TREATMENT OF ORGANIC POLLUTANTS ON ZEOLITES IN MOTOR TRANSPORTATION & AUTO REPAIR ENTERPRISES

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Abstract: *The objective of the present study was increasing the adsorption activities of zeolites for organic pollutants. For this purpose it was realize the using of modified by quaternary ammonium salts natural zeolite. Natural zeolites and them modified analogs can be made a renewable resource. The advantages of natural by-products in comparison with other sorbents are their low cost, availability of extraction, operational flexibility and control and others.*
Motor transportation and auto repairs station wastewaters include typical sewage from the petrochemical and petrol using industries, of course in smaller amounts.
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 Freundlich model for description of the adsorption data for activated carbon.

Keywords: *natural zeolites, modified zeolites, quaternary ammionium salt (Quat), adsorption, adsorbent, wastewater treatment, organic solution.*

Introduction

Organic compounds are major pollution problem in soil and groundwater. Their presence in water can create a hazard to public health and the environment.
Soil and groundwater pollution from small enterprise which have a relation with petroleum and this type of other products is becoming an important topic of interest as a result of the increasing public and regulatory concerns worldwide with problems of groundwater contamination and resultant impact on human health and ecological systems.
Nowadays for wastewater treatment in small enterprise wide application have found fine layer clarifier, in which height of upholding makes 100mm and less. The cost of such clarifier is pleased high and frequently comes nearer to cost usual clarifier. Therefore at the decision of a question of waste water treatment follows not only to find rational height of upholding, but also the appropriate component, which promotes fast upholding, moreover for sorption of petroleum. Last are in interaction in a flow of water, that results them agglomeration is especial at low meaning turbulence of a flow.
With the purpose of the sanction of a question of wastewater treatment from mentioned enterprises by us it is offered to apply clarifier with natural zeolites and them modified with quaternary ammonium salts analogs.
Taking into account that fact, that our small enterprises have no while the appropriate means, we offer the elementary technological circuit of clearing of drains. So, we offer to make special holes with the boxes, filled in them by zeolites, which further are used in building industry.
Motor transportation and auto repairs enterprises wastewater sources and characteristics:
For motor transportation and auto repair enterprises wastewater needs primary and tertiary treatments. Primary treatment includes screening the wastewater for removing the suspended large and small particles settling and skimming the oil from the top layer in the wastewater in the setting smaller tanks. Following the primary treatment the wastewater undergoes a tertiary treatment

which is mostly a physical process. In this case, the physical treatment includes adsorption by natural zeolites and them modified analogs.

Zeolites is used in water treatment plants for the removal of odors and tastes [1-3]. Natural zeolites and them modified analogs on the other hand, can be made a renewable resource. The advantages of natural by-products in comparison with other sorbents are their low cost, availability of extraction, operational flexibility and control and others. The effectiveness of natural zeolites and them modified analogs for the removal of organics by adsorption also is enhanced by its large surface area.

The characteristics of wastewater discharges form location to location depending upon the population and industrial sector served namely, land uses, groundwater levels and degree of separation between storm water and sanitary wastes. Motor transportation and auto repairs station wastewaters include typical sewage from the petrochemical and petrol using industries, of course in smaller amounts.

This type of wastewater usually is characterized by dark gray color and disagreeable odor. Chemically this wastewater composed of organic compounds as hydrocarbons, phenols, aniline and other aromatics.

Materials and methods

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/.The mineral composition for clinopilolite from Idjevan was generally clinpotilolite with tufas. This zeolite had an external surface area around 15 m^2/g. The zeolite was crushed and sieved to different grain size – 0.4 to 1.5 mm for laboratory batch and column experiments.

Here are we used the quaternary ammonium salts on the basis of N, N-dimethyl-N-ethanolamine [5]. From all of series of QUAT in this paper there is used N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide, which activity it`s possible to compare with the known QUAt as N, N, N-trimethyl-N-hexadecyl bromide (HDTMA) [4]. In other case N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide more thermal and basic stable than HDTMA [5].

The QUAT used in the laboratory experiments was produced by treating 100 g of clinoptiololite with 300 ml of a 0,01M QUAT or amine solution in water and shaking 24 h. The modified zeolites was rinsed with purified water 2 times and made air-dried. The final N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide loading was 6 gr (15,0 mmol) on 100 gr zeolite and monoethanolamine loading was 6 gr (100 mmol) on 100 gr zeolite.

The XRD patterns for sample with N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide show four Bragg peaks which indicating the long range order of these material.

Sorption of BTEX, phenol and aniline by zeolites proceedes in the unbuffered solutions (pH – 7,0). Sorption isotherm were prepared for benzene, phenol, anilin using different zeolites. 1 gr air dried zeolite was put in the into glass with 10 ml of benzene, phenol, aniline solutions in water (with the maximum solution in water for benzene, for phenol, aniline 0,1 N). The samples were shaken at 25^{o}C (room temperature) for 2 days a shaker table. After that was determined the rested amount of solute in water by refractometry, liquid chromatography and UV spectrometry analysis.

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.

Technological decision

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

Tertiary treatment: After primary treatment the above small enterprises wastewater is subjected to tertiary treatment. This process

includes adsorption of organic pollutants on sorbents. For treatment used natural zeolites and them modified analogs have in the powder form at 15– 25 mm size putting in the form of a bed.

Sorbent (zeolite) restoration: For this purpose it has been passed methylation or ozonation of sorpted organic compounds / see experiment/.

The other advantages of zeolites sieves is a catalytic activities in organic synthesis as catalysts. Zeolites can be used us useful catalysts for many chemical conversion, for instance in alkylation & oxidation reactions. This possibilities make a opportunity for zeolites reduction and them application as regenerative adsorbents in wastewater treatment processes.

Ozonation of aromatic compounds containing wastewater

Ozonation destroys toxics in industrial wastewater by breaking down molecular structures into simpler components organic molecules or such as water and carbon. The process is based on the discovery that organics will oxidize in water at relatively low temperatures as long as oxygen is present and the proper operating pressure is maintained. The research indicates that aromatic compounds will be oxidized under these conditions.

The processes in which ozone is involved basically two reaction pathways are of importance:

1. Ozone molecules will directly oxidize the organic compounds with an initial addition step,
2. Ozone dissociated by the reaction with hydroxyl and amino ions or hydroperoxyl anions

The objective of this study is to investigate the natural zeolites to be used as adsorbent in the simultaneous adsorption and ozonation processes under sequencing batch reactor operation to treat wastewater containing phenol.

Ozonization of the organics adsorbed on zeolite: For carrying out of experiments (diameter of 10 sm, height of 50 sm) loaded 25 ml of a mix into a reactor zeolite-water a solution of aniline after adsorption, further a mix barbotated an ozono-air mix. Ozono-air mixed moved from the generator of ozone developed for biomedical appointments. The ozone maintenance in an initial mix made 500 mg/m^3.

For the purpose of revealing of the most active sorbent we study adsorption of organics from water solutions according to this technique.

Results & discussion

Zeolites expose simultaneously hydroxyl groups, coordinatively unsaturated cations, as Lewis acid sites, and Lewis basic sites, anions, as O^{-2} ions, on their surface.

To retard the movement of organic species, materials with high affinity for organic molecules needed. It has been found recently that the surfactant modified (SMZ), a type of inexpensive cation exchanger, can fulfill this requirement [4]. The maximum loading of hexadecyltrimethylammonium (HDTMA) salts (with chloride, bromide or sulfate anion) can increase the sorption capacity of organic compounds with diminished the hydrophilic (water) substances sorption to the minimum. It`s known also, that the removal percentages for organobentonites to treat organic compounds from water were positively correlated to the length of alkyl chains of Quats [6].

At our opinion to make some of efforts to have with long chains alkyl group the additional hydroxyl groups and Lewis basic sites, anions, as O^{-2} ions, appears a possibilities to increase acid-basic properties of zeolites. One of the practice way for this problem decision is the modification of zeolites and its surface, so much the more with the organic compounds containing OH-groups as monoethanolamine and its derivatives.

This study evaluated the use of monoethanolamine and N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide, as modified agents for zeolite surface. The objective were determined the sorptive capacity of modified zeolites for organic compounds sorption from water solutions which results of research are in a processing stage.

Here was investigated the removal of organic compounds – BTEX, aniline, phenol sorption process from waste water by means of

modified clinoptilolite with ethanolamine and them ammonuim salts. 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.

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 research shows in the 1400-3700 cm^{-1} region for clinoptilolite (under treatments at 400^{o}C) 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.

The sorption of aniline on the modified sorbent of 3600 and 1050 sm^{-1} disappear, that testifies to occurrence instead of them additional coordination bonds between aniline and OH-groups.

An absorption peaks of 3050 sm^{-1} be conditional also can it is carried to O … H bonds, but weaker. Probably, therefore this connection is not realized with aniline, but it collapses at the subsequent regeneration of zeolite. Occurrence of absorption peaks in a spectrum recycled after sorption proves of 1050 sm^{-1} to zeolite aniline, that, first, really, given connection has been realized in superficial intra-complex with of aniline.

Previously the sorption of aniline on zeolites, for instance, sorption on montmorillonite was investigated by Israelien group of scientists [7]. They were identified various type of association between aniline and zeolite surface by FTIR. Aniline had been looked as selecting the better host for adsorption modes as a posterior in situ aniline polymerization. The aniline adsorption on to dehydrated NaY zeolite was investigated also by FTIR spectroscopy method [8].

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.

Previously it was investigated the adsorptive activities of zeolites at removal of phenol from tetrachloromethan solution / CCI_4 / - organic solvent which is more phenol on the geometrical sizes [3]. It has appeared that phenol removal it is better on ZSM-5 modified by Et_4N+Br. The *max* removal capability of phenol on zeolites is presented at the table 1.

Table 1.

Absorption of phenol from a CCI_4-solution on sorbents / 1 g phenol in 10 ml CCI_4 / Temperature 20^{o}C of measurements

N/N	Sorbent	The max removal capability g phenol/ 1g sorbent
1.*	Armenian natural zeolite – mordenite	0,16
2.*	Armenian natural zeolite – clinoptilolite	0,21
3.*	**C**linoptilolit modified by salts of Ba	0,27
4.*	ZSM-5 modified by Et_4N+Br [1]	0,31
5.	Clinoptilolite modified by monoethanolamine	0.30
6.	Clinoptilolite modified by N,N-dimethyl-N-hexadecyl-N-2-oxyethy-lammonium bromide	0.32

*) Zeolite from the family ZSM-5 with hydrophobic characteristics from the reference [3]

The measurements were carried out for phenolic water solutions in concentration limits from 0,1 up to 0,45 mol/L. It was earlier established, that the sorption in these limits grows and has linear dependence on factor of refraction in correction with the results of UV spectrum [3]. It was determined quantity of sorpted phenol by the graphic dependence concentration-molar refraction.

The amount of absorbed phenol is increasing in dependence of concentration of solutions. More active has appeared Clinoptilolite modified by N,N-dimethyl-N-hexadecyl-N-2-oxyethylammonium bromide.

All experiments were performed at the room temperature. Solutions were constantly stirred for one hours. After filtration quantity of adsorbed phenol was determined by UV-VIS spectrometry. The amounts of adsorbted pollutants were calculated from the differences between the amount of pollutants added and that remaining in the final equilibrium solution.In the table 2 presented the results for phenol sorption from water solutions.

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 Clinoptilolite modified by mono-ethanolamine g phenol. on 1 g sorbent	N_D^{20}after sorption on Clinoptilolite modified by N,N-dimethyl-N-hexa-decyl-N-2-oxyethylammoni-um bromide / g phenol. on 1 g sorbent	N_D^{20}after sorption on H-Clinoptilolite* / g phenol. on 1 g sorbent	N_D^{20}after sorption on ZSM-5* g phenol. on 1 g sorbent
0,05	1,3324	Full sorption	Full sorption	Full sorption	Full sorption
0,10	1,3328	Full sorption	Full sorption	1,3314/0,075	Full sorption
0,15	1,3342	1,3321/0,094	Full sorption	1,3322/0,085	Full sorption
0,20	1,3355	1,3320/0,107	1,3315/0,170	1,3329/0,103	1,3315/0,165
0,30	1,3371	1,3325/0,117	1,3317/0,247	1,3345/0,118	1,3318/0,245

*) from the reference [3]

Table 3

The sorption of aniline from a water solution on sorbents / an aniline concentration 0,01M, temperature 20°C,/**

N	Natural supporters	N_D^{20} after sorption	Time, hours	Aniline sorption, %
1.	H-Mordenite*	1,3291	4	75
2.	H-Clinoptilolite*	1,3289	4	100
3.	Clinoptilolite*	1,3290	4	98
4.	Clinoptilolite modified by mono-ethanolamine	1.3289	3	100
5.	Clinoptilolite modified by N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide	1.3289	2	100

*) from the reference [3]
**) N_D^{20} for initial aniline solution is 1,3300, for water N_D^{20} is 1,3289

The theoretical analysis of various types of isotherms of adsorption allows to receive a lot of helpful information on the adsorption mechanism. Adsorptive isotherms received of aniline adsorption from water solutions on zeolite it is possible to classify as type L3 [7]. This testifies that in this case influence of adsorption of solvent is expressed not brightly. The type of an isotherm of adsorption confirms that fact, that adsorption proceeds in a monolayer.

On the basis of the received data are calculated adsorption isotherms in co-ordinates of the equations of Freundlich and Langmuir. The deduced constants of the equations of The analysis of sorptived parameters, on calculated by equations of Freundlich and Langmuir has shown, that Freundlich's equation describes character of isotherms aniline sorption on zeolites is better. It proves to be true coincidence of experimental and settlement data (table 5.), that is not observed at application of Langmuir equation. The obtained data confirm that Freundlich's equation is applied for porous adsorbents.

Table 4

Freundlich and Langmuir parameters

Sorbent	Freundlich`s Equation		Langmuir`s Equation		
	β	**μ**	**Γ_{max} (calculated)**	**Γ_{max} (experimental)**	**K**
Clinoptilolite modified by N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide	0.60	0.5	2.2	0.045	500
H-Clinoptilolite	0.38	0.45	0.31	0.017	556

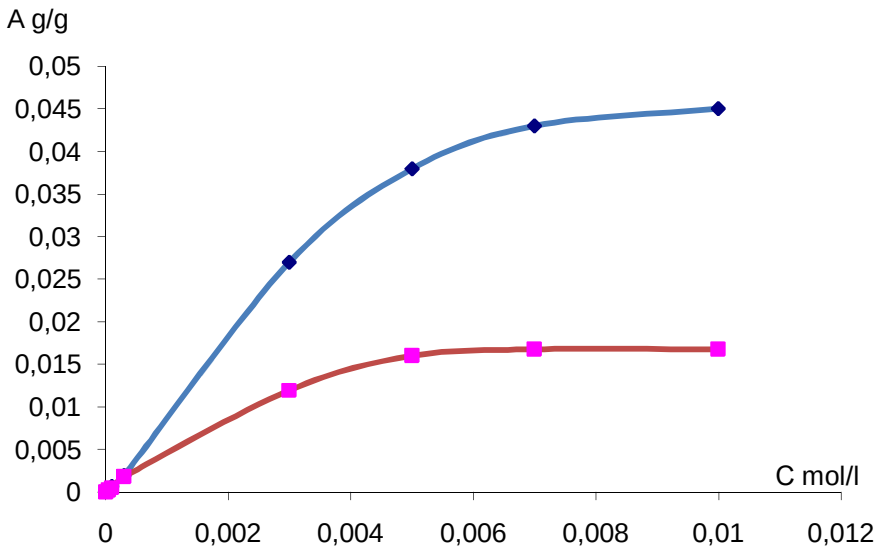

Fig.1 The adsorption istherm clinoptilolite modified by N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide / rhombic symbol / and H-clinoptilolite / square symbol /

Higher sorptive activity appears for the clinoptilolite modified by N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide. It can explained that large cationic surfactant molecules have a strong affinity for zeolite surface and replace positively charged inorganic counterions that neutralize the negative surface charge of the zeolite.the surfactant molecules impart hydrophobic properties to the zeolite surface organic compounds [7] is proportional to a specific surface hydroxyl group. Here is established, that sorption of aromatic compounds from solutions on the modified zeolites by monoethanolamine and N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromide occurs by means of formation of superficial connections with modifiers:

- In the beginning the modifier is adsorpted on a surface of grains of the natural not modified zeolite covered with groups Si-OH, .
- Then monoethanolamine co-operate with a structural lattice of zeolites, being fixed on a zeolite surface.
- Then N, N-dimethyl-N-hexadecyl-N-2-oxyethlammonium bromine co-operate with a structural lattice of zeolites, being fixed on a zeolite surface.
- During the sorption of aniline, phenol on modified zeolite appears, that OH-group of ethanolamine in zeolites forms a bonds with amino - or hydroxyl groups of adsorptives.

The kinetic researches of the sorption processes were spent basically on modeling solutions with initial concentration of aromatic connections of 0.01 mol/l. Always we have full sorption for aromatic compounds.

Conclusion

It has been found advantageous to go on with the researches in organic pollutants – BTEX, phenols, aniline make up a significant percentage of petroleum products sorption by Armenian natural zeolites and them modified analogs. In particular, such sorbents can be used in the poor countries for sewage treatment from small enterprises.

It is experimentally established, that sorption of organic compounds by the natural zeolites modified with N,N-dimethyl-N-hexadecyl-N-2-oxyethylammonium bromide higher effectual, it is satisfactory described by Friendlich's known equation.

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