THE USE OF BUILDING MATERIALS FOR WATER QUALITY MANAGEMENT

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INTRODUCTION

The increasing demand for ion-exchange materials as ecological problems simulated the intensive study of natural and modified zeolites [1-5] because they are considered to be cheap modified sorbents. The technological stability of building materials residues as sorbents is determined first of all by such characteristics as mineral and chemical composition, sorption ability and then mechanical, physical and following from them filtering properties.

Natural zeolites and building materials residues uses in the following fields of waste water cleaning:

1. removal and recovery of NH_4,
2. removal and storage of radionuclides,
3. removal and storage of heavy metals,
4. removal of organics.

The advantages of zeolite-tufa and volcanic tuff in comparison with other sorbents are their reserves in Armenia, a unique complex of technological properties / sorptional, molecular-sieving/ as well as their natural origin, possibilities of they modification in various directions, regeneration and utilization. The application of the Armenian volcanic material in the processes of water preparation has been scientifically approved according to the all-round evaluation of them mechanical, physical, physical-chemical, technological properties. It has been established that the natural zeolites and their combination with other systems is necessary to remove metal ions from water. There have been established the regularities of extraction processes of ions of iron, magnesium, calcium, zinc, copper, nickel, cobalt, lead and ammonium from water. The dependence of efficiency and mechanism of sorption of components from water, filtering parameters, length of contact liquid and solid phase's ratio and other factors are obtained.

Chemical stability and mechanical - strength of natural Armenian zeolites – Mordenite and Clinopilolite meet the requirements of filtering materials.

1. MATERIALS AND METHODS

The role of Lake Sevan was, and still is, very important in the national economy of Armenia. The lake water is used for hydroelectric power generation and agricultural land irrigation.

The problem of removal of hydrocarbons from the Sevan basin is an urgent task. Many manufacturing processes form organic pollutants (benzene, toluene, ethylbenzene, xylenes, phenol, aniline and their derivatives), which are toxic substances. Organic toxic substances are the main sources of anthropogenic pollution: agriculture (stock-breeding, farming, mineral fertilizers, poisonous chemicals), industry and household sewage waste waters.

The intensification of economic activity in Lake Sevan catchment basin is the cause of essential changes in the hydrocarbon chemical content of the rivers. The amount of dissolved organic matter in the water has grown up to 3 mg/l; the content of chlorides and sulfates has increased several fold; the concentration of nitrogen nitrate and ammonia forms have increased ten-fold; the total mineralization has grown from 130 to 190 mg/l. Noticeable changes took place in the concentration of mineral nitrogen which is the consequence of mineral fertilizers and stock-breeding development.

Ammonia concentrations have been determined for Lake Sevan. The some rivers of Sevan basin are most polluted with ammonia and heavy metals; the cleanest one in this respect is the river Arpa. All rivers are high in iron compounds (70-140 mkg/l) and low in manganese content (7-18 mkg/l).

The estimation of the water quality judging from average values does not reflect the alterations in the ecosystem of Sevan during the process of eutrophication.

Natural zeolite deposits of sedimentary origin are widespread in Idjevan / Clinopilolite / and Shirak / Mordenite / regions of Armenia. Tuff deposits are widespread in Arthik / Shirak region/. The natural zeolite-tufa - clinoptilolite and mordenite, and tuff were dehydrated at 110^oC.

In this study clinoptilolite and mordenite were prepared by heated pile method, using 0,5 and 1 N solution of $CaCI_2$ [3, 6]. Clinoptilolite modified

by monoethanolamine were prepared according to [6].

The ammonia adsorption by zeolites was investigated by IR spectroscopy [7]. 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.

Liquid chromatography is passed on HELCh /higher-effective liquid chromatography, detector Waters 486, controller Warers 600S, Pump, Waters 626, colon 250x4mm, Si-100 C 18, P 150 Bar, V 1ml/m, mobile phase acetonitryl-water (50:50), detector UV-254). UV spectrometry is passed on UV-Specord spectrometer.

Waste water treatment from organic impurities by zeolites/ static conditions/

1. On 1 gr of sorbent added on 10ml solutions of phenol in water. The mix was carefully shaken up within 4 hours. The measurements of molar refraction of a solution were carried out before and after sorption. On a difference of concentration of an organic solution expected amount of adsorpted phenol.Here it has been check the results by liquid chromatography and UV spectrum dates also.

2. The removal of organic substances is carried out as follows. The precisely weighed portions of sorbents are brought in to the certain volumes of organic substances in water, which initial concentration vary. The mix is carefully shaken up during 6 h. Further test is settled.

Waste water treatment from organic impurities by zeolites/ dynamic conditions/ Polluted by hydrocarbons water passes through a column filled with adsorbents. Hydrocarbons are taken from water, remaining in limits of adsorption column. The cleared water leaves a column for direct use or further treatment.

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

An improvement of water quality of Sevan lake**.** Creation of protective systems is offered at a confluence of river water of lake Sevan. It will consist of primary treatment system, and also tertiary treatment where on a watercourse protective walls filled are established by zeolite and building by products as volcanic tuff residues. Some walls with forward pools are supposed to create an opportunity of replacement of a sorbents

Primary treatment. This treatment involves settling clarifier pools, there settle able organic materials settle out and are pumped away, while oil floats to the top and is skimmed off.

Secindary treatment. After primary treatment river water is subjected to tertiary treatment. This process includes adsorption of organic pollutants on sorbents. For treatment there are used zeolites in the powder form at 10 – 25 mm size putting in the form of a bed.

2. RESULTS AND DISCUSSION

Waste water is often dumped directly into rivers. This fact is the primary cause of river water pollution in lake Sevan. Various attempts are now being made on a local scale to purify such waste river using simple methods. One of that is using natural zeolites for ammonia removing from wastewater.

At first the ability of proposed sorbents is compared to purify river waste water with normal river gravel. The tested sorbents (even tuff) had superiority over gravel in the oxidation of ammonium ions through nitrite ions into nitrate ions. The higher activity for ammonia sorption shows also treated by aminoethanole. The mentioned amine has microbial activity as one of product of mutagenesis.

In the present work the results of purposeful researches are submitted in the field solutions and waste water of application natural zeolites and tuff as sorbents for removal of organic substances from water. The higher adsorptivity shows natural clinoptilolite modified by monoethanolamine - about 100 % extraction of phenol from 0,015M solutions, and also rather high sorption activity of benzene, toluene, xylene from water solutions / from 50 up to 70 % /. The quantitative adsorption takes place in case of the H-form natural mordenite.

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 adsorbed phenol. The results are given in the Table 1. 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. It's visible from the given tables with increase of concentration of solutions the amount of absorbed phenol is increased. Fairly active has modifided clinoptilolite by monoethanolamine. The H-form of mordenite

Table 1. The adsorption of NH_3 [g] on the zeolite-tufa / natural and /modified and tuff /10g/.

N	Zeolite	1day	3day	5day	7day	10day
1.	Mordenite tufa	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.	Tuff residues	10.24	10.52	11.00	11.24	11.63
4.	Mordenite modified by monoethanol-amine	11,05	11,56	12,15	12,86	12,95

shows 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 zeolites – zeolites tuff, treating zeolites, modified zeolites. As zeolites were used clinoptilolite containing tuff from Idjevan deposits Armenia). They are modified by monoethanolamine.

The oil products content in water before and after the sorption was estimated by gravimetric method, after there was made a correction by gas-liquid chromatography. The results are presented in Table 3, 4.

It has been investigated the phenol and other aromatic sorption 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 after the sorption was estimated by gravimetric method, after there was made a correction by liquid chromatography.

Table - 2 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 tuff g phenol./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	-	-	Full sorption	Full sorption
0,10	1,3328	-	-	1,3314/0,0752	Full sorption
0,15	1,3342	1,3339/0,0017	1,3338/0,0019	1,3322/0,0846	Full sorption
0,20	1,3355	1,3347/0,0039	1,3346/0,0047	1,3329/0,1034	-
0,30	1,3371	1,3362/0,0061	1,3361/0,0063	1,3345/0,1175	-

Table- 3 Distribution coefficient of the oil products K_a (mg/g) during the sorption on sorbents

Sorbent	K_a / light organic[b]	K_a/ heavy organic
Clinoptilolite-tufa	50	300
Clinoptilolite-treating	160	540
Clinoptilolite- modified by monoethanolamine	450	780
Tuff	110	420

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

Table 4. Sorption of the oil from water solutions on sorbents.

Sorbent	Weight of sorpted oil product/ mg [b]	% of sorpted oil product
Clinoptilolite-tufa	20	30
Clinoptilolite-treating	32	45
Clinoptilolite- modified by monoethanolamine	75	89

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

CONCLUSION

It has been found advantageous to go on with the researches in ammonia and organic pollutants sorption by Armenian natural zeolites and tuff. It has been offered the convenient method for successful sorption of ammonia and organic pollutants from water. The given method can be applied at river water treatment processes by using domestic natural sorbents. The advantages of natural zeolite-tufa and tuff in comparison with other sorbents, such as technological stability, low cost, availability, filtering properties, etc are determined first for can use in the Sevan region.

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