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The Research on the Ammonium Concentrations in City Stocks and Further Sedimentation of Ion-Exchange Concentrate

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ABSTRACT
In this work, the exchange capacity and the selectivity of different ion-exchange products regarding the ammonium ions in treatment processes were measured; the regenerative preparation compounds influence on efficiency of conduction of ion-exchange products regeneration was determined. The adsorption processes were adapted to the known technological schemes of sewage and polluted surface water treatment that was polluted with ammonium ions. There were measured the technological aspects of water treatment by using adsorption on natural dispersed sorbents. The technological schemes of drain water treatment from ammonium ions were developed. The method of simultaneous removal of highly concentrated nitrogen and phosphorus was analyzed by physical and chemical precipitation, forming struvite, a by-product of magnesium ammonium orthophosphate hexahydrate. The analyses were conducted at various molar ratios of magnesium and phosphate ions and at various pH values. The comparative thermal analysis of chemical precipitation products and pure struvite was performed. The optimal conditions were identified to experience the maximum efficiency of simultaneous removal of ammonium nitrogen and phosphate ions from wastewater, forming $MgNH_4PO_4 \cdot 6H_2O$.

Keywords: environmental security, natural clay sorbents, adsorption, ion exchange, ammonium orthophosphate hexahydrate (struvite), thermal analysis

INTRODUCTION

Anthropogenic eutrophication and water pollution are the main processes that cause degradation of rivers, water reservoirs, lake systems and deterioration of the water quality. The main cause of both processes is the waste of economic activity entering the reservoir from the catchment area. Contamination of reservoirs with toxic substances of anthropogenic origin often complicates or makes it impossible to use water for drinking purposes.

The removal of ammonium nitrogen from water appears to be the most common problem. Usually, ammonium nitrogen can be found in water at pH level of 6–8. It infiltrates into the surface water with sewage; as a result of ammonification; decomposition of microorganisms of nitrogen-containing organic components (proteins, urea, nucleic acids, etc.), as well as fertilization into the soil. The presence of ammonium ions in water together with nitrates indicates recent water pollution with domestic sewage.

Assessment of surface water objects influenced by the contaminating components of effluents (Kulikova et al., 2016, as well as the analysis of natural of purification systems of effluents filtering from accumulation pounds in the "aeration nature zone-wastewater" system (Pavlichenko et al., 2013) proved to be important. Treatment of the water from various types of pollution by methods such as chlorination (Styskal et al., 2014), ozonization (Mosin, 2011), ultraviolet irradiation (Vronska et al., 2013), ion exchange (Malovanyy et al., 2013), electrodialysis (Gomelia et al., 2017, Shmandiy et al., 2017), biological purification

(Malovanyy et al., 2016, Malovanyy et al., 2018), adsorption on natural mineral sorbents (Sabadash et al., 2017, Malovanyy et al., 2013) and of plant origin (Danchenko et al., 2017, Bezdeneznych et al., 2009), typically requires expensive reagents and equipment, sometimes also introducing secondary hazardous contaminants to the system (chlorination and ozonation).

These methods are ineffective and difficult to apply. The wastewater from these industries is treated from biogenic elements by conventional biological methods (in aerotanks), while nitrogen compounds are virtually eliminated in them.

The development of new highly-efficient technological schemes for water treatment at the existing wastewater treatment facilities, as well as improvement of the existing wastewater treatment schemes, is one of the ways to solve the problem of discharging insufficiently treated wastewater into water bodies. The application of nitride-denitrification technology in conjunction with dephosphatization requires the improvement of reagent sewage treatment through a detailed study of the formation of weakly soluble magnesium ammonium orthophosphate $MgNH_4PO_4{\cdot}6H_2O$, which is a valuable fertilizer (Cahil et al., 2008) Implementing this technology under practical conditions, could significantly reduce the need for raw phosphate materials as well as phosphate fertilizer technologies.

The purpose of this study is to develop recommendations on the optimum conditions for the deposition of ammoniacal nitrogen from ion exchange regenerator for its further use as ammonium fertilizer, based on experimental data.

MATERIALS AND METHODS

The results of previous studies (Malovanyy et al. 2013) showed the possibility of concentration of ammonium ions from wastewater by means of ion exchange. In these studies, ion-exchange materials KU-2–8 or natural zeolite of the Sokirnitsky deposit (Zakarpattia) were saturated with ammonium ions from drain models in the fractioning column until a breakthrough was reached, after which the ion-exchange material was regenerated by pumping 30 g/l NaCl through it. The initial model solution contained 40 mg/dm^3 NH_4^+–N (prepared with NH_4Cl), pH = 6 with a total content of 2.46 mg/dm^3 cations. The results of saturation of cation exchanger KU-2–8 and natural zeolite with model solution and subsequent regeneration are presented in Table 1. The maximum saturation of ion-exchange material was determined by increasing the electrical conductivity of the solution at the exit from the column.

As a result of these experiments, we received the ion exchange concentrates, the characteristics of which are given in Table 2.

The research was held at room temperature using the chemical deposition method. Magnesium chloride ($MgCl_2{\cdot}6H_2O$) solution with Mg^{2+} – 10000 mg/l concentration and sodium hydrogen phosphate (Na_2HPO_4) with PO_4^{3-} – 9500 mg/l concentration were used as precipitators. In order to estimate the optimal conditions for ammonium nitrogen deposition, the experiments with different stoichiometric ratios Mg^{2+}: NH_4^+: PO_4^{3-} (1:1:1; 1,5:1:1; 1:1:1,5; 1,5:1:1,5; 1:1,5:1) were conducted. The pH of the reaction mass was adjusted to various values (7–11) using 10% NaOH. The pH of the reaction mass was determined using the method with pH meter HachSensIon 2 with electrode 51935–00. Substrate agents were added to the model solution in the required volumes to achieve the desired ratio Mg^{2+}:NH_4^+:PO_4^{3-}. Afterwards, we adjusted pH to the specified value. The reaction mass was stirred at 350 rpm 1 min (rapid mixing, reaction time), then at 20 rpm for 30 minutes (slow stirring, formation of the flocculus). The resulting suspension was protected for 1 hour. The suspension was then filtered, and the resulting filtrate was analyzed for the residual ammonium ions and phosphate ions content. The analy-

Table 1. The results of ion-exchange material saturation with ammonium and its further regeneration

Index	Cation exchanger usage КУ-2–8	Natural zeolite usage
Volume usage of model solution, 10^{-3} OK/c	11.4	9
Firsttraces NH_4^+in cleared water, OK	92	70
Dynamic exchange capacity, mg NH_4^+-N/г	10.1	4
Volume flow of solution for regeneration, 10^{-3} OK/c	1.9	2
Solution volume for regeneration, OK	13	120
Regeneration level, %	98	90

Table 2. Ion exchange concentrates

Ion-exchangematerial	Cationexchanger	Zeolite
NH_4^+-N, mg/l	550	470
Ca^{2+}, mg/l	280	260
Mg^{2+}, mg/l	240	240
pH	7	6.5

sis was held at photoelectric colorimeter with a method of photometric determination of ammonium ions using the Nessler's reagent in wastewater (KND 211.1.4.030–95, 2006) and method of photometric determination of phosphate ions in wastewater (KND 211.1.4.030–95, 2006).

The obtained data was compared to the initial concentrations in the model solution of the corresponding ions to determine the deposition efficiency.

RESULTS AND DISCUSSION

Due to the large number of variables in the experiments, it was decided to conduct studies in four groups (A, B, C, D) depending on the molar ratio of ions Mg^{2+}, NH_4^+, PO_4^{3-}: Group A – stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1, pH 7; 8; 9; 10; 11. Group B – stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1.5:1:1, pH 7; 8; 9; 10; 11. Group C – stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1.5, pH 7; 8; 9; 10; 11. Group D – stoichiometric ratio Mg^{2+}:NH_4^+:PO_4^{3-}= 1.5:1:1.5, pH 7; 8; 9; 10; 11.

Adjustment of the corresponding stoichiometric ratios Mg^{2+}: NH_4^+: PO_4^{3-} was carried out by mixing different volumes of working solutions according to the calculations. Sodium hydrogen phosphate was used as a precipitating agent (Na_2HPO_4),

The filtrate was analyzed for the content of residual phosphate ions. Therefore, while analyzing the results of the research, attention was drawn not only to the maximum degree of extraction of NH_4^+-N, but the degree of extraction of PO_4^{3-}.

The main results of precipitation are described in tables 3 and 4.

It was found that the optimal conditions for the process of reagent precipitation of ammonium nitrogen at the initial concentration NH_4^+-N – 550 mg/l is the stoichiometric ratio Mg^{2+}: NH_4^+:

Table 3. The results of the samples analysis of NH_4^+ and PO_4^{3-}content in solutions (while obtaining an ion exchange concentrate using cation exchanger КУ 2–8)

No.	pH	*Cm*(NH_4^+), mg	C(NH_4^+-N), mg/l	*Cm* (P_2O_5), mg	*C* (PO_4^{3-}), mg/l
Group A solutions					
1	7	3.9644	396.4	1.0506	157.04
2	8	0.9310	93.1	0.5223	77.47
3	9	0.4129	41.3	0.3237	48.39
4	10	0.6271	62.7	0.3766	56.29
5	11	2.2778	227.8	0.8484	126.82
Group B solutions					
1	7	3.7324	373.2	1.0306	154.05
2	8	0.3860	38.6	0.5314	79.43
3	9	0.3646	36.5	0.3401	50.85
4	10	0.4109	41.1	0.3036	45.39
5	11	2.3311	233.1	0.5751	85.97
Group C solutions					
1	7	2.0224	202.2	1.5607	233.30
2	8	0.7964	79.6	0.7063	105.57
3	9	0.4153	41.5	0.6225	93.05
4	10	1.7435	174.3	0.6917	103.35
5	11	1.8344	183.4	1.3968	208.79
Group D solutions					
1	7	3.0511	305.1	1.6026	239.56
2	8	0.6907	69.1	0.7773	116.20
3	9	0.3683	36.8	0.5228	78.15
4	10	0.3801	38.1	0.9559	142.89
5	11	1.8933	189.3	1.5881	237.38

Table 4. The results of the samples analysis for NH_4^+ and PO_4^{3-}content in solutions (at obtaining an ion exchange concentrate using zeolite)

No.	pH	*Cm*(NH_4^+), mg	C(NH_4^+-N), mg/l	*Cm* (P_2O_5), mg	*C* (PO_4^{3-}), mg/l
Group A solutions					
1	7	58.6526	456.19	2.7162	157.04
2	8	29.1789	226.95	1.2147	77.47
3	9	24.9684	194.20	0.9144	48.39
4	10	20.7579	161.45	1.9655	56.29
5	11	21.8105	169.64	2.1156	126.82
Group B solutions					
1	7	54.4421	423.44	1.2147	301.25
2	8	27.0737	210.57	1.0646	264.01
3	9	15.4947	120.51	0.9144	226.77
4	10	13.3895	104.14	2.2658	561.91
5	11	37.6000	292.44	3.0165	748.10
Group C solutions					
1	7	53.3895	415.25	3.0165	748.10
2	8	23.9158	186.01	2.2658	561.91
3	9	14.4421	112.33	1.5150	375.72
4	10	18.6526	145.08	1.0646	264.01
5	11	20.7579	161.45	0.7643	189.54
Group D solutions					
1	7	41.8105	325.19	1.3649	338.49
2	8	30.2316	235.13	1.2147	301.25
3	9	2.8632	22.27	0.9144	226.77
4	10	3.9158	30.46	0.4640	115.06
5	11	10.2316	79.58	0.7643	189.54
Group E solutions					
1	7	77.6000	603.56	0.7643	189.54
2	8	71.2842	554.43	0.6141	152.30
3	9	43.9158	341.57	0.6141	152.30
4	10	40.7579	317.01	0.9144	226.77
5	1	43.9158	341.57	1.5150	375.72

PO_4^{3-} = 1,5:1 :1 (option B). The results of the best option of lab research group were aggregated in a combined diagram, which shows the effectiveness of precipitation of NH_4^+-N depending on the pH (Figure 1).

This way, it was estimated that the maximum effectiveness of ammonia nitrogen removal is reached at a pH of about 9 and at a ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1.5:1:1.5. A change of ratio Mg^{2+}-:NH_4^+:PO_4^{3-}at 9 pH level leads to reducing effectiveness NH_4^+-N. A further growth of pH leads to a sharp decrease in the efficiency of removal of ammonium ions.

The results from group D, as the best lab sample, are reflected in a combined diagram, which shows the effectiveness of NH_4^+-N precipitation which depends on pH at Mg^{2+}: NH_4^+: PO_4^{3-}= 1.5 : 1 : 1.5 ratio (Figure 2).

It was established that the maximum efficiency of ammonium nitrogen removal at its initial concentration in the regenerate 470 mg/l is achieved at approx. 8.5 pH level with Mg^{2+}: NH_4^+: PO_4^{3-} = 1.5:1:1.5 ratio. The change of correlation Mg^{2+}:NH_4^+:PO_4^3 at 8.5 pH leads to a reduction of the NH_4^+-N removal efficiency. A further pH growth results in a high decrease of the NH_4^+-N removal efficiency. At a maximum level of ammonium nitrogen removal efficiency, the level of PO_4^{3-} removal is maximum too, at 8.5 pH level and Mg^{2+}: NH_4^+: PO_4^{3-} = 1.5:1:1.5 ratio.

On the basis of the results pertaining to the best options, deposition of real concentrates of ion exchange was carried out. The degree of NH_4^+-N ions deposition for concentrate excluded from cationite was 94.5%, and for the concentrate extracted from zeolite – 93.91%, which means that the results almost do not differ from the values of samples concentrates in which the proportion of adsorbed ions is NH_4^+-N – 93.91%.

The weight method was used to determine the moisture level of the precipitate. At the starting level 550 mg/l of NH_4^+-N concentration,

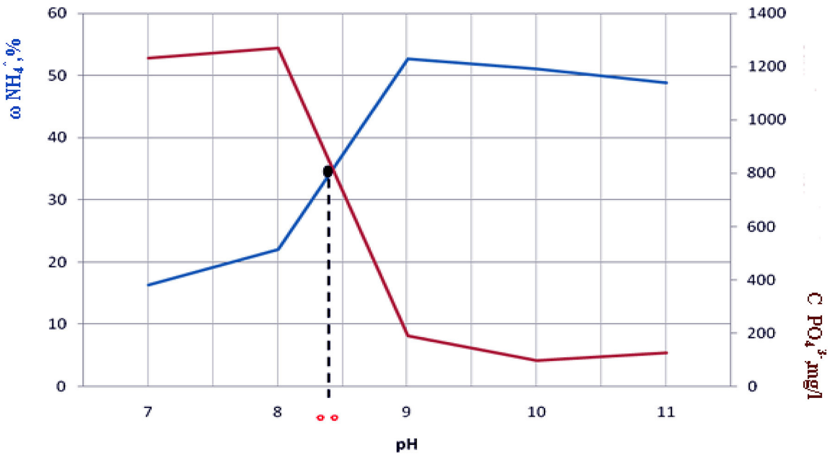

Figure 1. Optimal conditions of simultaneous removal of ammonium nitrogen and phosphate ions in solution B

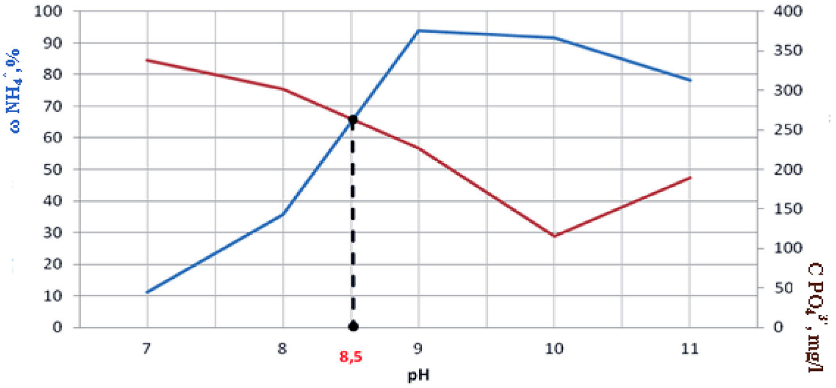

Figure 2. Optimal conditions for a simultaneous removal of ammonium nitrogen and phosphate ions in solution

obtained under the chosen optimal conditions (Mg^{2+of}: NH_4^+: PO_4^{3-} = 1.5:1:1, pH 9) it amounted to 33.07% moisture, but at the level 470 mg/l of NH_4^+-N concentration and optimal conditions Mg^{2+}: NH_4^+: PO_4^{3-} = 1.5:1:1.5, pH 8.5, the moisture level was 40.7%. The calculation of the moisture content of the precipitate enabled to establish a crystal hydrate formula: in the first case, it is $MgNH_4PO_4 \times 4.5H_2O$, in the other $MgNH_4PO_4 \times 4H_2O$.

The precipitate formed as a result of the physicochemical precipitation of ammonium and phosphorus ions was analyzed with a thermogravimetric method.

The differences in the chemical composition of the samples were determined by examining their thermal stability compared to the chemically pure crystalline matrix MgNH4PO4·$6H_2O$, a sample of SIGMA-ALDRICH, with a content of 99.997% of the basic substance (Tulaydan et al., 2017).

The thermograms of pure crystalline hydrate sample and a prototype are shown in Figures 3 and 4, respectively. The presented thermograms are a set of curves TG, DTG, DTA. The TG and DTG curves reflect the sample mass loss during heating and the mass loss rate, and the DTA curve depicts the changes in the sample temperature and reference substance temperature difference as well as characterizes the magnitude and type of thermal effect.

Similarity of the TG and DTG curves indicates the similarity of their mechanism of thermal destruction. By the nature of mass loss and total mass loss at the end of the process, the test sample is very similar to the sample of pure crystalline hydrate. The partial discrepancy of the sample mass loss of $MgNH_4PO_4 \cdot 4{,}5H_2O$ and $MgNH_4PO_4 \cdot 6H_2O$ at different stages of thermolysis, indicates a possible presence of a small amount of impurities in the sample in the form of magnesium hydroxide and calcium hydrophosphates. On the other hand, the difference in the amount of water characterizes the differences in the passage of the first stage. The presence of impurities is caused by the conditions of physical and chemical deposition analysis.

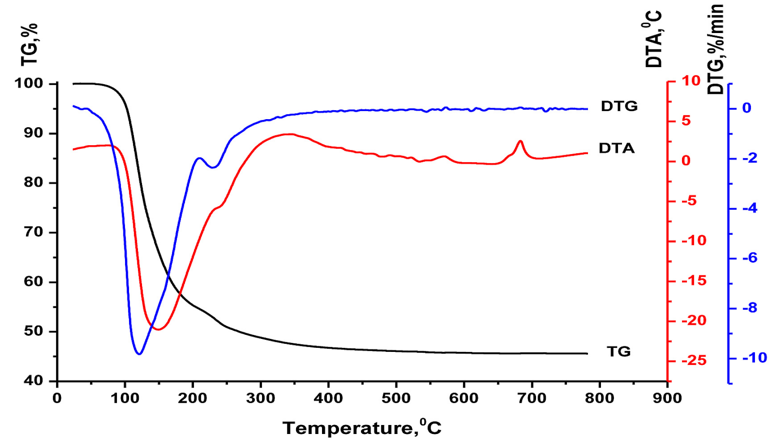

Figure 3. The thermogram of pure crystalline hydrate – $MgNH_4PO_4·6H_2O$

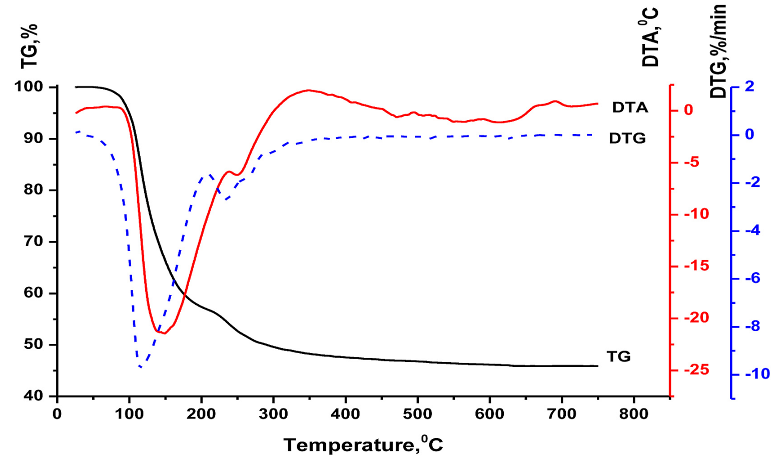

Figure 4. The thermogram of received crystalline hydrate – $MgNH_4PO_4·4.5H_2O$

The behavior of the resulting precipitate at thermal heating allows us to conclude that this product can be used as a fertilizer on the industrial level. During drying and granulation, the fertilizer does not lose nutrients. During the heating of fertilizers to more than 200°C, they can lose part of the crystallization – bound water, as well as a part of nutrient nitrogen in the form of ammonia.

CONCLUSIONS

1. A series of experimental studies were carried out on sample solutions. We obtained the following results:
2. The reagent method allows simultaneous removal of ammonia and phosphates with the achievement of the proportion of adsorbed ions up to 95% and up to 98%, respectively.
3. The most optimal conditions for the process of reagent precipitation of ammonia nitrogen at the initial concentration of NH_4^+ -N- 550 mg/l is pH 9 and the stoichiometric ratio is Mg^{2+}: NH_4^+: PO_4^{3-} = 1.5: 1: 1.5. In this case, the proportion of adsorbed ions is NH_4^+-N – 52.69%, PO_4^{3-} – 96.6%. At the initial concentration of NH_4^+-N – 470 mg/l, the optimum conditions for the process of reagent precipitation of ammonia nitrogen are pH 8.5 and the stoichiometric ratio is Mg^{2+}: NH_4^+: PO_4^{3-}= 1.5:1:1.5.
4. The moisture level was set during the drying of the mineral fertilizers. On the basis of the moisture values, we determined the content of the precipitate, which is close to the number of water molecules to the formula of fertilizer $MgNH_4PO_4·5H_2O$.
5. The behavior of the resulting precipitate obtained from the ion exchange concentrate, at thermal heating, suggests that the product can

be used as fertilizer on an industrial scale. Nutrients (nitrogen and phosphorus) would not be lost while drying and granulating fertilizer.

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