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Improvement of cadmium ion removal by base treatment of juniper fiber ☆

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Abstract

Juniper is a small-diameter underutilized lignocellulosic material. We evaluated the efficacy of base-treated juniper fiber (BTJF) for cadmium (Cd^{2+}) sorption and the viability of juniper fiber as a sorbent for removing Cd^{2+} from water. Fourier transform infrared spectroscopy analysis indicated that carboxylate ion is a major functional group responsible for Cd^{2+} sorption. The apparent ideal sodium hydroxide concentration for base treatment is approximately 0.5 M. A batch sorption isotherm test showed that equilibrium sorption data were better represented by the Langmuir model than the Freundlich model. After base treatment, the maximum Cd^{2+} sorption loading, Q_{max}, was greatly improved (9.18–29.54 mg/g), despite a decrease in specific surface area. A pseudo-second-order kinetic model fitted well for the sorption of Cd^{2+} onto BTJF. Initial metal ion concentration and treatment alkalinity were found to be major parameters influencing the kinetics of the sorption reaction. As a result of its strong ability to bind cadmium and its faster kinetics in low concentration, BTJF could be an inexpensive and efficient sorbent for removing heavy metals from stormwater runoff.
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Keywords: Cadmium; Juniper; Saponification; Fourier transform infrared (FTIR) spectroscopy; Isotherm; Kinetics

1. Introduction

Cadmium is one of the major heavy metal pollutants in stormwater runoff. It has been classified as a toxic heavy metal that can cause serious damage to the kidneys and bones [1]. All conventional methods of removing heavy metals, such as chemical precipitation, ion exchange, reverse osmosis, and adsorption on activated carbon, are expensive and are not suitable for low concentration, large volume waste streams such as stormwater runoff. Lignocellulosic fiber is an unconventional low-cost sorbent that has been examined for potential use in removing heavy metals [2]. However, the ion exchange or adsorption capacity of lignocellulosic fiber is lower than that of other sorbents. As a result, attempts have been made to modify various lignocellulosic fibers with different chemicals [3]. A simple and inexpensive base treatment (saponification) has recently been used to increase the capacity of lignocellulosic fibers to remove heavy metals [4,5]. Using X-ray absorption spectroscopic analysis (XANES and EXAFS), Tiemann et al. [5] showed that the carboxyl group plays an important role in the binding of heavy metals. However, few studies have examined the optimum base (sodium hydroxide) concentration in chemical modification.

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Nomenclature

b	Langmuir constant, L/g
h	initial sorption rate, mg/g min
k	equilibrium rate constant of second-order sorption, g/mg min
K	Freundlich constant (measure of sorption capacity, L/mg)
q_t	amount of Cd^{2+} sorbed at time t
Q_{max}	maximum adsorbate loading, grams adsorbate/grams adsorbent
$1/n$	Freundlich constant (measure of sorption intensity)

In this study, Fourier transform infrared spectroscopy (FTIR) was employed to quantify the carboxylic group that is the major functional group presumably responsible for removing cadmium ion (Cd^{2+}), to pinpoint the degree of alkalinity of substrate to maximize Cd^{2+} removal, and, at the same time, to minimize the exudation of extractives from the sample during the sodium hydroxide (NaOH) treatment process. In addition, a series of batch sorption tests were performed to investigate parameters that could affect the Cd^{2+} sorption reaction on the sorbents and to evaluate the viability of base-treated juniper fiber (BTJF) as a sorbent for removing Cd^{2+} from water.

Juniper was selected as an appropriate Cd^{2+} sorbent because its capacity to absorb heavy metals is relatively high compared to that of other lignocellulosic fibers [6]. In addition, juniper is a small-diameter and underutilized material. Juniper woodland, which is concentrated in the southwestern United States, covers approximately 24 million hectares of land. Over the years, large areas of rangeland have become overgrown with these trees [7].

2. Material and methods

2.1. Material

Juniper (*Juniperous monosperma*) trees were randomly collected from New Mexico. Bark and wood were chipped together and ground to pass through a 3-mm screen using a Wiley mill.

A 250-mL aliquot of 1 M NaOH solution was added to a 500-mL Erlenmeyer flask containing 20 g juniper powder. The mixture was agitated for 30 min (designated BTJF1-30 min) or 24 h (BTJF1-1 day). The excess alkaline solutions were decanted and media were washed continuously with distilled water until the pH of the wash water was less than 8. The BTJF samples were air dried at ambient temperature for 3 days.

2.2. Surface area measurement

The specific surface area of untreated juniper and BTJF samples was measured by the BET method [8] using an ASAP 2010 accelerated surface area and porositmetry system (Micrometrics, Norcross, GA) with nitrogen gas.

2.3. FTIR analysis

Milled samples were sieved through a 0.18-mm sieve and dried overnight at 105°C. Samples were pulverized with oven-dried potassium bromide and pressed into pellets. For FTIR analysis, samples were treated with different concentrations of NaOH solutions for 30 min. The concentrations were 0, 0.05, 0.20, 0.30, 0.50, and 1.00 M. The FTIR spectra were collected on a Mattson Galaxy 5020 (Mattson Instruments, Madison, WI) using 64 scans between 400 and 4000 cm^{-1}, triangular apodization, and resolution of 4 cm^{-1}. For comparison, spectra were baseline corrected at 840, 2000, and 4000 cm^{-1}. Absorbances of absorption bands were then measured from the baseline.

2.4. Sorption isotherm model

Juniper and BTJF sieved through a 0.18-mm sieve were used for the isotherm tests. Various concentrations of Cd^{2+} solution were prepared by serial dilution of standard 1000-mg/L reference solution between 0 and 200 mg/L. The mixture of 0.2-g BTJF with 50-mL Cd^{2+} solution of various concentrations was shaken at 150 rpm for 1 day at 25°C. The pH of initial solutions of the following isotherm and kinetic experiments remained 4.2 [9]. The equilibrium (final) pH of the batch test for juniper and BTJF1-1 day samples was increased from pH 4.2 to 6–7. In the pH range of 4–7, the uptake capacity (q_e) of the BTJF1-1 day is constant [9]. The mixture was then removed from the shaker, and the solution was filtered by a 0.45-μm (pore size) membrane filter using a syringe. The solution was then measured for dissolved Cd^{2+} concentration by means of inductively coupled plasma (ICP) emission (Jobin Yvon, Inc., Ultima ICP–AES, Edison, NJ). The final concentration (C_e), measured in mg/L, differed according to various C_0 values from zero to 100 mg/L. The uptake capacity (q_e), which is the amount of Cd^{2+} sorbed at equilibrium (mg/g), was calculated by mass balance between C_0 and C_e with duplicated batch samples.

A characteristic of the Langmuir isotherm is that the loading of sorbate onto the sorbent approaches a limiting value, Q_{max}, as the concentration increases. This corresponds to monolayer coverage of the adsorbent surface with a Langmuir constant, b, related to the free energy of adsorption:

$$q_e = \frac{bQ_{max}C_e}{1 + bC_e}, \quad (1)$$

where b is Langmuir constant (L/g) and Q_{max} is maximum adsorbate loading (grams adsorbate/grams adsorbent).

The Freundlich isotherm is empirical and is used for heterogeneous surface energies:

$$q_e = KC_e^{1/n}, \quad (2)$$

where K (L/mg), a measure of sorption capacity, and $1/n$, a measure of sorption intensity, are Freundlich constants. To obtain the best estimate of all constants for the Langmuir and Freundlich isotherms, data were fitted with nonlinear regressions using a least-squares fitting program (Origin 7.0, OriginLab Corp., Northampton, MA).

2.5. Sorption kinetic model

Juniper and BTJF samples between 1 and 3 mm were used for the kinetic study. One gram of medium was vigorously mixed in predetermined concentrations of 1 L Cd^{2+} solution with a magnetic stirrer throughout the experiment. Initial solution pH ranged from 4.2 to 4.5, and solution temperature was 25°C. After the media were mixed in the solutions, each 8 mL of filtered sample was collected at designated intervals and analyzed for metal elements by ICP.

All the correlation coefficients of the pseudo-second-order rate model gave the best fit compared with those of the simple first- and second-order reaction model, Lagergren first-order reaction model [10], and the pseudo-first-order rate model. Because of this, kinetic constant k for this study was determined from the pseudo-second-order rate equation. This model assumes that sorption follows the Langmuir equation [11].

The kinetic rate equations can be written as follows [11]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \quad (3)$$

where q_t is the amount of Cd^{2+} sorbed at time t (mg/g) and k is the equilibrium rate constant of the second-order sorption (g/mg min).

The initial sorption rate, h (mg/g min), is defined as

$$h = kq_e^2. \quad (4)$$

The q_e and h values were determined from a plot of t/q_t against t.

3. Results and discussion

3.1. Carbohydrate composition and characteristics of juniper fiber

Chemical characteristics of juniper fiber were analyzed for different anatomical parts of wood (Table 1). Base treatment (BTJF1-1 day) caused only a minor change in sugar and klason lignin composition and surface area compared to that of untreated fiber. In addition, despite a decrease in specific surface area from 0.2864 to 0.2450 m^2/g, q_e increased more than 2.5 times after base treatment. The q_e value of the bark was about

Table 1
Carbohydrate composition and characteristics of untreated and treated (BTJF1-1 day) juniper fiber[a]

Composition (%)	Sample				
	BTJF1-1 day	Untreated fiber	Bark	Sapwood	Heartwood
Klason lignin	34.8	36.5	35.3	36.1	39.9
Arabinan	2.76	2.76	2.81	1.01	1.09
Galactan	3.61	3.25	2.15	2.71	3.19
Rhamnan	0.44	0.49	0.49	0.23	0.26
Glucan	30.10	26.65	23.73	36.31	31.97
Xylan	6.56	5.92	5.04	7.55	7.29
Mannan	5.20	4.65	3.52	5.38	5.47
Total carbon	48.7	43.7	37.7	53.2	49.3
Total yield	83.7	80.5	73.8	89.3	89.2
q_e (mg/g)[b]	19.8 ± 0.233	7.8 ± 0.68	9.6 ± 0.04	1.1 ± 0.88	3.4 ± 0.62
Surface area (m^2/g)	0.2450	0.2864			

[a] Experimental procedures based on [12]. The batch test consisted of treating 0.1 g medium in 100 mg/L Cd^{2+} (50 mL), pH 4.2, for 1 day in a shaker.

[b] Mean and standard deviation of three determinations.

8.4 times higher than that of the sapwood and 2.8 times greater than that of the heartwood. The q_e value was obtained from the batch test.

3.2. FTIR analysis

FTIR analysis was performed to confirm the carboxyl group as the major functional Cd^{2+} removal group of BTJF and to determine the ideal NaOH concentration in saponification. The purpose of saponification is to increase the cation sorption capacity of wood fiber. Saponified ester groups in the wood fiber produce carboxylate, which can bind cations as shown in the following equation [5]:

$$\underset{\text{Ester}}{RCOOR'} + H_2O \xrightarrow{OH^-} \underset{\text{Carboxylate}}{RCOO^-} + \underset{\text{Alcohol}}{R'OH}. \quad (5)$$

The major band assignments are as follows. The region below 1550 cm^{-1} is the "fingerprint region," and the absorption cannot clearly be assigned to any particular vibration because it corresponds to complex interacting vibration systems. The region between 1800 and 3500 cm^{-1} presents two major absorption bands centered at about 3420 cm^{-1} (H-bonded OH group) and 2921 cm^{-1} (C–H stretching of CH_2 groups). The region between 1500 and 1800 cm^{-1} is a special range for evaluating the degree of saponification since this is the carbonyl and double-bond region [13–15].

The FTIR spectra of various BTJF samples are shown in Fig. 1. Although a major absorption band (wave number) shift was not observed, differences in absorption band height were observed between 1500 and 1800 cm^{-1} (Fig. 1a). In Fig. 1b, all spectra were set at the baseline equally. The 1500–1800-cm^{-1} range was magnified to investigate this region more closely. Two absorption bands were centered at 1620 and 1737 cm^{-1}. According to the literature, the absorption band wave number of the ester group and carboxyl acid groups in the organic compounds is approximately 1740 cm^{-1}, whereas the absorption band wave number of the carboxylate ion groups is about 1620 cm^{-1} [13–16]. Barker and Owen [17] assigned carboxyl groups an absorption band number of 1737 cm^{-1} for juniper (*J. virginiana*), and Brown et al. [18] assigned an absorption band number of 1620 cm^{-1} as a carboxylate. These absorption band numbers are identical to the numbers recorded in the study reported here. Therefore, it can be concluded from Fig. 1 that the absorption band at 1737 cm^{-1} is attributed to the absorption of carboxylic groups, except carboxylate in BTJF samples, whereas the absorption band at 1620 cm^{-1} corresponds to the absorption of the carboxylate. The pK_a values of the weak and strong carboxyl groups in base-treated sugar beet pulp are 6.10 and 4.6, respectively [4]. Since all juniper fiber was treated with NaOH solutions in which the pH was at least 12.5 and then neutralized to pH 8

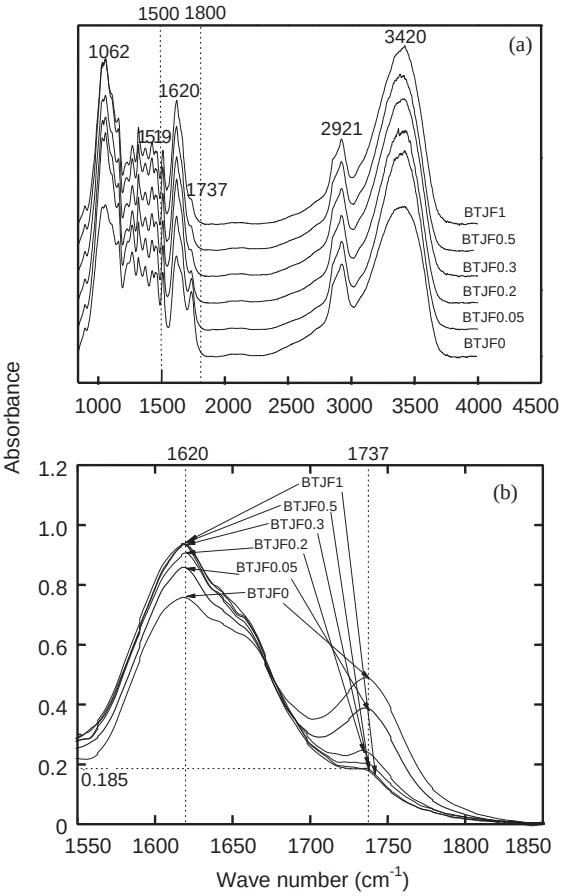

Fig. 1. FTIR spectra of treated juniper fiber: (a) spectra of various concentrations (M) of base-treated juniper, and (b) spectra of carbonyl group region from 1550 to1850 cm^{-1}.

and since the untreated fiber had a pH of approximately 8, it is clear that most of the non-esterified carboxylic groups were in the form of carboxylate at pH 8.

To quantify the relative changes in the spectral intensities of the carboxyl group in the juniper fiber treated with different concentrations of NaOH, the absorption band ratios of 1620 cm^{-1} (carboxylate) and 1737 cm^{-1} (ester) were calculated. Both the 1620/1737 (carboxylate/ester) ratio and q_e increased as NaOH concentration increased (Fig. 2a). There was a linear relationship between 1620/1737 and q_e (Fig. 2b). This result is explained by the saponification process (see Eq. (5)). Hydroxyl ions from NaOH converted the ester in the juniper fiber to carboxylate, which can bind Cd^{2+}. Thus, because high concentrations of NaOH were used for the base treatment, the amount of ester in the juniper fiber was reduced while the amount of carboxylate was increased. In addition, because no ester group that can convert to carboxylate remained when initial NaOH concentrations were higher than 0.5 M, both the

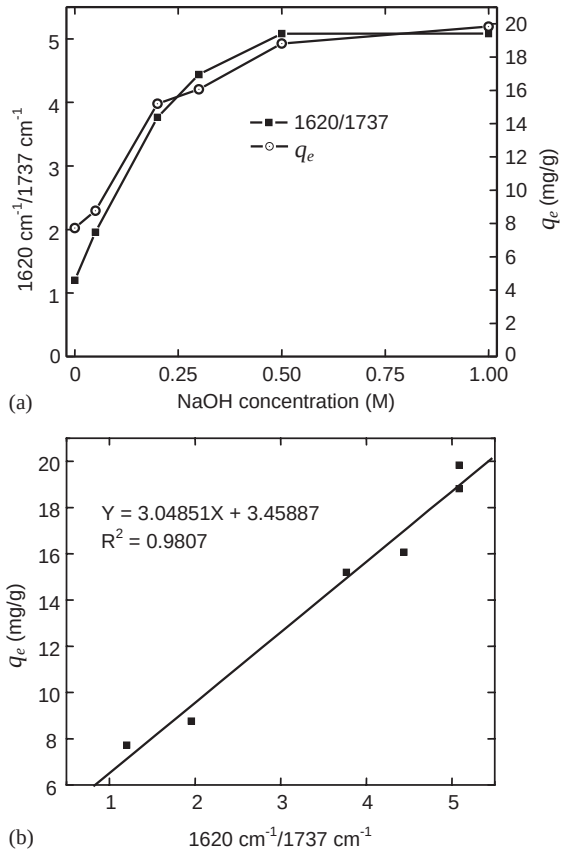

Fig. 2. Effect of base treatment on spectral intensities of carboxyl group: (a) effect of NaOH on carboxylate/ester ratio (1620/1737 cm^{-1}) and q_e, and (b) relationship between 1620/1737 ratio and q_e values.

1620/1737 ratio and q_e values were barely increased in the range tested (Fig. 2a). These data indicate that the ideal NaOH concentration for this base treatment is about 0.5 M.

3.3. Sorption isotherms

Sorption equilibria and sorption kinetics are two important physicochemical aspects of the sorption process as a unit operation. Fig. 3 shows the observed points of Cd^{2+} sorbed capacity (q_e) of untreated and treated (BTJF1-1 day) fiber in various effluent Cd^{2+} concentrations (C_e) in relation to the curves calculated from the constants in Table 2. The R^2 values in Table 2 show that the Langmuir isotherm model yielded a better fit than did the Freundlich isotherm model in the sorption of Cd^{2+} onto both untreated and treated fiber.

The sorption capacities of various sorbents tested by other researchers are summarized in Table 3 along with the results obtained in the study reported here. Cadmium ion sorption to the BTJF1-1 day sample with

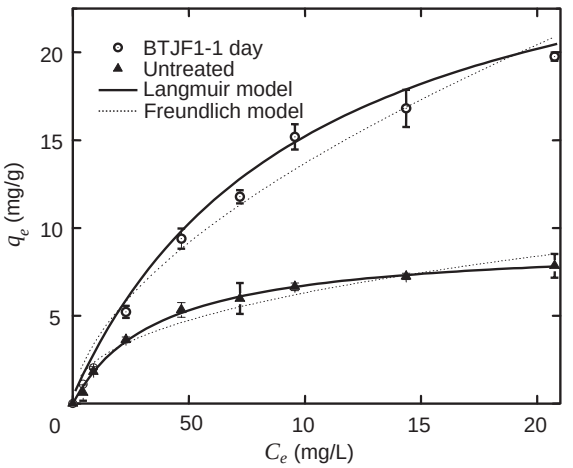

Fig. 3. Langmuir and Freundlich isotherms for Cd^{2+} sorption onto untreated and treated (BTJF1-1 day) juniper fiber.

the maximum sorption capacity of BTJF1-1 day was greater than that of the other sorbents, except for seaweed and chitosan. However, biomass such as seaweed has a tendency to easily collapse and swell, which prevents successful use in sorption columns [19]. Hsien and Rorrer [27] noted that the use of chitosan is limited by its solubility in acidic solution and its non-porosity.

3.4. Sorption kinetics

Sorption kinetics, which describes the solute sorption rate, is an important characteristic in evaluating the efficiency of sorption. Sorption data at different initial Cd^{2+} concentrations are shown in Fig. 4 and Table 4. The calculated q_e values from the pseudo-second-order rate model decreased from 7.26 ± 0.23 to 2.30 ± 0.01 mg/g and the h values decreased from 0.28 ± 0.00 to 0.10 ± 0.01 mg/g min, whereas the $k(\times 10^3)$ values increased from 5.4 ± 0.35 to 19.2 ± 2.94 g/mg min as the initial Cd^{2+} concentration increased from 3.2 ± 0.04 to 22.9 ± 0.653 mg/L. This indicates that initial heavy metal concentrations influenced the contact time necessary to reach equilibrium to a significant degree [11].

The change in q_e (from the pseudo-second-order rate model) of untreated and treated (BTJF1-1 day) fiber with time is shown in Fig. 5. C_0 values of untreated and BTJF1-1 day fiber were 9.8 ± 0.26 and 10.5 ± 1.11 mg/L, respectively. After base treatment, q_e increased from 1.7 ± 0.08 to 6.2 ± 0.05 mg/g, $k(\times 10^3)$ value decreased from 22.5 ± 3.00 to 7.3 ± 0.68 g/mg min, and h increased from 0.06 ± 0.01 to 0.28 ± 0.06 mg/g min. This indicates that base treatment of juniper increases Cd^{2+} removal capacity but also increases initial sorption rate h.

Table 2
Isotherm constants for Cd^{2+} adsorbed onto untreated and treated fiber

Sorbent	Freundlich isotherm			Langmuir isotherm		
	$1/n$	k (L/mg)	R^2	Q_{max} (mg/g)	b (L/g)	R^2
Untreated fiber	0.41±0.06	0.94±0.26	0.938	9.2±0.22	0.03±0.22	0.997
BTJF1-1 day	0.58±0.06	0.95±0.25	0.974	29.5±1.40	0.01±0.00	0.997

Table 3
Reported Cd^{2+} sorption capacities for various sorbents

Sorbent	q_e (mg/g)	Q_{max} (mg/g)	Source
BTJF1-1 day	—	29.5	Current study
Untreated juniper fiber	—	9.18	Current study
Walnut shell	1.5	—	[24]
Activated carbon	11.1	—	[20]
Geothite	—	3.08	[21]
Acid-treated bentonite	—	4.11	[22]
Sphagnum peat moss	—	5.8	[23]
Seaweed			
Ascophyllum andosum	67	—	[26]
Sargassum natans	—	100	[19]
Chitosan powder	420	—	[25]

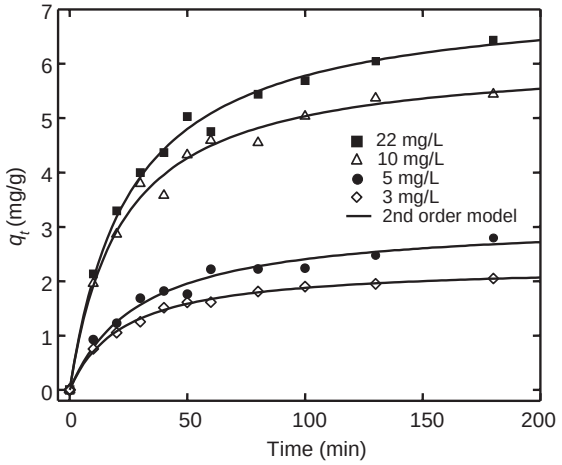

Fig. 4. Cd^{2+} removal capacity as function of time for various initial concentrations at 25°C, pH 4.2, and 1 g/L BTJF1-1 day.

The increasing reaction kinetics at low Cd^{2+} concentrations indicate that BTJF could be an excellent sorbent for treating even less than 5 mg/L of heavy metals and large volumes of waste streams such as urban stormwater runoff.

Table 4
Kinetic constants for effect of initial Cd^{2+} concentration

C_0 (mg/L)	q_e (mg/g)	$k(\times 10^3)$ (g/mg min)	h (mg/g min)	R^2
3.2±0.04	2.3±0.01	19.2±2.94	0.10±0.01	0.997
5.1±0.27	3.1±0.03	10.7±1.25	0.10±0.01	0.983
10.5±1.10	6.2±0.06	7.3±0.20	0.28±0.06	0.991
22.9±0.653	7.3±0.23	5.4±0.35	0.28±0.00	0.995

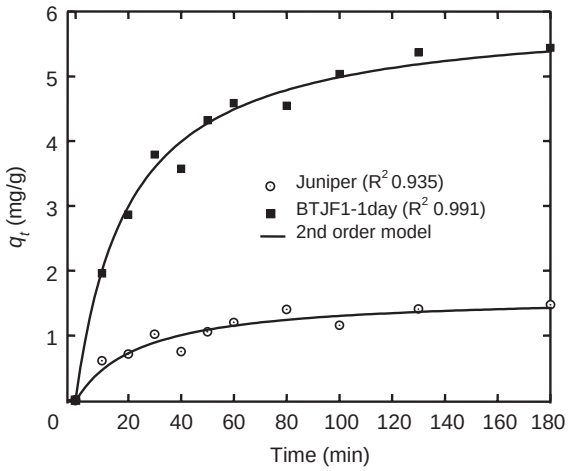

Fig. 5. Cd^{2+} removal capacity as function of time for untreated and treated (BTJF1-1 day) fiber at 25°C, 10 mg Cd^{2+}/L, and 1 g sorbent/L.

4. Conclusions

1. Carboxylate ion produced by saponification during base treatment was a major functional group responsible for cadmium (Cd^{2+}) sorption. The optimum NaOH concentration to maximize Cd^{2+} removal and to minimize the exudation of extractives during treatment was about 0.5 M.
2. The Langmuir theory was found to represent the sorption of Cd^{2+} onto both raw juniper fiber and BTJF better than does the Freundlich model. Based on the Langmuir theory, the base treatment raised Q_{max} about 3.2 times.

3. Initial metal ion concentration had a significant influence on the kinetics of the sorption reaction. A pseudo-second-order kinetic model was fitted for sorption of Cd^{2+} onto BTJF. The initial sorption rate of Cd^{2+} onto BTJF was about 5 times faster than that of control juniper sorbent.
4. BTJF appears to be an economical and effective sorbent for removing heavy metals from stormwater runoff because of its high removal capacity and fast kinetics in lower concentration.

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