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A BRIEF COMPARABLE LAB EXAMINATION FOR OIL REFINERY WASTEWATER TREATMENT USING THE ZEOLITIC AND CARBONACEOUS ADSORBENTS

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Abstract:
Two types of zeolite were briefly used to treat wastewater from a refinery i.e. one was natural zeolite of clinoptilolite type received from Slovakia and the other manufactured synthetic zeolite purchased abroad. Pollutants examined in this study for above adsorbent efficiencies were - petroleum hydrocarbons, heavy metals, sulfur and ammonia compounds. The removal efficiencies of these materials were compared to each other and with the two types of conventional activated carbons. The results showed that the zeolite performed some better properties in removal of ammonia compounds than activated carbons. It was concluded that the zeolite could be the best choice for some specific water treatment, however not for heavily contaminated refinery wastewater.

Key words: refinery wastewater, zeolite, activated carbon powdered and granulated, Valfor, clinoptilolite

1. Introduction

Zeolites are aluminosilicate minerals (natural or manufactured) usually with a 3-D structure based on polyhedra $[SiO_4]^{4-}$ – $[AlO_4]^{5-}$ networks. They have a unique structure and characteristics that make them to adsorb effectively a wide range of environmental pollutants. Their deep and wide pore openings are just one of few characteristics which enable to remove various water or atmosheric contaminants. Another characteristics of zeolite is their large surface area (20-50 m^2/g by natural species, however above 1000 m^2/g by synthetic ones). Both physisorption and chemisorption boundings may occur within the zeolite voids during the removal of pollutants. The most important benefit of the manufactured zeolite is that interior cavities can be sized during the manufacturing to the target molecules of a particular size. Zeolites, now-a-day can be used in almost all pollutants removal processes (atmospheric, municipal or industrial waste waters treatment and purification).

Tian[1] proposed a study for the removal of organic compounds and ammonia from municipal wastewater. The application involved the use of biological filtration with zeolite medium to elongate the life of the zeolite examined. The results showed an effectiveness of the new technology. Bourassa[2] used zeolite and bentonite as a micro particle system in the clarification of drinking water accompanied with dissolved air flotation.

Park[3] undertook a study of activated-sludge and a comparison between zeolite and activated carbon carriers on the nitrification process. In Drag's[4] publication about the preparation of zeolite-carbon adsorbents, these adsorbents were used to treat waste waters from carbonaceous deposits. Princz[5] studied the improvement of biological degradability of wastewaters using activated zeolites. In the course of this treatment process, zeolite was added to the influent water or directly into the aeration basin of an activated sludge system. The zeolite increased ammonium removal efficiency and the decomposition rate of the organic matters as well as the settling characteristics of the activated sludge (sludge-volume index, floc size). The main result of the study was that the use of clinoptilolite zeolite was recommended for removal of Cs^{+}, Ni^{2+}, Sr^{2+} and Ba^{2+}, from radioactive or municipal wastewater, as the affinity of the mineral for these cations was relatively high.

Ellis[6] tried to remove organics from retort waters derived from Stuart Oil Shale using the high silica zeolites. Removal of organics increased with the decreasing polarity of the adsorbate and was improved when free ammonia was firstly removed by air stripping. Zeolites were more effective than activated carbon, and were potentially useful for pretreatment of retort water before biological treatment.

Perona[7] proposed a simple model for the removal of radioactive contaminants in process wastewater using chabazite zeolite columns. The study showed that mass transfer zone lengths increased from 10 to about 30 cm, as the superficial velocity increased from 5.5 to 22 cm/min. Calculations with a multi-component model showed that the distribution coefficient remained the same, while the effectiveness of the zeolite was increased.

2. Experimental Runs

Materials

1. Natural zeolite of clinoptilolite type (ZEOCEM Company, Slovakia)
2. Manufactured zeolite (Valfor 100, Aluminosilicate)
3. Activated Carbon of particle size 0.85-1.7 mm (10-18 mesh) and powdered one
4. Local refinery wastewater of KNPC in Kuwait

Procedures

The refinery wastewater was split into 50 ml samples. One was kept as reference and the other were treated using 5 g of adsorbent materials available, namely the natural zeolite, Valfor 100 and activated carbon. Each sample was batch shaked for 20 minutes using electrical shaker and magnetic stirrer. The sample was then paper filtered and analysed. The results consisted of the following analyses: pH, COD, BOD (5 days, 20°C), TDS, ammonia NH_3-N, nitrate NO_3-N, petroleum hydrocarbons, SO_4^{2-} and S^{2-}. All test units were in mg/l. The analyses were performed using an IR-spectrometer (Perkin) and UV-spectrometer (Philips). For BOD and COD the standard method described by the International Organization for Standardization were used.

Zeolites used in this study were analysed by the Scanning electron microscope (SEM) JEOL-JXA 840A integrated with the Energy dispersive multichannel X-ray (EDX) microanalyser KEVEX equipped with Si(Li) detector.

SEM and EDX Analyses

Natural zeolite of clinoptilolite type (deposit Nižný Hrabovec) received from Slovakia was surface-analysed using the scanning electron microscope (SEM) as above mentioned. Its surface morphology (crystalline shape) with 3000x magnification shows Figure 1. The elemental spectrum image of this raw clinoptilolite is depicted in Figure 3. EDX weight analyses of natural zeolite (clinoptilolite) after refinery water treatment are presented in Figures 2 and 4, respectively. The corresponding spectrum images of Valfor-100 are shown in Figures 5 and 6 as well as their elemental weight analyses manifest Figures 7 and 8. Finally, analysis of zeolite weight percent before and after wastewater treatment summarizes Table 4.

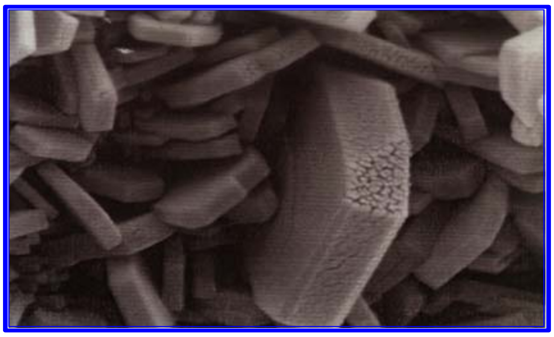

Figure 1. Natural zeolite by SEM under the 3000x magnification

3. Results and Discussion

Wastewaters from the local refinery (KNPC Kuwait) are mostly the effluents of various operational units that are mixed and treated before discharging to the closed sea. This mixture contains some heavy metals, petroleum hydrocarbons, NH_3-N and the other compounds (Table 1). Two million barrels of oil are being produced daily. Seventy percent (70%) of the oil production is being treated in three refinery plants. Oil refineries are located on the gulf. Presently, wastewater is treated by a skimming process and an aeration ditch, followed by a dillution process. This treatment is to match KU EPA requirements shown partially in Table 1. The analyses of the four potential adsorbents for this wastewater treatment presents Table 2.

Table 1 Partial analysis of effluent wastewater

Compound	mg/l	KU EPA limits
Iron	0.12	< 0.09
Aluminum	0.24	< 5
Copper	0.02	< 2
Nickel	< 0.01	<0.01
COD	160	2.5
BOD	40-60	30
Hydrocarbons HC's	4-10	5

Table 2 Batch experiment results of wastewater treated by various adsorbents

Test	Sample I	Sample II	Sample III	Sample IV	Sample V
COD mg/l	160	115.2	128	108.8	32
BOD mg/l	60	37.5	18	10	2
Ammonia NH_3 mg/l	63.5	9.9	20.5	26.6	53.4
Nitrate NO_3^- mg/l	0.037	0.043	0.018	0.138	0.012
Hydrocarbons HC's mg/l	4	1	2	0	0
SO_4^{2-} mg/l	240	230	180	160	175
S^{2-} mg/l	0.1	0.1	0.066	0.045	0.033

Sample I: Raw wastewater
Sample II: Treated using natural zeolite
Sample III: Treated using manufactured zeolite
Sample IV: Treated using granulated activated carbon
Sample V: Treated using powdered activated carbon

Based on the Tables 2 and 3 results, the natural zeolite performed better adsorption properties than the activated carbon in the removal of ammonia compounds (NH_3-N), but not as good ones in relation to the rest of examined pollutants. Comparing both the natural zeolite and Valfor 100, the natural zeolite was better adsorbent for ammonia compounds, only. Percentage removals of these brief tests summarizes Table 3. Considering the results of EDX analyses, both of zeolites i.e. natural clinoptilolite and manufactured Valfor seem to decrease some element contents from waters (Al, Si, Zn, Cu, Ti) Table 4, Figures 3-6.

Table 3 Percentage removal for each pollutant

% Change II	% Change III	% Change IV	% Change V
28.0	20.0	32.0	80.0
37.5	70.0	83.0	96.7
84.4	67.7	58.1	15.9
-16.2	51.4	-273.0	67.6
75.0	50.0	100.0	100.0
4.2	25.0	33.3	27.1
30.0	34.0	55.0	67

Table 4 Weight percentage of elements in zeolites before and after treatment

Element	Natural Zeolite 1	Natural Zeolite 2	Valfor 1	Valfor 2
C	-	-	13.73	2.07
O	60.82	57.64	52.39	51.28
Na	-	0.31	12.31	13.83
Al	4.98	5.21	10.76	15.32
Si	25.58	30.70	10.03	15.93
Cu	-	0.54	0.43	0.82
Zn	-	-	0.35	0.74
Fe	2.78	0.93	-	-
K	3.02	2.39	-	-
Ti	-	0.22	-	-
Ca	2.82	1.58	-	-
Mg	-	0.48	-	-

(2) zeolite samples enriched after water treatment

Zeolites, as it was confirmed, have many advantages as the pollution control agents. Natural and manufactured zeolite differs in their adsorption efficiencies. There is very important to know the nature of pollutants to be removed from contaminated media before deciding what a specific sorbent to select. In many applications, an activated carbon exhibits a sufficient capacity towards existing, especially organic water pollutants, however zeolite may adsorb some metals and ammonia more selectively.

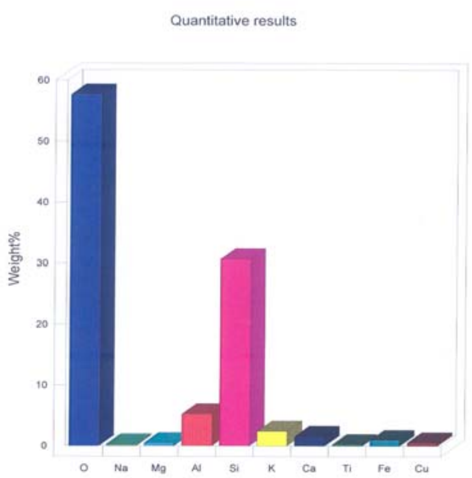

Figure 2. Elemental analysis of natural zeolite after treatment

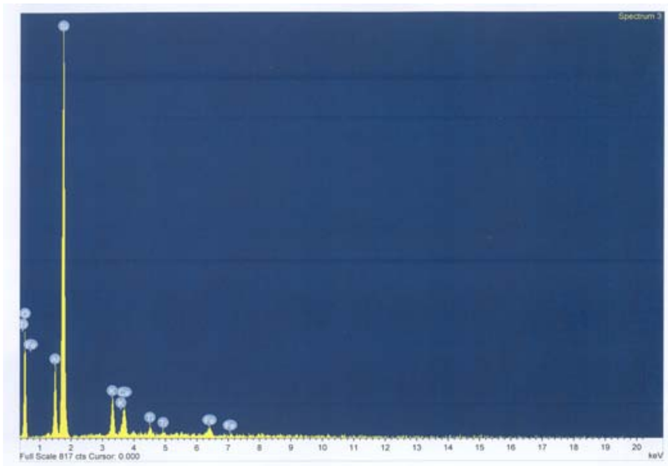

Figure 3. Spectrum image of natural zeolite before treatment

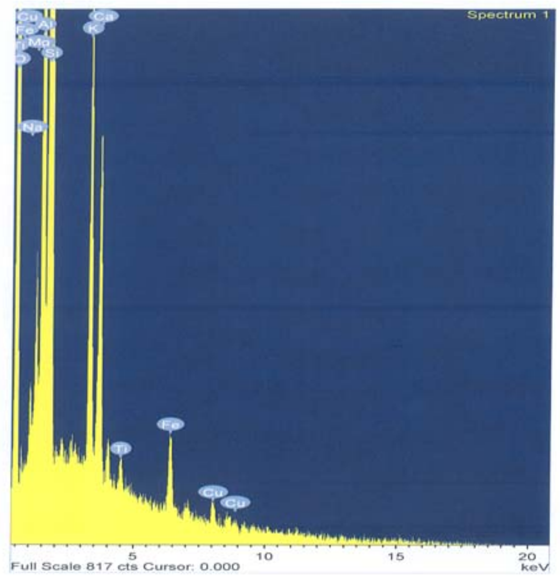

Figure 4. Spectrum image of natural zeolite after treatment

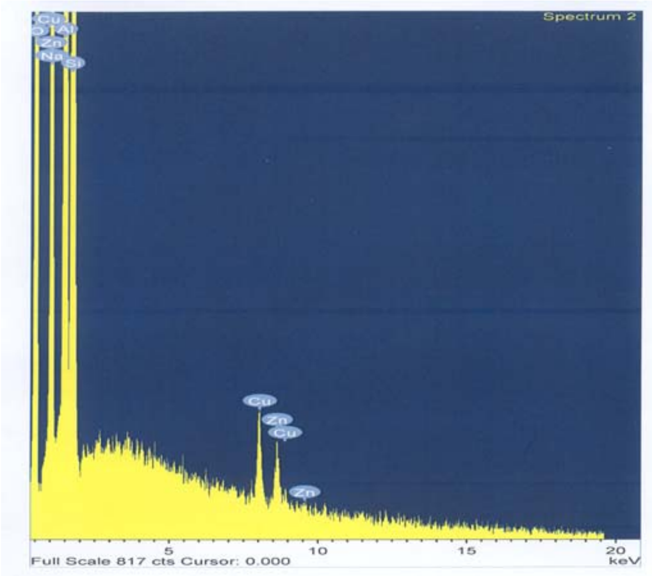

Figure 5. Spectrum image of Valfor-100 before treatment

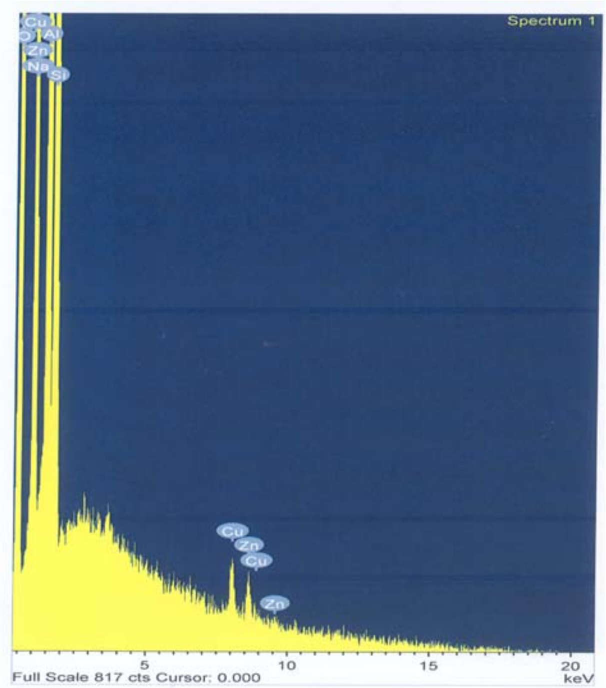

Figure 6. Spectrum image of Valfor-100 after treatment

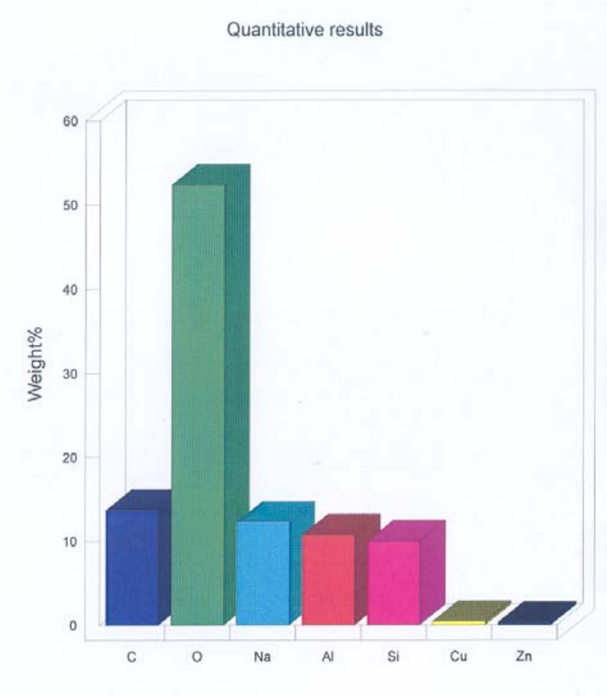

Figure 7. Elemental analysis of Valfor-100 before treatment

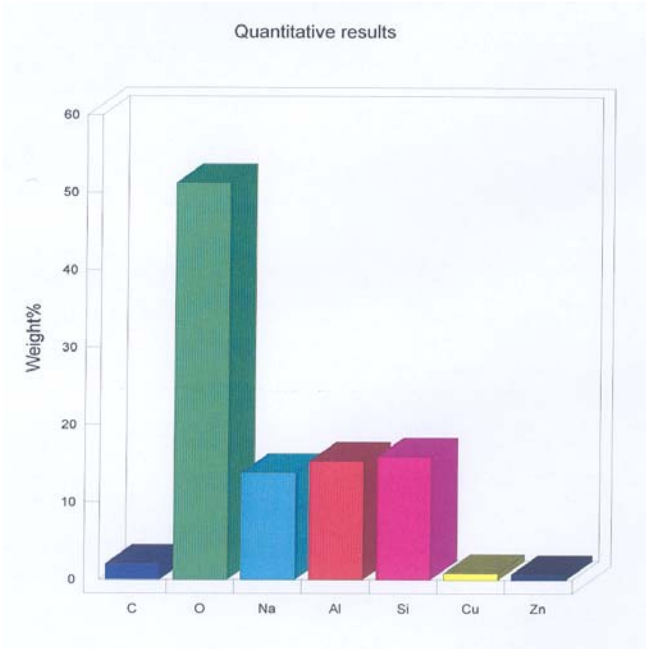

Figure 8. Elemental analysis of Valfor-100 after treatment

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4. References

[1] Tian, Wen-hua; Wen, Xiang-hua; Qian, Yi, J. Environ. Sci. (Beijing, China) 2004, 16, 1, 90-93.
[2] Bourassa, Caroline; Sain, Mohini; Daneault, Claude Cellul. Chem. Technol. 2003, 36, 1-2,193-202.
[3] Park, Se-Jin; Oh, Jang-Wook; Yoon, Tai-II, Process Biochem. (Oxford, U.K.) 2003, 39, 2, 211-219.
[4] Drag, Edwarda B., Pr. Nauk. Inst. Chem. Technol. Nafty Wegla Politech. Wroclaw. 2000, 57, 209-215.
[5] Princz, A Study Supported by NATO's Science for Peace Programme, 1999 NATO Project # SFP 972494.
[6] Ellis, J.; Korth, J.; Peng. Li, Fuel, 2001 74, 6, 860-864.
[7] Perona, J. J.; Coroneos, A. C.; Kent, T.E.; Richardson, S. A simple model strontium breakthrough on zeolite columns. Separation Science and Technology, 2003, 30, 7, 1259-1268.