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**WASTEWATER TREATMENT WITH NATURAL ZEOLITE
OF THE CLINOPTILOLITE TYPE**

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***Abstract:** In the present paper the possibility of wastewater's purification with natural zeolite of the clinoptilolite type was examined. The waste water from industrial companies was polluted with COD, BOD₅ and fats. The zeolite used was produced from the field in Beli Plast, North-East Rodopi Mountain.*

In the experiment described, zeolite has subjected to mechanical treatment in order to reach the appropriate size for industrial usage.

First, the wastewater was analyzed for containing of pollutants: COD, BOD₅ and fats, after that it has passed a triple adsorption with zeolite. It is found that the triple circulation passing of wastewater through a layer of zeolite has got a purifying effect as following: for fats - 41,5 %, for COD – 20,1 % and for BOD₅ – 26,59 %.

In summary, we can prove that zeolite, type clinoptilolite from the field in Beli Plast has significant purifying possibilities and can be used for cleaning of wastewater of industrial companies.

Key words: Zeolite, clinoptilolite, absorption of wastewater

INTRODUCTION

It is a known fact that biological methods of purification are based on the utilization of microorganisms, which during their metabolism break organic pollutants down to water and carbon monoxide or to low molecular weight, practically harmless, organic compounds [1,2]. Their application is more appropriate for the removal of organic contamination from household wastewater, although they are not always effective enough for the removal of organic pollutants from industrial wastewater due to the slow kinetics of the ongoing processes. [1, 2].

Natural zeolites are microporous bodies possessing significant adsorption properties attributable to their structure[3]. Zeolite adsorbents are characterized by a highly porous structure providing for a high efficiency during the course of the adsorption processes [4]. This unique property makes them very suitable for the treatment of drinking and wastewater from various toxic contaminants [5-7]. One of the advantages of the adsorption method in comparison to the other purification methods is the necessity for relatively small investments [2].

PRESENTATION

The present paper is related to research on the possibilities for utilization of natural adsorbents for wastewater treatment. Water (wastewater from industrial processes) was analyzed for the content of the contaminants COD, BOD₅ and fats. The adsorbent that we used is of the clinoptilolite type from the deposit at the Beliplast village in the Northeastern Rhodope Mountains. The chemical composition of the utilized clinoptilolite is specified in Table 1.

Table 1. Chemical composition of clinoptilolite from the Beliplast village, mass. %

Indicators	Chemical composition	
	Components	% mass.
Bulk weight, [g/cm ³] - 0,8295 – 0,8673	SiO ₂	66,05
	Al ₂ O ₃	11,22
Particle size (main fraction) - 1,0 – 2,5 mm - up to 95 %	Fe ₂ O ₃ and FeO	1,17
	CaO	3,69
	MgO	0,17

The performed Roentgen structural analysis showed the presence of only two phases. The diffractogram in Figure 1 shows peaks only of the minerals clinoptilolite [(Na,K,Ca)₆(Si,Al)₃₆O₇₂·20H₂O] and small amounts of quartz impurities. The performed quantitative analysis showed that the sample under examination contains:

98 % clinoptilolite –with formula [(Na,K,Ca)₆(Si,Al)₃₆O₇₂·20H₂O]

2 % quartz –with chemical formula SiO₂.

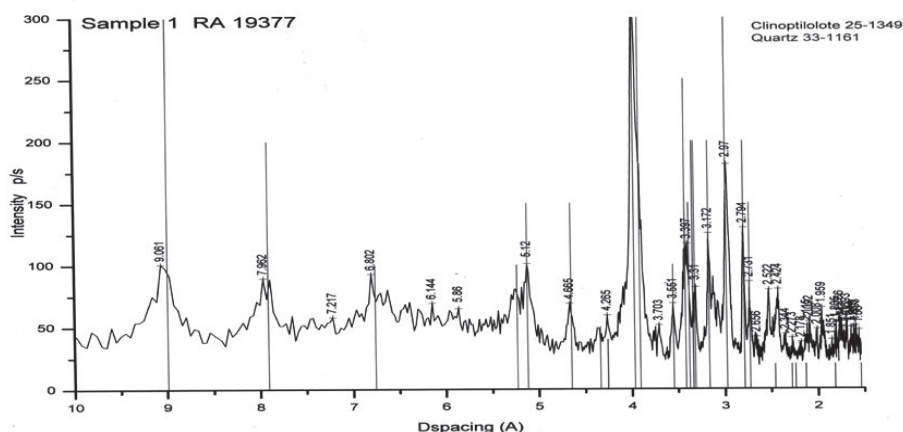


Figure 1. Diffractogram of natural zeolite from Beliplast village, clinoptilolite type.

EXPERIMENTAL

In accordance with the aims of the experiment, the zeolite goes through the following stages of processing:

- grinding in a planetary ball mill model “Retsch”,
- sifting through a Vibratory Sieve Shaker model „Retsch”,
- drying at 120 °C for 2 hours in a drying machine model “J.P.SELECTA, s.a.”,
- thermal activation at 400 °C for 2 hours in a furnace model “Carbolite CSF 1100”.

The so prepared zeolite is perfectly suited for the aims of the experiment.

The experiment was performed in an industrial plant with a capacity of the monthly wastewater - 1400 m³. The wastewater, which we used, was subjected to an initial analysis as follows:

COD /bichrome/ – according to the ISO 15705 methodology,

BOD₅ – according to the Bulgarian National Standard БДС EN 1899-1,

Fats – according to the Internal Laboratory Methodology

Table 2 presents the results from the wastewater analysis before the treatment and the results after the treatment with triple passage through the adsorption layer of zeolite, clinoptilolite type.

The maximum permitted levels to which the waters should comply with before being discharged into the water body are specified.

Table 2. Results from the analysis of untreated wastewater and of wastewater treated with zeolite

Name of the indicator	Measurement unit	Results from the testing of untreated wastewater	Results from the testing of wastewater treated with , clinoptilolite	Maximum permitted levels	Percent of purification
COD (bichrome)	mg.dm ⁻³	324,5	259,2	250	20,1 %
BOD ₅	mg.dm ⁻³	113,7	83,4	50	26,59 %
Fats	mg.dm ⁻³	28,2	16,5	10	41,5%

For the purposes of the experiment a pilot experimental installation was built. The principal scheme of the installation is shown in Figure 2.

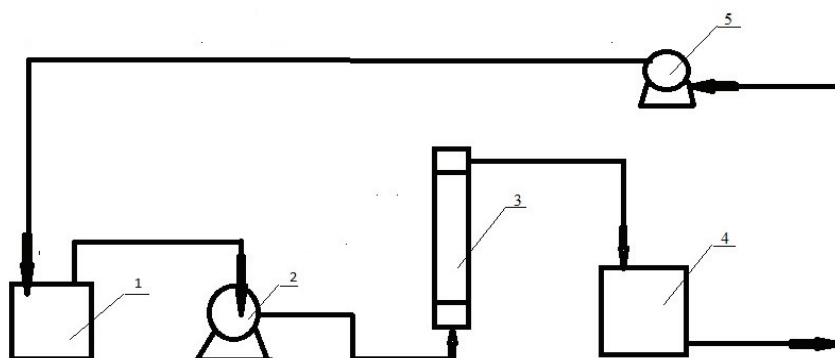


Figure 2. A principal scheme for the treatment of wastewater with natural zeolite of the clinoptilolite type.

The description of the scheme is the following: water for treatment at temperature 18-20 °C and pH = 7,4 - 8,2 enters reservoir 1. By means of centrifugal pump 2 the water flow is fed into adsorption zeolite column 3 with a volumetric capacity of 0,01 m³. The column is filled up with zeolite, clinoptilolite type, with fraction size of 2 - 2,5 mm. The wastewater quantity from reservoir 4 is transferred back three times by means of circulation pump 5 and passes through the zeolite column.

RESULTS AND DISCUSSION

In Table 3 an estimate is made of the quantity of clinoptilolite which will be necessary for usage for one month. The estimate is based on the adsorption capabilities of zeolite - clinoptilolite type.

Table 3. Quantity of contaminants in kg per month, before and after treatment

Contaminants	Before treatment kg. per month	After treatment with zeolite kg. per month	Difference kg. per month	
COD	410,0	324,3	85,7	
BOD ₅	366,6	269,1	97,5	
Fats	14,94	8,73	6,2	
total	791,5	602,1	189,4 - 24%	1000 kg zeolite per month

It is evident from the obtained results, presented in Table 3, that zeolite of the clinoptilolite type demonstrates the best purification of fats - 41,5%, BOD₅ – 26,59% and COD - 20,1 %. It

should be noted that these results were achieved after the triple fluidic passage of the wastewater through the zeolite column. The fluidic passage through the zeolite column was predetermined by the removal from the technological scheme of the reservoir for storage of wastewater before its entry into the zeolite column. First, this provides for the economy of space and compactness, second, it provides the ability to increase the debit of the entering wastewater, and third, the temporary storage of the wastewater could lead to the emergence of decay processes and the release of toxic gases, which would have additionally polluted the environment and additional capital resources would have also been needed for the construction of the necessary equipment for their removal. The analyses, however, allow us to observe that in order for the adsorption processes in the zeolite column to function, technological time for reaction is needed, as well as regulation of the flow with appropriate passage speed, sufficient for the capture of the specific contaminant. The performed material balance in Table 3 of the total quantity of pollutants presented in kilograms per month makes it clear that the total purification capability of zeolite of the clinoptilolite type is 24 % and the necessary quantity of zeolite for one month is around 1000 kg. depending on the entering contaminants' concentration.

CONCLUSION

The principal scheme of the performed adsorption purification with zeolite of the clinoptilolite type was described. The performed analyses established that the triple passage of wastewater through a zeolite layer has a purifying action for fats of 41,5 %, for COD – 20,1 % and for BOD₅ – 26,59 %.

The performed material balance of the total quantity of contaminants presented in kilograms per month makes it clear that the total purification capability of zeolite of the clinoptilolite type is 24 %. The necessary quantity of zeolite for one month is around 1000 kg. depending on the entering contaminants' concentration.

As a general conclusion we can state that the zeolite of the clinoptilolite type from the deposit at the village of Beliplast has significant purification capabilities and can be used for the treatment of wastewater from industrial facilities.

REFERENCES

- [1] Yang L., Lai C.T. 2000. Biological treatment of mineral oil in a salty environment. *Water Sci. Technol.*, 42 (7–8), 369–375.
- [2] Panayotova, M., Sokolova, E., Removal of organic pollutants from wastewater, *Annual of the university of mining and geology "St. Ivan Rilski"*, Vol. 56, Part II, Mining and Mineral processing, 2013.
- [3] Dubinin M., N.S.Lozhkova, B.A.Onusaytis, In the book: *Clinoptilolite "Metsniereba"* Tibilisi, 1977, 101-108.
- [4] Dobrevski I., V. Markov and others., *Technology water*, Part 2, Sofia 1987.
- [5] Michalev, T., I. Petrov, *The Removal of Heavy Metal Ions by Synthetic Zeolites: A Review*, *Proceedings, University of Ruse*, 2012, vol. 51, book 9.1, 79-84.
- [6] Michalev, T., I. Petrov and I. Pejchev, *Removal of lead and cadmium ions in aqueous solutions of natural zeolite (clinoptilolite): I. Thermodynamic*, *Proceedings, University of Ruse*, 2013, vol. 52, book 10.1, 225-229.
- [7] Michalev, T., I. Petrov and I. Pejchev, *The removal of Cu(II) ions from aqueous solutions on synthetic Zeolite NaA*, *XLIX international scientific conference on information, communication and energy systems and technologies*, 2014 r., Nis, Serbia

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