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## THEORETICAL EVALUATION OF THE POSSIBILITIES OF AMMONIA REMOVAL FROM POTABLE WATER BY LIGAND EXCHANGE

The process of the selective sorption of ammonia on the bed of strong acid cation exchanger exhausted with copper ions is considered theoretically. A quantitative influence of water temperature and ammonia concentration on ion exchange capacity is presented. An increase in temperature was found to result in the decrease of the quantity of ammonia being sorbed by the system. Similar results were obtained while decreasing the concentration of ammonia in water. Experimental data will be discussed in the authors' next paper.

### 1. INTRODUCTION

Excess ammonia nitrogen contained in surface waters causes serious disturbances in their self-purification and makes the direct use of polluted water for consumption purposes impossible.

Due to man's intensive activity in the field of technology and ever increasing population of people and animals the quantity of ammonia discharged to surface waters increases rapidly and often exceeds the permissible level of pollution. The majority of surface waters are, more or less, polluted with ammonia nitrogen compounds.

That is why new methods of nitrogen compounds removal from wastewater have been developed recently. The best known are the ones based on biological processes i.e. on the biochemical decomposition of nitrogen compounds or their assimilation by live organisms [1].

A method for the recovery of nitrogen compounds present in wastewaters discharged from nitrogen industry plants has been also developed. It consists in the sorption of ammonium ions in cation exchanger bed and of nitrate ions in anion exchanger bed. The regeneration of cation exchanger bed by means of nitrid acid and of anion exchanger bed by means of ammonia water solution allows to obtain the concentrate of ammonium nitrate which may be recirculated to production [1-4], [9,10]. The method, however, is not sufficient for the selective removal of ammonium and nitrate ions. It simply enables the remo-

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val and concentration of any ions contained in the solution. Hence, the method can be applied to wastewaters containing practically only ammonium and nitrate ions, i.e. those from nitrogen industry plants.

In many cases, however, of all the ions contained in wastes or water those of ammonium are few in number and there is no need to remove the remaining ones. Then selective processes must be applied such as the sorption of ammonia nitrogen in clinoptilolite bed [7, 8, 13]. However, a wide application of this method in Poland would require the development of the technology for obtaining clinoptilolite from the beds in the Carpathian Hills, which can not take place soon.

The method of ligand exchange seems to be very promising. It makes use of a cation exchanger with copper ions which, in their coordination zone, fix ammonia and so remove it from water. Interesting studies on the practical application of this method have been performed by SMITH and his co-workers [12].

Such complexes with ammonia are formed, among others, by copper. A schematic complex formation reaction is given by



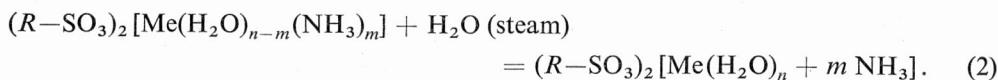
Constant instability is described by

$$K_n = \frac{[\text{Me}(\text{NH}_3)_n]^{+2}}{[\text{Me}(\text{NH}_3)_{n-1}]^{+2} \times [\text{NH}_3]}.$$

The stability of those complexes decrease with the increasing temperature. Therefore both the sorption of ammonia from water at ambient temperature and its desorption at higher (e.g. due to steam) temperature seem possible. The reactions of ligand exchange, that occur then, are characterized by the following equations:



desorption:



Considering the process from technological viewpoint the selective removal of ammonia nitrogen from wastes and water may be based on the reactions [11] and [9], what was confirmed by experimental studies [5, 12]. The process, however, lacks a full theoretical description which would allow to determine more precisely the relations that decide about the practical results. The present paper aims at filling up this gap.

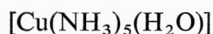
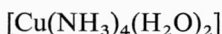
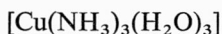
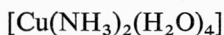
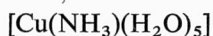
## 2. SORPTION OF AMMONIA ON SULPHONE ION EXCHANGER WITH $\text{Cu}^{++}$ IONS

In view of our considerations two phases must be distinguished, i.e. ion exchanger bead with the sorbed water and external solution. Since the copper affinity to cation exchanger is relatively high it is possible to attain a full ion exchange capacity of the cation

exchanger in relation to copper ions. The concentration of copper in internal ion exchanger solution is then equal to about 6 val/dm<sup>3</sup>. It may vary depending on the type of ion exchanger, the changes, however, being of little importance. What should also be noted is the fact that the bonds inside the ion exchanger are ionic in nature and hence the solution inside the ion exchanger bead may be treated as a completely dissociated electrolyte.

Moreover it is assumed that the coefficient of free ammonia distribution among the external and internal solutions equals 1, i.e. the concentrations of ammonia are the same in both solutions. This assumption may be approximately true taking account of the fact that ammonia is the molecule free of charge.

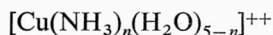
Our basic theoretical considerations refer to the temperature of 30°C. At that temperature copper forms the following complexes:



All the above-mentioned complex forms occur in equilibrium with one another and their mutual relationship depends on the concentration of ammonia and copper. The concentration of copper, however, is as a rule constant and dependent on the type of a cation exchanger applied to the sorption. Hence the only variable parameters are the concentration of ammonia and temperature. The necessary dependences may be analysed theoretically by means of properly transformed JACYMIRSKI's equation [6]:

$$\alpha_n = \frac{K_n [\text{C}_{\text{NH}_3}]^n}{1 + \sum_{i=1}^{i=5} K_i [\text{C}_{\text{NH}_3}]^i} \quad (3)$$

where  $\alpha_n$  is the mole fraction of the complex



and  $K_i$  is the constant instability of the complex  $[\text{Cu}(\text{NH}_3)_i(\text{H}_2\text{O})_{5-i}]^{++}$ .

By means of eq. (3) mole fractions of each complex were determined depending on ammonia concentration. The data are given in table 1.

At ammonia concentration  $10^{-6}$  m (0.014 ppm  $\text{N}_{\text{NH}_3}$ ) no complexes are formed because 99.29% of  $\text{Cu}^{++}$  ions remain uncomplexed. At the concentration  $\text{N}_{\text{NH}_3} = 10^{-5}$  m (0.14 ppm  $\text{N}_{\text{NH}_3}$ ) still 87.2% of  $\text{Cu}^{++}$  ions are uncomplexed. From the remaining 12.32% monoligand complexes are formed. At ammonia concentration  $10^{-4}$  m (1.4 ppm  $\text{N}_{\text{NH}_3}$ ) 34.55% of  $\text{Cu}^{++}$  ions remain uncomplexed, 48.77% form monoligand complexes, 15.4% biligand complexes, and 1.19% triligand complexes; the share of triligand complexes is rather small and equals 0.016%. At ammonia concentration  $10^{-3}$  m (14 ppm  $\text{N}_{\text{NH}_3}$ ) the

Table 1

Effect of ammonia concentration on the fraction (in %) of each complex of  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{5-n}]^{++}$  type for the temperature 303 K

Wpływ stężenia amoniaku na procentowy udział poszczególnych kompleksów typu  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{5-n}]^{++}$  dla temp. 303 K

$C_{\text{NH}_3}$	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\alpha_5$
$10^{-6}$	99.29	0.70	0.004	0.	0	0
$10^{-5}$	87.20	12.32	0.390	0.003	0	0
$10^{-4}$	34.55	48.79	15.400	1.190	0.016	0
$10^{-3}$	1.00	14.24	45.050	34.960	4.730	0.001
$10^{-2}$	0.001	0.16	5.170	40.170	54.310	0.001
$10^{-1}$	0	0	0.086	6.690	90.490	2.730

amount of the uncomplexed copper equals only 1%. The main part remains in the form of bi- (45.05%) and triligand (34.96%) complexes. At the concentration  $10^{-2}$  m (140 ppm  $N_{\text{NH}_3}$ ) the uncomplexed copper practically does not exist and mainly tri- (40.17%) and tetraligand (54.32%) complexes are formed. At ammonia concentration 0.1 m (1400 ppm  $N_{\text{NH}_3}$ ) mainly tetraligand complexes (90.49%) are formed.

Assuming the state of copper being fully complexed in the form of pentaligands as 100% one may determine the degree to which theoretical ion exchange capacity of ion exchanger is engaged:

$$Q\% = (0.2\alpha_1 + 0.4\alpha_2 + 0.6\alpha_3 + 0.8\alpha_4 + \alpha_5) \cdot 100\% \quad (4)$$

Since the mean capacity of sulphonic cation exchanger in relation to  $\text{Cu}^{2+}$  ions is equal to 1.2 val/dm<sup>3</sup> one may calculate the maximum theoretical ion exchange capacity of the sulphonic ion exchanger — copper ions system in relation to ammonia. It is equal to  $1.2 \cdot 5 = 6$  val/dm<sup>3</sup>. The influence of ammonia concentration on the theoretical ion exchange capacity  $Q_T$  is presented in table 2.

Table 2

Effect of ammonia concentration on the theoretical ion exchange capacity  $Q_T$

Wpływ natężenia amoniaku na teoretyczną pojemność wymienną  $Q_T$

$C_{\text{NH}_3}$	$Q_T$ [%]	$Q_T$ [val/dm <sup>3</sup> ]
$10^{-6}$	0.0016	$9.6 \cdot 10^{-5}$
$10^{-5}$	2.62	0.15
$10^{-4}$	16.6	0.996
$10^{-3}$	45.62	2.74
$10^{-2}$	69.65	4.18
$10^{-1}$	79.1	4.75
$10^0$	84.3	5.06

Another parameter that influences the sorption of ammonia by complex formation is temperature which affects the constant of complex instability. The relation between the constant of complex instability and temperature is given by

$$\lg \frac{K_1}{K} = \frac{\Delta H \cdot \Delta T}{2.303 \cdot R T T_1} \quad (5)$$

where  $K_1$  and  $K$  are the constants of complex instability at temperatures  $T_1$  and  $T$ , respectively,  $R$  is the gas constant  $H$  is the reaction thermal effect (for the sake of simplicity the influence of temperature on  $\Delta H$  is neglected). By means of eq. (5) the instability constants have been calculated for each complex in function of temperature. From the data given in table 3, it follows that the stability of complexes with greater number of ammonia

Table 3

Effect of temperature on the instability constants of  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O}_{5-n})]^{++}$  type complexes  
Wpływ temperatury na stałe nietrwałości kompleksów typu  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O}_{5-n})]^{++}$

$T$ [K]	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$
273	$2.79 \cdot 10^{4.15}$	$7.64 \cdot 10^{7.65}$	$21.3 \cdot 10^{10.54}$	$56 \cdot 10^{12.67}$	$143 \cdot 10^{12.15}$
283	$1.93 \cdot 10^{4.15}$	$3.70 \cdot 10^{7.65}$	$7.15 \cdot 10^{10.54}$	$13 \cdot 10^{12.67}$	$24 \cdot 10^{12.15}$
293	$1.37 \cdot 10^{4.15}$	$1.88 \cdot 10^{7.65}$	$2.58 \cdot 10^{10.54}$	$3.5 \cdot 10^{12.67}$	$4.7 \cdot 10^{12.15}$
303	$1 \cdot 10^{4.15}$	$1 \cdot 10^{7.65}$	$1 \cdot 10^{10.54}$	$1 \cdot 10^{12.67}$	$1 \cdot 10^{12.15}$
313	$0.74 \cdot 10^{4.15}$	$0.55 \cdot 10^{7.65}$	$0.41 \cdot 10^{10.54}$	$0.3 \cdot 10^{12.67}$	$0.2 \cdot 10^{12.15}$
333	$0.44 \cdot 10^{4.15}$	$0.19 \cdot 10^{7.65}$	$0.08 \cdot 10^{10.54}$	$0.04 \cdot 10^{12.67}$	$0.02 \cdot 10^{12.15}$
353	$0.26 \cdot 10^{4.15}$	$0.07 \cdot 10^{7.65}$	$0.02 \cdot 10^{10.54}$	$0.005 \cdot 10^{12.67}$	$0.002 \cdot 10^{12.15}$
383	$0.14 \cdot 10^{4.15}$	$0.02 \cdot 10^{7.65}$	$0.003 \cdot 10^{10.54}$	$0.00047 \cdot 10^{12.67}$	$0.00008 \cdot 10^{12.15}$

Table 4

Effect of temperature on the fraction (in %) of each complex of  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O}_{5-n})]^{++}$  type at ammonia concentration  $10^{-3}$  m

Wpływ temperatury na procentowy udział poszczególnych kompleksów typu  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O}_{5-n})]^{++}$  przy stężeniu amoniaku wynoszącym  $10^{-3}$  m.

$T$ [K]	$\alpha_0$	$\alpha_1$	$\alpha_2$ [%]	$\alpha_3$	$\alpha_4$	$\alpha_5$
273	0	2.85	24.68	53.43	18.95	0.01
283	0.20	5.43	32.92	49.34	12.11	0.006
293	0.47	9.23	39.96	42.53	7.79	0.003
303	1.00	14.24	45.05	34.96	4.73	0.001
313	1.94	20.24	47.58	27.50	2.72	0
333	5.36	33.90	45.48	14.85	1.00	0
353	11.74	43.12	36.72	8.13	0.27	0
383	25.10	49.70	22.50	2.50	0.05	0

Table 5

Effect of temperature on the fraction (in %) of each complex of  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{5-n}]^{++}$  type at ammonia concentration  $10^{-4}$  m

Wpływ temperatury na procentowy udział poszczególnych kompleksów typu  $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{5-n}]$

T [K]	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\alpha_5$
	[%]					
273	10.97	43.22	31.42	8.1	0.29	0
283	17.70	48.40	29.30	4.4	0.10	0
293	25.86	50.06	21.70	2.3	0.04	0
303	34.49	48.74	15.40	1.19	0.16	0
313	43.30	45.30	10.60	0.62	0.06	0
333	58.49	36.37	4.96	0.16	0.01	0
353	71.46	26.25	2.23	0.05	0.0017	0
383	82.86	16.39	0.74	0.009	0	0

particles decreases more rapidly. As a consequence the fraction (in per cent) of complexes with low content of ammonia particles increases with the increasing temperature. Exemplary data for the concentrations  $10^{-3}$  m (14 ppm  $\text{N}_{\text{NH}_3}$ ) and  $10^{-4}$  m (1.4 ppm  $\text{N}_{\text{NH}_3}$ ) are presented in tables 4 and 5, respectively.

As a result the amount of ammonia being sorbed in ion exchanger bed decreases. For example theoretical ion exchange capacities for various temperatures may be calculated basing on eq. (4). The data obtained are given in tables 6 and 7. The above mentioned data determine theoretical relations between temperature and ammonia concentration on the one hand and ion exchanger capacity on the other.

Table 6

Effect of temperature on the theoretical ion exchange capacity of ion exchanger at ammonia concentration  $10^{-3}$  m

Wpływ temperatury na teoretyczną pojemność wymienną jonitu przy stężeniu amoniaku wynoszącym  $10^{-3}$  m

T [K]	$Q_T$ [%]	$Q_T$
273	57.67	3.46
283	53.55	3.21
293	49.58	2.97
303	45.62	2.74
313	41.76	2.51
333	34.56	2.07
353	28.40	1.70
383	20.50	1.20

Table 7

Effect of temperature on the theoretical ion exchange capacity of ion exchanger at ammonia concentration  $10^{-4}$  m

Wpływ temperatury na teoretyczną pojemność wymienną jonitu przy stężeniu amoniaku wynoszącym  $10^{-4}$  m

$T$ [K]	$Q_T\%$	$Q_T$
273	26.3	1.6
283	24.2	1.5
293	20.1	1.2
303	16.75	1.0
313	13.7	0.8
333	9.3	0.6
353	6.17	0.4
363	3.58	0.2

When planning the process one should also consider the stability of  $\text{Cu}^{++}$  ions binding by ion exchanger in order to prevent  $\text{Cu}^{++}$  ions from penetrating into water. Since the sorption of  $\text{Cu}^{++}$  ions through the cation exchanger is a reversible process the ions, depending on their total concentration in water, may be to a smaller or greater degree leached from the ion exchanger. Generally speaking the higher is the total concentration of cations in water the more ions penetrate into water. The same happens when water contains cations of higher valence. Therefore it is necessary to consider the possibility of applying the double column system. The first column with  $\text{Cu}^{++}$  ions is a sorption column for ammonia, whereas the second one with sodium ions is rather small and functions as a filter for copper ions eluted from the first column.

### 3. CONCLUSIONS

From the above theoretical considerations it follows that strong acid cation exchanger exhauster with copper ions provide a sufficiently selective system for the sorption of ammonia from potable water. At the same time, from theoretical viewpoint, it is possible to obtain high enough ion exchange capacities.

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#### TEORETYCZNA OCENA MOŻLIWOŚCI USUWANIA AMONIAKU Z WODY PITNEJ METODĄ WYMIANY LIGANDÓW

W artykule przedstawiono teoretyczne rozważania nad procesem selektywnej sorpcji amoniaku na złożu silnie kwaśnego kationitu obsadzonego jonami miedziowymi. Przedstawiono ilościowy wpływ temperatury wody i stężenia amoniaku na pojemność wymienną układu. Stwierdzono, że wzrost temperatury powoduje spadek ilości zasorbowanego amoniaku przez układ. Podobne zjawisko obserwuje się przy obniżaniu stężenia amoniaku w wodzie.

Z przedstawionych danych wynika, że możliwe jest uzyskanie interesujących wyników praktycznych. Omówienie wyników doświadczalnych będzie celem pracy następnej.

#### THEORETISCHE ERWÄGUNGEN ZUM AMMONIAKENTZUG AUS TRINKWASSER MITTELS EINES LIGANDENTAUSCHES

Aus theoretischer Sicht ist die selektive  $\text{NH}_3$ -Sorptions auf einem stark sauren und mit Cu-Ionen besetzten Kationit möglich. Das Austauschvermögen wird von der Wassertemperatur und von der Ammoniakkonzentration beeinflusst; die Erhöhung der Temperatur hat eine Absenkung der sorbierten  $\text{NH}_3$ -Menge zur Folge. Dies wird auch bei einer Abnahme der  $\text{NH}_3$ -Konzentration beobachtet.

Aus den dargestellten Angaben folgt, daß praktisch akzeptable Ergebnisse zu erwarten sind; das soll im nächsten Beitrag nachgewiesen werden.



**ТЕОРЕТИЧЕСКАЯ ОЦЕНКА ВОЗМОЖНОСТИ УДАЛЕНИЯ АММИАКА ИЗ ПИТЬЕВОЙ ВОДЫ МЕТОДОМ ОБМЕНА ЛИГАНДОВ**

Представлены теоретические рассуждения о процессе избирательной сорбции аммиака на слое сильно кислого катионита с осажденными ионами меди. Представлено количественное влияние температуры воды и концентрации аммиака на обменную емкость системы. Обнаружено, что рост температуры вызывает снижение количества аммиака, сорбированного системой. Подобное явление наблюдается при снижении концентрации аммиака в воде. Из приведенных данных вытекает, что возможно получить интересные практические результаты. Обсуждению опытных результатов будет посвящена отдельная работа.