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ORIGINAL ARTICLE

Perspectives of integration the technology of ion-exchanging ammonium extraction from the system of municipal drain water purification

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The exchange capacity and the selectivity of different ion-exchange products regarding the ammonium ions in purification processeswere measured; the regenerative preparation compounds' influence on efficiency of conduction of ion-exchange products regeneration was learnt. The adsorption processes were adapted to known technological schemes of sewage and polluted surface water purification, that was polluted with ammonium ions. There were measured the technological aspects of water purification by using adsorption on natural dispersed sorbents. The technological schemes of drain water purification from ammonium ions were developed.
Key words: environmental security; natural clay sorbents; adsorption; ion exchange.

Introduction

Pollution of natural water reservoirs as a result of human economic activity is one of the most critical problems of the present. The development of the industrial production, the energy industry, increase of the territories used in agriculture and development of urban infrastructure require intensive exploitation of water resources, which is irreversibly associated with an increase in the load on water bodies due to discharge of wastewater there. (Kwok K.W. et al., 2014; Loganathan S., Murugan T., 2017; Dadi,D. et ai., 2017).

The anthropogenic load on water sources in Ukraine is close to a risk level, notwithstanding the decrease of water use in general. It should be noted that the most critical situation is observed in regions where agricultural and industrial capacities are concentrated (Nieder,R. at ai.,2018).

Contaminants that get into the water reservoir are the threat to the ecosystem life in general and the hydrobionts, in particular. Water pollution can be divided into such types: industrial, agrochemical and domestic, which is based on the nature of substances thathumans artificially put into water (Kok, J.W.K. et al., 2015; Wang Z.Y. et al., 2015; Pham,H.G. et al., 2017) Industrial contamination is caused by wastewater from facilities that throw various toxic and harmful substances that are normally difficult to access.

The main industrial sources of ammonium emissions are plants where ammonia, fertilizers and nitric acid are produced. The overall ammonia emission in Europe caused by industrial processes, fertilization and production wastes per year is estimated around $6{,}434 \cdot 10^6$ tones.

Ammonium is soluble in water, the solution has an alkaline reaction due to the formation of ammonium hydroxide. Its taste in water is felt at a concentration of 5-10 mg / l, and the smell at 0.037 mg / liter. [2].

Due to the excess amounts of ammonium compounds in the reservoirs, the primary productivity of Cianophyta and plankton algae is increased, for instanceMicrocystis, Merismopedia, Oscillatoria, Anabaena, Peranema, Euglena, Chlamydomonas. These algae are the indicators of eutrophication (the enrichment of a water body with nutrients, usually with an excess amount of nutrients). Thus, the concentration of Cianophyta may exceed 1 million cells per cubic centimeter of water. As a result, up to 2cm film of spores and dead Cianophyta appears on the surface of the water . This process dramatically affects the reduction of zooplankton. (Suominen, S. et al., 2017; Kennicutt, M.C. et al., 2017; Harke, M.J. and Gobler,C.J., 2015).

The pathogenic effect of Cianophyta on the livelihoods of fish has a complex nature: the functions of their organism are disturbed both by the influence of Cianophytaend toxins, toxic substances that are bacterial based, as well as because of the decay processes in the water that release toxic gases (methane, hydrogen sulfide, ammonium), which cause oxygen deficiency. Mostly, the firmness of fish towards the toxicants is determined by the ecological characteristics of the species, than their systematic situation. (Sukenik, A. et al., 2015; Overstreet,R.M. and Hawkins,W.E. 2017; Guzzella, L.M. et al., 2018; Ezekwe,C.I. and Edoghotu,M.I., 2015;) Fish species such as Misgurnus, carp, carassius, inhabited in slit waters, belong to the ecological group of fish with high resistance to the content of ammonium compounds in water. The group of medium-stable species

includetrench, common roach, common bream, gambusia, loach, scradinius. Species that inhabiting flowing waters are quite vulnerable to ammonium compounds (goby, perche, squalius,gobio)[3].
The manifestation of ammonium compounds toxic effects is showed in the reduced ability of fish's hemoglobin to bind oxygen. It is established that the toxic concentration is (mg / l): for young trout 0,2; adult rainbow trout 0.6; brown trout 0.8,tench and carp 2.0. toxic concentrations of ammonia is10 mg / l and more are capable of delaying embryonic development, in particular for roach.
The intoxication signs of fish are: seizures, excitement, bustle and plowing on the coast; death with wide open gills and mouth; the gills and trunk are covered with mucus. The mechanism of action of toxic effects of ammonium compounds is to excite the central nervous system, hemolysis of red blood cells and the effect of gill epithelium.(Das, M.K. et al., 2015; Awolusi, O. at ai,.2017).
It should be noted that the ammonium compounds contained in natural waters in the process of nitrogen circulation are gradually subjected to nitrification with the participation of microorganisms. So, bacteria Nitrosomonas oxidize ammonia to nitrates.

$NH_4^+ + 1,5O_2 \rightarrow NO_2^- + H_2O + 2H^+$ (1.1)

$NH_4^+ + 1,5\ O_2 + 2HCO_3^- = NO_2^- + 3\ H_2O + 2\ CO_2$ (1.2)

With the participation of bacteria Nitrobacter, there is a further conversion of nitrites to nitrates

$NO_2^- + 0,5O_2 \rightarrow NO_3^-$ (1.3)

Atthefinalstageofthecyclenitrineand nitrate ions undertheactionofbacteria-denitrificatorsshould be convertedintogaseouscompoundsN_2 or N_2O (Farges, B. et al., 2012; Bock, E. and Wagner M.,2013). .
The stability of the natural lifecycle of Nitrogen is violated by increased volumes of nitrogen-containing wastes of various industries and the growth of fertilizer usage. The consequence of this violation is the accumulation of nitrates and nitrites in the water reservoirs, which can lead to toxic poisoning. Nitrites and nitrates that come to the intestines of fish cause irritating effects on the mucous membrane and cause oxygen starvation of tissues after absorption into blood, thus hemoglobin loses the ability to bind and give oxygen. The osmoregulation of fish is disturbed (ions Na + and K + do not stay in the body of fish and are displayed outwards.

Materials and methods

It is extremely important to determine the method of purification from ammonium pollution, the source of pollution and further direction of the use of purified water. So, municipal and industrial drainage have a medium concentration of ammonium ions of 40 mg / dm3, and agrochemical pollution causes significantly higher concentrations in surface waters (70 mg / dm3), which leads to changes in the parameters of the main stages of the technology (adsorbent consumption, adsorption time, sedimentation time, and etc.). Purification of drinking water requires additional water disinfection. Generally such process (ultrasound, UV treatment) accelerates the sedimentation of used sorbent (Yurii Tulaydan, at ai.,2017) .
The rational methods of extracting ammonium from waste and surface waters should be recognized as sorption. The advantages of those are high efficiency and, if there is a national raw material base, low cost. The analysis of the known technologies of waste water purification from ammonium pollution verifies the promising use of natural sorbents for purification of water and expediency of the sorption methods.
There were conducted studies of the purification of urban wastewater from ammonium pollution by means of ion exchange (concentration of ammonium ions by clay sorbent), and by adsorption of ammonium ions by natural sorbents during constant stirring.
The most effective ion-exchange natural material in the ion-exchange process is zeolite, which has a fairly high dynamic volumetric capacity (3.0 mg NH^{4+} in the last cycle). Additionally, zeolite has a greater selectivity to exchange ammonium ions, with a high total salinity of wastewater. Thus, when using test solutions, wich are by cation content close to the real urban, the natural zeolite coefficient of selectivity is 13.1, 0.3 for synthetic zeolite. After a phase of saturation of natural zeolite, only less than ¼ exchange centers are occupied with calcium and magnesium ions. Therefore, with regard to the selectivity of ammonium sequestration, the best results can be achieved using natural zeolite, while other ion exchange materials are more selective to hard water (Andriy Malovanyy, at ai., 2014; Volodymyr Shmandiy at ai.,2017).

Results

We propose a basic technological technology scheme of ion exchange ammonium extraction from urban waste water. We analyzed possible variants of integration of the proposed technology into a comprehensive scheme of urban wastewater purification. In this case, all of the ammonium can be removed by ion exchange. The disadvantage of this scheme is that after its implementation, water needs further decontamination and purification from organic impurities. The biological method should be used for this. In this case, the drain water goes through the gratings, sand traps, primary settlers. After passing through the primary settler for wastewater and the filter, ammonium extraction is carried out with the ion-exchange processes. When ion-exchange material is regenerated by a NaCl solution of a given concentration, the resulting ion exchange concentrate is precipitated by the reagent method by adding a solution of magnesium salt and orthophosphoric acid to it (S.V. Vakal, and M.S. Malovanyy, 2016) .
The resulting suspension is precipitated for 1 hour. The suspension is then filtered. Precipitation, with an initial moisture content of 90.7%, is dried, and then packaged as ready-to-use fertilizer. The filtrate can be used to prepare a regenerative solution.

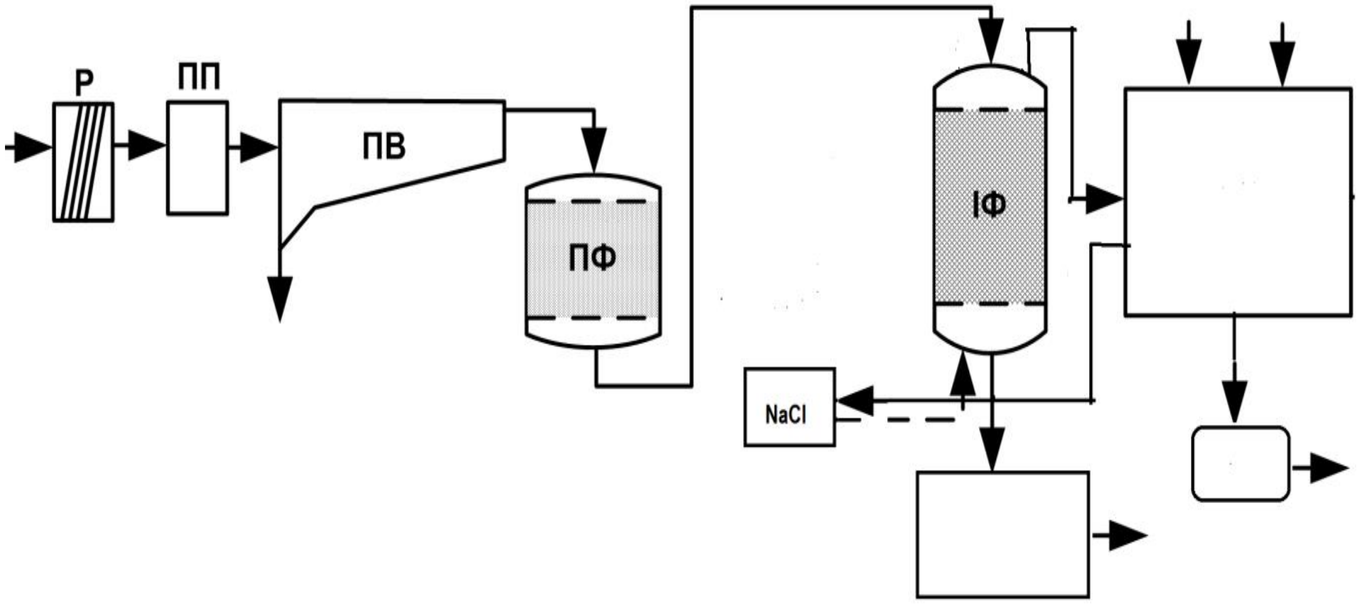

Fig. 1. Technological scheme of ammonium containing drain water purification from ammonium ions using ion exchange method: Р – grating; ПП – sand trap; ПВ – primary settler for wastewater; ПФ – sand filter; ІФ – ion-exchange filter; РО/К – reagent precipitation of concentrate; С – drier; ПР – receiver of purified water.

We proposed the technology of adsorption purification of ammonium-polluted industrial or municipal waste water. It consists of two following stages:

1. Adsorption of ammonium ions by natural sorbents in a device with a stirrer.
2. The separation of usedsorbents from purified liquids.

The temperature increase rarely can occur as the parameter of intensification of the first stage, which is economically unprofitable. In addition, in the case of temperature rise, the ammonium desorption from the contaminated liquid into the gas phase happens and causes secondary pollution of the atmosphere (the sealing of technological equipment is not only difficult to implement, but economically unprofitable). The effective parameter of the intensification of the adsorption process is the dispersion of the sorbent. Since with the increase of dispersion, the surface of mass transfer and the adsorption capacity of the applied natural sorbent increase. However, for the second stage, increasing dispersion leads to an increase in the time of the process, reduction of the degree of purification of the liquid from fine-grained mechanical contaminants. That is why the technology of purification of water from ammonia cal nitrogen by adsorption on natural disperse sorbents must be considered as integrated, and the conclusion on optimal conditions for its implementation should be made on the basis of a coherent analysis of both stages of the integrated process.

As for the comparison of the adsorption capacity of individual sorbents with respect to ammonium ions, experimental data shows that the maximum adsorption capacity is observed in zeolite and palygorskite. However, the adsorption capacity of glauconite is also quite high, which allows it to be recommended for use in technologies of drinking water purification from ammonium ions. The question of the choice of a specific adsorbent in each case should be solved by a feasibility study of possible options, taking into account the price of the sorbent, its adsorption capacity relative to the pollutant, the characteristics of the purification equipment (Myroslav Malovanyy, at ai., 2015; Elizaveta Kostenko at ai.,2017).

There is a technological scheme of periodic process of industrial wastewater purification from ammonium ions on Fig. 2.

According to the technological scheme, the ammonium-contaminated wastewater is fed from the collecting system to the collectorЗб-1, from which the it is pumped with the pump Н-1 into the reactor with a stirrer (M). A portion of the sorbent is loaded through the worm transporter ШТ-1and weight batch (ВД). The size of the portion is determined using the data of the above studies based on the concentration of ammonium ions in the effluents. The regulation valve ВР2 is used to control the correlation between the sorbent and the waste water.

After the reagents are loaded, the mixer is switched on for a certain time, which is determined using the data of the studies. The process of cleaning the effluents from the ammonium ions by the sorbent is going.

After the stage of the wastewater purification (the duration of which is determined based on the kinetic dependences we have obtained), the pulp enters the settler (В-1) through the regulating valve (ВР3). In ther settle the suspension is lit under the action of gravitational forces. The purified drains are pumped into the collector (Зб-1) with the pump Н-2. The surface water are bend through the valve ВР14 from the collector. The precipitate with the used sorbent from the settler В-1 enters the worm transporter ШТ-2.

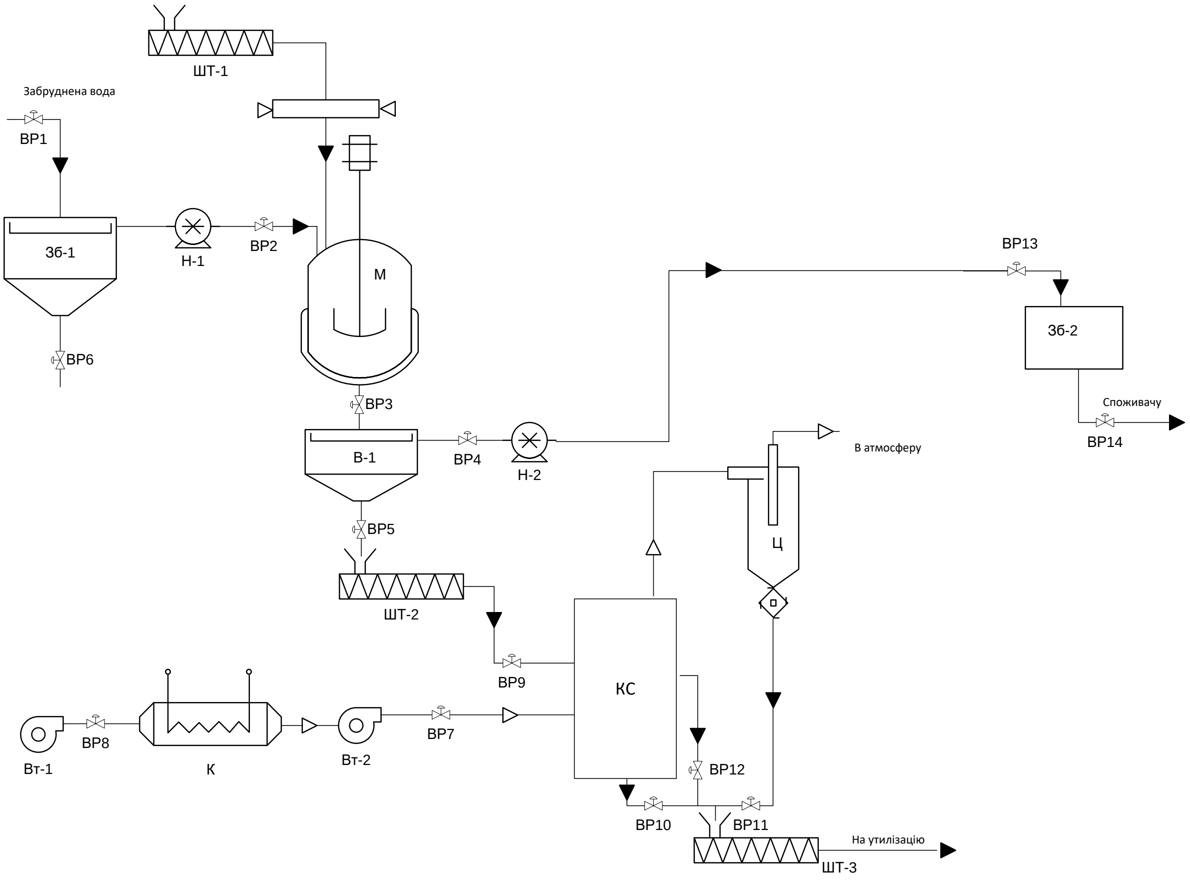

Figure 2. Principal technological scheme of ammonia-containing wastewater purification from ammonium ions using natural disperse sorbents:В-1 - the settler; ШТ-1, ШТ-2, ШТ-3 - the worm transporter; ВД –weight batch;
М – reactor with a mixer; Н-1, Н-2 – pulp; 3б-1, 3б-2 –collector; Вт-1,2 – fan; К – heater;С – drier; Ц – centrifugal separator; ВР-1-14 – regulation valve

For further usage of worked sorbent, for instance as a part of prolonged action fertilizers as a carrier of ammonium ions (one of the elements of plant nutrition), we offered to dry the sorbent in the drier (C). Air supply is made by fans Вт-1 and Вт-2 and regulated by valves ВР10, ВР12. Wet sorbent from worm transporter ШТ-2 is put with certain productivity, that is maintained with valves ВР10 and ВР12. The dried sorbent from the drier goes through worm transporterШТ-3 to the warehouse for further exploitation. As a result of drying process, the partial passing out of sorbent to the atmosphere happens. That is why we offer to clean air in centrifugal separator additionally and put extracted sorbent to worm transporter ШТ-3 through valve ВР11.

Discussion

The addition of excess amounts of ammonium compounds to the water reservoirs due to industrial processes, as well as usage of fertilizers and animal wastes leads to an increase of the primary productivity of Cianophyta and plankton algae, which leads to a decrease of zooplankton and the emergence of hypotonic conditions that cause the loss of hydrobionts.The article presents the technologies of adsorption purification of sewage and surface water in systems with natural disperse sorbents that ensure compliance the forms of preventing harmful effects on the environment and human life.
The principal technological scheme of the technology of ion exchange ammonium extraction from urban wastewater is proposed, possible variants of integration of the proposed technology into the integrated scheme of urban wastewater treatment are analyzed.The basic technological scheme of the process of adsorption of drain water purification or of urban effluents from ammonium ions with further utilization of wastes for production of ammonium nitrate has been developed.

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