УДК: 628.2

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USING OF ZEOLITE TO CLEAN THE EFFLUENTS OF MEAT ENTERPRISES

Ecological evaluation of effluents from meat enterprises shows that processing of agricultural production is accompanied by consumption of large amount of water which is saturated with organic substances and a number of biogenic elements (phosphorus and nitrogen compounds) during its industrial utilization. Effectiveness of natural sorbents klynoptylolit use for removing of such pollutants as ammonium and phosphate ions and protein fractions was theoretically substantiated and proved. Adsorptive capacity of sorbent concerning above mentioned pollutants during investigation of one-component system sorption was established; and influence of contamination of drains on equilibrium and speed of adsorptions during research of two- and three-component model systems was determined. Equation of isotherms of adsorption for one-, two- and three-component systems, based on the law of Henry, was proposed. Equilibrium values of adsorptive capacity of sorbent were investigated and kinetic curves were built, which made it possible to establish necessary time for removing of pollutants from drains. A mathematical model of pore-diffusion sorption is presented and diffusion coefficients: $D^*_{NH_4^+}= 2.84\times10^{-11}$ m^2/s, $D^*_{P_2O_5}= 2.92\times10^{-10}$ m^2/s, and $D^*_{alb.} = 6.54\times10^{-13}$ m^2/s, are determined. The efficiency of worked out sorbent application as fertilizer was experimentally proved.

Key words: sewage, meat enterprises, zeolite, cleaning, adsorption, fertilizer.

Здійснено екологічну оцінку стічних вод м'ясопереробних підприємств, яка вказує на те, що перероблення сільськогосподарської сировини супроводжується споживанням значної кількості води, яка після її промислового використання збагачується органічними речовинами, а також біогенними елементами, насамперед сполуками азоту та фосфору. Теоретично обґрунтовано та підтверджено експериментально ефективність застосування природного сорбенту – Сокирницького клиноптилоліту для вилучення таких забрудників зі стоку, як йони амонію, фосфати та білкові фракції. Встановлено адсорбційну ємність сорбенту щодо цих забрудників у результаті дослідження сорбції однокомпонентних систем та впливу супутніх забруднень стоків на рівновагу та швидкість адсорбції під час дослідження дво- та трикомпонентних модельних систем. Запропоновано рівняння ізотерм адсорбції для одно-, дво- і трикомпонентних систем, основані на законі Генрі. Досліджено рівноважні значення адсорбційної ємності сорбенту та побудовано кінетичні криві, за якими встановлено необхідний час вилучення забрудників зі стоків. Наведено математичну модель внутрішньодифузійної сорбції та визначено коефіцієнти дифузії: $D^*_{NH_4^+}$ = 2,84×10^{-11} м^2/с, $D^*_{P_2O_5}$= 2,92×10^{-10} м^2/с, $D^*_{білку}$ = 6,54×10^{-13} м^2/с. Експериментально підтверджено ефективність застосування відпрацьованого сорбенту для удобрення сільськогосподарських угідь.

Ключові слова: стічні води, м'ясопереробні підприємства, цеоліт, очищення, адсорбція, добриво.

The problem statement and its connection with important scientific or practical tasks

Industrial complexes are of great progressive importance in the development of cattle breeding, which, in turn, is economically effective and gives opportunity to supply population with meat products.

About 1.6 million tons of pork and beef and 0.5 million tons of poultry are produced in Ukraine every year. But development of agroindustrial complexes is connected with the environmental pollution.

Meat processing enterprises need a lot of clean water. To slaughter and processing one carcass of it is required 1500 l of water (beeves), 880 l (pigs), 550 l (calves). To meet technological demands one needs 4900 l of water for processing 1 ton of beef and 1100 l for processing 1 ton of pork. Due to this about 40 min m^3 of sewage per year - this equals to about 400 mln. m3 of urban sewage. Average concentrations of pollutions (mg/l) are as follows: suspended substances – 1200, fats – 200-500, NH_4^+ – 14-57, P_2O_5 – 7-60. The temperature varies from 12 to 27°C, depending on the season. They also contain a great numbers of microorganisms, pathogenic flora including [1,2].

About 95% of pollutants related to biological oxygen consumption from these enterprises processing waste are protein substances. Thus, when cleaning from protein fractions is not done properly, valuable food stuff is lost and environment suffers a lot. It is well known that protein substances and fats favor the development of different rotten microflora. Due to putrefaction of organic nitrous substances, which are a part of sewage, ammonia is formed; and organic protein components, which contain sulphur, in the process of putrefaction form sulfide. During aerobic decay of organic substances, oxidized products are formed, such as CO_2, HNO_3, HSO_4 et al. Under anaerobic conditions, during putrefaction of protein substances, peptones, amino acids, ammonia, sulfide, phenols and other substances are formed.

Pollution occurs not only because of improper cleaning but also due to a great number of biogene elements in organic substances, mainly nitrogen and phosphorus. Thus, when such elements get into water they cause eutrophication. In consequence of progressive development of phytoplankton, the level of dissolved oxygen becomes much lower, which leads to the disturbances in its self cleaning and destruction of aerobic flora and fauna [1,3].

The aim of investigation

Theoretical substantiation and experimental investigation regarding the use of zeolite from Sokyrnytskyi deposit with klynoptylolit in sodium form as the main constituent, concerning the ions of ammonia (NH_4+, phosphates (P_2O_5) and albumin in the process of their adsorption from sewage waters of meat processing enterprises; and also expediency of sorbent usage as fertilizer vegetation needs.

Review of recent research and publications

Ecological evaluation of quality of sewage from meat processing enterprises shows that content of a number of pollutants override the prescribed limiting rates as follows: ammonia nitrogen 1,15 times higher, phosphates 2,4 times higher, and the content of protein fractions is about 7 g/l. To reduce contamination level of water bodies, many different cleaning methods are used. One of them is using natural sorbents[4,5].

In the presented work zeolite, the main content of which was klynoptylolit in sodium form, was used. Statics and kinetics of sorption of ammonia ions, phosphates and protein on this sorbent, in the range of concentrations which is usual for sewage from meat processing enterprises, was investigated [6].

Method of determination

Conditions for determination of adsorptive capacity of zeolite related to ions of ammonium, phosphates and protein in model one-component systems, and two - and three-components systems were as follows: correlation water solution - sorbent : 200 ml of ammonia nitrate and phosphate solution and 100 ml of albumin solution, prepared in distilled water of different initial concentrations ($C_{NH_4^+}$= 0.55-3.33 mh-ekv/dm^3, ($C_{P_2O_5}$ = 0.035-0.211 mh-ekv/dm^3, C_{alb} = 0.015-0.15 mh-ekv/dm^3 (pH solutions containing protein components within 5.6-5.74) ~ 1 g of clinoptilolite.

Determination of static in the process of sorption takes place during mixing for two days at +(20 ± 0,5)°C. Conditions necessary for determination of exact time for absorption of ammonia nitrogen , phosphates and protein from sewage on clinoptilolite: to three formerly solution (capacity 1 cubic dm) - the first with ammonia nitrogen (Cfirst = 2.19 mh-ekv/dm^3), the second - model two-component solution with ion of ammonia (Cfirst = 2.17 mh-ekv/dm^3) and phosphates (Cfirst = 0.207 mh-ekv/dm^3), the third solution - three-component system with ammonia nitrogen (Cfirst = 2.17 mh-ekv/dm^3), phosphates (Cfirst = 0.213 mh-ekv/dm^3) and albumin (Cfirst = 0.077 mh-ekv/dm^3 (pH - 6.6)) added ~ 10 g of sorbent. The process was realized with the help of mechanical mixture for 20 min at + (20 ± 0,5) °C.

To investigate the influence of fertilizers on kinetics of growth there were made four experiments: substrate - without fertilizer (control); 10 g of natural zeolite; 10 to 20 g of worked out sorbent. In the process of plant growing there was given information concerning their nourishment and watering.

Experimental investigations

Taking into account obtained isotherms of sorption [6], we may confirm that the curves of isotherms lie in the field of low concentrations and are the first stage of Langmure isotherms that correspond to dependence and are described by means of Henry equalization: mh-ekv/dm^3: $0< C_{NH_4^+}< 2$, $0 < C_{P_2O_5}< 0,02$, $0 < C_{alb}< 0,13$:

$a^*_{pollutants} = m\, C_{pollutants}$: $a^*_{NH_4^+} = 0.271\, C_{NH_4^+}$; $a^*_{P_2O_5} = 6,91\, C_{P_2O_5}$, $a^*_{alb} = 0.014\, C_{alb}$,

where $a^*_{pollutants}$ ($a^*_{NH_4^+}$, $a^*_{P_2O_5}$, a^*_{alb}) – equilibrium concentration of pollutants adsorption on zeolite, mh-ekv/g; m - coefficient of proportionality in equation of Henry, dm^3/mh-ekv.

Investigation of sorption isotherms of two - and three-component systems where along with polluting components there were presented other pollutants, shows that when concentration of polluting compounds in solution is higher, adsorptive ability of sorbent to each of components is lower. Besides, concentration of adsorbate is larger and can absorb more polluting components from the solution. For two- (1) and three-component (2) systems the dependency is as follows:

$\sum a^* = f_1\, m_1\, C_{NH_4^+} + f_2\, m_2\, C_{P_2O_5}$, $\sum a^* = 0.69\, m_1\, C_{NH_4^+} + 0.778\, m_2\, C_{P_2O_5}$, (1)

$\sum a^* = f_{1,1}\, m_1\, C_{NH_4^+} + f_{2,1}\, m_2\, C_{P_2O_5} + f_3\, m_3\, C_{alb}$, $\sum a^* = 0.29\, m_1\, C_{NH_4^+} + 0.15\, m_2\, C_{P_2O_5} + 0.64\, m_3\, C_{alb}$; (2)

where f – degree of reduction in the adsorption capacity of zeolite.

According to kinetic curves of sorption of pollutants, it was stated [7,8,9] that in 20 minutes after contact of solution with sorbent concentration of ammonia nitrogen was two times lower compared with initial concentration and reached permissible concentration. Phosphate content was four times lower and reached permissible concentration. Concentration of protein was also low, but effectiveness of sorption depends on pH medium.

According to obtained results, there was described the mathematical model of sorption process of polluting components and calculated appropriate diffusion coefficients (D *):

$D^*_{NH_4^+} = 2.84 \times 10^{-11}$ m^2/s, $D^*_{P_2O_5} = 2.92 \times 10^{-10}$ m^2/s, $D^*_{alb} = 6.54 \times 10^{-13}$ m^2/s.

Thus, adsorptive ability of sorbent as to ammonia nitrogen is as follows: $a^*_{NH_4^+} = 0.000833$ g/g, $a^*_{P_2O_5} = 0.000922$ g/g, 1 g of sorbent after sorption process contains 0.0018 g of fertilizer. Besides, worked .out zeolite complex contains protein, which is of high value and its adsorptive ability is $a^*_{alb} = 0.153$ g/g. Given components are pollutants, but in agriculture they "improve" the yield. Zeolite and sorptive components fertilize the fields, which are why, their usage helps to solve the problem of fertilization and also to get the waste-free of technologies in the process of sewage cleaning.

Experiments showed, that plants fertilized with 10 and 20 g of worked out zeolite complex were two times heavier than those which were fertilized with only 10 g of zeolite and those which were fertilized none (Table 1) [10].

Table 1

Comparison of the obtained masses of plants that were grown at the different dosage of fertilizers to substrate

Item	Name of fertilizing component	Mass of plants, g
1	Without a fertilizer	0.061
2	10 gzeolite	0.05
3	10 gof worked out zeolite complex	0.08
4	20 gof worked out zeolite complex	0.136

Conclusion

Experimental investigations made on model solutions and real sewage of meat processing enterprise pointed at effective usage of natural zeolite and cleaning from nitrogen compounds, phosphates and protein. Worked out sorbent can be used as fertilizer for agricultural fields, as not only zeolite but its adsorbtive components are good fertilizers.

Paranjak R.P. Ekologhichna ocinka stichnykh vod m'jasopererobnykh pidpryjemstv ta fizyko-khimichni metody jikh ochyshhennja / R.P. Paranjak, O.V. Macusjka // Siljsjkyj ghospodar. – 2008. - №1 – 2. – S.38-42. 2. Savchenko Y.L. Okhrana sredы ot zaghrjaznenyja otkhodamy zhyvotnovodstva / Y.L. Savchenko, V.N. Blaghodatnyj. –K.: Urozhaj, 1986. – 128 s. 3. Ochystka stochnykh vod mjasnoj y molochnoj promyshlennosty / [S.M. Shyfryn, Gh.V. Yvanova, B.Gh. Mykulov, Ju.A. Feofanov]. – M.: Leghkaja y pyshhevaja promyshlenostj. – 1981. – 272 s. 4. Myronenko M.A. Sanytarnaja okhrana vneshnej sredy v rajonakh promyshlenno-zhyvotnovodcheskykh kompleksov / M.A. Myronenko, Y.F. Jarmolyk, A.V.Kovalenko // Ghyghyenycheskye osnovy okhrany okruzhajushhej sredy. – M.: Medycyna. – 1978. – 160 s. 5. Macusjka O.V. Ekologho-ekonomichna dociljnistj zastosuvannja kavitacijno-adsorbcijnogho sposobu ochyshhennja stichnykh vod m'jasopererobnykh pidpryjemstv/ O.V. Macusjka, R.P. Paranjak, V.V. Sabadash, Ja.M. Ghumnycjkyj // Naukovyj visnyk LNUVM ta BT imeni S.Z.Ghzhycjkogho. – Ljviv, 2013. – T.14. - № 1(55). – Ch.4. – S.123-127. 6. Macusjka O.V. Adsorbcyja komponentov stochnykh vod pryrodnymy sorbentamy / O.V. Macusjka, R.P. Paranjak, Ja.M. Ghumnyckyj // Khymyja y tekhnologhyja vody. - 2010. – T.42(4). – S.399-408. 7. Humnytskyy Y. Statics and kinetics of ammonium nitrogen sorption on natural zeolite under periodic conditions / Y. Humnytskyy,O. Matsuska // Chemistry and chemical technology. – 2011. – V.5. – №1. – R.7-11. 8. MacusjkaO.V. Statyka ta kinetyka sorbciji fosfativ na pryrodnomu ceoliti u periodychnykh umovakh / O.V. Macusjka, R.P. Paranjak, Ja.M. Ghumnycjkyj // Vodneghospodarstvo Ukrajiny. – 2011. – №2. – S.25-29. 9. MacusjkaO.V. Ochyshhennja stokiv vid bilka pryrodnymy sorbentamy / O.V. Macusjka, R.P. Paranjak // NaukovyjvisnykLNUVMtaBTimeniS.Z. Ghzhycjkogho. – 2011. – T.13. – №2(48). – Ch.2. – S.255-261. 10. MacusjkaO.V. Doslidzhennja fiziologhichnykh pokaznykiv roslyn pid chas jikh udobrennja sorbentom z komponentamy stichnykh vod / O.V. Macusjka, R.P. Paranjak, Ja.M. Ghumnycjkyj // Naukovyj visnyk LNUVMtaBT imeni S.Z. Ghzhycjkogho. – 2011. – T.13. – №4(50). – S.291-296.