Petroleum and Coal

Article **Open Access**

Yemeni Natural Zeolite as Adsorbent of Sulfur Compounds in Diesel Fraction

Fahed Salem Khamis[1], Yordanka Tsankova Tasheva[2], Galina Grigorova Khamis[1]*

[1] *Department of Oil and Gas Engineering, College of Oil and Minerals, Aden University, Ataq, Yemen*
[2] *Department of Industrial Technologies and Management, University " Prof. D-r Asen Zlatarov"-Burgas, Bulgaria*

Received March 18, 2021; Accepted August 3, 2021

Abstract

The presence of organosulfur compounds in middle distillate fuels not only leads to air pollution but are also a poison to catalytic converters, soot traps, and other harmful emission control technologies. A method has been developed for purification of sulfur compounds from diesel fraction from atmospheric distillation by adsorption with natural Yemeni zeolite from Al Al-Ahyuq area, Ta'iz governorate, Yemen and comparison of its adsorption ability with standard adsorbents - silica gel, alumina, and activated carbon. The performed adsorption processes of purification of gas oil fraction at different duration (from 30 to 360 minutes) and the ratio of raw material: adsorbent (1:10; 1:15 and 1:20) show that these methods could be used to obtain additional quantities of gas oil fuel for off-road and tractor equipment, according to the European norms.

Keywords: *Yemeni zeolite; Adsorption; Purification; Sulfur compounds; Diesel.*

1. Introduction

The presence of organosulfur compounds in middle distillate fuels not only leads to air pollution but are also a poison to catalytic converters, soot traps, and other harmful emission control technologies. Today in developed countries, the sulfur content is regulated in values lower than 10 ppm.

To remove organosulfur compounds from fuels, conventional hydrodesulfurization (HDS) in refineries requires extreme operating conditions such as high temperature and pressure, along with large amounts of catalysts and long residence times, but it is still ineffective in removing highly refractory sulfur types such as dibenzothiophene (DBT) and substituted DBT (e.g., 4.6 dimethyl dibenzothiophene). In this way, the production of diesel fuel with a sulfur concentration below 50 ppm by conventional HDS technology becomes uneconomical [1-2]. Many researchers have tried to develop alternative or complementary processes to conventional HDS. One of which is adsorption desulfurization, when silica gels, alumina, clay minerals (bentonite and montmorillonite), and zeolites, both natural and synthetic, are used as adsorbents.

The adsorption of dibenzothiophene, benzothiophene, 4,6-dimethyl dibenzothiophene, and other sulfur compounds was investigated on oxides of aluminum, zirconium, and magnesium. Adsorption has been found to occur mainly on acidic Lewis centers or on acid-base centers of the adsorbent. Alumina has the best adsorption activity, but due to steric factors, the adsorption of 4,6-dimethyl dibenzothiophene is difficult [3].

The adsorption of sulfur compounds in diesel fuel by selective adsorption on nickel nanoparticles deposited on silica gel mesopores was studied. It was found that the optimal content of nickel nanoparticles for the effective purification of sulfur compounds is 30% [4].

The selective adsorption of some types of sulfur compounds from raw materials in the production of oils using activated carbon and cobalt molybdenum contacts applied on activated carbon was studied [5-6]. In this work was shown that polyarene thiophenes are selectively and efficiently sorbed.

A method [7] was the purpose for the preparation of adsorption compositions for desulfurization using silica gels, bentonites, and montmorillonites, as well as molecular sieves with nitrate salts of transition metals.

It has been found [8] that the adsorption activity against organosulfur compounds increases in the order: thiophenes> aliphatic mercaptans> aliphatic disulfides> aromatic and cyclic thiols> aromatic disulfides> aliphatic and cyclic sulfides.

The adsorption of dibenzothiophene, quinoline, and naphthalene on nickel and cesium modified on ion-exchange zeolite Y was studied. It has been shown that when modified with nickel and cesium, the zeolite structure is partially amorphized, which leads to a slight decrease in the adsorption of dibenzothiophene [9].

A class of adsorbents has been developed which remove sulfur compounds by π-complex adsorption with thiophene compounds. It was found that Cu (I) –Y zeolite shows high selectivity for the adsorption of sulfur compounds from transport fuels. It was concluded that Cu + in Cu (I) –Y zeolite can remove sulfur compounds by π-complex adsorption with thiophene compounds [10].

Zeolitic tuff deposits in Yemen are found in three governorates: Ta'iz, Ibb, and Dhamar [11]. The natural zeolite deposits in the Ta'iz governorate are found mainly in two areas (Al-Adnah and Al-Ahyuq). The zeolite minerals occur in volcanic tuffs, and the kinds of natural zeolite minerals in Al-Adnah and Al-Ahyuq area are clinoptilolite, heulandites, and mordenite with rare stilbite [11].

The aim of the present work is to study the adsorption ability of natural Yemeni zeolite for purification of a gas oil component from sulfur compounds and comparison its ability with various standardized adsorbents.

2. Materials and methods

Our experiments were conducted in laboratory conditions. All reagents used for the experiments were commercially available and were not purified further. All solvents used in the experiments are standard, manufactured by Sharlau, Spain. Gasoil fraction, produced in Ma'reb refinery were used as raw materials. Its physicochemical properties are given in Table 1.

Table 1. Physicochemical properties of gas oil raw materials

No	Parameters	Methods	Gas oil
1.	Density at 20°C (kg/m^3)	EN ISO 3675:2004	832.0
2.	Distillation characteristics	EN ISO 3405:2019	
	-10 % (°C)		212
	-75 % (°C)		332
3.	Viscosity at 40°C (mm^2/s)	EN ISO 3104:2001	2,57
4.	Flash point (°C)	EN ISO 2719:2016	71
5.	Freezing point (°C)	ASTM D 97: 2017	-17
6.	Sulphur content (mg/kg)	EN ISO 8754:2006	524
7.	Arene content (%)	ISO 2977:2002	17
8.	Ash content (%)	EN ISO 6245:2004	0.011
9.	Water content (%)	ISO 3733:2003	neal
10.	Coke content (%)	ISO 6615:2002	0.0004
11.	Mechanical impurities (%)	St. of UMEA 2876:1981	neal
12.	Heat of combustion (MJ/kg)	St. of UMEA 3965:1983	42.735
13.	Characteristic groups	ASTM D 2007:2011	
	-alkane (%)		61.3
	-polar (%)		20.8
	-arene (%)		17.9

The hydrocarbon groups in gas oil raw materials were investigated by ASTM D 2007, too. Before determining the group hydrocarbon composition, raw gas oil fraction was deasphalted, because the presence of asphalt and mechanical impurities in the raw material would significantly impair the adsorption properties of the studied adsorbents due to the deactivation of their active centers. The deasphalting was carried out by treating the fractions studied by us

in an alkane solvent, during which the maltenes were dissolved, and the asphaltenes were precipitated and separated by filtration. For this purpose, 25 g of sample were weighed into an Erlenmeyer flask, and 10 times (by volume) amount of n-pentane was gradually added with constant stirring. The solution was allowed to stand for 4 hours, after which the precipitated asphaltenes were filtered through a pre-weighed and heated to a constant weight filter. The asphaltenes were washed again with n-pentane, the filter was first dried in air and then in a dryer at 105°C, and the filter was weighed again. The obtained filtrate was distilled to remove n-pentane and purged with air, and then subjected to adsorption separation.

The natural Yemeni zeolite used in our investigation is from the Al-Ahyuq area (Taʿiz governorate, Yemen), and it is characterized by a pore size of 200-230 mesh. The mineral composition of the analyzed sample shows that it is composed of 94 % clinoptilolite and 6 % quartz. The chemical data show that zeolitic tuff from the Al-Ahyuq area is composed mainly of SiO_2 (68.7%) and Al_2O_3 (11.98%), whereas Na_2O (0.61%), CaO (2.45%), and K_2O (3.69%) were the major single extra-framework cations in it.

To compare the adsorption ability of Yemeni zeolite, we performed similar experiments with standard silica gel 60, standard alumina 90 (manufactured by Valerus - Bulgaria with a certificate of Sigma Aldrich), and activated carbon obtained from us by pyrolyzed waste tires in previous experiments [12].

The activation of the selected adsorbents was performed by the following methods:

To activate the silica gel and zeolite, after loading them into the adsorption column, they were washed with ethanol and then air-dried. Thus prepared adsorbents were mixed with concentrated hydrochloric acid in a ratio adsorbent: concentrated hydrochloric acid (1:1.5), and the resulting mixture was heated for 3.5 hours while maintaining a constant temperature of 70°C ± 10°C (the temperature was kept constant by flask warmer). After removal of the acid, the adsorbent was washed first with distilled water (until chlorine ion-neutral) and then with 30% hydrogen peroxide solution. Then adsorbents were first dried for 6 hours at 50 ° C and then for a further 6 hours at 150°C.

The activation of the alumina was performed by heating it for 6 hours at a temperature of 750°C. The activation of carbon was performed by heating it first at 105°C for 6 hours and then for 6 hours at 450°C.

The experiments were performed according to the following procedure: After activation of the adsorbents, they were placed in the adsorption column and sealed by tapping with a rubber stopper. The column for the individual experiments was filled with adsorbents using the dry method. After loading the column, 10 g of the investigated gas oil component, previously dissolved in three times the solvent - n-pentane, was poured into it. The mass ratio of the investigated gas oil component to the input adsorbent varied (1:10, 1:15, and 1:20). The temperature of the individual adsorption processes is in the range of - 30-35°C. The collection rate of the individual filtrates was about 20 cm^3/min, depending on the duration of the individual adsorption processes and the amount of eluent. The eluents were fed successively in the following order: n-pentane, toluene, a 4:1 mixture of toluene and methanol (due to 4.6 dimethyl benzene and similar compounds, this mixture was fed) and ethyl alcohol. The individual fractions were collected in pre-weighed beaker cups, the solvent was evaporated on a water bath, and the resulting residue was weighed to constant weight. The sulfur content of the residues thus obtained was determined according to ISO 8754.

The used adsorbents were regenerated by removing the clear filtrate from the column, and then they were washed with distilled water. The washed adsorbent was placed in a beaker and mixed with hot distilled water. The mixture was refluxed for 30 minutes, after which the water was removed quantitatively. The adsorbent was flooded with hydrogen peroxide and left for 12 hours. After removal of the hydrogen peroxide (until neutral reaction with methyl orange), the washed adsorbent was dried first in the air, then for 1 hour at 80°C, 2 hours at 105°C, and finally for 2 hours at 450°C.

3. Result and discussion

A series of experiments with the following adsorbents – silica gel, alumina, activated carbon, and Yemeni zeolite were performed at the ratio of raw material: adsorbent were 1:10, 1:15, and 1:20. The results of the experiments are presented in Tables 2÷5.

Table 2. Experimental data with adsorbent silica gel

Type of adsorbent	Ratio of raw material: adsorbent	Sulfur content (mg/kg) obtained in an adsorption time, minutes					
		30	60	90	180	270	360
Silica gel	1:10	282	250	228	218	199	176
	1:15	259	232	223	204	186	155
	1:20	236	207	200	169	148	134

Table 3. Experimental data with adsorbent alumina

Type of adsorbent	Ratio of raw material: adsorbent	Sulfur content (mg/kg) obtained in an adsorption time, minutes					
		30	60	90	180	270	360
Alumina	1:10	275	242	223	213	181	162
	1:15	254	226	218	199	178	143
	1:20	224	200	174	165	144	125

Table 4. Experimental data with adsorbent activated carbon

Type of adsorbent	Ratio of raw material: adsorbent	Sulfur content (mg/kg) obtained in an adsorption time, minutes					
		30	60	90	180	270	360
Activated carbon	1:10	293	258	250	228	203	179
	1:15	266	239	232	211	196	178
	1:20	249	217	209	177	154	136

Table 5. Experimental data with adsorbent Yemeni zeolite

Type of adsorbent	Ratio of raw material: adsorbent	Sulfur content (mg/kg) obtained in an adsorption time, minutes					
		30	60	90	180	270	360
Yemeni zeolite	1:10	269	236	214	202	173	154
	1:15	248	218	207	183	164	131
	1:20	208	195	168	158	138	116

Based on the experimental data presented in the previous table, it can be seen that at the same ratio of raw material: adsorbent, Yemeni zeolite from the Al-Ahyuq area (Ta'iz governorate, shows the best adsorption properties - sulfur compounds in gas oil fraction decrease over four and a half times), while activated carbon shows the weakest adsorption properties to sulfur compounds (they decrease only 3.8 times). Intermediate results were obtained using silica gel as an adsorbent.

The study of the different duration of the process shows that with increasing contact time, the purification of sulfur compounds deepens, with the lowest degree of purification of the gas oil component shown at 30 min, and the best adsorption process is obtained at 360 minutes for all adsorbents used by us.

The conducted experiments indisputably show that the natural zeolite from the Al-Ahyuq apea can be successfully used for the production of diesel fuel for tractors and buses, which accorded the European standards for this type of fuel.

4. Conclusion

The performed adsorption processes for purification of gas oil fraction using silica gel activated carbon, alumina, and natural Yemeni zeolite at different duration and different ratios of

raw material: adsorbent shows that these methods could be used to obtain additional quantities of gas oil for off-road and tractor equipment which accorded the European standards for this type of fuel.

References

[1] Kumar S, Bajwa NS, Rana BS, Nanoti SM, Garg MO. Desulfurization of Gas Oil Using a Distillation, Extraction and Hydrotreating-Based Integrated Process. Fuel, 2018; 220: 754-762.

[2] Wang L, Sun B, Yang FH, Yang RT. Effects of Aromatics on Desulfurization on π-Complexation and Carbon Adsorbents. Chemical Engineering Science, 2012; 73: 208-217.

[3] Babich J, Moulijn. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. Fuel, 2003; 82 (6): 607-631.

[4] Corro G. Sulfur impact on diesel emission control-a review. Reaction Kinetics and Catalysis Letters, 2002; 75: 89-106.

[5] Mubic M, Sertiæ K. Alternative Processes for Removing Organic Sulfur Compound from Petroleum Fractions. Chemical and Biochemical Engineering Quarterly, 2013; 27(1): 101-108.

[6] Patil MS, Bhattacharyulu YC, Kulkarni SR. Desulphurization of hydrocarbon liquid fuels by adsorption. Journal of Engineering Research and Studies, 2011; 2 (1): 81-98.

[7] Serhiy P. Application of non-catalytic oxidative desulphurization process for obtaining diesel fuels with improved lubricity. Chemistry and chemical Technology, 2012; 6 (2): 229-235.

[8] Harlampidi HE. Seroorganicheskie soedinenia nefti, Metodi ochistki i modifikatsii. Himia, 2000; 6 (7): 42-46 (in Russian).

[9] Cooper B, Knudsen K. Ultra deep desulfurization of diesel: how an understanding of the underlying kinetics can reduce investment costs. Practical Advances in Petroleum Processing, 2006; 1: 297-316.

[10] Bhandari VM, Ko CH, Park JG, Han SS, Cho SH, Kim JN. Desulfurization of Diesel Using Ion-Exchanged Zeolites. Chemical Engineering Science, 2006, 61 (8): 2599-2608.

[11] Alshameri A, Xinghu W, Dawood AS, Xin C, Yan C, Assabri AM. Characterization of Yemeni Natural Zeolite (Al-Ahyuq Area) and its Environment Applications: A Review. Journal of Ecological Engineering, 2019; 20 (4): 157-166.

[12] Khamis FS, Khamis GG and Tasheva JT (2020), Obtaining of Dark Fuel from Thermal Cracking of Waste Tyre. International Research Journal of Modernization in Engineering Technology and Science 02 (11): 710-714.

To whom correspondence should be addressed: Dr. Galina Grigorova Khamis, Department of Oil and Gas Engineering, College of Oil and Minerals, Aden University, Ataq, Yemen, E-mail: *galinahamis@mail.bg*