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Sorption of lead from aqueous solutions by spent tea leaf

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An adsorbent was prepared using spent tea leaf and was used to remove lead (Pb) from solution. The Pb removal by the spent tea leaf adsorbent depended on pretreatment of spent tea leaf, adsorption contact time and adsorbent dosage. The optimum pretreatment conditions were confirmed to be that tea leaf was ground to 0.28-0.45 mm in diameter and then drenched in 0.3 M NaOH for 12 h. Adsorption kinetic study showed that the adsorption of Pb onto the spent tea leaf followed the pseudo-second-order model. The adsorption was time dependent and adsorbent dosage dependent. The optimum contact time was 8 h.

Key words: *Camellia sinensis*, spent tea leaf, adsorbent, lead removal, adsorption kinetics.

INTRODUCTION

Heavy metal pollution is an environmental problem of worldwide concern, among which lead (Pb) is one of the most common pollutants found in industrial effluents and is significantly toxic to human beings and ecological environments even at low concentrations. Heavy metals in solution are confirmed to be removed by methods of ion exchange, chemical precipitation, reverse osmosis and electrochemical processes, but these methods are often ineffective and/or very expensive when used for the reduction of heavy metal ions at very low concentrations (Rao et al., 2007). A number of investigations have been conducted to test the low cost adsorbents for heavy metal ion removal over the last few years. Such alternatives include agricultural biowastes (Park et al., 2008).

Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world. A big volume of spent tea leaf or tea leaf residue was disposed to environments through daily tea drinking and extractions of instant tea and ready-to-drink teas. Many investigations have been conducted to test tea waste, a fibrous by-product during tea processing, for many uses, such as adsorbent of heavy metals (Malkoc and Nuhoglu, 2006; Amarasinghe and Williams, 2007; Park et al., 2008), fertilizer (Ozdemir et al., 2007; Chong

et al., 2008) and mushroom growing medium (Gulser and Peksen, 2003; Toker et al., 2007; Baysal et al., 2007; Yigitbasi et al., 2007; Simsek et al., 2008). Lignocellulose prepared from tea stalk was used to prepare deca-ffeinated catechins (Ye et al., 2009). However, there has been few report on the utilization of the spent tea leaf. The present study aimed at using the spent tea leaves as adsorbent to remove lead from aqueous solutions.

MATERIALS AND METHODS

Materials

The spent tea leaf used was supplied by Hangzhou CinoTea Co. Ltd. (Hangzhou, China). It was the leaf residue after instant tea extraction. The leaf was dried at 60°C for 24 h and then ground using an EUPA TSK-927S grinder (Cankun Co., Ltd. Shanghai, China), sifted to particle size 0.28-0.45 mm, 0.45-0.90 mm and 0.90-1.25 mm in diameter, respectively. Sodium hydroxide was AR (analytical reagent) grade (Jinmei Biotech Corporation, Tianjin, China). The lead nitrate [Pb(NO3)₂] (Sigma Chemicals, St Louis, MO, USA) was purchased from market.

Pretreatment of spent tea leaf

In order to obtain optimum conditions for pretreatment of the spent tea leaf, orthogonal test with three factors including particle size (factor A), NaOH concentration (factor B) and pretreatment time (factor C). The three factors each (Table 1) was designed on soft-ware of the SAS System for Windows (version 8.01; SAS Institute

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Inc., Carry, NC, USA). The ground spent tea leaves were drenched in NaOH solutions of for 6, 12 and 24 h respectively, washed with water until the used water was colourless, and then washed with two volumes of distilled water for two times. The leaves were dried for 24 h at 60°C. The dried tea leaves were stored in sealed poly-thene bags till use.

Test of adsorption kinetics

Pb solution was prepared by dissolving $Pb(NO_3)_2$ in distilled water to a concentration at 600 mg L^{-1}. 0.5 g adsorbents pretreated under conditions A1 (0.28-0.45 mm in diameter), B2 (0.3 M NaOH) and C2 (12 h) was added into glass beaker flasks containing 50 ml of the Pb solution. The flasks were agitated at 150 rpm and room temperature on a H2S-H shaker (Donglian Electronic Technology CO., Ltd., Harbin, China). The solutions were sampled at time intervals 0.25, 0.5, 1, 2, 4, 8, 16, 24 and 32 h, and centrifuged at 4500 rpm for 5 min for Pb analysis.

The pseudo-first-order model and the pseudo-second-order model were used for the simulation of adsorption kinetics according to methods by Ho and McKay (1998a; 1998b). The pseudo-first-order model was described by the following equation (1):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Where q_e and q_t (mg g^{-1}) were the amounts of adsorbate (Pb) adsorbed on adsorbent (spent tea leaf) at equilibrium, and at sampling time t, respectively.
The k_1 was the rate constant (min^{-1}).
The pseudo-second-order model was based on following equation (2):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

On integration for boundary conditions as t = 0 to >0 and q = 0 to >0, the equation (2) becomes:

$$\frac{t}{qt} = \frac{1}{k_2 q e^2} + \frac{1}{q_e} t \tag{3}$$

where k_2 (g mg^{-1} min^{-1}) was the second-order rate constant, which were calculated from slopes and intercepts the plot of t/qt versus t (Figure 1). Initial sorption rate (h) was also a kinetic parameter for evaluating adsorption behaviours and it was calculated from the k_2 through the following equation (4):

$$h = k_2 q e^2 \tag{4}$$

Test of treatment time on Pb adsorption capacity

1 g of adsorbent pretreated under conditions A1 (0.28-0.45 mm in diameter), B2 (0.3 M NaOH) and C2 (12 h) was added into glass beaker flasks containing 50 ml of the Pb solution (600 mg l^{-1}). The flasks were agitated at 150 rpm and room temperature on a H2S-H shaker (Donglian Electronic Technology CO., Ltd., Harbin, China). The solutions were sampled and centrifuged as above for Pb analysis. The adsorption capacity was calculated by the following equation (5):

$$q = \frac{V(C_0 - C)}{G} \tag{5}$$

Where q was adsorption capacity of the adsorbent (mg g^{-1}) at equilibrium, C_0 and C were the initial and final Pb concentrations of the solution (mg l^{-1}), respectively. V was the Pb solution volume (ml) and G was weight of adsorbent used (g).

Test of spent tea leaf adsorbent dosage on Pb removal

The pretreated spent tea leaf with different amount (0.5, 1.0 or 0.25 g) was placed in a glass flask with 50 ml Pb solution (0.96 mg l^{-1}). The flasks were agitated on a shaker at 150 rpm and room temperature for 8 h. The solutions were centrifuged at 4500 rpm for 5 min for Pb analysis. The Pb removal was calculated by equation (6):

Pb removal (%) = $[(C_0-C)/C_0] \times 100$ (6)

where C_0 and C are initial and final Pb concentration (mg l^{-1}) respectively.

Determination of Pb

The Pb concentration was determined by a Model TAS-990F atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) with an injection volume set at 10 μl. The absorbance of a sample was read in triplicate.
All the tests were carried out in duplicate started from adsorption.

RESULTS AND DISCUSSIONS

Effect of pretreatment on Pb adsorption capacity of spent tea leaf

As shown in Table 1, there were significant differences in Pb adsorption capacity between treatments. Treatments No.7 (A1B2C3) and No.4 (A1B3C2) had the highest Pb adsorption capacity and No.9 (A3B1C3), No.6 (A3B2C2) and No.3 (A3B3C1) the lowest, with treatments No.8 (A2B3C3), No.1 (A1B1C1), No.2 (A2B2C1) and No.5 (A2B1C2) in between. When the individual tested factors were examined, it was found that the Pb adsorption capacity was decreased with decrease in spent tea particle size (Table 2). This increase can be attributed to the fact that the adsorbent surface area and adsorption sites of a same weight adsorbent with small particles were more than those of adsorbent with large size. Concentration of NaOH for pretreatment of the spent tea leaf had significant influence on the Pb adsorption capacity. The Pb adsorption capacity of 0.1 M NaOH treatment was significantly lower than those of 0.3 M NaOH and 0.5 M NaOH (Table 3). NaOH treatment time had significant impact on the Pb adsorption capacity. The Pb adsorption capacity of treatments of 12 and 24 h were significantly higher than that of 6 h. There was no significant difference in adsorption capacity between treatments 0.3 M NaOH and 0.5 M NaOH (Table 4).

Table 1. Effect of pretreatment of spent tea leaf on Pb adsorption capacity.

Pretreatment no.	A: Particle size (mm)	B: NaOH (m)	C: Time (h)	Pb adsorption capacity (mg g^{-1}) [a]
1=A1B1C1	A1=0.28-0.45	B1=0.1	C1=6	4.2b
2= A2B2C1	A2=0.45-0.90	B2=0.3	C1=6	3.8b
3= A3B3C1	A3=0.90-1.25	B3=0.5	C1=6	1.5c
4= A1B3C2	A1=0.28-0.45	B3=0.5	C2=12	13.4a
5= A2B1C2	A2=0.45-0.90	B1=0.1	C2=12	3.7b
6= A3B2C2	A3=0.90-1.25	B2=0.3	C2=12	2.1c
7= A1B2C3	A1=0.28-0.45	B2=0.3	C3=24	15.7a
8= A2B3C3	A2=0.45-0.90	B3=0.5	C3=24	5.5b
9= A3B1C3	A3=0.90-1.25	B1=0.1	C3=24	2.1c

[a]Data with different lower case alphabetic letters were significantly different at p=0.05.

Table 2. Effect of spent tea particle size on Pb adsorption capacity.

A: Particle size (mm)	Pb adsorption capacity (mg g^{-1})[a]
A1=0.90-1.25	1.90b
A2=0.45-0.90	4.33b
A3=0.28-0.45	11.10a

[a]Data with different lower case alphabetic letters were significantly different at p=0.05.

Table 3. Effect of NaOH concentration on Pb adsorption capacity.

NaOH concentration (m)	Pb adsorption capacity (mg g^{-1})[a]
B1=0.1	3.33b
B2=0.3	7.20a
B3=0.5	6.80a

[a]Data with different lower case alphabetic letters were significantly different at p=0.05.

Table 4. Effect of NaOH concentration on Pb adsorption capacity.

NaOH treatment time (h)	Pb adsorption capacity (mg g^{-1})[a]
C1=6	3.17B
C2=12	6.40A
C3=24	7.77A

[a]Data with different lower case alphabetic letters were significantly different at p=0.05.

Based on the above results, the optimum NaOH pretreatment conditions were A1 (0.28-0.45 mm in diameter), B2 (0.3 M NaOH) and C2 (12 h).
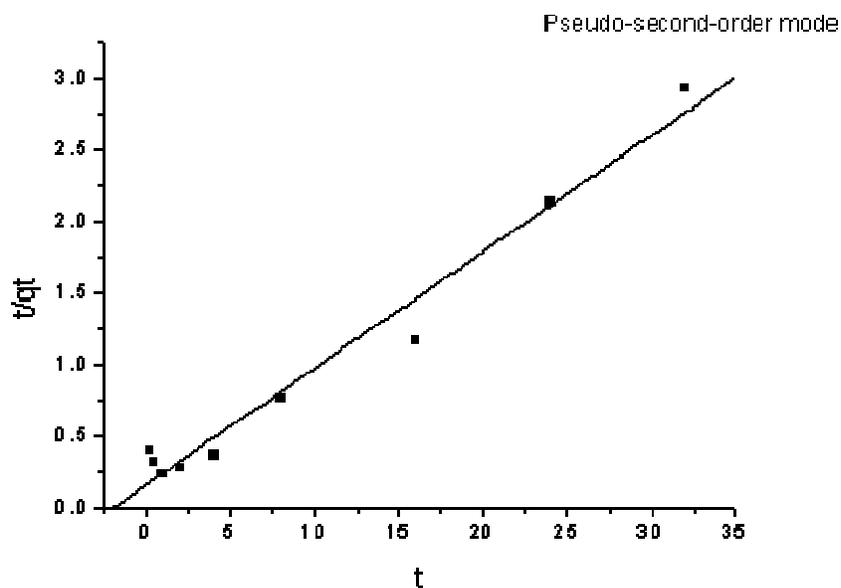
Adsorption kinetics

Adsorption kinetic study revealed that the adsorption system fitted well with the pseudo-second-order model (Figure 1). The determinant coefficient (square of correlation coefficient) for the pseudo-second-order model was 0,987, being significantly higher than that for the pseudo-first-order model (Table 5). It suggests that the Pb adsorption process of the spent tea leaf adsorbent was more fitted to the pseudo-second-order model than the pseudo-first-order model. The Pb adsorption capacity calculated according to the pseudo-second-order model was 13.750 mg g^{-1}, being similar to that experimental data 12.280 mg g^{-1} (Table 5).

Effect of adsorption contact time on Pb adsorption capacity of spent tea leaf

The Pb adsorption capacity of the spent tea leaf increased with adsorption contact time up to 8 h and then

Figure 1. Pseudo-second-order kinetics for the adsorption of Pb onto spent tea leaf.

Table 5. Pseudo-first-order and pseudo-second-order kinetic parameters at 298K[a].

Pseudo-first-order model		Pseudo-second-order model [b]				
k1 (h^{-1})	R^2	k2 (mgg^{-1} h^{-1})	H (mg g^{-1} h^{-1})	R^2	qe (exp) (mg g^{-1})	qe (cal) (mg g^{-1})
0.042	0.718	0.042	6.277	0.987	12.280	13.750

[a]Thermometric temperature scale K=273+celsiuss temperature (°C). Initial concentration of Pb was 600 mg L^{-1}.
[b]qe (exp): experimental data. qe (cal): theoretical value were calculated.
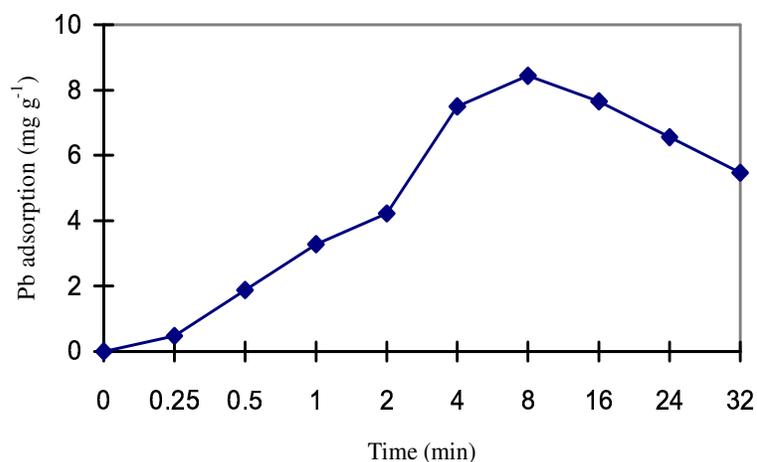
Figure 2. Effect of treatment time on Pb adsorption capacity.

decreased (Figure 2). This showed that sorption and adsorption took place simultaneously during the contact of spent tea leaf with Pb. At the early stage, the rate of adsorption was higher than that of adsorption, resulting in increase in Pb adsorption capacity of spent tea leaf.

However, the rate of adsorption was more quickly than adsorption in the late stage, leading to decrease in adsorption capacity. Several possible mechanisms were proposed to explain the sorption/adsorption of heavy metal on adsorbent that is diffusion of heavy metals into
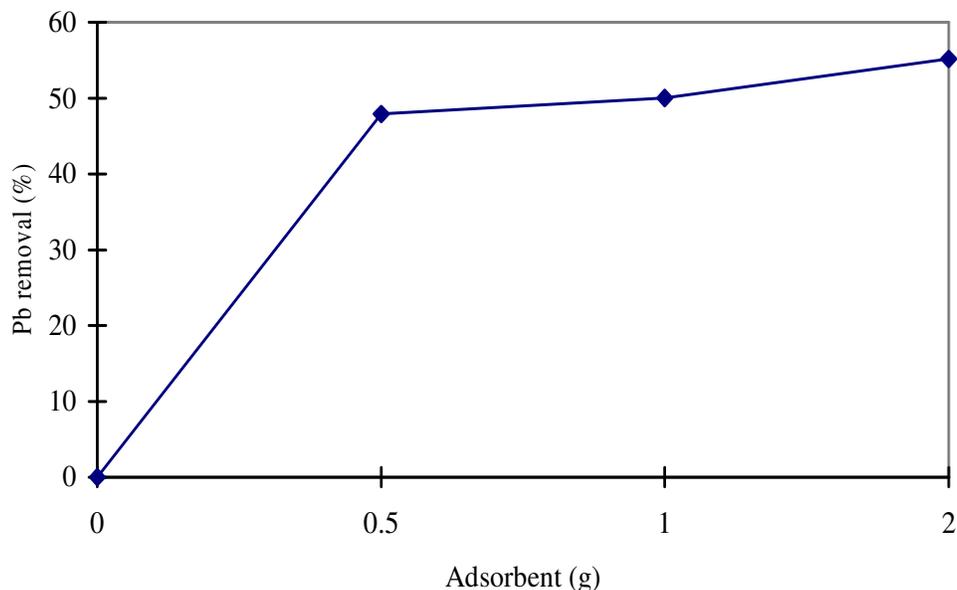
Figure 3. Effect of spent tea leaf dosage on Pb removal initial Pb concentration was 0.5 mg g^{-1}.

organic micropores, isomorphic substitution and forma-tion of a new surface polymer or precipitate (Gao et al., 2003). The biosorption of heavy metals was always accompanied with significantly high organic leaching (Yang and Chen, 2008). The organic leaching might lead to the changes in the adsorbent surfaces. This may explain that the Pb adsorption capacity of the spent tea leaf decreased. Biosorption was confirmed to be controlled by redox, ion exchange and coordination reactions, of which alcohol, carboxyl, amino and sulphonic groups play important roles. Chemical modification by 0.2% formaldehyde could modify seaweed and lowered the organic leaching, resulting in increase of metal biosorption (Yang and Chen, 2008). The effect of formaldehyde modification on the Pb adsorption capacity of the spent tea leaf remains to be further investigated.

Effect of spent tea leaf adsorbent dosage on Pb removal

The amount of removed Pb showed adsorbent dosage dependence. The percentage of removed Pb increased with the increase in spent tea leaf adsorbent dosage (Figure 3). This attributes to the increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the adsorbent. However, the relationship of removed Pb percentage did not show a linear regression relationship with the adsorbent dosage (Figure 3). Under the present experi-mental conditions, 47.9% of Pb was removed by 0.5 g spent tea leaf adsorbent and 55.2% Pb was removed by 2 g of the same adsorbent.

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