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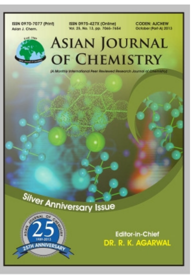

Adsorption of Ni(II), Cd(II) and Cr(III) on the Palm Thread Ash Burned at Low Temperature

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Adsorption of Ni(II), Cd(II) and Cr(III) from aqueous solutions was studied by using a novel adsorbent (ash-palm thread), palm thread (PT) burned at low temperature. The electron microscopy, infrared spectroscopy and X-ray diffraction were used to analyze the sorbent. The effects of contact time, adsorption temperature and initial pH on the adsorption were examined. The results showed that ash-palm thread had larger specific surface area and many active groups good to the adsorption; the adsorption reached the equilibrium *ca.* 480 min and was influenced by pH and temperature. The adsorption kinetics was better meet the Lagergren pseudo second kinetic model. The adsorption isotherms were better fitted Langmuir adsorption model. The sorption performance of ash-palm thread indicates that it is an effective biosorbent for removing heavy metals from aqueous solutions.

Key Words: Ash-palm thread, Adsorption, Kinetic, Isotherm, Nickel, Chromium and cadmium.

INTRODUCTION

With the accelerating process of industrialization and urbanization, the worldwide ecological risk is a growing problem. Due to the emissions of industrial waste, water pollution caused by heavy metals is a particularly serious problem[1,2]. Heavy metals in environmental media, are not biodegradable, but could be accumulated *in vivo* through the food chain. Some even could be transformed into more toxic chemical forms in some biological toxicity level and ultimately accumulated in the human body to endanger human health[3,4].

The treatment methods of wastewaters polluted by heavy metals have been extensively researched recently. The methods include chemical precipitation[5], electro-chemical precipitation[6], ion exchange[7], coagulation and flocculation[8], active carbon absorption[9,10] and biosorption[11-13]. Adsorption in a number of treatment methods is an easy to operate and economically viable, so the choice of the adsorbent is the key to this technology weather is feasible or not[14]. With the deepening of understanding on the circular economy and sustainable development concept, the natural adsorbents such as cocoa hull, lignin, chitosan and biomass, gradually have been focused on such studies[15-17]. Based on the above concept, we are trying to find a natural and environmentally friendly adsorbent. Palm thread (hereafter referred to as palm thread), taken from palm tree, is a porous and fine tubular biomaterial. In China, palm trees are common vegetation mainly found in the Qinling Mountains and the south of the Yangtze River, especially in Sichuan, Yunnan, Guizhou, Hunan, Hubei and Shaanxi provinces. Their wide distribution makes the palm thread (PT) a low cost and easy accessible biomaterial. The major constituents of palm thread are cellulose, lignin, pentosan and siliceous-cell. Ni(II) and Cd(II) adsorption onto palm thread and modified palm thread have been studied[18] by author.

In this study, the ash of palm thread burned at low temperature was prepared (labeled as ash-palm thread). The main purpose of this paper is to study the feasibility of Ni(II), Cd(II) and Cr(III) sorption on ash-palm thread. Surface properties of the adsorbents were characterized. Some influencing factors of adsorption were examined and the sorption performance was evaluated by kinetics and isotherm models.

EXPERIMENTAL

Palm thread (PT) was obtained from the located palm trees (Shanghai, China). The palm thread was washed several times with deionized water to remove dust and soluble impurities. Then it was dried for 12 h in an oven at 65 ºC. The palm thread, only washed by the deionized water, was labeled as palm thread. $NiNO_3·6H_2O$, $CdNO_3·4H_2O$, $CrNO_3·9H_2O$ and NaOH are of analytical grade and were purchased from

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The standard solutions and HNO_3 for AAS were guaranteed reagent and were purchased from Alfa Aesar A Johnson Matthey Company (NJ, USA).

Preparation of palm thread-ash burned at low temperature: palm thread-ash was prepared by burning the palm thread at *ca.* 600 ºC for 2 h and then transfered to a desiccator for cool down to the room temperature.

Characterization of sorbent: The surface configuration palm thread-ash was showed by scanning electron microscope JSM-6360LV (JEOL, Japan). Specific surface area was measured by time methylene blue adsorption method[19]. Fourier transform infrared spectroscopy Nicolet 5700 (Thermo Electron, USA) and X-ray diffractometer UltimaIV (Rigaku, Japan) were used to analyze the surface groups of the sorbent. The pH value was measured by a Mettler Toledo (Columbus, OH, USA) Delta 320 pH meter.

Batch mode sorption for Ni(II), Cd(II) and Cr(III): The ash-palm thread to adsorb Ni(II), Cd(II) and Cr(III) were examined by measuring the initial and equilibrium concentrations of Ni(II), Cd(II) and Cr(III) in a batch system.

Batch mode adsorption studies were carried out by shaking 60 mL screw cap vials with polytetrafluoroethylene sealer containing 0.02 g of sorbents and 50 mL of Ni(II), Cd(II) and Cr(III) solutions of desired concentration on an orbital shaker equipment at 120 rpm at 25 ºC. At the end of the adsorption, the supernatant solution was separated by centrifugation at 3000 rpm for 10 min. Effect of contact time, adsorption temperature and initial pH were studied. Langmuir and Freundlich isotherms were used to analyze the equilibrium adsorption data. The first order, second order kinetic models and Elovich model were used to analyze the adsorption kinetic data.

Analysis: After equilibrium was reached, the residual of Ni(II), Cd(II) and Cr(III) concentration was analyzed using Jena650P atomic absorption spectrophotometer (Jena, Germany) at wavelengths of 425.4nm. The uptake (q) of Ni(II), Cd(II) and Cr(III)was calculated from the mass balance as follows:

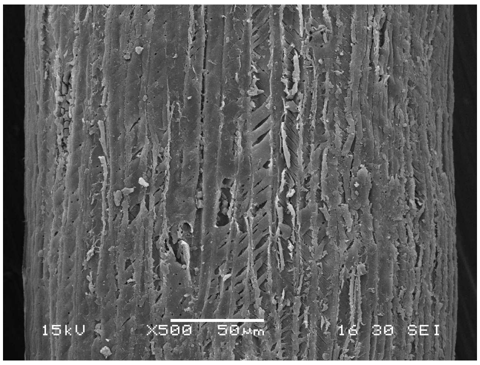
$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where q_e is the equilibrium sorption capacity (mg g^{-1}); V is the experimental solution volume (L) and m is the amount of adsorbent (g) used; C_0 and C_e are the initial and equilibrium concentrations of Ni(II), Cd(II) and Cr(III) (mg L^{-1}), respectively.

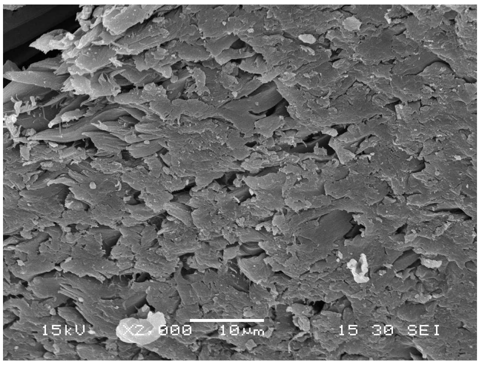
RESULTS AND DISCUSSION

Analysis of surface configuration: The SEM photos of palm thread and ash-palm thread are shown in Fig. 1(a-d). As shown in Fig. 1(a-b), palm thread has a complete fiber structure and the structure of these fibers formed the skeleton of palm thread. Compared to Fig. 1(a), ash-palm thread shown in Fig. 1(c) also remained the basic skeleton of palm thread, but it was more porous and honeycomb; compared to Fig. 1(b), as shown in Fig. 1(d) the regular structure of palm thread completely disappeared and replaced by irregular small floc and lamellar structure.

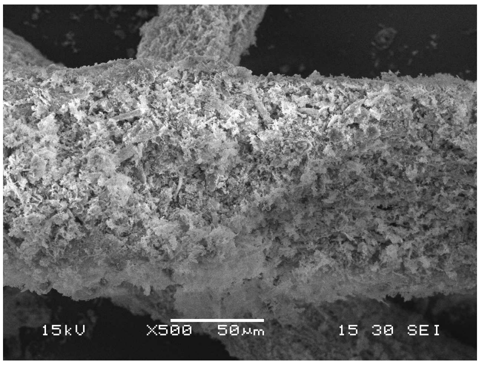
Analysis of specific surface area: The specific surface areas of palm thread and ash-palm thread were shown in Table-1.



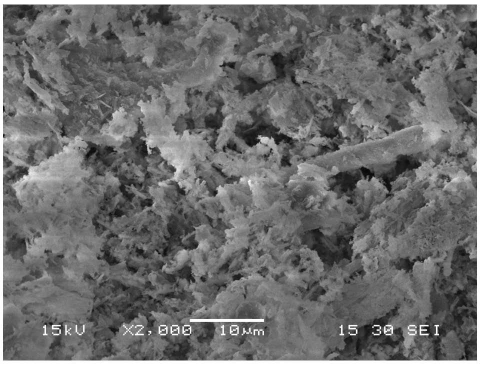
(a) Palm thread (× 500)



(b) Palm thread (× 2000)



(c) Ash-palm thread (× 500)



(d) Ash-palm thread (× 2000)

Fig. 1. SEM pictures of palm thread and ash-palm thread

TABLE-1
SPECIFIC SURFACE AREA OF PALM THREAD AND ASH-PALM THREAD

Adsorbent	Specific surface area (m^2 g^{-1})
Palm thread	0.57
Ash-palm thread	2.88

The results showed that comparing to palm thread, specific surface area of ash-palm thread greatly improved *ca.* 400 %. This proved that ash had more specific surface area, thereby increasing the contact area and contact probability of the adsorption material and heavy metal ions.

Analysis of fourier transform infrared spectroscopy (FTIR): The FTIR spectrum of ash-palm thread was shown in Fig. 2. Peaks at 3396, 2919, 1448, 1132, 877, 673 and 628 cm^{-1} are observed in the spectrum. The broad and strong band at 3396 cm^{-1} is attributed to the overlapping of O-H and N-H. Peak at 2919 cm^{-1} is the C-H stretching vibration. The peak at 1132 cm^{-1} can be assigned to O-Si-O stretching vibration. The peaks at 1448, 673, 628 and 877 cm^{-1} can be separately to carboxylic acid (O-H), alcohol (C-H), acetylenic hydrocarbons (C-H) and tertiary amine (N-H) all strengthened. All those surface functional groups are to the benefit of heavy metals adsorption.

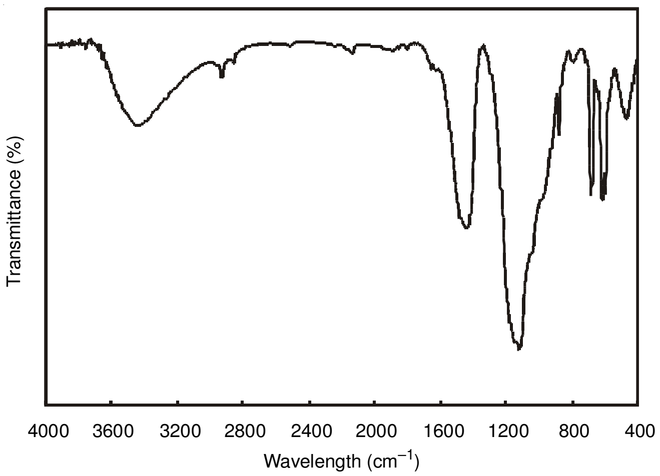


Fig. 2. FT-IR spectra of ash-palm thread

Analysis of X-ray diffraction (XRD): XRD spectra of ash-palm thread was shown in Fig. 3. As shown in Fig. 3, peaks at 25.44, 29.38, 31.36 and 48.66° are very narrow and are the characteristic peaks of SiO_2. The peak at 25.44° is the main peak of SiO_2 and is the sign of the high degree of crystallization of SiO_2, while weak peaks at 29.38, 31.36 and 48.66° the lower degree of crystallinity silica. This shows that the main ingredient of ash-palm thread is active SiO_2, which come to the same conclusion with the previous infrared spectroscopy. Active SiO_2 molecules have strong complexation with metal ions, making the ash-palm thread has a strong adsorption properties.

Effect of contact time on Ni(II), Cd(II) and Cr(III) sorption: As shown in Fig. 4, sorption amounts of Ni(II), Cd(II) and Cr(III) increased with increasing contact time. All curves have similar tendency and appear to be governed by two transport stages. During the first stage (0-60 min), the sorption rate was very high. Sorption amounts of Ni(II), Cd(II) and Cr(III) on ash-palm thread increased rapidly and all exceeded 50 % of the equilibrium sorption capacity. During the second stage (60-480 min), the sorption rate became much lower. The sorption amount increased slowly but gradually and approached equilibrium in about 480 min.

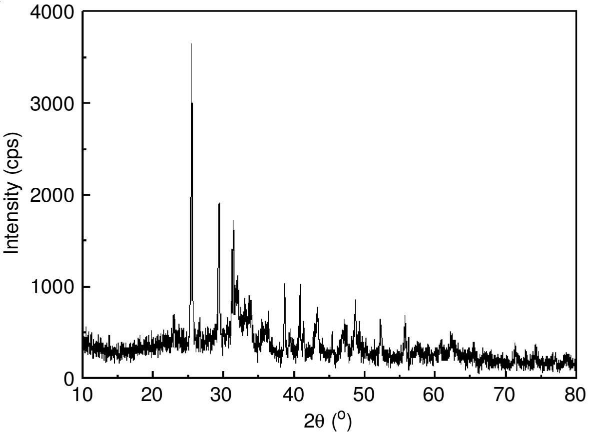


Fig. 3. X-Ray diffraction analysis of ash-palm thread

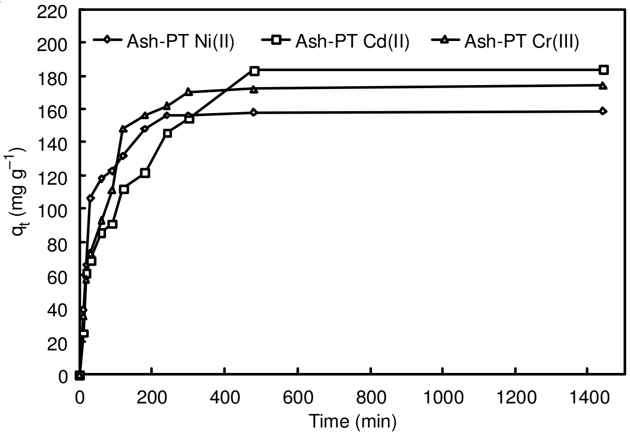


Fig. 4. Effect of contact time on adsorption capacity of Ni(II), Cd(II) and Cr(III) by ash-palm thread

At the beginning of adsorption, as the large surface of ash-palm thread and the high concentration of heavy metals, the adsorption rate was faster; as time past, the adsorption rate decreased as the reduction of adsorption sites of surface and the concentration.

Effect of adsorption temperature on Ni(II), Cd(II) and Cr(III) sorption: Fig. 5 showed that with the increasing temperature, the Ni(II), Cd(II) and Cr(III) adsorption capacity on ash-palm thread showed a gradually increasing trend. At 45 ºC, the Ni(II), Cd(II), Cr(III) adsorption capacity on ash-palm thread were 203.1, 222.7 and 213.5 mg g^{-1} and more than them at 25 ºC, respectively, 29.8, 20.8 and 23.3 %. This was also consistent with the general to slightly elevated temperatures conducive to adsorption[20]. Therefore, increasing temperature was good to the Ni(II), Cd(II), Cr(III) adsorption on ash-palm thread.

Effect of initial pH on Ni(II), Cd(II) and Cr(III) sorption: The initial pH of the solution determines the charge density of the adsorbent surface, thereby affecting the adsorption effect. The effect of initial pH on the Ni(II), Cd(II), Cr(III) adsorption capacity were examined and the results were shown in Fig. 6.

At strong acid medium ($pH < 3$), Ni(II), Cd(II), Cr(III) adsorption capacity increased rapidly with increasing pH. And Ni(II), Cd(II), Cr(III) adsorption capacity at $pH = 1$, respectively increased by 530, 520 and 960 % than at $pH = 3$. With

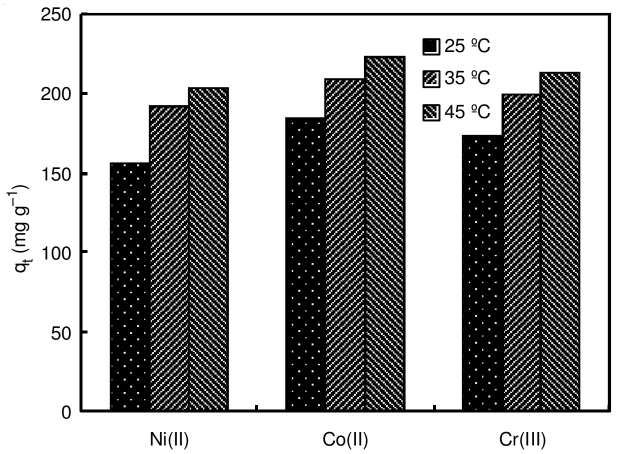


Fig. 5. Effect of temperature on adsorption capacity of Ni(II), Cd(II) and Cr(III) by ash-palm thread

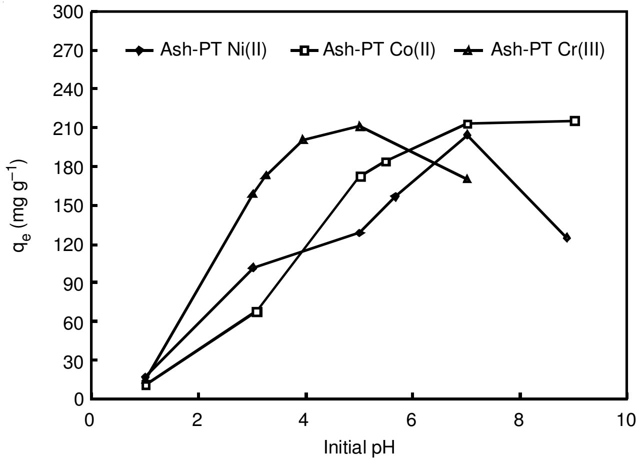


Fig. 6. Effect of initial pH on adsorption capacity of Ni(II), Cd(II) and Cr(III) by ash-palm thread

the rise of the initial pH, Ni(II), Cd(II), Cr(III) adsorption capacity continued to increase and reached the maximum value at pH 7, 9 and 5, respectively. Possible reason was that, under acidic conditions, a large number of H^+ were in solution and could combined with -OH and-COOH on the sorbent surface. This could change the affinity of the adsorbent and hindering the metal ions combined with the adsorbent surface, so the adsorption capacity was relatively low[21]; when the pH increased, the H^+ combined with the adsorbent surface functional groups was dissociative and surface potential density was reduced, so the adsorption capacity increased. As shown in Fig. 6, the Cr(III) and Ni(II) adsorption capacity decreased significantly at pH of 7 and 9. This could because that at this condition may be due to this condition Cr(III) and Ni(II) could be form the hydroxide precipitation and seriously affected them adsorption in the adsorbent surface[22].

Sorption kinetics of Ni(II), Cd(II) and Cr(III): Various models have been suggested to express the kinetics of adsorption of solute molecules onto a sorbent. We tested the probabilities of three kinetic models to describe the processes of Ni(II), Cd(II) and Cr(III) adsorption onto ash-palm thread. These models were a pseudo-second-order model, an intraparticle diffusion model and a pseudo-first-order model.

The pseudo-second-order kinetic model used is[23-25]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{2}$$

The Elovich model used is[26,27]:

$$q_t = a + b \ln t \tag{3}$$

The pseudo-first-order kinetic model used is[23,27]:

$$\ln(q_e - q_t) = \ln q_1 - k_1 t \tag{4}$$

In these models, k_2 (g mg^{-1} h^{-1}) is the rate constant for the pseudo-second-order model, a, b are the constants related to surface coverage and activation energy, k_1 (h^{-1}) is the rate constant for the pseudo-first-order model, q_e (mg g^{-1}) is the amount of solute adsorbed at equilibrium and q_t (mg g^{-1}) is the amount of solvent adsorbed at time t (min).

As shown in Table-2, the R^2 of fitted curve using the Elovich model kinetic model was between in 0.84-0.99. It indicates that this model could give a suitable description of the sorbent ash-palm thread to Ni(II), Cd(II) and Cr(III). Elovich model was more suitable for the idealized single molecule layer chemical adsorption process, so it was reputed that adsorption of ash-palm thread tends to be more idealized single molecule layer chemical adsorption. Fig. 7 shows the plots of sorption data fitted to pseudo-second-order equation.

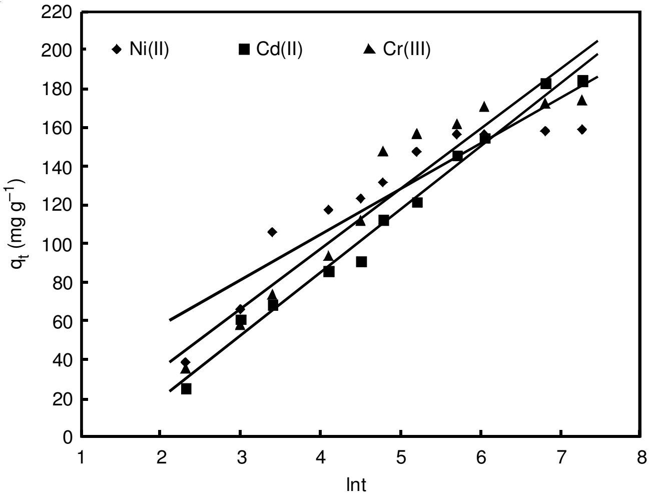


Fig. 7. Elovich kinetic curves

TABLE-2
KINETIC PARAMETERS FOR SORPTION DATA FITTED TO KINETIC MODELS

Heavy metal	Initial concentration (mg L^{-1})	Elovich model			Pseudo-first-order model		Pseudo-second-order model			
		a	b	R^2	k_1 [g (mg min)$^{-1}$]	R^2	k_2 [g (mg min)$^{-1}$]	q_e^b (mg g^{-1})	q_e^a (mg g^{-1})	R^2
Ni(II)	50	36.36	0.043	0.85	4.84E-03	0.88	2.79E-04	161.3	158.9	>0.99
Cd(II)	50	5.38E-14	0.693	0.98	5.30E-03	0.99	6.31E-05	196.1	184.4	>0.99
Cr(III)	50	13.3	0.032	0.91	5.30E-03	0.94	1.44E-04	178.6	174.2	>0.99

[a]Equilibrium sorption capacity from experimental results. [b]Equilibrium sorption capacity calculated from pseudo-second-order model.

The Pseudo-first-order kinetic curves were shown in Fig. 8. Table-2 also shows the R^2 of fitted curve using pseudo-first-order model and the R^2 was between in 0.87-0.99, indicating that the pseudo-first-order model could describe the Ni(II), Cd(II), Cr(III) adsorption process in a certain extent.

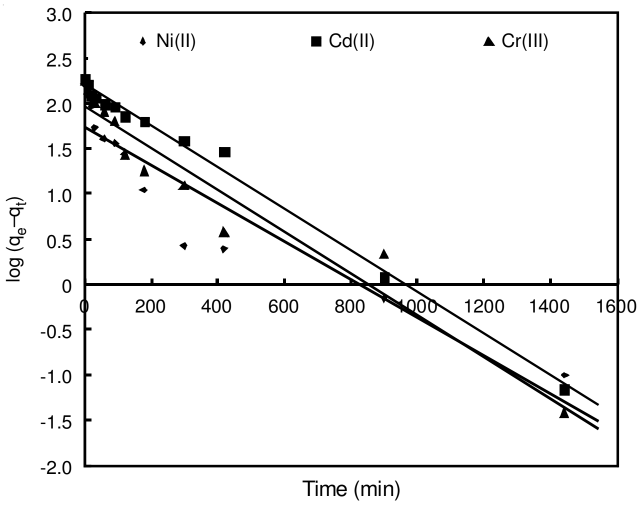


Fig. 8. Pseudo-first-order kinetic curves

As shown in Table-2, comparing to other kinetic models, the pseudo-second-order model was more fitted to the adsorption process, as R^2 were all over 0.99. This indicated that adsorption rate is proportional to the quadratic of the reactants concentration. And the curves were shown in Fig. 9.

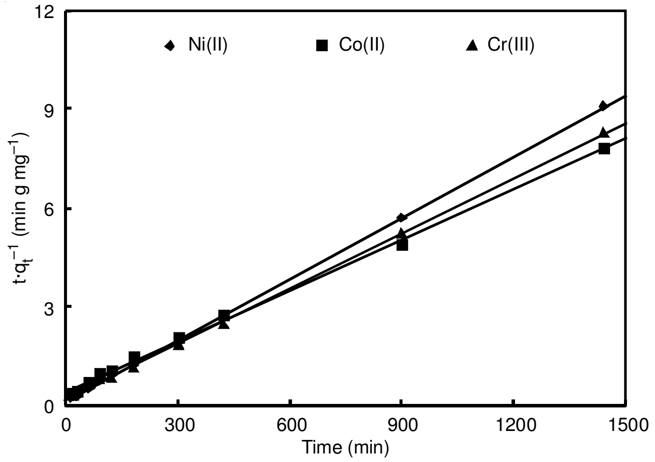


Fig. 9. Pseudo-second-order kinetic curves

Sorption isotherm of Ni(II), Cd(II) and Cr(III): The equilibrium sorption isotherm was used to quantify the sorption of Ni(II), Cd(II) and Cr(III) on ash-palm thread.

Freundlich model was used to describe the sorption isotherms:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

where K_F = sorption capacity coefficient ((mg g^{-1}) (L mg^{-1})1/n); n = Freundlich exponent that describes the non-linearity degree of sorption; C_e = equilibrium concentrations of Ni(II), Cd(II) and Cr(III) (mg L^{-1}).

Langmuir model was also examined to describe the sorption isotherms:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (6)$$

where K_L is Langmuir adsorption constant (L mg^{-1}); q_{max} is monolayer adsorption capacity (mg g^{-1}); C_e is equilibrium concentrations of Ni(II), Cd(II) and Cr(III) (mg L^{-1}).

Sorption coefficients and parameters of Freundlich and Langmuir model of Ni(II), Cd(II) and Cr(III) by ash-palm thread are shown in Table-3. All the sorption isotherms were better-fit to the Langmuir model than to Freundlich model due to R^2 values. As the Langmuir isotherm model is the ideal monolayer adsorption, the Ni(II), Cd(II), Cr(III) adsorption onto ash-palm thread met the monolayer adsorption in this concentration range.

Conclusion

This study investigated the surface properties, some influencing factors and sorption performance for Ni(II), Cd(II) and Cr(III) of the ash that palm thread (PT) burned at low temperature. Compared to palm thread, ash-palm thread remained the basic skeleton of the palm thread, but significantly improved the pore structure; specific surface area greatly improved about 400 %; the description of FIR and XRD indicated ash-palm thread contained large quantities of active SiO_2. These all were to the benefit of the Ni(II), Cd(II) and Cr(III) adsorption onto ash-palm thread. Adsorption temperature and initial pH both had effects on the adsorption. The adsorption kinetics better fitted to the Lagergren pseudo second kinetic model and the adsorption isotherm better fitted to Langmuir adsorption model.

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TABLE-3
FREUNDLICH AND LANGMUIR MODEL PARAMETERS OF Ni(II), Cd(II) and Cr(III) BY ASH-PT

Heavy metal	T (℃)	Freundlich model			Langmuir model		
		K_F (mg g^{-1}) L mg^{-1})$^{1/n}$	1/n	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
Ni(II)	25	58.4	0.3031	0.82	195.2	0.316	> 0.99
Cd(II)	25	117.5	0.1451	0.93	204.1	0.942	> 0.99
Cr(III)	25	75.6	0.2536	0.92	185.2	0.711	> 0.99

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