

## Removal of PAHs from n-Paraffin by Modified Clinoptilolite

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**ABSTRACT:** The ability of natural clinoptilolite and its modified forms were studied for removal of PAHs from n-paraffin. Surfactant modified zeolite (SMZ) was obtained by modifying clinoptilolite with hexadecyltrimethylammonium ion. Homoionic forms of zeolite were obtained by ion exchange process using inorganic salts of desirable cations (e.g. Ag<sup>+</sup>, Fe<sup>3+</sup> ...). Natural clinoptilolite and its cation exchanged forms show small affinity toward PAHs, due to their hydrophil nature, whereas SMZ removed more than 50 percent of the initial PAHs contents of n-paraffin. The structure of zeolite did not change upon modification. Regeneration of zeolite was performed efficiently with chloroform.

**KEY WORDS:** Clinoptilolite, Modified zeolite, n-Paraffin, PAHs, SMZ.

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a complex class of organic compounds containing two or more fused aromatic rings. PAHs are widespread environmental contaminants; a number of them are even known or suspected as carcinogens. These compounds accompanying n-paraffin must be removed from n-paraffin before it is used as food and pharmaceutical grade products.

Purification of n-paraffin from PAHs and other impurities is accomplished by different methods. In conventional method, paraffin is treated with oleum (sulfuric acid and sulfur trioxide). Separation of the acid tar residue which is produced in this method is difficult. Solvent extraction method is also used for paraffin purification. In this method the impurity level of final product exceeds 0.3% by weight which is higher than acceptable standard level [1].

The current method for PAHs removal is catalytic hydrogenation. The main disadvantage of this method is conversion of some naphtenic compounds to aromatics. Recently, intensive researches have been performed to destroy PAHs through oxidative degradation by microorganisms [2,3]. Surfactant-enhanced remediation (SER) has been suggested as a promising method for removal of PAHs from contaminated soil and groundwater [4,5]. Purification of n-paraffin has been studied by adsorbents such as aluminosilicate and activated charcoal, [6,7]. Surfactant-modified zeolites (SMZ) have been used as effective sorbents for removal of inorganic cations, inorganic anions and neutral organic materials [8-11]. SMZ prepared by hexadecyltrimethylammonium (HDTMA) is stable in high ionic strength and in a wide range of pH. More than 90% of HDTMA remains on the zeolite surface after regeneration.

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Table 1: Chemical analysis of purified clinoptilolite.

Composition	Wight Percentage
SiO <sub>2</sub>	68.65±1.2
Al <sub>2</sub> O <sub>3</sub>	10.43±0.92
Na <sub>2</sub> O	2.34±0.44
K <sub>2</sub> O	1.72±0.29
CaO	1.78±0.46
MgO	1.261±0.31
Fe <sub>2</sub> O <sub>3</sub>	0.88±0.08
H <sub>2</sub> O	12.94±0.06

## EXPERIMENTAL

Clinoptilolite was obtained from a deposit of Semnan region in center of Iran. The raw material was ground and screened (>250µm<420µm). The ground sample was refluxed with deionized water in order to remove soluble impurities.

The purified sample was characterized to be clinoptilolite using wet chemical analysis, X-ray diffraction (XRD) technique and thermal method of analysis (TA). To study the effect of zeolite modification on PAHs removal, different homoionic form of Fe<sup>+3</sup>, Ag<sup>+</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup> were prepared by ion exchange process. Surfactant modified zeolite was also prepared by mixing 36.5 g HDTMA in 1 liter deionized water and 100 g zeolite powder for 1 day at 25 °C. The samples are assigned as NZ for natural zeolite, NH<sub>4</sub>Z (treated with 0.1 M NH<sub>4</sub>Cl), FeZ (treated with 0.1 M FeCl<sub>3</sub>), AgZ (treated with 0.1 M AgNO<sub>3</sub>) and SMZ (treated with 0.1 M HDTMA).

The cation content of the modified samples was determined by atomic adsorption spectrometry using a Varian model 500 spectrometer. The surfactant content of the modified zeolite was determined by CHN analyzer (Leco 300 model). XRD patterns of the sample were taken by using D8 Advance Bruker X-ray diffraction instrument (Cu K<sub>α1</sub>=1.54439[Å]). TG and DTG curves of the samples were taken by a Mettler TA 4000 thermal analyzer to study thermal behavior of the samples. 10 mg of sample was heated with heating rate of 10 K.min<sup>-1</sup>. Start and end temperatures were 25 °C and 700 °C, respectively. Adsorption of PAHs by natural and modified samples was studied under different experimental conditions. The amount of adsorbed PAHs was evaluated

Table 2: XRD data of Clinoptilolite and reference [19].

Reference		Clinoptilolite	
d	I/I <sub>0</sub>	d	I/I <sub>0</sub>
8.883	100.0	8.877	100.0
7.831	40.0	7.824	27.4
5.0888	24.8	5.081	23.5
3.982	49.2	3.948	97.4
3.889	24.4	3.891	46.2
3.412	32.1	3.409	23.8
3.161	27.2	3.157	26.2
2.967	26.4	2.958	40.2
2.743	9.7	2.787	26.6

by measurement of PAHs by spectrophotometric method using a Varian UV-VIS spectrophotometer model CARY-500. Naphthalene was used as a standard material and chloroform as a solvent. The absorbance of water was measured at 269 nm. Standard addition method was used to plot the calibration curves. The dynamic range was obtained between 2-20 ppm of naphthalene. IR spectra of the samples were taken by a Buck-500 Scientific Co. spectrometer; to confirm the adsorbing of PAHs by zeolite. Regeneration of samples was performed 18 times by treating zeolite with chloro-form via Soxhlet method.

Impure paraffin was obtained from Isfahan Refinery Complex, which 2.32% aromatic, 73.84% paraffin, 23.47% naphthenic and 0.37% olefin compounds [12]. Separation of PAHs was performed by mixing of 5 g of sample with 50 ml of paraffin. The mixture was shaken at 80 °C for 10 minutes and the solid phase was separated by filtration. The absorbance of filtrate was measured at 269 nm.

## RESULTS AND DISCUSSION

Chemical analysis of the samples was performed by the method proposed by Maxwell [13] and data are given in (table 1). The X-ray pattern shows characteristic lines at d-values of 8.877, 7.824, 5.081, 3.948, 3.891, 3.409, 3.157, 2.958, and 2.787 with relative intensity of 100.0, 27.4, 23.5, 97.4, 46.2, 25.8, 26.2, 40.2 and 26.6, respectively (table 2). As represented in Fig. 1 some quartz and albite impurities were also observed.

DTG curves of natural sample showed a characteristic dehydration peak between 298-370 K. The weight loss

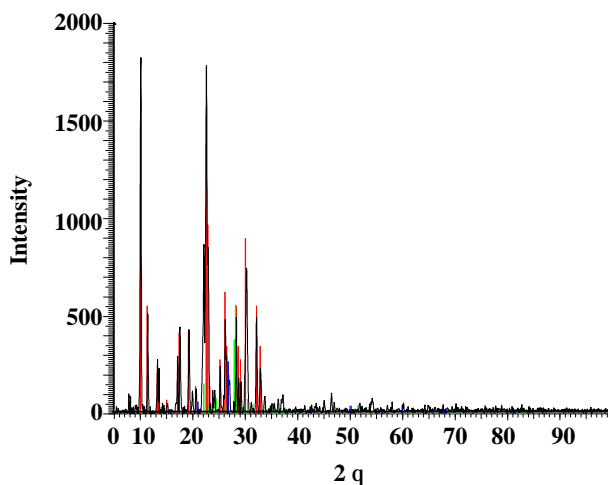


Fig. 1: XRD pattern of sample.

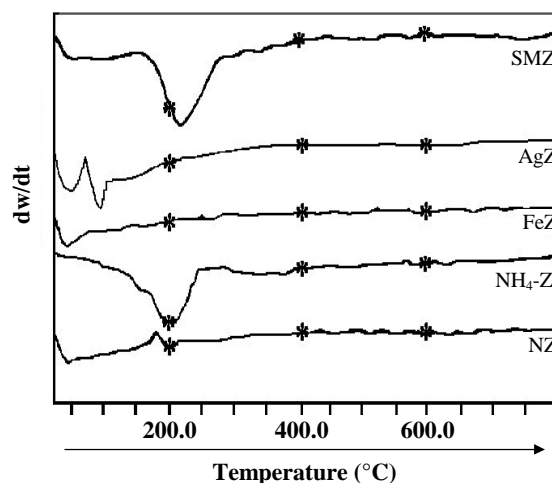


Fig. 2-a: DTG curves of modified samples.

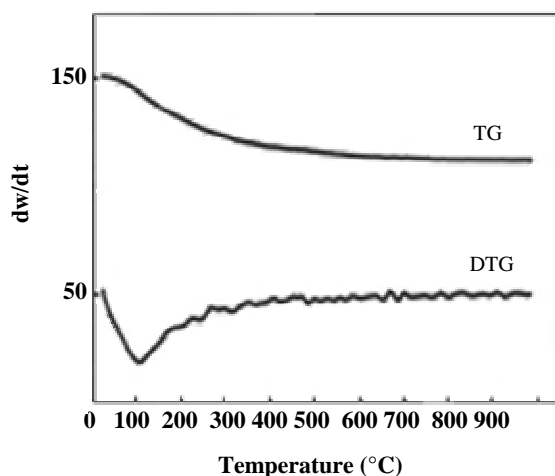


Fig. 3: DTG curves of raw clinoptilolite-rich tuff.

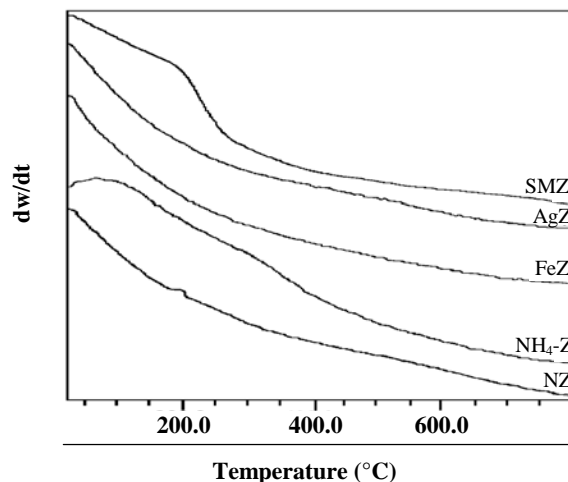


Fig. 2-b: TG curves of modified samples.

peak which occurred over a wide range of temperature is attributed to the loss of water molecules from different hydration sites. Setting of new cations into zeolite framework altered its water content and dehydration temperature. In AgZ samples the dehydration peak is splitted into two separate peaks indicating that the water molecules attached to silver ions are bonded more tightly than those bonded to sodium ions. In NH<sub>4</sub>Z sample the weight loss occurred between 340 and 550 K. This can be attributed to the slow release of NH<sub>3</sub> molecules. Due to the thermal decomposition of surfactant, a weight loss peak was observed between 425 and 580 K in SMZ sample as shown in Fig. 2-a and 2-b. The TG and DTG behaviors of standard clinoptilolite are shown in Fig. 3 [14].

The amount of adsorbed HDTMA was estimated by measuring the carbon and hydrogen contents of modified samples (table 3). As the particle size of the sample decreased, surfactant adsorption increased. It can be concluded that the surfactant molecules replace only those cations which are on the surface of zeolite.

According to the *Bowman's* work [15,16] in SMZ, surfactants micelles are formed through tail-tail interaction of the HDTMA which could create a positively charged interface on the organo-zeolite surface that could attract anions.

The paraffin molecules were captured most likely among tails and constitute a surfactant-paraffin lattice that is able to adsorb PAH molecules by using *van der Waals* forces (Fig. 4).

Table 3: Carbon and hydrogen content of the SMZ.

Sample	%C	%H	mmol HDTMA.g <sup>-1</sup> zeolite
>370 $\mu$ m < 850 $\mu$ m	3.16 $\pm$ 0.03	2.10 $\pm$ 0.02	0.05
>180 $\mu$ m <370 $\mu$ m	3.70 $\pm$ 0.03	1.94 $\pm$ 0.02	0.059
<75 $\mu$ m	8.17 $\pm$ 0.04	2.65 $\pm$ 0.05	.013
SMZ	5.94 $\pm$ 0.02	2.32 $\pm$ 0.01	0.094
SMZ + paraffin	8.32 $\pm$ 0.01	2.97 $\pm$ 0.03	-
SMZ + feed	8.34 $\pm$ 0.03	2.98 $\pm$ 0.01	-

Table 4: Effect of cation or surfactant content on dearomatization.

	NH <sub>4</sub> -Z	FeZ	AgZ	SMZ	NZ
Dearomatization(%)	18.64 $\pm$ 0.01	14.08 $\pm$ 0.03	14.90 $\pm$ 0.01	50.2 $\pm$ 0.02	9.58 $\pm$ 0.01
meq cation or surfactant.gr <sup>-1</sup> zeolite	1.81 $\pm$ 0.05	1.29 $\pm$ 0.02	1.66 $\pm$ 0.04	0.059 $\pm$ 0.02	-----
Dearomatization for each meq of cation or surfactant (%)	10.3	10.91	8.98	-----	-----
%Total adsorb (PAHs+paraffin)	49.70 $\pm$ 0.02	37.42 $\pm$ 0.01	38.50 $\pm$ 0.03	62.00 $\pm$ 0.01	21.60 $\pm$ 0.03
Regeneration (%)	49.74	37.62	38.26	62.48	21.69

The effect of temperature on dearomatization process was studied and the results are shown in Fig. 5. Process of dearomatization increases as temperature increases up to 353 K. At higher temperatures the adsorption capacity of the sample decreased. This can be attributed to the decrease of intermolecular forces at higher temperature.

The results of dearomatization are shown in table 4. The highest value is observed for SMZ sample (50.2%). Dearomatization by natural clinoptilolite and the exchanged forms was between 9.58 to 18.64%. It seems that attraction forces between surfactant and PAHs molecules are stronger than cation- aromatic  $\pi$  interactions [17] Fig. 6. The metals act as an electron donor and acceptor in the complexation interaction. An  $\sigma$  component of the bond results from overlapping of the cant outermost s atomic orbital of the metal with the full  $\pi$  (bonding) molecular orbital of the aromatic ring. This new molecular orbital, formed by donation of electron from aromatic ring to metal, has electron density concentrated between the bond members. In Ag (I) ions, the outermost s orbital is empty, because the single electron in the metal is also removed upon ionization to a +1 valence. In nonionizing facilitators, the metal is often bound to an electronegative atom. These electronegative atoms withdraw electron density from the metal, resulting in a partial positive charge and a substantially vacant

outermost s orbital. A  $\pi$  component of the metal-aromatic bond is formed by back donation of electrons from the full outer d atomic orbital of the metal to the vacant  $\pi^*$  (antibonding) molecular orbital of the aromatic [18]. This new molecular orbital has a nodal plane of electron density between the bond members (Fig. 6).

The adsorption of pure paraffin was studied as SMZ samples. DTG curves of the samples showed a new weight loss peak around 540 K which is possibly attributed to the release of paraffin at this temperature (Fig. 7).

The ratio of adsorbed PAHs to total adsorbed molecules (paraffin + PAHs) is considered as a scale to evaluate the efficiency of dearomatization. The ratios were between 0.38 to 0.40 for different samples (Fig. 8), it is concluded that the cation exchanged forms are not suitable adsorbents for PAHs because of low total capacity and low dearomatization ratio. In SMZ, although the total adsorption capacity is about 62% and the dearomatization ratio is 0.81, dearomatization is yet below the value needed for pharmaceutical applications (98% purity).

The regeneration of samples was conducted by Soxhlet method using chloroform as a solvent. The extracted solutions were examined by infrared spectroscopy. IR spectra of the extracted solutions were compared

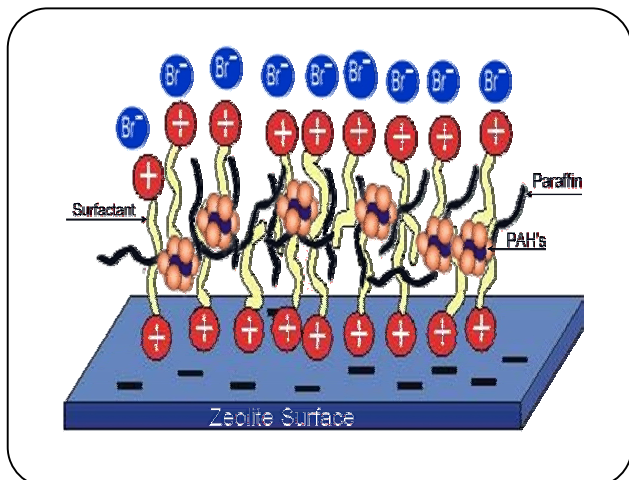


Fig. 4: Schematic representation of PAH adsorb by SMZ.

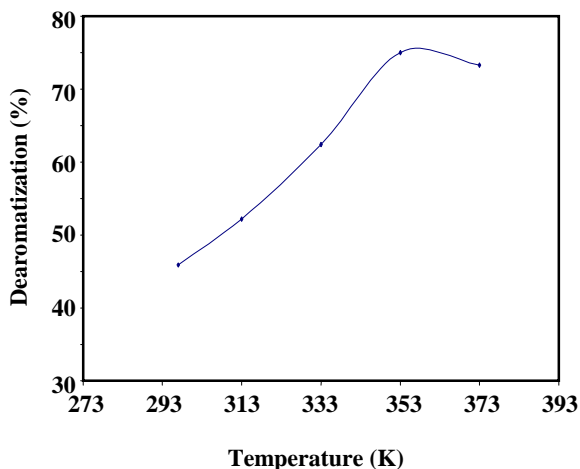


Fig. 5: Effect of temperature on dearomatization on SMZ.

to that of paraffin (Fig. 9). Both aromatic and aliphatic peaks are observed in the extracted solutions. =C-H aromatic rings stretching peaks appear, respectively, at 3004 and 3300  $\text{cm}^{-1}$  whereas C=C ring stretching peak appears as a doublet around 1475-1600  $\text{cm}^{-1}$ . As expected: In this experiment the absorption bands were observed at 1450  $\text{cm}^{-1}$ -1375  $\text{cm}^{-1}$  showing that regeneration was an efficient process.

FeZ sample contains 1.29 meq Fe per g (table 4) in which the cation content is less than those of AgZ and  $\text{NH}_4\text{-Z}$ , but AgZ has 8.98% dearomatization per mmol of cation in comparison to 10.91% and 10.30% per meq for FeZ and  $\text{NH}_4\text{-Z}$ , respectively. This behavior of AgZ is due to cation-aromatic  $\pi$  interaction. Because the outer d atomic orbital of the Ag is more available than atomic

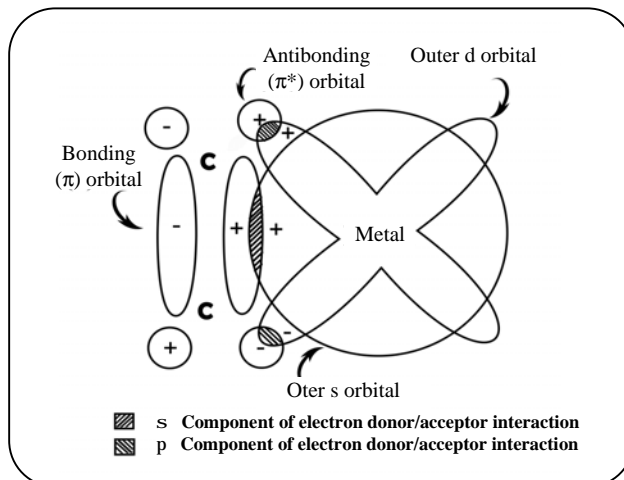


Fig. 6: Metal-aromatic interaction.

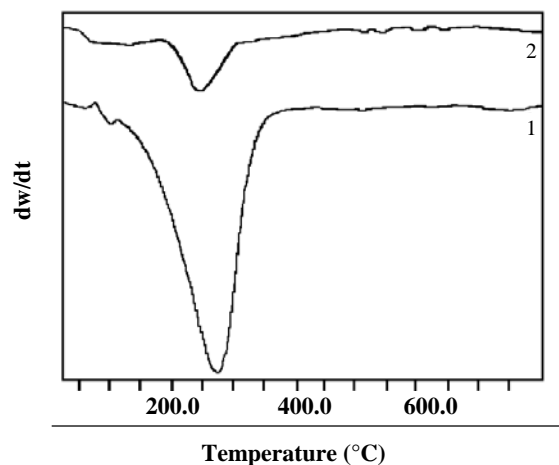


Fig. 7: DTG curves of samples: 1) SMZ after treatment, 2) SMZ before treatment.

orbital of other cations. In FeZ, the Fe cation has more hydrated radius than Ag, therefore, outer d atomic orbital of Fe is not available. As cation- $\pi$  interaction is stronger, the regeneration is lower.

In  $\text{NH}_4\text{-Z}$  sample where the exchange rate was 1.81 meq per g, and cation- $\pi$  interaction was weaker, the regeneration was higher. This may be contributed to the fact that the cation has not any empty outer orbital for aromatic  $\pi$  interaction.

Adsorption-desorption of PAH (Naphthalene) is represented in Fig. 10. The SMZ sample is able to adsorb more than 50% of naphthalene.

In this experiment, sample is SMZ and regeneration in A (-200 mesh) is 62%, B (-60+80 mesh) 58% and in C (-40+60 mesh) 56% from the extraction by chloroform.

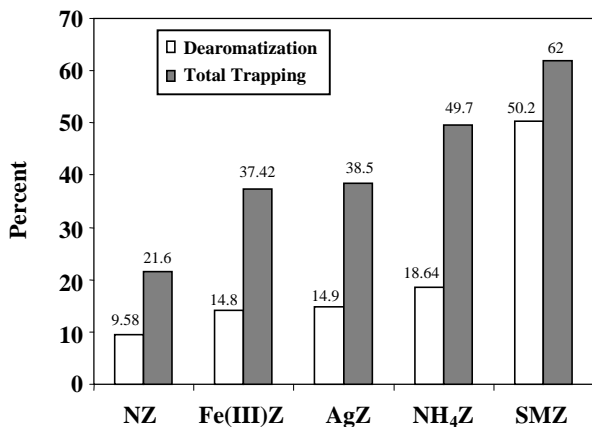


Fig. 8: Comparison of dearomatization and total trapping.

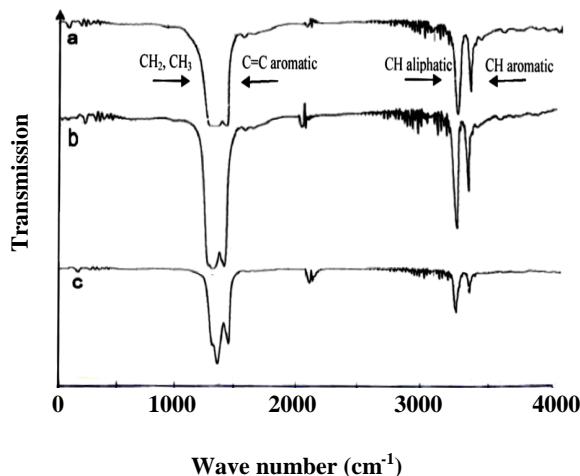


Fig. 9: IR Spectra of extracted solutions and impure paraffin.

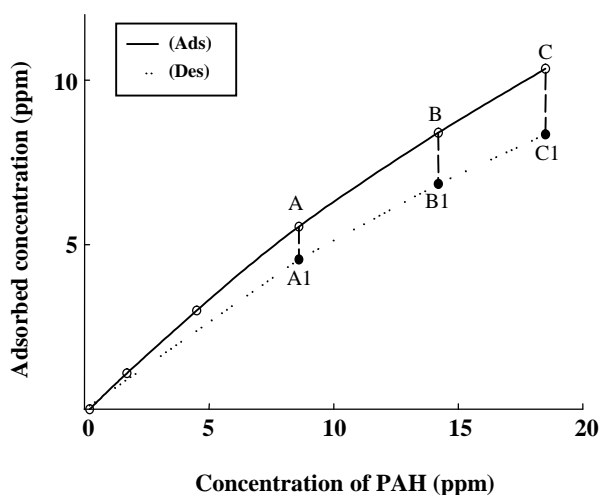


Fig. 10: Adsorption-desorption on SMZ.

For each region, it is possible to construct a "family" of releasing isotherms, each with a unique region on the adsorb branch.

## CONCLUSIONS

Surfactant modified clinoptilolite is able to remove more than 50% of PAHs from paraffin by a single treatment. In this method no liquid and gas wastes are produced and paraffin lost is also minimal. The regeneration of the sample can be performed by a single step.

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