IN SITU RIVER WATER TREATMENT WITH DOMESTIC MATERIALS USING AS SORBENTS

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Abstract: *Argichi river is the deepest river running into the lake Sevan. The river waters irrigate areas under crops of more of villages of Gegarkunik region in Armenia. The river Argichi is a habitat for reproduction brought in the Red book of fauna of Armenia for fishes. Hence, for the purpose of maintenance of safety of fauna of the rivers, it is necessary to treated river water. This research includes a situation of sewage in river Argichi, type and quantity of polluted materials and products, the attempts to present of the sewage treatment systems. and the development of technology for sorbent with polysorption properties with application of natural materials widespread on territories of Armenia.*
The results of purposeful researches are submitted in the field solutions and waste water of application natural zeolites as sorbents for removal of organic substances from water.
High level of adsorption of organic substances natural zeolites is provided with their initial saturation by ions of calcium and magnesia. It has been found advantageous to organic compounds sorption by natural zeolites. The advantages of natural zeolite in comparison with other sorbents are technological stability, low cost, availability, filtering properties. Thus, the sequence of operations in sorption will be the following: the first is sorption of metals and ammonia, the second is sorption of organic substances.

Keywords: *The Argichi river, Sevan, zeolite, modified zeolite, sorption, ammonia, organic substances,*

Introduction

The Argichi river has been the deepest river running into the lake Sevan and remains an important irrigate areas under crops of more of villages of Gegarkunik region in Armenia. The water situation in river Argichi and the type and quantity of polluted materials and products depend from many factor. The Argichi waters pollutes with metal ions, organic pollutants as petrol products and pesticides.
This study includes waste the attempts to present the wastewater treatment systems. One of the best method for wastewater treatment from pollutants is an application of inorganic and organic adsorbents. Current treatment processes usually involve also biological degradation or chemical oxidation of the waste organics.

Nowadays natural zeolites are focused in applications in the sector of wastewater decontamination, for instance for removal of ammonium from municipal sewages and abatement of radionuclides from effluents of nuclear power plants. There are many reasons for zeolites using in mentioned fields: good selectivity for many toxic cations and harmful compounds , as adsorbents organic compounds.
Zeolites occur in nature in specific kinds of rocks. Zeolite rich rocks are widespread in Northern part of Armenia, occurring in very extended geological formations. The zeolite types are exclusively clinopilolite - in Idjevan / Northern-East of Armenia / and mordenite in Shirak / Northern-West of Armenia/. Taking advantage of their high zeolite content, high cation exchange capacity and selectivity many

agricultural applications of Armenian zeolites have been proposed recently. Nowadays some of Armenian natural zeolites were characterized from the point of view of chemical composition, type of structure and chemical, thermal and radiation resistance. The ammonium in water and wastewater can be toxic to the aquatic life and should be removed to prevent environmental protection. Several processes are currently used for the removal of ammonium from aqueous solutions. Ion exchange on natural zeolites is among the methods most commonly employed.

Materials and methods

Nowadays natural zeolites are focused in applications in the sector of wastewater decontamination, for instance for removal of ammonium from municipal sewages and abatement of radionuclides from effluents of nuclear power plants [1-4]. There are many reasons for zeolites using in mentioned fields: good selectivity for many toxic cations and harmful compounds [1-2], as adsorbents organic compounds [5-7].

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Armenian natural zeolites - mordenite and clinoptilolite were dehydrated at 400^{o}C in vacuum (0.1 mm) for 3-4 hours. Clinoptilolite and mordenite were prepared by heated pile method, using 0,5 and 1 N solution of $CaCI_2$. Adsorptive isotherms were determined for the equilibrium status of water containing organic compounds in concentrations of 0.0025 to 0.070 mol/L on the zeolite sorbents. Adsorption was carried out at a temperature 27.0^{o}C, the average temperature in Argichi river around of Sevan in spring and autumn.

***The removal of the pollutants realized for each one separately by two type* :**

1) The precisely weighed portions of sorbents are brought in to the certain volumes of petroleum substances in water, which initial concentration vary. The mix is carefully shaken up during 6 h.

2) Polluted by hydrocarbons water passes through a column filled with adsorbents. Hydrocarbons are taken from water, remaining in limits of adsorption column. The treated water leaves a column for direct use or further treatment.

Further test is settled. The quantity of the besieged substance on zeolites is determined by the precipitated organic fraction in the filtered solution by the methods of UV Spectroscopy, Highly Effective Liquid Chromatography and Refractometry.

Example for phenol sorption. The linear dependence between concentration of phenol in a water solution and appropriate molar refraction is preset at 20^{o}C. The measurements were carried out in concentration limits from 0,05 up to 0,3 mol/L. It was earlier established, that the sorption in these limits grows and has linear dependence on molar refraction. From graphic dependence is determined amount of adsorpted phenol [5-7]. The results are given in the tables 1-3.

Zeolites as materials well known for they ability to remove ammonia from waste water preferentially [8 -12]. One of the goals of this work is to investigate ion exchange of ammonium ($NH_4)^+$ on zeolites obtained from mentioned here deposits in Armenia. The ion exchange capacity of natural zeolites, especially from Armenian deposits, offers the possibility of their application to the purification of ammonia-contaminated water.

Example for ammonia sorption. After sorption of ammonia vapour produced by 1 N NH_3 solution by natural zeolites and its treated forms for 10 days at room temperature the adsorption data were plotted.

The ammonia adsorption by zeolites was investigated by IR spectroscopy. The results are given in the table 4.

Results and discussion

Argichi river water mainly is polluted by oil, fat, detergents, ammonia, metals as vanadium, manganese, selenium and others.

Adsorption from wastewater with organic pollutants involves concentration of the solute on the surface. Here, it has been had adsorption and desorption process together which will attain an equilibrium state. We used Dubinin-Radushkevich model for description of the adsorption data.

In the present work the results of purposeful researches are submitted in the field solutions and waste water of application natural zeolites as sorbents for removal of organic substances. ammonia, metal ions from water.

It is necessary to note, that partial sorption of water /1-2ml from 10ml of a solution for 4 hours sorption of a solution on sorbents / takes place.

Here is investigated each polluted ions, molecules separately. As organic compounds here is presented the results for benzene, phenol and aniline removal results.

It was established that with increase of concentration of solutions the amount of absorbed phenol is increased. Fairly active has modifided clinoptilolite by $CaCI_2$ and $MgCI_2$. The H-form of mordenite shows activity, where, on all probability, the formation of hydrogen connections takes place. Here is obtained the same results for aniline sorption too. The H-form of mordenite and clinoptilolite show activity, where, on all probability, the formation of hydrogen connections takes place.

The sorption of water-soluble oil products are compared between different samples of natural zeolites. High level of adsorption of organic substances natural zeolites is provided with their initial saturation by ions of calcium and magnesia. The present is confirmed also processed by calcium chloride zeolites.

Zeolites expose simultaneously hydroxyl groups, coordinatively unsaturated cations, as Lewis acid sites, and Lewis basic sites, anions, as O^{-2} ions, on their surface. In this case some of efforts to have additional hydroxyl groups and mentioned sites, appears a possibilities to increase acid-basic properties of zeolites.

Here was investigated the removal of organic compounds – benzene, aniline, phenol sorption process from waste water by means of natural zeolites.

On superficial groups of hydro group and atoms of oxygen of zeolites processes of formation of chemical bonds owing to molecular interactions with groups of hydroxyl / for phenol/ and amino groups / for aniline / proceed. Here is specially investigated the aniline retain on zeolites. By the IR-spectroscopic method it is confirmed, that at zeolite modifying by monoethanolamine here is a considerable change of properties of its surface. IR-spectroscopic researches were spent on zeolite of the Noemberyan / east-north part in Armenia / deposit. As result IR shows in the 1400-3700 cm^{-1} region for clinoptilolite (under treatments at 400^oC) and aniline -clinoptilolite samples after sorption equilibrium at room temperature and heating in vacuum. The free electron pair on nitrogen is less able to hold proton aniline is a weak organic base than aliphatic amines. Aniline also an amphiprotic compound, it can react as proton acceptor (in general) and as donor.

Along with the valence and deformation with the specific frequencies belonging to the zeolite (3600, 3450, 1630 cm-^{1}), in zeolite structure absorption peak, which can be carried to valence and deformation vibrations in OH - and CN-bonds monoethanolamine (3750, 2230, 2150, 1050 cm^{-1}) are observed. The new absorption peaks testifying to formation of intermediate connections are found out also: 3600, 3050, 2710, 2600 sm^{-1}. The absorption peak of 3600 sm^{-1} corresponds to energy of formation of hydrogen bond O H.

It has been investigated the phenol and other aromatic sorbtion from water solution. Phenols and aromatics / benzene, toluene, xylenes and others/ are discharged in open reservoirs, they destroy the microflora and have negative effect on human health. The major way to diminish the discharge of phenols dissolved in water is strong purification and reuse.

The methods are offered for successfully sorption of phenols and other aromatics from waste water in natural and modified zeolites The given method can be applied at rather low initial concentration of phenols and aromatics.

The oil products content in water before and method, after there was made a correction by liquid chromatography.
Here was investigated also adsorption capacities of zeolites after sorption ammonia after the sorption was estimated by gravimetric ans calcium or manganese from them chlorieds water solution.

Table 1. The sorption of phenol from a water solution on sorbents

/ Temperature 20°C, duration 4 hours /

Concentration of phenol in water solution	N_D^{20} initial	N_D^{20} after sorption on clinoptilolite/ gphenol./g sorption	N_D^{20} after sorption on Mordenite g phenol./g sorption	N_D^{20} after sorption on H-Mordenite g phenol/g sorption	N_D^{20} after sorption on on clinoptilolite modified g phenol/g sorption
0,05	1,3324	1,3320/ 0,0236	-	Full sorption	Full sorption
0,10	1,3328	1,3320/ 0,0470	-	1,3314/ 0,0752	Full sorption
0,15	1,3342	1,3325/ 0,0710	1,3338/ 0,0019	1,3322/ 0,0846	Full sorption
0,20	1,3355	1,3335/ 0,0940	1,3346/ 0,0047	1,3329/ 0,1034	Full sorption
0,30	1,3371	1,3350/ 0,1034	1,3361/ 0,0063	1,3345/ 0,1175	-

Table 2. Distribution coefficient of the oil products K_a (mg/g) during the sorption on clinoptilolite and others.

Sorbent	K_a / light organic[b]	K_a/ heavy organic
Clinoptilolite-tuff	50	300
Clinoptilolite-treatied with $CaCL_2$	160	540
Clinoptilolite- after treated with ammonia	220	580

b) Conditions t= 2 days, concentration of oil product in water – 70 mg/l

Table 3. Sorption of the oil from water solutions on sorbents

Sorbent	Weight of sorpted oil product/ mg [b]	% of sorpted oil product
Clinoptilolite-tuff	20	30
Clinoptilolite-treatied with $CaCL_2$	32	45
Clinoptilolite- after treated with ammonia	40	55

b) Oil product concentration in water 70 mg/l, 100 gr sorbent, V water – 1000 ml

The ammonium in water and wastewater can be toxic to the aquatic life and should be removed to prevent environmental protection. Several processes are currently used for the removal of ammonium from aqueous solutions. Ion exchange on natural zeolites is among the methods most commonly employed. Zeolite as material well known for they ability removes ammonia from waste water preferentially [1,2]. One of the goals of this work is to investigate ion exchange of ammonium ($NH_4)^+$ on zeolites obtained from mentioned here deposits in Armenia. The ion exchange capacity of natural zeolites, especially from Armenian deposits, offers the possibility of their application to the purification of ammonia-contaminated water.

Table 4. The adsorption of NH_3 [g] on the zeolites /10g/

N	**Zeolite**	1day	3day	5day	7day	10day
1.	Mordenite	10.38	10.51	10.62	10.70	10.76
2.	Mordenite Treated by 0,5N $CaCI_2$	10.86	11.02	11.15	11.22	11.38
3.	Mordenite Treated by 1N $CaCI_2$	11.14	11.71	12.13	12.46	12.98
4.	Clinoptilolite modified by 1N $CaCI_2$	11,76	12,04	12,32	12,54	12,98

At first the ability of mordenite is compared to purify river waste water with normal river gravel. The tested zeolite had superiority over gravel in the oxidation of ammonium ions through nitrite ions into nitrate ions. The decrease in the amount of ammonium ions resulted not only exchange with Ca^{2+} mainly in the zeolites, but also the microbial oxidation on the surface of the zeolites. Thus, a long-term decrease in the amount of ammonium ions may be possible. This observation suggest that mordenite seems to promote purification with the help of microbial oxidation, with frequent exchange between Ca^{2+} and NH_4^+ at the zeolite surface.

The same capacity is allowed to treated sewage from metal ions. In this research is presented the results for manganese ion removal from water.

The analysis data for the clinoptilolite as sorbent for organic compounds from water system at a constant temperature were produced by UV spectrometry and liquid chromatography.

Proposal method for river water treatment we use during the flood, whish is happen any times in Argichi

The service provider treating floodwaters must take into account the following:

1. If the onsite wastewater treatment system has electrical components, the ability to restart the system will depend on the flood elevation.
2. If the floodwater only covers the tanks and the components in the tanks, it is possible to restart the system without further evaluation.
3. If the floodwater covers components located on the ground surface (air pumps, panels), the system should be inspected to determine whether it is safe to restart the electrical service and use the system.

Additionally, sorption materials can be placed on the floodplain, e.g., in ponds with mobile walls filled by adsorbents, and removed after the flood. There would be a primary treatment system and a secondary treatment where the containers filled with zeolite

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Conclusions

It has been shown that Armenian zeolites have polysorption capacity and can be used for river water treatment. Advantages of natural zeolite in comparison with other sorbents are that as technological stability, the low price, availability, filtering properties.

It has been found, that the sequence of operations in sorption will follow:

1. the sorption of metals and ammonia,
2. the sorption of organic substances.

This sequence can allowed to make cascade from permeable barriers from Armenian domestic zeolites for river water treatment.

References

1. Donald W.Breck Zeolite Molecular Sieves: Structure, Chemistry & Use. A Wiley-Interscience publication, John Wiley & Sons, New York, London, Sydney, Toronta, (1974) p.782.
2. C.Collela, Porous materials in environmentally friendly processes, in Studies in Surface Science and Catalysis, 1999, vol. 125, p.641-655,.
3. Zeolites and mesoporous materials at the dawn of the 21st century, Proceedings of the 13th International Zeolite Conference, Montpellier, France,8-13 July, 2001, Edited by A Galarneau, F.Di Renzo, F.Fajula, J.Verdine. Series Studies in Surface Science and Catalysis, Adisory Editors: B.Delmon and J.T.Jates, Vol.135.and Recent Research Repotrts for 13th IZC.
4. A. Dyer, A., An introduction to zeolite molecular sieves, John Wiley & Sons, Chichester, UK, 1988, p. 83.
5. Torosyan G.H., Water supply emergency for lake Sevan ,R.N.Hull and al (eds) Strategies to Enhance Environmental Security in Transition Country, Springer,.2007pp,.239-247,
6. Torosyan G., Isakov A.,.Aleksanyan A,.Zakaryan M,Use of natural materiales for municipal wastewater treatment, Y.Sharon at al (eds) Water Supply in Emergency Situations, Springer, 2007, 133-138,
7. Torosyan G., Harutyunyan S., Removing chlorine-containing organic compounds in the environment after floods, / J.Anthony A.Jones at al (eds) Threats to Global Water Security, Springer, 2009. 253-256,