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Adsorption of nickel ions from aqueous solution using butane tetracarboxylic acid modified cellulose extracted from peanut shell

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ABSTRACT

Adsorption of Ni(II) from aqueous solution by using the butane tetracarboxylic acid (BTCA) modified peanut shell cellulose as sorbent was examined in the batch system. The optimal modification conditions of cellulose were butane tetracarboxylic 0.05 g/g, sodium dihydrogen phosphate 0.15 g/g, reaction temperature 140°C, and reaction time 90 min. The nickel ions removal rate by the BTCA-modified cellulose increased with the increasing temperature in the range of 20°C–45°C. Ni(II) adsorption onto the BTCA-modified cellulose was successfully described by the pseudo-second-order kinetic and Langmuir isotherm models. According to the thermodynamic parameters, the results indicated that Ni(II) adsorption onto the BTCA-modified cellulose was spontaneous and endothermic in nature.

Keywords: Adsorption; Cellulose; Butane tetracarboxylic acid; Modification; Ni(II)

1. Introduction

Heavy metal pollution caused by industrial activities has been a serious worldwide environmental problem. The effluents containing heavy metals from a variety of essential industrial processes such as mining, iron making, metal processing, electroplating, pesticide, and medicine have a great impact on the aqueous ecosystem and human beings [1,2]. The heavy metals ions are toxic, nonbiodegradable, and in some cases, can combine with other toxins in the water to produce new more toxic organic substances. Meanwhile, heavy metal ions can accumulate in the human body through the food chain, thus causing serious harm to human health [3–5]. For example, as essential trace elements for the human body, the nickel ions intake over the permissible levels can cause grave diseases such as pulmonary fibrosis, renal edema, and skin dermatitis [6,7].

The conventional techniques for removing heavy metals generally include chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and electrochemical processes [8–10]. However, most of these methods encounter some disadvantages such as disposal of toxic sludge, high cost, high energy requirements, and inefficiency at low metal concentration [11,12]. Among those methods, adsorption is an attractive and effective method for the removal of heavy metal ions. Biomass materials, such as chitosan [13], cellulose [14,15], lignin [16], and microorganism [2,3,6], derived from nature or byproduct of agricultural and industrial processes have been reported to develop into various sorbents to remove heavy metals due to their environmental friendliness, high efficiency, low cost and easy availability [17]. As an important plant photosynthesis product, cellulose is composed of repeating glucose linked by β–1,4–glucosidic bonds, and the most abundant renewable natural biological resource. Cellulose derived

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agricultural waste such as straw, rice husk, and peanut shell provides wide application potentiality to remove heavy metal ions due to its abundance in quantity, renewability, and biodegradability.

However, cellulose as an absorbent used for the removal of heavy metal ions was limited due to low adsorption of heavy metal ions in practice. The cellulose with abundant hydroxy groups provides diversified modification possibilities for the improvement of adsorption capacity. Kumar and Sharma [18] synthesized cellulose extracted from rice husk grafted with N-isopropyl acrylamide and comonomer acrylic acid for removal of Ni(II), Cu(II), and Pb(II) ions. Li et al. [14] performed chemically modified orange peel cellulose including $C_6H_6O_7{\cdot}H_2O$, $H_2C_2O_4$, and H_3PO_4 modification for sorption of Co(II), Ni(II), Zn(II), and Cd(II). Cellulose grafted with the vinyl monomer glycidyl methacrylate and functionalized with thiosemicarbazide was used to adsorb Hg(II), Cd(II), and acid fuchsin from their aqueous solutions [19]. Yu, et al. [20] reported that multi-amino-functionalized cellulose was prepared by grafting glycidyl methacrylate and tetraethylenepentamine onto cotton cellulose and this modification improved the arsenic adsorption performances.

Peanut shell is more than 5×10^6 tons per year in China. The treatment and disposal of peanut shells are facing an enormous challenge. In this study, cellulose was extracted from a low-cost peanut shells to remove nickel ions from an aqueous solution. To improve the adsorption capacity of cellulose, polycarboxylic acid modification was investigated. The polycarboxylic acids by esterification with hydroxy groups on cellulose including dicarboxylic (malic and tartaric acid), tricarboxylic (citric acid), and tetracarboxylic acid (ethylenediaminetetraacetic and butane tetracarboxylic acid) can provide carboxyl groups as binding sites for heavy metal ions. However, the cellulose modified by different polycarboxylic acids and the butane tetracarboxylic acid (BTCA) for removal of nickel ions is rarely studied.

This study aims to assess the mechanism and potentiality of polycarboxylic acids modified cellulose for Ni(II) adsorption. The effect of different polycarboxylic acid modifications on Ni(II) adsorption was carried out. The optimum BTCA modification conditions of cellulose were investigated as a function of BTCA dosage, catalyzer (sodium dihydrogen phosphate) dosage, reaction temperature, and reaction time. The adsorption isotherms and thermodynamics for nickel ions adsorption onto BTCA-modified cellulose were evaluated.

2. Materials and methods

2.1. Cellulose extraction from peanut shell

The peanut shell was soaked in deionized water for 24 h to remove soluble substances and impurities, washed several times with deionization water, and dried for 24 h in an oven. The dry pretreated peanut shell was ground and passed through a 100-mesh sieve. The slurry dispersing 5 g of the obtained undersize in 75 mL of sodium hydroxide solution (1 M) was heated at 75°C in a water bath shaker for 4 h for removing hemicellulose from peanut shell and filtered. The content was washed with deionized water until neutral and then dispersed in 50 mL mixed liquor contained 15 g/L sodium hypochlorite and 30 mg/L acetic acid solution in equal volume. The mixture was heated for 1 h at 75°C and 130 rpm in a water bath shaker for removing lignin and filtered and the above acid cleaning process was repeated five times. Finally, the residue was washed with deionized water to neutralize and dried at 65°C as cellulose.

2.2. Surface modification of cellulose

Cellulose was modified by malic acid (MA), tartaric acid (TA), citric acid (CA), ethylenediaminetetraacetic acid (EDTA), and butane tetracarboxylic acid (BTCA), respectively, in the presence of catalyst NaH_2PO_4. Each of carboxylic acids (0.075 g), catalyst NaH_2PO_4 (0.1 g), cellulose (0.5 g), and deionization water (5 mL) were added into 100 mL beakers, then dispersed for 10 min by an ultrasonic cleaner (KQ-100VDB, Kunshan Ultrasound Instrument Co., Ltd., Kunshan, China). The mixture samples were put into a pressure cooker, boiled at 100°C for 60 min at atmospheric pressure, and then reacted in an oven at 120°C for 90 min. After esterification, the samples were washed several times to neutralize and dried at 65°C in an oven as modified cellulose. The optimum modification conditions of BTCA modified cellulose were carried out as a function of BTCA dosage (0.0125–0.075 g), catalyst NaH_2PO_4 dosage (0–0.1 g), reaction temperature (100°C–150°C), and reaction time (30–150 min). All the above chemical reagents are analytical grade. The esterification of the cellulose with BTCA can be expressed as follows:

$$\text{Cellulose} - \text{OH} + \text{HOOCCH}_2\left(\text{CHCOOH}\right)_2 \text{CH}_2\text{COOH} \xrightarrow[\Delta]{\text{NaH}_2\text{PO}_4}$$

$$\text{Cellulose} - \text{OOCCH}_2\left(\text{CHCOOH}\right)_2 \text{CH}_2\text{COOH}$$

2.3. Ni^{2+} adsorption experiments

The batch nickel ions adsorption experiments were carried out by varying solution pH from 1.5 to 8, sorption temperature from 20°C to 45°C and initial Ni(II) concentration from 10 to 90 mg/L with 50 mL nickel ions solution containing 1 g/L of sorbent in 150 mL Erlenmeyer flask at 130 rpm on a thermostatic oscillator. After sorption, the nickel ions concentration in solution was analyzed by the dimethylglyoxime spectrophotometric method using a 721E spectrophotometer (Shanghai Spectrum Instrument Co., Ltd., Shanghai, China) at λ_{max} 530 nm. All the batch experiments were conducted in triplicate in this study.

3. Results and discussion

3.1. Optimization of cellulose modification conditions

3.1.1. Effect of polycarboxylic acid

The influence of polycarboxylic acid modification on Ni(II) adsorption was investigated and the results are presented in Fig. 1. Ni(II) removal efficiencies by MA, TA, CA, EDTA, and BTCA modified cellulose were all higher than

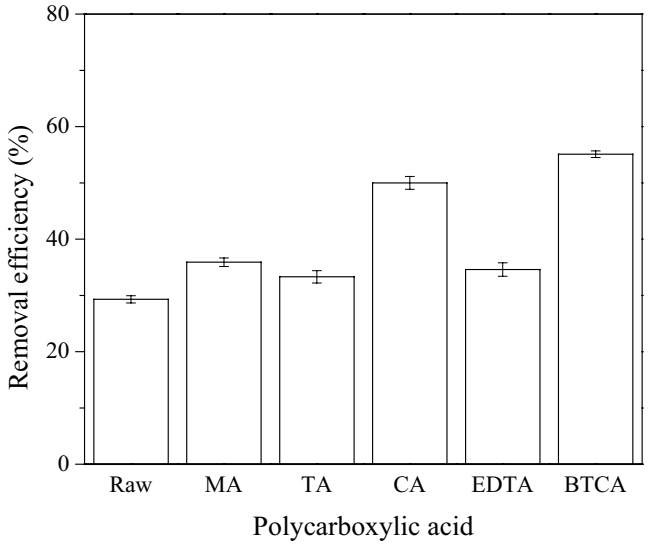

Fig. 1. Effect of carboxylic acid (sorbent dosage 1 g/L, Ni(II) 20 mg/L, temperature 30°C, contact time 180 min).

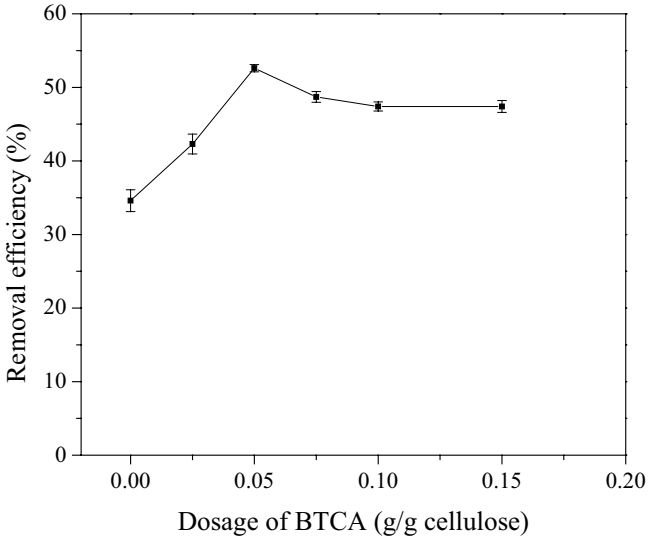

Fig. 2. Effect of BTCA dosage (sorbent dosage 1 g/L, Ni(II) 20 mg/L, temperature 30°C, contact time 180 min).

the raw. This indicated that the introduced carboxyl groups on the surface of cellulose by esterification played a role in Ni(II) adsorption. The order of Ni(II) removal rate from high to low is BTCA, CA, MA, EDTA, and TA-modified cellulose. In this study, the removal yield of Ni(II) onto BTCA-modified was 55.1%, higher than the other modified sorbents. This suggested that cellulose surface modified by BTCA with four carboxyl groups in molecular structure gained more carboxyl sites, which benefited the Ni(II) adsorption due to electrostatic attraction between the negatively charged sorbent and nickel ions at higher pH. The low uptake of Ni(II) onto the cellulose modified by EDTA also with four carboxyl groups may be ascribed to the low water solubility of EDTA, resulting in the low esterification efficiency. The BTCA was employed to modify the peanut shell cellulose in subsequent experiments.

3.1.2. Effect of BTCA dosage

The influence of BTCA dosage on Ni(II) uptake by BTCA-modified cellulose was investigated. As seen from Fig. 2, the removal yield of Ni(II) increased with a rise of the BTCA dosage from 0 to 0.05 g/g cellulose, and reached the maximum of 52.60% at 0.05 g/g cellulose, then gradually decreased until 0.15 g/g cellulose. The increase of Ni(II) adsorption with increasing BTCA dosage can be attributed to the increased carboxyl sites on the surface of BTCA-modified cellulose. As more BTCA molecules were grafted, the cellulose surface densely coated with BTCA molecules caused steric hindrance to prevent nickel ions from approaching binding sites on the cellulose surface or interior, leading to the lower Ni^{2+} uptake [21].

3.1.3. Effect of catalyst dosage

The Ni(II) adsorption onto BTCA-modified cellulose was carried out as a function of the dosage of catalyst by varying NaH_2PO_4 from 0 to 0.2 g/g and the results are shown in Fig. 3. The removal efficiency of Ni(II) onto cellulose modified by BCTA in the absence of catalyst was only 39.7%, slightly higher than that of the raw cellulose. As increased the dosage of catalyst from 0 to 0.15 g/g, the removal yield of Ni(II) climbed rapidly to peak value and the optimum dosage of NaH_2PO_4 was found to be 0.15 g per gram cellulose. The decrease with further increasing the catalyst dosage up to 0.2 g/g may be attributed to inaccessibility onto cellulose surface covered more BCTA molecules connecting by ester bonds.

3.1.4. Effect of reaction temperature

The grafting temperature of cellulose was explored in the range from 100°C to 150°C. As shown in Fig. 4, the removal of nickel ions by the BCTA-modified cellulose rapidly raised from 39.7% to 60.2% with the increase of reaction temperature from 100°C to 140°C. Subsequently, Ni(II) adsorption remained almost unchanged with a further increase in temperature. The higher Ni(II) adsorption at higher temperature can be due to the improvement of the esterification yield of cellulose with BCTA molecules, resulting in more carboxyl groups on cellulose. Mao et al. used citric acid to modify *Corynebacterium glutamicum* and found similar results that the increase of the uptake of Basic Blue 3 with the increasing reaction temperature in the range of 25°C–130°C. The authors thought that the added heat was likely used to form citric acid anhydride, which combines with hydroxyl groups of the biomass to form an ester linkage [22].

3.1.5. Effect of reaction time

The cellulose modification time was investigated in the range from 30 to 150 min. As presented in Fig. 5, the Ni(II) uptake of BCTA-modified cellulose was lower at 30 min, and then showed a rapid increase with the prolonging reaction time up to 90 min. When the reaction time was increased

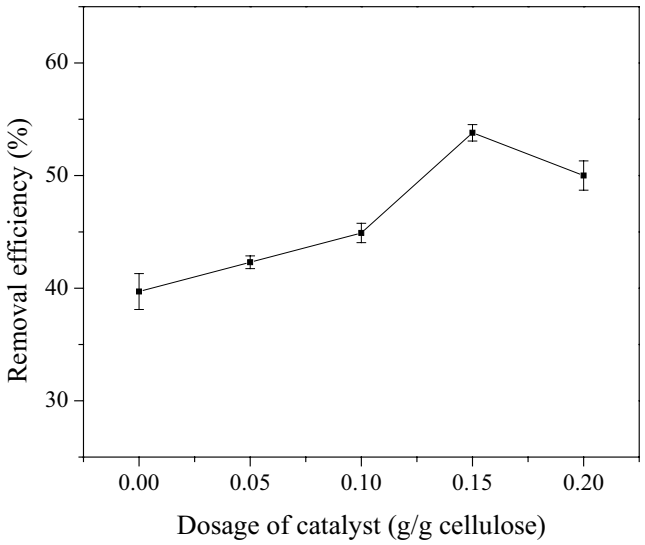

Fig. 3. Effect of catalyst dosage (sorbent dosage 1 g/L, Ni(II) 20 mg/L, temperature 30°C, contact time 180 min).

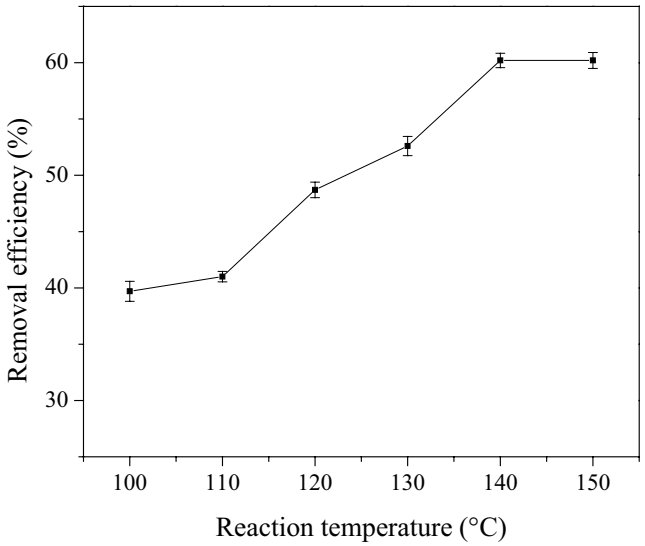

Fig. 4. Effect of reaction temperature (sorbent dosage 1 g/L, Ni(II) 20 mg/L, temperature 30°C, contact time 180 min).

from 90 to 150 min, the Ni(II) removal rate was slightly increased and a balance was almost reached.

Therefore, the optimal modification conditions per gram of cellulose were butane tetracarboxylic 0.05 g, sodium dihydrogen phosphate 0.15 g, reaction temperature 140°C and reaction time 90 min, and the removal yield of Ni(II) onto BCTA-modified cellulose was 65.8% at pH 7 under the optimal modification conditions.

3.2. Characterization of BTCA modified cellulose

Scanning electron micrograph (SEM) images for peanut shell, raw cellulose and BTCA-modified cellulose samples are presented in Fig. 6. It can be observed from the SEM image that peanut shell particles are irregular fragments

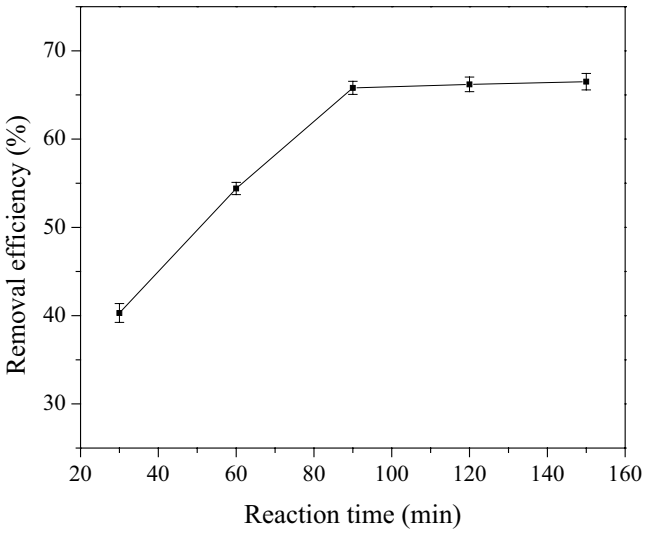

Fig. 5. Effect of reaction time (sorbent dosage 1 g/L, Ni(II) 20 mg/L, temperature 30°C, contact time 180 min).

(Fig. 6a). Cellulose particles extracted from peanut shells are dispersed and needle-like fibers with smooth surfaces and various lengths (Fig. 6b and c). After BTCA modification, the surface of cellulose fiber is rougher and fissured (Fig. 6d). The BET surface area and swelling ratio of BTCA-modified cellulose were determined as 14.51 m^2/g and 19.37%, respectively.

The Fourier transform–infrared spectroscopy (FT–IR) spectra of the raw, BTCA-modified, and Ni(II)-loaded BTCA-modified cellulose were analyzed and the results are presented in Fig. 7. It can be observed that the strong peak at 3,420 and 1,636 cm^{-1} represents the stretching and bending vibration of hydroxyl, –OH for raw cellulose. The peaks at 2,898 and 1,435 cm^{-1} could be attributed to the stretching vibration and bending vibration peaks of $–CH_2$, respectively. The skeleton stretching vibration peak of glycosidic bond (C–O–C) is observed at wave number 1,160 cm^{-1}. The absorption peak at 1,055 cm^{-1} should be assigned to O–H bending vibration of the primary alcoholic, $–CH_2OH$ [23–25]. The adsorption peaks of the hydroxyl group for BTCA-modified cellulose shifted from 3,420 to 3,440 cm^{-1} and the sharp decreases in the intensity of adsorption peaks at 3,440, 2,918, and 1,636 cm^{-1} occurred due to esterification with butane tetracarboxylic acid. Moreover, a new adsorption peak observed at 1,731 cm^{-1} was assigned to the >C=O stretching vibration peak, confirmed that carboxyl groups were introduced onto the cellulose by esterification with butane tetracarboxylic acid [22]. The small changes of adsorption peaks in the band ranging from 1,731 to 1,676 cm^{-1} for Ni(II)-loaded BTCA-modified cellulose indicated that chemical interactions were involved between the BTCA-modified cellulose and nickel ions and carboxyl groups on the surface of BTCA-modified cellulose played an important role in Ni(II) adsorption process.

3.3. Effect of pH

Solution pH value is one of the important factors for removing heavy metals from an aqueous solution [26].

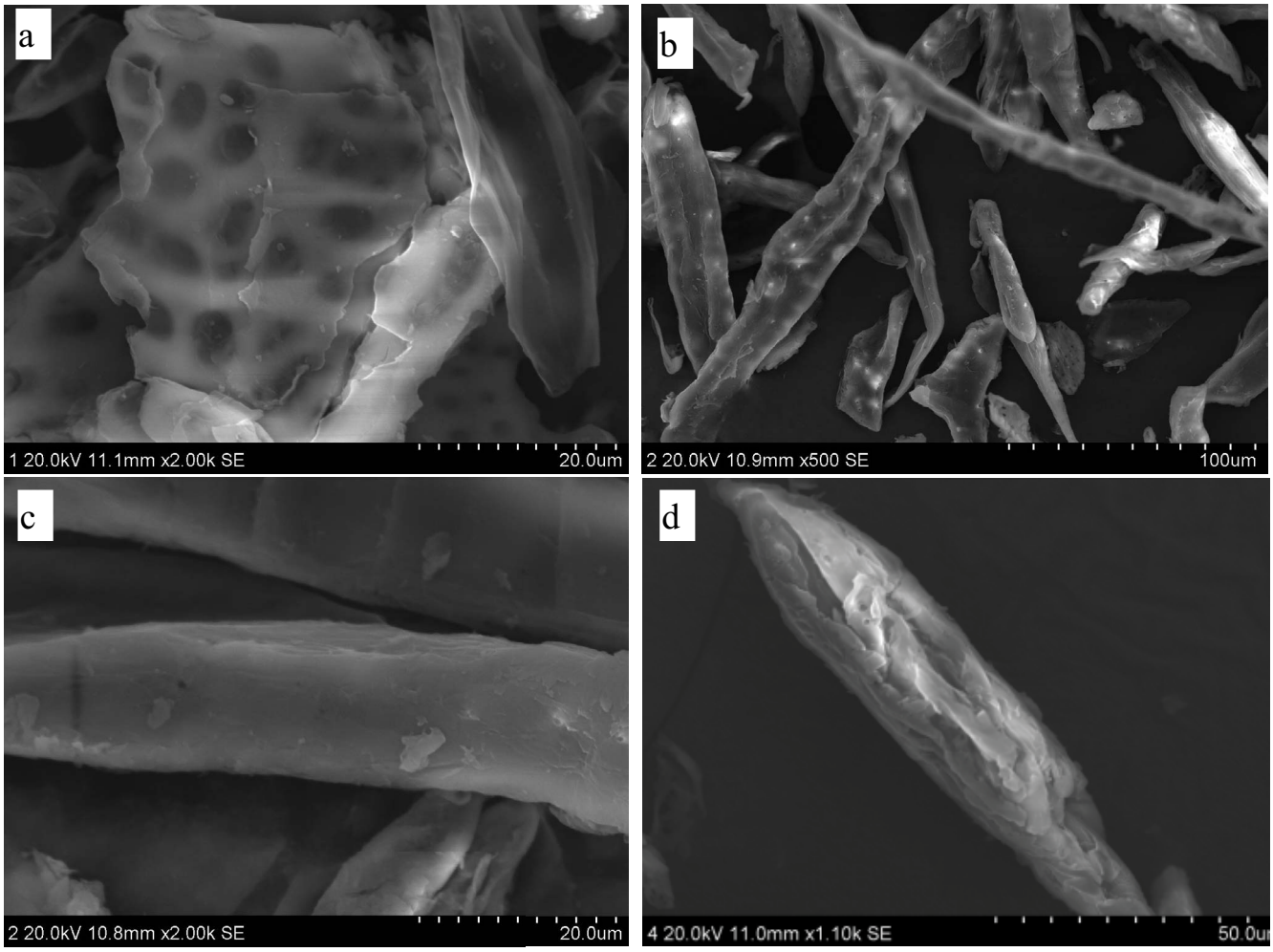

Fig. 6. Scanning electron micrograph images for peanut shell (a), cellulose (b, c) and BTCA modified cellulose (d).

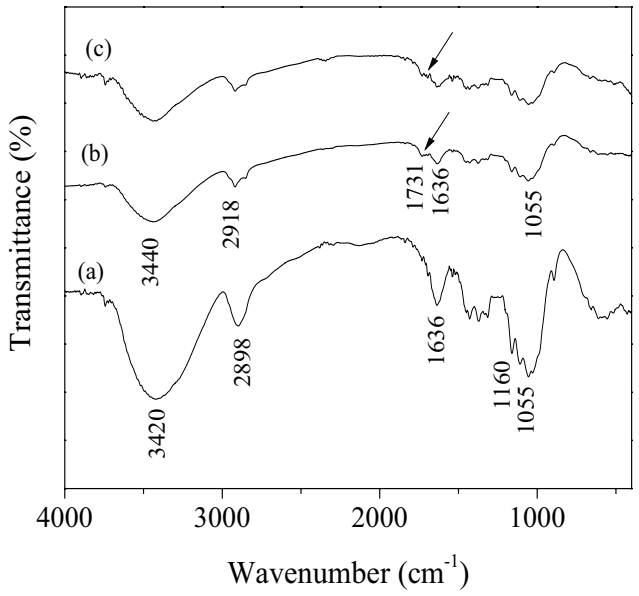

Fig. 7. FT–IR spectra of raw (a), BTCA-modified (b) and Ni(II)-loaded BTCA-modified cellulose (c).

The influence of the solution pH on nickel ions adsorption was explored in the range of 1.5–8.0 to ensure no precipitation of nickel ions. As seen from Fig. 8, the pH of the solution had a great influence on the adsorption of nickel ions. The removal efficiency of nickel ions was negligible at pH 1.5, and then sharply increased with the increasing pH from 1.5 to 7.0. As pH further increased up to 8, the Ni(II) adsorption by the BCTA-modified cellulose only slightly increased. The maximum removal efficiency of Ni(II) was observed as 66.7% at pH 8 in the studied pH range. Cellulose is a polymer of glucose units, containing a large number of hydroxyl groups. After modification, BTCA is linked to the surface of cellulose through an ester linkage, and its free carboxyl groups can provide adsorption sites. At lower pH, the functional groups such as hydroxyl groups on cellulose surface adsorbed the H^+ in the solution, resulted in the positively charged surface of cellulose, which decreased the adsorption of the positively charged nickel ions due to electrostatic repulsion. At higher pH, the functional groups on the surface of BTCA-modified cellulose such as carboxyl groups released H^+ at higher pH and became negatively charged carboxylate, resulting in the obvious increase of the removal yield of nickel ions due to

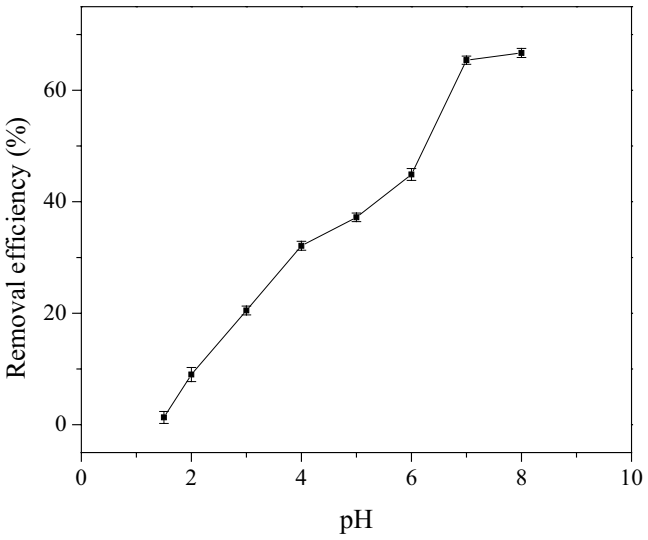

Fig. 8. Effect of pH (sorbent dosage 1 g/L, Ni(II) 20 mg/L, temperature 30°C, contact time 180 min).

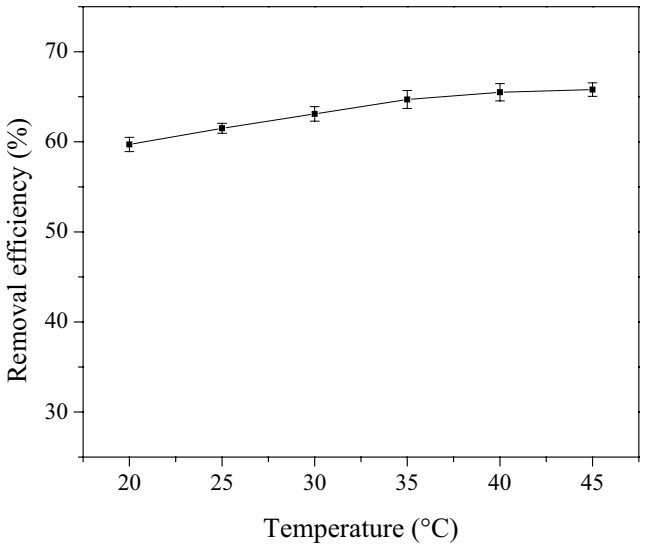

Fig. 9. Effect of temperature (sorbent dosage 1 g/L, Ni(II) concentration 20 m g/L, contact time 180 min, pH 7).

the electrostatic attraction between the BTCA-modified cellulose surface and nickel ions [27,28].

3.4. Effect of temperature

Effect of temperature of adsorption media on Ni(II) uptake by BTCA-modified cellulose was carried out at temperatures from 20°C to 45°C and the results are shown in Fig. 9. It was observed that nickel ions adsorption onto BTCA-modified cellulose increased with increasing temperature from 20°C to 45°C. The percentage of Ni(II) removal increased rapidly as the temperature rose from 20°C to 35°C, and then the percentage of Ni(II) removal slightly increased with further increasing temperature up to 45°C. The increase of Ni(II) removal rate with the temperature may be attributed to the increasing collision frequency between nickel ions and sorbent and the increasing activated binding sites [29–31]. Those results also indicate that Ni(II) adsorption is an endothermic process and thus the higher temperature of adsorption media is beneficial for Ni(II) adsorption onto BTCA-modified cellulose in the studied temperature range.

3.5. Adsorption kinetics

The influence of contact time on Ni(II) adsorption was examined at 20°C, 30°C, and 40°C, respectively. Fig. 10 illustrates that the adsorption capacity of nickel ions on BTCA-modified cellulose increased with an increase in contact time and temperature. Adsorption capacity increased sharply in the first 20 min and subsequently increased gradually until adsorption equilibrium was achieved at about 120 min. The increase of adsorption capacity during the initial period of 20 min may be associated with higher density of binding sites on the BTCA-modified cellulose surface which decreased with contact time [32,33].

The pseudo-first-order and pseudo-second-order kinetic models were often used to evaluate experimental data for heavy metal ions adsorption.

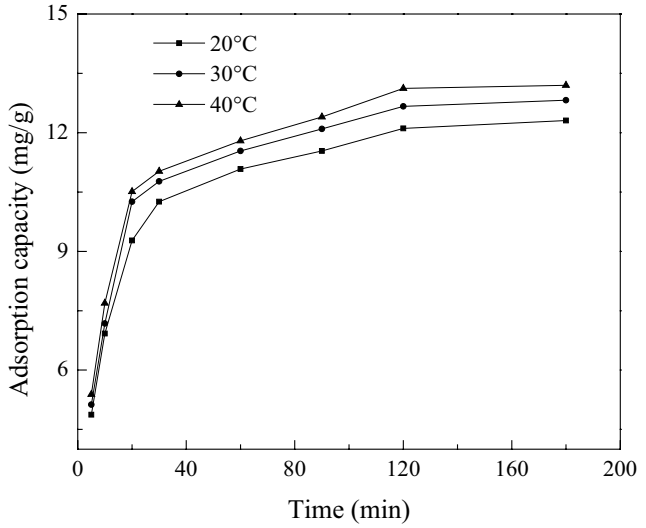

Fig. 10. Effect of contact time (sorbent dosage 1 g/L, Ni(II) concentration 20 m g/L, pH 7).

The pseudo-first-order equation by Lagergren is expressed as [3]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

where q_e and q_t (mg/g) are the amounts of nickel ions adsorbed at equilibrium and t (min), respectively. k_1 is the rate constant of the pseudo-first-order equation (1/min). k_1 and q_e were determined from the slope and intercept of the plot $\log(q_e - q_t)$ vs. t.

The pseudo-second-order kinetic model is given as [34,35]:

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

where k_2 is the rate constant of the pseudo-second-order equation (g/mg min). Values of k_2 and q_e were calculated from the intercept and slope of the plot t/q_t vs. t.

The kinetic parameters and linear regression correlation coefficients of the pseudo-first-order and pseudo-second-order models were listed in Table 1. The values of correlation coefficients for the pseudo-second-order model are low, less than 0.95 at the temperatures ranging from 20°C to 40°C. Moreover, the theoretical Ni(II) uptake capacity, q_{cal} determined from the pseudo-first-order model is not in line with the values of the experimental q_e. Whereas the correlation coefficients for the pseudo-second-order kinetic plots at studied temperatures are in the range from 0.9992 to 0.9996, significantly higher than that of the pseudo-first-order model and the values of q_{cal} determined from pseudo-second-order model are in agreement with experimental q_e values. The Ni(II) adsorption onto BTCA-modified cellulose followed the pseudo-second-order kinetic model. From these results, it can be easily concluded that the pseudo-second-order kinetic model is better than the pseudo-first-order in this work. The value of k_2 increases with the increase of temperature from 20°C to 40°C, further confirming that Ni^{2+} adsorption by BTCA-modified cellulose was the endothermic nature. Taşar et al. [36] investigated biosorption of lead(II) ions from aqueous solution by peanut shells and also observed that k_2 increased with an increase in temperature.

3.6. Adsorption isotherms

Adsorption isotherms for Ni(II) uptake onto BTCA-modified cellulose were investigated in the Ni(II) concentration range of 10–90 mg/L at temperatures from 20°C to 40°C. As seen from Fig. 11, Ni(II) equilibrium capacity increased with the increase of initial Ni(II) concentration and temperature. The increase of Ni(II) uptake with the initial concentration can be attributed to the driving force provided by the initial Ni(II) concentration to overcome mass transfer resistances of nickel ions from the aqueous to solid phases [37].

The Langmuir and Freundlich isotherm models are widely used for fitting the adsorption data. The Langmuir isotherm model based on assumption that adsorption occurs at specific homogeneous sites on adsorbent is used successfully in many monolayer adsorption processes and given by [38]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b}q_m \tag{3}$$

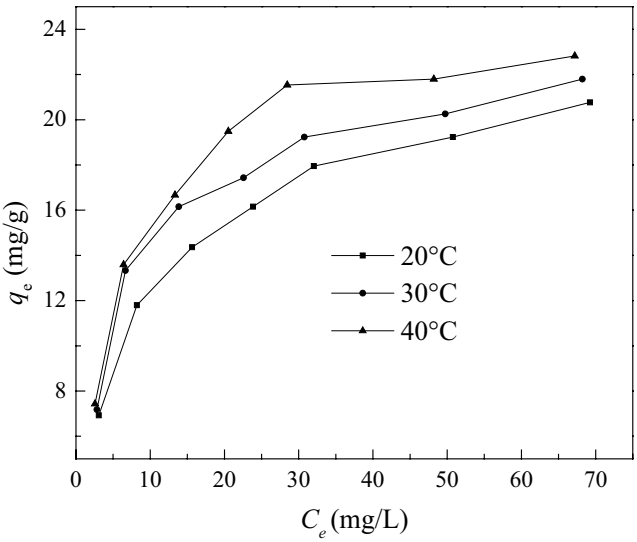

Fig. 11. Adsorption isotherm plots for Ni(II) adsorption (sorbent dosage 1 g/L, pH 7, contact time 180 min).

where q_m shows the maximum adsorption capacity (mg/g), b is the Langmuir constant (L/mg), C_e is the equilibrium Ni(II) concentration in the solution (mg/L), and q_e represents amounts of Ni(II) adsorbed on sorbent at equilibrium (mg/g).

The Freundlich isotherm model assumes a heterogeneous surface with nonuniform distribution of adsorption energy and the Freundlich linear equation is expressed as follows [39,40]:

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log K_F \tag{4}$$

where K_F and n represent isotherm constants of relative adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich equation constants are listed in Table 2. The correlation coefficients of the Langmuir isotherm model at different temperatures are all above 0.99, significantly higher than that of the Freundlich isotherm model, indicating that the Langmuir isotherm model can better describe Ni(II) adsorption onto BTCA-modified cellulose. The values of $1/n$ at temperatures from 20°C to 40°C are between 0 and 1, indicating that Ni(II) adsorption onto BTCA-modified cellulose is favorable at studied temperatures. According to the Langmuir isotherm

Table 1
Kinetic parameters for Ni^{2+} adsorption

T (°C)	Lagergren first-order model				Pseudo second-order model		
	k_1 (1/min)	q_e (mg/g)	q_{cal} (mg/g)	R^2	k_2 (g/mg min)	q_{cal} (mg/g)	R^2
20	0.0262	12.31	6.27	0.9145	0.0091	12.93	0.9995
30	0.0249	12.82	6.12	0.9156	0.0094	13.31	0.9992
40	0.0258	13.19	6.09	0.9456	0.0098	13.56	0.9996

Table 2
Adsorption isotherm parameters for Ni(II) adsorption

T (°C)	Langmuir model			Freundlich model		
	b (L/mg)	q_m (mg/g)	R^2	K_F	n	R^2
20	0.1179	22.87	0.9974	5.2591	2.9242	0.9592
30	0.1563	23.40	0.9978	6.2263	3.1383	0.8971
40	0.1787	24.69	0.9989	6.5169	3.0261	0.9002

model, the monolayer maximum equilibrium capacities, q_m, were determined as 24.69 mg/g in the studied temperature range. In this work, the maximum equilibrium capacity of BTCA-modified cellulose for Ni(II) is comparable with other low cost absorbents reported previously in the literature such as sugarcane bagasse [7], activated sludge [41], *Streptomyces coelicolor* [42], *Moringa oleifera* bark [43], and modified loquat bark [44] (Table 3). This indicates that the feasibility of Ni(II) adsorption onto BTCA-modified cellulose.

3.7. Thermodynamic analysis

Adsorption thermodynamic parameters provide information on the feasibility and spontaneous nature of the adsorption process [45]. To determine the thermodynamic mechanism of Ni(II) adsorption onto BTCA-modified cellulose, the thermodynamic parameters such as the Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were analyzed. The value of $\Delta G°$ can be calculated as follows [46]:

$$\Delta G° = -RT\ln K \tag{5}$$

where K is the adsorption equilibrium constant and T is the absolute temperature. The values of $\Delta H°$ and $\Delta S°$ can be obtained from the equation [46,47]:

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{6}$$

where the values of $\Delta H°$ and $\Delta S°$ can be determined from the plot of ln$K$ vs. $1/T$. The values of $\Delta G°$ are –2.42, –3.27, and –3.86 kJ/mol at temperature of 20°C, 30°C, and 40°C, respectively. The negative values of the Gibbs free energy change indicate a spontaneous nature of Ni(II) adsorption. The value of enthalpy change (18.75 kJ/mol) is positive, indicating Ni(II) adsorption process is endothermic. The positive value of entropy change (72.35 J/mol K) suggests increased randomness at the sorbent-metal solution interface during Ni(II) adsorption onto BTCA-modified cellulose [5,48].

4. Conclusion

Cellulose extracted from peanut shells modified by BTCA exhibited a higher Ni(II) removal rate than by MA, TA, CA, and EDTA. The optimum BTCA modification conditions of per gram cellulose were found to be butane tetracarboxylic 0.05 g, sodium dihydrogen phosphate 0.15 g, reaction temperature 140°C and reaction time 90 min the maximum Ni(II) removal yield for optimized BTCA-modified cellulose was about 66.7% at sorbent concentration 1 g/L in the studied pH and temperature ranges. Based on FT–IR spectra analysis, it was confirmed that the carboxyl groups were successfully introduced into cellulose by esterification with BTCA and played an important role in Ni(II) adsorption. According to the adsorption isotherms analysis, the Ni(II) adsorption onto BTCA-modified cellulose well followed Langmuir isotherm model. Thermodynamic parameters indicated that the Ni(II) adsorption process was spontaneous and endothermic in nature.

Table 3
Adsorption capacities for Ni^{2+} by different low-cost adsorbents

Aadsorbent	q (mg/g)	Reference
Sugarcane bagasse	2.23	[41]
Activated sludge	18.6	[42]
Streptomyces coelicolor	18.8	[43]
Moringa oleifera bark	26.84	[44]
modified loquat bark	27.548	[45]
BTCA modification cellulose	23.40	This work

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