Adsorption characteristics of Pb (II) on alkali treated tea residue

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ABSTRACT

The alkali treated tea residue (ATTR) was used as a novel adsorbent to remove Pb (II) from aqueous solution. The adsorption characteristics and underlying adsorption mechanism of Pb (II) on ATTR were investigated. Scanning electron microscopy (SEM) showed that ATTR had a highly porous surface structure. Comparative studies showed that the removal rate of Pb (II) on ATTR was significantly higher than that on green tea and green tea residue. Batch studies revealed that the solution pH was the key factor affecting Pb (II) adsorption and the maximum pH for efficient adsorption was about 4.5, and the adsorption equilibrium could be obtained within 90 min, and the adsorption kinetic followed the pseudo-second-order model. From the Langmuir isotherm, the maximum adsorption capacity for Pb (II) was 64.10 mg/g at 25 °C. Fourier transform infrared spectroscopy (FTIR) analysis revealed that carboxyl and hydroxyl functional groups were mainly responsible for the adsorption of Pb (II). These suggested that the low-cost ATTR could be used as a potential and appealing adsorbent for the removal of Pb (II) from aqueous solutions.

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1. Introduction

Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. It is well known that lead, a highly toxic metal, is considered as a priority pollutant.

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Lead is often discharged in a number of industrial processes, especially manufacturing batteries, electroplating, pigments and ammunition production, which can lead to water contamination in turn. Lead is not biodegradable and tends to accumulate in living organisms causing diseases and disorders [1]. Therefore, removal of lead from wastewater is currently one of the most important environmental issues being investigated. Treatment processes of Pb (II) removal from wastewater through adsorption or ion exchange of adsorbents have recently been studied [2,3]. However, application of such methods was sometimes restricted because of technical or economical constraints. It has become a challenge for researchers to seek cheaper and more effective adsorbents for lead removal.

Tea is the most widely consumed beverage after water throughout the world for its beneficial effects on health, such as antioxidant, anticarcinogenic, antimicrobial activities [4,5]. In China alone, the annual production of tea was close to 135 million tons in 2009 and is increasing by 8.7% per year. During the tea production procedure, high quality tea leaves are selected for the production of dried green tea or fermented tea, while low quality tea leaves are used for the production of tea beverages and for the extraction of tea polyphenol, caffeine, tea polysaccharide, etc. A great number of tea residues are produced for the production of tea beverages and extraction, and usually discarded into the environment without any treatment, which is not only a waste of resource, but also causes environmental hygiene problems during their degradation process. Therefore, it is desirable to reuse these tea residues.

It has been reported that tea residue is largely composed of cellulose, hemicelluloses, lignin, condensed tannins and structural proteins. Cellulose, hemicelluloses, lignin and condensed tannins have good potential as metal scavengers from solutions and wastewaters since they contain functional groups of carboxylate, aromatic carboxylate, phenolic hydroxyl and oxyl groups [6], which have relatively strong physical and chemical adsorption of metal ions [7]. Several researchers have stated that tea residue could be used as adsorbent for Cu (II), Cd (II) [8], Pb (II) [9], Zn (II) [10], and so on. However, the removal rate of metal ions is relatively low and can be improved by activated tea residue. Several studies [11,12] have reported that the activated tea residue showed very good promise for metal ions removal.

The objectives of the present study are to evaluate the following: (1) the removal rate of Pb (II) with alkali treated tea residue; (2) the adsorption characteristics of Pb (II) on alkali treated tea residue; and (3) the mechanism underlying the adsorption.

2. Materials and methods

2.1. Chemicals and materials

Pb (NO$_3$)$_2$, NaOH and HCl, obtained from Shanghai Chemical Reagent Company, are all analytical grade. Their purity is above 99.5%, above 96.0% and 36.0–38.0%, correspondingly. Synthetic wastewater solutions were prepared by dissolving Pb (NO$_3$)$_2$ in deionized water to obtain 1000 mg/L Pb (II) solutions. The solution was diluted to the required concentrations for experiments. The solution pH was measured and observed as (4.5 ± 0.2) and no chemicals were added to change the pH.

2.2. Preparation of adsorbent

Waste tea leaves, obtained from tea plant located in Huazhong agricultural university (China), were used for adsorbent development. Soluble and colored components were removed thoroughly from the tea by washing with boiling water. Then, the washed tea residues were soaked in 0.5 mol/L NaOH for 0.5 h to hydrolyze protein. The alkaline hydrolyzed sample was collected and rinsed with distilled water till the wash solution was neutral, and oven dried for 12 h at 80 °C. The dried sample was sieved to obtain the desired particle size (0.150–0.425 mm) and stored in a desiccator for further use.

2.3. Comparative study of Pb (II) removal on ATTR, green tea and green tea residue

A comparative study of Pb (II) removal from the solution on ATTR, green tea and green tea residue was conducted. The study was carried out at 25 °C by adding 0.1 g of different adsorbent into

a number of 250 mL glass stoppered conical flasks containing 100 mL of 50 mg/L Pb (II) solution. The flasks were placed on a rotary shaker at 160 rpm for 2 h. After centrifugation, the supernatant was analyzed for final Pb (II) concentration. Pb (II) removal rate was calculated as

$$Pb\ (II)\ \text{removal rate}\ (\%) = [(C_i - C_f)/C_i] \times 100 \tag{1}$$

where C_i and C_f are the initial and final Pb (II) concentration, respectively.

2.4. Batch adsorption experiments

Batch adsorption experiments included the effect of contact time, adsorbent dosage, initial Pb (II) concentration and initial solution pH. Batch experiments were carried out at 25 °C by adding known weight of ATTR into a number of 250 mL glass stoppered conical flasks on a rotary shaker at 160 rpm containing 100 mL Pb (II) solution of desired concentration. The effect of contact time was conducted by shaking 0.25 g of ATTR and 200 mg/L Pb (II) solution for different time (5, 10, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 180 min). The effect of adsorbent dosage was conducted by adding desired amounts of ATTR (0.1, 0.2, 0.3, 0.4, 0.5 g) to a series of concentrations (5, 10, 30 and 50 mg/L) Pb (II) solutions for 120 min. The effect of initial pH was conducted by mixing 0.25 g of ATTR with 200 mg/L Pb (II) solution at various pH values ranging from 2.0 to 6.0 for 120 min. Solution pH was adjusted with 0.5 mol/L HCl and NaOH solutions. The effect of initial Pb (II) concentration was conducted by adding 0.25 g of ATTR to Pb (II) solutions of various concentrations (100, 200, 400, 600, 800, 1000 mg/L) for 120 min.

2.5. Metal analysis and adsorbent characteristics

Atomic absorption spectrophotometry was used for Pb (II) analysis. Surface morphology of ATTR, green tea and green tea residue was identified by ALEO DSM 982 Gemini digital field emission scanning electron microscope (SEM, UK). The functional groups of the adsorbent were detected by FTIR spectroscopy (Thermo Nicolet AVATAR-330 Spectrometer, Thermo Nicole Corporation, USA). The point of zero charge (pH_{pzc}) of the adsorbent in aqueous phase was analyzed with ion adsorption measurements described by Uehara and Gillman [13].

2.6. Statistical analysis

All experiments were performed in duplicate and the mean values were presented. The data were analyzed by one-way analysis of variance (ANOVA) using SPSS 11.5 for Windows. The data was considered statistically different from control at $P < 0.05$.

3. Results and discussion

3.1. Adsorbent characteristics

SEM images of ATTR, green tea and green tea residue are shown in Fig. 1. These results revealed that their surface morphologies were obviously different. Green tea consisted of irregular particles ranging from 3 to 20 μm (Fig. 1a); green tea residue mainly consisted of fibers in diameter from 1 to 10 μm with open stomata (Fig. 1b); ATTR consisted of fibers with significant pore and uneven surface structure (Fig. 1c), which indicated that the surface area of green tea residue was increased for alkali treatment and the surface of ATTR was rougher than that of green tea and green tea residue. The surface of Pb (II)-loaded ATTR is shown in Fig. 1d, which indicated that the surface of ATTR was covered with Pb (II). The result in Fig. 2 shows that the surface charge of ATTR at pH 2.8 ± 0.1 was zero. Hence, the pH_{pzc} of ATTR was 2.8 ± 0.1.
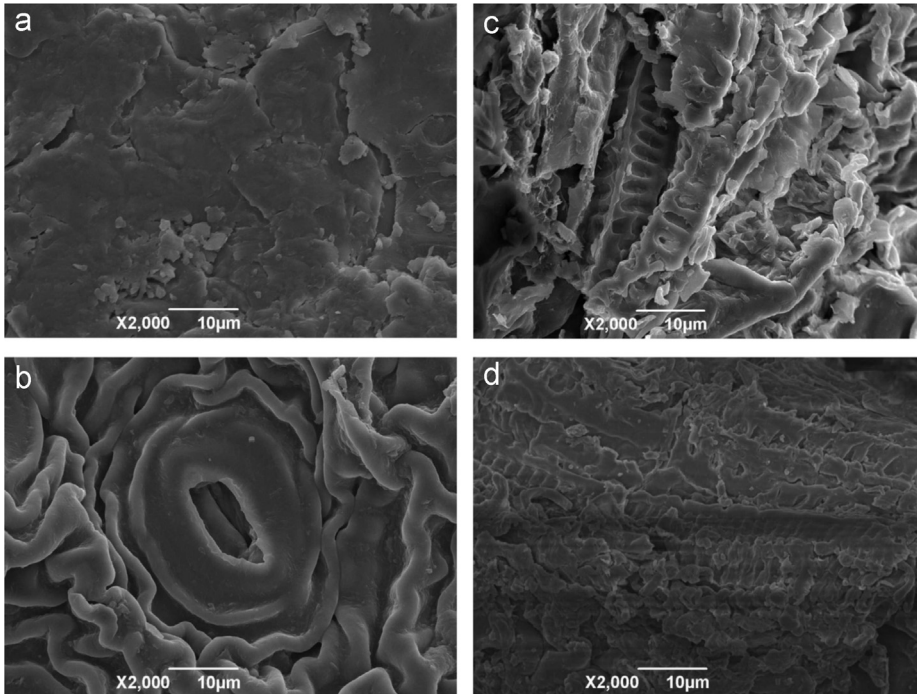
Fig. 1. SEM images of (a) green tea; (b) green tea residue; (c) ATTR; and (d) Pb (II)-loaded ATTR.
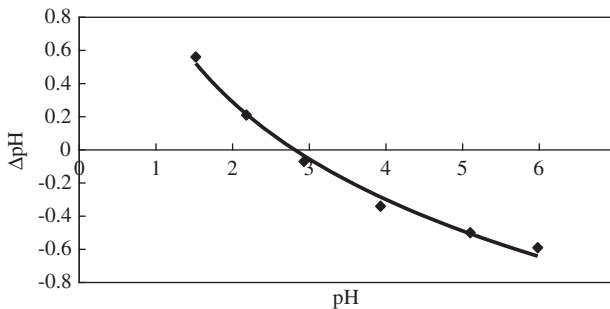

Fig. 2. pH of zero charge of ATTR.

3.2. Comparative study of Pb (II) removal on ATTR, green tea and green tea residue

The removal rates of Pb (II) on ATTR, green tea and green tea residue were conducted, respectively. The results showed that the removal rate of Pb (II) on ATTR (98.54%) was significantly higher than that on green tea (64.18%) and green tea residue (70.73%) at 50 mg/L of Pb (II) concentration ($P < 0.05$). Šćiban et al. [14] also reported that the adsorption capacity of sawdust after being treated with NaOH was significantly increased. It has been reported that the treatment with NaOH could remove the surface impurities of adsorbent and expose the active sites for metal adsorption [15]. Our SEM images also confirmed that the surface area of ATTR was larger than that of green tea and green tea residue. These might be the reason of the increase in Pb (II) adsorption on ATTR. Therefore, ATTR had the potential of being used as an efficient adsorbent.

3.3. Effect of contact time and adsorption kinetic

Fig. 3 shows the effect of contact time on the adsorption of Pb (II). It was observed that the adsorption capacity of ATTR increased with increasing contact time at the initial stage, and then gradually increased to reach an equilibrium value in approximately 90 min. The fast adsorption in the initial stage of adsorption was attributed to the large amount of active sites available. Thus, the progressive decrease of adsorption sites resulted in a slower adsorption reaction. According to these results, the contact time was fixed at 2 h for the rest of the batch experiments to make sure that the equilibrium was reached.

Pseudo-first-order and pseudo-second-order kinetic models are used to evaluate experimental data. The pseudo-first-order kinetic model is expressed as follows [2]:

$$\log(Q_e - Q_t) = \log Q_e - k_f t / 2.303 \tag{2}$$

The pseudo-second-order model is expressed as follows:

$$t/Q_t = 1/k_s Q_e{}^2 + t/Q_e \tag{3}$$

where Q_e is the amount adsorbed (mg/g) at equilibrium, Q_t the amount adsorbed (mg/g) at time t, k_f (min^{-1}) and K_s (g/mg min) the adsorption rate constants, respectively. The kinetic parameters calculated are given in Table 1. It was found that the pseudo-second-order model (0.998) provided a better coefficient than the pseudo-first-order model (0.910). This implied that the adsorption kinetic of Pb (II) on ATTR was fitted to the pseudo-second-order model. Similar phenomena have been observed in adsorption of methylene blue on tea waste [16].

3.4. Effect of initial Pb (II) concentration and adsorption isotherm

The adsorption capacity of ATTR for Pb (II) under different initial Pb (II) concentrations is shown in Fig. 4. It was clear that the adsorption capacity increased from 39.36 to 63.33 mg/g with an increase of initial Pb (II) concentration from 100 to 1000 mg/L until equilibrium was reached. This might be attributed to an increase in the driving force of the concentration gradient with the increase of initial Pb (II) concentration [17].
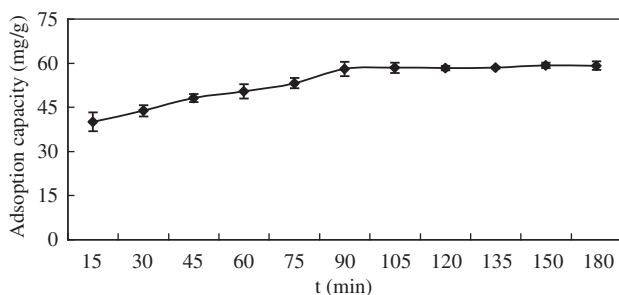

Fig. 3. Effect of contact time on the adsorption capacity for Pb (II) on ATTR (pH: 4.5; at 25 °C; adsorbent dosage: 2.5 g/L; initial Pb (II) concentration: 200 mg/L).

Table 1
Kinetic parameters of Pb (II) on ATTR (pH: 4.5; T: 25 °C; adsorbent dosage: 2.5 g/L; initial Pb (II) concentration: 200 mg/L).

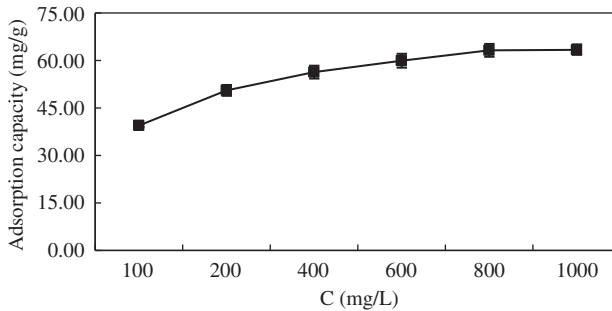| Kinetic constants	Pseudo-first-order model			Pseudo-second-order model		
	K_f (min^{-1})	Q_e (mg/g)	R^2	K_s (g/mg min)	Q_e (mg/g)	R^2
Magnitude	0.0325	40.570	0.910	1.260×10^{-3}	63.694	0.998

Fig. 4. Effect of initial Pb (II) concentration on the adsorption capacity for Pb (II) on ATTR (pH: 4.5; T: 25 °C; equilibrium time: 2 h; adsorbent dosage: 2.5 g/L).

Table 2
Langmuir and Freundlich isotherm constants for the adsorption of Pb (II) on ATTR (pH: 4.5; T: 25 °C; equilibrium time: 2 h; adsorbent dosage: 2.5 g/L).

Isotherm constants	Langmuir			Freundlich		
	Q_0 (mg/g)	b (L/mg)	R^2	K_F (mg/g)	$1/n$	R^2
Magnitude	64.103	0.0519	0.999	4.774	0.0802	0.990

Adsorption isotherm is important to describe how solute interacts with adsorbent. Two isotherm models, Langmuir and Freundlich, are used to describe the equilibrium adsorption isotherms. Langmuir isotherm model is expressed as follows:

$$C_e/Q_e = C_e/Q_0 + 1/bQ_0 \tag{4}$$

Freundlich isotherm model is expressed as follows:

$$\ln Q_e = \ln K_F + 1/n \ln C_e \tag{5}$$

where C_e is the equilibrium concentration of metal ion (mg/L), Q_e the amount of metal ion absorbed at equilibrium per unit mass of adsorbent (mg/g), Q_0 and b the Langmuir constants related to adsorption capacity and energy of adsorption, and K_F and $1/n$ the Freundlich model constants, indicating the adsorption capacity and adsorption intensity, respectively [18]. The linear plot of C_e/Q_e versus C_e shows that the adsorption obeys the Langmuir model. Q_0 and b are determined from the slope and intercept of the plot. The linear plot of $\ln Q_e$ versus $\ln C_e$ indicates the applicability of the Freundlich model.

The Langmuir and Freundlich constants and their correlation coefficients (R^2) evaluated from these isotherms are given in Table 2. The results showed that the maximum adsorption capacity was obtained with a value of Q_0 of 64.10 mg/g from the Langmuir model and with a value of K_F of 4.77 mg/g from the Langmuir model. The R^2 value is an important parameter for selecting the best isotherms model. The higher R^2 value suggests that the model describes the adsorption data more effectively [19]. The results in Table 2 revealed that both models were suitable for describing the adsorption equilibrium of Pb (II), while the adsorption process was well patterned by the Langmuir Isotherm. It is well known that the Langmuir equation is intended for a homogeneous surface and a good fit of this equation reflects monolayer adsorption. The Freundlich equation is suitable for homogeneous and heterogeneous surfaces, indicating a multi-layer adsorption [20]. These suggest that the adsorption of Pb (II) on the ATTR mainly takes place at specific homogeneous sites and is confined to one layer adsorption, which well explained that the increase in Pb (II) adsorption on ATTR is due to the increase of the surface area of ATTR compared to green tea and green tea residue.

To confirm the feasibility of the adsorption process followed the Langmuir isotherm, a dimensionless constant separation factor, R_L, is calculated by the following equation:

$$R_L = 1/(1 + bC_0) \tag{6}$$

where b is the Langmuir constant and C_0 is the initial concentration of Pb (II). R_L describes the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [21]. As seen in Table 3, the values of R_L at different concentrations of Pb (II) were between 0 and 1, which showed a favorable adsorption of Pb (II) on ATTR under study. The results were consistent with the report that the adsorption of Pb (II) on the activated carbon obeyed the Langmuir model [22].

3.5. Effect of initial pH

The initial pH value of a solution may change the surface charge of an adsorbent, the degree of ionization of an adsorbate molecule and the extent of dissociation of functional groups on the active sites of an adsorbent [23], thus affecting the adsorption capacity of the adsorbent. Therefore it plays an important role in the adsorption of Pb (II) on ATTR. As shown in Fig. 5, the adsorption capacity was only 1.18 mg/g at pH 2.0, and then it increased with increasing pH and reached up to a maximum value of 59.45 mg/g at pH 4.5. After that, it decreased very slowly up to the pH of 6.0. A similar behavior has been reported by [24] for the adsorption of Pb (II). This phenomenon can be explained by the surface charge of the adsorbent and the H^+ ions present in the solution. At pH $<$ pH$_{pzc}$, ATTR becomes positively charged due to the adsorption of H^+. Thus the electrostatic force of repulsion between ATTR and Pb (II) is prominent. In addition, the concentration of H^+ is high at low pH and they compete with Pb (II) in the solution for the active sites. Therefore the adsorption was very low. At pH $>$ pH$_{pzc}$, ATTR becomes negatively charged due to the adsorption of OH^- and the electrostatic attraction force between ATTR and Pb (II) is prominent. Moreover, as pH increases, the competition of H^+ with Pb (II) decreases as these surface active sites become more negatively charged [25]. Thus the

Table 3
Equilibrium parameter R_L at different initial Pb (II) concentrations (pH: 4.5; T: 25 °C; equilibrium time: 2 h; adsorbent dosage: 2.5 g/L).

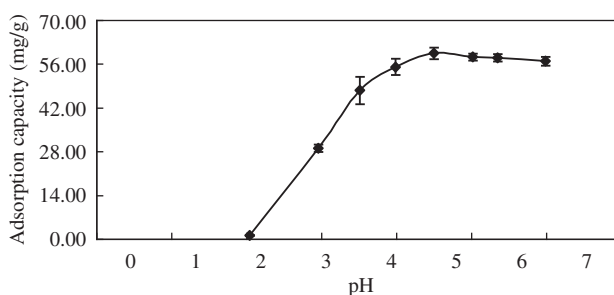| Concentration (mg/L)	Equilibrium parameter (R_L)
100	0.66
200	0.49
400	0.33
600	0.24
800	0.19
1000	0.15

Fig. 5. Effect of pH on the adsorption capacity for Pb (II) on ATTR (equilibrium time: 2 h; T: 25 °C; adsorbent dosage: 2.5 g/L; initial Pb (II) concentration: 200 mg/L).
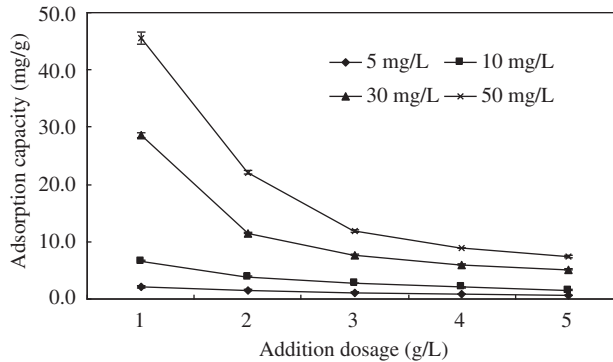
Fig. 6. Effect of adsorbent dosage on the adsorption capacity for Pb (II) on ATTR (pH: 4.5; T: 25 °C; equilibrium time: 2 h; initial Pb (II) concentration: 5, 10, 30 and 50 mg/L).

adsorption process is favored at high pH. A precipitate of lead hydroxide will play a leading role during heavy metal removal process at pH above 6.0 [26].

3.6. Effect of adsorbent dosage

The effect of ATTR dosage on the adsorption capacity at various initial Pb (II) concentrations is shown in Fig. 6. It was observed that the adsorption capacity of ATTR decreased from 2.09 mg/g to 0.63 mg/g with the increase of ATTR dosage from 1 to 5 g/L at an initial Pb (II) concentration of 5 mg/L. Similarly, the adsorption capacity decreased from 45.60 mg/g to 7.46 mg/g by the same increase of ATTR dosage at an initial Pb (II) concentration of 50 mg/L. The data indicated that the amount of Pb (II) adsorbed on ATTR decreased with the increase of ATTR dosage. This may be due to the fact that some adsorption sites remain unsaturated during the adsorption process when the number of available adsorption sites increases owing to the increase of the adsorbent dosage at high concentration of the adsorbent [1].

3.7. FTIR spectroscopy of ATTR and Pb (II)-adsorbed ATTR

The FTIR spectroscopy of ATTR before and after Pb (II) adsorption is shown in Fig. 7. It was seen that the peaks (Fig. 7a) could be assigned as follows: 3412 cm^{-1} (γ OH), (2919 and 2850) cm^{-1} (γ C–H asymmetric and symmetric in CH, CH$_2$, and CH$_3$ cm^{-1} (γ C=O), 1465 cm^{-1} (δ CH$_3$ and δ_S CH$_2$), 1737 cm^{-1} (δ CH$_3$ symmetric in CCH$_3$), 1059 cm^{-1} (γ C–O), where γ represented a stretching vibration, δ a blending vibration and δ_S a scissor vibration. An obvious change was observed on the spectrum of ATTR-adsorbed Pb (II). The adsorption bands at 3412, 2919, 2850, 1634, 1373 and 1059 cm^{-1} (Fig. 7a) had shifted, respectively, to 3399, 2920, 2851, 1636, 1383 and 1058 cm^{-1} due to Pb (II) absorption (Fig. 7b). These shifts might be attributed to ion exchange associated with carboxylate and hydryoxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, were predominant contributors in metal ion uptake [17].

4. Conclusions

ATTR was developed from tea residue, a tea production waste, treated with NaOH. SEM observation of green tea, green tea residue and ATTR indicated that ATTR had a relatively rough and irregular surface structure. The pH$_{pzc}$ of ATTR was 2.8 ± 0.1. Comparative study showed that ATTR displayed a significantly higher removal rate of Pb (II) than green tea and green tea residue. The results of batch equilibrium studies showed that the solution pH was the key factor affecting the adsorption characteristics. The adsorption capacity for Pb (II) increased as the solution pH increased and then
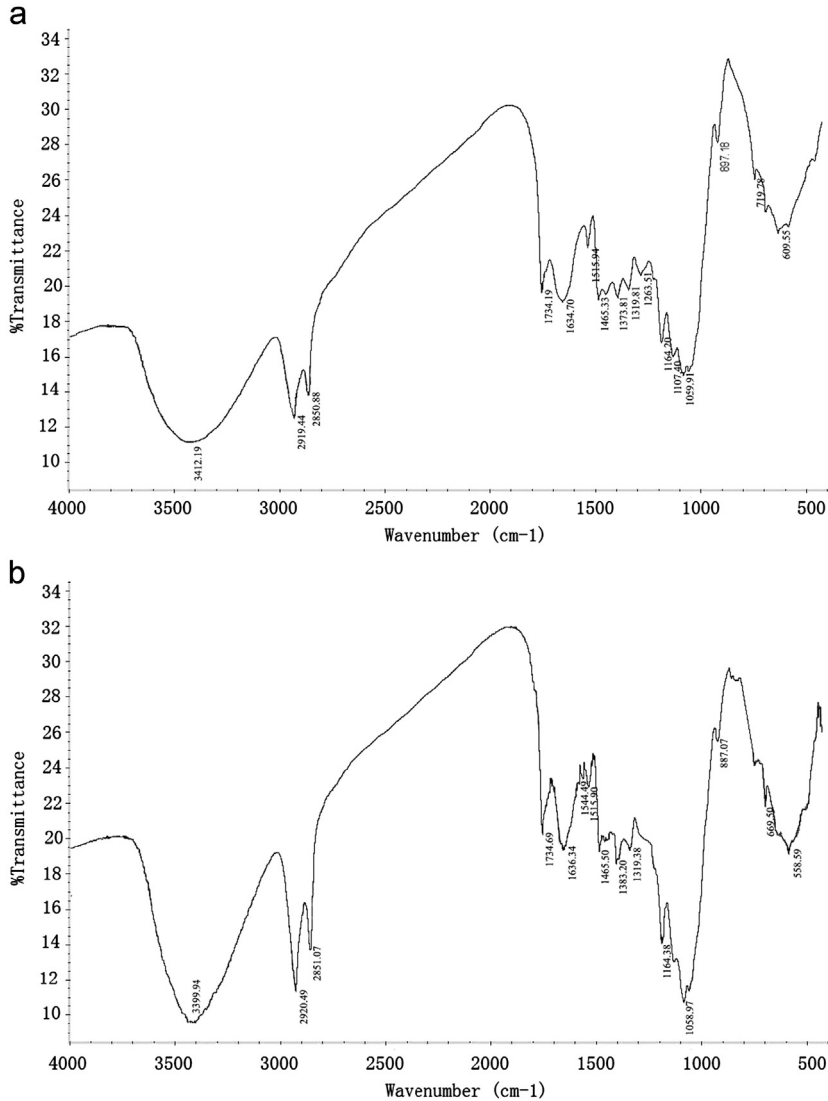
a

b

Fig. 7. FTIR spectra of (a) ATTR and (b) Pb (II)-adsorbed ATTR.

reached the maximum at pH 4.5. The adsorption capacity decreased as the adsorbent dosage increased at different initial Pb (II) concentrations. Several kinetic and isotherm equations were employed to model the adsorption of Pb (II). It was found that the kinetic fitted the pseudo-second-order model and the isotherm fitted the Langmuir model with high correlation coefficient. According to the Langmuir model, the maximum adsorption capacity for Pb (II) was obtained with a value of Q_0 of 64.10 mg/g.

FTIR spectroscopy studies showed that the adsorption bands of ATTR at 3412, 2919, 2850, 1634, 1373 and 1059 cm^{-1} before adsorbing Pb (II) had respectively shifted to 3399, 2920, 2851, 1636, 1383 and 1058 cm^{-1} after adsorbing Pb (II), which indicated that ATTR had adsorbed Pb (II). These suggested that ATTR could be used as a potential and appealing adsorbent for the removal of Pb (II) from aqueous solutions.

Acknowledgments

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