[f004]

(N-BUTYL-N-CHLOROPROPYL-N,N-DIMETHYL)AMMONIUM BROMIDE SALT OF CELLULOSE: PREPARATION AND ITS ABSORPTION OF ARSENIC IONS

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Abstract. Cellulose was modified by reaction with (N-butyl-N-chloropropyl-N,N-dimethyl) ammonium bromide (BCDMAB). The optimum reaction conditions were as follows: temperature 55°C, reaction time 3.2 h and mass ratio of cellulose:BCDMAB=1:2.5. Equilibrium adsorption capacity of modified cellulose for arsenate ion has been estimated. It's shown that this capacity increased with concentrations of arsenate ion. Structure of modified cellulose was confirmed by IR and SEM images.

Generally, ion exchangers are produced by polycondensation or polymerization [1] reactions which have several disadvantages such as long synthesis cycles, high costs, and reaction byproducts poisonous to the environmentand humans. Further development of ion exchangers has been investigated, and some studies have exhibited the preparation of ion exchangers fromAR, including sugarcane bagasse [2], peanut hull [3], apple pomace [4], sawdust [5], coconut husk [6], orange peel [7], banana pith [8] and pine bark [1].

Cellulose, hemicelluloses and lignin structures have a large amount of easily available hydroxyl groups; these hydroxyl groups can be used for the preparation of various functional polymers [10]. Research about tertiary amino anion exchanger prepared from AR(AR-TE) has been reported in previouswork [1,9,11], but there is no information concerning quaternary amino anion exchanger (QE) prepared from WR used for nitrate removal in the present literature. The main objective of this paper is to discuss the preparation of cotton quaternary amino anion exchanger (CT-QE) from by reaction with (N-butyl-N-chloropropyl-N,N-dimethyl) ammonium bromide (BCDMAB) in the presence of isopropanol and catalyst NaOH. The optimal synthesis conditions were determined by batch experiments of single influential factor and orthogonal tests. The characteristics of CT-QE and its property for asenate removal were studied.

MATERIALS AND METHODS

Reagent-grade chemicals were used to prepare all solutions. NanoActive alumina, with the mean aggregate size of 1.5_m and the BET area of 359m2 g−1 was purchased from NanoScale Materials, Inc., Manhattan, KS.

1. Materials

Cotton treated with 5% solution of NaOH for 3 h at 60-65°C, then filtered by suction,

washed with distilled water until neutral reaction and dried at 60°C for 6 h and cut into particles ranging from 100 to 250 mm.

2. Preparation of CT-QE

Batch experiments were conducted using cotton (0.5 g) with 8 ml of 30% solution of NaOH and 120 mL of isopropanol in a 250 ml three-neck round bottom flask at 50–55°C for 0,5 h. Batch amounts (11.9 g) of BCDMAB salt ere added for 30 min and the solutions were stirred for 3,5 h at 50–55°C. The primary product was filtered by suction, then washed with 500 mL of distilled water to remove the residual chemicals, then dried at 60°C for 12 h. The final product was obtained after a second cycle of washing, drying and sieving. It was used in all adsorption experiments [12,15]. Other batch samples were prepared by similar procedure (Table 1).

The synthetic reactions of CT-QE using cotton as a starting material are shown in Scheme 1 (cellulose as example). The reaction between BCDMAB salt and cellulose was induced after the hydroxyl groups in the cellulose molecule activated, producing hydroxy cellulose ether [16].

3. Determination of absorption of AsO_4^{3-}

Weighed 0.1 g. of modified cellulose (CT-QE) and added in 100-mL. conic flask. A volume of 50 mL. of 1000 ppm concentration of AsO_4^{3-} ion was added. The obtained mixture was stirred in 30 minutes and left in 24 hrs. and filtered. Took 2.5 mL. of obtained filtrate and diluted into 100 mL solution. Ion contents were determined using F/AAS method and capacity of absorption (q) was calculated by expression:

$$q = \frac{Co - C}{a} . V$$

where: q – amount of metallic ion absorbed on 1.0 gram of modified cellulose (mg/g); Co – initial concentration of metallic ion (mg/L or ppm); C – concentration of metallic ion on absorption equilibrium (mg/L or ppm); a – amount of modified cellulose (g); V – volume of absorption solution (L) (Table 1).

RESULTS AND DISCUSSION

1. Modifying cotton by BCDMAB salt

Modifying of cotton by BCDMAB salt was effected using reaction activated cellulose (in cotton) (Scheme 1). Structural changes of cellulose, modified with BCDMAB salt were confirmed by IR spectra (Fig. 1). IR spectrum of CT-QE shows absorption characteristic bands at 3466 cm^{-1} (ν_{OH} alcohol), 2924 cm^{-1} ($\nu_{CH\ sat.}$), 1644 cm^{-1} ($\nu_{C=O\ aldehyde}$), 1234 cm^{-1} ($\nu_{COC\ ether}$) and 1056 cm^{-1} ($\nu_{COC\ ether}$).
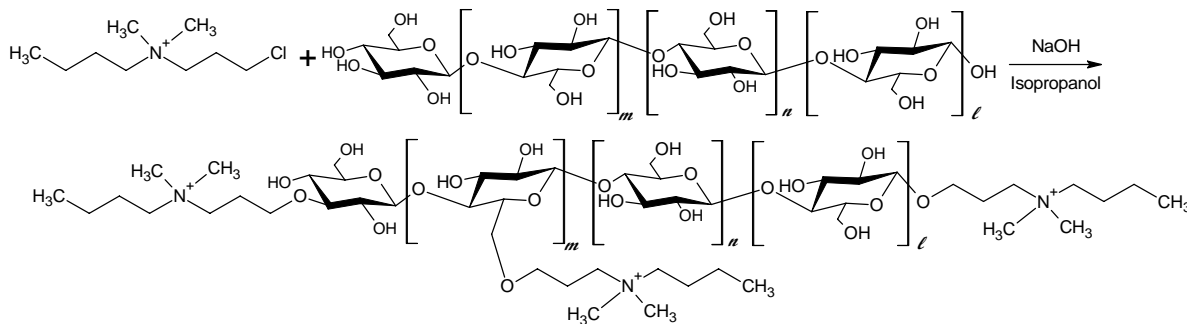
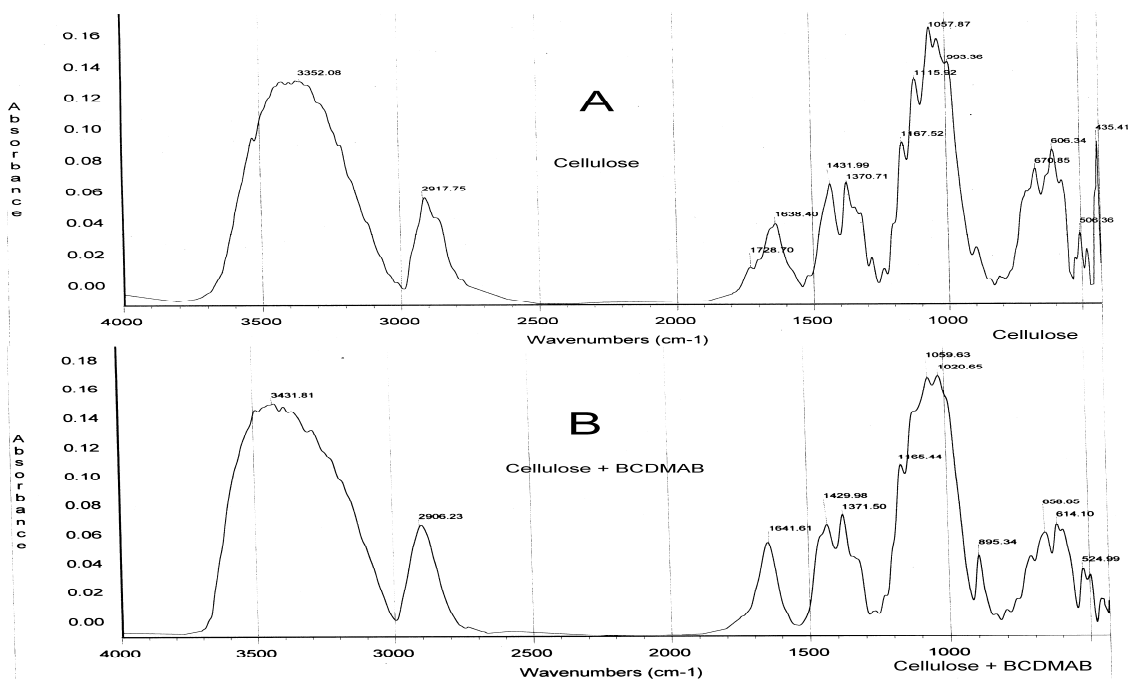**Scheme 1.** Reaction for modifying of cotton by BCDMAB salt.

Figure 1. *IR spectra of initial cotton (A) and CT-QE (B).*

2. Investigation of influence effects on absorption capacity of CT-QE products

Samples of CMC-g-MA/DEA synthesized with ratio CMC-g-MA:DEA=1:10 in reaction time changing from t_{rn}=1.67 h to 5 h. Obtained results indicated that reaction time t_{rn} affected to synthesized copolymer product amounts (m). Amount m changes for t_{rn} and achieved maximum amount with reaction conditions as follows: amount of cotton 2 g, reaction temperature 55°C and reaction time 3.5 h, with *q*= 225.5 mg/g and decreased gradually when reaction time increased (Table 1 and Fig. 2).
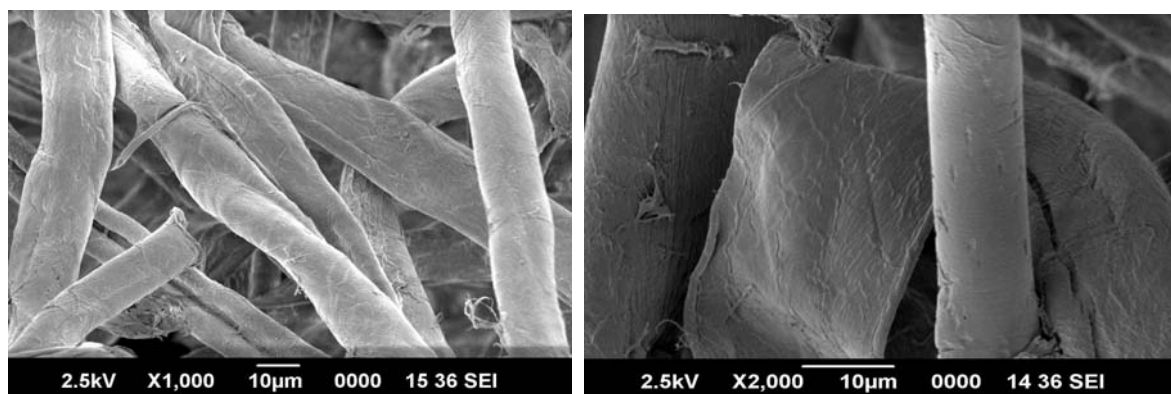
(A)   (B)

Figure 2. *SEM image of initial cotton (A) and CT-QE (B).*

Table 1. Absorption of AsO_4^{3-}ion at 1000 ppm concentration of BCDMAB-modified cotton (amount of cotton - reaction temperature – reaction time)

Entry	q (mg/g)	Entry	q (mg/g)
1, (1g - 40°C - 2h)	174.5	**9**, (3,2g - 55°C - 3.5h)	180.0
2, (3g - 40°C - 2h)	0.0	**10**, (0,8g - 5°C - 3.5h)	222.5
3, (1g - 70°C - 2h)	222.5	**11**, (2g - 73°C - 3.5h)	200.0
4, (3g - 70°C - 2h)	10.0	**12**, (2g - 37°C - 3.5h)	222.5
5, (1g - 40°C - 5h)	180.0	**13**, (2g - 55°C - 5.3h)	154.0
6, (3g - 40°C - 5h)	222.5	**14**, (2g - 55°C - 1.67h)	180.0
7, (1g - 70°C - 5h)	113.0	**15**, (2g - 55°C - 3.5h)	225.0
8, (3g - 70°C - 5h)	72.5		

3. Estimation of absorption capacity of AsO_4^{3-}ion in variable concentrations of CT-QE

The characteristics of CT-QE prepared in the optimal synthesis conditions were evaluated (Table 2 and Fig. 3). It shows that arsenate was significantly absorbed on modified cotton. The more the concentration of arsenate ion was, the more the absorption capacity increased. The relationship between equilibrium absorption capacity q and concentration of initial arsenate ion can be expressed by following regression equation:

$$q=0.112C_o+12.39 \text{ (with } R^2=0.99)$$

Table 2. *Independence of absorption capacity q on concentrations C_o*

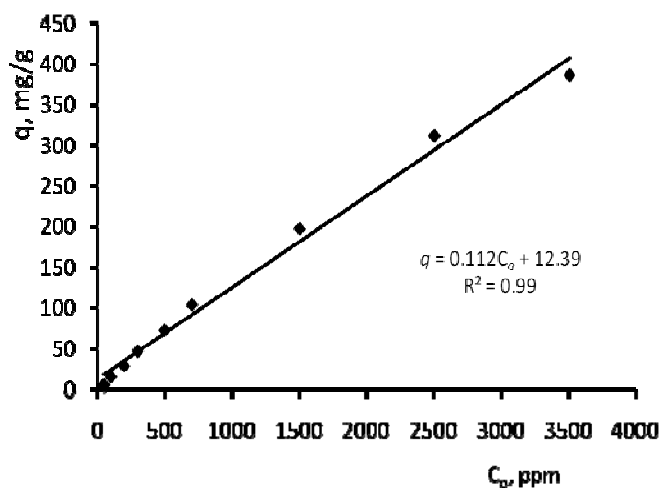| C_o (ppm)	AsO_4^{3-}	
	C (ppm)	q (mg/g)
50	28.662	5.330
100	38.250	15.430
200	86.088	28.478
300	114.750	46.310
500	210.324	72.419
700	286.824	103.294
1500	711.000	197.250
2500	1254.000	311.50
3500	1956.000	386.00

$q = 0.112C_o + 12.39$
$R^2 = 0.99$

Figure 3. *Independence of absorption capacity q on concentrations C_o.*

CONCLUSION

Optimal synthesis conditions for the preparation of CT-QE were determined by single influential factor experiments and orthogonal tests; the catalytic temperature was found to be the key influential factor. The characteristics of CT-QE prepared in the optimal synthesis conditions were evaluated. A large number of amino groups with positive charge were found in the

structure of CT-QE after the IR spectrums analysis.

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