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Removal of lead from aqueous solutions by condensed tannin gel adsorbent

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Abstract: Lead has caused serious environmental pollution due to its toxicity, accumulation in food chains and persistence in nature. In this paper, lead removal from aqueous solutions was investigated using condensed tannin gel adsorbent synthesized from a natural tannin compound. It is found that the adsorption is strongly affected by pH values of aqueous solutions. Within pH range of 3.5—6, when initial lead concentration is 100 mg/L, removal efficiency is more than 90%. Adsorption equilibrium is reached within 150 minutes. The adsorption isotherm fits well with the Langmuir equation, by which the saturated adsorption uptake of 190 mg Pb^{2+}/g dry tannin gel adsorbent is obtained. By means of thermodynamics analysis, it is revealed that the process is exothermic and the adsorption heat is up to 38.4 kJ/mol. With respect to high efficiency, moderate pH requirement and minimized second pollution, the tannin gel adsorbent exhibits a promising potential in the removal of lead from wastewater.

Keywords: lead removal; Mimosa tannin; synthesis; tannin gel adsorbent

Introduction

Many industries, such as petrochemicals, painting and coating, newsprint, smelting, metal electroplating, mining, plumbing and battery industries, discharge lead into the environment without adequate purification in some cases. Lead may be transported into water bodies by natural circulation and therefore threatens the human being due to its well-known toxicity, accumulation in food chains and persistence in nature. Hence, EPA of America lists it as a priority pollutant.

With respect to lead removal from water environment, particular attention has to be paid to the fact that such processes should be effective and simple. Traditional technologies used widely such as chemical precipitation, electrode deposition, ion exchange and reverse osmosis can not exhibit such performance in many cases. For example, chemical precipitation and electrode deposition always produce large amount of slurry. Ion exchange and reverse osmosis need high operation cost. While, some recent studies show that lead removal by low-cost adsorbent materials is accessible, such as by activated carbon (Reed, 1994; Akhtar, 1997), modified activated carbon (Mostafa, 1997; Lee, 1998), biosorbents (Kapoor, 1998) and even fly ash and red mud (Apak, 1998).

A similar kind of elimination is possible by means of novel tannin gel adsorbent. Condensed tannins are ubiquitous in species throughout the plant kingdom. They are not an isolated group of compounds, but a part of the vast collection of natural compounds and chemicals based on flavan-3-ol units. Flavanoid unites in tannin extracts are predominantly phloroglucinolic, resorcinolic or pyrogallolic A-rings and catecholic or pyrogallolic B-rings (Hemingway, 1989), as is shown in Fig.1. Tannins are reactive with formaldehyde due to their strong nucleophilicity of A-ring and are available to complex with metal ions because of the ortho-hydroxyls present in B-ring.

The original attempt in the removal of heavy metals from wastewater by tannin materials began in 1977 with the application of barks in the similar aspect. Later, some researchers synthesized adsorbents from commercial extracted tannins and applied them in removal of heavy metals, such as uranium (Sakaguchi,

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1998), americium(Matsumura, 1998), chromium (Yamaguchi, 1992a; Nakano, 2001) and copper (Yamaguchi, 1992b). After systematic study on lead removal from aqueous solutions using H-end tannin gel adsorbents, the authors of this paper put forward that ion exchange and surface precipitation are the main adsorption mechanisms of H-end tannin gel adsorbent (Zhan, 2001). Ion exchange takes place preferentially when initial lead concentration is not more than 60 mg/L and initial pH is not more than 6. Otherwise, surface precipitation predominates in high pH range. With respect to wastewater treatment, lead is often in acidic circumstance in case of any precipitation, so, it is challenging to develop a novel tannin gel adsorbent that is applicable at low pH. This is just the aim of this study.

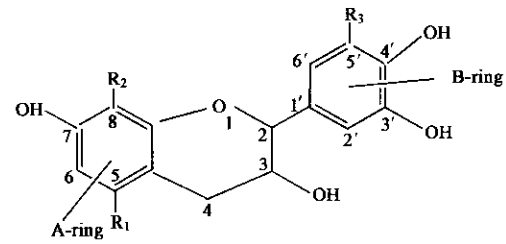

Fig.1 Flavanoid unit in condensed tannins
To A-ring R_1 = OH, R_2 = H, phloroglucinolic; R_1 = R_2 = H, resorcinolic; R_1 = H, R_2 = OH, pyrogallolic;
To B-ring R_3 = H, catecholic, R_3 = OH, pyrogallokic

1 Experimental methods and materials

1.1 Preparation of tannin gel adsorbent

A certain Mimosa tannin powder was equilibrated at room temperature with 65 ml KOH solution, which was based on distilled water spiked with 4.5 ml(6.25 mol/L) KOH and 4.2g $KMnO_4$ additionally. Then, tannin was gelated through polymerization with formaldehyde (37 wt%) at 353K for 1 hour in decahydronaphthalene solvent. After the extensive rinsing with acetone and distilled water, the obtained dark brown tannin particles were dried at 323K for 24 hours and then kept for following experiments.

1.2 Batch adsorption experiment

All adsorption experiments were conducted in a batch system. Synthetic wastewater was prepared from a standard lead solution ($Pb(NO_3)_2$, Nacalai Tesque, Inc., lead concentration = 1000 mg/L). The pH value of synthetic wastewater was adjusted by adding HNO_3 or NaOH solution. 50 ml solutions with known initial lead concentration and pH value were introduced into well-sealed 100 ml glass bottles with 0.05g tannin gel particles. The bottles were set in a thermostatic shaker for 24 hours. The shaking speed was 100 min^{-1} and the temperature was maintained at 298K. After adsorption, the suspensions were filtered and the filtrates were acidified by 10 mol/L HNO_3 to decrease pH to 2.5 in order to avoid lead precipitation before ICP measurement. Lead concentration in the filtrates was measured with an Inductively Coupled Plasma Spectrometer(ICPS, SPS4000, Seiko Instruments, Japan). Some bottles containing synthetic wastewater without tannin gel particles were functioned as the control experiment to study the effect of lead precipitation.

2 Results and discussion

2.1 Effect of pH on lead removal

Effect of pH on lead removal was studied within the range of 1 – 7. Fig.2 shows the pH-adsorption edge(the pH range in which lead removal efficiency is from 0 to nearly 100%) when initial lead concentration was fixed as 100 mg/L. Removal efficiency(η) in Fig.2 is defined as:

$$\eta = \frac{C_i - C_e}{C_i} \times 100\% . \quad (1)$$

In which, C_i is the initial lead concentration in aqueous phase (mg/L); C_e is the equilibrium lead concentration in aqueous phase (mg/L).

In acid solutions, lead removal can be promoted greatly with the increase of pH. When pH is 3.5, lead removal efficiency amounts to nearly 100%. In the control experiment, lead removal by precipitation

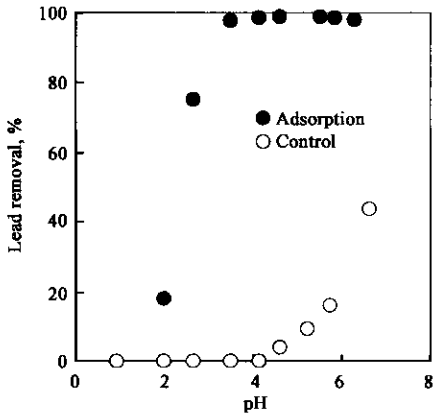

Fig.2 pH-adsorption edge (initial lead concentration = 100 mg/L; T = 298K; tannin gel adsorbent = 1 g/L)

and filtration happens at pH value of 4.2. Therefore, it can be concluded that adsorption is dominant when initial pH is below 6. This high adsorption efficiency is advantageous to lead removal because precipitation slurry can be avoided.

Distribution coefficient (K) is defined as:

$$K = X_e / C_e . \quad (2)$$

In which, X_e is the amount of lead adsorbed onto tannin gel adsorbent at equilibrium (mg Pb^{2+}/g dried tannin gel adsorbent). The development of K with pH value present in Fig.3 testifies to the fact that the optimum pH for lead removal is 4.2.

2.2 Sorption kinetics

Adsorption rate is an important factor evaluating the application of adsorbents. Fig.4 presents the distribution of lead in solid phase with shaking time. 90% of lead can be adsorbed within the initial 30 minutes. However, the uptake slows down with the development of time, with respect to the fact that only 5% was adsorbed in the later 100 minutes. The rapid stage corresponds to the adsorption on surface layer and the slow one corresponds to the adsorption in microporous. According to Fig.4, equilibrium can be reached after the shaking time of 150 minutes.

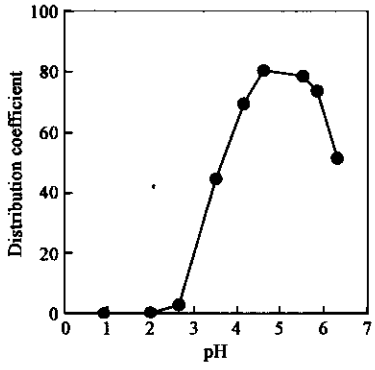

Fig.3 Effect of pH on distribution coefficient (initial lead concentration = 100 mg/L; T = 298K; tannin gel adsorbent = 1 g/L)

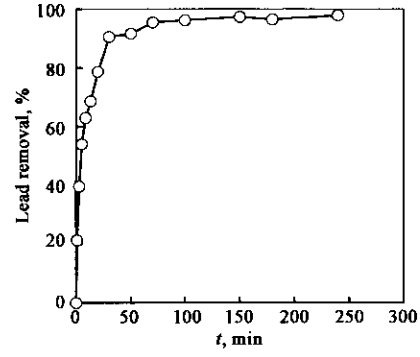

Fig.4 Plot of lead removal with the shaking time (initial lead concentration——100 mg/L; pH = 3.5; tannin gel adsorbent = 1 g/L

The plot of $\log(X_e - X)$ against time t within the initial 30 minutes can serve as a confirmation of adsorption rate expressed by Lagergren equation, which is shown in Fig.5:

$$\log(X_e - X) - \log(X_e) = - K_{ads} t/2.303 . \quad (3)$$

In which, K_{ads} is the first-order rate constant; X is the amount of lead adsorbed onto tannin gel adsorbent (mg Pb^{2+}/g dried tannin gel adsorbent).

In Fig.5, K_{ads}, the first-order rate constant, can be correlated as 0.079 min^{-1}. Compared with the data of Akhtar (Akhtar, 1997) (0.049 min^{-1}), the novel tannin gel adsorbent can exhibit better performance than activated carbon with respect to lead adsorption rate.

Adsorption rate is always defined by mass transport process. So, diffusion rate of lead onto tannin gel is very important. Diffusion rate(K_d) can be calculated with Morris-Weber equation:

$$X = K_d t^{1/2} . \quad (4)$$

Fig.6 lists the linear relationship between X and $t^{1/2}$. Plots of amount adsorbed expressed in terms of $t^{1/2}$ depict two distinct regions in all systems, namely an initial linear portion controlled by boundary layer diffusion effect and a final linear portion due to intrapartical diffusion as decisive stage. In the initial 30 minutes, K_d is 16.7 mg/g $min^{1/2}$, while it slows down to 0.7 mg/g $min^{1/2}$ in the later phase.

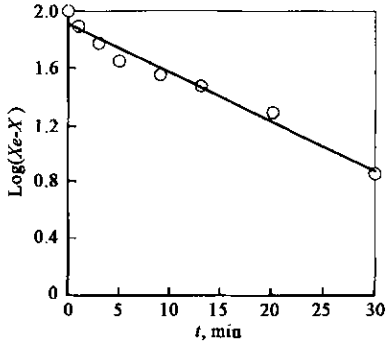

Fig.5 Plot of adsorption rate with Lagergren equation(initial lead concentration = 100 mg/l.; pH = 3.5; T = 298K)

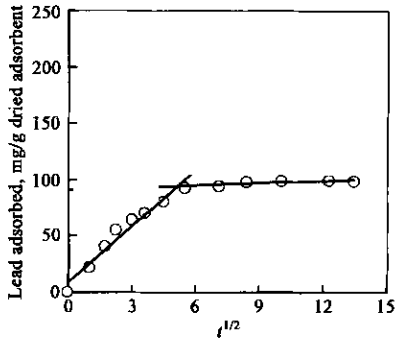

Fig.6 Lead adsorbed as a function of adsorption time(initial lead concentration = 100 mg/L; pH = 3.5; T = 298K)

2.3 Adsorption isotherm

Langmuir equation

$$X_e = X_m \frac{K_l C_e}{1 + K_l C_e} \tag{5}$$

and Freudlich equation

$$X_e = K_F C_e^{1/n} \tag{6}$$

are often used to express the adsorption isotherms in aqueous solutions(K_F, n are Freudlich coefficients and K_l is Langmuir coefficient). In this study, Langmuir equation fits the relationship very well, which can be confirmed by the plot of C_e/X_e against C_e shown in Fig.7. From Langmuir equation, the maximum amount adsorbed by the adsorbent is equal to 190 mg Pb^{2+}/g dried tannin gel adsorbent. This is much higher than lead removal by some other adsorbents reported, such as activated carbon (6—31 mg/g adsorbent(Reed, 1994); 23 mg/g adsorbent(Akhtar, 1997), modified activated carbon (0.6—25.9 mg/g adsorbent(Mostafa, 1997)); 8—32 mg/g adsorbent (Lee, 1998), bioadsorbent (10 mg/g adsorbent (Kapoor, 1998)). Furthermore, it is far more than that of H-end tannin gel particles (30—40 mg/g adsorbent(Zhan, 2001)).

2.4 Adsorption thermodynamics analysis

Based on distribution coefficient (K), the following equation could be established:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta = -RT\ln K, \tag{7}$$

in which, G^θ is the free energy of adsorption; H^θ is the adsorption heat; S^θ is the adsorption entraphy. So,

$$\log K = \Delta S^\theta/(2.303R) - \Delta H^\theta/(2.303RT). \tag{8}$$

From the linear relationship between $\log K$ and $1/T$, ΔH^θ and ΔS^θ could be calculated(Fig. 8).

From the slope and intersect of the line in Fig. 8, ΔH^θ and ΔS^θ are calculated as -38.4 kJ/mol and -108.6 kJ/(mol·K). The negative data of ΔH^θ means that the adsorption is exothermic. The value is much higher than that of copper adsorbed onto tannin resin noted by Yamaguchi(3 kcal/mol)(Yamaguchi, 1992b), which shows that the binding between tannin gel and lead is very strong.

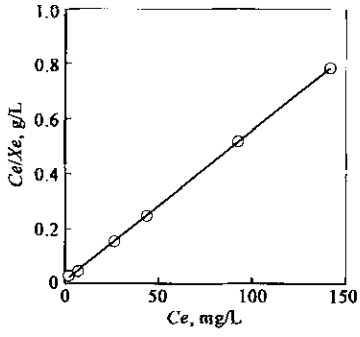

Fig. 7 Langmuir plot for lead adsorption isotherm (pH = 3.5)

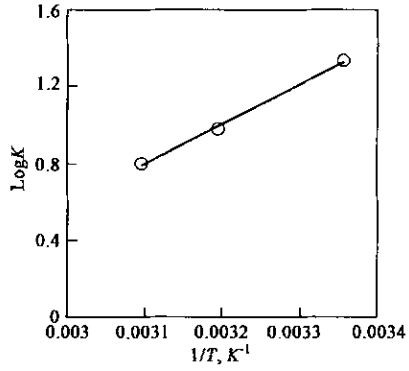

Fig. 8 Plot of $\log K$ as a function of $1/T$ (initial lead concentration = 100 mg/L, pH = 3.5)

3 Conclusions

The aim of this paper was to study the technique feasibility of lead removal by a newly synthesized tannin gel adsorbent. pH is an important factor influencing lead adsorption. Within the pH range of 2.5—6, this adsorbent can exhibit very promising properties in the uptake of lead from aqueous solutions. The optimum uptake occurs at pH value of 4.2. The adsorption equilibrium can be completed within 150 minutes. At the initial pH of 3.5, the Langmuir equation fits the adsorption isotherm well and the adsorbent has the saturated adsorption uptake of 190 mg Pb^{2+}/g dry tannin gel. The process is exothermic and the adsorption heat is calculated as 38.4 kJ/mol, as shows a strong binding between lead and the novel adsorbent. After adsorption, adsorbed lead can be recovered by combustion of tannin gel adsorbents, which can promote a zero-emission process for lead removal.

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