Environment Protection Engineering

Vol. 23 1997 No. 1–2

STEFAN SZTROMAJER*

THE CELLULOSE SKELETON ION EXCHANGERS PREPARED BY MEANS OF ELECTROLYTIC OXIDIZING

The modification of the cellulose skeleton materials allowing us to get the cation exchangers is presented. The modification consists in the electrochemical oxidation which converts the alcohol groups of the cellulose material into the carboxyl ones. The prepared materials acquire cation exchange properties and can be used to remove the heavy metals contained in the polluted water.

The expected advantages of the idea are its simplicity and low cost.

1. INTRODUCTION

The majority of ion exchangers are obtained chemically to get the polymer insoluble in water with the outside ionogen groups. In some cases, the reuse of the cellulose waste materials after some treatment as the ion exchangers seems to be possible.

Ion exchange resins are formed by chemical synthesis which has an adverse effect on the environment.

According to the idea presented, the natural polymer cellulose would replace the synthetic resin. The cellulose skeleton material will get the cation exchange properties after the electrolytic oxidizing.

The suggested way is a part of the general program to search the friendly methods in all branches of the human technical activity.

Obviously, this program is not easy, nor ready to be introduced just in time because of a lot of economical and technical problems; however, the author does believe it is the direction that makes our existence safer.

Nearly all the materials of the cellulose origin are distinguished by the ion exchange property. Probably it was stated for the first time during separation of the deposits by means of filtration through the filter paper. The solution changes its pH value as an effect of the exchange of the cations contained in the solution for the protons from the ionogenic groups.

---

* Chair of Geotechnics and Engineering Structures, Technical University of Łódź, al. Politechniki 6, 90-924 Łódź, Poland.

It is interesting that nearly all technological processes such as bleaching of paper, or the linen, or cotton textiles caused their partial oxidation. As the result an increase in the cation exchange capacity is observed. In particular, it is important when textiles have to be dyed.

An idea of the application of the cellulose skeleton as ion exchanger is not new. KULLGREN [9] measured the trace quantities of copper by means of the sulphite cellulose contained in the distilled (!) water.

According to CRANSTON and THOMPSON [1] the testing of copper contained in milk also by means of the sulphite cellulose was successful.

The cotton treated with the urea phosphate becomes an ion exchanger, while its properties as a textile are not vanished, as it was stated by MUENDEL and SELKE [12]. A textile treated in such a way and shaped as the transmission belt could be applied in the continuous operation, firstly in the separation process, next to the water bath, then to the acid solution, which acts as a regenerating agent, and finally to the first step – ion exchange [2], [3], [14].

According to the investigations presented by KIN [8] and SARNECKI [18] in 1956 and a bit later, in 1967, by MELMS ans SCHWENSON [11], the usefulness of the sulphite cellulose lye as the cation exchanger has been confirmed. In 1937, SZORYGIN and CHAIT [19] confirmed that cellulose is oxidizable by means of the nitrogen dioxide.

When the nitrogen dioxide is applied cautiously the treated paper still maintains its structure, while the strong oxidation leads to the water-soluble product [6], [7], [10], [13], [14], [15], [16].

According to IVANOV and LENSZINA [4], [5] the paper treated by means of the water solution of sodium chlorate, sodium iodate or the diluted nitric acid acquires the exchange capacity of ca. 2.80 mVal/g. (Such a value seems to be very high, taking account of the fact that in this case a half of all alcohol groups ($-CH_2OH$) can be converted to the carboxyl ones ($-COOH$) and such a product is soluble in water).

According to SAMUELSON and WENNERBLOM [17] as well as SIHTOLA [20] partly oxidized cellulose is insoluble in water when the content of carboxyl groups amounts to 2–3%.

According to the idea presented the wastes containing the cellulose skeleton after electrolytical treating can be applied as the cation exchangers to remove heavy metals from polluted water.

After the exchanger has been exhausted, it can be ashed and the metals recovered electrolytically. The main advantage of the method lies in the fact that no chemical reagents are discharged into the environment.

2. EXPERIMENTAL PART

In order to standardize the search, the cotton textile, denim, was chosen as the model cellulose skeleton material.

The several electrolytic baths were applied: 0.5 M water solutions of the sodium sulphate [21], sodium chloride, potassium iodide and potassium nitrate.

The electrochemical reactor, i.e., the cylindrical glass vessel, is divided into two parts by the barrel-shaped separator (figure 1). In the central part, the positively charged electrode, anode, is located, while the negatively charged electrodes, cathodes, are concentrically distributed on the other side of the separator (figure 2).

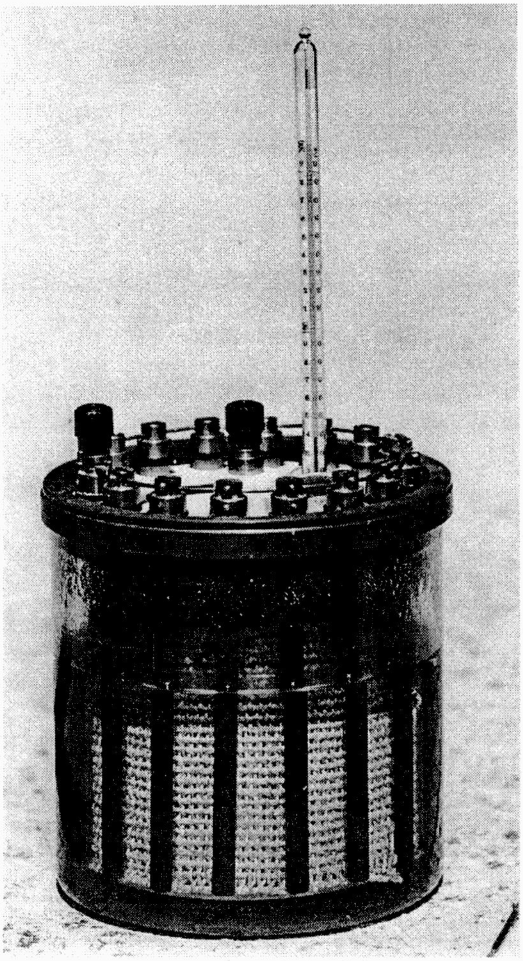

Fig. 1. Electrochemical reactor

The anode is made of the platinum, cylindrically shaped grid with the frame inside. The cathodes are made of the graphite rods (figure 3). The feeding rectifier is supplied indirectly from mains by the transformer, which allows us to control the current and thus to get its value as close to 5 A as possible.

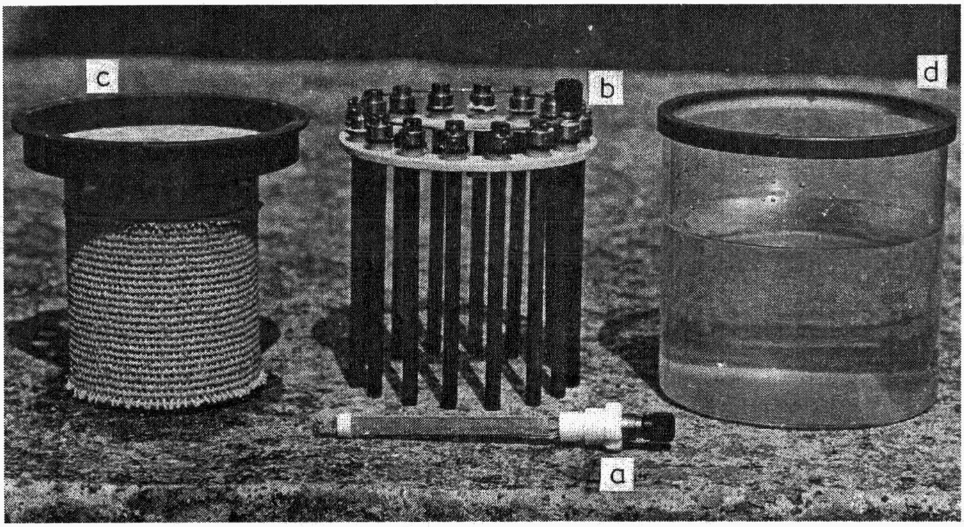

Fig. 2. Electrochemical reactor
a – anode, *b* – cathodes, *c* – separator, *d* – glass vessel

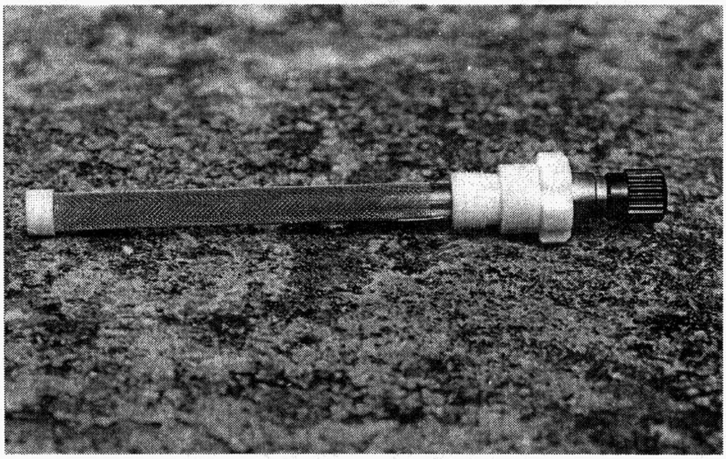

Fig. 3. Anode

The material prepared, i.e. denim, was directly wrapped around the anode to get the most efficient oxidizing effect.

The oxidizing process. Considering the formal balance of the anode oxidation in all water solutions, the reactions run as follows

$$H_2O \rightarrow H^+ + OH^-, \qquad (1)$$

$$2\,OH^- - 2e \rightarrow H_2O + O\,, \tag{2}$$

$$H^+ + H_2O \rightarrow H_3O^+\,. \tag{3}$$

The H_3O^+ ion travels to cathode and then electron is accepted:

$$H_3O^+ + e \rightarrow H_2O + H\,, \tag{4}$$

$$2\,H \rightarrow H_2\,. \tag{4a}$$

The only waste product, i.e. hydrogen, is liberated in the cathode area.

The oxygen liberated *in statu nascendi* on anode acts as strong oxidiser, hence the alcohol group reacts as follows:

$$-CH_2OH + 2\,O \rightarrow -COOH + H_2O\,. \tag{5}$$

This is the main reaction, the generation of the aldehyde group and partial depolimerisation of the cellulose skeleton were also observed.

The last reaction consists in breaking off the oxygen bonds between the elements of the chain of cellulose skeleton.

Probably the oxidation process is much more complex; it depends on the composition of the electrolyte. Supposedly some sort of catalysis takes place.

The baths after the salts' dissolution were neutral, but just after supply of electrochemical reactors, in the anode area the basic reaction was observed. It is obvious as the OH^- ions flow towards anode. (To be precise after 30 min of the whole bath processing on both sides of the separator there was an alkaline majority of the H_3O^+ ions which after discharging liberated a vessel as elementary hydrogen).

In the sodium chloride bath, oxidation of the cellulose was fast, but serious problem with the chlorine was observed.

The reactions probably proceeded as follows:

$$NaCl \rightarrow Na^+ + Cl^-\,, \tag{6}$$

$$2\,Cl^- - 2e \rightarrow Cl_2\,, \tag{7}$$

$$Cl_2 + 2\,OH^- \rightarrow Cl^- + ClO^- + H_2O\,, \tag{8}$$

$$-CH_2OH + 2\,ClO \rightarrow -COOH + H_2O + 2\,Cl^-\,, \qquad (9) \rightarrow (6)$$

$$ClO^- - e \rightarrow \frac{1}{2}Cl_2 + O\,, \qquad (10) \rightarrow (8)$$

$$-CH_2OH + 2\,O \rightarrow -COOH + H_2O\,, \tag{11}$$

$$2\,OH^- - 2e \rightarrow H_2O + O\,, \qquad (12) \rightarrow (11)$$

$$H_2O + O \rightarrow H_2O_2\,, \tag{13}$$

$$2\,H_2O_2 + -CH_2OH \rightarrow 3\,H_2O + -COOH\,, \tag{14}$$

in the cathode area

$$Na^+ + e \rightarrow Na, \tag{15}$$

$$2\,Na + H_2O \rightarrow 2\,NaOH + H_2, \tag{16}$$

$$NaOH \rightarrow Na^+ + OH^-, \qquad (17) \rightarrow (8) \rightarrow (12)$$

$$2\,H_3O^+ + 2e \rightarrow 2\,H_2O + H_2, \tag{18}$$

$$Na^+ + e \rightarrow Na. \tag{19}$$

Considering oxidation of the cellulose material we can state that the process is positive, but unfortunately the reaction (8) is not fast enough to allow absorption of all the chlorine liberated in the anode area (7). Therefore its excess can be considered as a serious pollutant. That is why such a way seems to be unprofitable.

The process in the potassium iodide bath is probably similar to the previous one.

$$KJ \rightarrow K^+ + J^-, \tag{20}$$

$$2\,J^- - 2e \rightarrow J_2, \tag{21}$$

$$J_2 + 2\,OH^- \rightarrow J^- + JO^- + H_2O, \tag{22}$$

$$-CH_2OH + 2\,JO^- \rightarrow -COOH + H_2O + 2\,J^-, \tag{23}$$

$$JO^- - e \rightarrow \frac{1}{2}J_2 + O, \tag{24}$$

$$J_2 + J^- \rightarrow J_3^-, \tag{25}$$

$$2\,J_3^- - 2e \rightarrow 3\,J_2, \tag{26}$$

$$-CH_2OH + 2\,O \rightarrow -COOH + H_2O, \tag{27}$$

$$2\,OH^- - 2e \rightarrow H_2O + O, \tag{28}$$

$$H_2O + O \rightarrow H_2O_2, \tag{29}$$

$$2\,H_2O_2 + -CH_2OH \rightarrow 3\,H_2O + -COOH, \tag{30}$$

in the cathode area

$$K^+ + e \rightarrow K, \tag{31}$$

$$2\,K + 2\,H_2O \rightarrow 2\,KOH + H_2, \tag{32}$$

$$KOH \rightarrow K^+ + OH^-. \qquad (33) \rightarrow (22) \rightarrow (28) \rightarrow (31)$$

As it was mentioned, the reactions are similar to those with sodium chloride. The essential difference consists in the liberation of the elementary iodide which does not escape from the reactor. The majority of the elementary iodide reacts with the OH^- ions (22), part of it reacts with the J^- ions (25) and the rest precipitates as a deposit. When the reactor is switched off, the elementary iodide still acts as an oxidizer until the iodide is reduced. In some cases, such an effect can be profitable.

When the material was treated in the potassium nitrate bath, no troubles arose. The reaction probably proceeded as follows:

$$KNO_3 \rightarrow K^+ + NO_3^-, \tag{34}$$

$$NO_3^- - e \rightarrow NO_2 + O, \tag{35}$$

$$-CH_2OH + 2O \rightarrow -COOH + H_2O, \tag{36}$$

$$2NO_2 \rightarrow N_2O_4, \tag{37}$$

$$N_2O_4 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O, \qquad (38) \rightarrow (35)$$

$$2NO_2^- - e \rightarrow NO_2, \qquad (39) \rightarrow (37)$$

$$2OH^- - 2e \rightarrow H_2O + O, \qquad (40) \rightarrow (36)$$

$$H_2O + O \rightarrow H_2O_2, \tag{41}$$

$$-CH_2OH + 2H_2O_2 \rightarrow -COOH + 3H_2O, \tag{42}$$

in the cathode area

$$K^+ + e \rightarrow K, \tag{43}$$

$$K_2 + 2H_2O \rightarrow 2KOH + H_2, \tag{44}$$

$$KOH \rightarrow K^+ + OH^-. \qquad (45) \rightarrow (35) \rightarrow (40) \rightarrow (43)$$

In the tests, 0.5 M solutions of the sodium chloride, potassium iodide and potassium nitrate were applied.

In the anode area, pH value was equal to 10–11 independently of the bath composition when the current of 2.5 A was switched on; the voltage had to be changed in the range of 7–12 V to maintain the current desired (the increase of the bath temperature caused the decrease of the resistance).

There were no troubles with maintaining the constant current when sodium chloride and potassium nitrate were used as the baths, but potassium iodide caused some difficulties. In this case, the liberated elementary iodine insulated partially anode, so the current decreased to ca 1–1.5 A. This phenomenon is similar to that observed when the chloride bath was applied: liberation of the elementary iodide (21) is faster than its ability to react with OH^- ions (22) and the parallel reaction of generating the J_3^- ion (25).

3. RESULTS AND DISCUSSION

The cotton textile after electrolytical oxidation became the cation exchanger. Its exchange capacity ranged from 0.38 to 0.44 mVal/g.

The theoretical exchange capacity of the cellulose amounts to 5.68 mVal/g, provided that all primary alcohol groups will be converted into carboxylic ones. Comparing this theoretical value to that achieved, which ranges from 0.38 to 0.44 mVal/g, we can establish that only about 6.7–7.7% of the alcohol groups are oxidized to the carboxylic ones.

It is possible to get higher exchange capacity, even exceeding 1 mVal/g, but in this case the structure of the textile will be destroyed, getting the gel structure.

Obviously such materials are not appropriate for our particular purposes. The treated textiles are less resistant compared to untreated.

The samples, shaped as belts of 30 mm width by means of a tensile tester, were tested. The tensile strength before treating was equal to ca. 533 N (177.7 N/cm), while the prepared textile was much less resistant: after processing its strength approaching 75–86 N (25–28.7 N/cm) was obtained.

As a matter of fact the presented process is very similar to the "classic chemical" one, when the water solutions of the sodium chlorate, sodium iodate, nitric acid [4], [5] or the nitrogen dioxide were applied [19].

The investigations confirm the SIHTOLA's [20] conclusion that the maximum content of the carboxyl groups introduced into the linear cellulose polymer is kept until the product is soluble in water (2–3% per weight, which is equal to ca. 7.7–11% of the oxidized alcohol groups).

It seems to be interesting to compare the fibres of the cellulose textile before and after processing under the scanning microscope (figures 4 and 5).

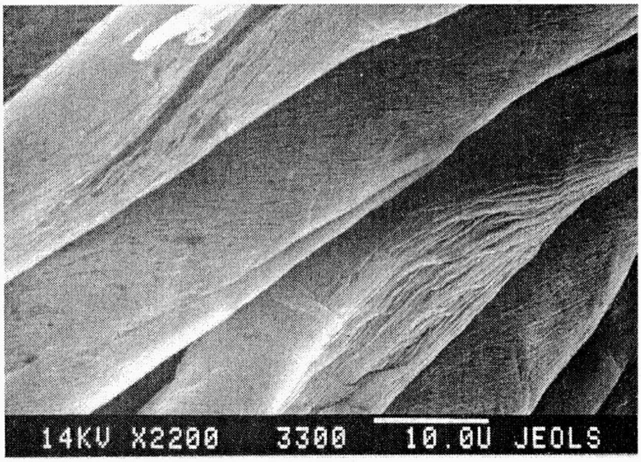

Fig. 4. Fibre before processing

The processed material is partly destroyed, so the value of its tensile strength is less than that of unprocessed one.

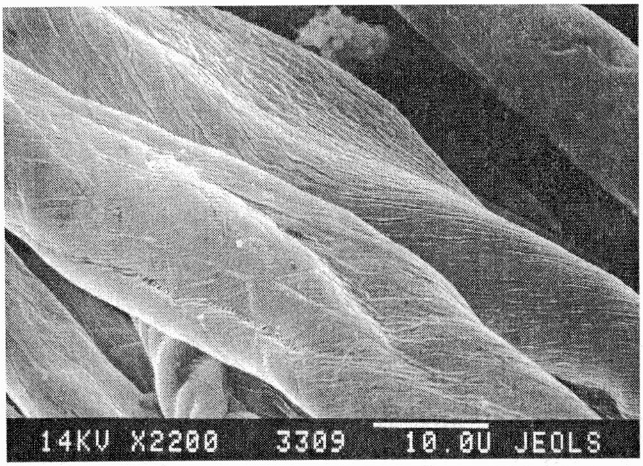

Fig. 5. Fibre after processing

It should be pointed out that some part of processed cellulose material owing to its depolymerisation becomes soluble in water. According to the content of the carbon compounds soluble in the electrolytical baths after the processing has been finished, about 9–15% of the cellulose was solved.

4. CONCLUSIONS

Our investigations confirmed the possibility of obtaining the cation exchangers by means of the electrolytical treating the cellulose materials. Comparing the exchange capacities of some commercial carboxyl-type exchangers [22] the results seem to be rather modest. However, the main idea of our investigations is to use the raw material and in such a way some waste products will be used. The advantages of the process described lie in the fact that no discharge of any substances, except hydrogen, into the environment takes place.

The cost of the device presented is substantially reduced if the platinum anode will be replaced by the platinum plated, graphite one.

REFERENCES

[1] Cranston H.A., Thompson H.A., Ing. Eng. Chem. Anal., 1946, **18**, 323.
[2] Guthric J.D., Ind. Eng. Chem., 1952, **44**, 2187.
[3] Hoffpair C.L., Guthric J.D., C. A., 1950, 11140.
[4] Ivanov V., Lenszina N., C. A., 1956, 12467.
[5] Ivanov V., Lenszina N., Ivanova V.S., C. A., 1957, 7801.
[6] Jackel J., Kenyon R.Z., J. Am. Soc., 1942, **64**, 121.

[7] KENYON R.Z., HASEK R.H., Ind. Eng. Chem., 1949, **41**, 2–8.
[8] KIN Z., Prace I.C.P., 1950, **4**, 40.
[9] KULLGREN C., Svensk Kem. Tid., 1931, **43**, 99.
[10] MC GEE P.A., SMITH J.Z., J. Am. Chem. Soc., 1947, **69**, 355.
[11] MELMS F. SCHWENSON, *Verwertunggebiete für Sulfitablauge*, Leipzig, 1967.
[12] MUENDEL C.H., SELKE W.A., C. A., 1955, 9330.
[13] PAYENS Th.A., C. A., 1956, 9101.
[14] REEVES W.A., GUTHRIC J.D., Text. Res. J., 1953, **23**, 522.
[15] ROGOVIN Z.A., TREJWAS M.G., SZORYGINA N.N., Zurn. Prakt. Chim., 1949, **22**, 1214.
[16] ROGOVIN Z.A., KONDRASZCZUK L., MALACHOV P.A., Zurn. Prakt. Chim., 1950, **23**, 418.
[17] SAMUELSON O., WENNERBLOM A., Svensk Papperstidn, 1995, 58.
[18] SARNECKI K., Przegląd Papiern., 1956, **12**, 345.
[19] SZORYGIN P.P., CHAIT E.W., Zurn Obszcz. Chim., 1937, **7**, 188.
[20] SITHOLA H., C. A., 1957, 15941.
[21] SZTROMAJER S., Green'93, *The preparation of the cellulose skeleton ion exchangers*, Balkema, Rotterdam/Brookfield, 1995.
[22] WINNICKI T., *Polimery czynne w inżynierii ochrony środowiska*, Arkady, 1978.

WYMIENIACZE JONOWE Z CELULOZOWYM SZKIELETEM OTRZYMANE W WYNIKU UTLENIANIA ELEKTROLITYCZNEGO

Opisano modyfikację materiałów ze szkieletem celulozowym, co pozwala otrzymać wymieniacze jonowe. Modyfikacja ta polega na elektrochemicznym utlenieniu, dzięki któremu grupy alkoholowe celulozy przechodzą w karboksylowe. Otrzymany w ten sposób materiał na właściwości kationitu i może być używany do usuwania metali ciężkich ze skażonych wód.

Prostota i mały koszt opisanej metody są jej głównymi zaletami.