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Comparative study on Pb(II), Cu(II), and Co(II) ions adsorption from aqueous solutions by arborvitae leaves

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ABSTRACT

In this study, the pretreatment feasibility of fallen leaves for the removal of heavy metals in aquatic environments was evaluated. The arborvitae leaves were selected as representative and characterized by Brunauer–Emmett–Teller (BET) and FT-IR. BET analysis showed that the surface area of arborvitae leaves was 29.52 m^2/g with the pore diameter ranging from 2 to 50 nm. Absorption bands in FT-IR were assigned to C–H, O–H, C–O, and C=O groups, which were the main sites for heavy metals adsorption. With the arborvitae leaves as a natural adsorbent, the removal of Pb(II), Cu(II), and Co(II) ions in the single and ternary component systems was studied by means of batch adsorption experiment. The results indicated that the adsorption amounts by arborvitae leaves increased sharply from 1.12 to 8.76 mg/g for Pb(II), 0.49 to 3.87 mg/g for Cu(II), and 0.44 to 2.28 for Co(II), respectively, with pH increasing from 1.79 to 4.26. The adsorption equilibrium was attained within 120 min, and the adsorption affinity order of the three heavy metals was Pb > Cu > Co in both of the single and ternary systems. All equilibrium data of Pb(II), Cu(II), and Co(II) ions obtained fit perfectly with Langmuir isotherm model compared with Freundlich isotherm model. Compared with the results in the single system, the adsorption capacity of Pb(II), Cu (II), and Co(II) ions on arborvitae leaves decreased from 35.84 to 9.32 mg/g, 7.94 to 3.07 mg/g, and 6.78 to 1.54 mg/g in the ternary systems, respectively. For the Dubinin–Kaganer–Radushkevich isotherm model, the sorption energy *E*-values for Pb(II), Cu(II), and Co(II) ions on arborvitae leaves were all below 8 kJ/mol in the single and ternary metal solution systems, indicating that the adsorption mechanism could be explained as the physical adsorption.

Keywords: Heavy metals; Adsorption; Arborvitae leaves; pH; Isotherm

1. Introduction

With the industrial development, a lot of wastewater containing heavy metals were discharged into the environment without appropriate treatment, which resulted in serious water pollution. Heavy metals, such as Pb(II), Cu(II), and Co(II) ions, widely existed in the industrial effluents from mining, metallurgy, electronics, electroplating, and petroleum fertilizer manufacturing

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[1]. Heavy metal contaminants are non-biodegradable and can be accumulated in human body through food chain, poisoning the bones, liver, and nerves [2]. Hence, heavy metal pollution has become a great concern in aquatic environments. The World Health Organization limitations for Pb(II) and Cu(II) ions in the drinking water are 0.01 and 4.0 mg/L [3], respectively, although the actual concentration of heavy metals in wastewater is as high as several hundreds of milligram per liter. Therefore, it is very important to remove heavy metals from water environment efficiently.

Hence, various water treatment technologies, such as chemical coagulation and precipitation, adsorption, membrane separation, ion exchange, and electrochemistry, have been applied to treat heavy metals contained in the wastewater [4,5]. Among them, the adsorption has been widely used in the removal of heavy metals due to its high efficiency, low price, and simplicity of operation [6].

In recent decades, the low-cost and unconventional adsorbents from a variety of agricultural byproducts or natural materials, such as cork waste [7], loofah fibers [8], rice husk ash [9], and Chinese bentonite [10], have been tested for the heavy metal sorption potential. Since previous experiments have shown that the leaves contain a large number of functional groups, potentials of many leaves, including castor leaf [11], fraxinus tree leaf [12], rubber leaf [13,14], and ricinus leaf [15], for the removal of heavy metals have been investigated in recent years.

Arborvitae is an excellent landscaping tree, which is very widespread in China, and can be grown in the ground or on the cliffs. Whether the fallen arborvitae leaves can be low-cost adsorbents for the heavy metal removal in suit has not been reported. In this work, the wild arborvitae leaves were selected as the natural adsorbent for the removal of Pb(II), Cu(II), and Co(II) ions by batch adsorption experiments, and the structural characters were analyzed by Brunauer – Emmett – Teller (BET) and Fourier Transform – Infrared spectroscopy (FT-IR). Furthermore, the effects of pH and contact time on adsorption were examined. At last, both of the single and ternary adsorption mechanisms of the heavy metals were investigated by the kinetic and equilibrium studies. The main aim of the work is to evaluate the pretreatment feasibility of fallen leaves for eliminating heavy metal contaminant in aquatic environments.

2. Experimental

2.1. Materials and reagents

The wild arborvitae leaves selected for adsorption experiments were collected in Shandong Province, China, which were washed with distilled water for several times, and dried in an air oven at 85℃ for 24 h, and then crushed into leaf powder to obtain uniform particle size of 20–50 mesh by screening. Finally, the obtained materials were preserved in the glass bottles as the adsorbents.

The synthetic solutions were prepared by diluting Pb(II), Cu(II), and Co(II) ions standard stock solutions (1,000 mg/L) in deionized water. All reagents were of analytical grade.

2.2. Characterization of adsorbents

The specific surface area of the arborvitae leaf sample was determined using the established Brunauer–Emmett–Teller (BET) method with a Micromeritics ASAP 2020 gas adsorption surface analyzer, meanwhile the features of pore structure were obtained according to Barrett–Joyner–Halenda method and *t*-plot.

The FT-IR spectrum of the adsorbent sample was measured with an EQUTNOX5 spectrometer using potassium bromide disks, and was recorded from 400 to 4,000 cm^{-1} at 4.0 cm^{-1} intervals in transmission mode.

2.3. Batch sorption experiments

To evaluate the effect of pH on Pb(II), Cu(II), and Co(II) ions adsorption, 0.10 g arborvitae leaves and 50 mL synthetized metal ion-contained solution (initial concentrations of 20 mg/L) were added in 150 mL Erlenmeyer flasks, and the initial pH was adjusted in the range from 1.79 to 5.88 with 0.1 mol/L HCl or 0.1 mol/L NaOH. The flasks were shaken for 300 min at 303 K and 150 rpm in the automatic shaker.

In the metal ions adsorption kinetic experiments, 2 g/L arborvitae leaves was added into 150 mL solutions with Pb(II), Cu(II), and Co(II) ions initial concentrations settled on 20 mg/L in single systems. Samples were shaken at 150 rpm and 303 K in an automatic shaker for 0–300 min.

In the adsorption isotherm studies, the effect of initial concentration of metal ions on adsorption capacities of arborvitae leaves was evaluated by varying the initial concentration of the metal ions solutions. For the single component adsorption experiment, tests were carried out with 0.1 g arborvitae leaves under the same conditions above, and the initial concentrations of Pb(II), Cu(II), and Co(II) ions were all from 5 to 30 mg/L, respectively. In order to investigate the competitive adsorption of Pb(II), Cu(II), and Co(II) ions on arborvitae leaves, 0.1 g of arborvitae leaves was dispersed into 50 mL solution with the each initial

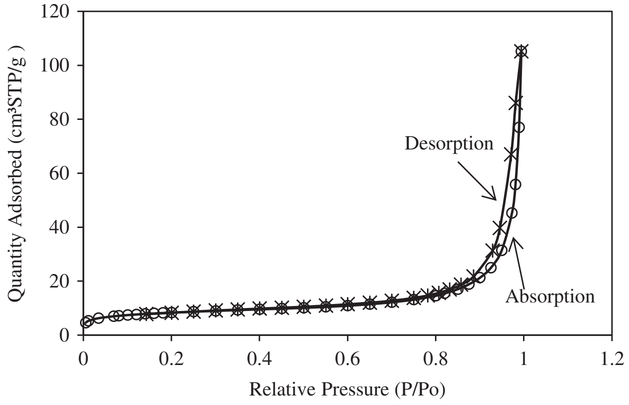

Fig. 1. Nitrogen adsorption/desorption isotherms for arborvitae leaves.

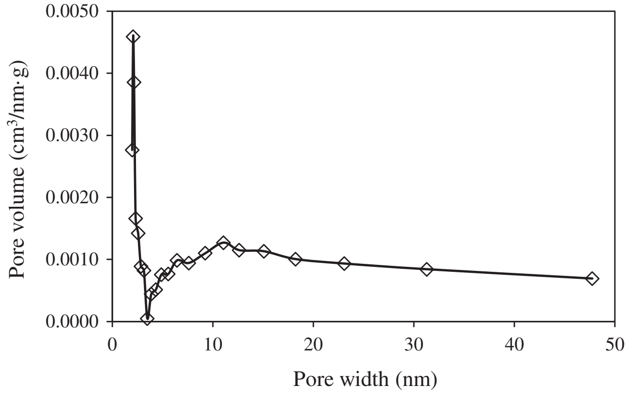

Fig. 2. Pore size distributions of arborvitae leaves.

concentration of three heavy metal ions in the range from 5 to 30 mg/L, and then conducted under the conditions consistent with the single-component adsorption experiment.

Except for experiments for evaluation of pH effect, the initial pH was adjusted to 5.5 with 0.1 mol/L HCl or 0.1 mol/L NaOH. Additionally, all experiments were conducted in triplicates, and a fourth flask containing only the metal ion solution (no arborvitae leaves) was set as a control.

Immediately after shaking, samples were taken with pipettes and then filtered through a 0.45-μm membrane. The filtrates were analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 5300DV, US) to detect the metal ion concentration. The sorption capacity q (mg/g) was calculated according to the following equation [16]:

$$q = [(C_0 - C_d)V/W] \tag{1}$$

where C_0 and C_d are the initial and detected concentrations (mg/L) of metal ions in the aqueous solution, respectively. V is the volume of synthetized metal ions-contained water and W is the mass of adsorbent.

3. Results and discussion

3.1. Material characterizations

3.1.1. BET surface area measurements

The adsorption properties of arborvitae leaves are dependent on the surface area and pore diameter.

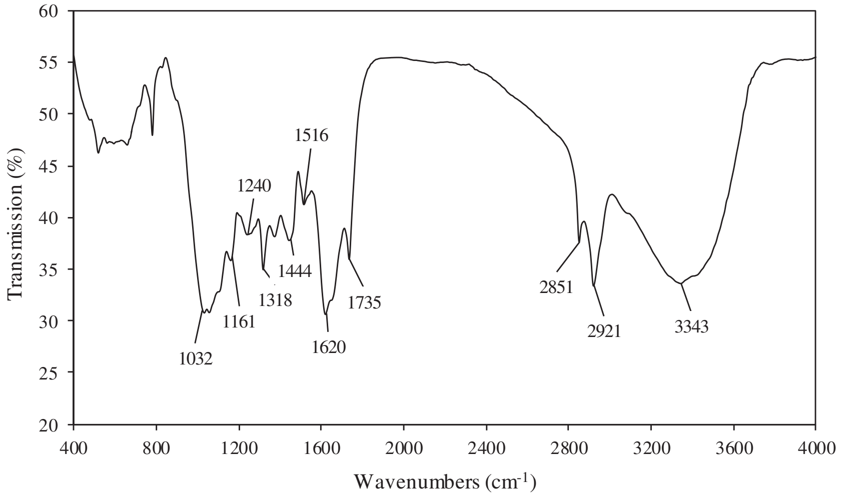

Fig. 3. FT-IR spectra of arborvitae leaves.

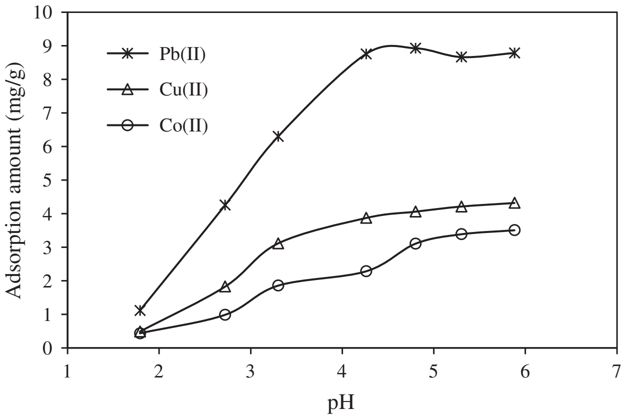

Fig. 4. Effect of pH on Pb(II), Cu(II), and Co(II) ions adsorption by arborvitae leaves (initial concentration of Pb(II), Cu(II), and Co(II) ions = 20 mg/L; reaction time = 5 h; absorbents dose = 0.1 g).

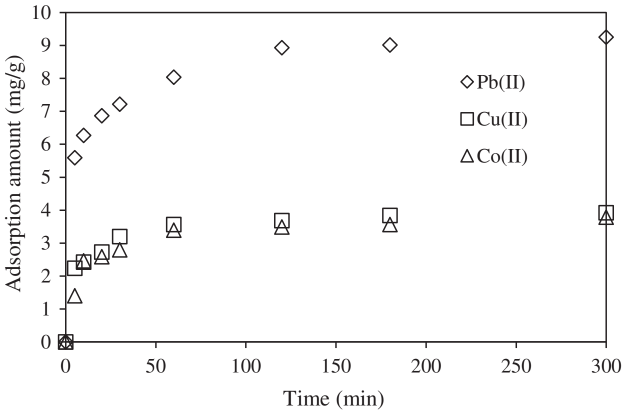

Fig. 5. Effects of contact time on the adsorption process in the Pb(II), Cu(II), and Co(II) single systems (initial concentration of Pb(II), Cu(II), and Co(II) ions = 20 mg/L; absorbents dose = 0.1 g; initial pH 5.5).

Fig. 1 shows the N_2 adsorption/desorption isotherms of the arborvitae leaves. Calculated from Fig. 1, the surface area of the arborvitae leaves was 29.52 m^2/g. Meanwhile, the pore diameters of arborvitae leaves were between 2 and 50 nm as shown in Fig. 2. With properties in terms of mesopores, the arborvitae leaves may serve as a promising material for the adsorption of heavy metal ions in water treatment [17].

3.1.2. FT-IR analysis

The FT-IR is commonly used to examine the surface groups of the adsorbents and to identify those groups responsible for the metal ions adsorption. The FT-IR spectrum of arborvitae leaves is given in Fig. 3. It can be seen that there are a number of absorption peaks, indicating numbers of active groups and bonds existed on the arborvitae leaves. The adsorption band at about 3,343 cm^{-1} was ascribed to the stretching vibrations of O–H group. The adsorption bands observed at 2,921–2,851 cm^{-1} were assigned to the C–H stretching, and the peaks around 1,735 and 1,620 cm^{-1} could be a characteristic of carbonyl group stretching from –COOH. The characteristic of C–O band absorption peak was observed in the range 1,300–1,000 cm^{-1} [17–20]. In general, oxygen functionalities (carboxyl and hydroxyl groups) on materials can involve in the binding of heavy metal ions [17], which suggested that the mechanisms of heavy metal ions adsorption on arborvitae leaves could also occur by cationic exchange and surface complexation.

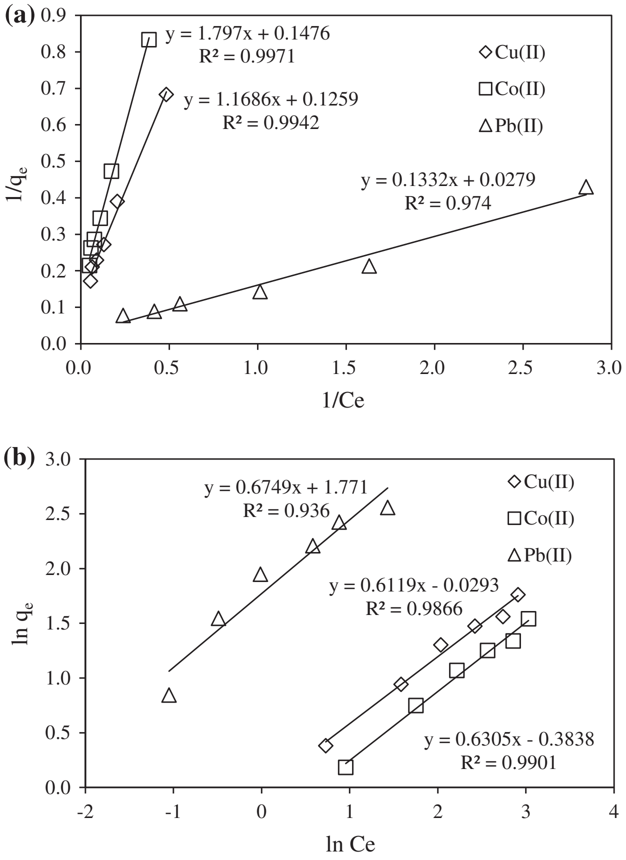

Fig. 6. Adsorption isotherms for single ions of Pb(II), Cu (II), and Co(II) ions onto arborvitae leaves: Langmuir(a) and Freundlich(b) (reaction time = 5 h; absorbents dose = 0.1 g; initial pH 5.5).

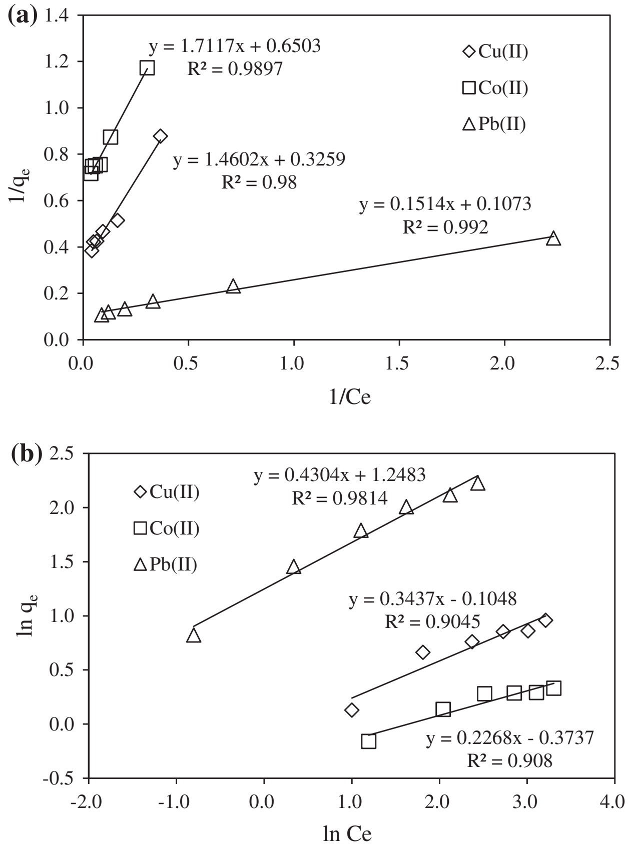

Fig. 7. Competitive adsorption isotherms for Pb(II), Cu(II) and Co(II) ions onto arborvitae leaves: Langmuir(a) and Freundlich(b) (reaction time = 5 h; absorbents dose = 0.1 g; initial pH 5.5).

3.2. *Effect of pH on adsorption of Pb(II), Cu(II), and Co(II) ions*

The pH of the solution plays an important role in the interaction between adsorbents and metal ions [21]. Fig. 4 shows the influence of the pH of the initial solution on the adsorption of Pb(II), Cu(II), and Co(II) ions onto arborvitae leaves in the pH range of 1.79–5.88. It can be seen from the graph that the adsorption amount by arborvitae leaves increased sharply from 1.12 to 8.76 mg/g for Pb(II), 0.49 to 3.87 mg/g for Cu (II), and 0.44 to 2.28 mg/g for Co(II) with an increase in the pH of the solution from 1.79 to 4.26, respectively. There was no significant increase observed at higher pH values, and the similar phenomena were demonstrated by another research [22]. When the pH value was low (less than 4.0), a high concentration of H^+ could compete with Pb(II) for exchangeable cations on the surface of adsorbents, resulting in the suppression of Pb(II) adsorption on the natural adsorbents surface [23]. In addition, most of the functional groups are protonated at low pH. At higher pH values, due to the weak competition effect of the H^+, more positively charged Pb(II) was adsorbed on the negatively charged sites [24]. According to the speciation diagrams for Pb(II), Cu(II), and Co(II) ions, when the pH value was below 6, Pb(II), Cu(II), and Co(II) ions exist mainly in form of ions. Besides, $PbOH^+$, $CuOH^+$, and $CoOH^+$ would exist, and then the precipitation of Pb (II), Cu(II), and Co(II) metal ions was occurred simultaneously with the increase in the pH value [25–27]. Hence, the optimum pH value was adjusted at 5.5 for the further experiments.

3.3. *Adsorption kinetics*

The adsorption kinetics can reflect the uptake rate of adsorbate in the solid–liquid interface. Fig. 5 shows the effects of contact time on the adsorption of single Pb(II), Cu(II), and Co(II) ions, respectively. The results revealed that the adsorption capacities increased with the increase in contact time for three kinds of metal ions, and the adsorption equilibrium time of Pb(II), Cu(II), and Co(II) ions was 120 min. The adsorption capacities were 9.25, 3.93, and 3.79 mg/g for Pb(II), Cu(II), and Co(II) ions, respectively.

3.4. *Adsorption isotherms*

Adsorption isotherms are powerful tools to study the adsorption capacity of adsorbents. The adsorption parameters were determined by the linearization of

Table 1
Langmuir parameters of single and competitive adsorption isotherm models for Pb(II), Cu(II), and Co(II) ions onto arborvitae leaves

	Single ion adsorption			Competitive ion adsorption		
Adsorbate	q_m (mg/g)	K_L (L/mg)	R^2	q_m (mg/g)	K_L (L/mg)	R^2
Pb(II)	35.84	0.209	0.974	9.32	0.709	0.992
Cu(II)	7.94	0.108	0.994	3.07	0.223	0.98
Co(II)	6.78	0.082	0.997	1.54	0.30	0.990

Table 2
Comparison of maximum adsorption capacities for Pb(II), Cu(II), and Co(II) ions removal

Adsorbent	Pb(II) (mg/g)	Cu(II) (mg/g)	Co(II) (mg/g)	Conditions	Refs.
Black carrot residues	–	8.745	5.350	pH 5.5; 293 K	[1]
Rice husks	–	6.262	–	pH 6.07; 298 K	[2]
Palygorskite	–	–	8.88	pH 6.0; 308 K	[27]
Recycled waste glass	11.68	6.68	–	pH 5.6; 298 K	[29]
Raw maize stover	19.65	–	–	pH 5.0; 293 K	[34]
Barley straw ash	–	6.04	4.15	pH 6.5; 298 K	[35]
Scolecite	5.8	4.2	–	pH 6.0; room temperature	[36]
Arborvitae leaves	35.84	7.94	6.78	pH 6.0; 298 K	Present study

the Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) isothermal adsorption models. Based on the different theory of hypothesis, the Langmuir adsorption isotherm model and the Freundlich adsorption isotherm model were based on the theory of monolayer adsorption and multiphase adsorption [28], respectively. However, since the Langmuir and Freundlich isotherms cannot provide any information about sorption mechanism, the DKR isotherm model was used to predict the nature of adsorption processes as physical or chemical [29]. Each isotherm model was expressed as relative certain constants, which characterized the surface properties and the adsorption capacity of the adsorbent [30].

Fig. 6(a) and (b) illustrated the Langmuir and Freundlich adsorption isotherms of single component onto arborvitae leaves. The experimental data of the metal ions adsorption fitted the Langmuir isotherm model better than the Freundlich isotherm model. All of the three species of metal ions had better correlation coefficient values for the Langmuir isotherm model (>0.97). The Langmuir and Freundlich adsorption isotherms models for the competitive adsorption of Cu(II), Co(II), and Pb(II) ions onto arborvitae leaves are shown in Fig. 7. The competitive adsorptions of Cu(II), Co(II), and Pb(II) ions on the adsorbent fitted the Langmuir isotherm model with the values of R^2 (0.98–0.99) and the Freundlich isotherm model with the values of R^2 (0.9045–0.9814). The results suggested that the experimental data fitted the Langmuir isotherm model better and the adsorbed metal ions of Cu (II), Co(II), and Pb(II) ions formed a monolayer coverage on the surfaces of arborvitae leaves [31].

The Langmuir isotherm parameters were listed in Table 1. In the single adsorption system, the adsorption affinity order of the three heavy metals was Pb > Cu > Co, which was in agreement with the order of electronegativity value (Pb(2.33) > Cu(1.90) > Co (1.88)) [32]. Compared with the single adsorption system, the adsorption capacity of the three species of heavy metals decreased significantly in the ternary component system. The adsorption capacity of the arborvitae leaves for Pb(II), Cu(II), and Co(II) ions decreased from 35.84 to 9.32 mg/g, 7.94 to 3.07 mg/g, and 6.78 to 1.54 mg/g, respectively. A similar trend of the decreased adsorption of the heavy metal ions in

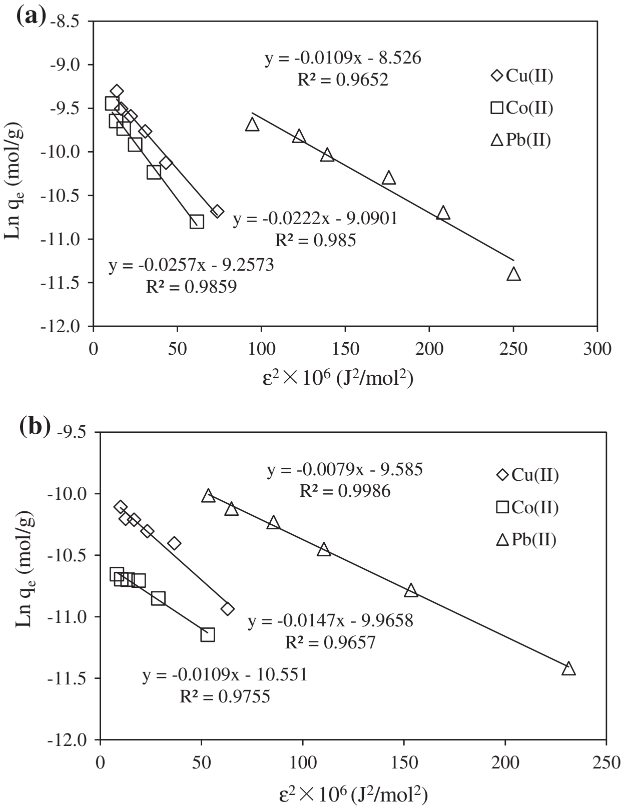

Fig. 8. The linearized DKR adsorption isotherms for Pb(II), Cu(II), and Co(II) ions onto arborvitae leaves: single component system (a) and ternary component system (b) (reaction time = 5 h; absorbents dose = 0.1 g; initial pH 5.5).

Table 3
Parameters DKR isotherms based on the adsorption of Pb(II), Cu(II), and Co(II) ions

	Single ion adsorption				Competitive ion adsorption			
Adsorbate	X_m (mg/g)	β (mol^2/J^2)	Sorption energy (E, kJ/mol)	R^2	X_m (mg/g)	β (mol^2/J^2)	Sorption energy (E, kJ/mol)	R^2
Pb(II)	41.04	-1.09×10^{-8}	6.77	0.9652	14.23	-7.9×10^{-9}	7.96	0.9986
Cu(II)	7.22	-2.22×10^{-8}	4.75	0.985	3.01	-1.47×10^{-8}	5.83	0.9657
Co(II)	5.63	-2.57×10^{-8}	4.41	0.9859	1.54	-1.09×10^{-8}	6.77	0.9755

binary or ternary systems was reported for *Spirodela polyrhiza* (L.) *Schleiden* [6] and activated carbon [33].

The results showed that the competition for the adsorption sites on arborvitae leaves existed among the different heavy metals, which had an antagonistic effect on the adsorption process.

The adsorption performance of arborvitae leaves for Pb(II), Cu(II), and Co(II) ions in this study was compared with that of other natural adsorbents reported in the literatures. The values are shown in Table 2. It is clearly noted that the arborvitae leaves had higher adsorption capacity than the previously reported adsorbents, which suggested that natural arborvitae leaves are promising adsorbents to remove Pb(II), Cu(II), and Co(II) ions from aqueous solutions in terms of adsorption capacity.

As shown in Fig. 8, the plot of ln q_e against ε^2 gave β (mol^2/J^2) and X_m (the sorption capacity, mg/g). Table 3 summarized the parameters and correlation coefficients for DKR isotherms of Pb(II), Cu(II), and Co(II) ions adsorption on arborvitae leaves. As shown in Table 3, the *E*-values were 6.77 for Pb(II), 4.75 for Cu(II), and 4.41 kJ/mol for Co(II) on arborvitae leaves in the single adsorption system, respectively, which were all below 8 kJ/mol indicating that a stronger physical adsorption existed [29,37,38]. Similarly, the *E*-values for Pb(II), Cu(II), and Co(II) ions on arborvitae leaves in the ternary metal solution system were 7.96, 5.83, and 6.77 kJ/mol, respectively, thus the adsorption type could also be explained as the physical adsorption.

4. Conclusion

The adsorption of Pb(II), Cu(II), and Co(II) ions onto the arborvitae leaves were investigated in the single and ternary component systems. The initial pH and contact time, the important variables, controlled the adsorption of heavy metals. The adsorption isothermal data fitted the Langmuir isotherm model better than the Freundlich isotherm model in both systems. Compared with those in the single adsorption system, the adsorption capacity of Pb(II), Cu(II), and Co(II) ions on arborvitae leaves in the ternary metal solution systems decreased from 35.84 to 9.32 mg/g, 7.94 to 3.07 mg/g, and 6.78 to 1.54 mg/g, respectively. For the DKR isotherm model, the sorption energy *E*-values for Pb(II), Cu(II), and Co(II) ions on arborvitae leaves were all below 8 kJ/mol in the single and ternary metal solution systems, and the adsorption mechanism could be explained as the physical adsorption. Conclusively, the preliminary results indicated that the arborvitae leaves could be used as the natural adsorbent for the heavy metals removal.

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