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Research on the regeneration of concentrated ammonium solutions from municipal wastewater

The conducted studies confirm the possibility and expediency of using the reagent method to remove ammonium nitrogen from wastewater in the form of slightly soluble magnesium-ammonium orthophosphate $MgNH_4PO_4 \cdot 5H_2O$, which is a high-quality fertilizer.

The most optimal conditions for the process of reagent precipitation of ammonium nitrogen at an initial concentration of NH_4^+ - N – 470 mg / l are pH 8.5 and the stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1,5: 1: 1,5.

It was determined that according to the chemical composition, properties and behavior during heating of the obtained magnesium-ammonium phosphate crystallohydrate corresponds to the biogenic mineral struvite and can be used as a mineral fertilizer of prolonged action.

It was found that the method of preserving struvite does not significantly affect the germination of the disease and the value of the humidity of germination.

Key words: *regenerate, ammonium nitrogen, magnesium-ammonium orthophosphate, fertilizer.*

Introduction. Over the past 20-30 years, effluents containing many compounds of nitrogen and phosphorus have been entering reservoirs. This is due to washout from fertilizer fields and waste discharges from enterprises. As a result, there is eutrophication of such reservoirs and increased development of phytoplankton, algae, etc. When the content of phosphorus and nitrogen in water exceeds a critical level, the life processes of aquatic organisms are accelerated. As a result, the mass development of planktonic algae ("blooming of water") begins. Water acquires an unpleasant odor and taste, its transparency decreases, its color increases, and the content of dissolved and suspended organic substances increases. In the deep zone, anaerobic metabolism increases, hydrogen sulfide, ammonia, etc. accumulate. Redox processes are disturbed and oxygen deficiency occurs. This leads to the death of valuable species of fish and plants, the water becomes unsuitable not only for food purposes, but also for household purposes. For water bodies, excessive intake of biogenic substances, which contain nitrogen and phosphorus, is no less dangerous than toxic water pollution. With an excess of organic matter in water, stable organomineral complexes with heavy metals are formed, in some cases more toxic than the metals themselves.

The most common problem is the removal of ammonium nitrogen from water. Ammonium nitrogen is found in water mainly at pH 6-8. Organic and mineral nitrogen compounds are present in wastewater from many industries: chemical, petrochemical, medical, microbiological, metallurgical, food, agrochemical, as well as in underground and domestic waters. Purification of water from nitrogen compounds by chlorination, ozonation, ultraviolet irradiation, ion exchange, electrolysis, demineralization requires expensive reagents and equipment, these methods are difficult to operate and ineffective. Wastewater from these industries is purified from biogenic elements by conventional biological methods, but the degree of extraction of nitrogen compounds is very low.

The development of new highly efficient technological schemes for water purification, as well as the improvement of existing ones, is one of the ways to solve the problem of discharging insufficiently treated wastewater into water bodies. The use of the nitro-denitrophication method in combination with dephosphatization requires the improvement of reagent wastewater treatment with the help of a detailed

study of the formation of poorly soluble magnesium ammonium orthophosphate $MgNH_4PO_4 \cdot 5H_2O$, which is a valuable fertilizer.

The purpose of the research is to develop recommendations on the optimal conditions for the precipitation of ammonium nitrogen from the ion exchange regenerate for its further use as an ammonium fertilizer based on experimental data.

Experimental part. For research, a strongly acidic cation exchanger KU-2-8 was used, which has a gel structure and contains only one type of ion-exchange groups - sulfo groups. KU-2-8 is distinguished by high chemical resistance in dilute solutions of alkalis and acids, organic solvents and some oxidizing agents.

In these studies, the KU-2-8 ion-exchange material was saturated with ammonium ions from model effluents in a column apparatus until breakthrough was reached, after which the ion-exchange material was regenerated by pumping NaCl with a concentration of 30 g/L through it [1, 2]. The characteristics of the obtained concentrate are presented in table 1.

Table 1. Characteristics of the ion exchange regenerate

Ion exchange material	KU-2-8
Ionite regeneration solution	NaCl - 30 g/l
NH_4^+-N, mg/l	470
Ca^{2+}, mg/l	260
Mg^{2+}, mg/l	240
pH	6.5

For research, a model solution was prepared, the composition of which corresponded to the composition of the ion exchange concentrate. The studies were carried out at room temperature by chemical precipitation. For this, solutions of magnesium chloride were used. ($MgCl_2 \cdot 6H_2O$) with a concentration of Mg^{2+} – 10000 mg/l and sodium hydrogen phosphate (Na_2HPO_4) with a concentration of PO_4^{3-} - 9500 mg / l. To determine the optimal conditions for the deposition of ammonium nitrogen, experiments were carried out at various stoichiometric ratios of 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) and pH 7-11.

Precipitating agents were added to the model solution in the required volumes to achieve the appropriate ratio of Mg^{2+} : NH_4^+: PO_4^{3-} . After that, the pH was adjusted to a predetermined value [3]. The reaction mass was stirred on a TYPE: OP-912/3 magnetic stirrer for 1 min at 350 rpm (rapid stirring, reaction time), then for 30 min at 20 rpm (slow stirring, floc formation). The resulting suspension was allowed to stand for 60 min, filtered (using an ashless blue ribbon filter with a pore size of 3μm). The resulting filtrate was analyzed for the content of residual ammonium ions and phosphate ions. The analysis was carried out on an FEK-56M photoelectrocolorimeter according to the methods of photometric determination of ammonium ions with Nessler's reagent in wastewater (KND 211.1.4.030-95) and photometric determination of phosphate ions in wastewater (KND 211.1.4.043-95). The obtained data were compared with the initial concentrations in the model solution of the corresponding ions to determine the precipitation efficiency.

Due to the large number of variable parameters during the experiments, a study was conducted in five groups (A, B, C, D, E) 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.
- Group E - stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1,5:1, pH 7; 8; 9; 10; 11.

Correction of the corresponding stoichiometric ratios Mg^{2+} : NH_4^+: PO_4^{3-} was provided by mixing different volumes of working solutions in accordance with the calculations.

Sodium phosphate (Na_2HPO_4) was used as the precipitant, so the filtrate was examined for the content of residual phosphate ions. When analyzing the research results, attention was paid not only to the maximum degree of extraction of NH_4^+-N, but also the degree of extraction of PO_4^{3-} .

Analyzing the results of laboratory studies of five groups, it was proved that the maximum efficiency of ammonium nitrogen removal is achieved at a pH of about 8.5 and a ratio of Mg^{2+} : NH_4^+ :

PO_4^{3-} = 1.5:1:1.5. A change in the ratio of Mg^{2+}:NH_4^+:PO_4^{3-} , as well as with an increase in pH above 8.5, leads to a decrease in the removal efficiency of NH_4^+-N. The maximum degree of extraction of PO_4^{3-} is also achieved under similar conditions [4].

Therefore, the most optimal conditions for the process of reagent deposition of ammonium nitrogen at the initial concentration of NH_4^+-N - 470 mg/l is pH 9 and the stoichiometric ratio Mg^{2+}:NH_4^+: PO_4^{3-} = 1.5:1:1.5. At the same time, the content of adsorbed NH_4^+-N ions is 93.91%, PO_4^{3-} - 95.26%.

The weight method was used to determine the moisture content of the sediment and for optimal conditions (Mg^{2+}:NH_4^+:PO_4^{3-} = 1.5:1: 1.5, pH 9) it is 40.7%. The calculation of the sediment moisture made it possible to establish the formula of the crystalline hydrate - $MgNH_4PO_4 \cdot 5H_2O$.

Magnesium-ammonium orthophosphate is a concentrated fertilizer that contains three nutrients: phosphorus, nitrogen and magnesium. $MgNH_4PO_4 \cdot 5H_2O$ can be used as a stand-alone fertilizer or to produce mixed fertilizers. This compound is one of the few fertilizers containing nitrogen in a water-insoluble form. Therefore, this fertilizer can be considered as a long-acting fertilizer.

The purpose of further of research was carrying out agronomic evaluations fertilizer obtained by the reagent method deposition of ionic concentrate exchange, and installation him suitability for use in organic production products crop production. Previously defined solubility magnesium -ammonium phosphate in water and in water solutions lemon acids of small concentrations. It is established that synthesized struvite has a solubility coefficient in water K_1^{20}=0.025, in 1% solution lemon acid K_2^{20}=0.068, in a 2% solution lemon acid K_3^{20}=0.203.

For the purpose of definition, biological efficiency struvite were conducted laboratory research by definition germination Raphanussativusvar. sativus radish seeds of the Saksa variety, manufacturer: Ukraine, also seeds watercress - salad. Efficiency effects of synthetic struvite determined by the following indicators as: resemblance seeds, energy germination for three days, duration germination. Also determined humidity germinated seeds.

For the germination analysis, three samples of 30 seeds in each variant were counted in a row, without selection. Seeds were germinated in Petri dishes at room temperature. Filter paper was used as a bedding. The reliability of the average germination rates was determined by the value of the least significant difference at the 5% significance level of $HI_{0.5}$.

The experimental data were varied according to the following scheme:

1 – control (distilled water).

1.1 – rate of application of magnesium-ammonium phosphate (MAF) 0.025 g/ml of distilled water;
1.2 – rate of application of MAF 0.068 g/ml of distilled water;
2.1 – rate of application of MAF 0.025 g/ml of 1% solution of citric acid;
2.2 – rate of application of MAF 0.068 g/ml of 1% solution of citric acid;
3.1 – rate of application of MAF 0.025 g/ml of 2% solution of citric acid;
3.2 – rate of application of MAF 0.068 g/ml of 2% solution of citric acid.

Table 2. Effect of struvite on germination of radish seeds

№ experiment	Seeds germination, %	Deviation from control, %	$HIP_{0,5}$	Duration of germination, days	The energy of germination
1.Control	90,0	-		1	90,0
1.1	93,3	3,3	1,07	2	93,3
1.2	93,3	3,3		2	93,3
2.1	90,0	0	0,86	2	90,0
2.2	86,7	-3,3		3	86,7
3.1	86,7	-3,3	1,85	3	86,7
3.2	80,0	-10		4	76,7

As a result of five days of germination of radish seeds, it was found that in the control variant with distilled water, the seeds germinated on the second day of the experiment. In variants with citric acid solution, seeds germination averaged 88.35% for variants of the second group and 83.35% for variants of group 3. In the variants with MAF solutions, higher germination rates were characteristic of aqueous solutions, but it is likely that stucco slows down germination. It can be definitely stated that the citric acid solution slows down the germination of radish seeds and reduces the germination rate to a greater extent due to acidification of the medium. The values of seeds moisture content (Fig. 1) confirm that citric acid

medium reduces the moisture content of germinated seeds, which indicates a decrease in the efficiency of their germination.

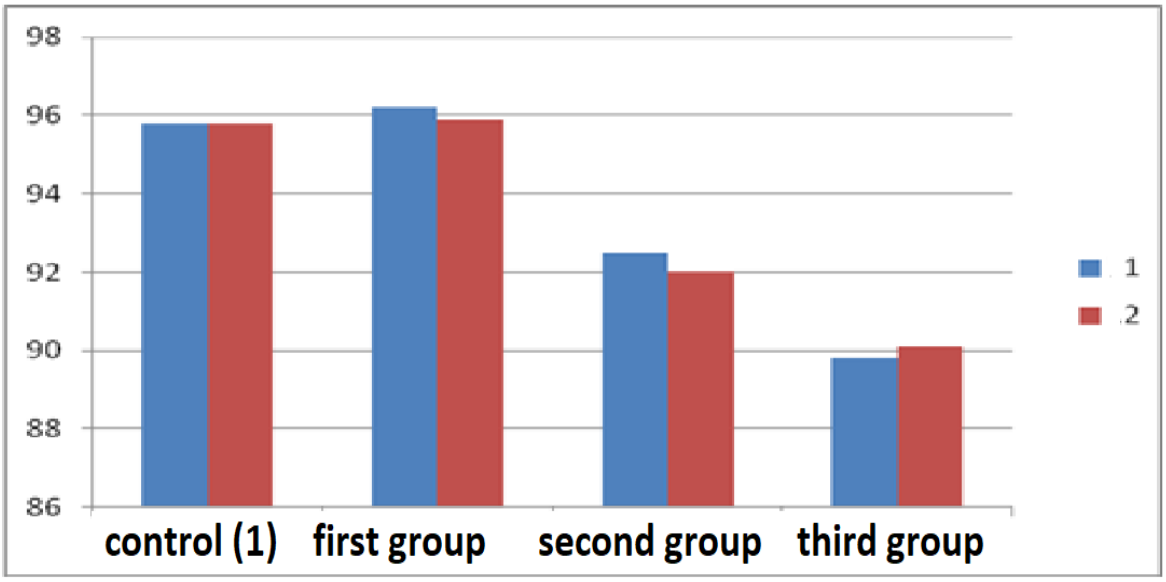


Fig.1 - Germination moisture values, %, for radish seeds

The results of watercress seeds germination are presented in Table 3. In all cases, seeds germination took place within 1-2 days, respectively; the values of the indicators of seed germination and germination energy are the same.

Table 3. Effect of struvite on watercress seeds germination

№ experiment	Seeds germination, %	Deviation from control, %	Duration of germination, days
1.Control	93,3	-	1
1.1	83,3	-10,0	2
1.2	80,0	-13,3	2
2.1	83,3	-10,0	2
2.2	76,7	-16,6	2
3.1	97,7	4,4	1
3.2	90,0	-3,3	2

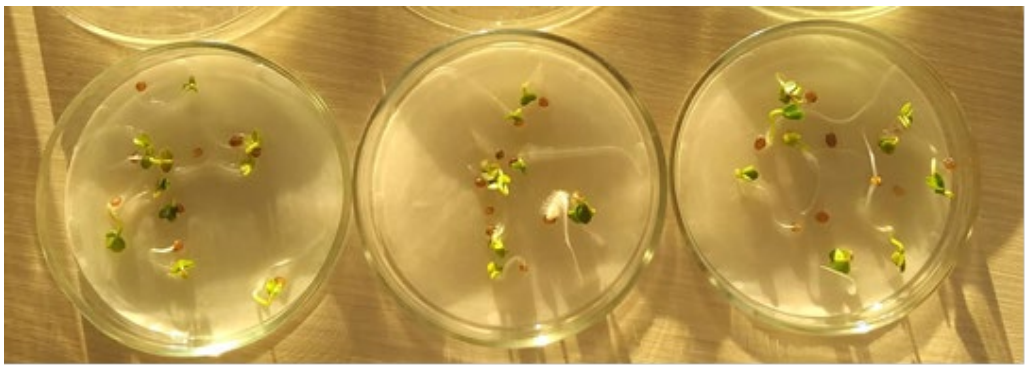
Research results indicate that the use of struvite reduces seeds germination and increases germination time. At the same time, the citric acid solution, on the contrary, promotes germination. Additional experiments on seed germination using only solutions of citric acid confirm the above: watercress seeds germinate in one day, and seed germination, respectively, is 93.3% when using a 1% solution of citric acid and 97.7% when using 2 % solution of citric acid. Therefore, the use of struvite at the stage of germination of watercress seeds is ineffective.

According to the best option for germination of radish seeds, a comparative agronomic evaluation of struvite mineral fertilizer obtained according to two options was carried out:

A. By reagent precipitation of ion exchange concentrate after purification of the model solution with natural zeolite or KU cationite with a concentration of ammonium ions of 40 mg/l.

B. By reagent precipitation of model solutions.

When using an aqueous solution with a dosage of 0.025 g/ml of Struvite, seed germination was 93.3% for both variants (Fig. 2).



A. B. 1-Control

Fig. 2. Germination of radish seeds on the 5th day after the start of the research.

The moisture content of germinated seeds was 96.20%±0.40 for variant A. and 96.00%±0.34 for variant B. Consequently, the reliable value of the experiment is [4]:

$$P_1 = \frac{1}{0{,}4^2} = 6{,}25; \qquad P_2 = \frac{1}{0{,}34^2} = 8{,}65;$$

$$\overline{X} = \frac{96{,}20 \cdot 6{,}25 + 96{,}00 \cdot 8{,}65}{6{,}25 + 8{,}65} = 96{,}08; \qquad (2)$$

The error of the result in case of uneven measurement is:

$$S_X = \left(\sqrt{6{,}25 + 8{,}65}\right)^{-1} = 0{,}2591; \qquad (3)$$

Since the error of the result does not exceed 3%, the measurement results for the two variants are reliable and close in value.

Conclusions. After conducting a set of experimental studies on model solutions established:

1. The reagent method allows extracting simultaneously ammonium ions and phosphate ions with the achievement of the degree of adsorption 93.91% and 95.26%, respectively.
2. The most optimal conditions for the process of reagent precipitation of ammonium nitrogen at an initial concentration of NH_4^+ - N – 470 mg / l are pH 8.5 and the stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{3-} = 1,5 : 1: 1,5.
3. The humidity of the mineral fertilizer under optimal conditions is 40.7%, respectively, the established formula of crystalline hydrate - $MgNH_4PO_4 \cdot 5H_2O$.
4. These data demonstrate the ability of synthetic struvite effectively to influence the germination of radish seeds and, obviously, the seeds of other plants of the radish genus of the cabbage family.
5. The need for further research to determine the effectiveness of struvite in terms of its impact on agricultural crops, as well as the ecotoxicological characteristics of the resulting fertilizer, was determined.
6. It was found that the method of obtaining struvite does not significantly affect seed germination and germination humidity.

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