Removal of Pb(II) from Vanillin Solution by Acid-modified Cattail Biomass

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The use of the aquatic plant cattail to produce an adsorbent for heavy metals will add value to wetlands. Cattail adsorbents were treated with multi-valent carboxylic acids to facilitate adsorption of Pb(II) from a vanillin solution. Fourier transform infrared (FTIR) spectroscopic analysis confirmed the formation of acid modifications by esterification. While unmodified cattail had a Pb(II) adsorption capacity of 3.21 mg/g, citric acid-, malic acid-, tartaric acid-, oxalic acid-, and iminodiacetic acid-modified cattail absorbents were able to adsorb 66.10, 55.42, 44.53, 52.32, and 36.82 mg/g, respectively, at the optimum pH of 4.9. The Pb(II) adsorption capacity increased as the concentration of Pb(II) increased without loss of vanillin during the adsorption process. Desorption of Pb(II) and regeneration of the adsorbents was achieved by 0.1 M HCl elution, which showed that the cattail adsorbents were regenerated easily and could be used repeatedly. The results suggest that acid-modified cattail biomass may be a promising adsorbent for heavy metal ion uptake in water-based cosmetics.

Keywords: Cattail biomass; Lead ion; Vanillin solution; Acid modification; Adsorption

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INTRODUCTION

It has been discovered through ancient texts and from archaeological digs that perfumes existed in some of the earliest human civilizations. Modern perfumery began in the late 19th century with the commercial production of aromatic compounds such as vanillin and coumarin (de Nicolaï 2008). Plants have long been used in perfumery as a source of essential oils and aromatic compounds. These aromatics are usually secondary metabolites produced by plants as protection against herbivores, infections, or to attract pollinators (Wang and Kays 2000).

The amount of heavy metals (such as Pb, Cd, Cr, Ni, *etc.*) released into the environment increases with rapid industrialization, poor emissions control, unorganized urbanization, and dense motor traffic. Heavy metal contamination of soil, water, and the atmosphere affects plants. Heavy metals can be absorbed from the soil by plant roots and transported to leaves, flowers, and seeds (Doganlar and Atmaca 2011). Perfumes from plants require the use of various methods to extract the aromatics from the raw materials; however, heavy metals tend to become concentrated in the perfumes throughout the extraction process (Popescu *et al.* 2008).

Plant perfumes have been widely used in personal care products and facial cosmetics, which are directly applied to human skin. The toxicity of heavy metals at high levels of exposure is well known (Sharma *et al.* 2011), but continual exposure to relatively low levels of heavy metals may also cause adverse health effects. An increase of Pb(II) may cause serious health hazards, such as acute and chronic poisoning (Hernandez and Margalida 2009).

In recent years, increasing emphasis has been placed on the minimization of environmental impacts. Research work prompted by these concerns has resulted in steady growth in the range and capability of natural and prepared materials capable of heavy metal removal (Biswal *et al*. 2013). In particular considerable work has been carried out on the use of both natural materials and their modifications. These natural materials, in many instances, are relatively cheap, abundant in supply, and have significant potential for modification and ultimately enhancement of their adsorption capabilities (Tang *et al*. 2013). Many researchers have reported on the use of the naturally occurring cellulosic materials, their modified forms, and their efficacy as adsorbents for the removal of heavy metals from waste streams (Hubbe *et al*. 2011). Adsorbents based on direct modification of cellulose have been evaluated, and modifications resulting from the grafting of selected monomers to the cellulose backbone with subsequent functionalization also have been assessed (Dimitrov *et al*. 2012). The heavy metal adsorption capacities for these modified cellulose materials were found to be significant, and levels of uptake were comparable, in many instances, to other naturally occurring adsorbent materials and commercial ion exchange type resins (Sulaymon *et al*. 2013). Many of the modified cellulose adsorbents proved regenerable and re-usable over a number of adsorption/desorption cycles, allowing recovery of the adsorbed heavy metal in a more concentrated form (Zewail and El-Garf 2010). In this work, dried cattail, *Typha angustifolia* (TA), a common aquatic plant with no economic value in the tropics and subtropics (Sharain-Liew *et al.* 2011), was used as a cellulosic adsorbent for lead removal from a vanillin solution, and the Pb(II) adsorption capacities of the cattail adsorbents *via* citric acid (CA), malic acid (MA), tartaric acid (TA), oxalic acid (OA), and iminodiacetic acid (IA) pretreatments were compared.

EXPERIMENTAL

Materials

The cattail biomass used in this study was collected from a local pond in Shanghai, China. It was washed with tap water to remove soil and dust, sprayed with deionized water, and dried to a constant weight at 75 °C. The dry cattail biomass was ground and sieved to obtain powder with particle sizes of 0.15 to 0.40 mm. Dried cattail biomass 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 °C for 12 h for further chemical processing. This unmodified cattail biomass was abbreviated *UC* in the following experiment. Its major chemical constituents are cellulose, hemicellulose, and lignin (Zhang *et al.* 2011). All the reagents used in the study were of analytical grade, and all solutions were prepared with deionized water.

Chemical Modification of Biomass

Modification of UC with acid (CA, MA, TA, OA, or IA) was carried out using the method reported by Marshall *et al.* (1999). UC powder (10 g) was added to 1.0 M acid solution (70 mL), and the acid/powder slurry was stirred for 30 min to mix completely, and then dried without stirring for 12 h at 50 °C. The material was subsequently heated at

120 °C for 90 min, then washed with 200 mL distilled water per gram to remove excess acid. The material was dried at 75 °C for 12 h. The citric acid-, malic acid-, tartaric acid-, oxalic acid-, and iminodiacetic acid-modified UC were abbreviated CC, MC, TC, OC, and IC in this experiment, respectively.

Characteristics of Adsorbents

Infrared spectra of cattail absorbents were obtained using a Fourier transform infrared spectrometer (Nicolet Nexus 470 FTIR). Samples were prepared using the KBr disk method, and the spectra were recorded in the 400 to 4000 cm^{-1} range. Surface morphology of the adsorbents was identified by use of a Philips XL-30 scanning electron microscope (SEM). Elemental analysis of cattail adsorbents was carried out using an VARIOEL3 Elementar instrument.

Physico-chemical Properties of Vanillin

Vanillin is a phenolic aldehyde, an organic compound with the molecular formula $C_8H_8O_3$. Its functional groups include aldehyde, ether, and phenol. It is the primary component of the extract of the vanilla bean. Synthetic vanillin, instead of natural vanilla extract, is sometimes used as a flavoring agent in foods, beverages, and pharmaceuticals. Solubility in water: 10 g/ L.

Pb(II) Adsorption Experiments

The adsorption of Pb(II), provided as lead nitrate ($Pb(NO_3)_2$), on cattail adsorbents was carried out by batch experiments in a shaker. Unless otherwise stated, the parameters were: temperature 293 K, solution volume 25 mL, adsorbent dose 0.03 g, contact time 4 h, initial pH 4.9, Pb(II) concentration 80 mg/L, and vanillin concentration 100 mg/L. The initial pH was varied from 2.0 to 6.0 using small volumes of 0.1 M HNO_3 or NaOH to investigate the effect of the initial solution's pH. The influence of the initial Pb(II) concentration was investigated in the range of 50 to 2000 mg/L, which was carried out in different vanillin contents (0 mg/L, 100 mg/L, 500 mg/L) while all other conditions were kept the same.

Desorption and Regeneration Tests

To investigate the possibility of repeated use of CC, desorption and regeneration experiments were also conducted. The lead-loaded CC was filtered, and Pb(II) content in solution was measured. The adsorbent (CC) was then transferred to another flask and stirred with 25 mL of 0.1M HCl solution for 3 h (Lasheen *et al.* 2012). It was again filtered, and the desorbed Pb(II) was determined in the filtrate. The adsorbent was washed several times with distilled water in order to remove excess acid and used for next adsorption cycle. The adsorption and desorption procedures were repeated using the same adsorbent.

Analytical Methods

Once the pre-set contact time was reached, the samples were withdrawn and centrifuged at 3000 rpm for 5 min. The supernatant solutions were analyzed for the residual Pb(II) concentration by titration with standard EDTA solution (0.1% xylenol orange was chosen as the indicator). The vanillin content was determined using the potentiometric titration method according to the Chinese standard (WS-10001-(HD-0540)-2002). All assays were carried out in triplicate and only mean values are presented.

RESULTS AND DISCUSSION

Characteristics of Cattail Adsorbents

The FT-IR spectra of cattail adsorbents before and after acid modification are shown in Fig. 1. It can be seen that the hydroxyl (–OH) stretching vibration bands are at a wave number of 3416 cm^{-1}. The peak at 2921 cm^{-1} is due to the asymmetric stretch of aliphatic chains (–CH). The peaks around 1624 cm^{-1} are due to C=C stretching that can be attributed to the presence of aromatic or benzene rings in lignin. The vibrations around 1420 to 1450 cm^{-1} could be due to aliphatic and aromatic (C–H) groups in the plane deformation vibrations of methyl, methylene, and methoxy groups (Feng *et al.* 2009). Comparing these results with the IR spectrum for the untreated cattail (UC), it could be seen that there was a strong characteristic stretching vibration absorption band for the carbonyl group at around 1737 cm^{-1} in IR spectra of all acid-treated cattail samples. This reflected esterification between the acid and –OH groups on the biomass (Gong *et al.* 2006). Because the acids employed contained multiple carboxylic acid groups, the ester formation provided covalent attachment of free carboxyl groups, and these groups appeared to be very effective in capturing Pb(II) from aqueous solution.

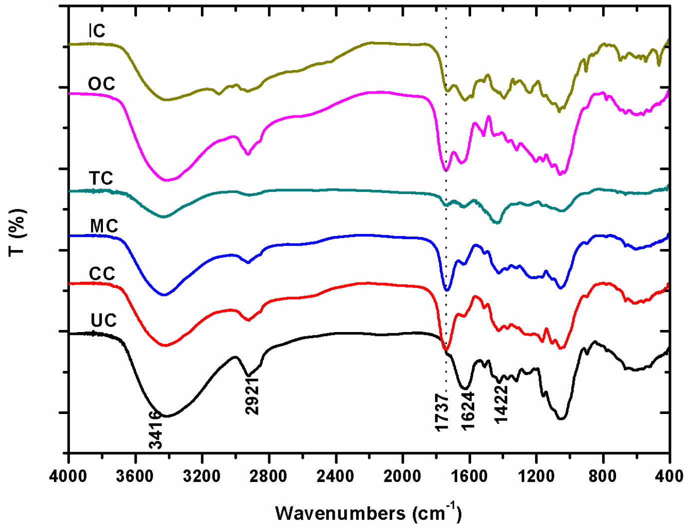

Fig. 1. FT-IR spectra of cattail adsorbents

Table 1. Band Shifts for Cattail Adsorbents Before and After Pb(II) Adsorption

		ν (–O–C)/ cm^{-1}	ν (–C=O) / cm^{-1}	ν (COO−)/ cm^{-1}	ν (–OH) / cm^{-1}
CC	before	1042	1645, 1736	1376	3416
	after	1045	1508, 1637	1242	3423
MC	before	1048	1628, 1730	1399	3437
	after	1058	1508, 1633	1247	3431
TC	before	1040	1639, 1742	1382	3420
	after	1046	1512, 1644	1251	3433
OC	before	1042	1619, 1728	1369	3415
	after	1047	1506, 1629	1240	3426
IC	before	1038	1653, 1740	1388	3433
	after	1044	1517, 1636	1244	3427

By comparing the spectra of CC before and after Pb(II) sorption, one can observe various shifts attributable to the adsorption of Pb(II). Because of the multiple subtle changes in many parts of the spectrum, no conclusion was drawn regarding which functional groups were responsible for the Pb(II) binding. Regarding FT-IR for CC after the Pb(II) uptake, it was found that, oxygen containing functional groups, methoxy –OCH_3, ketone –C=O and carboxylate ion –COO and phenolic –OH groups are affected after uptake process. This is judging from the shift in position or band intensity as follows: ν(–O–C) shifted from 1042 to 1045, ν(–C=O) from 1645 and 1736 to 1508 and 1637, ν(COO−) from 1376 to 1242 and ν(–OH) from 3416 cm^{-1} to 3423 cm^{-1}. On the other hand, for the FT-IR of MC after the Pb(II) uptake, it was observed that oxygen containing functional groups are affected after the uptake process as follows: ν(–O–C) shifted from 1048 to 1058, ν(–C=O) from 1628 and 1730 to 1508 and 1633, ν(COO−) from 1399 to 1247 and ν(–OH) from 3437 cm^{-1} to 3431 cm^{-1}. Band shifts for other adsorbents before and after Pb(II) adsorption were also shown in Table 1.

The elemental compositions of the cattail adsorbents are listed in Table 2. As is shown in Table 1, the oxygen content of CC is increased significantly from 47.04% to 48.86% by comparing to UC. The increase in oxygen content suggests that large amounts of acid groups had been grafted onto the CC.

Table 2. Elemental Composition of Cattail Adsorbents

	C(%)	H(%)	O(%)
UC	43.71	5.60	47.04
CC	42.51	5.20	48.86
MC	42.76	5.13	48.60
TC	42.78	5.41	48.32
OC	42.80	5.16	48.51
IC	42.95	5.32	48.17

The surface morphology of UC and CC are given in Fig. 2. UC was found to have a very smooth and compact surface, and some grains were observable along the vertical section.

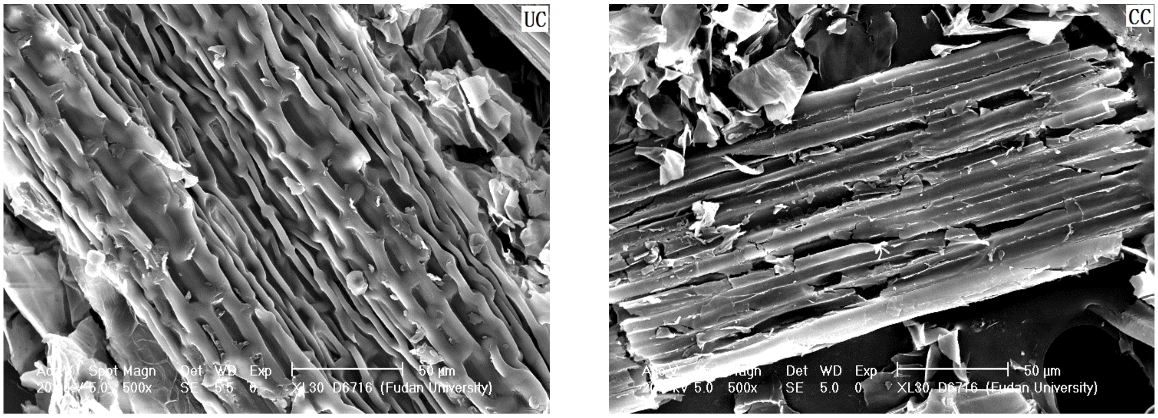

Fig. 2. SEM image of UC (left) and CC (right)

After reacting with acids, the surface of the adsorbent (CC) became rough, and some fractures and fragments were apparent. These changes are consistent with an increased surface area of CC, a change that would be expected to increase the adsorption ability of the CC.

Effect of Initial Solution pH

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. In the case of a low pH (< 6.0), positively charged Pb(II) species are dominant. In the case of high pH values (pH > 7.0), there are several Pb(II) species present with different charges. These species include $Pb(OH)^+$ and $Pb(OH)_2$, and thus the removal of Pb(II) may be accomplished by the simultaneous precipitation of $Pb(OH)_2$ and the adsorption of $Pb(OH)^+$ (Randelović *et al.* 2012). 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 2.0 to 6.0. A pH greater than 6.0 was not investigated to avoid lead precipitation.

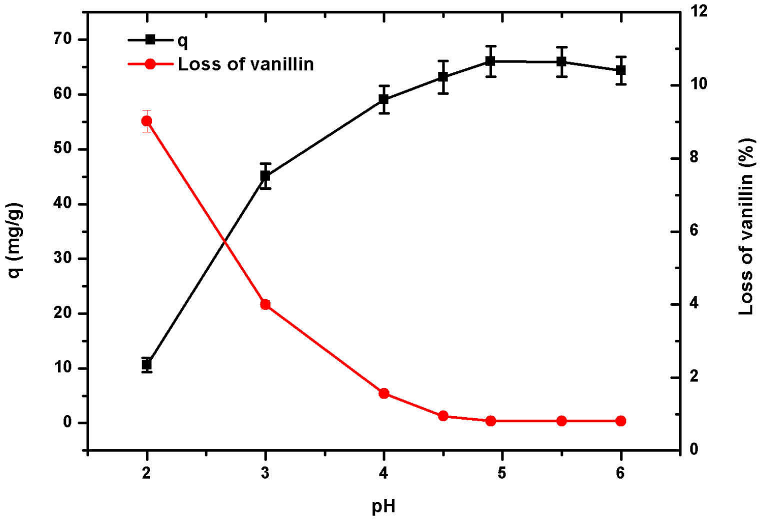

Fig. 3. Effect of initial solution pH on Pb(II) adsorption for citric acid-modified cattail adsorbent (weight: 0.030 g; solution: 25 mL; initial Pb(II) and vanillin concentration: 80 mg/L and 100 mg/L, 293K for 4 h).

As shown in Fig. 3, Pb(II) adsorption was increased when the pH was increased from 2.0 to 6.0 for CC. When the pH value was in the range of 4.5 to 6.0, the Pb(II) adsorption capacity of the adsorbent almost reached a maximum. The concentrations of lead after adsorption at pH = 2.0, 3.0, 4.0, 4.5, 4.9, 5.5, and 6.0 were 67.27, 25.87, 9.12, 4.21, 0.75, 0.86, and 2.73 mg/L, respectively. The low adsorption of metal ions at a low pH can be attributed to competition between H^+ and metal ions (Lu *et al.* 2009). Vanillin losses decreased as pH increased from 2.0 to 6.0. Based on a consideration of the adsorption of Pb(II) and the loss of vanillin, an initial pH 4.9 was chosen as the optimum pH in the subsequent experiments.

Effect of Initial Pb(II) Concentration and Vanillin Concentration

Figure 4 shows the Pb(II) adsorption capacity of CC at different initial Pb(II) and vanillin concentrations. The adsorption capacity of Pb(II) increased rapidly when the initial Pb(II) concentration was below 1000 mg/L. At lower Pb(II) concentrations, sufficient adsorption sites were available for adsorbing Pb(II). However, the numbers of Pb(II) ions were higher as compared to availability of binding sites at higher Pb(II) concentrations. Due to restriction of binding sites present on the surface of cattail biomass, adsorbents became saturated at a higher Pb(II) concentration. The increase in initial vanillin concentration made little contribution to Pb(II) adsorption at different Pb(II) contents. The vanillin content was not diminished by the adsorption process.

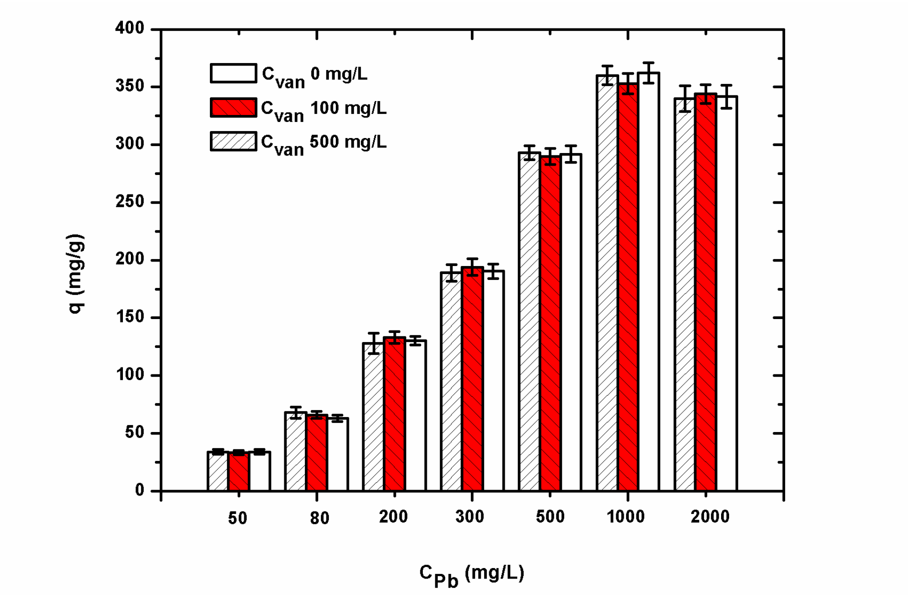

Fig. 4. Pb(II) adsorption capacity at different initial Pb(II) and vanillin concentrations for citric acid-modified cattail adsorbent (CC) (weight: 0.030 g; solution: 25 mL; initial pH: 4.9; 293K for 4 h).

Adsorption isotherm studies were carried out using the following conditions: weight of CC: 0.030 g; solution: 25 mL; initial pH: 4.9; initial vanillin concentration: 100 mg/L, 293K for 4h. Langmuir and Freundlich models were applied to describe the equilibrium sorption isotherm (Fig. 5).

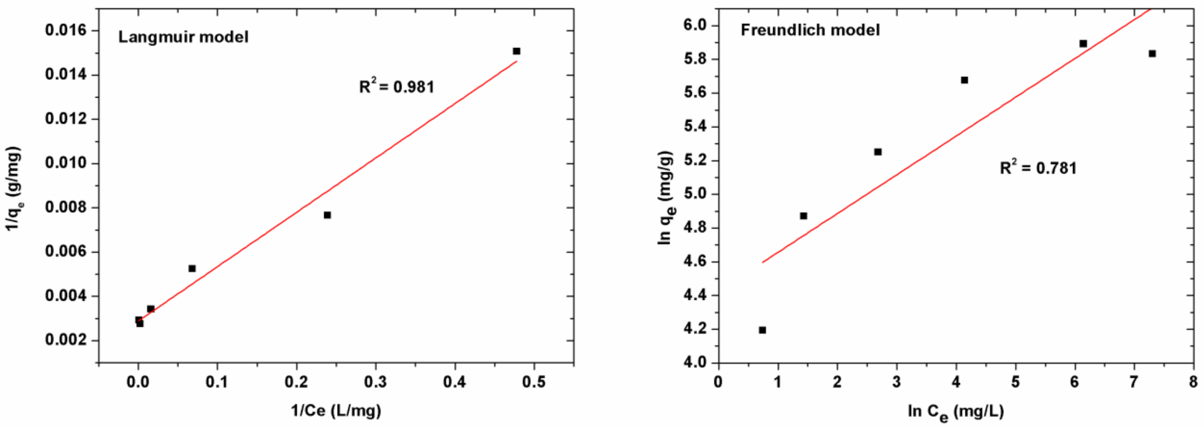

Fig. 5. Adsorption isotherms of Pb(II) by CC

Table 3. Langmuir and Freundlich Models Parameters for Pb(II) Adsorption

q_m (mg/g)	b	K_f	n	R^2	Adsorption model
351	24.36			0.981	Langmuir
		83.63	4.33	0.781	Freundlich

The Langmuir model can be given as, $1/q_e = 1/q_m + 1/(q_m b C_e)$, where q_e is the amount of Pb(II) adsorbed at the equilibrium time, C_e is the equilibrium concentrations of Pb(II) in solution, q_m is the maximum adsorption amount of metal ion per unit weight of adsorbent at C_e, and b is the affinity constant. The Freundlich model can be expressed as, $\ln q_e = (1/n)\ln C_e + \ln K_f$, where K_f and n are the Freundlich constants. Parameters of these models are given in Table 3 (R^2 is the linear regression coefficient of determination.). Table 3 indicates that the Langmuir model gave a good fit for Pb(II) adsorption behavior by CC, and the maximum adsorption capacity of CC for Pb(II) could be estimated as 351 mg/g.

Effect of Acid Modification on Pb(II) Adsorption

The adsorption efficiency of Pb(II) on UC and acid-modified cattail adsorbents was examined, and the results are shown in Fig. 6. The results clearly show that acid-modified cattail adsorbents were more effective than UC for the adsorption of Pb(II). This may be due to the superior ion exchange capacity and chelating capacity of the carboxyl-functionalized cattail adsorbent (Lu *et al.* 2009). The adsorption capacities of Pb(II) with different acid-modified cattail adsorbents decrease in this order: CC > MC > OC > TC > IC. The higher adsorption capacities of CC, MC, and OC could be due to more effective functional groups, such as carboxyl groups (Lu *et al.* 2009), for metal ion binding than TC and IC. From the FTIR spectra (Fig. 1), CC, MC, and OC show stronger carboxyl peak intensity at a wave number of 1737 cm^{-1} than TC and IC. This result coincides with the adsorption capacity order of these cattail adsorbents.

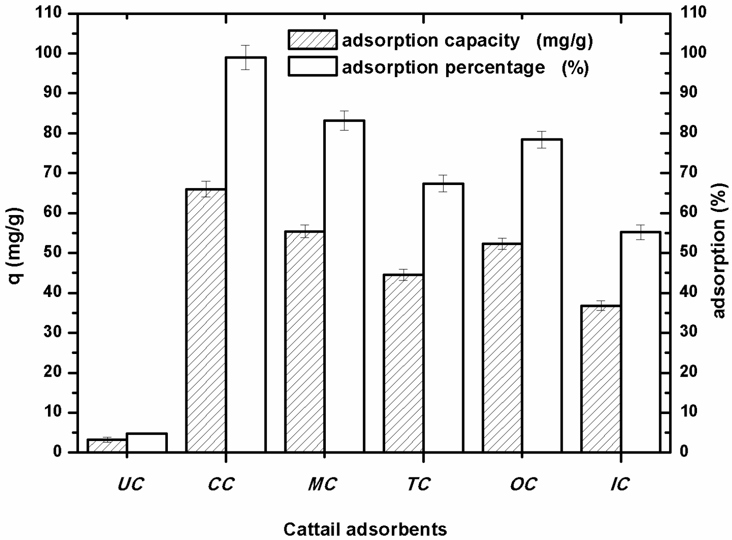

Fig. 6. Adsorption efficiency of Pb(II) on *UC* and acid-modified cattail adsorbents (weight: 0.030 g; solution: 25 mL; initial Pb(II) and vanillin concentration: 80 mg/L and 100 mg/L; initial pH: 4.9, 293K for 4 h)

Reuse of Adsorbent (CC)

Desorption and regeneration studies were carried out using 25 mL 0.1 M HCl as the eluant solution. The adsorbent was washed with water before each measurement. After four cycles, the Pb(II) adsorption capacity of CC decreased from 99.6% to 89.2%. This behavior indicates that the adsorbent can be used successfully four times after regeneration for the removal of Pb(II).

CONCLUSIONS

1. The introduction of carboxyl groups by esterification increased the Pb(II) uptake by modified cattail biomass.
2. Simple pretreatment, high Pb(II) adsorption performance without loss of vanillin, easy desorption, and high regeneration of cattail adsorbents were demonstrated in this study.
3. All of the appropriate features show that this modified plant material is feasible as an efficient adsorbent for Pb(II) removal in the perfume industry.

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