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Preparation and application of thiol wheat straw as sorbent for removing mercury ion from aqueous solution

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ABSTRACT

In this paper, thiol wheat straw (TWS) was prepared by esterifying mercaptoacetic acid onto cellulose in wheat straw. The potential feasibility of TWS as sorbent for removing mercury ion from aqueous solution was investigated in a batch system. The Hg^{2+} removal was found to be dependent on initial pH, sorbent dose, Hg^{2+} concentration, contact time, and temperature. The maximum value of Hg^{2+} removal appeared in the range of pH 4 to 7. The isothermal data of Hg^{2+} sorption conformed well to the Langmuir model and the maximum sorption capacity (Q_m) of TWS for Hg^{2+} was 72.46 mg/g. The equilibrium of Hg^{2+} removal was reached within 100 min. The Hg^{2+} removal process could be described by the pseudo-first-order kinetic model. The thermodynamic study indicated that the Hg^{2+} removal process was spontaneous and exothermic.

Keywords: Removal; Mercury ion; Esterification; Mercaptoacetic acid; Wheat straw

1. Introduction

Heavy metals are continuously released into the aquatic environment by natural and industrial processes. When excess of heavy metals introduced into aquatic ecosystems, water bodies have been polluted. Because having high affinity for thiol groups, carboxyl groups and/or amine groups, toxic heavy metals can bind to proteins, enzymes and nucleic acids, and interfere with their functions. Public concern over heavy metal pollution has grown constant since the outbreak of Minamata disease caused by mercury in Japan [1]. People's awareness of the hazards of heavy metals now covers a wide spectrum of heavy metals such as lead, mercury, cadmium, chromium, copper, zinc, nickel and arsenic.

The removal and recovery of heavy metals from wastewater is important in the protection of the ecological environment and human health. A number of techniques such as chemical precipitation [2], solvent extraction [3], flotation [4], electrodialysis [5], membrane separation [6], reverse osmosis [7], ion exchange [8], and sorption [9] have been employed to remove heavy metals from wastewater. But based on techno-economic considerations to conventional disposal methods, people still have been searching after new materials and techniques for heavy metal wastewater treatment.

In recent years, many agricultural wastes, including banana pith [10], apple waste [11], olive pomace [12], wheat shell [13], grape stalk waste [14], sawdust [15], carrot residue [16], sugar beet pulp [17], tree fern [18], rice husk [19], coffee husk [20], eucalyptus bark [21] and wool [22], had been used to sorb heavy metals from aqueous solution. The agricultural wastes

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being abundantly available with low cost mainly comprise of cellulose which is a natural biopolymer with sorption property. For improving the physicochemical properties or sorption capacities of agricultural wastes, various chemical modifications were employed [23–26].

Yu and coworkers employed cotton fiber modified by mercaptoacetic acid to preconcentrate 11 trace heavy metals [27]. This paper reported the preparation of thiol wheat straw (TWS) by esterifying mercaptoacetic acid onto cellulose in wheat straw. The resulting material with the high sorption capacity was subsequently investigated for its potential as sorbent for removing mercury ion from aqueous solution in a batch system. The purpose of this work was to exploit and utilize new modified agricultural waste for enhancing the treatment of heavy metal wastewater.

2. Materials and methods

2.1. Preparation of TWS

The TWS was prepared according to the similar method previously reported by Yu et al. [27]. In a wide mouth bottle, the following reagents were added in order: 100 ml of mercaptoacetic acid, 60 ml of acetic anhydride, 40 ml of 36% acetic acid, and 0.3 ml of concentrated sulfuric acid. The mixture was stirred thoroughly and cooled to room temperature, followed by adding 30 g ground wheat straw (420–850 μm), which subsequently was impregnated thoroughly in solution. After being cooled, the bottle was covered with the lid and kept at 40°C in a water bath for 3 days. The final reaction product was recovered by suction filtration and washed extensively with distilled water. After being dried at 40°C for 24 h, the TWS was kept at 4°C in a sealed dark bottle protected from sunlight. The thiol groups in TWS determined by iodimetry were 0.37 m mol/g [28].

2.2. Preparation of of Hg^{2+} solution

The stock solution of mercury ion corresponding to 350 mg/l of Hg^{2+} was prepared by dissolving 0.4737 g of mercury (II) chloride in distilled water and diluting to 1,000 ml in a standard volumetric flask. All working solutions were obtained by diluting the Hg^{2+} stock solution in accurate proportions to different initial concentrations (50–350 mg/l).

2.3. Removal experiments

Except for the experiments of temperature effect, other removal experiments were carried out in a rotary shaker at 150 rpm and ambient temperature using 250 ml shaking flasks containing 100 ml of different concentrations and initial pH values of Hg^{2+} solution. The initial pH values of the solution were previously adjusted with diluted HNO_3 or NaOH using a pH meter. Different doses of TWS were added to each flask, and then the flasks were sealed to prevent a change in volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and filtered through a membrane filter (0.45 μm). The concentration of residual Hg^{2+} in the filtrate was determined with flame atomic absorption spectrometry.

Because the precipitation of insoluble mercury compound occurred at pH value greater than 7, the effect of initial pH was studied over the pH range from 1.0 to 7.0 with other experimental parameters fixed as follows: Hg^{2+} concentration (150 mg/l), TWS dose (3 g/l), and contact time (120 min).

The influence of sorbent dose was investigated over the TWS dose range from 0.5 to 4.5 g/l with other experimental parameters fixed as follows: Hg^{2+} concentration (150 mg/l), contact time (120 min), and initial pH (6).

The effect of initial Hg^{2+} concentration was studied over the Hg^{2+} concentration range from 50 to 350 mg/l with other experimental parameters fixed as follows: TWS dose (3 g/l), contact time (120 min), and initial pH (6).

The influence of contact time was investigated over the time range from 0 to 180 min with other experimental parameters fixed as follows: Hg^{2+} concentration (150 mg/l), TWS dose (3 g/l), and initial pH (6).

The experiments were conducted in triplicate and negative control (with no sorbent) experiments were simultaneously carried out to ensure that sorption was caused not by the container but by the sorbent.

3. Results and discussion

3.1. Effect of initial pH

The effect of initial pH on removal percentage of Hg^{2+} is elucidated in Fig. 1, the amount of Hg^{2+} removal increased as the initial pH value of Hg^{2+} solution was increased from pH 1 to pH 4. The maximum value of Hg^{2+} removal appeared in the range of pH 4 to 7. For this reason, the pH 6 was selected for the other experiments.

3.2. Influence of sorbent dose

The influence of sorbent dose on the removal ratio of Hg^{2+} is shown in Fig. 2. For the Hg^{2+} solution at 150 mg/l initial concentration, the percentages of Hg^{2+} removed increased from 64.13% to 99.34% with

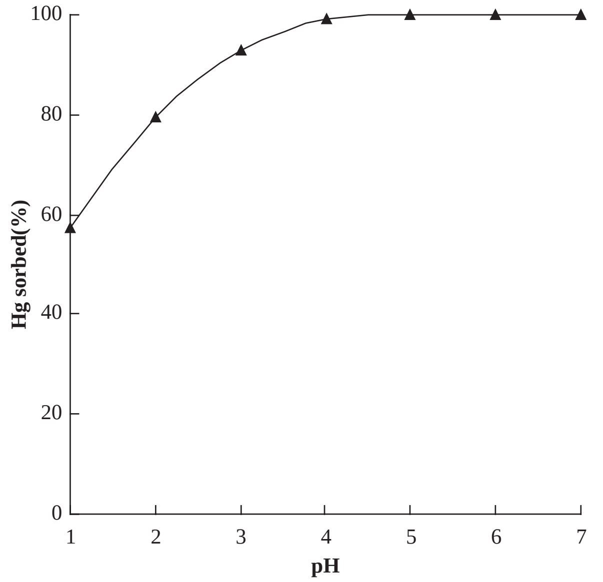

Fig. 1. Effect of initial solution pH on Hg^{2+} removal by TWS.

increasing the TWS dose from 0.5 to 3 g/l. Above 3 g/l of sorbent dose, all Hg^{2+} in the solution almost was completely removed. So, the TWS dose of 3 g/l was chosen for subsequent experiments.

Because the surface area of sorbent (number of sorbent sites) correspondingly increases with the increase of sorbent dose, the percentage of sorbate removed increased along with increase of sorbent dose. But after the sorption equilibrium, the removal ratio of sorbate kept constant.

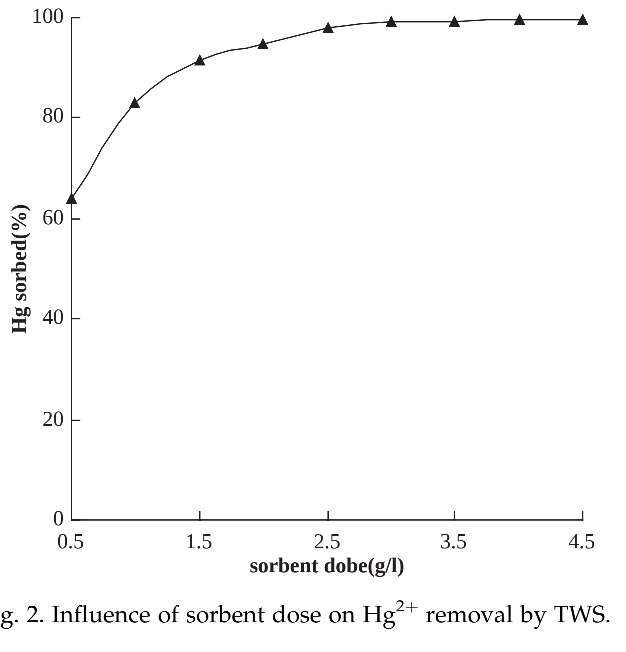

Fig. 2. Influence of sorbent dose on Hg^{2+} removal by TWS.

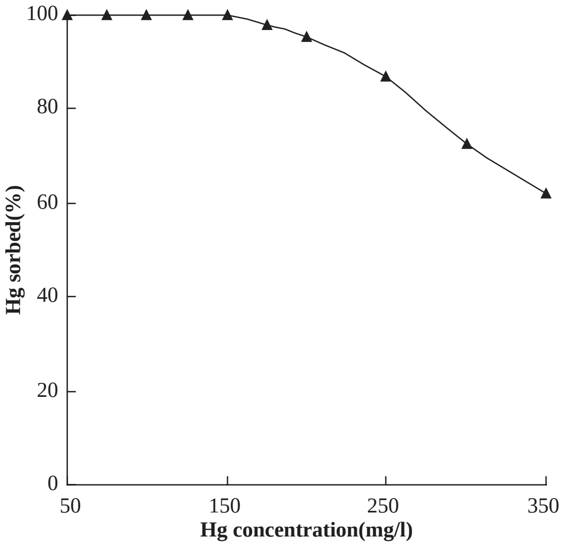

Fig. 3. Effect of initial Hg^{2+} concentration on its removal by TWS.

3.3. *Effect of initial Hg^{2+} concentration*

The effect of Hg^{2+} concentration on its removal percentage is shown in Fig. 3. When the Hg^{2+} concentration was in the range of 50–150 mg/l, All Hg^{2+} in the solution almost could be removed by 3.0 g/l of TWS. With further increase of Hg^{2+} concentration up to 350 mg/l, the percentage of Hg^{2+} removed by TWS decreased to 55.86%. The decrease of Hg^{2+} removal could be attributed to the lack of available active removal sites required for the high initial Hg^{2+} concentration.

With the data in Fig. 3, Langmuir equation was employed to study the sorption isotherm of Hg^{2+}. The linearized Langmuir equation was shown as follows:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m, \tag{1}$$

where C_e (mg/l) is the concentration of the Hg^{2+} solution at equilibrium, q_e (mg/g) is the amount of Hg^{2+} sorbed at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is Langmuir constant. The Q_m and a values were obtained from the slope ($1/Q_m$) and intercept ($1/aQ_m$) of the linear plot of C_e/q_e versus C_e.

The Langmuir sorption isotherm of Hg^{2+} sorbed on TWS is shown in Fig. 4. The good linear correlation coefficient indicated that the sorption isotherm of Hg^{2+} on TWS followed the Langmuir model. The sorption capacity (Q_m) of TWS for Hg^{2+}, which was obtained from the slopes ($1/Q_m$) of linear Langmuir equation,

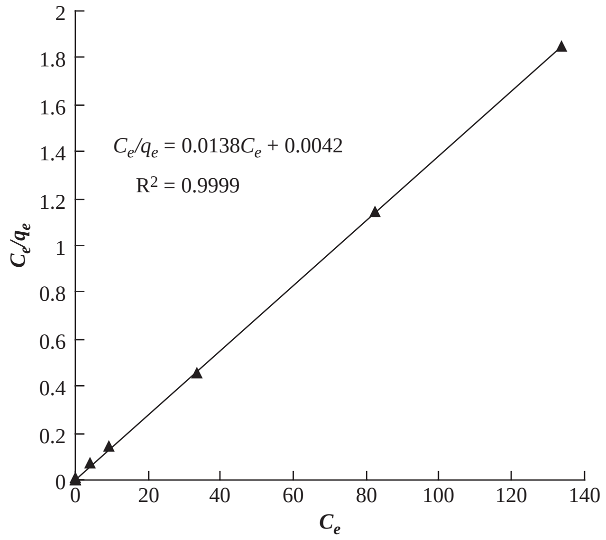

Fig. 4. The Langmuir sorption isotherm of Hg^{2+} by TWS.

was 72.46 mg/g. The sorption capacities (Q_m) of various sorbents for Hg^{2+} are compared in Table 1.

3.4. Influence of contact time and sorption kinetics

The influence of contact time on Hg^{2+} removal by TWS is illustrated in Fig. 5. The rate of Hg^{2+} removal was very rapid at the initial stage of sorption, caused by the fast diffusion and sorption of Hg^{2+} ion onto the external surface of sorbent. After that, the Hg^{2+} removal rate declined gradually and reached the equilibrium value at about 100 min. This process was controlled by the pore diffusion velocity of Hg^{2+} ion into the intraparticle matrix of sorbent.

To examine the kinetic model of Hg^{2+} removed by TWS, The data in Fig. 5 are treated with the following Lagergren's pseudo-first-order rate equation:

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t, \tag{2}$$

where q_e and q_t (mg/g) refer to the amount of Hg^{2+} removed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constants k_{ad} could be calculated from the slope of the linear plot of lg ($q_e - q_t$) versus t.

Table 1
The sorption capacities (Q_m) of various sorbents for Hg^{2+}

Sorbent	Q_m (mg/g)	Reference
Carboxyl banana stem	90.88	[25]
TWS	72.46	Present study
Activated carbon (sago waste)	55.6	[9]
Rice husk	36.1	[19]
Eucalyptus bark	33.11	[21]
Tree fern	26.5	[18]

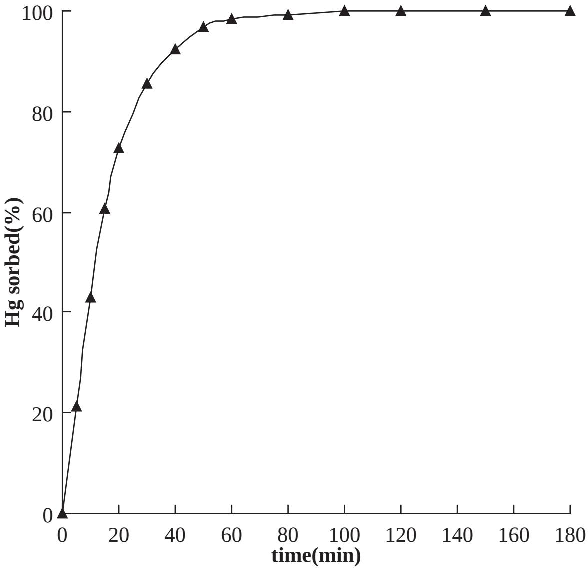

Fig. 5. Influence of contact time on Hg^{2+} removal by TWS.

The above kinetic data were also treated with the following intraparticle diffusion rate equation:

$$q_t = k_{id}t^{1/2} + C, \tag{3}$$

where q_t (mg/g) is the amount of Hg^{2+} removal at time t (min), k_{id} is the intraparticle diffusion rate constant, and C is the intercept. The k_{id} and C values were obtained from the slope and intercept of the linear plot of q_t versus $t^{1/2}$. When the line passed through the origin ($C = 0$), the intraparticle diffusion will be the sole rate control step. If the plot does not pass through the origin, it implies that intraparticle diffusion is not the only rate control step and other processes may control the rate of sorption.

The pseudo-first-order rate and intraparticle diffusion rate equations, values of constants and correlation coefficients for Hg^{2+} removal by TWS are shown in Table 2. The high value of correlation coefficients indicated that the Hg^{2+} removal process could be described by the pseudo-first-order kinetic model. The intraparticle diffusion was also involved in the removal process, although it was not the only rate control step.

3.5. Sorption thermodynamics

The thermodynamic experiment was carried out at 308.15, 313.15, 318.15, and 323.15 K with other experimental parameters fixed as follows: Hg^{2+} concentration (150 mg/l), TWS dose (3 g/l), contact time (120

Table 2
The pseudo-first-order rate and intraparticle diffusion rate equations, values of constants and correlation coefficient for Hg^{2+} removal by TWS

Sorbate	Pseudo-first-order rate			Intraparticle diffusion rate		
	$\ln(q_e - q_t) = -0.0689t + 3.9976$			$q_t = 11.654t^{1/2} - 15.378$		
	q_e (mg/g)	k_{ad}	R^2	k_{id}	C	R^2
Hg^{2+}	54.47	0.0689	0.9974	11.654	−15.378	0.9987

min), and initial pH (6). The thermodynamic parameters, $\Delta H°$ and $\Delta S°$, were obtained from the following Van't Hoff equation:

$$\ln(q_e/C_e) = S°/R - H°/RT, \tag{4}$$

where q_e/C_e is the equilibrium constant (ml/g), $\Delta S°$ is standard entropy (J/mol·K), $\Delta H°$ is standard enthalpy (J/mol), T is the absolute temperature (K), and R is the gas constant (8.314 J/mol·K). From Fig. 6, the $\Delta H°$ and $\Delta S°$ values could be calculated from the slope ($-\Delta H°/R$) and intercept ($\Delta S°/R$) of the linear plot of ln (q_e/C_e) versus $1/T$.

The thermodynamic parameter, $\Delta G°$, was calculated from the following Gibbs-Helmholtz equation:

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

where $\Delta G°$ is the standard free energy (kJ/mol). The $\Delta G°$ values under different temperatures as well as $\Delta H°$ and $\Delta S°$ values are presented in Table 3. The negative values of $\Delta G°$ and $\Delta H°$ indicated that the Hg^{2+} removal were spontaneous and exothermic. Lower temperatures were favorable for the removal process.

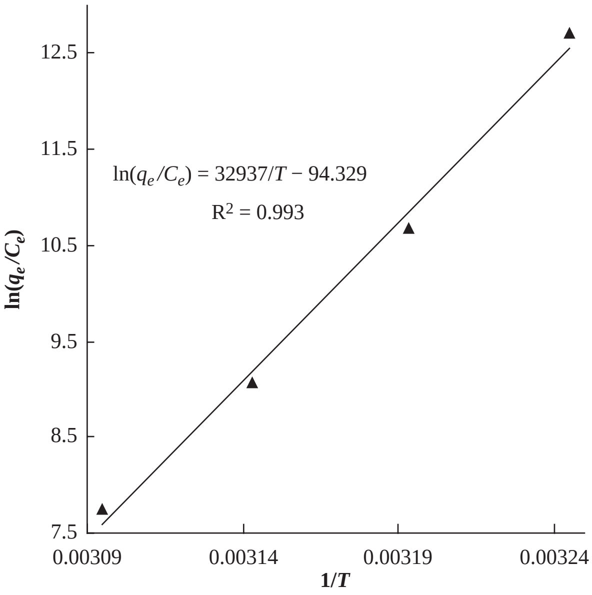

Fig. 6. The plot of ln q_e/C_e vs. $1/T$ for Hg^{2+} removal by TWS.

4. Conclusions

This study confirmed that TWS was an excellent heavy metal sorbent. The maximum value of Hg^{2+} removed by TWS appeared in the range of pH 4 to 7. The 3 g/l or up of TWS almost could completely remove Hg^{2+} from 150 mg/l of its aqueous solution. The removal percentage of Hg^{2+} kept above 99% over a range from 50 to 150 mg/l of Hg^{2+} concentration when 3.0 g/l of TWS was used. The isothermal data of Hg^{2+} sorption conformed well to the Langmuir model, and the maximum sorption capacity (Q_m) of TWS for Hg^{2+} was 72.46 mg/g. The equilibrium of Hg^{2+} removal was reached within 100 min. The Hg^{2+} removal process could be described by the pseudo-first-order kinetic model. The kinetic result indicated that intraparticle diffusion was not the only rate control step in Hg^{2+} removal process. The thermodynamic study indicated that the Hg^{2+} removal process was spontaneous and exothermic.

Table 3
The values of thermodynamic parameters for Hg^{2+} removal by TWS

Sorbate	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol·K)	$\Delta G°$ (kJ/mol)			
			308.15 K	313.15 K	318.15 K	323.15 K
Hg^{2+}	−273.84	−784.25	−32.17	−28.25	−24.33	−20.41

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