

ANNALES  
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA  
LUBLIN — POLONIA

VOL. XXXV, 11

SECTIO AA

1980

Instytut Chemii UMCS  
Zakład Technologii Chemicznej

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**Urea Decomposition by Nitrites**

Rozkład mocznika za pomocą azotynów

Разложение мочевины при помощи нитритов

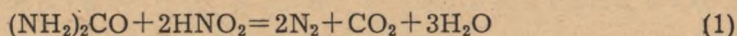
INTRODUCTION

Large amounts of wastewater from nitrogen industry constitute a substantial hazard for local surface water. Therefore, many attempts have been undertaken to eliminate nitrogen compounds from this wastewater. The best developed methods are biological ones consisting either in decomposition of these compounds or their assimilation by microorganisms. A great sensitivity of microorganisms to environmental conditions (concentration, *pH*, temperature, content of other pollutants) results in disturbances of their purification activity. Therefore, studies on finding physicochemical methods are of great concern, which from technological point of view are easier and stable in industrial practice. Among them, ion exchange methods for recovering of water and chemicals (ammonia and nitrates) which have been developed are simple and economical [1—5].

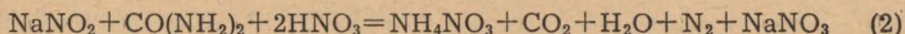
Although a method of decomposition of urea by its hydrolysis at a high temperature and under increased pressure has been developed, it is, however, economically not attractive because of a high use of energy. Thus there arises the need to find other methods of urea decomposition in wastewater.

The starting point of the studies is analytical reaction of urea determination [6], the principle of which is urea decomposition according to the reaction:





There is also known the method of neutralization of nitrogen oxides by their sorption in NaOH, followed by acidification of the solution and with added urea. In such a medium the following reaction takes place [7]:



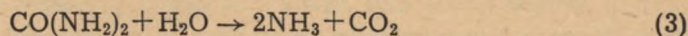
The above information point to the possibility of implementing these reaction to remove urea from wastewaters, which justifies further studies on the reaction of urea with nitrites.

## EXPERIMENTAL

### Studies on the effect of acidity

A mixture of urea with sodium nitrite at a stoichiometric ratio according to reaction (2) was prepared. Then nitric acid in an appropriate amount was added and the mixture was intensively mixed during the measurement (temperature 20°C). Solution samples of 1 cm<sup>3</sup> to 10 cm<sup>3</sup> (in relation to the urea content in the initial solution) were collected and then each sample was neutralized with NaOH. Next, demineralized water was added, reaching a volume of 50 cm<sup>3</sup>. On mixing it a 10 cm<sup>3</sup> sample was taken for determination of N<sub>NH<sub>3</sub></sub>, and a 5 cm<sup>3</sup> sample for determination of N<sub>(NH<sub>2</sub>)<sub>2</sub>CO</sub>. The content of N<sub>NH<sub>3</sub></sub> was determined by the colorimetric method with Nessler's reagent [8], whereas the content of N<sub>(NH<sub>2</sub>)<sub>2</sub>CO</sub> was analysed according to the following procedure.

A sample of solution was taken in a 50 cm<sup>3</sup> volumetric flask, and 1 cm<sup>3</sup> solution of urease stabilized with buffer solution of NaOH-EDTA of pH 7. Next, the sample was kept at 36°C for 12 hours, when the whole amount of urea hydrolysed according to the reaction:



Then, the content of N<sub>NH<sub>3</sub></sub> was determined by the colorimetric method with Nessler's reagent. The amount of ammonia formed from urea is the difference between total content of ammonia determined after hydrolysis of urea, and that formed in reaction between urea and nitrite.



## Influence of temperature

The solution containing stoichiometric (according to reaction 2) mixture of urea and sodium nitrite was acidified with  $\text{HNO}_3$  using its stoichiometric amount in the first series and 100% of its excess in the second series of investigations (according to reaction 2). Next, the solution was transferred to a flask and put in a thermostat with set up suitable temperature, where the solution was stirred. The solution samples from  $1 \text{ cm}^3$  to  $10 \text{ cm}^3$  (depending on urea content) were collected in a  $50 \text{ cm}^3$  volumetric flask, where they were immediately neutralized by  $\text{NaOH}$  and made up to the mark with demineralized water. From such prepared solution  $10 \text{ cm}^3$  samples were collected for determination of ammonia content and  $5 \text{ cm}^3$  samples for determination of urea. The analysis was done according to the procedure described in 2.1.

## RESULTS AND DISCUSSION

It was found that acidity greatly affects the reaction between urea and nitrite which is illustrated in Fig. 1. One can see that the increase in the concentration of nitric acid significantly intensified the course of this reaction, the influence being particularly visible at a low concentration of urea. However, when the concentration of urea increases the intensity of the reaction also increases even at a low concentration of nitric acid (see Fig. 2).

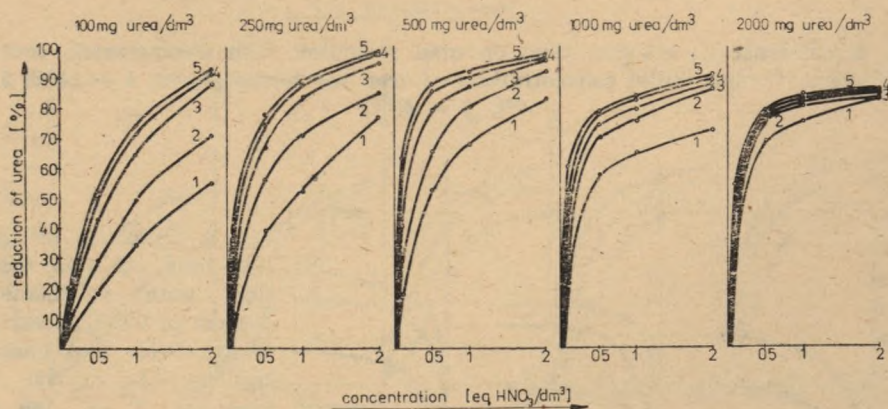


Fig. 1. Influence of acidity on urea reduction at its various initial concentrations and time of reaction (temperature  $20^\circ\text{C}$ ); 1 — for time of reaction: 0,5 h, 2 — 1 h, 3 — 2 h, 4 — 3 h, 5 — 5 h



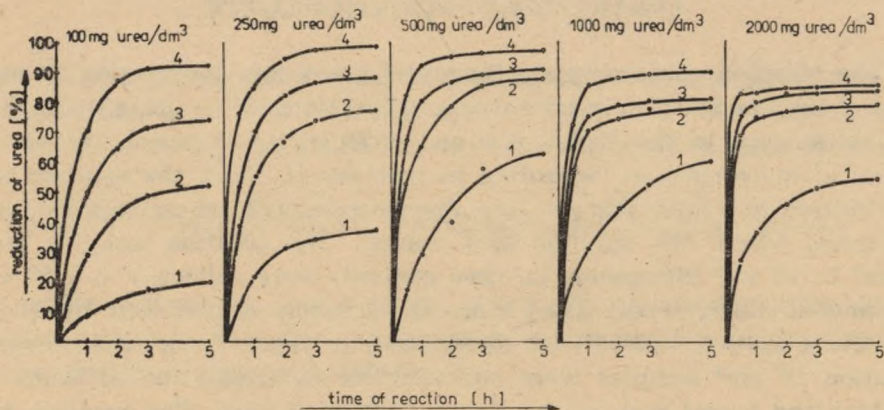


Fig. 2. Influence of reaction time on urea reduction at its various initial concentrations and acidity of environment (temperature 20°C); 1 — for HNO<sub>3</sub> concentrations 0,1 eq HNO<sub>3</sub>/dm<sup>3</sup>, 2 — 0,5 eq HNO<sub>3</sub>/dm<sup>3</sup>, 3 — 1 eq HNO<sub>3</sub>/dm<sup>3</sup>, 4 — 2 eq HNO<sub>3</sub>/dm<sup>3</sup>

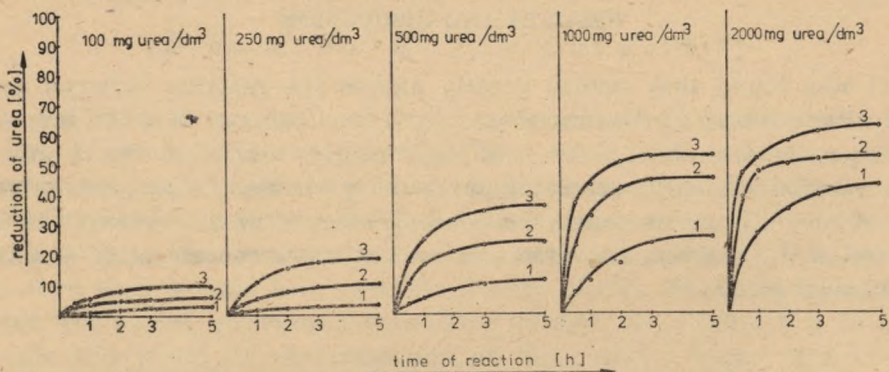


Fig. 3. Influence of reaction time on urea reduction with stochiometric content of HNO<sub>3</sub> at various initial concentrations of urea and temperatures; 1 — 20°C, 2 — 40°C, 3 — 60°C

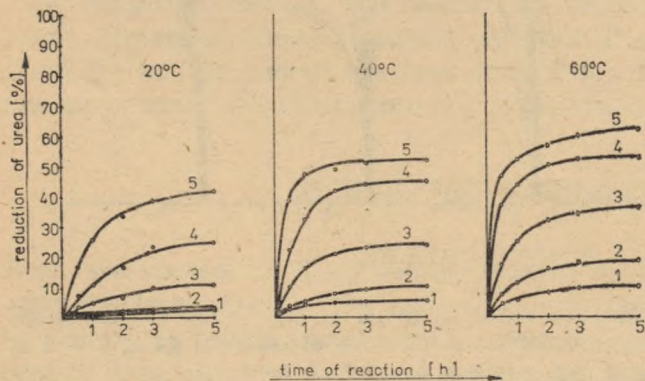


Fig. 4. Influence of reaction time on urea reduction with stochiometric content of HNO<sub>3</sub> at various temperatures and concentration; 1 — 100 mg urea/dm<sup>3</sup>, 2 — 250 mg urea/dm<sup>3</sup>, 3 — 500 mg urea/dm<sup>3</sup>, 4 — 1000 mg urea/dm<sup>3</sup>, 5 — 2000 mg urea/dm<sup>3</sup>

The influence of time of the reaction on the reduction of urea at temperatures: 20°C, 40°C and 60°C, and at the following concentrations of urea: 100; 250; 500; 1000 and 2000 mg/dm<sup>3</sup> with a stoichiometric (according to reaction 2) content of nitric acid is illustrated in Figs. 3 and 4. It can be seen that the rise in temperature by 20°C increases the reduction of urea by about 10%. At a higher concentration of urea its reduction is more efficient (see Fig. 5). Also an increase in the content of nitric acid increases the reduction of urea (compare Figs. 5 and 6).

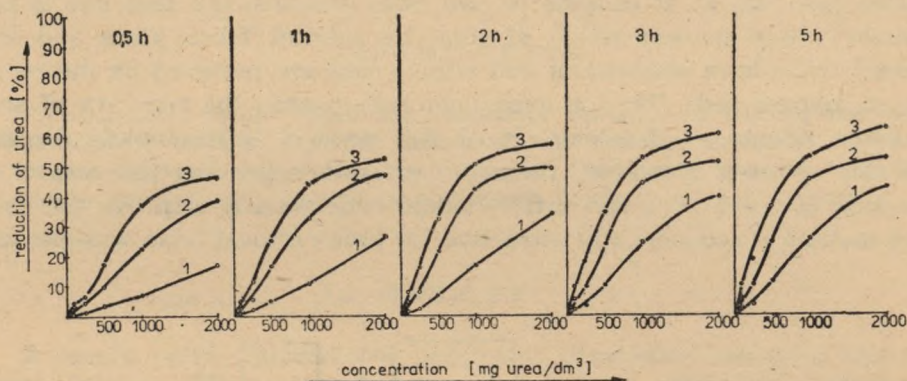


Fig. 5. Influence of initial concentration of urea on its reduction with stoichiometric content of  $\text{HNO}_3$  at various reaction times and temperatures; 1 — 20°C, 2 — 40°C, 3 — 60°C

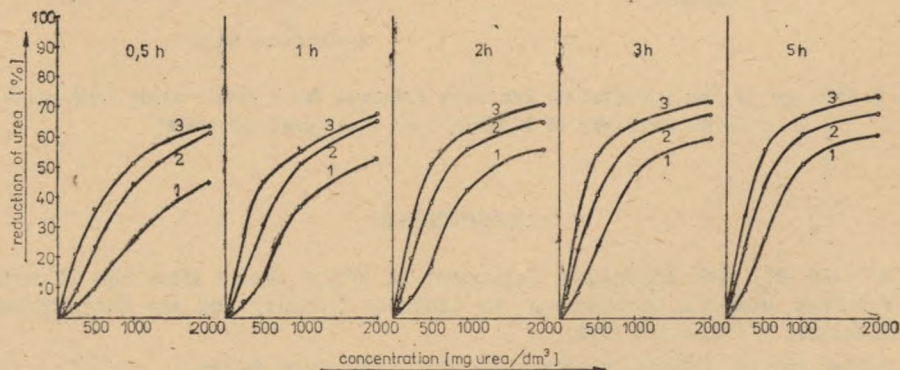


Fig. 6. Influence of initial concentrations of urea on its reduction with 200% stoichiometric content of  $\text{HNO}_3$  at various reaction times and temperatures; 1 — 20°C, 2 — 40°C, 3 — 60°C



## SUMMARY

The data obtained confirm that nitrites in acid media decompose urea and this reaction may constitute the basis for the technical process of urea removal from wastewater, particularly when its concentration is high enough because the reaction efficiency increases significantly with the concentration of urea. Also an increase in temperature intensifies urea decomposition by nitrites.

As a result, a method of urea removal from wastewater may be suggested (see Fig. 7). It consists of two main sections: the first one is the reactor where decomposition of urea by nitrites takes place and the second one where ammonium and nitrate ions are removed by means of ion exchanger beds. The ion exchanger beds permit the recovery of ammonium nitrate. A disadvantage of this process is incomplete decomposition of urea. However, finding a catalyst improving the course of reaction between urea and nitrite would substantially improve the process making it economically attractive for urea removal from wastewater.

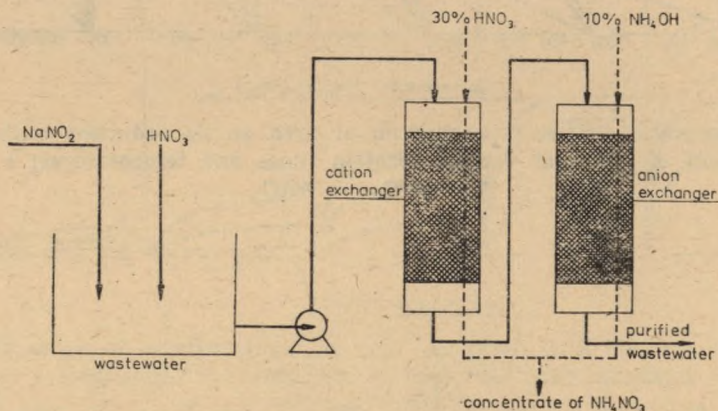


Fig. 7. Scheme of the installation for urea removal from wastewater with simultaneous recovery of  $\text{NH}_4\text{NO}_3$  and demineralized water

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### STRESZCZENIE

Przedstawiono wyniki badań nad rozkładem mocznika za pomocą azotynów. Stwierdzono, że reakcja może być zastosowana do redukcji zawartości mocznika ze ścieków, które zawierają go w dużych ilościach. Efektywność usuwania mocznika ze ścieków zawierających mocznik w niewielkich ilościach jest jednak niska.

### РЕЗЮМЕ

В данной работе представлены результаты разложения мочевины при помощи нитритов. Исследования показали, что реакция может быть применена к раскислению мочевины из стоков, которые содержат большое количество мочевины. Эффективность удаления мочевины из стоков, содержащих небольшое количество мочевины, бывает низкая.



