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Adsorption of Ni(II), Cd(II) from Aqueous Single Metal Solutions by the Palm Thread Impregnated with Sodium Dodecyl Benzene Sulfonate

WENGANG LV, YANBO ZHOU, BING HE, HAIBING QIU and JUN LU*

College of Resource & Environmental Engineering, East China University of Science & Technology, No. 130, Meilong Road, Shanghai 200237, P.R. China

*Corresponding author: Tel: +86 13764365741; E-mail: shimily666@163.com; lujun@ecust.edu.cn

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Adsorption of Ni(II) and Cd(II) from aqueous solutions was searched by using palm threads (PT) impregnated with anionic surfactant sodium dodecyl benzene sulfonate (SDBS). Two types of palm threads were used/applied; one was untreated palm threads (UPT) and the other was basified with NaOH *i.e.*, basified palm threads (BPT). When treated with surfactant-impregnated basified palm threads (SDBS-BPT) the removal of Ni(II) and Cd(II) was up to 21.0 and 25.3 mg g^{-1}, which was more better than the Ni(II) and Cd(II) removal performance of untreated palm threads with surfactant (SDBS-UPT) (*i.e.*, 9.2 and 16.6 mg g^{-1}). The kinetics of the adsorption of Ni(II) and Cd(II) onto the surfactant-impregnated palm threads were best described by the pseudo-second-order model and after being pretreated with NaOH. The sorption rate constants (k_2) of Ni(II) and Cd(II) increased from 0.5499 and 0.2017-1.5023 and 0.7274 g mg^{-1} h^{-1}, respectively and the total basicity also increased from 310.5-530.8 μeq g^{-1}. The isotherm was described better by the Freundlich adsorption isotherm than by the Langmuir model. The active groups and the total basicity enhanced significantly. when it was pretreated with NaOH and impregnated with SDBS, which resulted in the improved sorption rate and sorption capacity for Ni(II) and Cd(II). The sorption performance of SDBS-BPT indicates that it is an effective biosorbent for removing heavy metals from aqueous solutions.

Key Words: Palm thread, Adsorption, Impregnate, Sodium dodecyl benzene sulfonate, Basicity, Nickel and cadmium.

INTRODUCTION

Water contamination caused by heavy metal pollution has been a very important environmental issue for the past several decades and heavy metals are among the most important pollutants in source and treated water. Several treatment methods have been proposed to remove them from the wastewaters. The methods include chemical precipitation[1], electro-chemical precipitation[2], coprecipitation[3], ion exchange[4], membrane separation[5,6], coagulation and flocculation[7], complexation[8], active carbon absorption[9,10], double hydroxides adsorption[11,12] and biosorption[13-15].

Considerable attention has been devoted to the study of the removal of heavy metal ions from solutions by means of adsorption, because it is inexpensive, widely applicable/feasible and creates relatively little sludge. Conventional sorbents such as activated carbon and resin are widely used and showed acceptable performance in heavy metals sorption. However, the high cost and complex manufacturing procedures may limit their applications. Thus, research and development of excellent and low cost/cheap adsorbent is still the core problem of the adsorption method that urgently need to be solved. The biomaterials especially agricultural materials such as waste wool, nut wastes, tree barks, cotton and sawdust are used as adsorbents. Many agricultural byproducts such as bark and sawdust are low cost/extremely cheap materials. Though the sorption performances of natural biomaterials are not satisfactory, they can be improved through minor chemical alteration. Activated carbon produced from almond shell, sawdust based GAC, tree bark treated with formaldehyde and sulphuric acid, sulphurized activated carbon, ozonized activated carbon, chemically treated GAC, rice hulls and rice bran, pine bark, treated sawdust and agricultural wastes with or without pre-treatment have been widely used for the removal of heavy metals[13]. Therefore, the chemical modified biomaterials could be a new alternative in water treatment.

Palm thread (PT), 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 a low cost and easy accessible biomaterial. The major constituents of palm thread are cellulose, lignin, pentosan and siliceous-cell. Some preliminary investigations on the removal of heavy metal ions with

sawdust have been reported[15]. Sodium dodecyl benzene sulfonate (SDBS), a common and inexpensive anionic surfactant, is amphipathic substance with lyophobic and lyophilic groups, it can complex/react/combine with heavy metals and form the micelle in the aqueous solution, so it is widely used in water treatment with ultrafiltration and has been applied to modify the surface properties of solid[16-18]. Considering these characteristics, surfactant-modified adsorbents are not only superior in terms of removal efficacy than the conventional adsorbents, but also suggests selective adsorption[19]. Their use in the chemical modification of adsorbents can lead to selective separation and recovery of precious and noble metals as well[20].

In this study, based on the characters of palm thread and SDBS, a novel adsorbent for Ni(II) and Cd(II) was prepared by the combination of amphiphilicity of SDBS and the heterogeneous structure of palm thread. We modified the surface of the palm thread by impregnating it with SDBS in two different ways one was directly and the other indirectly. The direct one is carried out by no pretreated palm thread, while the indirect one is carried out by pretreating palm thread with sodium hydroxide solution. The main purpose of this paper is to study the feasibility of Ni(II) and Cd(II) sorption on palm thread impregnated with SDBS. Surface properties of the palm thread before and after impregnated were characterized. The sorption performance was evaluated by kinetics and isotherm models.

EXPERIMENTAL

Palm thread was obtained from local palm trees (Shanghai, China). The content of cellulose and lignin was 77.9 and 18.7 %, respectively. 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 and cut into pieces of length of 1-3 mm. The palm thread, only washed by the deionized water, was labeled as UPT. $NiNO_3 \cdot 6H_2O$, $CdNO_3 \cdot 4H_2O$, HNO_3 and NaOH are of analytical grade and were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The surfactant SDBS is chemical pure and was purchased from Lingfeng Chemical Co. (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 SDBS impregnated palm thread: SDBS impregnated UPT was prepared by mixing 10 g of palm thread with 1 L of 0.05 mol L^{-1} SDBS solution. The mixtures were shaken by Boxun (Shanghai, China) HHS-4 water bath oscillator for 12 h at 25 ºC, then the liquid was discharged and the impregnated palm thread was washed with distilled water several times to remove superficially held surfactant and it was re-dried as described above. Basified palm thread was prepared by steeped UPT in NaOH solution (5 % w/w) for 24 h, then washed with deionized water until the pH was neutralized (pH 7). Then it was dried for 12 h at 65 ºC and was labeled as BPT.

SDBS impregnated BPT was prepared with BPT under the same conditions of the SDBS-UPT prepared and was labeled as SDBS-BPT.

Characterization of sorbent: The surface configuration of UPT, SDBS-UPT, BPT and SDBS-BPT was showed by scanning electron microscope JSM-6360LV (JEOL, Japan). Carbon and hydrogen contents of adsrobents were determined by semi-automatic carbon-hydrogen measurement equipment type BHC-1 (Jiangsu, China) and their sulphur content was determined by coulomb sulfur analyzer type CLS-2 (Beijing, China). The analysis of elements show the changes of elements before and after impregnation. The identities of the functional groups on activated carbon were determined using Boehm titration to determine their acidities and basicities[21]. For measurement, 0.1 g of sorbent was mixed with 10 mL of basic or acidic solutions in 50 mL capped conical tubes. The mixtures were shaken at 160 rpm at 20 ± 1 ºC for 72 h and then passed through 0.45 μm PTFE syringe filter. To measure acidities, the solutions were 0.025 N $NaHCO_3$, Na_2CO_3, NaOH or $NaOC_2H_5$. The filtrates were titrated up to pH4.5 using a 0.025 N H_2SO_4 solution. To measure basicities, the solution was 0.025 N HCl. The filtrates were titrated up to pH 11.5 using a 0.025 N NaOH solution. The pH value was measured by a Mettler Toledo (Columbus, OH, USA) Delta 320 pH meter. Ash contents were measured by heating the samples at 815 ± 10 ºC for 2 h in the muffle furnace.

Batch mode sorption for Ni(II) and Cd(II): The UPT, SDBS-UPT and SDBS-BPT to adsorb Ni(II) and Cd(II) were examined by measuring the initial and equilibrium concentrations of Ni(II) and Cd(II) in a batch system.

Batch mode adsorption studies were carried out by shaking 60 mL screw cap vials with polytetrafluoroethylene sealer containing 0.2 g of sorbents and 50 mL of Ni (II) and Cd(II) solutions of desired concentration on an orbital shaker equipment at 150 rpm, 25 ºC and at an initial pH 5.8. At the end of the adsorption period, the supernatant solution was separated by centrifugation at 3000 rpm for 10 min. Effect of contact time was studied by withdrawing the samples from the shaker at predetermined time intervals. 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.

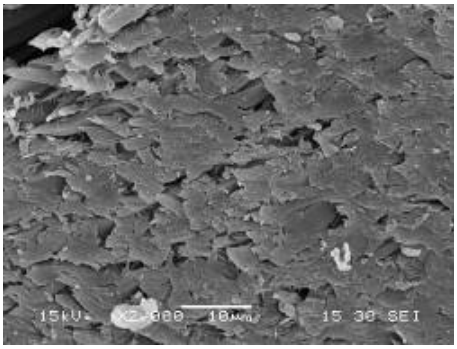
Analysis: After equilibrium was reached, the residual of Ni(II) and Cd(II) concentration was analyzed using AA-400 atomic absorption spectrophotometer (Jena, Germany) at wavelengths of 232.0 and 228.8 nm. The Ni (II) and Cd(II) uptake (q) was calculated from the mass balance as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

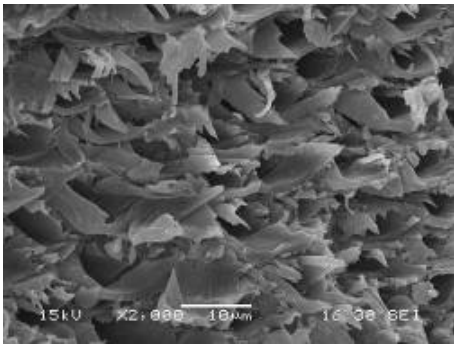
where q_e is the equilibrium sorption capacity (mg g^{-1}); V is the experimental solution volume (L) and m is the amount of adsorbent (g) used; C_0 and C_e are the initial and equilibrium concentrations of Ni(II) and Cd(II) (mg L^{-1}), respectively.

RESULTS AND DISCUSSION

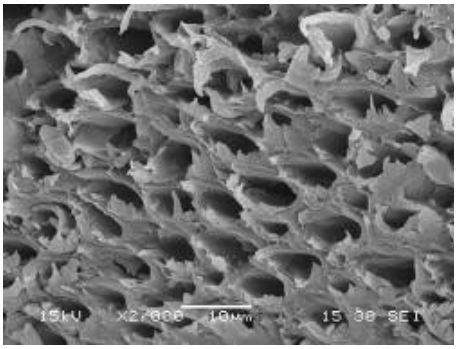
Analysis of surface configuration: The SEM photographs of UPT, SDBS-UPT, BPT and SDBS-UPT are shown in Fig. 1(a-d). As shown in Fig. 1(a), UPT has a complete fiber structure and the structure of these fibers formed the skeleton of UPT, therefore it has certain mechanical strength. The fiber structures of SDBS-PT remained intact, indicating that SDBS did not damage the fiber backbone, keeping good mechanical



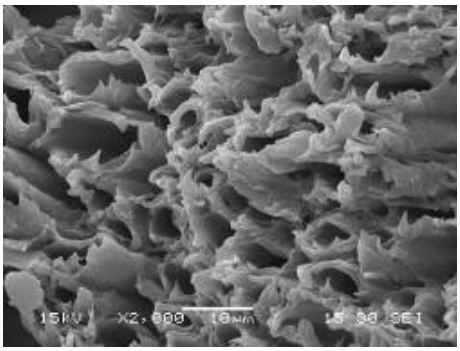
(a) UPT (×2000)



(b) SDBS-UPT (×2000)



(c) BPT (×2000)



(d) SDBS-BPT (×2000)

Fig. 1. (a)-(d) The SEM photo of UPT, SDBS-UPT, BPT and SDBS-UPT

strength. Comparing to the UPT, SDBS-UPT became more rough and its microtubule structure expanded. Fig. 1(c) shows that the surface became significantly rough and its microtubule structure also expanded. These features could be due to the formation of alkali cellulose as a result of the reaction of NaOH with cellulose. Comparing to BPT, the surface of SDBS-BPT had no significant changes.

Elemental analysis: Table-1 provides to the differences of elemental contents in UPT, SDBS-UPT, BPT, SDBS-BPT. Comparing to UPT,the carbon, hydrogen and sulphur contents of SDBS-UPT increased slightly,and indicated that SDBS was hardly attached onto the palm thread matrix. On the contrary, comparing to BPT, carbon, hydrogen and sulphur contents of SDBS-BPT increased obviously. A possible cause could be that palm thread was treated by NaOH and NaOH not only could make the surface of palm thread deprotonation but also could expand the aperture between the cellulose to make SDBS easily access to the inner body of the cell.

TABLE-1
ELEMENTAL COMPOSITION OF U-PT, SDBS-UPT, B-PT AND SDBS-B-PT

Sorbent	C (%)	H (%)	S (%)
UPT	50.08	3.13	0.161
SDBS-UPT	50.94	3.21	0.207
BPT	50.80	3.17	0.064
SDBS-BPT	54.90	3.84	0.180

Acidity and basicity analysis: Since the component of palm thread is so complex,the total acidities and basicities were determined instead of functional groups. The total acidities and basicities of UPT, SDBS-UPT, BPT and SDBS-BPT are showed in Table-2. Comparing to UPT, the SDBS-BPT has the lowest acidity (40.3 μeq g^{-1}) and highest basicity(530.8 μeq g^{-1}); SDBS-UPT only slightly changed total acidity(18 %) and total basicity (24 %).

TABLE-2
THE TOTAL ACIDITIES AND BASICITIES OF U-PT, SDBS-UPT, B-PT AND SDBS-B-PT

Sorbent	Aciditiy (μeq g^{-1})	Basicity (μeq g^{-1})
UPT	220.1	256.1
SDBS-UPT	180.4	310.5
BPT	70.5	443.2
SDBS-BPT	40.3	530.8

Acidic functional groups sequester heavy metals ions due to mainly by adsorption[22-24]. For this reason, many researchers have tried to increase the total quantity of surface functional groups and to make the surface charge more favorable for adsorption of cationic heavy metals. In this study, impregnation of palm thread with SDBS reduced its total acidity and increased its total basicity (Table-2). This result means that these anionic surfactants successfully covered the surface of palm thread. Specifically, total acidity of the palm thread was decreased because the surfactants covered surface acidic groups. Meanwhile, the hydrophilic heads of the surfactants could act as basic functional groups. In aqueous solutions, the bound anionic surfactants can be dissociated and then the protons bind to the hydrophilic heads, resulting in the increase of the SDBS-UPT's and SDBS-BPT's total basicities.

Effect of contact time on Ni(II) and Cd(II) sorption: As shown in Fig. 2 sorption amounts of Ni(II) and Cd(II) increased with increasing contact time. All curves have similar tendency and appear to be governed by two transport stages. During the first stage (0-2 h), the sorption rate was very high. Sorption amounts of Ni(II) and Cd(II) on SDBS-UPT and

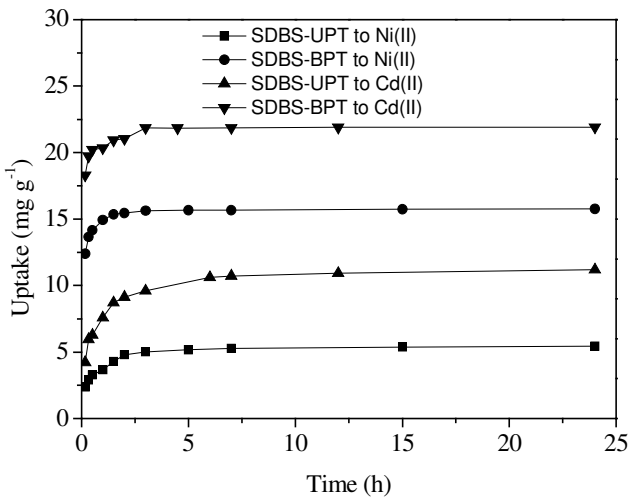


Fig. 2. Effect of contact time on Ni(II) and Cd(II) sorption on SDBS-UPT and SDBS-BPT

SDBS-BPT increased rapidly and all exceeded 90 % of the equilibrium sorption capacity, which indicates a quick partitioning of Ni(II) and Cd(II) from aqueous solution to active sites on palm thread surface. During the second stage (2-7 h), the sorption rate became much lower. The sorption amount increased slowly but gradually and approached equilibrium in about 7 h. Such results suggest that SDBS-UPT and SDBS-BPT both have rapid sorption rate for Ni(II) and Cd(II), which may benefit its application in water treatment.

Fig. 2 also shows that sorption capacity of SDBS-BPT are superior to that of SDBS-UPT. The equilibrium sorption capacities of SDBS-BPT for Ni(II) and Cd(II) were 15.7 and 21.9 mg g^{-1}, while those of SDBS-UPT for Ni(II) and Cd(II) were 5.4 and 11.2 mg g^{-1}, respectively. This indicates that the sorption capacity of palm thread was improved after being pretreated with NaOH.

Sorption kinetics of Ni(II) and Cd(II): 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) and Cd(II) adsorption onto SDBS-UPT and SDBS-BPT. These models were a pseudo-second-order model, an intra-particle diffusion model and a pseudo-first-order model.

The pseudo-second-order kinetic model used is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (2)$$

The Elovich model used is:

$$q_t = a + b \ln t \quad (3)$$

The pseudo-first-order kinetic model used is:

$$\ln (q_e - q_t) = \ln q_1 - k_1 t \quad (4)$$

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 (h). The initial adsorption rate in the pseudo-second-order kinetic model is $h = k_2 q_2^2$.

As shown in Table-3, the R^2 of fitted curve using the pseudo-first-order kinetic model was between in 0.82-0.92. It indicates that this model could not give a suitable description of the sorbent SDBS-UPT and SDBS-BPT to Ni(II) and Cd(II). Table-4 also shows the R^2 of fitted curve using Elovich model and the R^2 of SDBS-UPT seems to be better than SDBS-BPT. Elovich model was more suitable for the idealized single molecule layer chemical adsorption process, so it was reputed that adsorption of SDBS-UPT tends to be more idealized single molecule layer chemical adsorption.

Since the sorption reached equilibrium in about 7 h, the pseudo-second-order model was applied on sorption data between 0.17-7.00 h. Fig. 3 shows the plots of sorption data fitted to pseudo-second-order equation and indicates that pseudo-second-order model fitted all the kinetics sorption data. The pseudo-second-order model parameters were summarized in Table-4. The R^2 were all above 0.995 and the qe values calculated from the model were very close to the values obtained from the experimental results. It suggests that the sorption of Ni(II) and Cd(II) onto SDBS-UPT and SDBS-BPT follows the pseudo-second-order model.

As shown in Table-4, at specified initial concentration, k_2 value for SDBS-BPT is greater than that for SDBS-UPT. It can be easily seen in Fig. 3 that SDBS-BPT reached sorption

TABLE-3
PSEUDO-FIRST-ORDER MODEL AND ELOVICH MODEL KINETIC PARAMETER

Heavy metal	Sorbent	Initial concentration (mg L^{-1})	Pseudo-first-order model		Elovich model		
			k_1 (h^{-1})	R^2	a	b	R^2
Ni(II)	SDBS-UPT	46	0.46	0.92	3.88	0.84	0.96
	SDBS-BPT	46	0.69	0.84	14.56	0.85	0.86
Cd(II)	SDBS-UPT	51	0.33	0.92	7.66	1.78	0.98
	SDBS-BPT	51	0.76	0.84	20.46	0.91	0.91

TABLE-4
KINETIC PARAMETERS FOR SORPTION DATA FITTED TO PSEUDO-SECOND-ORDER MODEL

Heavy metal	Sorbent	Initial concentration (mg L^{-1})	q_e^a (mg g^{-1})	q_e^b (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	R^2
Ni(II)	SDBS-UPT	46	5.4	5.5	0.5496	0.999
	SDBS-BPT	46	15.6	15.7	1.5023	0.999
Cd(II)	SDBS-UPT	51	11.2	11.4	0.2017	0.998
	SDBS-BPT	51	21.9	21.9	0.7274	0.999

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

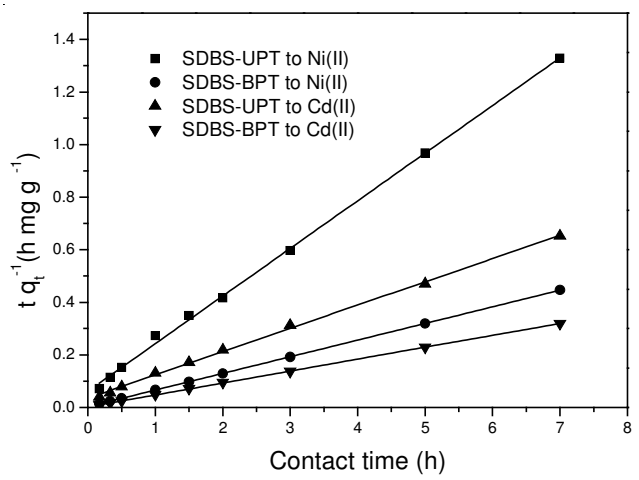


Fig. 3. Pseudo-second-order plots for sorption of Ni(II) and Cd(II) on SDBS-UPT and SDBS-BPT

equilibrium more quickly than SDBS-UPT. These results indicate that the sorption rate of heavy metals on SDBS-BPT was higher compared to that on SDBS-UPT. It could be explained as; more SDBS was attracted to the BPT than UPT and SDBS could complex the heavy metals very quickly according to the complex reaction. And at the same time, the total basicity of SDBS-BPT was much greater than that of SDBS-UPT, so the heavy metals could be attracted more quickly.

Sorption isotherm of Ni(II) and Cd(II): The equilibrium sorption isotherm was used to quantify the sorption of Ni(II) and Cd(II) on SDBS-UPT and SDBS-BPT.

Freundlich model was used to describe the sorption isotherms:

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

where K_F is the sorption capacity coefficient ((mg g^{-1}) (L $mg^{-1})^{1/n}$); n is the Freundlich exponent that describes the nonlinearity degree of sorption; C_e is equilibrium concentrations of Ni(II) and Cd(II) (mg L^{-1}).

Langmuir model was also examined to describe the sorption isotherms:

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

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) and Cd(II) (mg L^{-1}).

Sorption coefficients and parameters of Freundlich and Langmuir model of Ni(II) and Cd(II) by SDBS-UPT and SDBS-BPT are shown in Table-5. All the sorption isotherms better-fit to the Freundlich model than to Langmuir model and due to R^2 values the processes of SDBS-BPT could not use the Langmuir model to describe the kinetic involved. This result suggests that the heterogeneity of SDBS-UPT and SDBS-BPT surface and bidentate type adsorption process might be conducted between Ni(II) and Cd(II) ions and the negatively charged groups of surfactant onto palm thread.

Conclusion

This study investigated the effect of impregnated with SDBS on palm thread (PT) untreated and pretreated by NaOH on the surface properties and its sorption performance for Ni(II) and Cd(II) adsorption. Attachment of SDBS to palm thread increased the total basicity, especially when pretreated by NaOH, which maked the surface of the sorbents content more negatively charged, according to negatively charged groups in the hydrophilic head of SDBS. These groups made the surface charge more negative, resulting in more favorable conditions for Ni(II) and Cd(II) adsorption and could adsorb Ni(II) and Cd(II) more and faster. In other words, SDBS-BPT has greater sorption capacity and faster sorption rate comparing to SDBS-UPT. Therefore, the sorbent, palm thread pretreated by NaOH and then impregnated with SDBS was effective in adsorping Ni(II) and Cd(II) and could be better applied to the heavy metals treatment.

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TABLE-5
FREUNDLICH AND LANGMUIR MODEL PARAMETERS OF Ni(II) AND Cd(II) BY SDBS-UPT AND SDBS-BPT

Heavy metal	Sorbent	Langmuir model			Freundlich model		
		k_L (L mg^{-1})	q_{max} (mg g^{-1})	R^2	k_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	1/n	R^2
Ni(II)	SDBS-UPT	0.177	7.15	0.925	8.29	0.252	0.995
	SDBS-BPT	–	–	0.529	0.750	0.577	0.996
Cd(II)	SDBS-UPT	0.193	15.5	0.976	3.5481	0.376	0.990
	SDBS-BPT	–	–	0.632	16.3832	0.115	0.986

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