Copper removal from aqueous solutions by sugar beet pulp treated by NaOH and citric acid

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Abstract

Sugar beet pulp was converted into effective copper sorption material by treating subsequently with NaOH and citric acid. Compared with the untreated sugar beet pulp, the cation exchange capacity of the modified sugar beet pulp increased from 0.86 to 3.21 mequiv. g^{-1}. Swelling capacity and COD values of modified sugar beet pulp were found to be decreased in the ratio of 38% and 61%, respectively, compared to the corresponding values of native sugar beet pulp, meaning that modification causes stabilization. Sorption characteristics of the modified sugar beet pulp towards copper ions were studied with batch experiments. Pseudo-first, pseudo-second-order and intraparticle kinetic models were applied to the kinetic data and it was found that the sorption processes followed the pseudo-second-order rate kinetics with activation energy of 16.34 $kJ\,mol^{-1}$. The equilibration data fit best with the Langmuir isotherm the maximum copper sorption capacity of which is 119.43 $mg\,g^{-1}$. The mean free energy of copper sorption process calculated from Dubinin–Radushkevich model and the Polanyi potential concept was found to be in the range of 10.91–11.95 $kJ\,mol^{-1}$ showing that the main mechanism governing the sorption process is ion exchange. The negative values found for enthalpy change ($-14.797\,kJ\,mol^{-1}$ over the range of 25–55 °C) and free energy change ($-19.361\,kJ\,mol^{-1}$ for 25 °C) indicate that the sorption process is exothermic and spontaneous in nature.

1. Introduction

One third of the world sugar production is based on sugar beet. After the extraction of sucrose, about 50 kg sugar beet pulp (on a dry weight basis) per tonne sugar beet processed is left as a by-product, which is primarily composed of hemicellulose, pectin and cellulose. These constituents account about 85% of its dry matter. It also contains small amounts of protein, salts, lignin and residual sugar [1]. Traditionally, sugar beet pulp is dried and mainly utilized for ruminant nutrition as a low value product. There has been a continuous interest in finding new applications for sugar beet pulp, which is recently evaluated for its ability to bind metal ions. It has been reported that sugar beet pulp and pectin extracted from pulp exhibited high cation sorption capacity due to the carboxyl groups on galacturonic acids, which are the main components of pectins [2]. In recent years,

sugar beet pulp and its modified products have been investigated for heavy metal removal from aqueous solutions [3–8]. Dronnet et al. [4] have indicated that the hydration of beet pulp is too great to allow its direct use. It has been reported that modification of sugar beet with epichlorhydrine and formaldehyde reduced the swelling capacity and enhanced the sorption capacity [4,5]. Laszlo and Dintzis [8] have shown that the treatment of sugar beet with epichlorohydrin improved its cation exchange capacity and physical stability. In some attempts, sugar beet pulp has converted into activated carbons and investigated for heavy metals and phenol removal from aqueous solutions [9–11].

It has been showed that treating agricultural materials with poly acids (citric, tartaric, phosphoric i.e.) at mildly elevated temperatures enhanced their sorption capacity for metal ion [12–18]. By such a treatment, some extra acidic groups can be introduced to the material by forming an ester linkage. Some cellulosic materials including sugar beet pulp have been modified with commercial phytic acid which is an organic polyphosphoric acid and calcium exchanging capacity of the modified product obtained from sugar beet pulp has been found

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as 2.72 mequiv. g^{-1} [18]. Marshall et al. [14] have compared the copper sorption ability of soybean hulls modified with different polycarboxylic acids and reported that the use of citric acid (tricarboxylic acid) in modification process gives better results than the use of succinic, tartaric, malic and maleic acids (dicarboxylic acids). It has been reported that an estimated production cost for citric acid-modified soybean hull is \$1.17/kg versus typical retail costs \$4–40/kg for commercial, petroleum-based cation exchange resins when purchased in bulk quantities [17].

The objective of this study was to determine the copper sorption ability of sugar beet pulp treated with NaOH and citric acid by a method applied for soybean hulls by Marshall et al. [13]. For this purpose, sugar beet pulp was subjected to alkaline treatment with NaOH solution and subsequently heating together with citric acid for improving the cation binding properties. The sugar beet modified was characterized and subjected to a systematic copper sorption study. For this aim, the effects of pH, contact time, copper concentration and temperature were investigated and sorption equilibria were analyzed. The experimental data were correlated to sorption models and the characteristics related to binding capacity, kinetics, thermodynamics and the mechanisms of sorption are discussed.

2. Materials and methods

2.1. Materials

Sugar beet pulp was obtained from a local sugar factory in Elazig, Turkey. The coarse humidity of sugar beet pulp was removed by air blowing for 24 h. It was then dried in an oven at 50 °C for further 24 h. The dried pulp was ground in a blender. The grinded material was sieved and the fraction between 16 and 30 mesh (0.6 mm < x < 1.2 mm) was used in the experiments. This sample was named as sugar beet pulp (SBP).

2.2. Modification of sugar beet pulp

Modification of SBP was carried out in two stages using a similar method reported by Marshall et al. [13]. First is a base extraction with NaOH solution and second is an esterification with citric acid. Marshall et al. [13] have reported that extracting soybean hull and corncob with 0.1N NaOH and modification of base extracted material with 0.6 M citric acid gives best results to enhance their metal sorption capacities. From this standpoint, the conditions around these bases were used to modify sugar beet pulp.

One hundred grams of SBP was mixed with 2 l of 0.1 M NaOH solution in a 5 l PE jar. The mixture was shaked at 200 rpm for 2 h at ambient temperature. The base-treated pulps were poured onto a perforated ladle and rinsed with distilled water. The pulps were added to 2 l of distilled water in jar and shaked at 200 rpm for 1 h at room temperature to remove excess base. The washed SBPs were poured onto the perforated ladle, rinsed and added to 2 l of fresh distilled water. This procedure was repeated until no pH variation in the wash water could be detected. This product is nominated as NaOH-treated sugar beet pulp (NTSBP). A portion of this product was dried at 50 °C until constant weight. This was set aside for characterization tests. Another portion of NTSBP was exposed to air blowing for 6 h in order to remove excess humidity. Then, NTSBP was subjected to a citric acid (CA) esterification procedure the condition of which is an optimal of the study conducted by Marshall et al. [13]. For this purpose NTSBP was mixed with a 0.6 M citric acid in a ratio of 1.0 g material to 7.0 ml citric acid solution. NTSBP completely imbibed the CA solution within a couple of hour. The acid–NTSBP mixture was cooked for 12 h at 50 °C. The cooked NTSBP–acid mixture was then finaly heated at 120 °C for 90 min. Modified product was added to hot distilled water at about 50 °C in a water/solid ratio of 20 and shaked at 200 rpm for 1 h to remove unreacted acid. The mixtures were poured onto the perforated ladle, rinsed and added to new hot distilled water. This procedure was repeated to ensure the complete removal of unreacted citric acid. The presence of citric acid in wash waters was tested by adding 0.1 M lead(II) nitrate solution [14]. Washing was terminated when no turbidity from lead(II) citrate was observed. The modified pulp was coarsely dried by air blowing and then dried in an oven at 50 °C until constant weight and final product is referred to as NaOH and citric acid-treated sugar beet pulp (NCTSBP). This sample was subjected to characterization tests and copper sorption study.

2.3. Copper sorption study

A stock solution of copper was prepared in the concentration of 0.25 M by dissolving appropriate amount of $CuCl_2 \cdot 2H_2O$ in distilled water. Working solutions were prepared from this stock solution by appropriately diluting with water or buffer solution (0.07 M sodium acetate–0.03 M acetic acid).

In the preliminary study, initial pH of 5 mM Cu^{2+} solutions was adjusted to desired value by adding 0.1N HCl solution. A weighed amount of NCTSBP (corresponding to 5 g l^{-1} sorbent dosage) was added to the solution and the sorption tests were carried out at 25 °C for a contact period of 24 h. The rest of the study was carried out with the copper solutions prepared in the buffer solution of 0.07 M sodium acetate–0.03 M acetic acid (pH 4.8).

The experiments were conducted in 300 ml Erlenmeyer flasks containing 1.25 g of NCTSBP and 250 ml of copper solutions in varying concentrations from 5 to 25 mM. The flasks were agitated on an orbital shaker at 200 rpm and at constant temperature for different time and temperature. Samples were taken at pre-determined time intervals (5–1440 min) for determination the residual copper ion concentration in the solutions. Before analysis the samples were filtered through the Advantec (No. 6) filter paper and the supernatant fraction was analyzed for the remaining copper ions. Blank experiments showed that the copper sorption of filter paper is negligible since the experimental solutions have high copper concentrations. Uptake values were determined from the difference between the copper concentrations of initial and final solutions and calculated on a dry weight basis of NCTSBP. All experiments were carried out in duplicates and the mean values were used for further calculations.

2.4. Methods of analysis

ASTM D 2187-74 method [19] was used to determine cation exchange capacity. Swelling capacities were measured by bed-volume technique [20]. Water retention capacities were determined by measuring of watersaturated weight of samples by using centrifugation method [21]. Chemical oxygen demand, which is a measure of pollution potential originated from adsorbent, was determined by using dichromate method [22]. Throughout the copper sorption study, copper ions in the solutions were analyzed by using atomic absorption spectrophotometry (Perkin-Elmer PE 370).

3. Results and discussions

3.1. Modification of sugar beet pulp

Table 1 summarizes some properties of sugar beet pulp (SBP), NaOH-treated sugar beet pulp (NTSBP) and NaOH and citric acid-treated sugar beet pulp (NCTSBP). As seen from Table 1, SBP has a considerable cation exchange capacity. Subjecting the SBP to a simple base extraction significantly enhance the cation exchange ability. The pre-treatment of pectocellulosic materials with dilute NaOH solution may lead to saponification of esters associated with pectic chains (methylated carboxyls), which results in the increasing number of free carboxylate groups in pectic structure. This treatment may also set free primer alcohol groups esterified in cellulose molecules. In addition, extraction with dilute NaOH solutions at mild conditions may provide stability to the material by removing soluble substances with low molecular weight. This deesterification process increases both the cation uptake ability of pectic fraction and the number of primary alcohol groups which are appropriate sites in cellulosic fraction to be esterified with citric acid. In a study [4] sugar beet pulp has been subjected to a saponification with NaOH following by a modification with formaldehyde and epichlorohydrine. Authors have reported an increase in cation exchange capacity of base extracted sugar beet pulp due to the decrease in methylation and acetylation degrees in pectic structure. It has been reported no decrease in swelling capacity. In our study, about 34% decrease in swelling capacity and about 65% increase in

cation exchange capacity were observed for a base extracted sugar beet pulp.

In the citric acid treatment stage, cellulose enriched in free primary alcohol groups may bind some extra carboxyl groups. Thus, this treatment may further enhance the cation uptake ability of sugar beet pulp. Findings show that citric acid modification applied after the base extraction is much more effective for enhancing cation exchange capacity which rised to 3.73-fold compared to SBP (Table 1).

A lower value of chemical oxygen demand, which is a measure of organic pollution due to the solubilization of some organic materials, for base extracted sample may show the stabilization. Much lower values of swelling and water retention capacities for NCTSBP indicate that sugar beet pulp gains further stabilization via citric acid treatment. This may be due to crosslinking the cellulose fibrils through the carboxyl groups of citric acid. Although chemical oxygen demand value of NCTSBP is higher than that of NTSBP, it is still about three-fold lower than that of SBP.

It can be briefly noted that a base treatment and a subsequent citric acid modification stabilize the SBP due to crosslinking and increase its cation uptake ability stemming from carboxylic groups inserted into molecules.

3.2. Copper sorption study

Sorption of metal ions by the active sites on the surface of an ion exchanger resin or an adsorbent is affected by several factors such as pH of solution, initial metal ion concentration, contact time, temperature, agitation speed and the amount and particle size of resin. To evaluate metal uptake behaviour, it is required to observe kinetics and equilibria of sorption. From the results of some preliminary experiments, particle size, dosage of resin and agitation speed were selected as 0.6–1.2 mm (16 mesh $> d >$ 30 mesh), 5 g l^{-1} and 200 rpm, respectively, and kept constant throughout the study.

The pH of the aqueous solution is an important variable for the sorption of metals on sorbents. As a beginning, in order to check the effect of pH on the copper uptake by NCTSBP, sorption experiments were realised at several pHs (2.25, 3.50 and 4.80) by using a 5 mM copper solution for a contact time of 24 h (Table 2). As expected, the copper sorption capacity increases with pH probably due to the fact that the H$_3$O$^+$ ions compete with copper ions for the binding sites on sorbent surface, thereby partially releasing the copper ions at lower pHs. On the other hand, dominant species of copper in the range of pH 3–5 are Cu^{2+} and Cu(OH)$^+$, while the copper ions at higher pH values

Table 1

Some properties of sugar beet pulp (SBP), NaOH-treated sugar beet pulp (NTSBP) and NaOH and citric acid-treated sugar beet pulp (NCTSBP)

Parameter	SBP	NTSBP	NCTSBP
Moisture content (%)	6.36	8.45	7.97
Ash content[a] (%)	4.31	6.12	5.56
Bulk density (g ml^{-1})	0.279	0.294	0.326
Conductivity[b] (μs cm^{-1})	145	120	162
pH[b]	4.81	8.74	3.90
Chemical oxygen demand[b] (mg-O$_2$ l^{-1})	167.8	35.6	66.0
Cation exchange capacity[a] (mequiv. g^{-1})	0.86	1.42	3.21
Swelling capacity (ml g^{-1})	6.70	4.40	4.15
Water retention capacity (g g^{-1})	7.90	6.85	5.10

[a] On dry basis (at 105 °C).

[b] Values for water (100 ml) contacted with 1 g material for 24 h.

Table 2

Effect of pH for the sorption of Cu^{2+} onto NCTSBP (NCTSBP dosage: 5 g l^{-1}, initial Cu^{2+} conc.: 5 mM, time: 24 h, shaking rate: 200 rpm)

Experiment	Initial pH	Final pH	Copper sorption, q (mg g^{-1})
1	2.25	2.34	16.10
2	3.50	3.29	27.40
3	4.80[a]	4.73	58.85

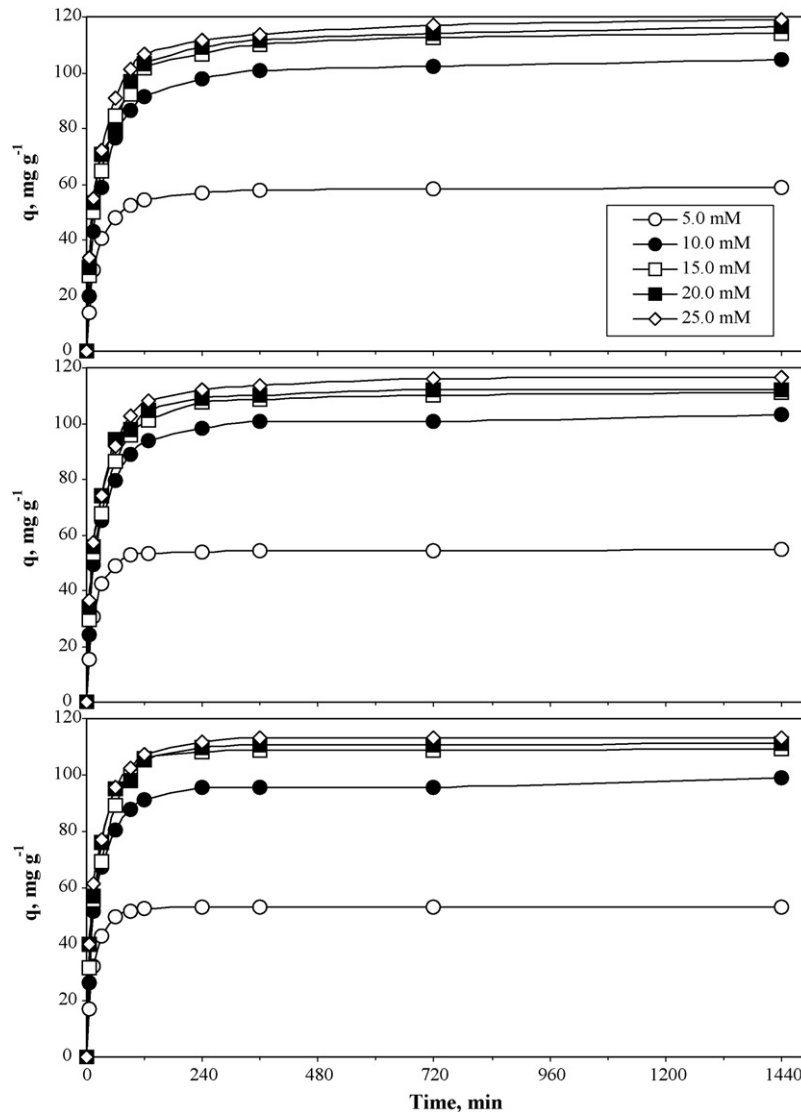[a] In the medium of 0.07 M sodium acetate–0.03 M acetic acid buffer solution.

Fig. 1. The variations in the copper uptake with contact time at 25, 40 and 55 °C for different initial copper concentrations (NCTSBP dosage: 5 g l^{-1}, pH: 4.8, shaking rate: 200 rpm).

may be hydrolysed into insoluble Cu(OH)$_2$ [23]. This makes the sorption study complicated. In the rest of the study, therefore, pH of solution was kept constant at about 4.8 by using a buffer solution (0.07 M sodium acetate–0.03 M acetic acid).

The first step performed in the copper sorption studies is the evaluation of the contact time required to reach equilibrium at different initial copper concentrations. Fig. 1 shows the results of sorption kinetics at different temperatures for initial copper concentrations varying from 2.5 to 25 mM. The results show that the copper uptake by the NCTSBP is biphasic, showing an initially fast, followed by a slower copper sorption rate. Equilibrium time required for the removal of copper by NCTSBP for the initial copper concentrations of 2.5, 5.0 and 7.5 mM is 2–3 h. However, for higher initial copper concentrations, considerable sorption continued up to 12 h. It can be stated that a satisfactory equilibria are attained within 12 h at 25, 40 and 55 °C for the studied concentration range of 2.5–25 mM. On the other hand, in all cases, copper uptake slightly decreases with increasing temperature in the range of 25–55 °C.

Fig. 2 represents the adsorbed amounts of copper ions from aqueous solutions of various initial concentrations onto NCTSBP at the end of 12 h for different temperatures. From Figs. 1 and 2, it is seen that copper uptake at the equilibrium increases with the initial concentration. However, for the sorbent dosage of 5 g l^{-1} studied, it reaches to saturation beyond 12.5 mM copper concentration. The time necessary to reach equilibrium of sorption at the temperatures studied is practically the same. These results are in agreement with those of the study carried out by Marshall et al. [13], which has been reported that there is no advantage at the temperatures higher than 25 °C for copper removal by modified soybean hulls. Aksu and Isoglu [6] have found the same temperature-adsorption relationship for copper sorption by native sugar beet pulp. The thermodynamic results derived from temperature effect will be presented in following sections. As can be seen from Fig. 2 representing a L-type isotherm, a saturation limit is attained at higher adsorbate concentrations. In such cases that q_e attains to a plateau, a monolayer formation is thought [24]. In these cases, Langmuir
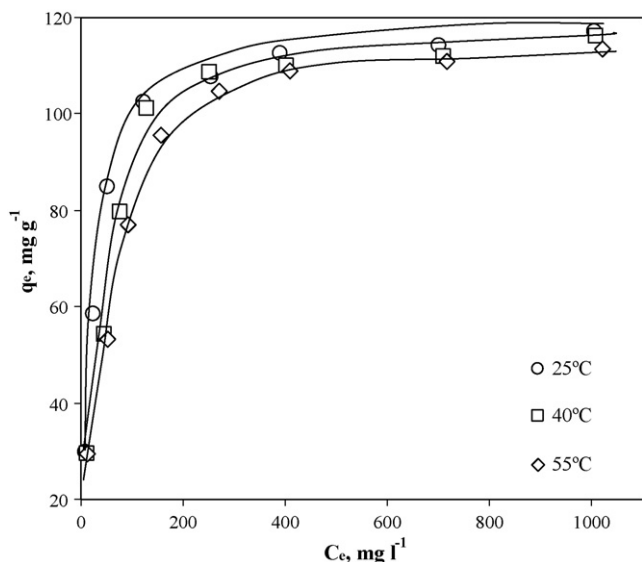
Fig. 2. Equilibrium copper uptake capacities of NCTSBP at different temperatures (NCTSBP dosage: $5\,g\,l^{-1}$, initial pH: 4.8, equilibration time: 12 h, shaking rate: 200 rpm).

Fig. 3. Langmuir Plot for Cu sorption by NCTSBP.

equation [25] can be used to calculate some useful parameters, which are given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (1)$$

where C_e and q_e are the equilibrium copper concentrations in the aqueous ($mg\,l^{-1}$) and solid phases ($mg\,g^{-1}$), respectively, and Q_0 and b are constants that are considered to be the maximum sorption capacity ($mg\,g^{-1}$) and a constant related to the affinity of binding sites or bonding energy, respectively. Plots of C_e/q_e versus C_e values obtained at different temperatures for the sorption of copper on NCTSBP are given in Fig. 3.

The equilibrium sorption data were applied to the linearized Freundlich equation [26] (Eq. (5)).

$$\ln q_e = \frac{1}{n}\ln C_e + \ln K_f \qquad (2)$$

where K_f and $1/n$ are constants that are considered to be relative indicators of sorption capacity and sorption intensity, respectively.

The sorption equilibrium data were also tested for Dubinin–Radushkevich (D–R) model which is widely used to evaluate the nature of sorption. D–R model equation [27] is given by the following equation:

$$\ln q = \ln q_m - \beta \varepsilon^2 \qquad (3)$$

where q_m is the maximum amount of ion that can be sorbed onto unit weight of sorbent ($mg\,g^{-1}$), β the constant related to sorption energy ($mol^2\,kJ^{-2}$) and ε is the Polanyi potential which is equal to $RT\ln(1 + 1/C_e)$, where R and T are the gas constant ($kJ\,mol^{-1}\,K^{-1}$) and the absolute temperature (K), respectively. The plot of $\ln q$ versus ε^2 results a straight line. The slopes of the D–R plots give β constant and q_m value is calculated from the intercept of the plot.

Langmuir, Freundlich and D–R constants calculated are listed in Table 3. The copper sorption capacity of $119.43\,mg\,g^{-1}$ ($3.76\,mequiv.\,g^{-1}$) obtained from Langmuir isotherm (Table 3) are slightly higher than cation exchange capacity ($3.21\,mequiv.\,g^{-1}$) (Table 1). This result is in good agreement with a similar result reported by Reddad et al. [7] for modified sugar beet pulps has been attributed to the some neutral functional groups (like hydroxyl or carbonyl) which may play an extra role in copper binding process. Reddad et al. have reported 0.33, 0.57 and 0.457 mmol g^{-1} (0.66, 1.14 and 0.91 mequiv. g^{-1}) copper sorption capacity for native, saponified and base extracted sugar beet pulps, respectively. In another study [6], copper sorption capacity of native sugar beet pulp, based on Langmuir isotherm, has been found as $31.4\,mg\,g^{-1}$ ($0.99\,mequiv.\,g^{-1}$). Compared to the results of present study with those of above-mentioned studies, it can be noted that citric acid treatment enhances copper sorption capacity of sugar beet pulp in a great extent.

Table 3
Calculated isotherm parameters for Cu^{2+} sorption by NCTSBP

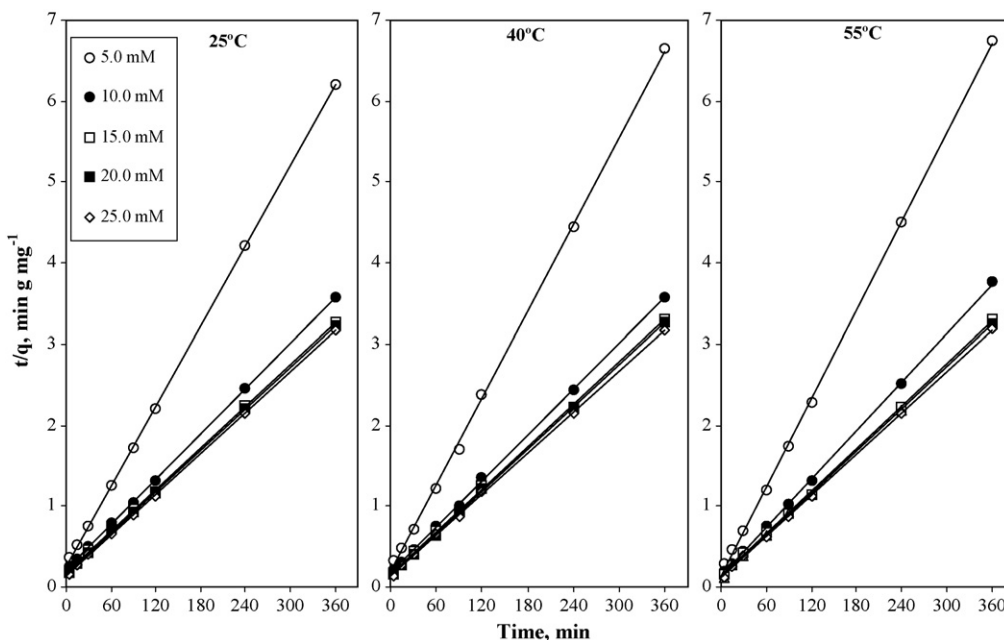| Temperature (°C)	Langmuir isotherm			Freundlich isotherm			D-R isotherm		
	Q_0 ($mg\,g^{-1}$)	b ($l\,mg^{-1}$)	R^2	K_f	$1/n$	R^2	q_m ($mg\,g^{-1}$)	β	R^2
25	119.43	0.039	0.9999	23.15	0.262	0.8108	198.76	0.0035	0.8659
40	119.05	0.027	0.9990	18.25	0.297	0.8546	199.75	0.0039	0.9029
55	118.48	0.023	0.9993	16.45	0.307	0.8924	204.32	0.0042	0.9079

Fig. 4. Application of pseudo-second-order kinetic model to copper sorption by NCTSBP.

The thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy changes (ΔS°) for the sorption process can be determined using following equations:

$$\ln b = \ln b' - \frac{\Delta H^\circ}{RT} \tag{4}$$

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^\circ}{RT} \tag{5}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{RT} \tag{6}$$

where b is the Langmuir constant, b' energy parameter, T absolute temperature (K) and R is the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$).

The calculated values of the thermodynamic parameters for Cu^{2+} sorption by NCTSBP are listed in Table 4. The negative value of ΔH° ($-14.797\,\mathrm{kJ\,mol^{-1}}$) suggests the exothermic nature of the process. The negative value of ΔG° shows that the process is spontaneous. The positive values of ΔS° may be attributed to the increasing randomness at the NCTSBP solution interface during the sorption.

The mean free energy of sorption can be calculated from D–R isotherm parameter β by the following equation [28]:

$$E = (2\beta)^{-1/2} \tag{7}$$

Table 4
Thermodynamic parameters for Cu^{2+} sorption by NCTSBP

Temperature (°C)	Thermodynamic parameters		
	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
25		−19.361	0.0153
40	−14.797	−19.396	0.0147
55		−19.827	0.0153

The calculated E values are the energy required to transfer 1 mol of a sorbate to the surface from infinity in solution. The value of E is used to estimate the reaction mechanism occurring. If the magnitude of E is between 8 and $16\,\mathrm{kJ\,mol^{-1}}$, the sorption process proceeds by ion exchange, while for values of $E < 8\,\mathrm{kJ\,mol^{-1}}$, the sorption process is of a physical nature [29,30]. In the present study, E values were calculated as 11.95, 11.32 and $10.91\,\mathrm{kJ\,mol^{-1}}$ at the temperatures of 25, 40 and 55 °C, respectively. Thus, it may be concluded that the copper removal mechanism is mainly governed by ion exchange.

The copper sorption kinetics of NCTSBP may be described by pseudo-first-order and pseudo-second-order type kinetic models. Integrated pseudo-first-order [31] and pseudo-second-order [32] type expressions are given in the following equations:

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{8}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where q_e and q are the amounts of copper adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively. k_1 and k_2 are the rate constant of sorption in the pseudo-first-order and pseudo-second-order type kinetic models, respectively.

Since the sorption process was accomplished with sufficient mixing of aqueous copper solution and NCTSBP particles, the pore diffusion may be the rate-limiting step. For the confirmation of sorption mechanism, kinetic data can also be evaluated according to intraparticle diffusion model [33]:

$$q = f\left(\frac{Dt}{r_p^2}\right)^{1/2} = k_{id} t^{1/2} \tag{10}$$

where r_p is the diameter of resin particle, D the effective diffusivity of copper ion within the particle and k_{id} is the intraparticle

Table 5
Calculated model parameters and regression coefficients for pseudo-first-order, pseudo-second-order and intraparticle diffusion models for all studied concentration at various temperatures

Temperature (°C)	Initial conc. (mM)	Actual q_e values (mg g⁻¹)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model	
			k_1 (min⁻¹)	q_e (mg g⁻¹)	R^2	k_2 (g mg⁻¹ min⁻¹)	q_e (mg g⁻¹)	R^2	k_{id} (mg g⁻¹ min⁻¹ᐟ²)	R^2
25	5.0	58.33	0.0123	26.80	0.9477	0.00108	60.61	0.9999	2.31	0.7285
	10.0	102.28	0.0107	57.77	0.9607	0.00041	107.53	0.9999	4.51	0.8075
	15.0	112.35	0.0097	58.94	0.9391	0.00042	116.28	0.9995	4.68	0.8195
	20.0	114.20	0.0094	57.33	0.9260	0.00044	117.65	0.9989	4.58	0.8197
	25.0	116.92	0.0087	52.19	0.8849	0.00052	119.05	0.9997	4.52	0.7878
40	5.0	54.20	0.0207	21.12	0.9592	0.00171	55.87	0.9995	1.96	0.6350
	10.0	100.98	0.0144	58.08	0.9772	0.00051	105.26	0.9997	4.14	0.7801
	15.0	110.00	0.0116	54.15	0.9432	0.00049	113.64	0.9994	4.43	0.7996
	20.0	111.91	0.0107	47.42	0.9098	0.00051	116.28	0.9992	4.23	0.7661
	25.0	115.94	0.0096	48.53	0.8809	0.00054	119.05	0.9996	4.37	0.7814
55	5.0	53.31	0.0253	21.99	0.9815	0.00229	54.95	0.9996	1.78	0.6097
	10.0	95.68	0.0235	64.51	0.9976	0.00075	100.10	0.9998	3.67	0.7254
	15.0	108.90	0.0179	58.09	0.9725	0.00060	113.64	0.9993	4.33	0.7589
	20.0	110.75	0.0165	56.37	0.9863	0.00067	114.94	0.9997	4.00	0.7646
	25.0	113.41	0.0148	53.47	0.9789	0.00066	117.65	0.9998	4.06	0.7674

diffusion coefficient. When plotting of q versus $t^{1/2}$, diffusion parameter k_{id} can be calculated from the slope.

The values of the k_1, k_2 and k_{id} were calculated from the slope of the linear plots and are presented in Table 5. Comparing the correlation coefficient values (R^2) in Table 5, it can be stated that the uptake of copper ions on the NCTSBP follows a pseudo-second-order kinetic model governing the sorption process (Fig. 4). Due to these results, the equilibrium sorption capacities (q_e) calculated from the pseudo-second-order equation are reasonably close to experimental values than those from the pseudo-first-order equation. Additionally, it should be emphasized that linear plots obtained for intraparticle diffusion model does not pass through the origin. From these results, it can be stated that the intraparticle diffusion is not solely responsible for the rate controlling.

Based on the data from pseudo-second-order kinetics, the activation energy for the sorption system of copper ions onto NCTSBP was found as 16.34 kJ mol⁻¹ from the slope of $\ln k_2$ against $1/T$ linear plot in the temperature range studied.

4. Conclusion

In the present work, the copper sorption characteristics of sugar beet pulp modified by treating with NaOH and citric acid were examined. Characterization tests confirm that the modified sugar beet pulp exhibits enhanced cation exchange capacity and stabilized hydration and solubilization properties. Batch sorption experiments were conducted to examine the efficiency of the modified sugar beet pulp on copper binding. The equilibrium data were analyzed using Langmuir, Freundlich and Dubinin–Radushkevich isotherm models depending on temperature. The Langmuir model correlates the experimental data the best. The mean free energy of sorption calculated from Dubinin–Radushkevich isotherm and Polanyi potential confirms that the main mechanism governing sorption process is ion exchange. Kinetic evaluations show that the copper sorption process follows the pseudo-second-order kinetic model. The temperature dependence and thermodynamic findings indicate an exothermic and spontaneous process. Overall, this study showed that sorbent with high copper removal capacity could be prepared from sugar beet pulp through simple treatment methods.

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