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# COMMUNICATION

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# UREA SORPTION ON CATION-EXCHANGE BED

#### 1. INTRODUCTION

Discharge of urea into the receiving surface waters is limited due to the fact that an excessive concentration of this substance leads to serious disturbances in hydrobiological processes occurring in water. Hence the urea removal from wastewater is indispensable.

The earliest known methods of urea removal are the biological ones which consist in its biodegradation or assimilation by the appropriate microorganisms. The chief shortcoming of biological methods is their sensitivity to changes in wastewater composition and temperature variations.

There is also a method of urea degradation by its hydrolysis to ammonia and carbon dioxide in elevated temperature and under higher pressure. This process is, however, energy-consumptive and requires the construction of special reactors.

The methods mentioned above allow to achieve the main goal, i.e. the environment protection, since they result in the removal of undesirable urea from wastewater. Considering, however, the fact that the natural resources are constantly depleting, the technologies allowing the recovery of pollutants contained in wastewater should be preferred.

So far a partial utilization of urea is possible with biological methods of assimilation (e.g. culture of algae). Biomass produced in this process may be used as a fodder for fish. Hydrolytic method allows to recover ammonia which is the product of urea degradation. Thus, in both the cases the products are much less valuable than urea.

The most desired process is recirculation of the urea concentrate to technological processes, since then the fully valuable material is recovered. Thus, it is advisable to look for the methods allowing the separation of urea from wastewaters and its concentration.

The present work is aimed at determination of the sorption ability of a cation-exchanger with respect to the urea contained in wastewaters.

#### 2. EXPERIMENTAL

Laboratory-scale investigations have been performed under dynamic conditions, using as an absorbent the cation-exchanger Wofatit KPS (produced in G.D.R.) in its standard hydrogene form. Synthetic waste-water prepared for investigations contained 50, 100, 250, 500, 1000, 1500, 2000, and 2500 mg of urea/dm<sup>3</sup>.

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The measurements were taken at  $20^{\circ}$ C,  $40^{\circ}$ C,  $60^{\circ}$ C, and  $80^{\circ}$ C for each of the above specified concentrations. The wastewaters were pumped through the cation-exchange beds at the velocity of 6.35 m/h. The set of apparatus used for investigations shown in fig. 1 consists of: ultrathermostate, peristaltic pump and thermostated glass column. Wastewater solution was pumped from the flask placed in the thermostate,



Fig. 1. Scheme of laboratory setup I – column with ion-exchange bed, 2 – water mantle of the column, 3 – glass spiral, 4 – ultrathermostate, 5 – flask with urea solution, 6 – peristaltic pump, 7 – receiver

Rys. 1. Schemat laboratoryjnego zestawu badawczego

1 – kolumna ze złożem jonitowym, 2 – płaszcz wodny kolumny, 3 – spirala szklana, 4 – ultratermostat, 5 – butelka z roztworem mocznika, 6 – pompa perystaltyczna, 7 – odbieralnik

through a glass spiral (also placed in the thermostate) to the column filled with a cation-exchanger. Prior to each experiment the whole system was thermostated for 2 h. This time was sufficiently long to achieve the required temperature. The effluent from the column was collected in form of fractions of the volume of 50 cm<sup>3</sup>, 100 cm<sup>3</sup> or 200 cm<sup>3</sup>, depending on the initial concentration of urea.

The column used for investigations had the following dimensions: the cross-section area equalled  $3.01 \text{ cm}^2$  and the height was 90 cm (bed height was 60 cm and its volume  $-0.181 \text{ dm}^3$ ). The concentration of urea in the fraction collected was analysed according to the following procedure:  $0.2 \text{ cm}^3$  to  $10 \text{ cm}^3$  of the effluent was poured into a measuring flask, adding 1 cm<sup>3</sup> of a solution of urease stabilized with the pH 7 buffer EDTA-NaOH. The sample was heated at  $36^{\circ}$ C for 12 h to cause a total hydrolysis of urea by urease, according to reaction

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$
.

The quantity of ammonia produced was determined by the standard colorimetric method, using the Nessler reagent.

#### 3. RESULTS AND DISCUSSION

Urea sorption on cation-exchange bed from the wastewaters of the urea concentrations of 50 mg/dm<sup>3</sup> and 2500 mg/dm<sup>3</sup> is illustrated in figs. 2 and 3, respectively. From the data presented it follows that with the increasing temperature the amount of urea absorbed decreases and the breakthrough curves become more and more sharp (vertical) which means that at higher temperature the time required to achieve the equilibrium is shorter. In general, the height of working zone decreases with the increasing temperature and urea concentration in wastewaters.

Urea sorption on cation-exchange bed



Fig. 2. Characteristics of breakthrough curves for urea sorption on cation-exchanger Wofatit KPS at various temperatures; initial concentration of urea equal to 50 mg/dm<sup>3</sup>
Rys. 2. Charakterystyka krzywych przebicia sorpcji mocznika na złożu kationitowym Wofatit KPS o stężeniu wyjściowym 50 mg CO(NH<sub>2</sub>)<sub>2</sub>/dm<sup>3</sup> w różnych temperaturach



Fig. 3. Characteristics of breakthrough for urea sorption on the cation-exchanger Wofatit KPS at various temperatures; initial concentration of urea equal to 2500 mg/dm<sup>3</sup>

Rys. 3. Charakterystyka krzywych przebicia sorpcji mocznika na złożu kationitowym Wofatit KPS o stężeniu wyjściowym 2500 mg CO(NH<sub>2</sub>)<sub>2</sub>/dm<sup>3</sup> w różnych temperaturach

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The effect of temperature on the sorption capacity of breakthrough  $q_B$  and on the maximal sorption capacity  $q_M$  is quantitatively illustrated in figs. 4 and 5, respectively. From the data presented it follows that the temperature affects significantly the sorption capacities which decrease with its increase. Owing to such a correlation a thermal regeneration of the ion-exchanger is possible. In such a regeneration sorption capacity is equal to the difference in sorption capacities for 20°C and 80°C.



Fig. 4. The effect of temperature on sorption capacity of cation-exchanger Wofatit KPS breakthrough

concentration of urea in wastewater:  $I = 50 \text{ mg/dm}^3$ ,  $2 = 100 \text{ mg/dm}^3$ ,  $3 = 250 \text{ mg/dm}^3$ ,  $4 = 500 \text{ mg/dm}^3$ ,  $5 = 1000 \text{ mg/dm}^3$ ,  $6 = 1500 \text{ mg/dm}^3$ ,  $7 = 2000 \text{ mg/dm}^3$ ,  $8 = 2500 \text{ mg/dm}^3$ 

Rys. 4. Wpływ temperatury na pojemność sorpcyjną przebicia kationu Wofatit KPS stężenie mocznika w ściekach:  $1 - 50 \text{ mg/dm}^3$ ,  $2 - 100 \text{ mg/dm}^3$ ,  $3 - 250 \text{ mg/dm}^3$ ,  $4 - 500 \text{ mg/dm}^3$ ,  $5 - 1000 \text{ mg/dm}^3$ ,  $6 - 1500 \text{ mg/dm}^3$ ,  $7 - 2000 \text{ mg/dm}^3$ ,  $8 - 2500 \text{ mg/dm}^3$ 



Fig. 5. Effect of temperature on the maximal sorption capacity of cation-exchanger Wofatit KPS

concentration of urea in wastewaters: *I* - 50 mg/dm<sup>3</sup>, *2* - 100 mg/dm<sup>3</sup>, *3* - 250 mg/dm<sup>3</sup>, *4* - 500 mg/dm<sup>3</sup>, *5* - 1000 mg/dm<sup>3</sup>, *6* - 1500 mg/dm<sup>3</sup>, *7* - 2000 mg/dm<sup>3</sup>, *8* - 2500 mg/dm<sup>3</sup>

Rys. 5. Wpływ temperatury na maksymalną pojemność sorpcyjną kationitu Wofatit KPS stężenie mocznika w ściekach:  $1 - 50 \text{ mg/dm}^3$ ,  $2 - 100 \text{ mg/dm}^3$ ,  $3 - 250 \text{ mg/dm}^3$ ,  $4 - 500 \text{ mg/dm}^3$ ,  $5 - 1000 \text{ mg/dm}^3$ ,  $6 - 1500 \text{ mg/dm}^3$ ,  $7 - 2000 \text{ mg/dm}^3$ ,  $8 - 2500 \text{ mg/dm}^3$  Sorption capacity resulting from the partial desorption of urea occurring at elevated temperature allows the sorption of urea at lower temperature and regeneration of the ion-exchanger at elevated temperature. A certain sorption capacity displayed in this process by the ion-exchanger is defined as thermal sorption capacity  $q^T$ .

The values of thermal sorption capacities of breakthrough  $q_B^T$  and those of the maximal thermal sorption capacities  $q_M^T$  are listed in table. It can be seen that the thermal sorption capacities increase with the urea concentration in the solution from which it is being removed, but the values of those capacities are rather small, since the maximal sorption capacity obtained by us amounted to 7.3 mg of urea per 1 dm<sup>3</sup> of the cation-exchanger.

Table



Thermal sorption capacities of cation-exchanger Wofatit KPS as a function of urea concentration Zestawienie termicznych pojemności sorpcyjnych dla kationitu Wofatit KPS uzyskanych przy różnicach temperatur między 20°C i 80°C w funkcji stężenia



Urea sorption on cation-exchange bed

The increase in sorption capacity with the increasing concentrations of urea in treated wastewater (fig. 6) does not improve significantly the efficiency of the process, since the amount of wastewater treated on one volume of ion-exchange bed remains constant and in all the cases is equal to several (below 7) bed volumes.

## 4. SUMMARY

The performed investigations of urea sorption on the cation-exchange bed have shown that this method of wastewater treatment is theoretically possible. It has also been shown that the differences in sorption capacities for  $80^{\circ}$ C and  $20^{\circ}$ C exist. Although they do not exceed the value of 7.3 g CO(NH<sub>2</sub>)<sub>2</sub>/dm<sup>3</sup> of cation-exchanger, the thermal regeneration of cation-exchange bed is possible. However, the efficiency of this process is too low to recommend it at its present state for an industrial application.