

Preparation of the ramulus mori-based adsorbent and its adsorption performance for heavy metals ions

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Abstract: The waste Ramulus Mori generated from sericulture process was chemically modified with succinic acid to prepare Ramulus Mori-based adsorbent for removal of heavy metals from aqueous solution. The as-prepared adsorbent was characterized by Fourier Transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The isoelectric point, specific surface area and oxygenic groups of the as-prepared adsorbent were measured and the adsorption behavior for heavy metals including Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} were investigated. The results show that a lot of oxygenic groups were grafted into the as-prepared adsorbent. The Ramulus Mori-based adsorbent exhibited highly efficient and rapid adsorption for heavy metals. The adsorption isotherm of the four heavy metals could be well fitted by Langmuir and Temkin model and the maximum adsorption capacity of the prepared adsorbent for Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} was estimated, by Langmuir model, to be 67.57, 50.25, 46.95 and 50.51mg/g, respectively. The adsorption may be governed by chemisorption involving coordination between heavy metals and the oxygen in oxy groups on the surface of the adsorbent and ion exchange between cationic heavy metals and carboxylic group on the surface of the adsorbent by electrostatic attraction. The competitive adsorption between the four heavy metals was in the order of $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. The Ramulus Mori-based adsorbent could be regenerated effectively and reused.

1. Introduction

Lead, cadmium, copper and zinc are the most common heavy metals in effluents discharged from many industries such as electroplating, printing, mining, non-ferrous metal processing and papermaking, etc.[1]. Heavy metals are nonbiodegradable in environment. They can enter human body via food chain or drinking water and damage human health, resulting in mental retardation, nervous illness or cancer [2]. At present, adsorption, ion exchange, flocculation, chemical precipitation, oxidation-reduction, microbial decomposition etc. have been employed to remove heavy metals from wastewater. Of these, adsorption and ion exchange are considered as a most effective technique. Activated carbons and ion exchange resins are common adsorbents used in removing heavy metals from wastewater. However, they are costly and limited in wide application. To reduce the cost of adsorption, a variety of biomass materials, such as fruit peels, corncobs, bagasses, peanuts, drying algae and ferns etc., have been developed to be low-cost and effective substitutes in removing heavy metals [3-8].

In China, a great numbers of waste Ramulus Mori have been generated from sericulture. These



Ramulus Mori had once been discarded or burned as fuel, resulting in waste of resource and low efficiency of sericulture. At present, to save resource, waste Ramulus Mori has been used in cultivation of edible fungi and manufacture of artificial silk, cotton and pulp. However, Ramulus Mori contains 49.1% of celluloses and 28.1% of lignin [9]. There are lots of highly active alcohol hydroxyl groups in molecular of celluloses and lignin. In our research group, waste Ramulus Mori was used to prepare Ramulus Mori-based adsorbents by esterification between succinic acid and hydroxyl in celluloses from Ramulus Mori. The schematic illustration of preparation route for the Ramulus Mori-based adsorbents was as follows. Firstly, succinic acid was dehydrated at high temperature to obtain a reactive anhydride, then anhydride combined with the hydroxyl groups of celluloses by ester bonds and carboxylic acid groups were introduced into Ramulus Mori-based adsorbents. Finally, the carboxylic acid of the adsorbents was converted to sodium carboxylate by neutralization with sodium bicarbonate. Adsorption of dyes by the Ramulus Mori-based adsorbents prepared in our laboratory had ever been reported [10]. In this study, the removal of heavy metals from aqueous solution by Ramulus Mori-based adsorbents was investigated for the first time.

2. Experimental materials and methods

2.1. Experimental materials

Ramulus Moris were collected from Sericulture Research Institute, Chinese Academy of Agriculture Science. The Ramulus Mori-based absorbent is prepared according to the literature [10].

Potassium dichromate, zinc chloride, lead nitrate, cadmium chloride, copper chloride dihydrate were purchased from Chemical Reagent Co. Ltd. Sodium bicarbonate, sodium hydroxide, hydrochloric acid were obtained from Chemical Reagent Factory, Tianjin. All chemical reagents are of analytical grade.

2.2. Characterization of the absorbent

The morphology of the Ramulus Mori s-based absorbent was observed by scanning electron microscopy. Functional groups on the surface of Ramulus Mori-based absorbents were characterized by Fourier Transform infrared spectroscopy. The specific surface area of the Ramulus Mori-based absorbent sample was measured by nitrogen adsorption/desorption method. The oxygenic groups on the surface of the Ramulus Mori-based absorbent were determined by Boehm titration [11]. Zeta potential of the sample was determined by electrophoresis.

2.3. Batch Adsorption

Adsorption of heavy metal ion was carried out by using batch adsorption experiments. 100mL aqueous solution of heavy metals with the concentration of 50mg/L was added into a flask. A given amount of Ramulus Mori-based absorbents were added and were then shaken at 180r/min in the rotary oscillator until the adsorption equilibrium. The samples were taken out and separated by centrifugation for 10min. Then the concentration of heavy metal ions in the supernatant was measured by AA-6320 atomic absorption spectrophotometer. The percentage removal (R) and the adsorption capacity (q_e) was calculated by Eq.(1) and Eq.(2), respectively.

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (2)$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium. C_0 and C_e (mg/L) are the initial and equilibrium concentration of the heavy metal ions, respectively. V (L) is the liquid volume; W (g) is the mass of the absorbent.

2.4. Competitive adsorption experiments

The mixture solution containing 50mg/L of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} was added into a flask. 0.8g of

the Ramulus Mori-based absorbents was added into the flask and then shaken at 180r/min until the adsorption equilibrium.

2.5. Regeneration of the adsorbent

The Ramulus Mori-based absorbent which reach adsorption saturation was filtered and then was added to 100ml of HCl solution with the concentration of 0.01mol/L in a flask. The flask was stirred at 180r/min for 60min to carry out desorption. After desorption was finished, the adsorbents were centrifugally separated, washed with deionized water until neutrality and then dried for the next adsorption experiment. Five cycles were repeated to evaluate the reuse of Ramulus Mori-based absorbent.

3. Results and discussions

3.1. Characterization of Ramulus Mori-based adsorbents

3.1.1. SEM analysis

SEMs of the Ramulus Mori-based absorbents were presented in Fig.1. As shown in Fig.1, The samples of raw Ramulus Moris and Ramulus Mori-based adsorbent are both porous. Chemical modification didn't significantly change the morphology of the adsorbent. But, the chemically modified Ramulus Moris existed as honeycomb and had more abundant porous cavities, which can increase the surface area and pore volume of the adsorbent. It is beneficial for the adsorption of heavy metal ions.

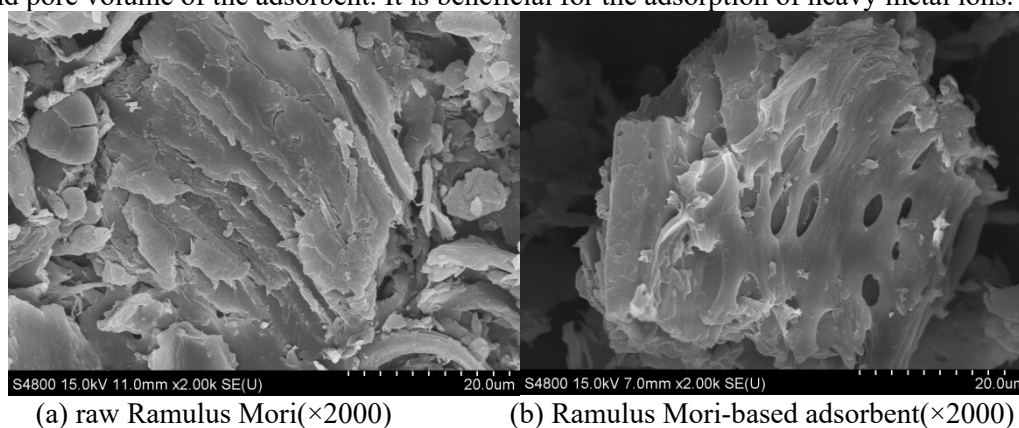


Fig.1. SEM of Ramulus Moris-based adsorbent

3.1.2. FT-IR spectra analysis

FT-IR spectra of the Ramulus Mori-based adsorbent and raw Ramulus Moris were shown in Fig.2. As seen in spectrum of raw Ramulus Moris powder (Fig. 2a), the adsorption peak at 3373cm^{-1} is attributed to the -OH stretching vibration. The peak at 2912cm^{-1} is due to saturated hydrocarbon C-H stretching vibration. A weak peak were observed at 1714cm^{-1} and can be attributed to C=O stretching vibration of -COOH groups. adsorption peaks at 1616cm^{-1} , 1495cm^{-1} , 1367cm^{-1} is due to C=O asymmetrical and symmetrical stretching vibration of -COO⁻ groups, respectively. The characteristic adsorption peak near 1043cm^{-1} is due to stretching vibration of C-O groups in primary hydroxy from the Ramulus Mori cellulose. The Fig.2b is the spectrum of Ramulus Mori-based adsorbent. Compared to Fig. 2a, -OH stretching vibration at 3373cm^{-1} was shifted to 3406 and weaken, It is indicated that -OH group reacted with modifier Succinic acid. The two strong adsorption peak at 1734cm^{-1} , 1236cm^{-1} is attributed to C=O bond stretching vibration and -C-O-C stretching vibration of open chain anhydride, respectively. It is indicated that the reaction of succinic acid with cellulose formed a new -C-O-C bond (the latter carbon atom is the cellulose carbon atom). The carboxylic groups were introduced into the adsorbent during preparation of the adsorbent.

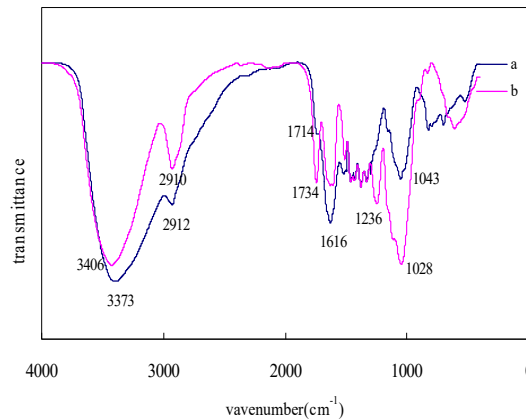


Fig.2. FT-IR spectra of Ramulus Mori -based adsorbent

3.1.3. The oxygenic groups

The content of the oxygenic groups, such as carboxylic, phenolic hydroxyl and lactonic groups on the surface of the Ramulus Mori-based adsorbent were measured by Boehm titration. The results were listed in Table.1.

As exhibited in Table.1, the content of carboxylic groups and lactonic groups of the Ramulus Mori-based adsorbent were significantly more than that of the raw Ramulus Mori powder. Moreover, the oxygenic groups of Ramulus Mori-based adsorbent existed in large amount of carboxylic groups, a few of lactonic groups and hardly little of phenolic hydroxyl groups. Hence, the peak of aromatic group was not found in FT-IR infrared spectrum in section 3.1.2.

Table1. Content of oxygenic groups on Ramulus Mori-based adsorbent

Adsorbent		carboxylic group (mmol/g)	lactonic groups (mmol/g)	Phenolic hydroxyl group (mmol/g)	Total (mmol/g)
Raw Mori	Ramulus	0.52	0.06	0.08	0.66
prepared adsorbent		2.60	0.17	0.08	2.85

3.1.4. Specific surface area

The specific surface areas of the Ramulus Mori-based adsorbent and the raw Ramulus Mori powder were determined, by N₂ adsorption/desorption method, to be 1.6933m²/g and 0.9757m²/g, respectively. Compared with the raw Ramulus Mori powder, the specific surface areas of the Ramulus Mori-based adsorbent increased, suggesting that the Ramulus Mori-based adsorbent has higher adsorption capacity than the raw Ramulus Mori.

3.1.5. Zeta potential

The relationship between zeta potential of Ramulus Mori-based adsorbents and pH was presented in Fig.3. It can be seen from Fig.3, zeta potential decreased with increasing pH. When pH value is 4.2, the zeta potential is zero. When pH of solution is less than 4.2, the surface of Ramulus Mori-based adsorbent was positively charged. As pH is more than 4.2, Ramulus Mori-based adsorbent was negatively charged. Therefore, the isoelectric point of Ramulus Mori-based adsorbent was 4.2.

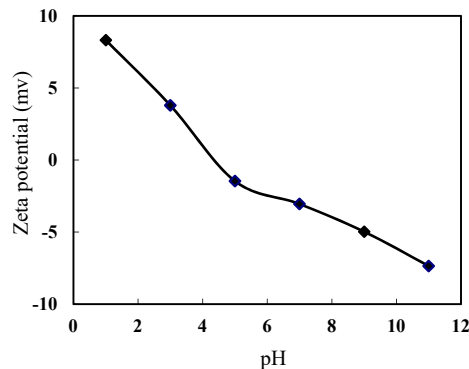


Fig.3. Zeta potential values of Ramulus Mori-based adsorbent

3.2. Effect of pH on adsorption efficiency

Initial pH can influence the adsorption sites of Ramulus Mori-based adsorbent and existing forms of heavy metal ions during adsorption [12]. To investigate the effect of initial pH on the adsorption properties of heavy metal ions, adsorption was performed at pH less than critical pH at which heavy metal ions can hydrolyze to form hydroxide precipitation. The effects of pH on adsorption efficiencies were shown in Fig.4.

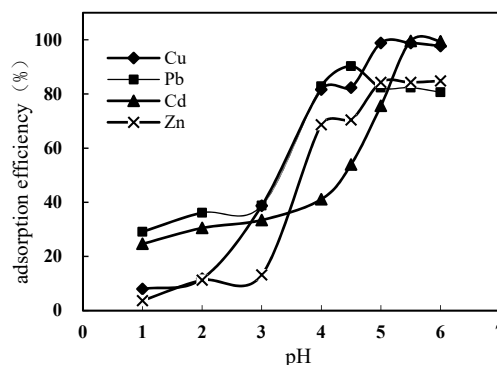


Fig.4. Effects of initial pH on adsorption efficiency

As given in Fig.4, The adsorption efficiencies of Ramulus Mori-based adsorbent for Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} increased with increasing initial pH under acidic condition. At pH 4.5, the adsorption rate of Ramulus Mori-based adsorbents for Pb^{2+} reach maximum value 90.3%. At pH 5.5, the adsorption efficiencies reaches maximum value 99.5%, 98.8% and 84.8% for Cd^{2+} , Cu^{2+} and Zn^{2+} , respectively.

The isoelectric point of adsorbents was measured to be 4.2 in 3.1.5 section. When pH value of solutions was below 4.2, the dissociation of carboxylic groups was restrained. So, most of carboxylic groups exist in the form of $-\text{COOH}$, resulting in the decreases in the adsorption site which produce electrostatic attraction with heavy metal ions. Adsorption was performed only through coordination between oxygen from lactonic groups and carboxylic groups with heavy metal ions, which bring about low adsorption capacity. When pH exceed pKa values or isoelectric point pH, the dissociation of carboxylic groups $-\text{COOH}$ made carboxylic groups exist in the form of $-\text{COO}^-$, enhancing the electronegativity on the surface of the Ramulus Mori-based adsorbent. The positively charged heavy metal ions could be adsorbed via not only coordination but also electrostatic attraction, resulting in significantly enhanced adsorption efficiency.

3.3. Adsorption isotherms

The adsorption isotherms of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} on the adsorbent at 25°C were given in Fig.5.

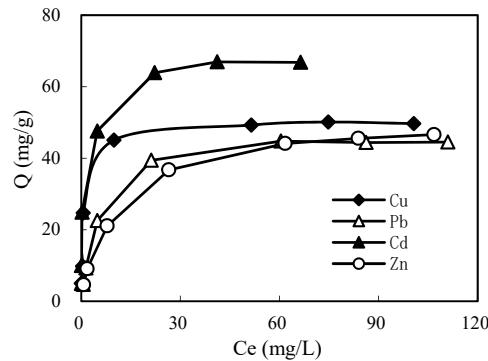


Fig.5. Adsorption isotherm of heavy metal ions at 25°C

Fig 5 shows that the adsorption capacity of the Ramulus Mori-based absorbent for Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} increased significantly with increasing equilibrium concentration of heavy metal solutions. The data were fitted with representative adsorption isotherm models, such as Langmuir, Freundlich, Dubinin–Radushkevich (D-R) and Temkin models which is expressed by eq.(3), eq(4), eq(5) and eq (6), respectively[14-17].

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{1}{Q_0} c_e \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (4)$$

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln c_e \quad (6)$$

Where C_e is the equilibrium concentration in solution; q_e is the equilibrium adsorption capacity; Q_0 is the maximum adsorption capacity; b_L is the Langmuir constant related to the free energy of adsorption; K_F is the Freundlich constant related to the adsorption capacity of the adsorbent; n is the Freundlich constant related to the intensity of the adsorbent; β is the constant related to the adsorption energy; b is the Temkin constant related to the change of the adsorption energy; K_T is the Temkin constant related to the corresponding maximum binding energy.

The obtained model parameters and linear regression coefficients (R^2) were presented in Table.2. It can be seen from Table.2 that Langmuir and Temkin models both can simulate the adsorption process of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} well. And the highest linear regression coefficient is obtained by Langmuir model. All of R^2 values exceed 0.999 for the four ions, indicating the adsorption process is monolayer adsorption and the adsorption capacity is in the order of $\text{Cd}^{2+} > \text{Zn}^{2+} \sim \text{Cu}^{2+} > \text{Pb}^{2+}$. The calculated R_L values are in the range of 0-1, indicating adsorption is favorable.

Table 2. The adsorption isothermal parameters

Ions	Langmuir			Freundlich			D-R			Temkin		
	Q_0	R_L	R^2	k_F	$1/n$	R^2	q_m	B ($\times 10^{-3}$)	R^2	k_T	b	R^2
Cu^{2+}	50.25	0.0167	0.9998	17.44	0.2701	0.8974	35.95	2.140	0.6921	74.76	0.432	0.9322
Pb^{2+}	46.95	0.0894	0.9994	8.039	0.4155	0.9135	35.20	3.736	0.8356	2.943	0.2900	0.9725
Cd^{2+}	67.57	0.0173	0.9993	22.60	0.3167	0.8873	59.42	4.14	0.9825	49.49	0.2847	0.9906

Zn²⁺ 50.51 0.1527 0.9993 6.577 0.4589 0.9631 33.87 4.873 0.7940 142.28 22.74 0.9888

3.4. Adsorption kinetics

At 25°C, the adsorption rate curves of the adsorption of Ramulus Mori-based absorbent for Cu²⁺, Pb²⁺, Cd²⁺ and Zn²⁺ were depicted in Fig.6. As presented in Fig.6, the adsorption was rapid and reached equilibrium after 30min.

To further study the adsorption mechanism, the pseudo-first order, pseudo-second order and intraparticle diffusion equations, which is expressed as eq.(7), eq.(8) and eq.(9) respectively[18-21], are employed to fit the adsorption data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

$$q_t = k_p t^{1/2} + C \quad (9)$$

Where, q_e indicates the equilibrium adsorption capacity (mg/g); q_t represents the adsorption capacity at time t (mg/g); k_2 is the second order reaction rate constant (g/mg/min); k_1 is the first order reaction rate constant (min⁻¹). k_p represents the constant of the adsorption rate (mg g⁻¹ min^{-1/2}); C represents the intercept, the value of C reflects the boundary layer thickness.

The model parameters and correlation coefficients obtained from linear regression were listed in Table 3. It can be seen obviously from table 3 that the pseudo-second order kinetic model shows excellent linear correlation with correlation coefficients more than 0.99 for the four ions, indicating that adsorption process is mainly chemical adsorption [22].

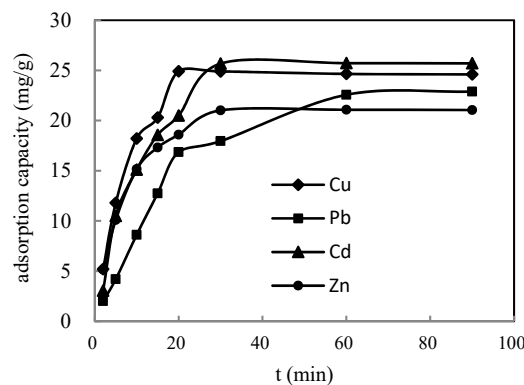


Fig. 6. Effect of adsorption time on the adsorption property at 25°C

Table 3. The kinetic adsorption parameters

Metal ions	pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	K_1	q_{e1}	R^2	K_2	q_{e2}	R^2	k_d	C	R^2
Cu ²⁺	0.0204	4.48	0.5857	0.0128	25.13	0.9994	1.1036	13.03	0.5311
Pb ²⁺	0.0573	26.03	0.8920		27.03	0.9910	1.8591	3.89	0.8373
Cd ²⁺	0.0268	6.09	0.6195		25.91	0.9989	1.3807	10.19	0.6450
Zn ²⁺	0.0211	4.72	0.6216		21.74	0.9995	0.9733	10.95	0.6018

Notes: (1) q_{e1} and q_{e2} in mg/g. (2) K_1 in min⁻¹, K_2 in g/mg·min and k_d in mg/g·min^{1/2}.

3.5 Competitive adsorption experiments

Under the coexistence of heavy metal ions Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} , adsorption capacity of Ramulus Mori-based adsorbent for heavy metal ions are shown in Table.4.

Table 4. Adsorption capacity of competitive adsorption

ions	competitive adsorption q (mg/g)	single adsorption q(mg/g)
Cu^{2+}	41.49	50.25
Pb^{2+}	33.17	46.95
Cd^{2+}	63.24	67.57
Zn^{2+}	27.92	50.51

As given in Table.4, when adsorption was carried out under the coexistence of the four ions, the adsorption capacity of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} decreases by 17.43%, 29.35%, 6.41%, 44.72%, respectively, compared with single adsorption. It is indicated that the competitive adsorption phenomenon occurred between the four ions. Furthermore, the preferential adsorption of the four ions is in the order of $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$.

3.6 Regeneration and reuse

Ramulus Mori-based adsorbent saturated by heavy metal ion was regenerated by using 0.01 mol/L HCl solution as desorbent, and the regenerated Ramulus Mori-based adsorbent were employed to adsorb the heavy metal ion once more. Adsorption-desorption was repeated for 5 cycle, the ratio of q_i/q_e was employed to evaluate regeneration efficiency (q_i and q_e represent the adsorption capacity of every cycle and the first adsorption, respectively), and the results were listed in Fig.7. As given in Fig.7, for every recycle, adsorption capacity of the four heavy metal ions decrease slightly. Nevertheless, after cyclic regeneration for 5 times, the ratios of q_i/q_e are still more than 80%. Considering the adsorption capacity decrease resulted from a certain loss of adsorbent due to solid-liquid separation during the regeneration, it is, therefore, concluded that the Ramulus Mori-based adsorbent can be regenerated efficiently and reused.

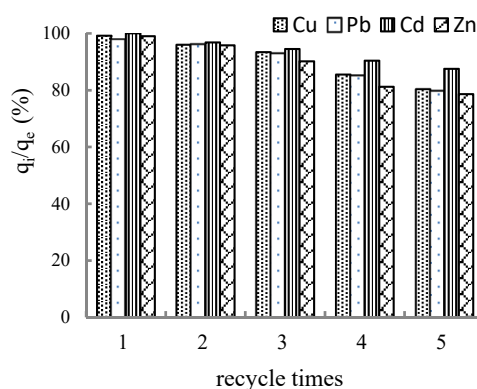


Fig. 7. Cyclic reuse of Ramulus Mori-based adsorbent

4. Conclusion

The waste Ramulus Mori was modified with succinic acid to prepare Ramulus Mori-based adsorbent with specific surface areas of $1.6933\text{m}^2/\text{g}$ and the isoelectric point of 4.2. A large number of oxygenic groups were introduced into Ramulus Mori-based adsorbents. The oxygenic groups exist in form of lots of carboxylic groups and a few of lactonic groups and hardly little of phenolic hydroxyl.

The Ramulus Mori-based adsorbent showed highly efficient and rapid adsorption for Cd^{2+} , Cu^{2+} ,

Pb^{2+} and Zn^{2+} . Adsorption equilibrium time was 30min. The maximum adsorption capacity for Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} was estimated to be 67.57, 50.25, 46.95 and 50.51mg/g, respectively. The adsorption may be governed by chemiadsorption involving not only coordination between heavy metals and the oxygen in oxy groups but also ion exchange between cationic heavy metals and carboxylic group on the surface of the absorbent by electrostatic attraction. The competitive adsorption between the four heavy metals was in the order of $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. The Ramulus Mori-based absorbent can be regenerated with 0.01mol/L HCl and reused.

Acknowledgements:

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