Preparation, Characterization, and Utilization of Cationized Hemp as Anion Exchanger for Removing Permanganates and Dichromate Anions

H. M. Fahmy,[1] R. Kohler[2]

[1]Textile Research Division, National Research Center, Dokki, Cairo, Egypt
[2]Institute of Applied Research, Reutlingen University, Reutlingen, Germany

ABSTRACT: Using a software experimental design strategy and through 25 experiments, steam exploded hemp bast fibers (HBF) as well as their shives were cationized by the exhaustion method using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride solution. The results obtained revealed that at pH 13, raising the temperature of a bath containing 100 g/L cationizing agent aqueous solution at liquor to substrate ratio 1/15 to 80°C for 90 min produces the cationized forms of HBFs as well as their shives with percent nitrogen content 0.2240 and 0.4893 respectively. The statistical analysis for the results indicated that the percent nitrogen content is significantly influenced by factors of time, pH, and primarily the cationizing agent concentration. The cationized forms of HBFs as well as their shives, having amino contents 76 and 104 mequiv/100 g respectively, were characterized by studying their potentiometric titration and were analyzed by thermogravimetric analysis. Both of these cationized substrates were utilized as anion exchangers for adsorption of permanganate and dichromate anions from their acidic aqueous solutions. Adsorption dynamics of the removal of such anions were first-order reactions whereas the adsorption isotherms showed that the adsorption of those anions on all the aforementioned anion exchangers was favorable. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2584–2592, 2007

Key words: hemp; cationization; computer software for experimental design; anion exchanger; permanganates and dichromate anions

INTRODUCTION

During recent years, interest has been increasingly focused on environmental pollution. The problem of removing pollutants from water and waste water has grown with rapid industrialization.

Heavy metals contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations, and tanneries. Heavy metals, such as cadmium, chromium, lead, and mercury, are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders.[1] Various methods exist for the removal of toxic metals from aqueous solution, such as ion-exchange, reverse osmosis, adsorption, complexation, and precipitation.[2–5] Adsorption is the most effective and widely used method.

Among all the natural polymers, cellulose could be considered promising as ion exchanger because of its low cost, renewable resources, biodegradability, and wide application spectrum, both in natural as well as modified form.[6] Hemp bast fibers (HBF), as a cellulosic material, are very similar to flax, but less regular. Flax swells much more in sodium hydroxide, giving an 85% increase in diameter, while with hemp it is only 25%, reflecting the highly crystalline structure of its fibers.[7] Many studies have demonstrated that quaternized cellulosics can be used as anion exchangers for removing pollutants such as dyes,[8,9] heavy metals cations,[10] and nitrates[11] from waste water. In continuation, the present work aims to cationize steam exploded hemp bast fibers (SHBF) using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride solution. Steam explosion is a special treatment for HBFs more effective than the conventional scouring.[12] Additionally, raw hemp shives, the woody part residues resulting from decortications of the hemp stalks (without steam explosion treatment), have been also cationized. An experimental design strategy as well as statistical analysis for the results is used to find the optimal conditions for the cationization process with a minimum number of experiments. The thermal gravimetric analysis of both steam exploded hemp and its cationized form were discussed. Furthermore, utilization of these cationized substrates as anion exchangers for adsorption of permanganate and dichromate anions were studied.

Correspondence to: H. M. Fahmy (aukal34@yahoo.com).

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TABLE I
Layout of D-Optimal Response Surface Design for Cationization of Steam Exploded Hemp and the Resulting Percent Nitrogen Contents

Standard order	Run order	Temp. (°C)	Time (min)	Quat-Conc. (g/L)	pH	Nitrogen content (%)
1	1	80	90	100	13	0.2240
2	9	80	30	65	13	0.0440
3	18	40	90	65	13	0.1177
4	25	40	90	100	11	0.1743
5	5	40	90	30	11	0.0543
6	13	80	90	30	11	0.0778
7	15	80	30	30	11	0.0427
8	6	80	90	30	13	0.0763
9	16	40	30	30	13	0.0405
10	24	40	30	65	11	0.0820
11	17	40	60	100	13	0.2170
12	8	60	60	30	12	0.0485
13	10	80	60	100	11	0.1086
14	3	80	30	100	12	0.1230
15	22	60	30	100	11	0.0966
16	21	60	60	82.5	12	0.1000
17	23	40	30	100	12	0.0925
18	19	60	30	100	13	0.1250
19	2	40	60	65	12	0.0660
20	12	80	60	65	12	0.0854
21	14	40	90	100	11	0.1382
22	4	80	90	100	13	0.1960
23	20	40	30	30	13	0.0571
24	11	40	90	65	13	0.1000
25	7	80	30	30	11	0.0601

Liquor ratio 1/15 for all trials; factor labels and ranges: A = temperature (40–80°C); B = time (30–120 min); C = Quat concentration (50–150 g/L), D = pH (9–13).

EXPREMENTAL

Materials

Steam exploded hemp bast fibers (SHBF) and its shives (HV) were kindly supplied by the Institute of Applied Research (IAF), Reutlingen University, Germany.

Chemicals

Sodium hydroxide, potassium permanganate, potassium dichromate, and acetic acid were of laboratory grade chemicals. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride, 66% aqueous solution, under the commercial name Quab-188 (Quat) was kindly supplied by Degussa Company.

Steam explosion of hemp

Hemp bast fibers (HBF) were treated by steam explosion using the individually designed and built steam explosion installation[12] at IAF.

Cationization of hemp fibers

HBF or its HV were cationized using Quat aqueous solution by the exhaustion procedure. The cationization process was performed by introducing a specific amount of SHBF or its HV into an aqueous solution of sodium hydroxide of specific concentration to maintain a desired pH in an ''Ahiba'' Apparatus (AG CH-8305 Dieticon/Zurich, Type TU600). The reaction temperature is raised gradually until a required temperature, then Quat solution of a specific concentration was added and the cationization reaction was left to proceed for a specific time. At the end of the reaction, both of the cationized forms of SHBF (CSHBF) or shives (CHV) were washed several times with cold water and neutralized with 1% aqueous solution of acetic acid. Finally, the neutralized products were washed with distilled water and dried at ambient conditions.

Computer software for experimental design

To explore the effects of factors supposed to influence the degree of cationization of SHBF as well as the possible interactions between these factors, a D-optimal response surface design for statistical evaluation was chosen using the software Design Expert, Version 6, (Stat-Ease, USA). The design suggested 25 experiments, which were run in a random sequence (see Table I), with every factor set to specified levels. The

studied factors and selected ranges respectively, were time, 30–120 min; temperature, 40–80°C; pH, 9–13; and Quat concentration, 50–150 g/L.

Analytical and test methods

The nitrogen content obtained after cationization was determined by the Kjeldahl method. The amino content was determined according to Fisher and Kunin.[13] Potentiometric titration was conducted as per Benerito et al.[14] Water solubility was carried out by measuring the percent weight loss after 10, 20, and 50 cycles of water extraction in a soxhlet.[15] Water swellability was performed by evaluating the percent increase in volume after 24 h and 1 week of water impregnation in a measuring cylinder.[15] Thermogravimetric analysis (TGA) was carried out in a temperature range 50–500°C under nitrogen atmosphere with a heating rate of 10°C/min using Perkin-Elmer TGA-7.

Permanganate and dichromate anions removal

A 0.5 g sample of CSHBF or CHV was added to a 100 mL stopped glass bottle containing 50 mL of potassium permanganate or potassium dichromate aqueous solution of specific concentrations and at different pHs.[16] The bottle was shaken at 200 rpm for different intervals of time. Then, the content of the bottle was filtered on sintered glass crucible, and the concentration of the remaining anions in the filtrate was deter-

mined colorimetrically at the wave length of maximum absorption of the aforementioned anions solutions (which was 500 and 420 nm for permanganate and dichromate solutions respectively) using a photoelectric colorimeter, Model 581, China.

Desorption and reuse

A desorption study was carried out by agitating 0.5 g of CSHBF or CHV with 50 mL of potassium permanganate or potassium dichromate aqueous solution of specific concentrations at pH 6 for specific interval of time, after which the sorbent was filtered, washed with distilled water and dried at 80°C for 4 h.

The sorbent samples were then regenerated by 0.1M NaOH at liquor to material ratio 1 : 100 for 24 h and then reused for the adsorption purpose at pH 6. The adsorption and regeneration cycle was repeated five times. After adsorption in each cycle, the permanganate or dichromate anions remaining in the filtrate were analyzed colorimetrically as mentioned earlier.

RESULTS AND DISCUSSION

It has been established that cellulose can undergo cationization through its reaction with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride in basic medium.[17] A suggested mechanism for cationization of hemp, as a cellulosic material, is represented in the following equations:
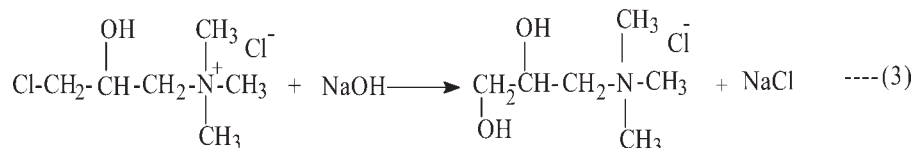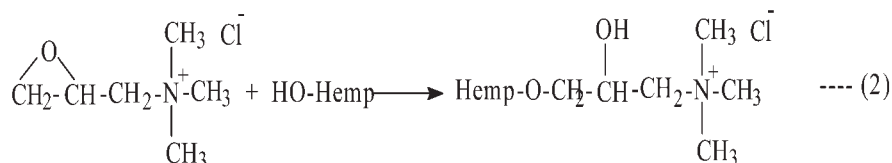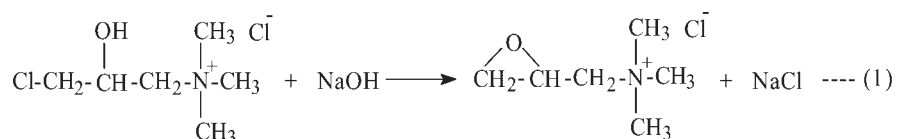
The above reaction scheme features the following points: (a) The chlorohydrin form of the reagent is converted to the epoxy intermediate (2,3-epoxypropyl trimethyl ammonium chloride; eq. (1)); (b) the epoxy intermediate reacts with the hemp (eq. (2)); (c) the chlorohydrin form is converted via hy-

drolysis to the nonreactive 2,3-dihydroxy derivatives (eq. (3)).

Factors affecting cationization of SHBF as well as a statistical analysis of the results obtained were studied using the software ''Design Expert'' accompanied with an appropriate discussion later.
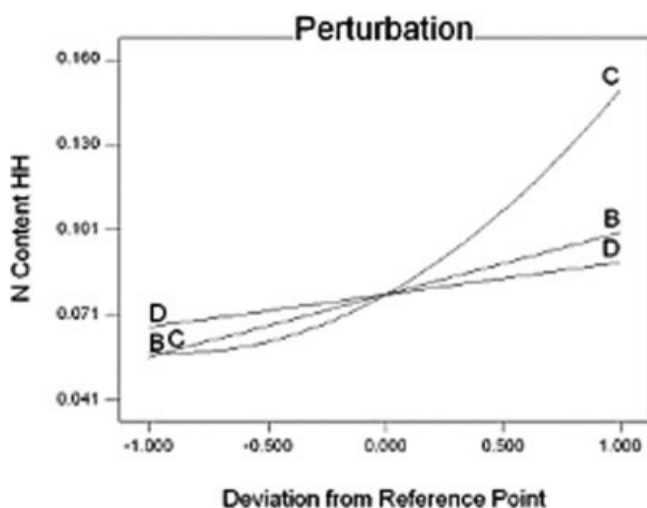
Figure 1 Effect of cationization factors on the percent nitrogen content. Actual factors: A, temperature = 60°C; B, time = 60 min; C, Quat concentration = 65 g/L; D, pH = 12.

Experimental design for cationization of SHBF

Within the aforementioned selected ranges of factors affecting the cationization of SHBF, Table I shows that the extent of cationization, expressed as percent nitrogen content, reaches a maximum at standard 1/run 1 whereas it is a minimum at standard 9/run 16.

Statistical evaluation of the results of cationization suggests a model describing the significant effects of the aforementioned different factors. The first step of this statistical evaluation is testing the aforementioned factors for statistical significant effects on the results of cationization. In a second step the experimental results are modeled by a "response surface." The model equation is actually a linear regression equation which has been numerically fitted to the experimental results by mini-
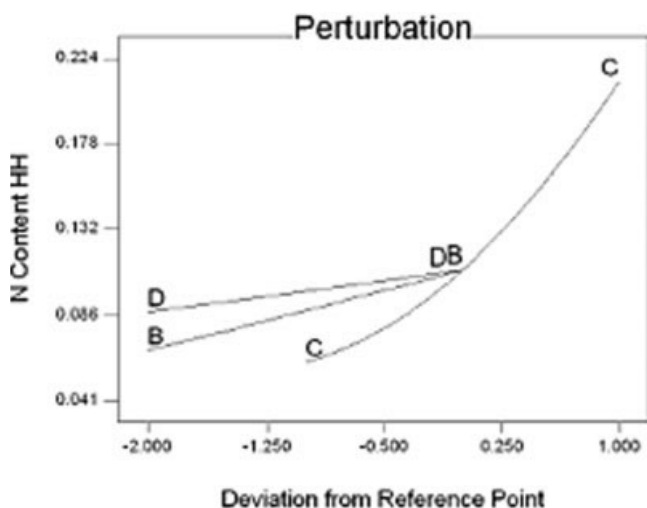

Figure 2 Effect of cationization factors on the percent nitrogen content. Actual factors: A, temperature = 60°C; B, time = 90 min; C, Quat concentration = 65 g/L; D, pH = 13.
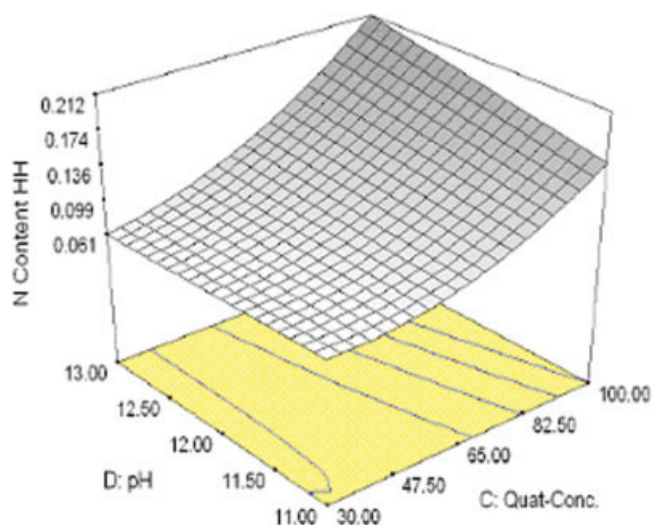

Figure 3 Three-dimensional plot for nitrogen contents at temperature 60°C and time 90 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mizing the residuals. The equation generally includes only the factors that are statistically significant or necessary to keep the model hierarchical.

The best model obtained is given by the following equation (all factors normalized to the range −1 to +1):

$$\text{Nitrogen Content} = +0.078 + 0.022^*B + 0.046^*C \\ + 0.011^*D + 0.026^*C^2 + 0.014^*B^*C \\ + 0.015^*C^*D$$

It is obvious that the nitrogen content is significantly influenced by the factors time (B), and pH (D), and
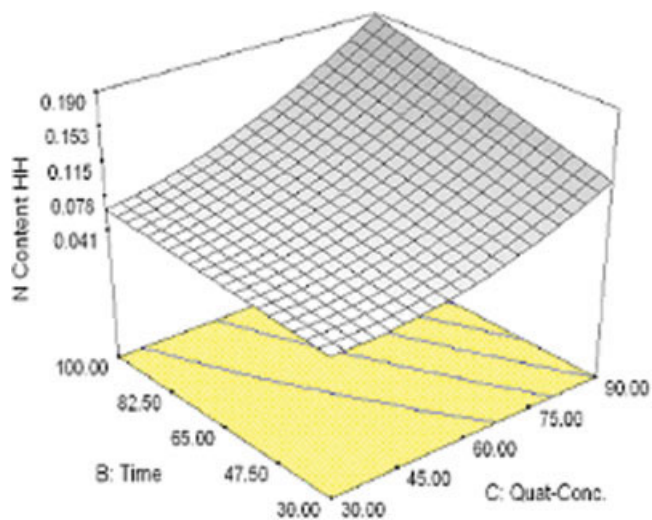

Figure 4 Three-dimensional plot for nitrogen contents at temperature 60°C and pH 13. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
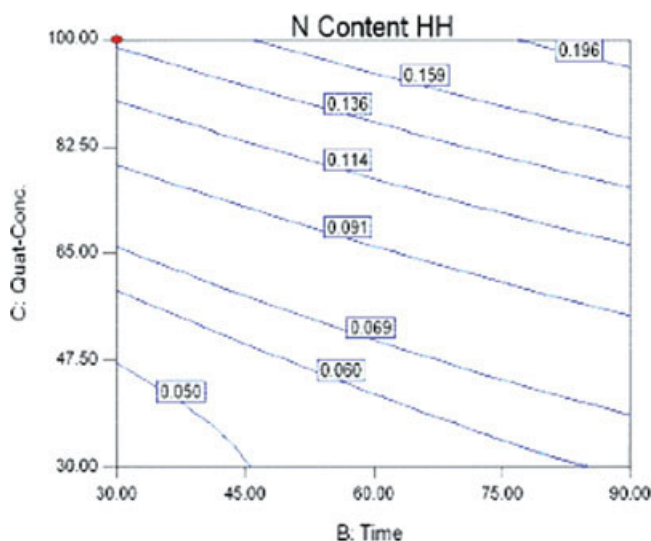
Figure 5 Contour plots for nitrogen contents at temperature 60°C and pH 13.

that the Quat concentration (C) has the highest influence. This is underlined by the fact that the square of this factor has also a significant contribution. The pH has the smallest effect and the influence of temperature is not significant. Furthermore the significant interactions BC and CD mean that the effect of Quat concentration depends slightly on time and pH. Figures 1 and 2 are perturbation plots, calculated using the aforementioned model equation and showing the effects of the factors on the nitrogen content. It is clear from Figure 1 that the Quat concentration has the highest influence on the nitrogen content whereas pH has a minor effect. Figure 2 shows the interaction between Quat concentration and pH and time respec-

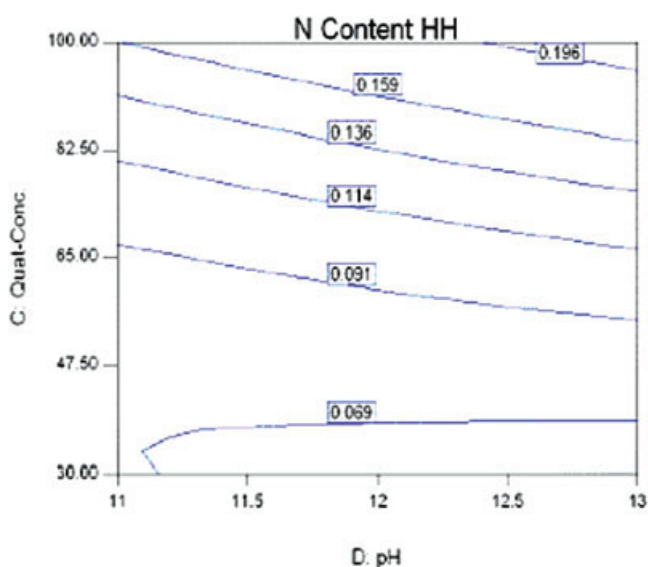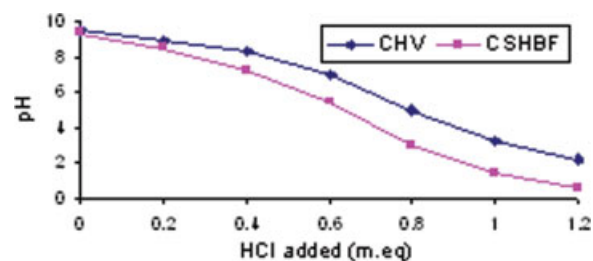**Figure 6** Contour plots for nitrogen contents at temperature 60°C and time 90 min.

Figure 7 Potentiometric titration curves of CHV and CSHBF anion exchangers. Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; temp., 28°C; 1 mm > particle size of shives > 500 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tively. At high pH and with long treatment time the effect of Quat concentration increases.

Figures 3 and 4 are three-dimensional plots that give qualitative pictures of the factor effects on the nitrogen content. Figure 3 shows that the highest nitrogen content is obtained at high Quat concentration and high pH, whereas Figure 4 shows that the highest nitrogen content is obtained at long time of treatment with high Quat concentration. Figures 5 and 6 are another illustration of the results represented by contour plots. These are section lines across the response surface connecting points of same nitrogen content.

Characterization of cationized hemp and cationized shives

Both of the CSHBF and CHV, having amino contents 76 and 104 mequiv/100 g respectively, are characterized by potentiometric titrations, water solubility, and swellability whereas CSHBF and SHBF are analyzed thermogravimetrically (TGA).

Potentiometric titration

Figure 7 shows the two potentiometric titrations corresponding to the CSHBF as well as the CHV according to Benerito et al.[14] It is clear that both potentiometric titrations are consistent with the behavior of a strong monobasic base, revealing that both CSHBF and CHV are strong anion exchangers.[18]

Water solubility

Table II shows water solubility of CSHBF and CHV anion exchangers. It is clear that these cationized substrates manifest little solubility during the first 10 cycles then their weights remain approximately unchanged and the solubility of CHV is higher than CSHBF, which reflects the role of steam explosion treatment (as a pretreatment step for HBF) in the re-

TABLE II
Water Solubility of CSHBF and CHV

Number of cycles	% Loss in weight	
	CSHBF	CHV
10	0.21	0.37
20	0.1	0.15
50	0.1	0.1

Nitrogen content of CSHBF, 0.2240 mequiv/100 g; Nitrogen content of CHV, 0.4893 mequiv/100 g; 1 mm > particle size of shives > 500 μm.

moval of the soluble natural impurities before cationization.

Water swellability

Table III shows water swellability of CSHBF and CHV anion exchangers. It is clear that the swellability of the HCl salt form of both substrates is higher than the free form and CHV swells more than that of CSHB. This state of affair is most probably due to the differences between both substrates in their physicochemical properties, crystallinity/amorphousity ratios as well as location, distribution, and extent of cationic active sites.

Thermogravimetric analysis

Figure 8 shows two curves representing the TGA of SHBF and CSHBF. It is obvious from the figure that both curves are consisting of three parts, the first one starts from 50°C to about 257 or 268°C with loss of weights of 4.800 and 5.966% for SHBF and CSHBF respectively, and represents a dehydration stage for both materials.

The second part represents the first stage of the thermal degradation of both substrates and includes the maximum weight losses as a result of pyrolysis.[19] In this stage, the degradation starts at 257.4°C and ends at about 368.1°C with a weight loss of 60.3% for SHBF, whereas it starts at 268°C and ends at about 355.3°C with weight loss of 63.653% for CSHBF.

TABLE III
Water Swellability of CSHBF and CHV

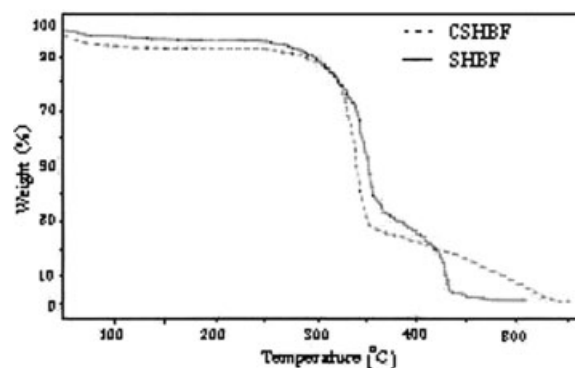| Anion exchanger	% Increase in volume
CSHBF	
Free	30
HCl	50
CHV	
Free	40
HCl	70

Figure 8 Thermal gravimetric curves of SHBF and CSHBF.

The third part of both curves represents the conversion of the remaining materials to carbon residues.[19] This stage ends at 509.11°C with weight loss of 34.100% for SHBF whereas it ends at 554.6°C with weight loss of 28.010% for CSHBF. The residual weights of both samples at the end of the combustion process are 0.8 and 2.371% at final degradation temperatures 509.11 and 554.6°C for the SHBF and CSHBF respectively.

Utilization

CSHBF was investigated for its ability to act as an anion exchanger by studying the removal of permanganate and dichromate anions at different pHs. The results and discussion are given later.

Removal of permanganates and dichromates anions at different pHs

Table IV shows the removal of permanganate and dichromate anions by the CSHBF anion exchanger from aqueous solutions at different pHs. It is clear that, within the range studied, the percent removal of both anions is enhanced in the acidic medium and the more acidic the medium, the more removal will occur. This result can be explained on the basis that in the acidic medium the fixation sites of CSHBF are protonated, allowing the permanganate or dichromate anions to be fixed, and the more protonation the more fixation capacities for anions will be.[10] Also, it is evident from Table IV that both anion exchangers remove permanganate anions more readily than dichromate anions, the point which can be explained on the basis of smaller size, weight, and valence of permanganate anions.[20]

Adsorption dynamics

Figures 9 and 10 show Lagergren's plots for the removal of permanganate and dichromate anions

TABLE IV
Effect of pH on Percent Removal of Potassium Permanganate or Potassium Dichromate by SHBF, CSHBF, HV, and CHV

	% Removal by SHBF		% Removal by CSHBF		% Removal by HV		% Removal by CHV	
pH	MnO_4^-	$Cr_2O_7^{2-}$	MnO_4^-	$Cr_2O_7^{2-}$	MnO_4^-	$Cr_2O_7^{2-}$	MnO_4^-	$Cr_2O_7^{2-}$
4	41	2.5	100	22	47	4.5	100	33
6	33	1.0	100	15	42	3.0	100	27
8	27	0.5	95.3	4	31	1.25	96.5	20

Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; concentration of potassium permanganate or potassium dichromate, 100 mg/L; time of agitation of potassium permanganate, 3 min; time of agitation of potassium dichromate, 2 h; LR, 100 L/kg; agitation speed, 200 rpm; temp., 28°C; 1 mm > particle size of shives > 500 µm; λ_{max} of potassium permanganate, 500; λ_{max}. of potassium dichromate, 420.
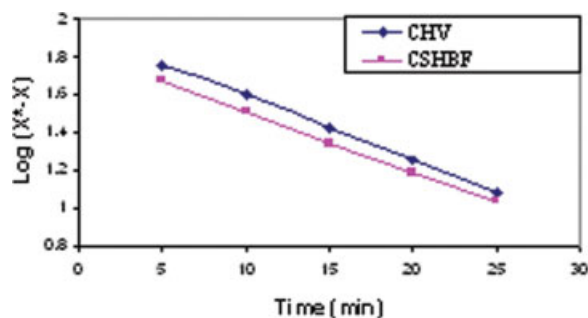

Figure 9 Adsorption dynamic of potassium permanganate on CSHBF and CHV. Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; concentration of potassium permanganate, 300 mg/L; pH, 5; LR, 100 L/kg; agitation speed, 200 rpm; temp., 28°C; 1 mm > particle size of CHV > 500 µm; λ_{max} of potassium permanganate, 500. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

respectively, by the aforementioned anion exchangers. The rate constants, k_a of adsorption can be estimated using Lagergren's equation:[20]
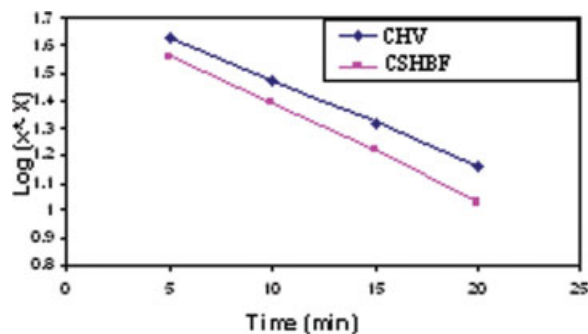
$$\frac{X^* - X}{X^*} = e^{k_a t}$$

Figure 10 Adsorption dynamic of potassium dichromate on CSHBF and CHV. Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; concentration of potassium dichromate, 100 mg/L; pH, 5; LR, 100 L/kg; agitation speed, 200 rpm; temp., 28°C; 1 mm > particle size of CHV > 500 µm; λ_{max} of potassium dichromate, 420. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Adsorption Kinetics of Permanganate and Dichromate Anions on CSHBF and CHV

	k_a of adsorption	
Substrates	MnO_4^-	$Cr_2O_7^{2-}$
CSHBF	6.3×10^{-2}	3.6×10^{-2}
CHV	6.67×10^{-2}	3.2×10^{-2}

where X^* and X are the amounts of anions adsorbed (mg/L) at equilibrium and at time t (minutes), respectively. Plotting $\log(X^* - X)$ versus time gives a straight line and the slope of this line is k_a. The rate constants of the adsorption of permanganate and dichromate anions on CSHBF or CHV were depicted and tabulated in Table V. Results in Table V lead to the conclusion that the removals of the aforementioned anions on both anion exchangers are first order reactions.

Adsorption isotherms

Figures 11 and 12 show the adsorption isotherms of permanganate and dichromate anions respectively on the aforementioned anion exchangers. It is clear from both figures that the adsorption of both anions obeys
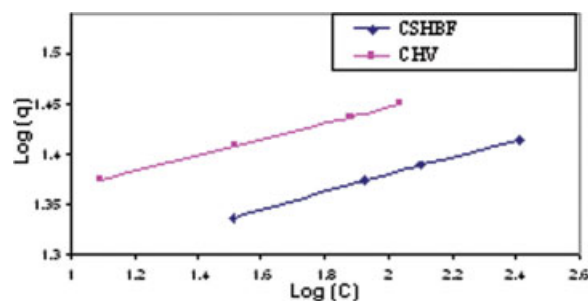

Figure 11 Adsorption isotherms of potassium permanganate on CSHBF and CHV. Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; concentration of potassium permanganate, 250–400 mg/L; pH, 5; LR, 100 L/kg; agitation speed, 200 rpm; temp., 28°C; 1 mm > particle size of CHV > 500 µm; λ_{max} of potassium permanganate, 500. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
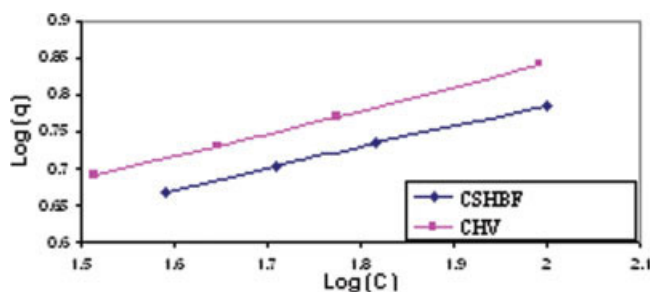
Figure 12 Adsorption isotherms of potassium dichromate on CSHBF and CHV. Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; concentration of potassium dichromate, 80–160 mg/L; pH, 5; LR, 100 L/kg; agitation speed, 200 rpm; temp., 28°C; 1 mm > particle size of CHV > 500 μm; λ_{max} of potassium dichromate, 420. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Freundlich type of adsorption,[20] which can be represented by the following equation:

$$q = K_{ads}C^{1/n}$$

where q is the amount of anions (mg/g) adsorbed per unit weight of anion exchanger corresponding to the equilibrium concentration of anions in solution C (mg/L), whereas K_{ads} and n are constants. Table VI shows Freundlich parameters, $1/n$ and K_{ads} where n is the slope of each straight line and K is the intercept of each straight line with log q axis at a value of log C equals 0 in Figures 10 and 11. The results in Table VI indicate that the adsorption capacity of such anions is much higher on CHV than on CSHBF, whereas the values of $1/n$, which is less than unity, leads to the conclusion that the adsorption of these anions on all the aforementioned anion exchangers is favorable.[8]

Regeneration of CSHBF or CHV

To make the adsorption process more economical, it is necessary to regenerate the spent adsorbent. Results mentioned above indicated that CSHBF or CHV as anion exchangers are effective to remove permanganate than chromates anions from their aqueous solutions. To demonstrate the reusability of the CSHBF

TABLE VI
Freundlich Parameters of the Adsorption of Permanganate and Dichromate Anions CSHBF and CHV

Substrates	Adsorption parameters			
	MnO_4^-		$Cr_2O_7^{2-}$	
	K_{ads}	$1/n$	K_{ads}	$1/n$
CSHBF	18.19	0.15	1.32	0.67
CHV	23.44	0.10	1.8	0.625

TABLE VII
Percent Sorption and Desorption of Potassium Permanganate and Potassium Dichromate Anions by CSHBF and CHV After Repeated Cycles of Use

No. of cycles	CSHBF (MnO_4^-		CHV (MnO_4^-	
	% Sorption	% Desorption	% Sorption	% Desorption
1	100	94	100	95
2	98	93	99	94
3	96	93	99	94
4	96	92	98	93
5	95	91	96	92

Capacity of CSHBF, 76 mequiv/100 g; capacity of CHV, 104 mequiv/100 g; concentration of potassium permanganate, 100 mg/L; time of agitation of potassium permanganate, 3 min; LR of adsorption or desorption, 100 L/kg; pH of adsorption or desorption, 6; desorption, 0.1M NaOH; desorption time, 24 h; temp., 28°C; agitation speed, 200 rpm; 1 mm > particle size of shives > 500 çm; λ_{max} of potassium permanganate, 500.

and CHV, the adsorption–desorption cycle of permanganate anions was repeated five times for CSHBF and CHV (Table VII). It is obvious from Table VII that either the adsorption or desorption capacities by CSHBF or CHV did not change remarkably and these anion exchangers could be repeatedly used in permanganate adsorption with slight losses in their initial adsorption capacities.

CONCLUSIONS

From the previous discussion the following points can be concluded:

1. Using an experimental design strategy it is found that SHBF can be cationized to a nitrogen content of 0.2240% by treating them in a bath together with 100 g/L Quat aqueous solution at pH 13, at liquor to hemp fibers ratio 1/15 and raising the temperature, to 80°C for 90 min.
2. The statistical analysis of the results indicates that the nitrogen content is significantly influenced by the factors time and pH, and primarily by the Quat concentration.
3. Potentiometric titration curves of CSHBF and CHV reveals that they are strong anion exchangers.
4. The solubility of CHV is higher than CSHBF.
5. The swellability of the HCl salt form of both substrates is higher than the free form and CHV swells more than that of CSHB.
6. The removal of permanganate and dichromate anions, from their acidic aqueous solutions, by adsorption on these anion exchangers is favorable and follows a first-order reaction.
7. CSHBF or CHV could be repeatedly used in permanganate adsorption with slight losses in their initial adsorption capacities.

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