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Adsorption study of Pb(II) by chemically modified cattail stem

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ABSTRACT

A series of new chemically modified cattail stem adsorbents were prepared and the feasibility of adsorbents to remove Pb(II) ion from aqueous solution was examined. Structural and textural modifications of cattail stem powder which occurred during the synthesis of adsorbents were confirmed by infrared spectroscopy (IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetry (TG). The effectiveness of the adsorbents in Pb (II) removal from aqueous solutions at different initial concentrations, pH, and temperature of the solutions was studied. Higher pH favors higher Pb(II) removal in acid solution. Increase in temperature results in a larger Pb(II) loading per unit weight of the adsorbents. The equilibrium adsorption data were analyzed using two widely applied isotherms: Langmuir and Freundlich. The isothermal data for CC and MC (cattail stem powder modified by 1.0 M citric acid and malic acid, respectively) were fairly well fitted with Langmuir equations. The maximum adsorption capacities obtained from Langmuir model were 352.2 and 299.2 mg/g by using CC and MC. The thermodynamic parameters of the cattail adsorbents, ΔH, ΔS, and ΔG, were calculated. The negative ΔG values of Pb(II) at various temperatures confirmed the adsorption processes were spontaneous.

Keywords: Modified cattail stem adsorbent; Lead ion; Adsorption; Kinetics; Isotherm

1. Introduction

Growing attention is being given to health hazards caused by the existence of heavy metals in the aqueous environment and their accumulation in living tissues poses a serious health problem. Lead has been considered as one of the most toxic pollutants and because of its suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, causing sterility, kidney problem and high blood pressure to the public, it has become a serious health concern. The presence of lead ion (Pb(II)) in some water bodies for human consumption and in industrial wastewater has been the cause of great attention and called for development of several new materials with great potential to treat such waters for Pb(II) removal [1–4]. Generally, the techniques employed for lead ion removal include reduction and precipitation, coagulation, lime softening, adsorption, and ion exchange [5,6]. Although, all these techniques afford moderate to efficient Pb(II) removal, due to ready availability and cost effectiveness, the biological waste materials such as starch [7], straw [8], tea waste [9], peat moss [10], sugar cane pulp [11], coconut hulls [12], as well as aquatic plant materials [13] have attracted the attention of investigators in the area of Pb(II) adsorption.

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Cattail is an aquatic plant and has been widely used in artificially constructed wetlands for the removal and mineralization of phenol [14], treatment of high-strength wastewater [15], and removal of phosphorous and heavy metals [16]. However, the cattail biomass produced in the phytoremediation probably becomes a potential pollution source like water hyacinth if it is not properly managed. Previous studies have shown that cattail biomass could be subjected to a feedstock for biofuel production [17]. Cattail stem has a porous structure and a large surface area, which might be utilized as adsorbent to treat Pb(II) wastewater. However, the use of chemically modified cattail stem for removal of Pb(II) from aqueous solution has not been described. Thus, providing useful information about the removal characteristics of cattail stem may be essential for understanding its lead ion removal capacity and gives us a new direction to select biological materials which are competent for the remediation of lead pollution.

The aims of the present investigation are to detect the performance of cattail stem powder on Pb(II) removal from aqueous solution and to evaluate the effect of various parameters including pH, initial Pb (II) concentration, temperature, solid/liquid ratio, and contact time. Furthermore, adsorption isotherms are conducted and the mechanism of cattail adsorbents for the removal of Pb(II) is discussed.

2. Materials and methods

2.1. Adsorbents

2.1.1. Raw material

Cattail stem used in this study was collected from a local pond in Shanghai, China. The stem was washed with tap water to remove soil and dust, sprayed with deionized water, and dried to a constant weight at 75℃.The dry cattail stem was ground and sieved to obtain powder with particle sizes of 0.15–0.40 mm. Dried cattail stem powder (40 g) and 700 mL 20% isopropyl alcohol were added together into a beaker and stirred for 24 h at room temperature, then filtered and washed with deionized water until the filtrate was colorless. The filter residue was dried in an oven at 75℃ for 12 h and used in our experiments as raw material, hereafter abbreviated as RC.

2.1.2. Modified with NaOH

RC (4 g) was treated with 0.1 M NaOH (100 mL), stirred for 10 min, and left overnight. It was then filtered and washed with deionized water to remove excess lignin-containing alkali. The filter residue was dried in an oven at 75℃ for 12 h. This alkali-treated cattail powder was abbreviated as AC.

2.1.3. Modified with citric acid

Modification of RC with citric acid was carried out using the method reported by Marshall et al. [18]. RC was mixed in a ratio of 1 g powder to 7 mL of 1.0 M citric acid and the acid/powder slurry was dried overnight at 50℃. The material was subsequently heated at 120℃ for 90 min, then washed with 200 mL distilled water per each gram to remove excess citric acid, and was dried at 75℃ for 12 h. This citric acid-treated cattail powder was abbreviated as CC.

2.1.4. Modified with malic acid

Another adsorbent was prepared by the above pretreatment with only a change of 1.0 M malic acid instead of citric acid. This malic acid-treated cattail powder was abbreviated as MC.

2.1.5. Modified with tartaric acid

The last adsorbent was obtained by the same treatment process of citric acid modification with only a change of 1.0 M tartaric acid instead of citric acid. This tartaric acid-treated cattail powder was abbreviated as TC.

2.2. Reagents and measurements

The stock solution of Pb(II) was prepared by dissolving a weighed quantity of lead nitrate in 10 mL 3% HNO_3 and 10 mL 25% hexamethylene tetramine buffer solution (pH 5.0) and diluting quantitatively to a volume of 250 mL. Before mixing with cattail powder adsorbents, initial pH of each solution was adjusted to an appropriate value by adding 0.1 M HNO_3 or/and NaOH solutions. All the reagents were of analytical grade. A PHS-3C model acidity meter (made in China) was used to measure pH values of all solutions. The concentration of Pb(II) was titrated with standard EDTA solution, 0.1% xylenol orange was chosen as indicator, and 25% hexamethylene tetramine was used as buffer solution.

2.3. Instruments used for characterization

The infrared spectra of the cattail powder adsorbents were recorded with a Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrophotometer using potassium bromide disks. X-ray diffraction (XRD) was measured by a Bruker-D8 Advance wide angle X-ray diffractometer (WAXD) at scan speed of 9°/min. Surface morphology of the adsorbents was identified by Philips XL-30 scanning electron microscope (SEM). The thermal characteristics of the adsorbents were examined by TG peaks using a TG 209 F1 Iris instrument.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted by agitating 0.030 g of adsorbent with 20 mL of lead ion solution of desired concentration in 50 mL flask for specific time. The effect of solution pH on the equilibrium adsorption of Pb(II) was investigated under similar experimental conditions between pH 2.1 and 6.1. In the kinetic experiments, 1.00 mM lead ion solution was used. The adsorption time was varied between 5 and 240 min. In the isotherm experiments, 0.030 g of adsorbent was added in 20 mL of lead solution at various concentrations (0.48–9.65 mM). Once the preset contact time reached, the samples were withdrawn and centrifuged at 3,000 rpm for 5 min and the supernatant solutions were analyzed for the residual metal ion concentration by titration with standard EDTA solution (0.1% xylenol orange was chosen as indicator). All the adsorption experiments were conducted in duplicate, and the mean values were reported.

2.5. Analysis

The adsorption amount (q) and the removal percentage (E%) were calculated according to Eqs. (1) and (2):

$$q = (C_0 - C_e) \times V/W \tag{1}$$

$$E\,\% = (C_0 - C_e) \times 100/C_0 \tag{2}$$

where q is the adsorption amount of metal ion (mmol/g), W is the weight of adsorbent (g), V is the volume of solution (L), and C_0 and C_e are the initial and equilibrium concentrations of Pb(II) in solution, respectively (mM).

2.5.1. Kinetics models

Pseudo-first-order kinetic model [19] is generally expressed as Eq. (3):

$$\ln((q_e - q_t)/q_e) = -K_1 t \tag{3}$$

where q_t and q_e are the amounts of Pb(II) adsorbed (mmol/g) at the time t and equilibrium time, K_1 is the pseudo-first-order rate constant (L/min).

Pseudo-second-order kinetic model [20] is expressed as following formulation:

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \tag{4}$$

where K_2 is the pseudo-second-order rate constant (g/(mmol min)).

2.5.2. Isotherm models [21]

Langmuir model:

$$1/q_e = 1/q_m + 1/(q_m b C_e) \tag{5}$$

where q_m is the maximum adsorption amount of metal ion per unit weight of adsorbent at C_e, b is the affinity constant.

Freundlich model:

$$\ln q_e = (1/n) \ln C_e + \ln K_f \tag{6}$$

where K_f and n are the Freundlich constants.

3. Result and discussion

3.1. Characters of cattail adsorbents

The FTIR spectra of cattail adsorbents are shown in Fig. 1. In all spectra, the broad and intense absorption peaks at 3,419 cm^{-1} correspond to the O–H stretching vibrations of cellulose, pectin, absorbed water, hemicellulose, and lignin [22]. The peaks

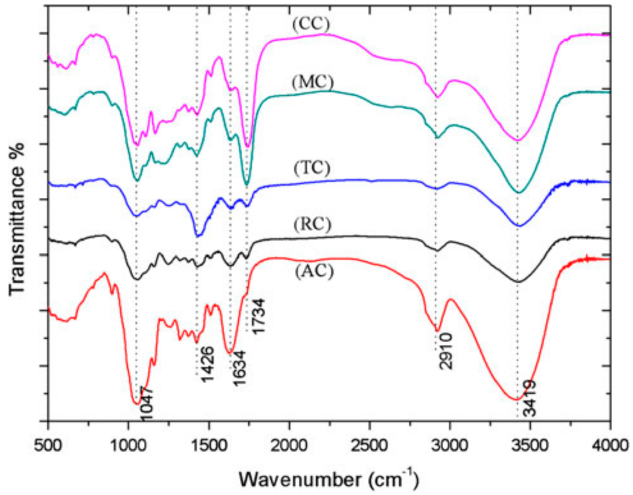

Fig. 1. FTIR spectra of cattail adsorbents.

observed at 2,910 cm^{-1} can be attributed to the C–H stretching vibrations of methyl, methylene, and methoxy groups. The peak at 1,734 cm^{-1} in the RC spectrum shows the carbonyl (C=O) stretching vibration of the carboxyl groups of pectin, hemicellulose, and lignin in RC. The peaks around 1,634 cm^{-1} are due to the C=C stretching that can be attributed to the presence of aromatic or benzene rings in lignin. The vibrations around 1,426 cm^{-1} can be due to aliphatic and aromatic (C–H) groups in the plane deformation vibrations of methyl, methylene, and methoxy groups. The bands around 1,047 cm^{-1} can be assigned to the C–O stretching vibration of carboxylic acids and alcohols. Comparing AC to RC, it is observed that the peaks at 3,419, 2,910, 1,634, and 1,047 cm^{-1} become stronger, revealing more active groups appear on AC after alkali treatment. For TC, it has similar spectrum as RC, except that the peak at 1,426 cm^{-1} becomes broad and strong, indicating cattail substrate really reacts with tartaric acid. Comparing with the IR spectrum of RC, it can be seen that there is a strong characteristic stretching vibration absorption band of carboxyl group at 1,734 cm^{-1} in spectrum of CC or MC. It reflects the result of citric acid or malic acid esterification [23]. Through changes of different peaks, it discloses that some functional groups (–COOH and –OH) have been successfully introduced into the surface of adsorbents after chemical modification.

The XRD patterns of cattail adsorbents are presented in Fig. 2. The diffractions at RC of 14.9°, 22.3°, 24.5 °, 30.2, °and 38.4° are observed, which are attributed to the typical crystalline form of stem or straw of many natural plants as reported in the references [24,25]. For other adsorbents (AC, CC, MC, and TC), the peak positions do not change. However, comparing with RC, the peak intensity of all the modified samples at 24.5° declines markedly, indicating the decrease in crystallinity. This may be due to the reactions between the chemical reagents (NaOH, citric acid, malic acid, and tartaric acid) and RC, which translate crystalline regions into noncrystalline regions. Thus, the accessibility and reactivity of functional groups on the cattail adsorbents are improved observably.

The surface morphology of the unmodified and modified cattail adsorbents is given in Fig. 3. RC has a very smooth and compact surface, and some grains are observable along the vertical section. The surface of AC is quite similar to that of RC, except that some lignin constructions [26] on its surface are cleaned. After reacting with acids, the surface of the adsorbents (CC, MC, and TC) becomes rough and some fractures and fragments are emerged. Thus, the surface area of these samples is greatly enlarged indicating the adsorption ability of CC, MC, and TC will be predictably improved. Comparison of the micrographs reveals that modification significantly changes the morphology of the surface structure of RC. Due to the irregular surface, it makes possible the adsorption of metals in different parts of these cattail materials [27].

The TG analysis of RC, AC, CC, MC, and TC was done in order to address their thermal stability and the results are shown in Fig. 4. The TG curves indicate the better thermal stability of RC with respect to other materials. The decomposition temperature, T_D, is

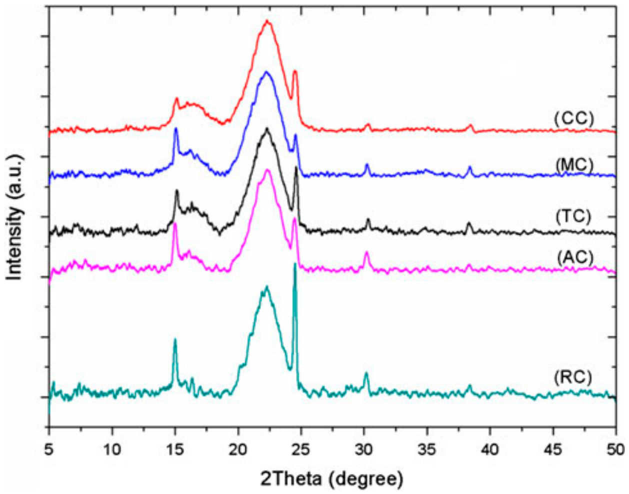

Fig. 2. XRD patterns of cattail adsorbents.

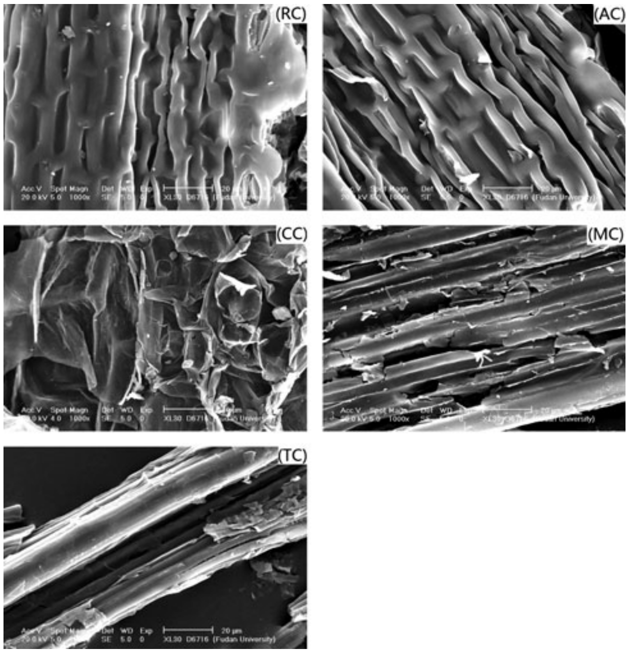

Fig. 3. SEM images of cattail adsorbents.

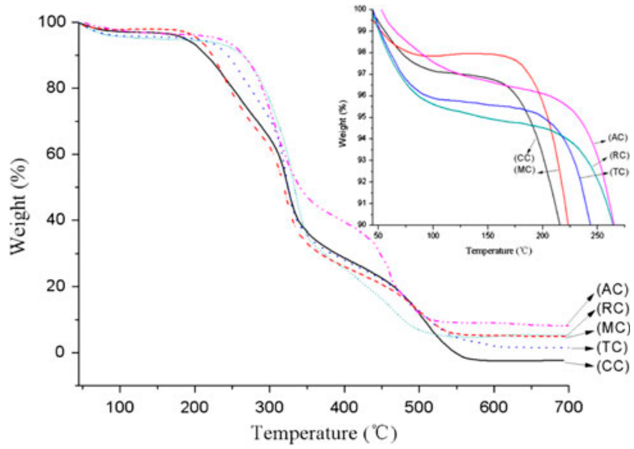

Fig. 4. TG curves of cattail adsorbents.

found to be 332, 325, 323, 321, and 305℃ for RC, CC, TC, MC, and AC, respectively. The temperature for 10.0% weight loss (T_{10}) is a basic criterion used to indicate the thermal stability of materials (Fig. 4, insert picture) [28]. The values of T_{10} are found to be 264, 215, 244, 223, and 265℃ for RC, CC, TC, MC, and AC, respectively. From the results of T_D and T_{10}, it can be concluded that after treating with chemical reagents, the thermal stability of raw cattail substrate is deteriorated greatly.

So, based on the crystallinity, porous structure and irregular surface, thermal stability, as well as high amounts of introduced functional groups, it can be concluded that chemical modified cattail adsorbents present adequate physical and chemical characteristics to adsorb lead ion.

3.2. Effect of pH on Pb(II) adsorption

The pH is a significant factor in determining the form of the metallic species in aqueous media. It influences the adsorption process of metal ions as it determines the magnitude and sign of the charge on the ions. The distribution of Pb(II) species as a function of pH is displayed in Fig. 5. In the case of a low pH (<7), positively charged Pb(II) species are dominant [29]. In the case of high pH values (pH = 7–11), however, there are several Pb(II) species present with different charges. These include Pb $(OH)^+$ and $Pb(OH)_2$, and thus the removal of Pb(II) may possibly be accomplished by the simultaneous precipitation of Pb $(OH)_2$ and the adsorption of $Pb(OH)^+$. Furthermore, pH is also one of the most important parameters for controlling the surface charge of the adsorbents. In this experiment, the influence of pH on the adsorption capacity was studied over a range of pH values from 2.1 to 6.1 and not more than 6.1 to avoid lead precipitation. As shown in Fig. 5, it is observed that Pb(II) adsorption increases when the pH increases from 2.1 to 6.1 for cattail adsorbents. When the pH value is about 5.5, the adsorption capacity of the adsorbent almost reaches a maximum. This result indicates that the adsorption ability of these samples for Pb(II) is strong in near-neutral conditions and poor in strongly acidic conditions. Herein, the optimum pH range is chosen to be 5.5 ± 0.1. The solution pH diminishes after adsorption, which indicates that ion-exchange mechanism is involved in the adsorption process.

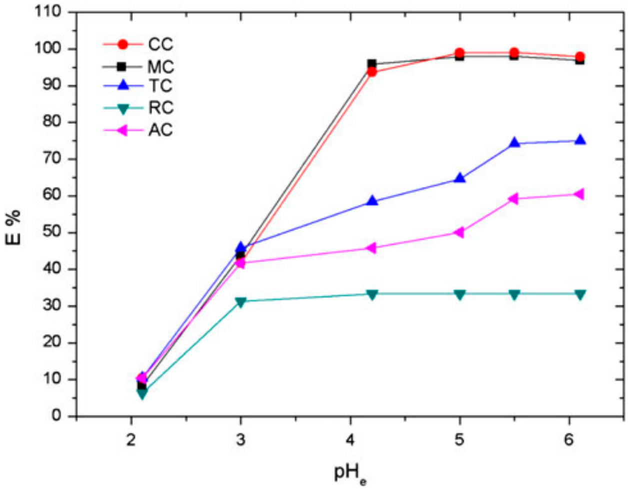

Fig. 5. Effect of pH on Pb(II) adsorption by different cattail adsorbents (weight: 0.030 g, Pb(II) solution: 20 mL, initial Pb(II) concentration: 1.00 mM, 20℃ for 4 h).

3.3. Effect of contact time and adsorption kinetics

Fig. 6 shows the effect of contact time on batch adsorption of 1.00 mM Pb(II) at 20℃. The amount of Pb(II) adsorption sharply increases with increasing contact time in the initial stage (0–20 min), and then gradually increases to reach an equilibrium value in approximately 120 min. According to the results in Fig. 6, the contact time was fixed at 4 h for the rest of the batch experiments to make sure that the equilibrium is reached.

In order to investigate the mechanism of adsorption of Pb(II) by cattail adsorbents and the potential rate-controlling steps, such as mass transport and chemical reactions, kinetic models were applied to evaluate the experimental data. For this purpose Lagergren's pseudo-first-order kinetic model and pseudo-second-order kinetic model were used. Pseudo-first-order model is rendered the rate of occupation of the adsorption sites to be proportional to the

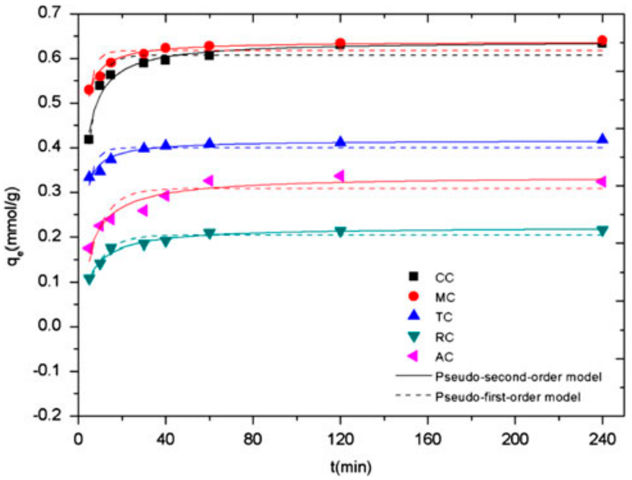

Fig. 6. Effect of contact time on Pb(II) uptakes by different cattail adsorbents (weight: 0.030 g, Pb(II) solution: 20 mL, initial Pb(II) concentration: 1.00 mM, initial pH: 5.5, 20℃).

number of unoccupied sites; pseudo-second-order kinetic model is assumed the chemical reaction mechanisms, and that the adsorption rate is controlled by chemical adsorption through sharing or exchange of electrons between the adsorbate and adsorbent [30,31].

Parameters of two kinetic models are given in Table 1. The best-fit model is selected based on both linear regression correlation coefficient (R^2) and the theoretical $q_{e(cal)}$ value. The pseudo-second-order rate equation for adsorption of Pb(II) onto cattail samples agrees well with the data for $R^2 = 0.922–0.977$. In addition, the theoretical $q_{e(cal)}$ values are closer to the experimental $q_{e(exp)}$. It can be said that the pseudo-second-order kinetic model provides a good correlation for the adsorption of Pb(II) onto cattail samples in contrast to the pseudo-first-order model. Therefore, the adsorption behavior of Pb(II) onto cattail adsorbents belongs to the pseudo-second-order kinetic model and the adsorption process is a chemical process.

Besides adsorption at external surface of adsorbents, there is a possibility of intraparticle diffusion from the external surface into the pore of adsorbents; this possibility is explored by plotting of q_t vs. $t_{1/2}$, according to Weber–Morris model, $q_t = K_{id}\ t_{1/2}$, [32] where K_{id} is the intraparticle diffusion coefficient. The plots are shown in Fig. 7. It can be seen that these plots are multilinear curves with three distinct regions. The initial curve stage relates the adsorption of external surface. The second region corresponds to the gradual uptake, which reflects intraparticle diffusion as the rate-limiting step. Final plateau region indicates equilibrium uptake. It shows that the intraparticle diffusion is not the only rate-controlling step [33].

3.4. Effect of initial Pb(II) concentration

Several experiments were undertaken to study the effect of initial Pb(II) concentration on the Pb(II) removal from the solution. The results obtained are shown in Fig. 8. For all the adsorbents, the data show that the metal uptake increases and percentage adsorption of the Pb(II) decreases with increase in initial Pb(II) concentration. For example, for MC, the percentage decrease is between 99.98 and 24.14% where the initial concentrations are increased between 0.48 and 9.65 mM. This is because at low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, at high concentrations, the driving force, i.e. concentration gradient is stronger, and the amount of Pb(II) adsorbed per unit weight of adsorbent, q_e, is higher. As a result, the cattail adsorbents are more efficient for the wastewaters of low ion concentrations, and the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations [34]. Under the condition of 1.50 g/L adsorbent, the ratio of Pb(II) adsorbed on CC or MC keeps above 90% over a range from 0.48 to 2.00 mM of lead concentration.

Table 1
Kinetic parameters of the pseudo-first- and pseudo-second- order model for Pb (II) adsorption

Adsorbent		The pseudo-first-order model			The pseudo-second-order model		
	$q_{e(exp)}$ (mmol/g)	R^2	$q_{e(cal)}$ (mmol/g)	K_1 (min^{-1})	R^2	$q_{e(cal)}$ (mmol/g)	K_2 (g/(mmol.min)
CC	0.633	0.922	0.607	0.223	0.965	0.639	0.668
MC	0.640	0.625	0.617	0.360	0.963	0.638	1.391
TC	0.417	0.569	0.399	0.311	0.925	0.416	1.630
RC	0.217	0.911	0.204	0.129	0.977	0.222	0.875
AC	0.330	0.754	0.308	0.129	0.922	0.336	0.569

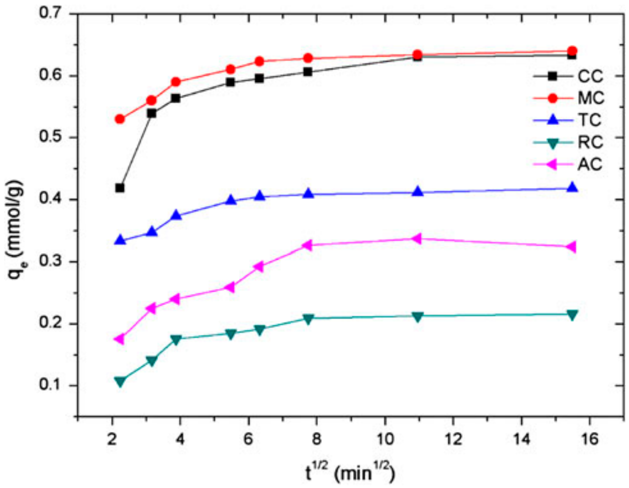

Fig. 7. Intraparticle diffusion plots on Pb(II) adsorption by different cattail adsorbents (weight: 0.030 g, Pb(II) solution: 20 mL, initial Pb(II) concentration: 1.00 mM, initial pH: 5.5, 20˚C).

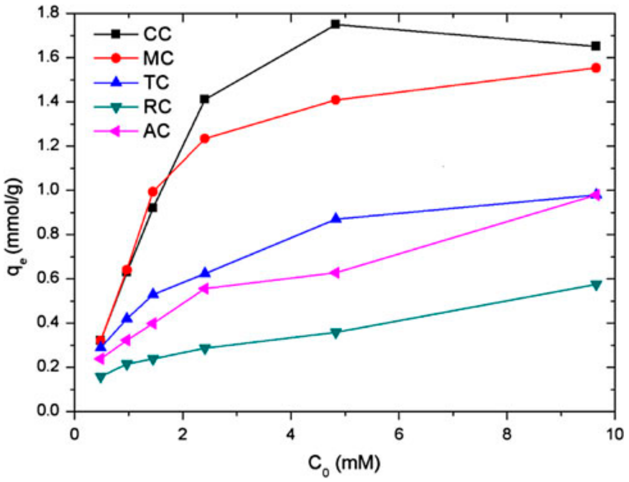

Fig. 8. Effect of initial Pb(II) concentration on Pb(II) adsorption (weight: 0.030 g, Pb(II) solution: 20 mL, initial pH: 5.5, 20˚C for 4 h).

Adsorption isotherms of lead ion adsorption by the cattail adsorbents are given in Fig. 9. In this study, the adsorption isotherms were generated at pH 5.5 with concentrations ranging from 0.48 to 9.65 mM and the adsorption data were described using the Langmuir and Freundlich isotherm models. The results of these analyses, using linear regression procedures, are shown in Table 2.

Table 2 indicates that Langmuir model gives good presentations for Pb(II) adsorption behavior by CC and MC ($R^2 = 0.979$ and 0.970, respectively), and poor presentations by TC, RC, and AC ($R^2 = 0.754$, 0.809, and 0.750, respectively). Comparatively, Freundlich isotherm model gives better descriptions for Pb(II) adsorption data of TC, RC, and AC ($R^2 = 0.982$, 0.954, and 0.960, respectively). However, worse descriptions are obtained for CC and MC ($R^2 = 0.827$ and 0.778, respectively) from Freundlich isotherm model.

Freundlich parameters (K_f and n) indicate whether the nature of adsorption is either favorable or unfavorable [35]. The intercept is an indicator of adsorption capacity and the slope is an indicator of adsorption intensity. A high value of the intercept, K_f, is indicative of a high adsorption capacity. A relatively slight slope indicates that adsorption intensity is good (or favorable) over the entire range of concentrations studied. Since the K_f values, reported in Table 2, can be used to indicate the relative adsorption capacity of the adsorbents, the adsorption capacity for the Pb(II) can be estimated as: TC > AC > RC. Using the Langmuir model, the maximum adsorption capacity of the cattail adsorbents for Pb(II) can be estimated as: 1.700 mmol/g or 352.2 mg/g of CC and 1.444 mmol/g or 299.2 mg/g of MC. Expectedly, q_m values, which are extrapolated for all metal concentrations, do not correspond to the experimental ones (q_e),

Table 2
Langmuir and Freundlich models parameters for Pb(II) adsorption equilibrium (20˚C, 4 h, 20 mL solution, 0.030 g adsorbents)

Adsorbent	q_m (mmol/g)	b	K_f	n	R^2	Adsorption model
CC	1.700	24.38			0.979	Langmuir
			0.240	0.279	0.827	Freundlich
MC	1.444	59.99			0.970	Langmuir
			1.236	5.531	0.778	Freundlich
TC	0.676	14.58			0.754	Langmuir
			0.587	4.000	0.982	Freundlich
RC	0.376	2.74			0.809	Langmuir
			0.243	2.961	0.954	Freundlich
AC	0.596	5.07			0.751	Langmuir
			0.445	3.028	0.960	Freundlich

Table 3
Maximum adsorption capacities of different modified plant adsorbents for Pb(II)

Adsorbent	Modifying agent(s)	Q_{max} (mg/g)	Reference
Rice husk	Tartaric acid	120.48	[36]
Peanut husk	Sulfuric acid	29.14	[37]
Banana stem	Formaldehyde	91.74	[38]
Imperata cylindrica leaf powder	Sodium hydroxide	13.50	[39]
Alfalfa biomass	Sodium hydroxide	89.2	[40]
Azolla filiculoides	H_2O_2–$MgCl_2$	228	[41]
Sugarcane bagasse	Sodium bicarbonate	196	[42]
	Ethylenediamine	164	[42]
	Triethylenetetramine	313	[42]
Nipah palm shoot biomass	Mercaptoacetic acid	52.86	[43]
Lawny grass	Citric acid	320.9	[44]
Cotton	Thioglycolic acid	28.67	[45]
Buckwheat hull	Thioglycolic acid	44.84	[45]
Wood sawdust	Thioglycolic acid	43.14	[45]
Posidonia oceanica	Hydrochloric acid	140	[46]
Soybean hulls	Sodium hydroxide	217	[47]
Triticum aestivum bran	Unmodified	87.0	[48]
Agave sisalana	Unmodified	1.34	[49]
Cornstalk	Unmodified	24.65	[50]
	Citric acid	245.8	[50]
	Citric acid -Sodium hydroxide	251.9	[50]
	Cyanex272	235.6	[50]
	Citric acid -Cyanex272	274.5	[50]
	Citric acid -Sodium hydroxide- Cyanex272	276.6	[50]
Cattail stem	Malic acid	299.2	Present study
	Citric acid	352.2	Present study

which are specific for a given C_0. These results are similar to those obtained by other authors, apart from a few variances resulting from different experimental conditions [1,9].

The basic assumption of Langmuir model is based on monolayer coverage of the adsorbate on the surface of adsorbent and which is an indication of the fact that the adsorption of lead ion onto the cattail materials (CC and MC) generates monolayer formation. Adsorption capacities of different adsorbents collected from the references are listed in Table 3 along with the values corresponding to CC and MC for comparison. From Table 3, CC exhibits a relatively higher adsorption capacity compared with other adsorbents.

3.5. Effect of adsorbent dose

The effects of adsorbent dose on the Pb(II) removal ratios are presented in Fig. 10. Along with the increase in adsorbent dose from 0.25 to 2.00 g/L, the percentage of Pb(II) adsorbed on cattail adsorbents increases from 39.61, 37.53, 18.78, 4.21, and 10.45% to 98.96, 99.17, 75.01, 37.53, and 60.43% for CC, MC, TC, RC, and AC, respectively. Increase in the Pb(II) adsorption ratio with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. Above 1.50 g/L of adsorbent dose, the maximum uptake value of Pb(II) adsorbed on CC is reached and the Pb(II) removal ratio only vibrates between 97.92 and 98.96%. In terms of high removal percent and cost effect, optimum solid/liquid ratio is pitched on 1.50 g/L.

3.6. The thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The thermodynamic parameters can be obtained using the following equations [51]:

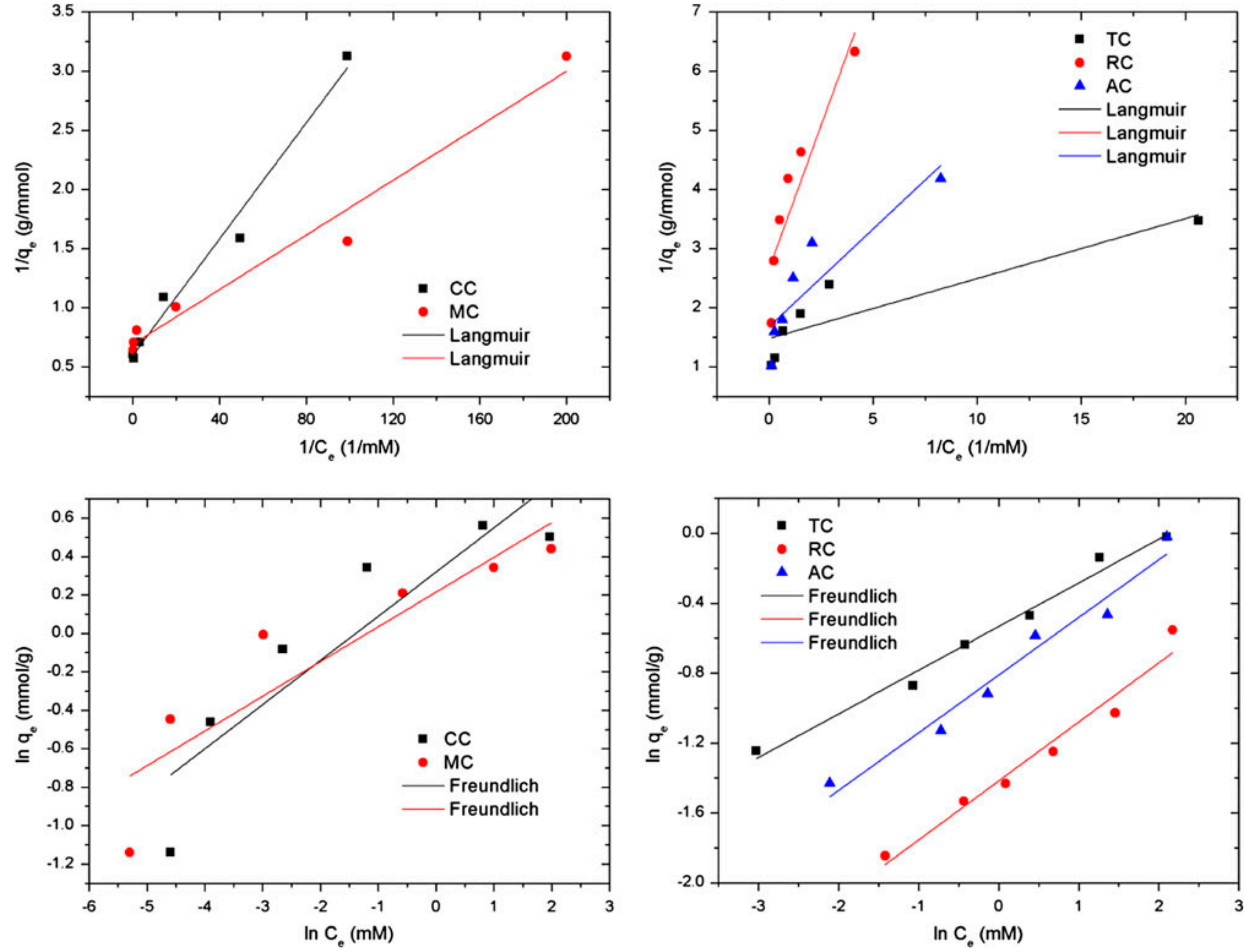

Fig. 9. Adsorption isotherms of Pb(II) by different cattail adsorbents (weight: 0.030 g, Pb(II) solution: 20 mL, initial pH: 5.5, 20°C for 4 h).

$$\ln K_D = -\Delta H/RT + \Delta S/R \ (\mathrm{kJ/mol}) \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \ (\mathrm{kJ/mol}) \tag{8}$$

where R is the universal gas constant, $T(K)$ is the temperature. Moreover, K_D is the equilibrium constant ($K_D = q_e/C_e$). The results are presented in Fig. 11, which is the plot of $1/T$ vs. $\ln K_D$. Table 4 summarizes the values of these thermodynamic parameters.

The positive value of ΔH indicates endothermic nature of adsorption process. The positive value of ΔS shows an affinity of these adsorbents and the increasing randomness at the solid–solution interface during adsorption process of Pb(II). The negative value of ΔG reveals a feasibility and spontaneous nature of this adsorption process. The values of ΔG are found to increase as temperature increases indicating more driving force and hence resulting in higher adsorption capacity. Compared with ΔG for the adsorption of Pb (II) on MC, the adsorptive forces are stronger on CC disclosing more spontaneous thermodynamically process due to the specific recognition sites on CC.

3.7. Adsorption mechanism

Different chemical reagents were applied to modify cattail stem powder in order to enhance its adsorption ability. Firstly, 20% isopropyl alcohol was used to discolor and remove organic compound and organic small molecule. Then filtered and washed repeatedly with deionized water in order to remove water-soluble residue, impurity, and polarity compound. Finally, RC was obtained; major chemical constituents of which are cellulose, hemicellulose, and lignin. For enhancing the number of functional groups on cellulose, a series of chemical modifications were further

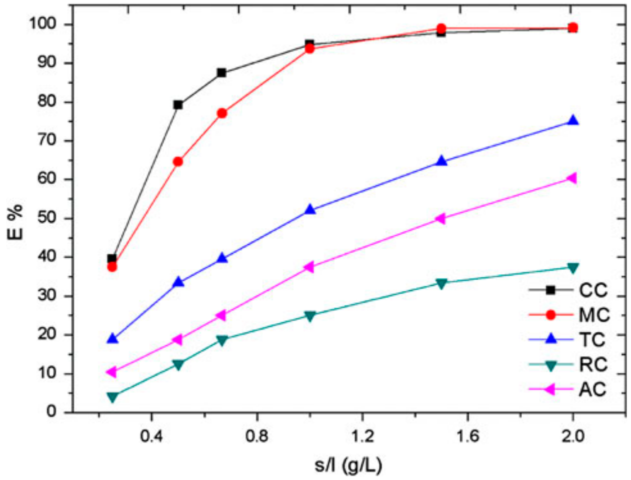

Fig. 10. Effect of solid/liquid ratio on Pb(II) adsorption by different cattail adsorbents (initial Pb(II) concentration: 1.00 mM, initial pH: 5.5, 20℃ for 4 h).

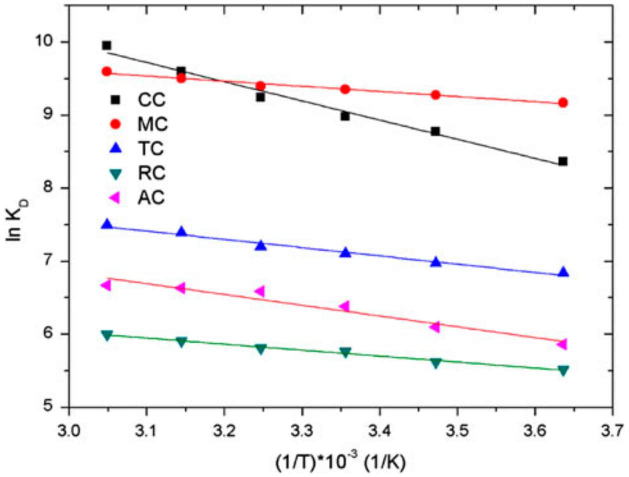

Fig. 11. Plots of $1/T$ vs. $\ln K_D$ on Pb(II) uptakes by cattail samples (weight: 0.030 g, Pb(II) solution: 20 mL, initial Pb (II) concentration: 1.00 mM, initial pH: 5.5, contact time: 30 min).

performed. In the modified process, 0.1 M NaOH was utilized to make carboxylic groups on the surface of cellulose bare and convert H^+ type of functional groups into Na^+ type so that Pb(II) can react with them more easily. Citric acid, malic acid, and tartaric acid were chosen to introduce carboxylic groups to RC for increasing the amount of surface functional groups upon cellulose. The reactive anhydride was combined with cellulosic hydroxyl groups so as to form an ester linkage and introduce carboxyl groups to the cellulose. The addition of carboxylic function groups increases adsorbents' abilities of binding with positively charged metal ions [52]. The Pb(II) adsorption by these cattail adsorbents occurs through ion-exchange reaction. Functional groups such as –COOH and –OH of cellulose can react with Pb(II) to form complexes by releasing protons. The reaction equations are described in Fig. 12.

From the experimental results in the text, it is clear that the adsorption capability for Pb(II) removal has the following order: CC > MC > TC > AC > RC. The reason can be explained: ion exchange is the main mechanism for these absorbents to adsorb Pb(II) from solution, then the adsorption capability depends on the amount of the active sites. CC has more carboxylic acid groups on the cattail cellulose than other absorbents (MC, TC, AC, and RC), which results in the highest Pb(II) loading per unit weight of the adsorbents. Comparing MC to TC, malic acid is easier to be changed into anhydride at high temperature (120℃, in this paper) than tartaric acid, so more carboxylic acid groups may be grafted to the cattail cellulose by malic acid treating process, which leads to a better Pb (II) removal property for MC than TC. From the reaction equation, it can be seen that, tartaric acid modification provides additional active groups (–OH and –COOH) to the cattail substrate, so TC has more active sites than AC, and a stronger Pb(II) absorption capacity can be expected for TC by comparing to AC.

Table 4
Thermodynamic parameters for Pb(II) adsorption

Adsorbent	ΔH (kJ/mol)	ΔS (kJ/mol K)	ΔG (kJ/mol)					
			278 K	288 K	298 K	308 K	318 K	328 K
CC	0.0218	0.148	−40.81	−42.74	−44.22	−45.71	−47.19	−48.68
MC	0.0059	0.097	−26.79	−28.06	−29.03	−30.01	−30.98	−31.95
TC	0.0094	0.091	−24.98	−26.16	−27.07	−27.98	−28.89	−29.80
RC	0.0068	0.070	−19.38	−20.29	−21.00	−21.70	−22.41	−23.11
AC	0.0123	0.094	−25.76	−26.98	−27.91	−28.85	−29.79	−30.73

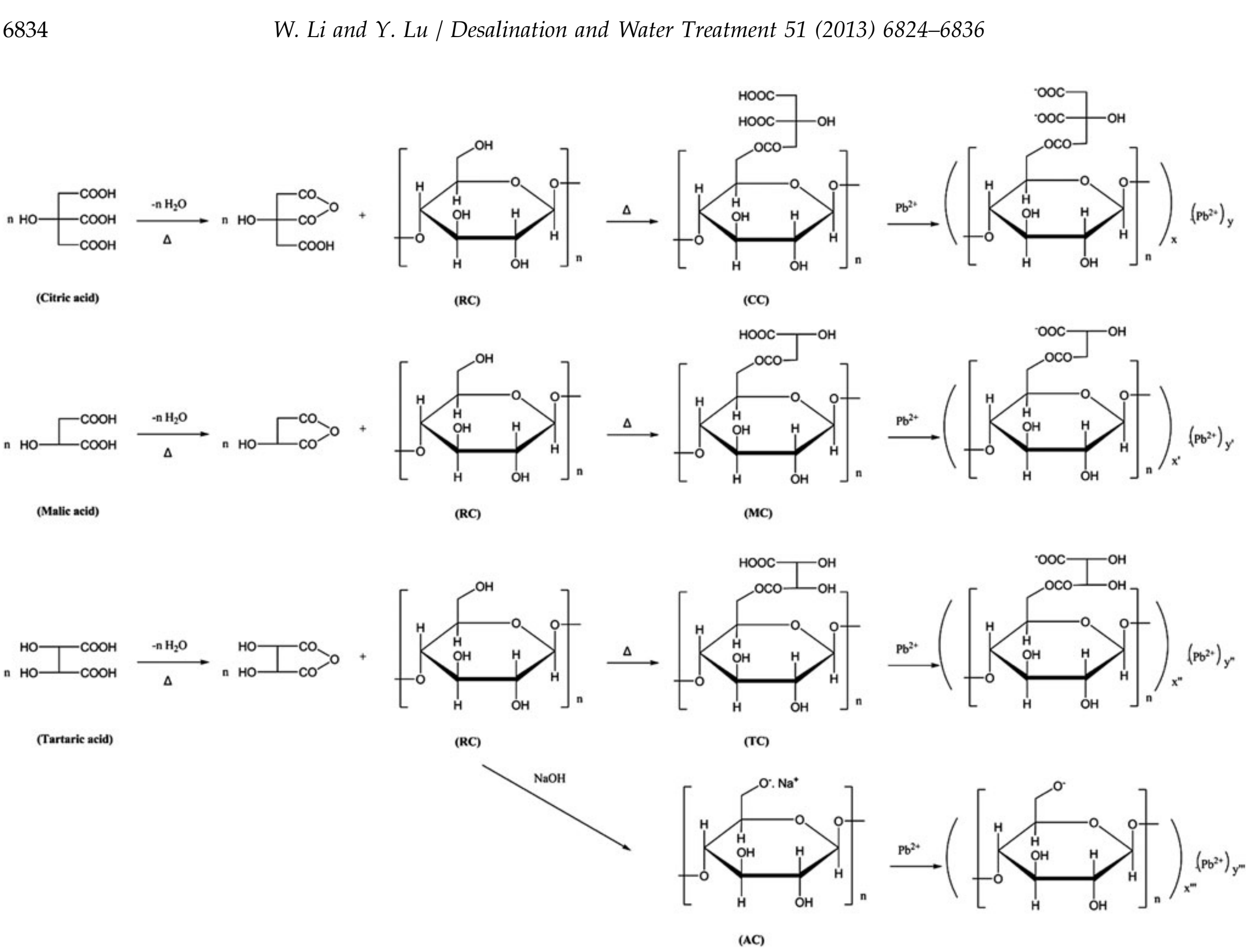

Fig. 12. Preparation and Pb(II) adsorption process of different cattail adsorbents.

3.8. Desorption

One important requirement of commercial adsorbents is that they should be capable of being regenerated by elution and recovery of the adsorbed metal. To evaluate the property of regeneration of the adsorbents, 0.1 mol/L HCl was tested as eluent. The results of regeneration indicated that there was a noticeable loss of adsorption capacity after the first reuse cycle and the adsorption capacities of Pb(II) at equilibrium for MC and CC decreased from 299.2 to 251.1 and 352.2 to 296.7 mg/g, respectively. However, the adsorption capacities decrease slowly after the second reuse cycle. After the tenth reuse cycle, the adsorption capacities of Pb(II) at equilibrium for MC and CC were 238.3 and 270.3 mg/g, respectively.

4. Conclusion

In this study, CC, MC, TC, and AC were prepared by treating raw cattail stem powder (RC) with citric acid, malic acid, tartaric acid, and NaOH. The spectra, morphology, structure, and stability of these cattail adsorbents were indicated by FIIR spectroscopy, SEM, XRD, and thermogravimetry (TG). The initial pH of solution has significantly affected adsorption of Pb(II) on cattail adsorbents; the optimal pH for favorable adsorption is 5.5. Under the condition of 1.50 g/L adsorbent, the ratio of Pb(II) adsorbed on CC or MC keeps above 90% over a range from 0.48 to 2.00 mM of lead concentration. The isothermal data of CC or MC fits the Langmuir model. The adsorption capacities are calculated to be 1.700 mmol/g or 352.2 mg/g of CC and 1.444 mmol/g or 299.2 mg/g of MC, respectively. CC exhibits a higher adsorption capacity when compared with other reported plant adsorbents. The adsorption processes follow the pseudo-second-order rate kinetics. Therefore, cattail adsorbents are of great potential to be efficient and economical biosorbents for the removal of dissolved Pb(II) from solution.

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