applied to the determination of trace mercury in surface water samples with satisfactory results.

EXPERIMENTAL

Modified organobentonite with dithizone(D-O-bentonite) was prepared according to our previous work[6]. Stock solutions of Hg(II) (0.1 mol L^{-1}) was prepared by dissolving $Hg(NO_3)_2{\cdot}H_2O$ in 3 % HNO_3 to avoid hydrolysis. Nitric acid solution and acetic acid/sodium acetate buffer solution were used for pH adjustment. All the reagents were analytical grade and distilled water was used to prepare all the solutions.

The concentration of Hg(II) was determined using a hydride generation-atomic absorption spectrometry (HG-AAS), a WYX-9003A-model atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co., Ltd.), the operating parameters are as follows: lamp current, 3.0mA; slit width, 0.4 nm; wavelength, 253.7 nm; Burner height, 5.0 mm; a WHG-102A hydride generator.

The pH values were measured with a PHS-3C acidometer (Shanghai REX Instrument Factory, Shanghai, China) supplied with a combined electrode.

A constant temperature bath shaker (Jintan Experiment Instrument Factory, Jiangsu China).

Adsorption experiments: Mercury(II) solution was added into a 50 mL calibrated colorimetric cylinder with plug. The pH was adjusted to 5 with HNO_3 or ammonia solution. After adding 2 mL pH 5.0 buffer solution, dilution to the mark with water, then 0.5 g of D-O-bentonite was added. After being shaken for 15 min, the solution was separated from the adsorbent. Then the concentrations of Hg(II) were determined by HG-AAS and absorption capacity was calculated.

After adsorption experiments, the Hg(II) loaded samples was washed with water to remove any unadsorbed Hg(II). The adsorbed Hg(II) was eluted with 5 mL of 3 mol·L^{-1} HCl. The concentration of the Hg(II) in the eluent was determined by hydride generation-atomic absorption spectrometry. Recoveries were calculated from concentrations of eluent.

RESULTS AND DISCUSSION

Effect of pH on the adsorption: The pH of medium has been the most important variable governing metal ion adsorption onto adsorbent. The pH value of the medium governing the complexation of dithizone with Hg(II) (Fig. 1). The result shows the effect of pH on the adsorption of Hg(II) onto D-O-bentonite. It could be seen that the adsorption percentage increased with increasing pH and reached a plateaue value at around pH 5. So, in this study, the pH 5 was selected as the optimal condition.

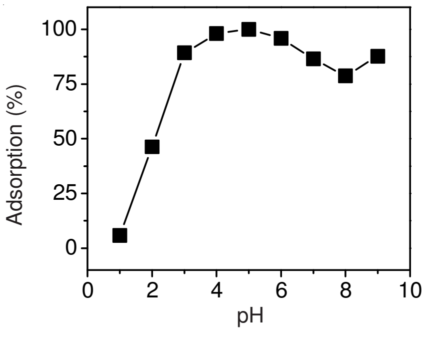

Fig. 1. Effect of pH on the adsorption

Effect of shaking time: The influence of shaking time on the adsorption of Hg(II) onto D-O-bentonite (Fig. 2) was investigated. Fig. 2 showed that the amount of adsorption increased with increasing the shaking time. The maximum adsorption capacity was observed after 15 min, beyond which there was almost no further increase in the adsorption. So, in this study, the shaking time was 15 min.

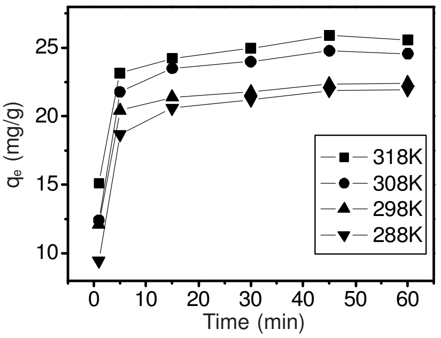

Fig. 2. Effect of contact time on adsorption at various temperatures

Isotherm analysis: In order to investigate the sorption isotherm, two equilibrium models were analyzed: the Langmuir and the Freundlich isotherm equations. Following the models of Langmuir and Freundlich, mercury adsorption isotherm data starting at different initial concentrations were investigated[8].

The expression of the Langmuir model is

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

where q_e is the equilibrium Hg(II) concentration on the adsorbent (mg/g), C_e is the equilibrium Hg(II) 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

$$\ln q_m = \ln K_F + \frac{1}{n}\ln C_e \qquad (2)$$

where 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 Hg(II) on D-O-bentonite at various temperatures (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 Tables 1 and 2, respectively.

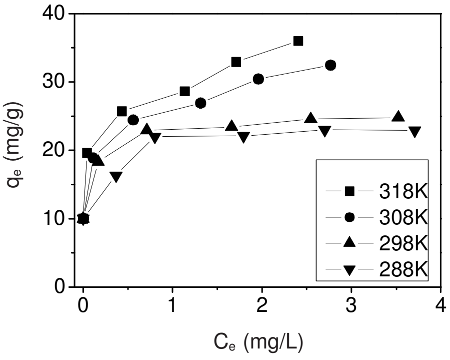

Fig. 3. Adsorption isotherms

TABLE-1
PARAMETER EQUATIONS FOR LANGMUIR ISOTHERMS

T (K)	Equations	q_m	K_L	R^2
288	y = 0.0842x + 0.1007	23.76	117.9	0.9991
298	y = 0.0656x + 0.1869	30.48	81.61	0.9622
308	y = 0.0594x + 0.1119	33.68	150.4	0.9915
318	y = 0.0545x + 0.0855	36.70	214.6	0.9849

TABLE-2
PARAMETER EQUATIONS FOR FREUNDLICH ISOTHERMS

T (K)	Equations	1/n	K_F	R^2
288	y = 0.1558x + 1.9630	0.156	7.121	0.7645
298	y = 0.0975x + 2.1918	0.098	8.951	0.9291
308	y = 0.1627x + 2.2228	0.163	9.233	0.9815
318	y = 0.1403x + 2.3852	0.140	10.861	0.9558

It could be seen, the Langmuir isotherms have best fitted for the sorption of Hg(II) on D-O-bentonite at various temperatures ($r^2 > 0.99$). This indicates that the adsorption of Hg(II) by the D-O-bentonite was monolayer-type. The monolayer capacity of the adsorbent, q_m, increased as temperature increased, indicating that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.

The parameters inclusive adsorption enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) for the adsorption process can be gained from the van't Hoff equation and Gibbs-Helmholtz equation[8]

$$\ln C_e = -\ln K_0 + \frac{\Delta H}{RT} \tag{3}$$

$$\Delta G = -RT \ln C_e \tag{4}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{5}$$

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. 3-5, respectively (Table-3).

TABLE-3
PARAMETERS OF ADSORPTION THERMODYNAMIC

T (K)	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (J/(mol K))
288	14.20	-11.423	88.97
298		-10.908	84.26
308		-12.840	87.79
318		-14.197	89.30

The positive value of ΔH for the processes further confirms the endothermic nature of the process; Gibbs free energy change (ΔG), is negative, this suggests the adsorption process is spontaneous at a given temperature. The positive entropy change (ΔS) 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[8]. First-order rate equation based on solid capacity is generally expressed as

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{6}$$

where K_1 (min^{-1}) is the equilibrium rate constant of the first-order adsorption and q_e and q_t (mg/g) are the amounts of Hg(II) adsorbed at equilibrium at any time t.

TABLE-4
ELUTION CONDITIONS

Desorption agents	Volume (mL)	Concentration	Recovery (%)
HNO_3	5	1 moL L^{-1}	17.2
HNO_3	5	2 moL L^{-1}	20.5
HNO_3	5	3 moL L^{-1}	31.5
HCl	5	1 moL L^{-1}	87.6
HCl	5	2 moL L^{-1}	96.3
HCl	5	3 moL L^{-1}	99.4
Thiourea solution	5	2 % (m/V)	0
EDTA solution	5	2 % (m/V)	0

A pseudo-second-order adsorption kinetic rate equation is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

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 mercury adsorption onto the D-O-bentonite was calculated by using the logarithmic expression of the Arrhenius equation

$$\ln K_2 = \ln K_0 - \frac{E_a}{R} \cdot \frac{1}{T} \tag{8}$$

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 14.06 kJ mol^{-1}.

$$\ln K_2 = -1691.3\left(\frac{1}{T}\right) + 12.942 (R^2 = 0.9861) \tag{9}$$

For the magnitude of the activation energy can indicate the type of sorption, the adsorption with activation energy of less than 40 kJ/mol, the main interaction between the Hg(II) and dithizone is probably coordination bond.

TABLE-5
PRECONCENTRATION AND RECOVERY OF Hg(II)

Volume of the solution (mL)	The quantity in eluent (µg)	Recovery (%)	Enrichment factor
25	0.973	97.3	5
50	1.040	104.0	10
100	0.956	95.6	20
200	0.921	92.1	40
500	0.907	90.7	100

Elution and regeneration conditions: After adsorption under the optimized adsorption conditions, four different desorption agents such as nitric acid solution (1, 2, 3 moL/L), hydrochloric acid solution (1, 2, 3 moL/L), 2 % thiourea and 2 % EDTA were chosen to be eluents in the desorption of

TABLE-6
CONCENTRATION OF Hg(II) IN RIVER WATER SAMPLES (n = 6)

Samples of water	Back ground (µg/L)	RSD (%)	Added (µg/L)	Found (µg/L)	Recovery (%)
Liao He river 1	0.1084	3.52	0.1	0.2018	93.4
Liao He river 2	0.0983	2.87	0.1	0.2006	102.3
Hun He river 1	0.1277	4.08	0.1	0.2244	96.7
Hun He river 2	0.1359	2.96	0.1	0.2331	97.2

Hg(II) adsorbed on D-O-bentonite. The recovery results are given in Table-4. The recovery results showed that recovery of using 3 moL/L hydrochloric acid solution was up to 99 %. Therefore, in this work, 5 mL 3 moL/L hydrochloric acid solution was chosen.

After regeneration, the D-O-bentonite was dried under 50 ºC and reused 10 times. Its adsorption performance did not decrease, indicating that D-O-bentonite was stable.

Enrichment factor and detection limit: For exploring the possibility of enriching low concentrations of Hg(II) from large volumes, 1 µg of Hg(II) was dissolved in various volume of water together. The pH was adjusted to 5.0 with HNO_3 or ammonia solution, respectively. The samples were eluted with 5 mL of 3 moL/L HCl after adsorption. The amounts recovered are listed in Table-5. It could be seen that when the solution volume was 500 mL and the concentration of Hg(II) was 2 µg L^{-1}, the recovery was above 90 %. The enrichment factor was 100. The detection limit of Hg(II) was 3.2 ng L^{-1}.

Effects of coexisting ions: The effects of common coexisting matters on the recovery of Hg(II) was studied. In this work, the potential interfering ions were added to solution of 0.2 mg/L Hg(II). The experimental results showed that recoveries of the Hg(II) remained above 95 % even in the presence of ions in the following concentrations: 2000 mg/L for Na^+, K^+, NH_4^+ and NO_3^-; 1000 mg/L for Ca^{2+} and Mg^{2+}; 500 mg/L for Al^{3+}, Cr(VI) and Cl^-; 200 mg/L for Cr(III), Ag^+, Co^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+}; 100 mg/L for Cd^{2+} and Fe^{3+} and 1.0 mg/L for Zn^{2+}, indicating that the adsorbent has a good selectivity.

Application in real samples: The proposed method was applied to the determination of Hg(II) in the river water samples. River water samples collected from Liao He river and Hun He river (shenyang, China), were filtered through a 0.45 µm membrane filter. According to general procedure, Hg(II) were adsorbed on the adsorption. Then it was eluted and determine by hydride generation-atomic absorption spectrometry. Meanwhile, the recovery tests were also conducted. The results were given in Table-6. The recoveries were reasonable for trace analysis, in a range of 93.4-102.3 %.

Conclusion

D-O-Bentonite has been successfully applied in mercury enrichment and separation and determined using a hydride generation-atomic absorption spectrometry. In the medium of pH 5, the adsorption time was 15 min, the Hg(II) could be adsorbed on the D-O-bentonite. The adsorbed quantity was affected by the pH value of medium and contact time. 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 14.20 kJ/mol. The Gibbs free energy changes (ΔG) were negative and entropy changes (ΔS) were positive. The activation energy (E_a) was 14.06 kJ/mol for the adsorption. The mercury adsorbed on the D-O-bentonite could be completely eluated by using 3 mol/L HCl. The proposed method has been applied to the pre-concentration/ separation of Hg(II) in river water samples with satisfied results.

REFERENCES

1. S. Tunali, T. Akar, A.S.Ozcan, I. Kiran and A.Ozcan, *Sep. Purif. Technol.*, **47**, 105 (2006).
2. H. Seiler and H. Sigel, Handbook on Metals in Clinic and Analytical Chemistry, Marcel Dekker, New York (1994).
3. D.P. Torres, M.A. Vieira, A.S. Ribeiro and A.J. Curtius, *J. Anal. Atom. Spectrom.*, **20**, 289 (2005).
4. Z. Long, J. Xin and X. Hou, *Spectrosc. Lett.*, **37**, 263 (2004).
5. J.C.A. Wuilloud, R.G. Wuilloud, A.P. Vonderheide and J.A. Caruso, *Spectrochim. Acta B*, **59**, 755 (2004).
6. D. Zhang, G.J. Ren and L.Z. Xu, *J. Chem. Ind. Eng.*, **59**, 1535 (2008).
7. D. Zhang, J. Zhang, L.Z. Xu and G.J. Ren, *Metallurg. Anal.*, **28**, 57 (2008).
8. D. Zhang and Y. Cheng, *Asian J. Chem.*, **24**, 5279 (2012).
9. D. Zhang and Y.L. Zhang, *Adv. Mater. Res.*, **230-232**, 888 (2011).