Removal of Emulsified and Dissolved Traces of Organic Compounds from Industrial Wastewaters Using Natural and Synthesized (NaA and NaM) Zeolites

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ABSTRACT: *The main object of this study was to compare the natural and synthetic(NaA and NaM) zeolites as absorbents in removing emulsified and dissolved traces of organic compounds, which appear in the wastewater of power plants, refinery and petrochemical complexes. The specific objectives of the work was: a) to select the best species that have the highest amount of absorption; b) to measure the rate of absorption of traces of organic compounds and emulsions on the natural and synthesized zeolites; c)to establish the absorption isotherms for the organics and emulsions with selected samples; d) to select readily available regenerants, and e) to examine the pH dependence of the process and to establish a simple and practical method to detect and to measure the pollutants after the treatment process. The BOD and COD of the treated and feedwaters were compared.*

KEY WORDS: *Zeolites, Wastewater, Removal, Synthetic, Natural, COD, TOC, BOD, Absorption, Isotherm.*

INTRODUCTION

Majority of industrial wastewaters contain traces of organic and emulsified compounds which may appear in the forms of linear or non – linear organic salts. The latter would be more soluble than the former and for this reason they are probably most abundant species in wastewaters found in petrochemical and oil industry complexes. There is also a wide range of industrial complexes such as textile, cement, power plants which consume large amounts of mineral oils, e.g. lubricants used in cooling or rotating systems in production lines. The pollution, mostly arises from or through the leakage from machinaries or directly from their usages. In textile mills, a large number of detergents as well as dyes and softening oils are ejected in effluents, polluting the environment. Most of these emulsified compounds and aromatic oils, as well as surfactants and detergents used in industry are non – biodegradable and are thus unfavourable in terms of

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BOD requirements [1-6]. Three non – activated soils (Talc, Mica, Kaolin) were used to remove detergents from wastewater. Investigators have shown a minimum of 40% absorption during a 24 h period for all these good soils [7]. A comprehensive research on absorption processes of natural minerals as absorbents and catalyzers has been reported [8-14]. The main objective of this study was to evaluate the rate and extent of the absorption of real and laboratory prepared samples of organics and emulsified oils present in wastewaters on natural and synthetic zeolites (NaA and NaM). The main aim was to open up new vistas of research for some easy and handy treatment methods.

EXPERIMENTAL

Two natural and laboratory water samples were selected. The first was taken either from Soufian Cement Factory's lower phase of untreated industrial wastewater lagoon or from dyestuff wastes of textile manufacturers and the second was made by saturating a mixture of hydraulic brake oil, transformer oil, motor oils and lubricants. The factories mentioned are located in Tabriz, Iran. The lower phase of mixed oils, as described previously, was taken as the laboratory made sample. The natural soil samples (with two different mesh sizes) were examined after being activated thermally and chemically, as well as the activated and unactivated synthesized (NaA and NaM) zeolites. The soil's fixed bed load was about 20 cm^3.

All experiments were carried out in filtrating glass tubes. The intake and output TOC were measured on the basis of or through the solvent extractions by diethylether grade – Analar [15-18]. To achieve the highest surface effectiveness of the ore, it was heated below 500 ^oC to be calcined and kept in 1% HCl, in order to remove any pore blocking inorganics for some days. It should be mentioned, that the stabilities of such minerals (the synthetics and non-synthetic minerals) in different acidic media were reported [9], and no structural deformation or distortions were observed at such low acid concentrations. The same was done with the synthetic samples so that a comparison of results could be made. The synthetic materials were obtained from Chemical and Petrochemical Academy of Baku.

RESULTS AND DISCUSSION

Selection of zeolites

The percent of absorption of the two series of samples (wastewater samples), i.e. C_ns and C_as, (C_n and C_a, refer to real and laboratory prepared water samples, respectively) on natural zeolite, as well as with those of synthesized were obtained almost for l hour of absorption time [13-14]. The three samples of selected soils showed a minimum of at least 85% absorption, i.e. the natural one 85%; NaA 89%, and NaM around 93%. Two samples of different mesh (≈5μ and ≈2μ) were selected, though it was expected that the high mesh sizes (the granules of small sizes) would improve the results, but very surprisingly, both sizes showed almost the same absorption data. Also, unexpectedly, the absorption data, as described previously, were more or less in the same range, and in the case of NaM only 8% was higher than the two others. This can be viewed as a good economical advantage for applying the natural sample instead of synthetic (NaA or NaM) zeolites which show only a slightly more absorption.

Rates of absorption

The rate of absorption of C_ns and C_as (which are labled Nat. and Lab. wastewaters on diagrams) on the soils with reaction time of 15 – 60 minutes are shown in Fig.1 and Fig.2. These indicate the fact that the absorption was fast and occurred at about an hour or less. Figure 3 shows a similar behaviour via the removal percentages of total emulsions and organics dissolved traces, according to the time coordinate. Figure 4 shows the equilibrium absorption of soils for the real water samples, which depends on the equilibrium concentrations. From this and Figs. 1-3 we can deduce that the rate of adsorption depends on the total concentrations and samples selected, i.e. as the concentration of total organics and emulsified components increase, the rate of absorption increases accordingly and vice versa. The following general statements can be deduced from the observed experimental data.

1) The reaction rates were fast and completed in about one hour.

2) The half – life time for absorption was in the range of minutes.

3) The reaction rates were comparably fast in NaM,

but more or less the same for all absorbents.

4) The reaction rate showed a similar behaviour in both cases of laboratory made and real water samples.

5) Figure 1 showed that the absorption reaction is considered as the rate limiting step, for all cases and that catalytic effect of the natural and synthesized zeolites (particularly that of natural zeolite) was not the predominant process, under the different conditions and temperatures studied (room temperature, 40 and 60°C). It was also shown that this kind of catalytic reactions are mostly predominant at high temperatures and thay have fairly enduring effects [19, 18, 8, 15]. Contrary to the facts mentioned previously, no detectable effect was observed at higher reaction times, shown in Figs. 1-2.

Effect of pH

The effect of pH on the absorption of 3 absorbents was investigated in two ranges of neutral and alkaleic pHs. The results, as shown in Figs.5 and 6, indicate that the absorption is fast in alkaline state for the natural zeolite. A similar behaviour, though a bit more, was observed for the cases of NaA or NaM which are synthesized zeolites. One possible explanation is fact that although the catalytic characteristics are not dominating during filtration process, such activity might have been slightly trigerred under alkaline conditions. Another explanation might be that the emulsion's slight saponification and the dissociation of the salts produced under alkaline solutions. This promotes the attraction of positively charged ions produced on negatively charged porous active surface sites on the absorbents.

Changes consequent to wastewater treatment

The biological and chemical factors, such as BOD and COD were determined for the neutral and alkaline samples. Some results are shown in Tables l to 4. Once more, the NaM is distinguished as the best sample for such experiments. These biodegradable and some non – biodegradable oil additives (which contain some aromatics and cyclics, and are only slightly biodegradable) would increase the rate of biological reactions, and therefore cause a higher demand for oxygen to activate the micro-organisms. As a consequence of absorption of traces of aromatics, as well as removal of most of soluble organics and emulsions during the filtration process, a decrease in BOD is expected.

Tabel 1: BOD, COD values obtained in natural zeolite for real wastewater sample (C_n) at pH ≈ 7.0

Sample	COD (mg/l)	BOD (mg/l)
Input	220	105
Output	140	20

Tabel 2: BOD, COD values obtained in NaA zeolite or laboratory sample (C_a) at pH ≈ 7.0

Sample	COD (mg/l)	BOD (mg/l)
Input	20	9.5
Output	11	2.0

Tabel 3: BOD, COD values obtained in NaM for natural sample (C_n) at pH ≈ 7.0

Sample	COD (mg/l)	BOD (mg/l)
Input	220	105
Output	15	11

Tabel 4: BOD, COD values obtained in NaA for natural sample (C_a) in alkaline solution (pH ≈ 10)

Sample	COD (mg/l)	BOD (mg/l)
Input	220	105
Output	65	8

The decrease in COD values can be explained in the same manner. The distinguished behaviour of NaM, in comparison with the other two, is not very surprising due to the high porosity and preactivation, during its synthesis.

Equilibrium isotherms

The equilibrium data obtained for the natural and synthesized zeolites are shown in Table 5. These equilibrium data are totally consistent with Langmiur's and Freundlich's absorption isotherms, [2,7].

CONCLUSIONS

Based on the findings of this work, the following conclusions can be drawn.

1- Among the three samples, the synthesized NaM proved the best absorbent with an absorption capacity higher than 97%.

2- The rates of absorption in selected samples and absorbents were relatively the same, but a little greater in the case of NaM.

Table 5: Freundlich absorption parameters for the treatment of C_n, C_a by different zeolites

Samples	Zeol.	n	K_f	1000xb
C_n	Nat.zeol.	3.4	4.01	2.30
C_n	NaA	2.52	2.10	2.90
C_n	NaM	2.90	2.10	3.00
C_a	Nat.zeol.	1.1	1.8	-----
C_a	NaA	1.1	2.10	-----
C_a	NaM	1.21	2.2	-----

n = Freundlich equilibrium constant multiplier, K_f = Freundlich equilibrium constant, b=Langmuir equilibrium constant

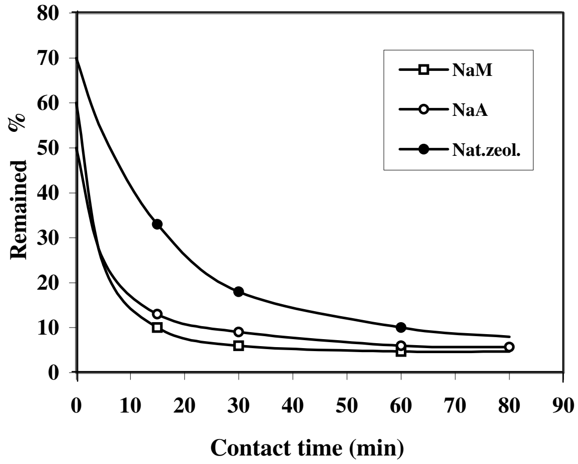

Fig. 1:Absorption rate of dissolved trace organics and emulsions (real water sample;C_n) on zeolites with 5 micron meshes

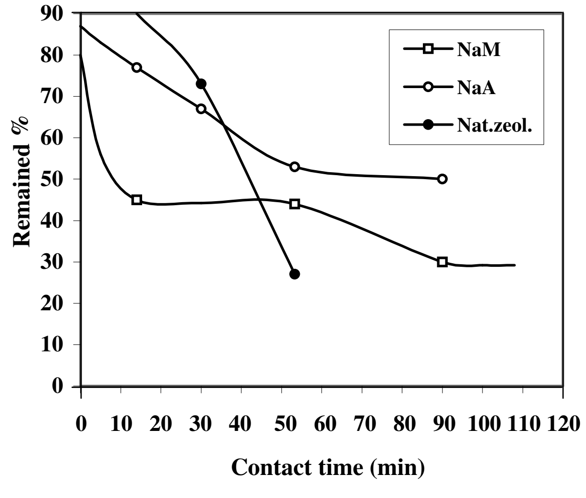

Fig. 2: Adsorption rate of dissolved trace organics and emulsions (real water sample; C_n) on zeolites with 2 micron meshes

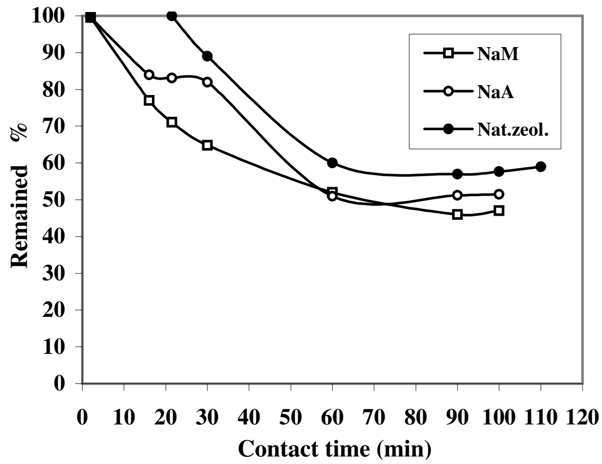

Fig. 3:Absorption rate of dissolved trace organics and emulsions (lab. water sample; C_a) on zeolites with 5 micron meshes.

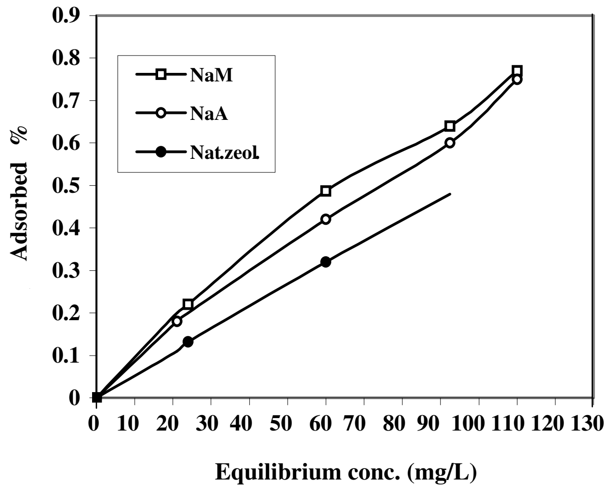

***Fig. 4:** Equilibrium absorption of dissolved trace organics and emulsions (lab. water sample; C_a) by zeolites with 5 micron meshes, ambient temperature and pH~7.0*

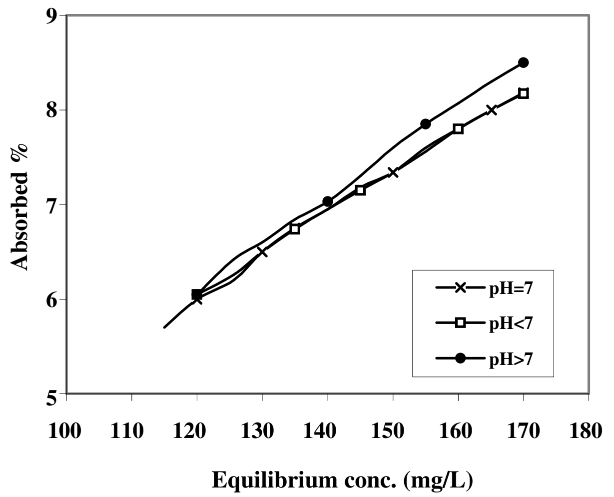

***Fig. 5:** Absorption rate of real water sample (C_n) by nat. zeol. with ~2 micron at diff. pHs*

3- The equilibrium absorption for both C_n and C_as on all the soils followed the Freundlich's isotherms. The range of parameter n, 1<n<3 indicates a favourable absorption for almost all selected absorbents.

4- After saturation in filtration processes the absorbents are regenerable with suitable regenerants, (e.g. with aqueous NaCl or NH_3).

5- Absorption is the same at all pHs, but slightly better under alkaline conditions.

6- It was proved that the NaM was the most suitable compared to the other two.

7- The lowering of BOD was observed under neutral and alkaline conditions and NaM, proved having a better lowering capacity (BOD and COD parameters).

8- Neither any particular chemical treatment nor any other alternatives are proposed for biochemical or biological wastewater treatment, while using these minerals as the filtering media. From the economical viewpoin, although NaM shows slightly higher absorption capacity, the natural zeolite is being proposed for industrial application.

9- The absorption reaction is the rate – limiting step and the catalytic effect is the rate – determining for all the samples studied [18,19].

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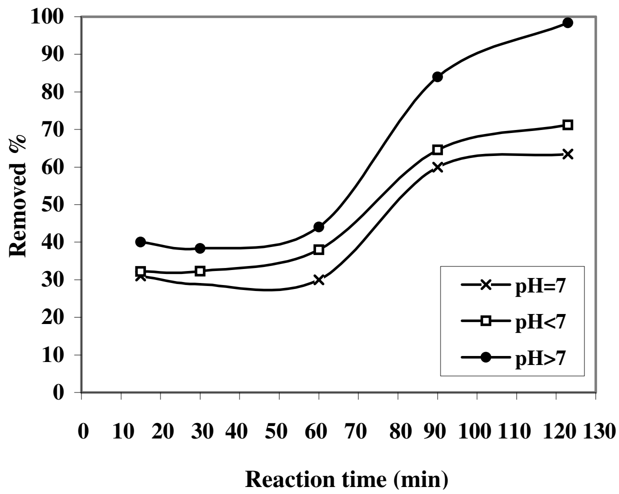

***Fig. 6:** Absorption rate of dissolved trace organics and emulsions (real water sample; C_n) by NaM with 5 micron meshes at diff. PHs*

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