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Fly Ash Derived Zeolites in the Removal of Toxic Compounds

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Abstract

The present paper describes the previous obtained results concerning purification of gases, water and sewages from toxic components such as mercury, radionuclides and petroleum substances. The tested materials constitute synthetic zeolites obtained in hydrothermal reaction, i.e., Na-X, Na-P1, and natural zeolite clinoptilolite. The zeolites (Na-X, Na-P1 and clinoptilolite) needed for mercury capture were activated by silver ions; however, for the removal of petroleum substances (Na-X and Na-P1) as well as radionuclides (Na-P1) raw zeolite materials were used. The review of the results have shown that zeolites used both for mercury capture and the removal of radionuclides, as well as petroleum substances, can be considered promising sorbent materials.

Keywords: fly ash, na-X, na-P1, clinoptilolite, mercury, radionuclides, petroleum substances

1. Introduction

The chemical impact on the environment as well as human health constitutes an increasing concern [1]. Therefore, the awareness of relationships between ecosystem and human health and their distribution in the environment [2] is growing worldwide. Considering chemicals that are toxic and harmful for the organisms, Plant et al. [1] distinguished four main groups of pollutants, i.e., (1) inorganic elements such as heavy metals, i.e., As, Cd, Hg, or Pb but also Se, I, NO_x, Ga and PGEs; (2) radioactive substances such as ^{238}U, ^{226}Ra, ^{222}Rn as well as process materials, i.e., depleted uranium or isotopes ^{137}Cs, ^{90}Sr, ^{243}Am and ^{240}Pu; (3) persistent organic pollutants such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs),

polybrominated diphenyl ethers (PBDEs), perfluorooctane sulphonate (PFOS); and (4) human and veterinary pharmaceuticals.

The European Environment Agency and the United Nations Environment Programme articulated the problem of chronic exposure to potentially toxic chemicals [3]. The increasing concern about harmful compounds in the environment is also reflected by the growing number of European Union (EU) Directives and national and international conventions related to chemicals [1].

For the removal of toxic pollutants in the environment, many sorbents and materials are investigated. One of the promising materials considered over the years is zeolites (alumino-silicates of alkali and earth metals). Due to their crystalline, infinite and three-dimensional crystal structure, they possess many important properties that are helpful in environmental and chemical sciences among others, such as, adsorption, dehydratation-rehydratation, ion-exchange molecular sieve and catalytic properties [4].

The various potential applications of both synthetic and natural zeolites depend on their fundamental physical and chemical properties that are in turn directly related to the chemical composition and crystal structure of individual species [5].

The present work describes the evaluation of zeolite materials for three toxic compounds, namely, mercury from flue gases, and radionuclides from mine waters and petroleum substances.

2. Zeolites as mercury sorbents

2.1. Characteristic of mercury pollutions in flue gas

Mercury in various forms (for example, Hg^0, HgCl and HgO) is one of the most important and dangerous environmental contaminants and has received special attention because of its high volatility, high toxicity and bioaccumulation ability [6].

It is believed that coal combustion is one the main sources of mercury emissions in the atmosphere, accounting for 60%, or even more, of the total mercury emissions [7]. The rest of the emissions originate from cement clinker production, and primary production of ferrous and non-ferrous metals is a predominant source of global anthropogenic mercury emission. Annual emissions of mercury to air form current anthropogenic sources are responsible for about 30% [8].

Considering combustion of fuels, the mercury in coal is volatilized and converted into elemental mercury (Hg^0) vapour in the high-temperature regions of coal-fired boilers. During cooling of flue gas, a series of complex reactions take place converting Hg^0 into ionic mercury (Hg^{2+}) compounds and/or Hg compounds (Hg_p) that are in a solid phase at flue gas cleaning temperatures or Hg that is adsorbed onto the surface of other particles. The presence of chlorine in flue gas causes the formation of mercuric chloride ($HgCl_2$) at flue gas cleaning temperatures. Nevertheless, Hg^0 is speciation; as a result, Hg enters the flue gas cleaning device(s) as a

mixture of Hg^0, Hg^{2+} and Hg_p. It is thought that majority of gaseous mercury in bituminous coal-fired boilers constitutes Hg^{2+}. But, the majority of gaseous mercury in subbituminous- and lignite-fired boilers is Hg^0 [9].

In conclusion, mercury in flue gas is found in three major chemical forms: gaseous elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}) and particulate-bound mercury (Hg_p). The mercury amount adsorbed on the particles of ash ranges from 5 to 10% of the total quantity of Hg released during the combustion processes. The remaining 90–95% of the mercury is released in the gaseous form. Mercury concentrations of flue gas from coal combustion generally range from 5 to 10 $\mu g/m^3$, with a large range in the relative proportions of Hg^0, Hg^{2+} and Hg_p. The most dangerous and the most stable mercury form that accounts for over 90% of the total mercury in the atmosphere is the elemental form. It is hazardous due to long residence time in the atmosphere (from 6 months to 2 years) but it could also be as short as hours to weeks under specific environmental conditions [10, 11] and due to migrating hundreds of kilometres from the source of emission. The gaseous form of Hg^{2+} lasts for only several days to several weeks in the atmosphere [12–14].

Another problem is that mercury is insoluble in the water, thus making inefficient the existing methods of their removal from flue gases [15]. To remove mercury-activated carbons (AC) commercially, their high cost and instability of the structure (degradation) in the exhaust gas temperatures are the major problems. In addition, these materials are not very efficient for removing mercury in the elemental form. Consequently, a large number of studies have focused on the possibility of using new techniques based on zeolites for removing gaseous elemental mercury species [16, 17]. The other forms of mercury (oxidized and gaseous divalent mercury Hg^{2+}) can react with ash particles to form the solids. These two forms, as compared to Hg^0, are efficiently removed from the gas stream by the conventional purification methods (wet desulphurization or bag filter) [14, 18–21].

2.2. Sorption mechanism of Hg on zeolites

Many materials are under examination because of their potential oxidation, capture and catalysis of mercury. The most frequently studied are, among others, palladium, gold, iridium, platinum, iron, fly ash and activated carbons [22].

Previous studies on removing gaseous forms of mercury (mainly Hg^0) from zeolites showed negligible adsorption of mercury vapour compared with the commercially used activated carbons. This may be related to the lack of chemical affinity of zeolites to mercury or a stronger affinity to the other, main components of exhaust gas (including water vapour present in the exhaust gas, which is rapidly adsorbed in the zeolite structure). Therefore, it can be concluded that the adsorption of gaseous forms of mercury is not a pure physical adsorption. In addition to zeolites, sulphur-activated carbons did not effectively adsorbed mercury, whereas sulphur-impregnated activated carbons are good sorbents of Hg and currently they are commercially used [23].

Silver activation of zeolite materials significantly improves their adsorption capacity with respect to mercury [17, 24–26], which is related to chemical affinity of silver to mercury. The

magnetic properties of Fe-activated zeolites also significantly influence the adsorption of mercury [27]. Manganese-oxidized mercury, Hg^0 to HgO, compounds are more easily adsorbed [28]. On the other hand, silver has a high affinity for mercury [17]. Mercury in contact with the silver-activated zeolite is bonded to the zeolite structure as a silver amalgam. Then, mercury is released from the structure of zeolite during the heating of zeolite to a temperature of about 400°C, indicating the possibility of regeneration of the material. An example for silver-impregnated zeolites is that the magnetic composite zeolite-containing silver nanoparticles were able to capture mercury from the flue gases in large scale from coal-fired power plants [26]. In order to improve the sorption of mercury on different sorbents, the bromine chloride (BrCl) to oxidize Hg^0 to $HgCl_2$ was used [29]. Nowadays, the introduction of selective catalytic reduction (SCR) increases the efficiency of the oxidation of Hg^0 to Hg^{2+} [30].

2.3. Results of mercury capture

Considering the results obtained by other authors, so far many materials have been observed and studied for their potential to remove mercury from exhaust gases. Others activated carbons (impregnated with iodine, bromine and sulphur) and carbon-based materials are fly ash, metals (such as silver, gold, copper and lead), and their oxides and sulphides, calcium species (lime) and zeolites [10, 15, 21, 31–35]. Unfortunately, most of these sorbents are less effective at higher temperature, in addition they have low capacities, cannot be regenerated and are easily deactivated by flue gas components such as sulphur oxides (SO_x) [36, 37], which means that the search for the ideal mercury sorbent is far from over [38].

Other raw materials for the capture of mercury zeolites were tested both synthetically and naturally. However, compared with the activated carbon, they showed much less adsorption capacity relative to the gaseous form of mercury. Therefore, significant attempts have been taken to activate them in order to improve their adsorption capacity.

The sorption tests of mercury compounds were performed by Wdowin et al. [17] at laboratory scale in pure mercury stream wherein nitrogen was used as carrier gas. Similar experiments were carried out by Wdowin et al. [6] in flue gas stream wherein gas mixtures were composed of SO_x, NO_x, CO_2, HCl, HF and CO.

The tested materials in the experiments carried out by Wdowin et al. [17] constitute Na-X, Na-P1, clinoptilolite. In order to enhance their sorption capacity to mercury, the investigated materials were activated with silver by using the ion-exchange method.

The first experiment was carried out in a pure stream of Hg^0 wherein nitrogen was used as carrier gas. The tested raw zeolite materials were not able to remove more than 10% (by weight) of mercury; therefore, their sorption capacity at the breakthrough of the bed could not be calculated.

Table 1 clearly shows that the addition of Ag^+ to the tested samples significantly improves the performance of the zeolite with respect to mercury capture. The best results were observed for the sample of Ag-X, which is associated with the highest BET surface area and the largest volume of micro- and mesopores. This result suggests that both micro- and mesopores are essential for the mercury capture. Moreover, in this case multilayer adsorption is an important

parameter, but only to some extent, because Ag-P1 possesses a larger volume of meso- and macropores and Ag^+ ions, but this zeolite captures lower amount of mercury. The results were compared with commercially available activated carbons.

Sorbents	Flow rate N_2 (ml/min)	Evaporation (mg/min)	Time to breakthrough (5%)[*] (min)
Na-X	80	0.00288	2
Ag-X	80	0.00288	13017
Ag-X	160	0.005766	5327
Na-P1	80	0.00286	0
Ag-P1	80	0.002883	1536
Clinoptilolite	80	0.00286	2
Ag-Clinoptilolite	80	0.00286	5
AC/Br	80	0.002883	2538

Breakthrough when 5% of Hg passed through the sorbent bed without being captured.

Table 1. The results of Hg^0 capture on the raw and silver-activated zeolites [17].

From **Table 1** it can be concluded that Ag-X zeolite found very promising results because it has achieved five times better result of Hg capture as compared with AC/Br zeolite material.

Moutsatsou et al. [39] obtained similar results of Hg capture on clinoptilolite; it was very low especially compared with the synthetic zeolites. It also was not improved by silver-activated clinoptilolite.

The removal of the gaseous forms of mercury from exhaust gases was carried out by Wdowin et al. [6] on the zeolite Na-X-activated silver (Ag-X) in an especially designed oven. The tested zeolite beds were in the granular and powder form. The Hg flow rate was established at 85 dm^3/h. The estimated exhaust gas composition at an oxygen concentration of the order of 4–8% was as follows: CO_2 = 11–17%, CO = 20–50 ppm, NO = 70–100 ppm, SO_2 = 650–1000 ppm. The fixed gas stream was passed through a sorbent bed.

Studies that remove gaseous forms of mercury from the exhaust gas at the Ag-X zeolite in the form of powder and granulate showed that granulation enhances the efficiency of the tested material. The average penetration of mercury was 15% in the test lasting about two hours, whereas the presence of other components (mainly sulphur compounds in the flue gases) reduces the efficiency of the tested sorbent in comparison to tests carried out in a clean gas stream of Hg (carrier gas N_2). The better results were obtained for granulated zeolite materials.

Hsi et al. [40] studied fly ash and zeolites of types A and Y in terms of the removal of elemental Hg and $HgCl_2$ in the flue gases. They studied both starting materials and sulphur-activated materials. Studies have shown negligible adsorption of Hg compounds by initial fly ash and sulphur-activated materials. These results explained that the adsorbents' porous structure, mainly as micropores, is one of the important factors for Hg^0 and $HgCl_2$ adsorption. In addition,

the authors point out that the reason for these results is the water content in the structure of the zeolite. Therefore, prior to impregnation it is necessary to get rid of H_2O from the zeolite structure. Studies show that too small size of the zeolite channels is also a cause of low adsorption of Hg compounds.

Morency et al. [41] investigated the use of a low-cost additive to improve the capability of a high surface area sorbent such as zeolite to remove all forms of mercury vapour from power plant flue gases. They examined treated zeolite wherein preliminary research led to the conclusion that a zeolite material could achieve substantial mercury removal at a significant cost reduction over current mercury control technologies. They carried out the adsorption test of Hg compounds at 150°C on activated natural zeolite (clinoptilolite) and synthetic (A, X, Y, ZSM-5) zeolites. The results proved to be similar to the results obtained on the active carbons. In addition, the zeolites used in the experiments captured all forms of mercury present in the flue gas. This material is also much cheaper than the commercially used activated carbons for this purpose. These authors also found that synthetic zeolites are better for the removal of mercury compounds due to the constant size of the channels and chambers, whereas sizes of natural zeolites are variable and are often associated with a number of network defects; however, natural zeolites are much cheaper material. In addition, after the Hg adsorption experiment on zeolites, these authors conducted leachability test on this material wherein they obtained positive results, i.e., the tested sorbent can be safely disposed in a landfill if sale of the ash is not an option.

In addition, Morency et al. [42] conducted a successful Hg adsorption test on two types of treated zeolites. The experiment was conducted at a temperature of 130–200°C of flue gas and a concentration of 30–60 μm/m^3 of Hg. Studies have shown almost 100% adsorption of Hg at an Hg ratio of 25,000.

Morency et al. [16] carried out experiment on adsorption of Hg compounds of the flue gases on activated carbons and raw and treated zeolites using appropriate chemical reagents. The results showed that in the case of treated zeolites, they show similar results to those of active carbons whereas their efficiency is greater than 90% at a ratio of injected mercury 25,000 g/g.

Pavlish et al. [43] have studied the adsorption of mercury compounds wherein A class of magnetic zeolite composites with supported silver nanoparticles has been tested for elemental mercury removal from power plant flue gas. As a result, this type of activation mercury capture levels of 45–92% was achieved at high ratios of sorbent to mercury ranging from 20,000 to 100,000, with no decrease in capture observed and an increase in gas temperature between 130 and 200°C. In Addition, high dose rates of zeolites, which are composed of aluminosilicate, will not degrade the commercial value of fly ashes used as a substitute for cement in concrete or as filler in plastics.

In many reports on the removal of mercury from flue gas, it is underlined that zeolite-based sorbents are not as efficient as activated carbons but can be much more economical to use than the commonly used carbons.

Mercury sorption experiments on the non-carbon materials at 110°C were conducted by Jurng et al. [23]. For this purpose, they used zeolite and bentonite materials with a relatively low

surface area (less than 30 m^2/g), which were sulphur activated in order to improve the sorption. As an activating agent, CS_2 solution was used. The results showed 50% of the sorption of Hg compounds for both the starting and activated zeolites and bentonites.

3. Zeolites as radionuclide sorbents

3.1. Characteristics of radionuclides in mine water

The development in the field of nuclear science and technology, generation of electricity in nuclear power plants, nuclear weapons testing, and the use of radionuclides in a research and medicine have led to the increase in the production of various wastes (both liquid and solid) containing radionuclides and release of artificial radionuclides into the environment. It is thought that radiocaesium ^{134}Cs and ^{137}Cs are one of the most abundant radionuclides in nuclear fission products and is considered as hazardous element [44, 45].

One of the most important sources of radionuclide pollution is the mine waters. Some mines have a serious problem with utilization of mine water rich in the radionuclide elements among others Silesia mines in Poland. There are also other areas all over the world where significant radioanomalies are present, including a coal mining district in Germany where radium-bearing waters occurred with ^{226}Ra concentration up to 63 kBq·m^{-3}. One of the major sources of radiation in such areas is related with hard coal mining activity. Sometimes in radium-bearing mine water barium ions are also present, in some mines in concentrations of up to 2 g·dm^{-3}. Contrary, in other waters no barium can be found but radium and sulphate ions are present. The presence of barium in mine waters is the most important factor for the further behaviour of radium isotopes in mine galleries or on the surface. From waters with radium and barium these elements always co-precipitate as sulphates, when such waters are mixed with any water, containing sulphate ions [46]. Coal, deep circulation groundwater, and deposits contain significant quantities of ^{226}Ra and ^{228}Ra as a member of the uranium chain.

In addition, natural waters with similarly high radium concentrations are observed, especially in oil fields. For example, hot springs in Iran contain up to 330 kBq·m^{-3} of ^{226}Ra [47].

3.2. Sorption mechanisms of radionuclides on zeolites

In the case of radionuclide sorption onto zeolite such mechanisms are quite simple in comparison to mercury capture. Zeolites due to their ion-exchange properties have received great attention, especially for application in radioactive liquid waste treatment [48, 49]. The radioisotopes in the form of cations, present in the liquid effluents of low and intermediate levels of liquid waste, are removed by the ion exchange with the Na$^+$ ions present in the zeolite structure in ion-exchange positions. Zeolite materials are characterized by high exchange capacity, selectivity and specificity, and good resistant to radiation, which is very important with respect to the immobilization of radionuclides and final disposal when compared with organic ion exchangers [45, 49–51].

The results of Remenárová et al. [52] on the removal of radionuclide from solution have shown that maximum sorption capacity is achieved though high values indicating that the physical adsorption is not the main binding mechanism. So far many studies [45, 53–56] based on the chemical nature of zeolites stated that ion exchange is the dominating mechanism of metal cation sorption in which cations in the zeolite framework are replaced by metal cations present in water.

Some author modified the surface properties of zeolite in order to enhance the sorption capacity for the removal of radionuclides. For example, Singh and Dutta [57] modified the surface of the zeolite Y type using *n*-octadecyltrichlorosilane for the extraction of ^{137}Cs and ^{90}Sr from aqueous to organic phases [35, 57].

The removal of radionuclides such as ^{137}Cs and ^{134}Ba onto zeolites was investigated by Chmielewská-Horváthová [58]. The examinations were carried out on synthetic aqueous solutions using clinoptilolite and mordenite. In this process, the predominant reaction was also related to the ion exchange of cations that occur in mineral structure, i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+. Results have also shown that pH of tested solutions is also important in the sorption capacity of tested zeolites, where the best pH values of sorption are almost neutral.

In addition, Elizondo et al. [59] studied the effects of pH solution and particle size on the removal of ^{137}Cs and ^{90}Sr by natural zeolite (clinoptilolite) from liquid radioactive wastes and observed that natural zeolite is an effective filter for the radionuclides from a liquid radioactive waste solution with a pH value of 8.

Consequently, Faghihian [60] used modified zeolites for the removal of radioactive iodine (^{121}I and ^{131}I) with different quaternary alkylammonium ions to replace the exchangeable cations from the zeolite surface.

3.3. Results of radionuclide sorption

The third experiment on radionuclides for the removal of (^{226}Ra and ^{228}Ra) from mine water taken from a hard coal mine KWK Piast was carried out by Chałupnik et al. [61]. The effectiveness of tested zeolite (Na-P1) with regards to the removal of radionuclides was measured in an experiment performed under dynamic conditions.

The effectiveness of zeolite sorbent with regards to the removal radionuclides was measured under dynamic conditions wherein the used mine water (KWK Piast, Poland horizon 650 m) contained the following concentrations of isotopes: ^{226}Ra 4.216 ± 0.534 [kBq·m^{-3}], ^{228}Ra 7.81 ± 1.46 [kBq·m^{-3}] (thermal conductivity was 119,000 μS·cm^{-1} and salinity was 110 g·dm^{-3}). In this experiment, the column of about 30 cm in diameter was filled with 26 kg of sand and 2 kg of tested zeolite.

The results obtained by Chałupnik et al. [61] on the removal radionuclides (^{226}Ra and ^{228}Ra) have shown high efficiency of up to 98% of the tested zeolites. After passing 120 dm^3 of mine water through the zeolite bed in the column, the concentration of ^{226}Ra decreased to a value of 0.017 kBq·m^{-3}, and in the case of isotope ^{228}Ra decreased to a value of 0.05 kBq·m^{-3}. It has been concluded that despite the adsorption of about 500 Bq of ^{226}Ra and about 1000 Bq of ^{228}Ra still

no breakthrough of zeolite bed had occurred. They also carried out preliminary laboratory tests on "synthetic waters" and found that for waters with a similar concentration of radium ions as in the experiment a column breakthrough could only occur after passing approximately 1200 dm^3 of water through it with similar characteristics as in the present experiment [61].

The analysis of the water samples obtained after the process of removing radium ions showed that using Na-P1 zeolite for the removal of radionuclides has no effect on the level of calcium or magnesium concentration in the purified water where their concentrations before and after the experiment are similar. The same tested zeolite also did not cause significant changes in the concentration of monovalent metals (sodium and potassium) as well as iron, strontium and manganium in the solution. Moreover, no change was observed in the concentrations of anions (chloride, sulphate, or bicarbonate ions), which are not adsorbed by Na-P1 that is related to the negative charge on their surface [61].

Other authors carried out the removal of radiounuclides using different zeolites among others natural zeolites. Gallant and Prakash [62] carried out dynamic experiment onto the removal of radionuclides such as ^{137}Cs, ^{60}Co and ^{90}Sr from water effluents also rich in Cu, Cd and Zn from nuclear operations using clinoptilolite and chabazite. Experiments have shown that in multication solution caesium is easily removed by both zeolites, so it would be economical to remove caesium first from such solutions using low-cost zeolites [62].

In 2014, Remenárová et al. [45] used synthetic zeolites from fly ash for the removal of caesium from the solution of CsCl under static conditions. They have examined the influence of pH on the sorption of radionuclides and the results have shown that the better sorption was found at pH values ranging from 4 to 5. Nevertheless, the carried out experiments have shown that synthesized zeolite materials could be suitable sorbents for the removal of radiocaesium from liquid radioactive wastes. Moreover, Moattar and Hayeripour [46] have examined natural zeolite (clinoptilolite) for the removal of ^{137}Cs, ^{60}Co and ^{54}Mn from low-level radioactive liquid waste under static and dynamic conditions. In such experiments, zeolites showed the same promising results in the removal of caesium.

El-Naggar et al. [49] used A type synthesized zeolite and evaluated it as an inorganic ion-exchange material for the removal of ^{137}Cs and ^{90}Sr ions from aqueous solutions in both batch and fixed bed column operations. The results have shown that the total ion uptake of these metals and the overall bed capacity decreased by increasing the flow rate and increased by increasing the initial ion concentrations and bed depth. The removal of caesium was also investigated by the International Atomic Energy Agency [63] where tests of the removal of ^{137}Cs ions for aqueous solution were carried out using synthetic NaA-X zeolite. This synthetic zeolite showed a promising sorption behaviour.

Soelberg et al. [64] impregnated zeolite of silver in order to enhance the uptake of volatile radioactive iodine and krypton. Silver impregnated zeolites showed high iodine decontamination factors as high as 105, iodine loading capacities and other adsorption parameters including adsorption rates.

4. Zeolites as petroleum substance sorbents

4.1. Characteristics of petroleum substances

Crude oil belongs to the group of natural hydrocarbon fuels, such as natural gas or coals, which was created as a result of biochemical, chemical and geochemical transformations of organic matter derived from dead plant and animal organisms. It is the liquid mixture of hydrocarbons, oxygen and sulphur compounds, containing trace amounts of various inorganic compounds and elements. The conventional crude oil is mainly composed of hydrogen and carbon in an atomic relation H/C ~ 1.85. Other elements such as sulphur, nitrogen and oxygen are usually not less than 3% (by weight) of its content. The remaining components of the crude oil are usually trace amounts of phosphorus, arsenic, selenium and heavy metals such as vanadium, nickel, iron, cobalt, copper and mercury.

The composition of the hydrocarbons in crude oil consist of paraffinic hydrocarbons (aliphatic), cycloparaffinic (naphthenic) and aromatic among which the cycloparaffins dominate (approximately 50% content). Aliphatic hydrocarbons are the second group of the hydrocarbons present in crude oil in substantial quantities. It is assumed that crude oil comprises *n*-aliphatic (straight) hydrocarbons with the number of carbon atoms from 1 to 60. Except *n*-aliphatic hydrocarbons, branched chain hydrocarbons are present in significant amounts. Their boiling point is lower than the boiling point of unbranched equivalents. Aliphatic hydrocarbons (straight and branched) have lower density and are more volatile than their naphthenic analogues.

Aromatic hydrocarbons contain at least one benzene ring in the molecule. Crude oil usually contains up to 15% of arenes. This type of compounds are typically concentrated in fractions boiling at a higher temperature, such as lubricating oils and residues, where the concentration may exceed 50%. Among the aromatic hydrocarbons, toluene and *m*-xylene are present in the crude oil to the largest quantities. Monocyclic aromatic hydrocarbons constitute a valuable component of the fuel. It should be emphasized that the benzene and its alkyl derivatives (ethyl benzene, toluene and xylene) are compounds with carcinogenic properties and very high toxicity. These features and the relatively good water solubility make them a group of substances that is very hazardous to the environment. On the other hand, polycyclic aromatic hydrocarbons (PAHs) are concentrated in petroleum products such as diesel oils boiling at high temperatures, lubricating oils and residues distillation. They have the ability to accumulate in tissues of living organisms and exhibit the carcinogenic properties [65].

Petroleum distillates are components of commonly used refined products such as gasoline, aviation fuel, diesel fuel and motor oils, hydraulic oils, fuel oils, base oils for lubricants, petroleum waxes, asphalt, petroleum coke and petrochemical raw materials.

Currently, there is a special emphasis on the preparation of such petroleum products that have a minimum negative impact on the environment. Interaction depends on many factors that include the physical, chemical and toxic properties of the product, the manner of its use, scale of consumption and method of disposal. Fuels accounts for about 80% V/V of the processed crude oil and therefore they are the biggest source of oil pollution of the environment [52].

Other products representing approximately 1.5% of processed crude oil pose a smaller risk, albeit not without significance for the environment. In fact, there is still a problem with waste oil and other petroleum waste, which are the substances of potentially dangerous status from the point of view of ecology.

Undesirable effects of petroleum substances are due to their physicochemical properties, including viscosity, density, lipophilicity and hydrocarbon composition that determines these properties.

Among the petroleum compounds particularly dangerous to life and health of living organisms, volatile aromatic hydrocarbons, such as benzene, toluene, ethylbenzene and xylene (BTEX), can be distinguished. These compounds are components of many solvents or fuels, such as petrol or diesel oil [66–68]. They tend to accumulate in groundwater and are also soil or air pollutants [69]. They are carcinogenic, irritate the mucous membranes, cause changes in haematology, central nervous system disorders, respiratory problems, abnormal liver function and kidney function. They act toxic even in small concentrations, and their inhalation or ingestion may result in death [69, 70].

4.2. Sorption mechanisms of petroleum substances on zeolites

Several mechanical, biological and chemical methods are used to liquidate oil spills from water and paved roads [11, 33, 71–76]. Among these methods, one of the most popular is the sorption method using sorbents of different origins. Sorbents are solids with developed surface and able to bond molecules on their surface (from liquid or gaseous phase). These sorption features are characteristics of zeolite minerals.

The most commonly used adsorbents for oil spills on paved surfaces (roads, asphalt and land) are those of mineral origin. For this type of materials, the sorption process takes place according to the physical sorption including two main mechanisms. The first one is a stage of sorption associated with filling of the available pores in the material and the capillary pores between the grains of the sorbent according to mechanism involving capillary (mass transport). Capillarity depends on, among others, the effective diameter of the capillary, or surface energy of the interior wall of the capillary and viscosity of the oil. After this step, sorption occurs on the outer surface and an oily film layer is created around the grain of sorbent (or optionally around the agglomerate grains). On the surface of the sorbent grains, oil can create a uniform layer (film) or irregular aggregates, depending on the morphology of the material surface, its irregularities and the properties of the oil [77].

The adsorption of petroleum compounds from aqueous solutions (e.g., solubilized form of organic compounds such as BTEX) on porous sorbents involves diffusion process, the course of which may include transport of the molecules in the vicinity of the adsorbent, the diffusion in a boundary layer, the diffusion in sorbent's capillary, surface diffusion and intra-particle diffusion.

4.3. Results of petroleum substances sorption

Some relevant papers concerning removal of petroleum substances indicate the possibility of using zeolites for this purpose, including those derived from fly ash.

A comparison of sorption properties in relation to diesel fuel (Biodiesel and Verva ON) of zeolites from fly ash on the zeolite types of structures of Na-P1 and Na-X and natural clinoptilolite as well as on commercial silica-based sorbent (Absodan) was presented by Bandura et al. [78, 79]. They received the sorption capacity of the order of 1.24–1.40 g/g for Na-P1 zeolite, 0.91–1.13 g/g for Na-X zeolite and 0.31 g/g for clinoptilolite. For commercial sorbent, the sorption capacity was 0.83–0.95 g/g (**Figure 1**).
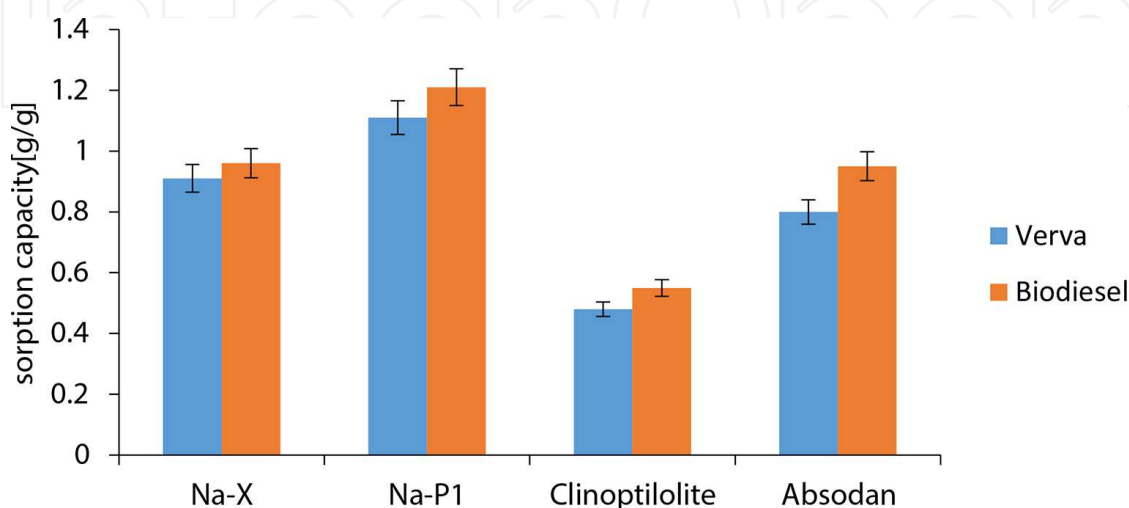

Figure 1. Sorption capacity of zeolite materials.

Na-P1 and Na-X zeolites also showed good sorption properties with respect to oils similar to sepiolite and vermiculite and some commercial sorbents. Importantly, Na-P1 and Na-X zeolites have higher sorption capacity with respect to oil in comparison of zeolites tested in the works of Carmody et al. [77] and Ankowski [80]. The zeolites from the fly ash, i.e., Na-X and Na-P1, can also be used as absorbents of volatile organic compounds [81].

In this direction, Ankowski [80] examined zeolites from fly ash granulated with clay, whose capacity to diesel fuel was 0.51–0.57 g/g. In addition, the capacity of sodium aluminium silicate and commercial sorbents Eco-dry and dry-Lite was determined, which amounted to 0.27–0.43, 1.11, 0.77 g/g, respectively.

Sakthivel et al. [82] synthesized zeolites from fly ash by hydrothermal conversion and fusion methods, and then zeolite products were modified by organic compounds. The sorption capacity of zeolites without modification was 0.37 g/g for zeolite obtained by the hydrothermal method and 1.22 for zeolite obtained by fusion. It is worth noting that the sorption capacity of zeolites modified was in the range of 0.21–1.15 g/g, lower than those that were not modified. These results indicate that organic modification of zeolites is not in all cases profitable with respect to the removal of petroleum substances. It turned out that this type of modification of the sorbent surface blocks the pores of the zeolite, thus reducing its specific surface area and limiting the access of oil into the pores.

The results of this research indicate the possibility of the use of zeolites from fly ash as a mineral sorbent to remove oil spills from paved surfaces.

5. Conclusions

The present results have shown that zeolite can be considered promising materials for the removal of toxic compounds, such as mercury, radionuclides, and petroleum substances.

The results of mercury removal in pure stream of gas have shown that silver impregnation greatly improves zeolites efficiencies. The highest uptake achieved Na-X Ag-impregnated that adsorbed significantly more mercury than the commercial available activated carbon with bromine. For the removal of mercury in flue gas only Na-X Ag-impregnated was tested (powder and granulate). The tested zeolite reduced the level of mercury in the flue gas where the long-time mercury breakthrough ranges from 15 to 40% depending on the experimental conditions. The better results were obtained for granulated material.

Results of removing radium isotopes indicate high efficiency of the process at a level of 98% which indicates a high application potential of synthetic zeolites for the purification of mine water from radionuclides. Other radionuclides, mainly caesium and strontium, tested by other authors are also removed perfectly from various solutions using zeolites (natural and synthetic).

Results have shown that the sorption of diesel fuels and used oil on clinoptilolite, Na-P1 and Na-X, and commercial sorbent mainly constitutes physical characters. Synthetic zeolites have around twice higher sorption capacity for oils than commercial sorbents. Higher sorption capacities were achieved for oils of higher densities.

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