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Zeolites for water and wastewater treatment: An overview

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Abstract:

Zeolites are natural or synthetic microporous crystalline aluminosilicates, which have unique ion exchange and sorption properties, and are widely used in a large number of water treatment processes, such as water softening and purification from ammonia, heavy and radioactive metals. In the same time, they have been extensively researched for variety of new applications, e.g. as adsorbents for removal of organic substances, microorganisms and anions, for seawater desalination membranes and fill materials for reactive permeable barriers.

The objective of this paper is to review the research concerning the application of zeolites in water and wastewater treatment. The first part of the manuscript gives a brief description of natural and synthetic zeolites, most often exploited in (waste)water treatment practice. An accent is put on the synthesis, properties and practical potential of some cost-effective, environmental-friendly zeolites, obtained on the base of industrial, municipal and agricultural wastes.

The second part of the study is focused on the application of the zeolites in various (waste)water treatment processes. The discussion confers the general aspects of each application and reviews some recent studies. The most important experimental results concerning the performance of zeolites in different water treatment processes are summarized in a table format.

Keywords: zeolites, zeolitization, water treatment, wastewater purification, waste utilization.

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1. INTRODUCTION

The extremely fast growth of the world population in the last century, in addition to the industrial revolution, reflected in a considerable rise in both fresh water consumption and wastewater production. Fresh water demand has already exceeded supply, and currently special treatment is more and more often required in order to obtain drinking water of high qualityas well as to produce environmentally acceptable effluents.

Water from natural, industrial, municipal or agricultural origin may contain variety of suspended, dissolved, colloidal or emulsified organic and inorganic impurities, some of which could be successfully separated out, using special class of inorganic compounds, called “zeolites” (from the Greek “ζέω” = "boil" and “λίθος” = "stone").

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Zeolites are crystalline microporous aluminosilicates, built up of a 3-dimentional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, linked by sharing oxygen atoms [1], and weakly bonded (readily exchangeable) cations and water molecules in the pores and voids of the structure. Cations sorption is determined by the uncompensated negative charge, resulting from the substitution of Si (IV) by Al (III) in the tetrahedra. Cation exchange capacity (CEC) is a measure of the number of cations per unit weight available for exchange, usually expressed as milliequivalents per gram of material. As a rule, the greater the Al content (i.e. the more extra framework cations needed to balance the charge), the higher CEC of the zeolite [2]. The sorption capacity and selectivity for water and/or other molecules are defined by zeolite porosity, pore size distribution, and specific surface. The composition of zeolites can be represented by the general formula $M_{x/n}[(AlO_2)x(SiO_2)y].zH_2O$, where n is the charge of the cation M, and the values of x, y and z depend on the type of zeolite [3]. The number of naturally occurring zeolite types is about 40 [4], but owing to the artificially synthesized zeolites, almost 200 [5] unique frameworks have been identified so far.

Due to their unique properties, zeolites have found a broad range of industrial applications as catalysts, adsorbents, molecular sieves and ion exchangers with a growing global market, estimated of about 4 million tonnes for 2010. They have been used in a large number of water treatment processes such as water softening and purification from ammonia, heavy metals, radioactive species, dissolved or emulsified organic substances, toxic anions, odour and solids. Thousands of scientific articles, books, patents and technical notes, dealing with different aspects of zeolite utilization in (waste)water treatment processes, were published in the last few decades, but still numerous laboratory researches and pilot-plant studies are ongoing.

The general objective of the current paper is to overview the state-of-the-art knowledge concerning the use of different kinds of zeolites in (waste)water treatment processes and to summarize the most important properties of natural, synthetic and waste-derived zeolites, relevant to these applications, in order to facilitate their comparison and give an outstanding point that could assist the right choice of materials for practical purposes.

2. METHODOLOGY

The study was done on the base of a review of over 300 scientific articles, published in the last 10-15 years and available through the international scientific databases. Books, patents, commercial articles and company documentation were not reviewed and were mentioned only in a few occasions. The reproduction of details of some of the reference articles was consciously avoided in order to prevent the overlapping of the content of the present paper with those of the already published papers reviewing similar topics, as well as to keep the volume of the article in reasonable limits. Instead, an attempt to summarize and compare the most important properties of natural, synthetic and waste-derived zeolites (which are usually discussed in separate studies) was made. For this purpose, the data reported in different researches were generalized, recalculated (if necessary) to obtain the same dimension, and summarized in a table format. Since most of the reviewed studies have been carried out at more or less different conditions (i.e. system parameters, measurement/analytical methodology and equipment, etc.), these data should not be used for direct comparison, but rather as an outstanding point for the evaluation of the potential for the application of different zeolites in variable (waste)water treatment processes.

The first part of the manuscript gives a brief description of natural and synthetic zeolites, most often exploited in (waste)water treatment practice. Their composition, occurrence or methods for production as well as some physical properties, such as theoretical or measured cation exchange capacities, are presented. An accent is put on the synthesis, properties and practical potential of some cost-effective, environmental-friendly zeolites or zeolitic materials, obtained on the base of industrial, municipal and agricultural wastes. The second part of the study is focused on the application of the zeolites in various (waste)water treatment processes, including water softening, and removal of ammonia, heavy and radioactive metals, phosphates and other anionic species, dissolved or emulsified organic compounds and dyes, pathogen microorganisms removal, etc. The discussion confers the general aspects of each application and reviews some recent studies and such, containing essential results. The most important experimental results concerning the adsorption capacity, efficiency and selectivity for different water contaminants of natural, synthetic and waste-derived are compared and summarized in a table format.

3. RESULTS AND DISCUSSION

3.1. Zeolites origin, synthesis and basic properties

3.1.1. Natural zeolites

Natural zeolites are formed by an interaction of volcanic rocks and ash with alkaline underground water. Since the discovery of the first mineral (stilbite, $Na_2Ca_4Al_{10}Si_{26}O_{72}\cdot30H_2O$), classified as a zeolite by the Swedish mineralogist Axel Fredrik Cronstedt in 1756, natural zeolites have been intensivly explored, investigated and mined.

In naturally occurring zeolites, the cations are mainly of the alkali (Na and K) and alkaline earth (Ca and Mg) metals. The most common natural zeolites are analcime, chabazite, clinoptilolite, erionite, faujasite, ferrierite, heulandite, laumontite, mordenite and phillipsite. Their typical formulae and selected physical properties and theoretical CEC as given by Mumpton [2] are listed in Table 1.

Table 1. Typical formulae, structure type and selected physical properties of some natural zeolites

Zeolite	Representative unit-cell formula	Structure type	Void volume, % *	Channel dimensions, Å	CEC, meq g^{-1}**
Analcime	$(Na_{10})(Al_{16}Si_{32}O_{96}).16H_2O$	ANA	18	2.6	4.54
Chabazite	$(Na_2Ca)_6(Al_{12}Si_{24}O_{72}).40H_2O$	CHA	47	3.7 x 4.2	3.84
Clinoptilolite	$(Na_3K_3)(Al_6Si_{30}O_{72}).24H_2O$	HEU	34	3.9 x 5.4	2.16
Erionite	$(NaCa_{0.5}K)_9(Al_9Si_{27}O_{72}).27H_2O$	ERI	35	3.6 x 5.2	3.12
Faujasite	$(Na_{58})(Al_{58}Si_{134}O_{384}).24H_2O$	FAU	47	7.4	3.39
Ferrierite	$(Na_2Mg_2)(Al_6Si_{30}O_{72}).18H_2O$	FER	28	4.3 x 5.5 4.0 x 5.5	2.33
Heulandite	$(Ca_4)(Al_8Si_{28}O_{72}).24H_2O$	HEU	39	4.4 x 7.2 4.1 x 4.7	2.91
Laumontite	$(Ca_4)(Al_8Si_{16}O_{48}).16H_2O$	LAU	34	4.6 x 6.3	4.25
Mordenite	$(Na_8)(Al_8Si_{40}O_{96}).24H_2O$	MOR	28	2.9 x 5.7 6.7 x 7.0	2.29
Phillipsite	$(NaK)_5(Al_5Si_{11}O_{32}).20H_2O$	PHI	31	4.2 x 4.4 2.8 x 4.8 3.3	3.31
Scolecite**	$Ca_2Al_2Si_3O_{10}.3H_2O$			3.9	5.10

*Void volume determined from water content. **Theoretical value, calculated from unit-cell formula, *** [6].

The environmental applications of natural zeolites have been widely researched. In the last 1-2 decades several hundred technical papers and scientific articles, including few reviews [7-9], were devoted to (waste)water treatment by natural zeolites from different deposits. Although clinoptilolite has relatively low CEC, it has demonstrated high selectivity for NH_4^+ [7,8,10,11], some heavy metals [7,12, 13] and radionuclides [14-16] and has become the major natural zeolite used in (waste)water purification practice [2]. Good selectiveness for NH_4^+, transition and radioactive elements has been demonstrated also by mordenite, chabazite and phillipsite [7,12].

World reserves of natural zeolites are not determined but are evaluated to be large [17]. The world production of natutal zeolites for 2010 is estimated of about 2.75 million tones [17]. China is the major source, with production of 2.0 million tones, followed by Korea (210 000 t), Japan (150,000 t), Jordan (140 000 t), Turkey (100 000 t), Slovakia (85 000 t), and the USA (59 000 t) [17]. Zeolite deposits are available also in Cuba, South Africa, Iran, Italy, Hungary, Bulgaria, Argentina, Australia, Germany, Indonesia, Ukraine, and some other republics from the former U.S.S.R.

Natural zeolites from different deposits may vary widely in purity (from 15-20 up to 90-95%), chemical composition, crystal size, porosity, pore diameter and other properties, determining their sorption and ion exchange capacity [9]. The actual CEC values of natural zeolites are usually lower than calculated. CEC values of clinoptilolite from different deposits are presented in Table 2.

Table 2. CEC of clinoptilolite from different deposits

Zeolite	Country of origin	CEC, meq g^{-1}	Reference
Clinoptilolite	Australia	1.20	[18]
Clinoptilolite	Bulgaria	1.42	[19]
Clinoptilolite + Mordenite	Chile	2.05	[20]
Clinoptilolite	China	1.03	[21]
Clinoptilolite	China	1.20	[22]
Clinoprtilolite	China	1.20	[23]
Clinoptilolite	Croatia	1.45	[24]
Clinoptilolite + Mordenite	Iran	1.20	[25]
Clinoptilolite	Romania	1.37	[22]
Clinoptilolite	Slovakia	1.17	[26]
Clinoptilolite	Turkey	1.6-1.8	[27]
Clinoptilolite	Turkey	1.84	[28]
Clinoptilolite + Mordenite	Turkey	1.65	[29]
Clinoptilolite	Ukraina	0.64	[30]
Clinoptilolite	Ukraina	1.63	[31]

The main advantages of natural zeolites are their low price and availability, however they could not gain the commercial water treatment niche-market of the synthetic forms, possessing tailored composition, structure and properties.

3.1.2. Synthetic zeolites

Synthetic zeolites are generally produced by alkali treatment of silica and alumina – bearing row materials of synthetic, natural or waste origin. The first synthetic zeolite, ZK-5 ($Na_2Al_2Si_{4\text{-}6}O_{12\text{-}16}.6H_2O$), unknown as natural mineral, was obtained in the late 1940s by Richard Barrer who investigated the conversion of minerals under the action of strong salt solutions at high temperatures (≈170÷ 250°C) [31]. Later, Milton pioneered the use of more reactive starting materials, enabling milder reaction conditions and leading to the discovery of zeolite A [32] which has become the most important synthetic zeolite, commercially used as a water softener in detergent industry, in radioactive waste treatment, and in the purification of industrial wastewaters. The formulae, structure type and CEC of some of the most important synthetic zeolites are given in Table 3.

Conventional zeolite synthesis involves the hydrothermal (HT) crystallization of aluminosilicate gels or solutions in the presence of cations and basic environment (pH>10). The crystallization is usually carried out in closed systems at increased temperature and duration varying from few hours to several days. The type, yield, purity and disperse composition of the obtained zeolite is affected by the nature and pretreatments of the reactants, composition of the reaction mixture (Si/Al ratio, presence of seeds or templates, pH of the system), pre-reaction seeding, heating regime, pressure, preliminary or post-heating ageing, hydrodynamic conditions, etc. [33-36].

Table 3. Typical formulae, structure type and selected physical properties of some synthetic zeolites

Zeolite	Representative unit-cell formula	Structure type	Channel dimension, Å	CEC, meq g^{-1}*
Zeolite NaA	$Na_{12}\,Al_{12}Si_{12}O_{48}.27H_2O$	LTA	4.2	5.48
Zeolite NaX	$Na_{86}Al_{86}Si_{106}O_{384}.264H_20$	FAU	7.4	4.73
Zeolite NaY	$Na_{20}Al_{20}.Si_{48}O_{136}.89H_2O$	FAU	7.4	3.26
Zeolite NaP	$Na_2Al_2Si_{2\text{-}5}O_{8\text{-}14}.5H_2O$	GIS		3.51
Zeolite NaP1	$Na_6Al_4Si_4O_{24}.4H_2O$	GIS	2.6	7.37
ZSM-5	$Na_nAl_nSi_{96-n}O_{192}.16H_2O$, $0<n<27$	MFI	5.3 x 5.6; 5.1 x 5.5	2.07
Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2.2H_2O$	CAN	5.9	9.19
Hydroxisodalite	$Na_6Al_6.Si_6O_{25}.4H_2O$	SOD	2.3	

*Theoretical value, calculated from unit-cell formula.

The preparation of zeolites from chemical sources of Si and Al (e.g. colloidal SiO_2, Na_2SiO_3, $Na_2Al_2O_4$, $Al(OH)_3$) is expensive, but has the advantage to produce materials of high-purity, with precisely engineered chemical and physical properties, suitable for some specific applications in pharmacy, electrochemistry, photochemistry, nanotechnologies as well as for academic research purposes. For multi-ton, industrial production of zeolites, some cheaper natural materials such as clay minerals, sand, volcanic ash and natural zeolites are commonly used as Si or Si-Al sources.

3.1.2.1. Synthetic zeolites from natural materials

Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply raw materials for zeolites synthesis is virtually unlimited.

Clay minerals, such as kaolin [37-41], illite [42], smectite [43, 44], interstratified illite–smectite [45], montmorillonite [46,47], bentonite [48,49], perlite [50-51] have been used frequently for zeolites synthesis, due to their high contents of silicon and aluminum, which easily dissolve and form zeolite under alkaline conditions [52]. The zeolitization is realized via HT methods and typically includes the application of suitable pretreatments (e.g. grinding, acid washing, calcination, fusion with additives) of the starting materials.

A variety of zeolites (A [38,53,54], X [53-56], LSX [37,39], N [47], P [41] etc.) has been synthesized using kaolin as an aluminosilicate source. It is usually first calcinated (at 550-950°C) in order to obtain the more reactive metakaolin, which is then subjected to alkali HT treatment for zeolite crystallization [41,57,58]. Similar methods have been applied for the synthesis of zeolites (NaY and NaP) from natural mordenite [53] and NaP1 [58,59] and NaA [60] from natural diatomite. Zeolites NaP, NaX, NaP and NaA with high CEC were obtained by fusion of low-grade natural clinoptilolite [52,61], halloysite [62] and illite [42] with NaOH prior to hydrothermal treatment.

Another approach in the utilization of natural minerals for zeolite production is based on chemical treatments, aiming at the conversion of Si- and/or Al- ingredients of the rocks into alkaline silicates and aluminates, and subsequent HT synthesis of zeolites from these solutions [61]. Zeolite ZSM-5 with high specific surface area has been successfully synthesized from Korean serpentine as a source of amorphous Si [63]. Pure NaA zeolite has been prepared from a mixture of metasilicate and aluminate solutions, prepared by alkaline dissolution of Tunisian sand and aluminium scraps, respectively [64].

The main disadvantages of most of the methods for zeolite synthesis from natural minerals are the application of high energy-consumption processes like grinding, calcination and fusion, and the landscape-destructive effect of raw materials mining. The last is avoided when zeolites are synthesized from waste materials, having the additional advantage of zero or even negative price.

3.1.2.2. Synthetic zeolites from waste materials

3.1.2.2.1. Zeolites from coal fly ash (CFA)

Over 500 million tones of CFA are generated every year in the world as a by-product of coal combustion in thermal power plants [65]. More than 65% of this fine-powdered waste is disposed of in landfills and ash ponds creating serious problems with air and water pollution. On the other hand, CFA contain significant amount of crystalline and amorphous aluminosilicates that could be utilized for zeolite production. Since the initial study on the conversion of CFA into zeolite, published in 1985 by Höller and Wirsching [66], a large number of scientific articles have been devoted to the development and optimization of HT methods for CFA zeolitization. Generally, these methods are based on alkaline activation of CFA (with or without preliminary fusion with alkali) aiming at he dissolution of Al and Si - bearing phases, and precipitation of zeolites [1,67-76]. In most studies, the CFA activation is carried at temperatures in the range 100 - 200 ºC, conversion time 3 - 48 h, alkali concentration 0.5 - 5 M and liquid/solid ratio 1 - 20 ml g^{-1} [1]. They have demonstrated that, at different treatment conditions, more than 15 types of zeolite (e.g. NaA, NaX, NaY, NaP1, K-chabazite, Linde F, etc. [1,67,68,72]) could be synthesized, and that the type and the yield of zeolite obtained, are strongly influenced by chemical and mineralogical composition the CFA used [77]. CEC of CFA-derived zeolite material varies in a large range and depends upon the type, form (Na-exchanged, K-exchanged, etc.), purity and content of the zeolite in it. The experimental CEC values reported for some CFA-derived zeolites are presented in Table 4.

Table 4. Measured CEC of some CFA-derived zeolite materials

Zeolite	Conversion method	CEC, meq g^{-1}	Reference
Sodalite	Direct HT treatment	0.3	[1]
Analcime	Direct HT treatment	0.6	[1]
Linde F	Direct HT treatment	1.9	[1]
KM	Direct HT treatment	1.9	[1]
Herschelite	Direct HT treatment	2.1	[1]
NaP1	Direct HT treatment	2.7	[1]
NaP1	Direct HT treatment	2.4	[78]
NaP1	Obtained from supersaturated silicon and aluminium alkali extracts from fused CFA	4.5	[79]
NaP1	Direct HT treatment	2.4	[14]
NaA	Obtained from supersaturated silicon and aluminium alkali extracts from fused CFA	4.4	[79]
NaA	Obtained from silicon and aluminium alkali extracts of CFA	1.8	[80]
NaA	Fusion with alkali prior to HT treatment	≈ 3.5	[81]
NaA	Obtained from silicon and aluminium alkali extracts of CFA	≈ 5.7	[81]
Blend of NaA and K-A	Direct HT treatment	1.1	[82]
Blend of NaA and NaX	Obtained from silica extracts from CFA	4.7	[1]
Blend of NaA and NaX	Obtained from Si-Al extracts from fused CFA	4.6	[83]
NaX	Room temperature synthesis	2.5	[84]
NaX	Fusion with alkali prior to HT treatment	2.2	[85]
NaX	Obtained from supersaturated silicon and aluminium alkali extracts from fused CFA	3.2	[79]
NaX	Fusion with alkali prior to HT treatment	≈ 3.2	[81]
NaX	Obtained from silicon and aluminium alkali extracts of CFA	≈ 5.0	[81]
Blend of NaX, HS, and	HT treatment of low-calcium CFA	2.8	[86]

traces of NaP and NaA			
Blend of NaP and calcium silicate hydrate	HT treatment of high-calcium CFA	0.7	[86]
Blend of unnamed zeolite, ZSM18, LTL and erionite	Direct HT treatment	1.2	[82]

3.1.2.2.2. Zeolites from municipal solid waste incineration ash (MSWIA)

MSWIA have been also researched [87-92] as potential starting materials for the synthesis of zeolites, due to their high specific surface and the content of SiO_2 and Al_2O_3, even though in less quantity than in CFA. One of the first reports on the zeolitization of MSWIA was published by Yang and Yang [91] who applied HT alkaline processing, very similar to that used for CFA activation. The zeolites formed were mainly gismondine and unnamed sodium alumina silicate hydrate. Small quantity of NaX was also detected in some samples but CEC of the produced materials did not exceed 0.64 meq g^{-1}. Successful synthesis of zeolites NaA, NaP and sodalite from the MSWIA by fusion prior HT treatment was also reported [90] but the CEC obtained was again unsatisfactory (maximum 1.09 meq g^{-1}). Later, the investigations of Sallam [87] confirmed that the direct HT treatment of MSWIA is inefficient in producing of zeolites of commercial quality, but the application of preliminary fusion under optimized conditions could considerably increase the CEC of the final product - a blend of NaA, sodalite and unnamed zeolite - up to value of 2.45 meq g^{-1}, which is within the commercial range.

3.1.2.2.3. Zeolites from oil shale ash (OSA)

Since 2004, several studies dealing with zeolite synthesis from OSA, a high-volume by-product fly ash from oil shale processing, have been published [93-95]. Shawabkeh et al. [93] first reported the synthesis of zeolite (NaP1) by HT treatment of OSA. The activation was performed at different temperatures (25-160°C) using 8 M NaOH. The maximum CEC of 1.66 meq g^{-1} was obtained at the highest temperature 160 °C and treatment time 24 h. The linead increase of the CEC with temperature rise indicated that it could be improved by furher optimization of the treatment conditions. Purified (milled, calcinated and acid-washed) OSA was used as a raw material for synthesis of zeolites by alkaline fusion (at 350°C) followed by two different crystallization procedures – refluxing and HT treatment, both realized at 100°C [94]. The largest amount of crystalline zeolites (≈ 92%) has been obtained at 2 h 30 min of and at 12 h respectively. In both procedures, the synthesis products were mainly composed of NaX zeolite, whose content was influenced by the crystallization time, and of NaA zeolite, with a practically constant content, limited by the content of Al_2O_3 in OSA.

3.1.2.2.4. Zeolites from rice husk ash (RHA)

Pure, high-grade zeolites could be synthesized from silica-rich (85-98% SiO_2) RHA generated during the burning of rice husk (RH), one of the largest agricultural wastes with annual world production of about 120 million tonnes. The composition of RHA and its zeolitization behaviour depend mainly on calcination temperature. As a rule, the complete RH burning at high temperatures (800-1000°C) produces white, carbon-free, low-reactive crystalline SiO_2, while the incomplete roasting at lower temperatures (500-700°C) yields in a so called carbonized RHA, containing carbonaceous material and highly reactive amorphous SiO_2 [96], which is more easily dissolvable in alkaline medium. For this reason, carbonized RHA is the preferred starting material for preparation of alkaline silicate solution, which is then mixed with standard aluminate solution and processed via classic HT methods to produce the desired zeolite. The main RHA-derived zeolites are NaA, [97-103], NaX, [98,104,105], NaY, [98,106-108], ZSM-5, [109-114], ZSM-48 [114], and zeolite-beta [115,116]. Measured CEC values of some zeolites, obtained from RH are presented in Table 5.

A synthesis of pure zeolite NaA from silicate solution, obtained by direct leaching of RH at 150°C in autoclave, was also reported [96]. The obtained solution was mixed with standard Al-solution and subjected to HT crystallization for 5 h at 100°C in autoclave.

Table 5. CEC of some RHA-derived zeolites

Zeolite	HT treatment conditions	CEC, meq g^{-1}	Reference
NaA	3 h at 90 °C in autoclave	5.79	[104]
NaA	3 h at 100 °C in autoclave	5.72	[100]
NaA	6 h at 100 °C in autoclave	5.43	[100]
NaA	12 h at 100 °C in autoclave	5.00	[100]
NaX	6 h at 90 °C in autoclave	4.61	[104]
NaY	24 h ageing, seeding, 22 h at 100 °C	3.15	[98,107]

3.1.2.2.5. Zeolites from other wastes

Synthesis of zeolite NaP1 having high CEC from paper sludge ash and diatomite was reported by Wajima et al. [117]. Conversion of waste porcelain into Zeolite-13X with high specific surface area (412 m^2 g^{-1}) was achieved by alkali fusion at 600° C (6 h) followed by HT treatment at 80° C (12 h) [118]. The prospects for the utilization of several other industrial wastes, such as cupola slag [3,119] and exhausted fluid cracking catalysts [120,121] for the synthesis of valuable zeolites (ZSM-5, NaA, NaX) have been also considered as technically feasible and environmentally appropriate alternative to their disposal. In addition, some municipal solid wastes such as non-recyclable glass and thin-walled aluminium scrap (i.g. Al-foils and cans) which recycling is usually less effective also could be utilized as Si- and Al-sources in zeolite synthesis.

Regardless of their origin, zeolites have found broad range of (waste)water treatment applications, related to their unique native or designed properties. The CEC and selectivity are definitely the most important characteristics of zeolites, because a substantial part of (waste)water treatment processes are based on the selective sorption of metal cations, ammonium or polar organic compounds. In addition, cation exchange properties of zeolites can be exploited to modify their surface chemistry such that other classes of compounds can also be retained [122].

3.1.3. Modified natural and synthetic zeolites

An interesting class of materials, extending the area of application of zeolites in (waste)water treatment, is surfactant-modified zeolites (SMZ) [8,122], which combine the cation sorption properties, typical for zeolites, with the ability to sorb anionic species (e.g. arsenates, chromates, iodides, nitrates, phosphates, perchlorates, antimonates) and non-polar organics (e.g. benzene, toluene, ethylbenzene, and xylenes (BTEX), phenoles, pesticides, herbicides, dyes, etc.) for which untreated zeolites have little or no affinity [8,123,124]. The most frequently used modifying agents are quaternary amines (e.g. hexadecyltrimethylammonium (HDTMA), cetyltrimethylammonium bromide (CTMA), octadecyldimethylbenzyl ammonium (ODMBA), N-cetylpyridinium (CPD), benzyltetradecyl ammonium (BDTDA), stearyldimethylbenzylammoniumchloride (SDBAC), etc.), which form on the zeolite surface a bilayer-like structure [8]. The positive surface charge provides sites for sorption of anions, whereas the organic-rich surface layer provides a partitioning medium for sorption of non-polar organic compounds [8]. Although the modified zeolites have anion exchange properties, they keep the ability to adsorb inorganic cations. It is because the modifiers are relatively large molecules, which remain on the external surface of the zeolite crystal and do not enter the zeolite channels [125], where the local surface charge remains negative. Similar anion sorption properties are demonstrated by polymer-modified zeolites (e.g. by polyhexamethylene-guanidine) [8,126,127] and metal cation-modified zeolites [128-130]. The SMZ are stable in water and aggressive chemical solutions [122]. Their relatively low cost makes them a viable alternative to other commercial adsorbents such as activated carbon and ion exchange resins. The most relevant applications of natural SMZ were reviewed in [123].

3.2. (WASTE)WATER TREATMENT APPLICATIONS OF ZEOLITES

3.2.1. Water softening

The largest commercial market of synthetic zeolites, estimated of about 1.3 million tons per annum, is as water softening "builder" in detergent formulations. In 1973 the German company "Henkel" patented formulations incorporating zeolite NaA as a water softener [131]. In 1978 "Procter and Gamble" introduced zeolite NaA in its laundry detergents [132], and nowadays, most of the commercial washing powders, contain zeolite, instead of harmful phosphates, banned in many parts of the world because of the risk of water eutrophication [133]. Zeolite NaA does not contribute to the eutrophication potential of surface waters and is nontoxic to freshwater and marine aquatic communities [134]. Moreover, some zeolites, for example, zeolites, obtained from high-calcium CFA or in Ca-exchanged forms, have been successfully applied for elimination of phosphate contamination via precipitation of Ca-phosphates [135-137]. Zeolite A possesses high affinity for exchange of Na^+ with the "hard" Ca^{2+} ions in a broad range of pH values [138]. However, whilst calcium ions diffuse relatively easily into the interstices of zeolite A, the smaller magnesium ions are impeded by a hydrate shell [139], and are therefore incorporated more slowly [140,141]. At higher temperatures, when the hydrate shell of the Ca^{2+} ion is gradually removed, the rate of exchange increases. Similar behaviour was reported for zeolite NaP when tests were performed at room temperature, whereas, at 60◦C the affinity of the material toward Mg^{2+} increased to acceptable levels [142]. Due to its larger pore diameter of 0.74 nm, zeolite X has significantly higher magnesium binding capacity compared to zeolite A and zeolite P [139] and was successfully introduced into detergents market 14 years ago [143]. Other zeolites, such as zeolite 13X [144] and clinoptilolite [145, 146], have been also reported for use in detergent formulations. The experiments of Culfaz et al. [146] showed that zeolite A and zeolite X were more effective in cleaning than clinoptilolite at low temperatures, while all these builders had the same effectiveness at high temperatures. A relatively new and effective zeolite for water softening applications is so called zeolite AX. It represents a co-crystallite comprised of 80% zeolite X and 20% zeolite A, which has Ca^{2+} and Mg^{2+} exchange properties better than those of a blend of the pure zeolites [147].

Since detergent ingredients have to be pure, synthetic zeolites, obtained from chemical reagents or high-grade natural row materials are commonly used for this purpose. Nevertheless, some recent studies have demonstrated that some waste-derived zeolites, obtained by appropriate technology, could compete the commercial products in this application. For example, Hui and Chao [148] succeeded to obtain single-phase zeolite 4A (NaA) samples in pure form with a high crystallinity (up to 95%) by applying step-change of synthesis temperature during HT treatment of CFA. The calcium binding capacity of these zeolite 4A samples and the commercial detergent grade zeolite 4A (Valfor 100) were tested for usage as a detergent builder (see Table 6). The results show that

Table 6. Ca^{2+} sorption properties of commercial and CFA-derived NaA according [148]*

Zeolite	Zeolite origin	Ca^{2+} conc., mg l^{-1}	Ca^{2+} sorption, mg g^{-1}	Ca^{2+} removal, %
NaA	Commercial	40	40	100
NaA	CFA- derived	40	37-41	100
NaA	Commercial	80	76	100
NaA	CFA- derived	80	57-75	82-94

* Some values are recalculated and/or rounded.

zeolite 4A obtained from CFA behaved similarly as the commercial one in removing calcium ions during the washing cycle. Moreover, the leaching tests performed for evaluation of the toxicological safety of the synthesized materials showed that CFA-derived 4A samples leached the same elements as the commercial one with the concentrations in the same order of magnitude.

Alongside their main function (that of softening water) zeolites also have other proven effects in the laundering process. Zeolite A, for instance, promotes the inhibition of graying through heterocoagulation with dirt particles. Zeolites can remove dyes from the washing liquor by heterocoagulation and adsorption. In conjunction with the relatively low sodium concentration associated with zeolite as compared with soluble builders, this leads to a reduced risk of dyes discolouring other items [139].

The main disadvantage of the use of zeolites in as water softener in detergent formulations, is that since zeolites are insoluble in water they lead to increase in sewage sludge mass. Experimental measurements and model calculations have shown that zeolite A typically accounts for an increase of approximately 10% in the dry mass of the sewage sludge [139]. However, field studies have indicated that zeolite-based detergents do not cause any increase in the volume of sewage sludge, which is more important with respect to sludge handling and disposal. On the contrary, in the presence of zeolite A the sedimentation and dehydration properties of the sludge are improved which can facilitate the operation of the sewage treatments plants [149].

Due to the advantageous builder properties of zeolites combined with their human and environmental safety, they have been included in an extensive range of detergent formulations [139]. In Europe, the USA, Japan and several regions of East Asia, zeolites have almost entirely replaced phosphates [150]. Zeolites are widely used in industrial water softening systems and in domestic "on the tap" filters, since the "hard" cations-loaded zeolite could be easily regenerated by treatment with concentrated sodium solutions.

3.2.2. Ammonia removal

Another industrial application of zeolites is for separation of ammonia from drinking or wastewater. The term ammonia includes the non-ionized (NH_3) and ionized (NH_4^+) species. Ammonia in the environment originates from metabolic, agricultural and industrial processes and from water disinfection with chloramine. Natural levels in groundwater and surface water are usually below 0.2 mg l^{-1} [151] but intensive rearing of farm animals can give rise to much higher levels in surface water. Ammonia in water is an indicator of possible bacterial, sewage and animal waste pollution. Ammonia may have harmful effect on human and animal health [125], it contributes to the eutrophication and oxygen depletion in receiving waters [9], and in addition attacks the rubber components of water plumbing systems. In the Guidelines for drinking-water quality of the World Health Organization (WHO) [151], no health-based guideline value for ammonia is recommended, but the it is stated that ammonia could cause taste and odour problems at concentrations above 35 and 1.5 mg l^{-1} respectively. Existing methods and technologies for the removal of this pollutant/contaminant, i.e. biological [152] (biological filter, biological contact oxidation, etc.) and physicochemical [153,154] (air stripping, break-point chlorination and ion exchange, etc.), are constantly being adapted and improved, but still some limitations in these methods exists. For example, biological filter is very effective for ammonia removal, however it is sensitive to temperaure and climat conditions, it requires high costs for construction of the filter and there is a higher risk to safety during the subsequent processing [23]. The traditional ion exchange using ion exchange resins also has high running costs and has been limited to application in smaller quantities, because ammonia could be exchanged by other high-valence ions presented in wastewater [23]. Compared with the above-mentioned methods, safety, low cost, and high affinity for NH_4^+ are three of the attributes that are attracting an increasing focus on the use of zeolite as ion exchanger for ammonia removal from water.

The removal of ammonia by natural zeolitic materials was widely investigated in the last few decades and the most important results were reviewed in several papers [7-9,125,155]. They indicate that clinoptilolite and mordenite are the most effective natural zeolites for ammonia removal [8,10,11,24,29,156], due to their high selectivity for ammonium ion in the presence of competing cations (such as K^+, Ca^{2+} and Mg^{2+}), across a wide range of NH_4^+ concentrations [156]. The maximum ammonia adsorption capacity of natural zeolites from different deposits varies from 2.7 mg g^{-1} (Chinese clinoptilolite) to 22.9 mg g^{-1} (Canadian clinoptilolite) [9] and is generally lower than that of synthetic zeolites (e.g. Na–P [158,159], Na–Y [108,158,160], NaX [162], NaA [63,161,162]), whose adsorption capacities are typically in the range 20-50 mg g^{-1}. The ammonia uptake capacity of clinoptilolite could be improved to a certain degree by application of suitable pre-treatments, such as grinding, sieving, acid washing, heating, and pre-exchange strong Na^+ solutions. [20,163]. The last is applied in order to obtain homionic Na-form of the clinoptilolite, which has higher ammonia exchange capacity than K^+ and Ca^{2+} forms, according to the order of affinity of clinoptilolite to alkaline and earth-alkaline cations: $K^+ > NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+}$ [24].

The actual ammonia adsorption capacity and efficiency of NH_4^+ removal process depend upon the type of zeolite used, contact time, initial concentration of ammonia, temperature, the amount of zeolite loading, its particle size and presence of competitive ions [125,155]. The influence of these factors has been discussed in several researches on the kinetics and equilibrium of ammonia sorption from model solutions or real effluents [20,62,156,158,160,164-166,207]. Summarized experimental data for the ammonia adsorption performance of some natural and synthetic zeolites are presented in Table 7.

Table 7. Ammonia adsorption on some natural and synthetic zeolites

Zeolite	Zeolite origin	NH_4^+ conc. mg l^{-1}	Zeolite dosage g l^{-1}	NH_4^+ sorption mg g^{-1}	NH_4^+ removal, %	Reference*
Blend of heulandite, montmorillonite and illite	China	80	24	2.9	83	[167]
Mordenite	Nutural			18	80	[168]
Mordenite	Powdered	50	2.5	15.3	42	[107]
Mordenite	Granulated	50	2.5	14.6	48	[107]
Mordenite	New Zealand	10-200	10	1.3-14.4	92-56	[156]
Clinoptilolite	New Zealand	10-200	10	1.3-11.9	98-46	[156]
Clinoptilolite	Australia			5.8	96-98	[10]
Clinoptilotite	Chile	121	2.5	13.4	-	[20]
Clinoptilotite	Chile, modified with NaCl	121	2.5	18.3	29	[20]
Clinoptilolite	Iran, mm-sized	90-3610	3.3	11.3	88-10	[157]
Clinoptilolite	Iran, nm-sized	90-3610	3.3	13.3	92-11	[157]
Clinoptilolite	China	80		6.1-1.2	83-96	[167]
Clinoptilolite	China			21.7		[158]
Clinoptilolite	China	250	10	10.5		[160]
Clinoptilolite	USA	5.4		18.4		[169]
Clinoptilolite	Croatia	130	10	7	61	[11]
Clinoptilolite	Croatia	640	10	16.7		[11]
Clinoptilolite	Croatia	800		17.7	75	[24]
Clinoptilolite	China,	5		0.15		[23]

Clinoptilolite	modified Turkey			5.2-8.1		[170]
Clinoptilolite+ mordenite	Turkey	88	10	1.39	>85	[29]
Clinoptilolite/ heulandite + mordenite	Turkey	60-150	20	9.6	94-75	[164]
Clinoptilolite/ heulandite + mordenite	Turkey	60	10		80	[164]
Fauyasite	CFA-derived	144		19.2		[161]
NaA	Synthetic	144		50.2		[161]
NaA	CFA-derived	144		15.5		[161]
NaA	From halloysite	50-300	10	9-35	76-6	[62]
NaA	Commercial	285	9.6-49.6	5.1-1.4	17-35	[162]
NaA	Commercial	3372	26-76	19.5-14.3	19-32	[162]
NaA	CFA-derived	285	9.8-47.4	5.0-1.8	17-29	[162]
NaA	CFA-derived	3372	23-74	25.4-17.7	17-39	[162]
NaX	Commercial	285	12-50	3.0-1.0	13-17	[162]
NaX	Commercial	3372	26-74	16.5-19.6	16-43	[162]
NaX	CFA-derived	285	9.2-51.2	7.3-2.2	23-40	[162]
NaX	CFA-derived	3372	26-79	23.4-18.5	18-43	[162]
NaP1	CFA-derived	285	11.2-51.6	5.3-2.5	20-45	[162]
NaP1	CFA-derived	1600		6-19		[171]
NaX with small amounts of HS and NaP	CFA-derived	43-348	4	7-27.3	66-28	[86]
NaP	CFA-derived	200	10		45	[165]
NaP	CFA-derived, acid washed	200	10		60	[165]
NaP	CFA-derived		3.5	35-47	60-80	[159]
NaP	From Clinoptilolite			64.4		[158]
NaP and calcium silicate hydrate	CFA-derived	130	4	2.5		[166]
Blend of NaX, HS, NaA, NaP	CFA-derived	130	4	18.2		[166]
NaY	From Clinoptilolite			49.5		[158]
NaY	From Clinoptilolite	250	10	19.3		[160]
NaY	RHA-derived	50	2.5	42.7	71	[207]

* Some values are recalculated and/or rounded.

Rozic et al. [11] investigated the NH_4^+ removal from water with natural and modified bentonite clay and Croatian clinoptilolite. The results showed that natural zeolite had much higher removal efficiency (61.1 wt% at 100 mg N-NH_4^+ l^{-1}) when compared with that of the clay (<47 %) at the same conditions. With the increase of the initial concentration of ammonia, the removal efficiency rapidly decreased. A contact time of 60 min was found to be sufficient for quantitative removal of NH_4^+ by zeolite. Cooney et al. [172] undertook a laboratory study of Australian clinoptilolite, to remove ammonia from water. They investigated the equilibrium and kinetic characteristics of ammonia exchange in the zeolite under binary and multi-component conditions. The results revealed that the highest ammonia removal efficiency was achieved with the sodium form of zeolite. For a multi-component system there was a competitive effect between ammonia and other cations such as Ca^{2+}, Mg^{2+}, K^+ and the zeolite's selectivity for ammonium ions was over other cations typically present in sewage. Malekian et al. [157] studied the ammonia removal from aqueous solutions with different Na^+ concentrations (0.03, 0.1, and 0.3 M) by Iranian clinoptilolite in millimeter and nanometer particle sizes. The maximum NH_4^+ exchange capacity by the zeolite at equilibrium was obtained for the lowest sodium concentration in the solution - 11.31 and 13.27 mg NH_4^+ g^{-1} for millimeter- and nanometer-sized zeolite, respectively.

Weatherley and Miladinovic [156] compared the ammonia uptake performances of New Zealand clinoptilolite and mordenite in the concentration range of 0–200 mg NH_4^+ g^{-1}. The results showed that the mordenite exhibited higher overall uptake at equilibrium compared with clinoptilolite at solution concentrations greater than 80 mg l^{-1}. The influence of other cations (K^+, Ca^{2+} and Mg^{2+}) present in water upon the ammonia uptake was estimated to be relatively small and smaller for mordenite. In all cases, the ammonium ion showed the highest uptake on to both zeolites, wich is in a contrast with the majority of other researches reporting that clinoptilolite exhibits higher affinity for K^+ than for NH_4^+. Other components in the solution such as heavy metal ions and organics also may affect ammonia exchange due to competitive adsorption [9,24], as indicated the investigation of Farkas et al. [24] who studied the adsorption of ammonium ions and organic pollutants on clinoptilolite from leakage waters from waste dumps. Without pre-treatment of leakage water, the exchange of NH_4^+ on the zeolite was found to be 4.2 mg NH_4^+ g^{-1}, while in pure ammonia solution, the exchange was 17.70 mg NH_4^+ g^{-1}, suggesting that organic pollutants and K^+ and Ca^{2+} ions in leakage water prevents the exchange of NH_4^+ ions.

Englert and Rubio [20] studied ammonia exchange by natural and modified Chilean clinoptilolite. The ammonia uptake tests were conducted with 0.25 g zeolite, 100 ml of 100 mg NH_3-N l^{-1} solution, for 2 h and varying the feed solution concentrations. The Langmuir isotherm model provided best correlation of the equilibrium data reaching saturation values at 0.68 meq NH_4^+ g^{-1}. Results from batch experiments at different pH (2-12) of the suspension showed optimal pH=6, while at acidic and basic conditions the removal was decreased. Optimal pH values in the close to neutral range (pH=5-8) were obtained in a number of other studies [62,86,107,164,165,167], as well. Theoretically, according to the equilibrium reaction ($NH_3+H_2O\leftrightarrow NH_4OH$), ammonia removal should be greater at lower pH and smaller at higher pH values, as the cation exchange mechanism occurs only by means of the ammonium ion. The steep reduction of ammonia uptake at alkaline conditions (pH>9) thus could be partially explained by the presence of significant amount of electrically neutral NH_3 [20] in the solution. Although it could be expected that the volatilization of NH_3 contributes to the elimination of ammonia at alkaline pH values, the data obtained by Zhang et al. [165] indicated that only about 5% of the ammonia is lost by volatilization for a solution of 25 mg $N.l^{-1}$ and pH=11.4. Partial dissolution of the zeolite is suggested as another possible reason contributing to the reduction of ammonia uptake of natural zeolites pH > 8 [167]. The observed reduction of ammonia removal at acidic conditions (pH<5) is probably a result from the competition between NH_4^+ and H^+ for the exchangeable sites on zeolite [20,165]. Quite acidic conditions (pH<2) could cause structural degradation of the zeolite [173], as well.

The sorption kinetics studies of Englert and Rubio [20] showed that the ammonia removal proceeded very rapidly (rate constant of 0.3 min^{-1}), indicating approach to chemical equilibrium in approximately 15 min. Similar kinetic results were obtained by Demir et al. [174] with a clinoptilolite from Turkey, and by Zhao et al. [62] with NaA zeolite. Saltali et al. [164] studied the removal efficiency of NH_4^+ ion from aqueous solution using the natural Turkish zeolite, containing clinoprtoloite, heulandite and mordenit. The experiments were carried out using batch method (60 mg NH_4^+ and 10 g zeolite per liter) at room temperature and pH=8. The results showed that removal efficiency of NH_4^+ ion increased with increasing shaking time and 75% of NH_4^+ ion removal was completed within 15 min. It reached up 80% within 30 min and than became very slow. The kinetics studies have clearly demonstrated that the rate of NH_4^+ ions removal by zeolite is initially very high, but thereafter significantly reduces. This change in the adsorption rate could be explained with the fact that initially all adsorbent sites are vacant, and the solute concentration gradient is high, but afterwards the decrease in adsorption sites and concentration gradient lead to rate decrease in NH_4^+ uptake rate [62]. The contact time is particularly important for continuous process operation, because lower resident times are required to reduce footprint installations using compact units [20]. Sarioglu [29] investigated the ammonia uptake from drinking water by natural zeolite in column tests performed at different flowrates. It was found that the system saturated within 5 min. The highest adsorption capacity (1.08 mg NH_4^+-N g^{-1}) was obtained at a contact time of 40 min (at pH=4 and 0.5 ml min^{-1}). For influent concentration of NH_4^+-N 5 mg l^{-1} 100% removal efficiency was achieved, but it was not possible to reach such high values when initial concentration of 12 mg l^{-1} NH_4^+ were used.

Huang et al. [167] studied ammonia removal from aqueous solutions by using natural zeolitic material containing 46% heulandite, 24% montmorillonite and 30 % illite. The optimum pH was found to be 8 and the pH dependence of absorption followed similar trend to that of clinoptilolite. The effect of other cations on the removal of ammonia followed the order of preference $Na^+>K^+>Ca^{2+}>Mg^{2+}$ at identical mass concentrations, and the effect of the presence of individual anions followed the order of preference $CO_3^{2-}>Cl^->SO_4^{2-}>HPO_4^{2-}$. It was observed that NH_4^+ removal efficiency rose from 67.4% to 81.1% with reduction in the zeolite particle size range from 0.2-0.3 mm to 0.074-0.125 mm, due to the increase of specific surface. Sorption equilibrium was attained after approximately 180 min of adsorption for all zeolites of different particle size ranges. Equilibrium isotherm data was fitted better to the Freundlich model. At optimal conditions, NH_4^+ removal rose from 61.4% to 96% with the increase of zeolite dose from 8 to 64 g l^{-1}.

Wang et al. [160] investigated the equilibrium uptake behaviour of NH_4^+ in the concentration range of 50–250 mg l^{-1}onto clynoptilolite and obtained from it zeolite NaY. It was established that due to its bigger aperture and lower Si/Al molar ratio zeolite NaY had much (almost twice) higher ammonium exchange capacity than the natural zeolite (see Table 7). Adsorption isotherms of the two materials were similar and fitted good to Freundlich model. In order to establish the influence of K, Ca and Mg ions alone upon NH_4^+ uptake, further equilibration experiments were conducted with metal cation concentration of 100 mg l^{-1}, which equals to 2.6 meq K.l^{-1}, 5 meq Ca.l^{-1} and 8.3 meq Mg l^{-1}. The results showed that in both cases the presence of additional cations leads to significant reduction in the equilibrium uptake of ammonia. For the natural zeolite, the reduction followed the order of $K^+>Ca^{2+}>Mg^{2+}$ (opposite to the order of equivalent concentrations used), which is consistent with the results obtained by Farkas [24]. For zeolite NaY the order of preference was $Mg^{2+}>Ca^{2+}>K^+$, i.e. corresponding to the their equivalent concentrations. This indicates that zeolite NaY exhibits lower selectivity for these cations than the natural clinoptilolite. The reason for this is that NaY has much bigger aperture and the ionic strength in the solution turns into the principal factor in ion exchange. Another study of the same authors [158] on the NH_4^+ exchange with natural clinoptilolite and synthetic zeolites NaY and NaP confirmed that although the two synthetic materials have much higher CEC than the natural one, the latter has the highest selectivity for NH_4^+ among the three materials. Calculated thermodynamic parameters indicated that ammonia adsorption on zeolite at ambient conditions is an exothermic and spontaneous process, which was confirmed by several other investigation [62,86].

Zhao et al. [62] investigated the adsorption behaviour of ammonium ions from aqueous solution onto zeolite NaA, synthesized from natural halloysite, as a function of equilibrium time, pH, initial NH_4^+ concentration, temperature and competitive cations. A maximum adsorption capacity deduced from Langmuir isotherm was 44.3 mg NH_4^+ g^{-1}. The equilibrium adsorption was reached within 15 min. The effect of the presence of competitive cations was studied at 288 K, 0.2 g l^{-1} adsorbent and initial NH_4^+ concentration of 100 mg l^{-1}. It was found that the adsorption capacities of NH_4^+ on NaA zeolite were significantly reduced by the presence of competitive cations. When the concentration of Na^+, K^+, Ca^{2+} and Mg^{2+} increased from 0 to 0.1 mol l^{-1}, the NH_4^+ adsorption capacities decreased from 22.06 to 0.50, 0.51, 0.56 and 7.66 mg g^{-1}, respectively. This indicates that the selectivity order of ammonia over other cations was $Na^+>K^+>Ca^{2+}>Mg^{2+}$, which is consistent with the result reported for natural zeolite (heulandite + montmorillonite) [167], but does not match the order of selectivity reported for clinoptilolite ($Ca^{2+}>K^+>Mg^{2+}$) [156] and CFA-derived NaX ($K^+>Ca^{2+}>Na^+>Mg^{2+}$) [86]. These findings suggest that different type of zeolites, and even different zeolites of the same type [156], may exhibit different cation selectivities. In the case of NaX obtained from CFA [86], the increase of Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations from 0 to 10 meq.l^{-1} decreased the removal efficiency of NH_4^+ from 69.9% to 44.9%, 64.4%, 53.8%, and 41.5%, respectively. When the initial ammonium ion concentration increased from 2.56 to 25.07 meq l^{-1} with CO_3^{2-}, Cl^-, and SO_4^{2-} individually present in the solution, the ammonia removal decreased from about 68.7% to 26.5%, 28.3%, and 38.4%, respectively, i.e. the order of anion effects on ammonia uptake was $CO_3^{2-}>Cl^->SO_4^{2-}$, which is in agreement with the results obtained by other authors [167].

Otal et al. [162] investigated the application of several synthetic zeolites to the decontamination of leachate produced in a MSW treatment plant and to liquid waste from a pig farm. The reduction of organic matter, ammonia and total nitrogen, phosphorus and metals contents was evaluated. Commercial zeolites (NaA and NaX) and CFA-derived zeolitic materials (containing NaA, NaX and NaP1) were tested in a stirred tank and in a column experiments. For the different types of zeolites tested, the maximum elimination percentages ranged from 16.7 to 45.0% in the case of the landfill leachate and from 32.2 to 43.4% in the case of the pig slurry. In general, the behaviour of any given zeolite with regard to the elimination of nitrogen was always slightly superior in the case of the pig slurry samples, which had almost ten times greater concentration of NH_4–N. It was found that the performance of CFA-derived zeolites was similar to those of the commercial zeolites of the same type (see Table 7). Authors estimated the total manufacturing cost of 1.7 EUR per kg of pure zeolite NaA, which could be considered competitive to other commercial adsorbents. Zeolite (NaP1 with small amounts of analcime and chabazite), synthesized from CFA, was used a bench-scale study both as a decantation aid reagent and as an adsorbent of COD and NH_4−N [159]. The leachate was collected directly from a storage unit of the organic fraction of MSW, before it was composted. The sludge was recirculated to enhance the removal efficiency of nutrients as well as to optimize flocculant saving and to decrease sludge production. The results showed that it is possible to remove 43%, 53% and 82% of COD, NH_4−N, and suspended solids, respectively.

Yusof et al. [107] performed recently kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by RHA-synthesized zeolite NaY and powdered and granulated mordenite. They showed that NaY presents the superior adsorption capacity, which is 3 times greater than that of mordenite. The maximum monolayer adsorption capacity, obtained from the Langmuir plots for NaY, powdered mordenite and granulated mordenite were 42.37, 15.13, 14.56 mg NH_4^+ g^{-1}, respectively. The initial uptake of ammonia occurred rather fast for NaY and powdered mordenite and reached equilibrium in less than half and hour, and two hours, respectively. Inversely, granular mordenite demonstrated slower ammonia uptake and reached equilibrium in about 24 h. Adsorption kinetics can be best represented by a pseudosecond-order model with initial sorption rate being highest for adsorption on zeolite Y. Authors concluded that zeolite Y synthesized from RHA can be utilized as an alternative sorbent to remove ammonia from water owing to its rapid adsorption rate, high adsorption capacitiy and low production cost.

Since the ammonia-removal efficiency of zeolite decreases after operating for a long duration, due to the depletion of the free ion exchange sites, the investigation of zeolites regeneration behavior is of a great practical interest. For this purpose, number of methods for the regeneration of ammonium-loaded zeolite have been elaborated and tested. They includes heating (at 200–500ºC in air stream) leading to NH_3 evaporation [23], biological regeneration by nitrifying bacteria which converts NH_4^+ to NO_3^- on the surface of zeolite in oxygen-enriched air [155,175], acid washing leading to the ion exchange of NH_4^+ with H^+ [23,62], treatment with sodium salt to obtain Na-zeolite [23,29,62,86,155], and electrochemical regeneration (using a Ti/IrO_2–Pt anode and Cu/Zn cathode) in the presence of chloride ions aiming the convertion of ammonia into nitrogen gas [176]. The comparison of the reported results indicated that treatment with NaCl solution (0.5-2.0 mol.l^{-1}) for a period varying from half an hour to several hours is probably the most effective and feasible method for regeneration NH_4^+- loaded zeolite.

Li et al. [23] have tested heating (at 200 °C for 24 h), acid washing (with 1.0 mol.l^{-1} HCl solution for 24 h) and NaCl treatment (2.0 mol.l^{-1} for 24 h) method for the regeneration of natural and modified Chinese clinoptilolite used for ammonia removal from drinking water. Their experiments showed that the adsorption capacity of the modified clinoptilolite after three regeneration cycles was only 4 % lower than that of the fresh material, while the other two methods gave much worse results. Zhao et al. [62] studied the reusable ability of synthetic zeolite NaA. For this aim the adsorption experiments were performed using 0.2 g NaA zeolite and 50 ml 100 mg l^{-1} NH_4^+ at 288K for 30 min, and desorption of adsorbed NH_4^+ onto NaA zeolite was studied using 100ml 1mol. l^{-1} NaCl solution at 288 K for 30 min. Consecutive adsorption–desorption cycles were repeated six times. The results showed only 2.2 % decrease in adsorption capacity - from 16.72 mg g^{-1} for the first cycle to 16.35 mg g^{-1} for the last cycle. Similar results were obtained when 1M NaCl solution was used for regeneration of ammonia -saturated CFA-derived NaX [86]. The mixture (25 ml NaCl solution and 2 g zeolite) was stirred at 180 rpm at 25 °C for 1.25 h, dried and sieved. The results show that the patterns of ammonia uptake by the regenerated zeolite with different pH values (3–12) and adsorbent dosages (0.5–20.0 g l^{-1}) were similar to those of original zeolite. To examine the recyclization of the synthesized zeolite, the regenerative zeolite was further used to treat wastewater from a sewage treatment plant containing competitive ions (K^+, Ca^{2+}, and Mg^{2+}). The results showed that the regenerated zeolite had almost the same ammonia uptake capacity as the original zeolite. Malekian et al. [157] investigated the kinetics of the ammonia release from NH_4^+- loaded Iranian clinoptilolite in NaCl solutions of different ionic strengths and established that the process was rapid for the first 60 min and nearly complete within 150–200 min at all ionic strengths. The amount of NH_4^+ released in 0.3 MNa^+ was almost two-fold greater than that in 0.03 M Na^+, and the NH_4^+ release of deionized water was negligible. Authors suggested that the exhausted NH_4^+- saturated zeolite could be utilized as a controlled-release ammonia fertilizer.

On the base of the reviewed investigations on ammonia removal by zeolites, it could be summarized that ion exchange of NH_4^+ by zeolite is feasible, spontaneous and exothermic in nature process. Increased temperature has unfavorable effect on NH_4^+ sorption. At ambient conditions, NH_4^+ adsorption on zeolite surface is a diffusion-controlled process, which rate is limited mainly by heterogeneous diffusion on the zeolite-solution interface. Decrease in particle size of zeolites and intensive stirring of the suspension enhance the adsorption of NH_4^+. Most of batch studies reported that feasible degree of ammonia uptake from wastewaters is achieved in one hour or less, while the equilibrium is reached within 2-3 hours. The complete removal of ammonia requires longer treatment duration (up to several days), and is usually achieved by higher zeolite dosage and lower initial concentration of NH_4^+. At higher NH_4^+ concentration in the solution the ammonia adsorption capacity of zeolites is higher, but the degree of removal is lower, while with the increase of the zeolite dosage NH_4^+ removal efficiency increases at the expense of adsorption capacity. The optimal zeolite dosage varies from several grams up to several dozens grams per liter ammonia solution and depends upon the concentration ammonia in the influent, the desired degree of its reduction, and the presence of competitive ions. Maximum ammonia uptake is usually achieved at pH of the suspension in the neutral or close to the neutral area (pH=5-8). With the increase of pH above the optimal area NH_4^+ removal quickly decreases, due to the transformation of NH_4^+ into the neutral NH_3. The decrease of pH below the optimal range leads to a slower decrease in NH_4^+removal, due mainly to competitive adsorption of H^+. At acidic conditions partial dissolution of the zeolite is also possible. The presence of competitive alkali metal and alkaline earth metal ions in the solution affects the removal of ammonia ion. This influence is related to the selectivity of the zeolite used, which is different for different zeolites. Natural clinoptilolite has higher selectivity for NH_4^+ ion than synthetic zeolites. Potassium ion has the strongest negative effect on ammonia uptake, due to higher affinity of clinoptilolite to K^+ than to NH_4^+. For other types of natural zeolite, ion exchange with NH_4^+ is similar to clinoptilolite. Sodium form of both natural and synthetic zeolites is the most appropriate for ammonia removal. Ammonium-loaded zeolite could be easily and almost entirely regenerated. The regenerated zeolite could be re-used several times without noticeable affect of its performance. The spent NH_4^+-loaded zeolites could be utilized as a fertilizer with controlled ammonia release. Despite of their lower selectivity to ammonia ion, synthetic zeolites, namely types A, X and Y, have much higher ammonia exchange capacity than naturally occurring zeolites. Some synthetic zeolites, obtained from waste materials (e.g. CFA and RHA) performed well in ammonia removal processes and are considered as a good alternative of the natural zeolites and the other commercial adsorbents.

3.2.3. Heavy metals removal

Heavy metals are generally considered to be those whose density exceeds 5 g cm^{-3} [177]. A large number of elements fall into this category, but the ones of relevance in the environmental context are Cd, Cr, Cu, Ni, Zn, Pb and Hg [177]. Heavy metals are well known with their toxicity. Some of them tent to accumulate in living organisms, and may cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and even death [151]. The recommended maximum content of some heavy metals according to the WHO's guidelines for drinking-water quality [151] are presented in Table 8 along with the possible negative effects of heavy metals over-exposure on human health.

Table 8. Maximum heavy metals content and possible negative effects on humah health

Metal	Effect on human health	Max. content, mg l^{-1}
Cd	Carcinogenic, accumulates in the kidney and has a biological half-life in humans of 10–35 years	0.003
Cr(VI)	Genotoxic and carcinogenic	0.05
Cu	Affects gastrointestinal tract	2
Hg	Damages the kidney and causes haemorrhagic gastritis and colitis	0.006 for inorganic Hg
Mn	Neurological	0.4
Mo	Not reported	0.07
Ni	Carcinogenic	0.07
Pb	General toxicant that accumulates in the skeleton and interferes with calcium metabolism, both directly and by interfering with vitamin D metabolism	0.01
Sb	Genotoxic	0.02
U	Carcinogenic	0.015

Treatment processes for the removal of heavy metals from wastewater include coagulation, carbon adsorption, ion exchange, precipitation, reverse osmosis, etc. The new trends in removing heavy metals from industrial wastewater were reviewed by Barakat [177]. Zeolites have beed widely explored for heavy metals immobilization form natural or industrial water. The applicability of many natural and synthetic zeolites for the uptake of different heavy metal ions from variety synthetic and real wastewater compositions was extremely extensively researched in the last few decades. The number of the scientific articles devoted on this problem in the past ten years exceeds one hundred. Some of those concerning the application of natural zeolites for heavy metals removal have been reviewed in [9]. It is known that the immobilization of heavy metal ions from aqueous solutions by zeolites is quite a complicated process, consisting of ion exchange and adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface. Similarly to the sorption of ammonia, the heavy metal cations removal efficiency depends upon the type, dose and grain size of zeolite used, contact time, pH, temperature, initial metal concentration and to a significant extent to the presence of competitive ions. Experimental data for the sorption of heavy metal cations by natural and synthetic zeolites are presented in Table 9. Table 10 summarizes data for cation exchange selectivity of heavy metal ions on natural and synthetic zeolites.

Table 9. Heavy metals adsorption on some natural and synthetic zeolites

Metal ion	Zeolite	Zeolite origin	Metal conc. mg l^{-1}	Zeolite dosage, g l^{-1}	Metal sorption, mg g^{-1}	Metal removal, %	Refe-rence*
Ag^{+}	Clinoptilolite	Bulgaria	500	5	32.2	43	[19]
Ag^{+}	Na-clinoptilolite	Bulgaria	500	5	82.1	84	[19]
Ag^{+}	Beneficiated clinoptil.	USA	1072	4		84	[178]
Ag^{+}	Beneficiated erionites	USA	1072	4		94-96	[178]
Ag^{+}	Beneficiated chabazites	USA	1072	4		88-90	[178]
Ag^{+}	Beneficiated mordenites	USA	1072	4		38-75	[178]
Cd^{2+}	Natural scolecite	Brazil	50	17	2.5-8.9	84-59	[179]
Cd^{2+}	Na-scolecite	Brazil	15	5	0.18		[180]
Cd^{2+}	Na-clinoptilolite	Croatia	1124	10	23.6		[181]
Cd^{2+}	Clinoptilolite	Croatia	1124	10	13.5		[181]
Cd^{2+}	Clinoptilolite	Greece	100	10	4.1		[182]
Cd^{2+}	Beneficiated clinoptil.	USA	1124	4		41-46	[178]
Cd^{2+}	Beneficiated erionites	USA	1124	4		61-85	[178]
Cd^{2+}	Beneficiated chabazites	USA	1124	4		53-65	[178]
Cd^{2+}	Beneficiated mordenites	USA	1124	4		29-32	[178]
Cd^{2+}	Mordenite	New Zealand	0.025	10		45	[183]
Cd^{2+}	NaP	Synthetic	0.025	10		100	[183]
Cd^{2+}	NaP1	From CFA	100	10	50.8		[182]
Cd^{2+}	NaP1	From CFA	11	0.1		85	[184]
Cd^{2+}	NaP1	From OSA	100	1	95.6		[93]
Cd^{2+}	NaA	Commercial	25-100	25		98-73	[185]
Cd^{2+}	NaA	From kaolin	20	8		>99	[54]
Cd^{2+}	NaA+ tobermorite	From MSWIA	3.5	2		>99	[186]
Cd^{2+}	Blend of NaA and KA	From CFA	100	200		100	[82]
Cd^{2+}	13X	Commercial	25-100	25		97-71	[185]
Cd^{2+}	NaX	From kaolin	20	8		>99	[54]
Cd^{2+}	NaX + activated carbon	From CFA	500	2	129.3		[187]
Co^{2+}	Na-scolecite	Brazil	15	5	0.23		[180]
Co^{2+}	Clinoptilolite	Turkey	50	20	2.0	78	[188]
Co^{2+}	NaA	From CFA	50-100	1	16.8-5.5		[80]
Cr^{3+}	Natural scolecite	Brazil	50-250	17	3.0-14.5	100-96	[179]
Cr^{3+}	Clinoptilolite	Greece	100	10	4.1		[182]
Cr^{3+}	Natural mordenite		500	5	3.5		[53]
Cr^{3+}	Blend of NaX and NaA	From kaolin	500	5	71.1		[53]
Cr^{3+}	Blend of NaY and NaP	From mordenite	500	5	83.2		[53]
Cr^{3+}	NaP	From mordenite	500	5	52.0		[53]
Cr^{3+}	NaP1	From CFA	100	10	43.6		[182]

Cr^{3+}	Hydroxysodalite	From kaolin	500	5	34.7		[53]
Cr^{3+}	13X	Commercial	500	5	60.7		[53]
Cr^{3+}	NaY	Commercial	500	5	36.4		[53]
Cr^{3+}	NaA	Commercial	500	5	53.7		[53]
Cr^{3+}	NaA	From CFA	50-100	1	38.7-56.4		[80]
Cr^{3+}	NaA+ tobermorite	From MSWIA	11	2		>99	[186]
Cr^{3+}	Blend of NaA and K-A	From CFA	100	200		100	[82]
Cu^{2+}	Clinoptilolite	Bulgaria	50	10	2.9	57	[189]
Cu^{2+}	NaOH-modified clinoptilolite	Bulgaria	50	10	4.8	95	[189]
Cu^{2+}	CH_3COONa - modified clinoptilolite	Bulgaria	50	10	4.7	93	[189]
Cu^{2+}	Na-clinoptilolite	Bulgaria	50	10	4.8	95	[189]
Cu^{2+}	Na-clinoptilolite	Ecuador	635		19.2		[190]
Cu^{2+}	Clinoptilolite	Ecuador	635		0.8		[190]
Cu^{2+}	Clinoptilolite	Egypt	10-100	5		91-50	[191]
Cu^{2+}	Clinoptilolite	Greece	100	10	5.3		[182]
Cu^{2+}	Heulandite	Ecuador	635		3.9		[190]
Cu^{2+}	Stilbite	Brazil	635		2.1		[190]
Cu^{2+}	Beneficiated clinoptilolite	USA	635	4		30-35	[178]
Cu^{2+}	Beneficiated erionites	USA	635	4		63-82	[178]
Cu^{2+}	Beneficiated chabazites	USA	635	4		43-59	[178]
Cu^{2+}	Beneficiated mordenites	USA	635	4		8-18	[178]
Cu^{2+}	Mordenite	New Zealand	0.25	10		53	[183]
Cu^{2+}	NaP	Synthetic	0.25	10		98	[183]
Cu^{2+}	NaP1	From CFA	100	10	50.5		[182]
Cu^{2+}	NaP1	From CFA	6.4	0.1		89	[184]
Cu^{2+}	Zeolite type 13A	Synthetic	63.5-635	4		99-78	[178]
Cu^{2+}	Zeolite type 3A	Synthetic	63.5-635	4		61	[178]
Cu^{2+}	Zeolite type 5A	Synthetic	63.5	4		56	[178]
Cu^{2+}	Zeolite type 4A	Synthetic	63.5	4		64	[178]
Cu^{2+}	NaA	From kaolin	20	8		>99	[54]
Cu^{2+}	NaA	From CFA	200	5	38.0		[81]
Cu^{2+}	NaA	From CFA	50-100	1	39.8-72.0		[80]
Cu^{2+}	Blend of NaA and K-A	From CFA	100	200		100	[82]
Cu^{2+}	Chabazite	From CFA	25-54	10		87-97	[192]
Cu^{2+}	NaX	From kaolin	20	8		>99	[54]
Cu^{2+}	NaX	From CFA	200	5	28.9		[81]
Cu^{2+}	NaX + activated carbon	From CFA	500	2	101.7		[187]
Fe^{3+}	Natural phillipsite	Jordan	400	20	14.6	73	[193]
Fe^{3+}	Clinoptilolite	Turkey	400	37-150	6.4-2.6	59-97	[13]
Fe^{3+}	Chabazite	From CFA	24-49	10		99-61	[192]
Fe^{3+}	NaP1	From CFA	5.6	0.1		29	[184]
Hg^{2+}	Beneficiated clinoptil.	USA	2006	4		5-6	[178]
Hg^{2+}	Beneficiated erionites	USA	2006	4		7-9	[178]
Hg^{2+}	Beneficiated chabazites	USA	2006	4		3-6	[178]
Hg^{2+}	Beneficiated mordenites	USA	2006	4		1-2	[178]
Hg^{2+}	Blend of Faujasite, Sodalite and zeolite A	From filtrate from CFA and AMD co-disposal	0.00047	20		64	[194]
Mn^{2+}	Natural scolecite	Brazil	50	17	2.3-9.4	75-63	[179]
Mn^{2+}	Clinoptilolite	Turkey	50	20	0.5	20	[188]
Mn^{2+}	Clinoptilolite	Turkey	20	37-150	0.52-0.13	95-99	[13]
Mn^{2+}	Clinoptilolite	Greece	4-100	10	up to 7.69	65-30	[195]
Mn^{2+}	Fe-clinoptilolite	Greece	4-100	10	up to 27.1	100-93	[195]
Mn^{2+}	Na-clinoptilolite	Serbia	50-400	10	5.0-8.0		[196]

Mn^{2+}	NaOH-modified (clinoptilolite + mordenite)	Chile	100	2.5	20.3		[197]
Mn^{2+}	Na-(clinoptilolite + mordenite)	Chile	100	2.5	13.0		[197]
Mn^{2+}	Na-(clinoptilolite + mordenite)	Chile	100	25	12.4		[198]
Mn^{2+}	MnO_2-(clinoptilolite + mordenite)	Chile	100	1-6	15.1-11.8	42-99	[198]
Mn^{2+}	MnO_2-(clinoptilolite + mordenite)	Chile	100	25	30.2		[198]
Ni^{2+}	Natural scolecite	Brazil	50	17	2.9-6.0	96-40	[179]
Ni^{2+}	Na-scolecite	Brazil	30	5	0.9		[180]
Ni^{2+}	Na-Clinoptilolite	Serbia	100-600	10	6.0-10.6		[199]
Ni^{2+}	Beneficiated clinoptilolite	USA	587	4		20-23	[178]
Ni^{2+}	Beneficiated erionites	USA	587	4		15-17	[178]
Ni^{2+}	Beneficiated chabazites	USA	587	4		20-25	[178]
Ni^{2+}	Beneficiated mordenites	USA	587	4		8-10	[178]
Ni^{2+}	Clinoptilolite	Greece	100	10	2.0		[182]
Ni^{2+}	NaP1	From CFA	100	10	20.1		[182]
Ni^{2+}	NaX	From kaolin	20	8		>99	[54]
Ni^{2+}	NaX + activated carbon	From CFA	500	2	132.1		[187]
Ni^{2+}	NaA	From kaolin	20	8		>99	[54]
Ni^{2+}	NaA	From CFA	50-100	1	11.5-6.1		[80]
Ni^{2+}	Blend of NaA and K-A	From CFA	100	200		100	[82]
Pb^{2+}	Na-scolecite	Brazil	30	5	5.8	97	[180]
Pb^{2+}	Clinoptilolite	Greece	1036	20	33.7	65	[200]
Pb^{2+}	Clinoptilolite	Croatia	2072	10	78.7		[181]
Pb^{2+}	Clinoptilolite	Ecuador	2072		40.4		[190]
Pb^{2+}	Na-clinoptilolite	Croatia	2072	10	91.2		[181]
Pb^{2+}	Na-clinoptilolite	Ecuador	2072		73.4		[190]
Pb^{2+}	Heulandite	Ecuador	2072		20.4		[190]
Pb^{2+}	Stilbite	Brazil	2072		8.8		[190]
Pb^{2+}	Beneficiated clinoptil.	USA	2072	4		42-69	[178]
Pb^{2+}	Beneficiated erionites	USA	2072	4		92-94	[178]
Pb^{2+}	Beneficiated chabazites	USA	2072	4		92-96	[178]
Pb^{2+}	Beneficiated mordenites	USA	2072	4		10-17	[178]
Pb^{2+}	Mordenite	New Zealand	0.05	10		89	[183]
Pb^{2+}	NaP	Synthetic	0.05	10		100	[183]
Pb^{2+}	NaP1	From CFA	21	0.1		98	[184]
Pb^{2+}	NaP1	From CFA	200	2.4		>95	[201]
Pb^{2+}	NaP1	From OSA	100	1	70.6		[93]
Pb^{2+}	NaX	From kaolin	20	8		>99	[54]
Pb^{2+}	NaX + activated carbon	From CFA	100	2	228		[187]
Pb^{2+}	NaA	From kaolin	20	8		>99	[54]
Pb^{2+}	NaA+ tobermorite	From MSWIA	22	2		>99	[186]
Pb^{2+}	Blend of NaA and K-A	From CFA	100	200		100	[82]
Pb^{2+}	Blend of Fauja site, Sodalite and zeolite A	From filtrate from CFA and AMD co-disposal	0.00323	20		95	[194]
Pb^{2+}	Hydroxysodalite	From CFA	200	2.4		>95	[201]
Pb^{2+}	Hydroxysodalite	From CFA	21	0.1		65	[184]
Pb^{2+}	Analcime	From CFA	21	0.1		65	[184]
Pb^{2+}	Cancrinite	From CFA	21	0.1		45	[184]
Pb^{2+}	Chabazite	From CFA	25-49	10		99-100	[192]
Pb^{2+}	Faujasite	From CFA	0.00323	20		88	[194]
Pb^{2+}	Faujasite	From CFA	21	0.1		90	[184]

Zn^{2+}	Beneficiated mordenites	USA	654	4		22-23	[178]
Zn^{2+}	Clinoptilolite	Greece	100	10	3.1		[182]
Zn^{2+}	Mordenite	New Zealand	0.5	10		42	[183]
Zn^{2+}	NaP1	From CFA	100	10	32.6		[182]
Zn^{2+}	NaP1	From CFA	6.5	0.1		65	[184]
Zn^{2+}	NaP	Synthetic	0.5	10		97	[183]
Zn^{2+}	13X	Commercial	25-100	25		95-79	[185]
Zn^{2+}	NaX	From kaolin	20	8		>99	[54]
Zn^{2+}	NaX	From CFA	200	5	22.4		[81]
Zn^{2+}	NaA	Commercial	25-100	25		97-87	[185]
Zn^{2+}	NaA	From kaolin	20	8		>99	[54]
Zn^{2+}	NaA	From CFA	200	5	29.7		[81]
Zn^{2+}	NaA	From CFA	50-100	1	40.4-19.6		[80]
Zn^{2+}	Blend of NaA and K-A	From CFA	100	200		100	[82]
Zn^{2+}	Chabazite	From CFA	25-43	10		97-33	[192]

* Some values are recalculated and/or rounded.

Bektas and Kara [210] studied the removal of Pb^{2+} from aqueous solution using natural clinoptilolite. The effects of initial metal concentration (10–100 mg l^{-1}), pH (2–7), agitation speed (100–225 rpm), particle size (315–1600 μm) and temperature (25 – 50◦C) on the uptake process were investigated. The sorption isotherms were described well by the Langmuir model with the maximum sorption capacity of 166 mg g^{-1} of lead on clinoptilolite. At the maximum temperature, and equilibrium lead concentration of about 1000 mg l^{-1} a sorption capacity of approximately 180 mg g^{-1} was reached. The sorption kinetics study indicated that the Pb^{2+} uptake process followed the pseudo-second order rate expression, which is consistent with the results obtained for Mn and Zn sorption on cliniptilolites [197,199]. Stylianou et al. [202] performed fixed bed experiments for the removal of Pb, Cu and Zn from aqueous solutions by clinoptilolite from Greece. Experiments were performed at volumetric flow rates of 5, 7 and 10 bed volume h^{-1}, under a total normality of 0.01N, at initial pH = 4 and ambient temperature. It was found that the removal efficiency increased when decreasing the flow rate. The obtained selectivity order was Pb>Zn≥Cu, which is in agreement with some of the results reported for clinoptilolites [203,204,206,211] but does not match the order of selectivity (Pb>Cu>Zn) obtained for other clinoptilolites [188,205,207], and other natural zeolites like chabasite [206,207] and mordenite [183]. These discrepancies could be explained with the specific composition of natural zeolites from different deposits and with the differences in the experimental methods used. Conductivity measurements showed that Pb removal follows mainly ion exchange mechanism, while Cu and Zn removal involves sorption mechanism as well [202].

Erdem et al. [188] investigated adsorption behaviour of clinoptilolite from Western Anatolia with respect to Co^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} removal from aqueous solutions. Batch method was employed, using metal concentrations in solution ranging from 100 to 400 mg l^{-1}. It was found that the adsorption phenomena depend on charge density and hydrated ion diameter. According to the equilibrium studies, the selectivity sequence can be given as Co>Cu>Zn>Mn. The maximum adsorption capacities for Co, Cu, Zn and Mn, according to the Langmuir equation were 244, 141, 134 and 77 mmol kg^{-1} in the same order.

Motsi et al. [13] studied the adsorption behaviour of clinoptilolite in order to determine its applicability in treating acid mine drainage (AMD) containing 400, 120, 20, 20 and mg l^{-1} of Fe^{3+}, Zn^{2+}, Cu^{2+}, and Mn^{2+} respectively. Tests to determine both the rate of adsorption and the uptake at equilibrium were performed under batch conditions from single and multi-component solutions. The optimum conditions for the treatment process were investigated by observing the influence of pH levels, the presence of competing ions zeolite dosage and thermal modification of the natural zeolite. The adsorption studies showed rapid uptake for the first 40 min, corresponding to about 80% total removal. Approximately 80%, 95%, 90% and 99% of Fe^{3+}, Mn^{2+}, Zn^{2+} and Cu^{2}

respectively, were adsorbed from single component solutions. Only Fe^{3+} adsorption of was unaffected by the presence of competing ions, which was explained with the precipitation mechanism of Fe^{3+} removal. The adsorption of the other 3 cations from multi-component solutions of concentration 40 mg l^{-1} decreased with 30-40%. Promising results were obtained from the preliminary tests using real AMD, as well. The process of continuous elimination of Pb^{2+}, Cu^{2+}, Zn^{2+} from AMD wastewater by natural stilbite, heulandite, and clinoptilolite was investigated by Calvo et al. [190]. The general order of effective CEC obtained from breakthrough curves of these zeolitic tuffs, was the following: clinoptilolite > heulandite > stilbite. The raw clinoptilolite sample showed very good exchange capacity for Pb^{2+} (40.4 mg g^{-1}), and also a high exchange capacity for Cu^{2+} (19.2 mg g^{-1}) and Zn^{2+} (7.8 mg g^{-1}) when conditioned with 2M NaCl. The sorption of Pb^{2+} on the Na-clinoptilolite reached 73.4 mg g^{-1}, witch value is comparable only with that obtained for the unmodified Croatian clinoptilolite [181].

Table 10. Cation exchange selectivity of heavy metal ions on natural and synthetic zeolites

Zeolite	Zeolite origin	Selectivity order	Reference
Clinoptilolite	Greece	$Pb^{2+} > Zn^{2+} \geq Cu^{2+}$	[202]
Clinoptilolite	Greece	$Pb^{2+} > Cr^{3+} > Fe^{3+} \geq Cu^{2+}$	[203]
Clinoptilolite	Greece	$Cu^{2+} > Cr^{3+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$	[182]
Clinoptilolite	Turkey	$Co^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$	[188]
Clinoptilolite	Turkey	$Fe^{3+} > Zn^{2+} > Cu^{2+} > Mn^{2+}$	[13]
Clinoptilolite	Turkey	$Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$	[204]
Clinoptilolite	Croatia	$Pb^{2+} > Cd^{2+}$	[181]
Clinoptilolite	Italy	$Pb^{2+} > Cu^{2+} > Cd^{2+} \approx Zn^{2+}$	[205]
Clinoptilolite	Italy	$Pb^{2+} > Cd^{2+} > Zn^{2+} \approx Cu^{2+}$	[206]
Clinoptilolite	Commercial	$Cs^{+} > Cu^{2+} > Sr^{2+} > Zn^{2+} > Co^{2+}$	[207]
Natural chabazite	Commercial	$Cs^{+} > Sr^{2+} > Cu^{2+} > Zn^{2+} \approx Co^{2+}$	[207]
Natural chabazite	Italy	$Pb^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+}$	[206]
Natural chabazite	Italy	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+}$	[206]
Natural scolecite	Brazil	$Ni^{2+} > Cr^{3+} > Cd^{2+} > Mn^{2+}$	[179]
Natural scolecite	Brazil	$Cu^{2+} > Zn^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$	[180]
Natural mordenite	New Zealand	$Pb^{2+} > Cu^{2+} > Zn^{2+} \approx Cd^{2+}$	[183]
NaP1	From CFA	$Cr^{3+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$	[182]
NaP1	From CFA	$Ba^{2+} > Cu^{2+} > Cd^{2+} \approx Zn^{2+} > Co^{2+} > Ni^{2+}$	[78]
NaP1	From CFA	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$	[184]
NaA	Commercial	$Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+}$	[80]
NaA	From CFA	$Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+}$	[80]
NaA	From kaolin	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$	[54]
NaX	From kaolin	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2}$	[54]
NaY	Commercial	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+}$	[208]
NaY	From CFA	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$	[187]
Faujasite	From CFA	$Fe^{3+} > As^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$	[209]
Cancrinite	From CFA	$Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$	[6]

Coruh [212] investigated Zn^{2+} removal from aqueous solutions by raw and NaCl conditioned (10 ml 2M NaCl solution per gram zeolite) clinoptilolite. The pre-treatment was performed by three different methods: at room temperature, at 70°C and with a preliminary treatment with 0.1 M HCl to wash out carbonates and clays. The results prove that the conditioning improved both the exchange capacity and the removal efficiency [212,181]. It was found that the increase of temperature from 10 to 90°C resulted in a rise of removal efficiency from 90.7 to 99.7%. The maximum sorption capacity, calculated from the Langmuir equation for the sample conditioned at increased temperature was 22.2 mg g^{-1}, while for the raw zeolites it was 17.9 mg g^{-1}. The change of pH from 4 to 8 had a negligible effect on the performance of the conditioned sample, while the effect for the raw one was significant.

Panayotova examined the kinetics and thermodynamics of Ni^{2+}[213], Cu^{2+} [189] and Cd^{2+} [214] removal from wastewater by use of raw and modified Bulgarian clinoptilolite [189]. It was found that the modification of zeolite with NaOH, NaCl, and CH_3COONa increased significantly metal ions uptake, whereas the HCl treatment has negative effect on the process. The uptake equilibriums of Ni^{2+} and Cu^{2+}were best described by the Langmuir adsorption isotherm, while the uptake of Cd^{2+} fitted better to Freundlich isotherm. The uptake of Cu^{2+} by zeolite from neutral wastewater has proved to be as effective as precipitation of copper hydroxide. The simultaneous presence of Ca^{2+} and Mg^{2+} did not significantly influence the uptake of Cu^{2+}, however the uptake of Cd^{2+} was considerably decreased in the presence these ions. Desorption experiments showed that Cu^{2+} ions were strongly immobilized by zeolites modified with NaOH, NaCl and CH_3COONa, while the immobilization by natural sample was weaker. Loaded natural and modified cliniptilolites were easily regenerated by 2M NaCl solution [189]. Panayotova and Velikov [215] further studied the kinetics of the uptake of Cd, Pb, Cu, Ni and Zn from single ion solutions and from their mixture. It was found that Pb^{2+} were strongly immobilised by the zeolite, in single ion and mixed solutions, as well as in soft and in hard water. It was also reported that pre-treatment of zeolite with NaCl increased the rate of heavy metal ions' uptake and the distribution coefficients, but does not change zeolite selectivity sequence for the ions in multi-component solutions [216].

Bosso and Enzweiler [180] investigated the potential of natural Brazilian scolecite as a new material for heavy metal removal (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+}) from aqueous. Samples were pre-treated with 2M NaCl solution. The experiments were carried out under constant agitation for 24 h, at ambient temperature. The quantity of cations retained per mass of scolecite was evaluated as a function of initial concentration (5–60 mg l^{-1}), pH (4–6), liquid/solid ratio and particle size. The results indicated a great affinity of scolecite for Cu^{2+} with a retention value of 0.13 meq g^{-1} at pH= 6, initial Cu^{2+} concentration mg l^{-1} and liquid/solid ratio of 200. In the same conditions, the maximum retention measured for the other ions was 0.064 meq g^{-1} (Zn^{2+}), 0.056 meq g^{-1} (Pb^{2+}), 0.031 meq g^{-1} (Ni^{2+}), 0.00.8 meq g^{-1} (Co^{2+}) and 0.0032 meq g^{-1} (Cd^{2+}). The selectivity sequence calculated in milliequivalents per gram of zeolite is therefore Cu>>Zn>Pb>Ni>>Co>Cd. The maximum uptake was for all the ions studied was obtained at pH=6. Dal Bosco et al. [179] further studied the cation exchange capacity of the same material for the sorption of Cr^{3+}, Ni^{2+}, Cd^{2+}, and Mn^{2+} in single-metal synthetic solutions. The results demonstrated that removal of metals from specific metal solutions is best described by a Freundlich isotherm. The sorption capacity of scolecite for metals at 298 K followed the series Cr>Mn>Cd>Ni. This order could be related to such properties as the radius of hydration and the hydration enthalpy of the cations. There was a significant enhancement in the sorption of metals at high temperature values for the metals tested, except for Ni. Thermodynamic data indicated the spontaneity of the endothermic cation exchange process and suggested the following selectivity series at 298 K: Ni>Cr>Cd>Mn.

The adsorption of Mn^{2+} onto natural and activated Chilean zeolites was investigated by Taffarel and Rubio [197]. Zeolite activation was carried out by treatment of 5g zeolite with 1l 1M solutions of NaCl, NH_4Cl, Na_2CO_3 or NaOH for 24 h at room temperature. It was found that zeolite modification by treating with all the above listed chemicals increased the Mn^{2+} uptake capacity from 0.26 meq g^{-1} (raw zeolite) to 0.67-0.77 meq g^{-1}. Solution alkalinity influenced significantly the Mn^{2+} adsorption rate and capacity and the best results were obtained at pH=6–6.8. The adsorption onto the activated zeolite followed the pseudo-second-order kinetic model. Activation with NaOH resulted in the highest reaction rate. The same authors [198] further investigated the removal of Mn^{2+} from aqueous solution by Chilean natural zeolite coated with MnO_2. The results showed that the coated zeolite has almost 2.5 higher Mn^{2+} adsorption capacity than the Na-form and that it is able to remove up to 99% of Mn^{2+} from solution with initial concentration of 3.64 meq.l^{-1}. Kinetic and thermodynamic data obtained, indicated that Mn^{2+} capturing onto zeolite is the result of a combination of several interfacial reactions namely, ion exchange, chemisorption, and adsorption. The maximum Mn^{2+} adsorption capacity was 1.12 meq g^{-1}.

Rajic et al. tested NaCl-modified Serbian clinoptilolite as adsorbent for Ni^{2+} [199] and Mn^{2+} [196] ions from aqueous solutions. It was found that Ni^{2+} sorption at 298 K varies from 1.9 mg g^{-1} to 3.8 mg g^{-1} at initial Ni^{2+} concentrations in the range of 100-600 mg l^{-1}. At 338 K roughly three-fold increased sorption capacities - up to 6 mg g^{-1} (for 100 mg l^{-1} Ni^{2+}) and 10.6 mg g^{-1} (for 600 mg l^{-1} Ni^{2+}) were observed. For Mn^{2+} the increase of temperature also led to significant increase in sorption rate and capacity. The sorption isotherm for both elements on clinoptilolite was best represented by the Sips model, and the kinetics followed the pseudo-second-order model. It was found that the sorption involved film diffusion, intra-particle diffusion, and chemical cation exchange processes [199]. The sorption of both metals was found to be an endothermic and spontaneous in the temperature range studied. Maximum Mn^{2+} adsorption was achieved at pH=6.

Dimirkou and Doula [195,217,218] tested natural and Fe(III)-overexchanged clinoptilolite in Zn^{2+} and Mn^{2+} removal from drinking water samples. The Fe-overexchanged clinoptilolite was prepared by mixing 20 g of clinoptilolite, 100 ml 1M $Fe(NO_3)_3x9H_2O$ solution, and 180 ml of 5M KOH solution, suspension delution to 2l and subsequent thermal treatment 70ºC for 60 h. Batch adsorption experiments were carried out to determine the effectiveness both adsorbents in the removal of Zn and Mn from drinking water. The maximum adsorbed Mn amount for raw clinoptilolite was 7.69 mg g^{-1}, whereas that for the Fe-clinoptilolite system it was much higher - 27.1 mg g^{-1}. The respective values for the adsorption of Zn were 71.3 mg g^{-1} and 94.8 mg g^{-1}. The maximum adsorption efficiency of the raw zeolite is observed at initial metal concentration of 4-5 ppm for both cations, while the Fe-modified samples showed > 90% removal efficiency in a broad range of concentrations – from 4 to 100 ppm for Mn and from 5 to 200 ppm for Zn. The tests for simultaneous removal of Cu, Mn and Zn from drinking water showed that both substrates reduced Mn adsorption in the presence of Cu and Zn.

Katsou et al. [219] recently investigated the potential regeneration of natural zeolite, which had been contaminated with Pb, and Zn contained in aqueous solutions, treated secondary effluent and primary treated wastewater. The adsorption experiments were conducted in batch reactors at initial heavy metals concentration of 320 mg l^{-1} and zeolite dosage 10 g l^{-1}. Several desorbing solutions were examined for the removal of Pb and Zn and KCl (at 3M and 1M concentration, respectively) was found to be the most effective exhibiting very high desorption efficiencies (>98.5%) for both metals. Successive regeneration cycles resulted in the reduction of desorption efficiency by more than 50% after 9 and 4 cycles for lead and zinc, respectively. Kinetics examination showed that desorption was slower than adsorption. Adsorption was characterized by a three-stage diffusion process, while desorption followed a two-stage diffusion process.

Although the above-reviewed investigations demonstrated that under appropriate conditions natural zeolites, could be very effective in the uptake of some heavy metals from (waste)waters, several comparative studies [182,183] clearly indicated that generally synthetic zeolites have much better removal performance than natural ones. Alvarez-Ayuso et al. [182] studied the sorption behaviour of natural zeolite (predominantly clinoptilolite) and zeolite NaP1, obtained from CFA, with respect to Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in order to consider their applicability for purification of metal electroplating wastewaters. The batch method was employed using metal concentrations in solution ranged from 10 to 200 mg l^{-1} and zeolite ratios dose from 2.5 to 10 g l^{-1}. It was found that synthetic zeolite exhibited about 10 times greater sorption capacities than natural zeolite, and that while the metal sorption on natural zeolite increased with time, the sorption on NaP1 zeolite appeared to be practically instantaneous. The metal amounts, sorbed by NaP1 in the first half an hour, corresponded to 100% of equilibrium amounts. Metal sorption affinity was found to follow the sequence: Cr>Cu>Zn>Cd>Ni for NaP1 and Cu>Cr>Zn>Cd>Ni for the natural zeolite. The main factors responsible for the retention sequences were recognized to be CEC of zeolites and the strength of the hydration shells of cations. Zeolite NaP1 showed the same high sorption capacity values when used in the purification of real metal electroplating wastewaters. Pitcher et al. [183] conducted batch experiments with natural mordenite and synthetic NaP zeolite to test their ability to remove dissolved heavy metals (Zn, Cu, Pb, Cd) from simulated and spiked motorway stormwater. Synthetic NaP zeolite showed almost complete removal (>91%) of the studied heavy metals from both solutions and did not appear to be affected by the calcium present in the motorway stormwater, while mordenite was less effective at reducing the levels of heavy metals (42–89% in synthetic solution, 6-44% in motorway stormwater).

Purna Chandra Rao et al. [185] compared the sorption of Cd^{2+} and Zn^{2+} by bentonite and commercial zeolites 13X, 4A in a batch tests at different equilibrium time, pH (2-8) and sorbent dose (5-30 g l^{-1}). They reported the metals sorption by zeolite 4A was higher than that by zeolite 13X and bentonite. The sorption peak values for all the sorbents were obtained at pH 6.0 and 6.5 for Cd^{2+} and Zn^{2+}respectively and the sorption followed the Freundlich model. More than 70% sorption occurred within 20 min and equilibrium was attained at around 90 min for the three sorbents. The experimental data revealed that with an initial concentration of 25 ppm, the removal of Cd at pH 6 was 0.088 mmol/g with zeolite 4A, 0.086 mmol/g with zeolite 13X and 0.084 mmol/g with bentonite. With an initial concentration of 25 ppm, the removal of Zn at pH 6.5 was 0.148 mmol/g with zeolite 4A, 0.145 mmol/g with zeolite 13X and 0.141 mmol/g with bentonite. The maximum percentage desorption was obtained using 10% NaCl solution and was 76% for Cd and 80% for Zn. The presence of competitive cations (Ca^{2+}, Mg^{2+} and Fe^{2+}) in the solution reduced the efficiency of Cd^{2+} and Zn^{2+} uptake wit about 10% for all studied sorbents.

Covarrubias et al. [53] investigated Cr(III) exchange on zeolites obtained by HT synthesis from kaolin (hydroxisodalie, and a blend of zeolites X and A) and from natural mordenite (a blend of zeolites Y and P2, and pure zeolite P). Batch experiments were carried at initial Cr^{3+} concentration of 500 mg l^{-1}, adsorbent dosage of 5 g l^{-1}, room temperature, continuous agitation and 24 h treatment time. It was found out that the Cr^{3+} exchange of synthesis products was determined by zeolite type and the fraction of amorphous phase in the solid product. The highest Cr^{3+} exchange capacity was obtained for the products containing FAU-type zeolites (X and Y), which could be explained with the larger pore opening, which facilitates the diffusion of large hydrated chromium ions into the internal cation exchange sites. The synthesized zeolites products presented higher Cr(III) exchange capacity (4.1 and 4.8 meq g^{-1} for zeolites X and Y respectively) than commercial zeolites types 13X, 4A and NaY (2.1, 3.1, and 3.5 meq g^{-1}).

In addition to the type of zeolite, its cation form was found to play an importat role in the heavy metals exchange process. Keane [220] investigated the removal of Cu^{2+} and Ni^{2+} from aqueous solution using Li-, Na-, K-, Rb-, and Cs-exchanged Y zeolites under competitive and non-competitive conditions. The results indicated that the extent of transition metal removal is dependent strongly on the nature of the out-going alkali metal cation with the overall preference of the zeolite for exchange with both metals decreasing in the order LiY>NaY>KY>RbY>CsY, corresponding to the order of increase of the size of the bare alkali metal cation. As this size increases, the charge density decreases, the solid phase ions are present in a less hydrated state, interacting more strongly with the zeolite lattice and, consequently, are more resistant to exchange with external cations. The heavy metal removal was found to be is independent of the nature of the anion, coming from heavy metal salt used [208], however it is dependent of the heavy metal hydrated ion diameter [184,221]. Jamil et al. [54] performed series of experiments in order to determine the optimum conditions for removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+} using zeolites A and X prepared from kaolin. Metal removal was investigated using synthetic solutions at initial concentrations of 20 mg l^{-1} of individual metals and mixture of metals with concentration of 20 mg l^{-1} for each, at 25°C and pH = 7.5. It was found that the optimum contact time for removal of Cd, Cu, Pb and Zn was 30 min and for Ni was 60 min for both zeolite types. At the optimum time the efficiencies of zeolite A and X were almost equal and above 99% for all the cations studied. In the second part of the investigation [221] authors reported that according to the equilibrium studies, the selectivity sequence of both zeolites can be given as Pb>Cd>Cu>Zn>Ni, which is in conformity with the orders obtained for commercial and CFA-derived zeolite A [80], and zeolite Y [208,220], but does not match those reported for zeolite NaP1 [78,182,184], which was found to be less selective to the Cd^{2+} ion.

The intensive research on the applicability of the zeolitized CFA as ion exchangers for water decontamination has shown that CFA-derived zeolites are also very effective in the removal heavy metals from industrial wastewaters and that, although initial CFA usually contain heavy metals, the synthesized zeolites are environmentally safe, due to the immobilization of heavy metals by sorption in the zeolite framework or by precipitation of insoluble hydroxides [78].

Hui et al. [80] performed a comparative study on the uptake Cu^{2+}, Cr^{3+}, Zn^{2+}, Co^{2+} and Ni^{2+} from mixed metal ions solution by commercial zeolite 4A (Valfor 100) and CFA-based pure zeolite 4A. Batch method was employed to study the influential parameters such as initial metal ions concentration, adsorbent dose, contact time and initial pH of the solution on the adsorption process. The experimental data were well fitted by the pseudo-second-order kinetics model (for Co^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+} ions) and the pseudo-first-order kinetics model (for Ni^{2+} ions). The equilibrium data for both NaA zeolites were well fitted by the Langmuir model and showed the same affinity order: Cu>Cr>Zn>Co>Ni. It was found out that the increase of the initial concentration from 50 to 300 mg g^{-1} of the mixed metal ions led to significant decrease in the sorption of Zn^{2+}, Co^{2+} and Ni^{2+} ions, which could be attributed to the higher selectivity of the zeolite to Cu^{2+} and Cr^{3+} ions. The adsorption process was found to be pH and concentration dependent. It was demonstrated that the sorption rate and capacity of metal ions could be significantly improved by increasing pH value. Commercial grade zeolite 4A and the CFA-4A showed very similar heavy metals uptake behaviour, despite its lower crystallinity and specific surface. For CFA-prepared zeolite, the equilibrium sorption capacities obtained were 50.45 mg g^{-1} for Cu^{2+}, 41.61 mg g^{-1} for Cr^{3+}, 30.80 mg g^{-1} for Zn^{2+}, 13.72 mg g^{-1} for Co^{2+}, and 8.96 mg $g^{-1}$for Ni^{2+}. For commercial zeolite 4A, they were 53.45 mg g^{-1} (Cu^{2+}), 45.29 mg g^{-1} (Cr^{3+}), 31.58 mg g^{-1} (Zn^{2+}), 11.52 mg g^{-1} (Co^{2+}), and 7.9 mg g^{-1} (Ni^{2+}).

Wang et al. [81] synthesized two pure-form zeolites (A and X) from CFA by a two-stage method and tested their potential as adsorbents for Zn^{2+} and Cu^{2+} uptake from wastewater. The results from comparative studies showed that zeolite A was more effective in removing both ions, Cu^{2+} and Zn^{2+}, compared to zeolite X. The influential parameters were studied for the removal performance of metal ions on three adsorbents: CFA-derived pure zeolite A, hydroxisodalite, obtained from raw CFA, and commercial zeolite A. All the adsorbents showed effective adsorption with higher capacity for Cu^{2+} than for Zn^{2+}. The greatest removal efficiency, obtained for the three zeolites were respectively 99.7%, 89.6% and 99.1% for Cu^{2+}, and 93.2%, 81.5%, and 96.1% for Zn^{2+}.

Jha et al. [187] prepared composite materials of activated carbon and zeolite X have by fusion of CFA with NaOH at 750ºC in N_2 followed by HT treatment. The samples were subjected to Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} uptake experiments by a batch method at room temperature, solid/solution ratio 0.1 g 50 ml^{-1}, initial metal ion concentrations 20-500 ppm of Ni^{2+}, Cu^{2+}, Cd^{2+} and 100–2000 ppm of Pb^{2+}, and treatment time of 24 h. The kinetic experiments were performed at 500 ppm for Ni^{2+}, Cu^{2+}, Cd^{2+} and 1000 ppm for Pb^{2+} for times of 0.5–6 h. The relative selectivity of the sorbent for the various ions was found to be Pb>Cu>Cd>Ni, with equilibrium uptake capacities of 2.65, 1.72, 1.44 and 1.20 mmol.g^{-1}, respectively. The sorption isotherm fitted to the Langmuir isotherm. The overall sorption is pseudo-second order with an initial rapid and quantitatively predominant sorption followed by a second slower and quantitatively insignificant sorption. Although the uptake amounts of metal ions in multi-component systems were decreased by competitive reactions, the total uptake was increased. The adsorption isotherms [222] of the obtained NaX based on the characteristics required to remove Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} were examined in multi-metal systems. Thus obtained experimental data suggested that the Langmuir and Freundlich models are more accurate compared to the Dubinin–Kaganer–Radushkevich model. Further, in going from a single- to multi-metal system, the degree of fitting for the Freundlich model compared with the Langmuir model was favored due to its basic assumption of a heterogeneity factor.

Lee et al. [184] investigated Pb^{2+} sorption from aqueous solutions using five different zeolites (NaP1, faujasite, hydroxy sodalite, analcime, and cancrinite) obtained by HT treatment of CFA under different conditions. It was found that all the zeolites synthesized have greater adsorption capabilities for heavy metals than the original CFA and natural zeolites. NaPl exhibited the highest adsorption capacity with a maximum value of about 1.29 mmol Pb g^{-1} and had a strong affinity for Pb $^{2+}$ ion. They also studied the sorption of Cu^{2+}, Cd^{2+} and Zn^{2+} by NaP1 and found that the metal ion selectivity of NaP1 decreases in the order: Pb>Cu>Cd>Zn, which is consistent with the decreasing order of the radius of hydrated metal ion. The experiments of Woolard et al. [201] also proved that CFA-derived zeolite NaP1 is more effective at removing Pb^{2+} than hydroxysodalite. The maximum Pb^{2+} sorption capacities calculated, using Langmuir's model were 0.985 mmol.g^{-1} for NaP1 and 0.628 mmol.g^{-1} for hydroxisodalite, while for the untreated CFA it was 0.217 mmol.g^{-1}. Zeolite NaP1 demonstrated high removal efficiency (>95%) in abroad range of pH (3-8.5), while for hydrixisodalite the maximum efficiency was reached at pH above 5.5, and could be attributed to the precipitation of PbO. Steenbruggen and Gollman [78] tested the ability of zeolitized CFA containing 45% zeolite NaP1 to remove heavy metals and ammonia from aqueous solutions in batch and column tests. Batch sorption experiments indicated that the selectivity series for NaP1 is Ba>Cu>Cd≈Zn>Co>Ni. Column experiments results indicated that, besides cation exchange reactions, precipitation of hydroxides also played a role in the immobilization of heavy metals. Column leaching tests showed that compared to the original CFA, the zeolitized CFA is of a better environmental quality.

Rios et al. [209] compared the performance of CFA, natural clinker and synthetic zeolites in heavy metals removal from AMD generated at the Parys Mountain Cu–Pb–Zn deposit, North Wales. Zeolites were prepared by two methods: by classic HT synthesis using natural clinker (producing Na-phillipsite), and by alkaline fusion prior to HT treatment using both CFA and natural clinker (producing faujasite type zeolites). Faujasite showed higher heavy metal removal efficiency than Na-phillipsite. The results indicated that pH play an important role in the process. The higher adsorbent dose promoted an increase in pH, which led to a reduction in metal concentration. This result is inconsistent with the results reported by Endres et al. [192], whose investigations on the removal of Fe^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} from wastewaters using CFA-derived chabazites clearly indicated that heavy metals removal is enhanced at the lower pH. Qiu and Zheng [6] studied the removal of Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} from water by a cancrinite-type zeolite synthesized from CFA. Adsorption equilibriums of the metals on the zeolite were studied in synthetic solutions and were well represented by Langmuir isotherms. The increase of pH levels during the adsorption process suggests that the uptake of heavy metals on ZFA inolves ion exchange. It was found that the maximum exchange level followed the order: Pb>Cu>Ni>Co >Zn. Comparison with previous studies shows that the sorption capacity of CFA-derived cancrinite is higher than the commonly used natural zeolites; and it is also comparable to (or higher than) several synthetic zeolites (NaP1, NaY, NaA), and ion exchange resins (IRN 77, SKN 1, Ca-alginate-resin). Koukouzas et al. [82] tested four zeolitic materials (containing zeolites NaA, KA, erionite, ZSM-18 and Linde L) obtained form Polish bituminous and South African CFA for removal of Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Cr^{3+} from aqueous solutions. The results showed that at initial cation concentration of 100 mg l^{-1} and adsorbent dose of 200 mg l^{-1}, all the materials synthesized were able to remove completely (99.8-100%) the studied heavy metals in two hours of contact time.

Somerset et al. [194] studied the removal of Hg^{2+} and Pb^{2+} ions from wastewater by zeolites obtained from CFA and from the filtrate of co-disposal of CFA and AMD. The results showed that the second material was more effective. At 20 g l^{-1} adsorbent dosage this zeolite material reduced Pb^{2+} concentration from 3.23 to 0.17 μg kg^{-1} and Hg^{2+} from 0.47 to 0.17 μg kg^{-1}.

Pena et al. [186] examined the retention of Cs^{+}, Cd^{2+}, Pb^{2+} and Cr^{3+} by zeolitic materials formed as a result of the HT treatment of the bottom ash from fluidized-bed incineration of MSW. The amount of Cs^{+} retained was considerably lower than those for Cd^{2+}, Pb^{2+}, and Cr^{3+}, independently of the type of compounds, formed by the different bottom ash treatments. The higher percentage of Cs^{+} retained (31%), occurred after treatment of the bottom ash in NaOH at 200°C, where zeolite NaA was the major compound, together with aluminum tobermorite. In the case of Cd^{2+}, Pb^{2+} and Cr^{3+}, the removal efficincy was about 99% under all of the conditions studied.

Shawabkeh [93] tested zeolite NaP1, obtained from OSA, as ion exchanger for Pb^{2+} and Cd^{2+} cations from aqueous solutions. The adsorption capacities were estimated to be 70.58 mg g^{-1} Pb^{2+} and 95.6 mg g^{-1} for Cd^{2+} when the initial concentration for both ions was 100 mg l^{-1}. For Cd the best fit was obtained with the Sips model while, for Pb the Sips models fits the experimental data adequately. Based on the results obtained, it was concluded that the treated OSA possessed strong potentials for zeolite production used in wastewater treatment.

On the base of the reviewed investigations, it could be summarized, that heavy metals uptake capacity and selectivity depend mainly upon the zeolite type, its cation form, and the hydrated radius of the heavy metal ion. Good performance in the treatment of waters contaminated with heavy metals was demonstrated by Brazilian scolecite and some modified clinoptilotites. However, yet again, synthetic zeolites (types P1, A, X, and Y), including zeolites and zeolitic materials, obtained from wastes such as CFA and MSWIA have higher heavy metal uptake capacity than naturally occurring zeolites. For practical purposes the sodium form of both natural and synthetic zeolites is the most appropriate for heavy metals removal. Most of zeolites have high sorption capacity and selectivity for Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+}, whereas their affinity to sorb Mn^{2+}, Ni^{2+}, Co^{2+}, especially from multi-component solutions, is smaller. Several mechanisms, including ion exchange, chemisorption, adsorption and precipitation, could be involved in the heavy metals uptake from aqueous solutions by zeolites, but even so, generally, the sorption of heavy metals on zeolites is a feasible, spontaneous and endothermic in nature process, which is enhanced by temperature increase. The sorption of heavy metals onto zeolite surface is a diffusion-controlled process, therefore the decrease in particle size of zeolites and intensive stirring have positive affect the process positively. The optimal zeolite dosage varies from several grams up to several dozens grams per liter wastewater and depends upon the concentration of heavy metal in the influent, the desired degree of its reduction, and the presence of competitive ions. Most of batch studies reported that acceptable degree of heavy metals uptake from wastewaters is achieved in less than one hour, while the equilibrium is reached within a few hours. The complete removal of heavy metals requires longer treatment duration and higher zeolite dosage. Maximum metal uptake is usually achieved at initial pH of the suspension in the neutral range (pH=6-8). In batch condition, longer time of contact between zeolite and heavy metal solution leads to an increase in the alkalinity, which in turn facilitates heavy metal removal via precipitation of insoluble metal hydroxides onto zeolite surface. Heavy metals-loaded zeolite could be partially regenerated and recycled.

3.2.4. Radioactive species removal

Various processes used in the nuclear fuel cycle and in the application of radionuclides in industry, medicine, and research generate low or intermediate level liquid wastes, containing radioactive isotopes (e.g. ^{137}Cs, ^{90}Sr, ^{60}Co, ^{45}Ca, ^{51}Cr, ^{111m}Cd, ^{110m}Ag). Such effluents usually require treatment to remove radioactive contaminants or to reduce them to levels, which allow safe discharge. One of the first publications on the utilization of zeolites for the sorption of radioactive species was probably the patent of Ames [14] who proposed a method for removal of cesium from aqueous solutions by sorption with clinoptilolite. Table 11 summarizes some of the more recently reported results for radioactive metals uptake by zeolites.

Table 11. Radioactive elements adsorption on some natural and synthetic zeolites

Metal ion	Zeolite	Zeolite origin	Metal conc. mg l^{-1}	Zeolite dosage, g l^{-1}	Metal sorption, mg g^{-1}	Metal removal, %	Uptake distr. coef. ml g^{-1}	Refe-rence*
U^{6+}	HEU - type	Greece	20000	10	8.7	0.43	0.4	[223]
U^{6+}	HEU - type	Greece	1000	10	4.7	4.7	5.0	[223]
U^{6+}	HEU - type	Greece	250	10	3.5	13.9	16.1	[223]
U^{6+}	HEU - type	Greece	100	10	1.6	16.0	19.1	[223]
U^{6+}	HEU - type	Greece	50	10	1.0	19.6	24.5	[223]
Th^{4+}	HEU - type	Greece, Na-exchanged	20000	10	11.0	0.55	0.6	[223]
Th^{4+}	HEU - type	Greece, Na-exchanged	1000	10	12.4	12.4	14.2	[223]
Th^{4+}	HEU - type	Greece, Na-exchanged	250	10	12.1	48.2	93.4	[223]
Th^{4+}	HEU - type	Greece, Na-exchanged	100	10	6.6	65.6	192.9	[223]
Th^{4+}	HEU - type	Greece, Na-exchanged	50	10	1.6	31.4	46.2	[223]
I^{+}	Clinoptilolite	Iran	635	40			74-152 x10^{3}	[224]
I^{+}	Mesolite	Iran	635	40			165 x10^{3}	[224]
I^{+}	Analsite	Iran	635	40			119 x10^{3}	[224]
Mo^{2+}	Clinoptilolite	Iran	480	40			199-230 x10^{3}	[224]
Mo^{2+}	Mesolite	Iran	480	40			313 x10^{3}	[224]
Mo^{2+}	Analsite	Iran	480	40			206 x10^{3}	[224]
Mo^{2+}	NaA ZM	Synthetic	96			99.8		[225]
La^{3+}	Clinoptilolite	Iran	695	40			TA**	[224]
La^{3+}	Mesolite	Iran	695	40			506 x10^{3}	[224]
La^{3+}	Analsite	Iran	695	40			TA	[224]
Nd^{3+}	Clinoptilolite	Iran	721	40			400 x10^{3}-TA	[224]
Nd^{3+}	Mesolite	Iran	721	40			545 x10^{3}	[224]
Nd^{3+}	Analsite	Iran	721	40			TA	[224]
Sm^{3+}	Clinoptilolite	Iran	752	40			926-5470 x10^{3}	[224]
Sm^{3+}	Mesolite	Iran	752	40			1760x10^{3}	[224]
Sm^{3+}	Analsite	Iran	752	40			3070 x10^{3}	[224]

Cs^+	NaA ZM	Synthetic	133			99.4		[225]
Cs^+	Clinoptilolite	USA	1329		220.6			[14]
Cs^+	Blend NaA-X	CFA-derived Si and Al	133	1	37.8	76	390	[83]
Cs^+	Blend NaA + tobermorite	MSWIA-derived	26	2		31	222	[186]
Cs^+	Clinoptilolite	Turkey	Total	10	186.1-252.5			[16]
Co^{2+}	Clinoptilolite	Turkey	activity	10	26.5-32.4		3.75-4.45	[16]
Ag^+	Clinoptilolite	Turkey	8.45x10^5	10	107.8-151.0		x10^3	[16]
Sr^{2+}	Clinoptilolite	Turkey	Bq.l^{-1}	10	74.5-96.4			[16]
Sr^{2+}	NaA ZM	Synthetic	88			99.8		[225]
Co^{2+}	Erionite	Mexico	1.5	10	32.4			[226]
Co^{2+}	NaA	Synthetic	1.5	10	58.9			[226]
Co^{2+}	NaX	Synthetic	1.5	10	73.7			[226]
Co^{2+}	NaY	Synthetic	1.5	10	38.3			[226]
Co^{2+}	ZSM-5	Synthetic	1.5	10	26.5			[226]
Cd^{2+}	NaA	Synthetic	2.8	10	157.4			[226]
Cd^{2+}	NaX	Synthetic	2.8	10	207.9			[226]
Cd^{2+}	NaY	Synthetic	2.8	10	140.5			[226]
Cd^{2+}	ZSM-5	Synthetic	2.8	10	84.3			[226]

* Some values are recalculated and/or rounded; **TA- total adsorption.

Misaelides et al. [223] studied the uptake of thorium and uranium from their aqueous solutions by untreated and NaCl-pre-treated HEU type zeolite-bearing rock from Greece using batch method. The preliminary experiments had indicated NaCl pretreatment of the materials improved the thorium but not the uranium uptake. Therefore, the raw zeolite was used for the U and NaCl-pretreated form was used for Th uptake experiments. Eight solutions of different concentrations ranging between 20 000 mg l^{-1} and 50 mg l^{-1} were used. The absolute Th uptake was between 1.57 and 12.41 mg g^{-1}, while for U it was between 0.98 and 8.70 mg g^{-1}. Kd values obtained showed that the relative Th^{4+} and U^{6+} uptake was higher for initial concentrations below 250 mg l^{-1}. The zeolitic materials showed high resistance to the initial low pH (2.16 for Th and 2.78 for U) of the solutions, which was significantly increased during the experiments, due to the simultaneous adsorption of H^+. The authors discussed in details the aqueous chemistry of the elements and concluded that thorium and uranium uptake is quite a complicated phenomenon, because the various metal species (depending on the concentration and the pH of the solutions) are bound through different uptake processes, such as ion exchange, adsorption and surface precipitation. Nevertheless, the ability of the materials to remove U and Th is mainly due to the microporous ingredients (zeolites, clay minerals and micas).

Nilchi and collaborators [224] studied natural Iranian zeolites from five different deposits in Iran as ion exchangers for radioactive waste management. Kd measurements were used to investigate the uptake of ^{131}I, ^{99}Mo, ^{153}Sm, ^{140}La and ^{147}Nd onto zeolites under circumstances appropriate to the nuclear industry. They found that all the zeolites, except mesolite from Arabad Tabas, had extremely high absorption value towards ^{140}La, while just some of them showed good sorption of the other elements. For instance, clinoptolite from Mianeh and analsite from Ghalehkhargoshi showed good absorption for ^{147}Nd, while clinoptolite from Semnan and from Firozkoh showed high absorption for ^{153}Sm. Authors stated that the natural zeolites used, showed a similar pattern to those of synthetic ion exchangers and in some cases have an extremely high selectivity towards certain radioactive elements. Osmanlioglu [16] studied clinoptilolites from five zeolite formations in Turkey for the removal of ^{137}Cs, ^{60}Co, ^{90}Sr and ^{110m}Ag from liquid radioactive waste in a combined process, including chemical precipitation and adsorption. Clinoptilolite were shown to have a high selectivity for radioactive Cs^+ and Ag^+. All zeolites showed highest ion exchange capacities for Sr^{2+}

and lowest for Co^{2+}. Gordes clinoptilolite was the most suitable natural sorbent for all radionuclides studied. At the end of the liquid waste treatment, decontamination factor achived with 0.5 mm clinoptilolite, at 30◦C and pH=10 was 430.

Garcia-Sosa and Solache-Ríos [226] determined CEC of synthetic zeolites A, X, Y, ZSM-5 and natural Mexican erionite and compared the results obtained with the results for the retention of Cd^{2+} and Co^{2+} on these zeolites. It was found that the retention of Co and Cd decreases as follows: X>A>Y>erionite>ZSM-5. This behavior is similar to that observed for the determined CEC, except that zeolite X retains more cobalt than zeolite A, which could be due to several parameters such as window size and selectivity. Dyer and Abou-Jamous [227] examined synthetic zeolites X and Y for their abilities to uptake ^{60}Co, ^{63}Ni and ^{65}Zn radioisotopes from aqueus solution. Distribution coefficients (Kd) were determined, with and without competing cations, at various pH values. The effects of sea and ground waters were checked using synthetic solutions. Elution studies on radioisotopes-loaded zeolites considered the effect of acid and alkaline conditions, calcination and cement encapsulation. Results showed slight differences between zeolites X and Y reflected the higher Si/Al ratio in zeoliteY and the order of uptake Zn>Ni>Co mirrored that of increasing cation size. The general conclusion was that both were suitable for decontamination of aqueous wastes containing Co, Ni and Zn. Zeolite/cement composites were stable and yielded low leach rates, but no advantage accured from pre-calcination.

El-Naggar et al. [36] synthesized zeolite NaAX blend from silica extracts obtained from CFA by alkaline leaching and investigated the sorption potential of the synthesized zeolite for the removal of Cs from aqueous solutions. The influence of pH (pH=2-9), contact time (up to 90 min) and temperature (T=298-333K) was investigated. It was found that the acidic medium had an inhibitory effect on the sorption process, due to the competition behaviour between H^+ and studied ions for sorption onto the synthesized powder. The uptake was continuously increased from 18.6% to 62.6% with the increase in pH value. The maximum uptake of 64.1% was observed at pH range from 6.0 to 8.0. The obtained time-dependence of the Cs^+ uptake showed that a higher initial rate of removal within the first 30 min was followed by a slower subsequent removal rate till reaching equilibrium. The metal ions fraction sorbed and the calculated corresponding Kd values increased with increasing temperature indicating the endothermic nature of Cs^+ sorption process. Both of pseudo second-order and homogeneous particle diffusion models were found to correlate well with the experimental sorption kinetics data. Some of the parameters obtained indicate that the sorption process is diffusion-controlled and that the sorption reaction of the Cs^+ is an associative mechanism.

The possibility of using zeolitic membranes (ZM) to remove ions from aqueous solutions by reverse osmosis (RO) has been considered an alternative to polymeric membranes for desalination of complex wastewaters which contain organic solvents and heavy metals or radioactive elements, or when high temperature operation is desired [228]. Malekpour et al. [225] studied NaA ZM, prepared by hydrothermal synthesis on a porous α-alumina support, for the desalination of simulated radioactive wastes through pervaporation process. The influence of several operating parameters such as synthesis time, number of zeolite layers and seeding procedure was investigated. Results showed that membranes, which were prepared in a four-stage process, yield the best separation. For all the ionic solutions including 0.001 M of Cs^+, Sr^{2+} and MoO_4^{2-} very high rejection factors (>99%) were obtained. With increasing the time, the water flux was decreased, due to the partial fouling of membranes. The lowest amount of flux was obtained for molybdate solutions although their rejection factor was high. This fact could be explained with the bigger kinetic radius of MoO_4^{2-} compared with Cs^+ and Sr^{2+}. Authors concluded that NaA ZM could be used for treatment of low-level radioactive wastes as well as for desalination and volume reduction of these solutions, especially through the pervaporation process.

Several practical examples for successful use of zeolites for radioactive species immobilization have to be mentioned, as well. A mixture of synthetic zeolite A and natural chabazite was used to take up ^{90}Sr and ^{137}Cs, respectively, from contaminated waters after the nuclear accident at Three Mile Island (U.S.A.) and about 0.5 million curies of radiation was removed [229]. About 500 000 tons natural zeolite from the Trans-Carpathia area was used after the Chernobyl accident in for decontamination of rivers polluted with ^{137}Cs and ^{90}Sr [230,231]. Clinoptilolite, currently, is used in the Sellafield Ion Exchange Effluent Plant to remove ^{137}Cs and ^{90}Sr from low-level effluents generated in a nuclear power plant before they are released to the Irish Sea in U.K. [232]. Both clinoptilolite and chabazite have been used in the removal of radioactive ^{137}Cs and ^{90}Sr from high level radioactive processing wastes at the Henford Atomic Energy Project in the USA [229].

Some of the main advantages of using zeolites for nuclear wastewater are their resistance to degradation in the presence of ionizing radiation, their low solubility and that they can be used for long term storage of long-lived radioisotopes after drying the radionuclide-exchanged zeolite at 200ºC, and sealing in a stainless steel containers [7]. The ‘‘saturated’’ zeolite can be also transformed into concrete, glass, or ceramic bodies, and stored indefinitely [2].

3.2.5. Removal of inorganic anions

Nitrates, phosphates, arsenates, chromates and fluorides are among the most common anionic water contaminants. As it has been mentioned, raw zeolites are negatively charged, and thus have no affinity for sorption of anionic species. However, some cation-modified zeolites, having positive net charge, are able to adsorb anions by means of electrostatic interaction. Summarized data for the performance of some natural and modified zeolites for anionic contaminant removal from water are presented in Table 12.

Table 12. Anionic species adsorption on some natural and synthetic zeolites

Anion	Zeolite	Anion conc. mg l^{-1}	Zeolite dosage, g l^{-1}	Anion sorption, mg g^{-1}	Anion removal, %	Refe-rence*
As (III)	Natural zeolites from Mexico	0.1–4.0		0.003-0.017		[233,234]
As (III)	Natural zeolite from Hungary	0.1–4.0		0.002		[233,234]
As (III)	Fe-modified clinoptilolite	8-10	20	>0.95		[235]
As (III)	Fe-modified clinoptilolite	0.36		0.012	99	[236]
As (V)	Natural zeolites from Mexico	0.1–4.0		0.025-0.1		[233,234]
As (V)	Natural zeolite from Hungary	0.1–4.0		0.006		[233,234]
As (V)	Fe-modified clinoptilolite	8-10	20	>0.40		[235]
As (V)	Fe-modified clinoptilolite	0.23		0.006		[236]
As (V)	Iron oxide modified clinoptilolite	100	0.5-10	21-9	11-96	[237]
As (V)	H-Beta	5	100		>95	[238]
As (V)	NH_4-ZSM-5	5	100		<5	[238]
As (V)	NH_4-Ferrierite	5	100		<30	[238]
As (V)	H-Y (Si/Al=40)	5	100		<40	[238]
As (V)	H-Y (Si/Al=6)	5	100		>99	[238]
As (V)	NH_4-Y (Si/Al=6)	5	100		>99	[238]
As (V)	NH_4-Y (Si/Al=6)	5	100		>99	[238]
As (V)	H-MFI-24	10-150	20		75-70	[239]
As (V)	H-MFI-90	10-150	20		79-73	[239]
As (V)	NH_4-Y (Si/Al = 4)	0.74	10		85	[128]
As (V)	Al-modified W (Si/Al = 3.5)	0.74	10		99	[128]
As (V)	Zeoite 5A	2.3	0.2-5	4.1		[130]
As (V)	NaY	2.3	0.2-5	1.4		[130]
As (V)	CFA-derived cancrinite	2.3	0.2-5	5.1		[130]
As (V)	Al-modified CFA-derived cancrinite	2.3	0.2-5	34.5		[130]

As (V)	Ce-P, obtained from RHA	500	7.5	23.4		[129]
As (V)	Ce-P, obtained from RHA	33.2	0.15-0.6		87-99	[129]
Cr(VI)	CPB - modified Iranian clinoptilolite	16.7	15	0.20		[25]
Cr(VI)	HDTMA-modified synthetic clinoptilolite	16.7	15	0.16		[25]
Cr(VI)	HDTMA-modified ZSM-5	16.7	15	0.07		[25]
Cr(VI)	CPB-modified ZSM-5	16.7	15	0.09		[25]
Cr(VI)	APTES-modified Y/Maghemite composite	52-78	1	26		[240]
Cr(VI)	HDTMA-modified clinoptilolite from New Mexico, fraction < 0.4 mm	2.9-4.0	250	0.42		[241]
Cr(VI)	HDTMA-modified clinoptilolite from New Mexico, fraction 3.6-4.8 mm	2.9-4.0	250	0.08		[241]
Cr(VI)	HDTMA-modified nanozeolite A	1	2	0.25	51	[242]
Cr(VI)	HDTMA-modified nanozeolite A	100	5	8.6	43	[242]
Cr(VI)	HDTMA-modified nanozeolite A	>300		10-11		[242]
F^-	Unmodified natural zeolite from China	70	5-100	0.7-0.07	5-10	[243]
F^-	Ca-modified natural zeolite from China	70	5-100	1.8-0.7	13-94	[243]
F^-	Ca-modified natural zeolite from China	100	50	1.8	90	[243]
F^-	Fe(III)- modified stilbite	10	10		≥90	[244]
NO_3^-	Chinese clinoptilolite		50	0.19		[243]
NO_3^-	HDTMA-modified Chinese clinoptilolite		50	1.48		[243]
NO_3^-	HDTMA-modified Australian clinoptilolite		50	1.49		[243]
NO_3^-	HDTMA-modified USA clinoptilolite		50	3.47		[243]
NO_3^-	HDTMA-modified Croatian clinoptilolite		50	2.79		[243]
NO_3^-	HDTMA-modified clinoptilolite	50	2-30	6.2-1.7	25-100	[246]
NO_3^-	HDTMA-modified Clinoptilolite	100	36		>90	[247]
NO_3^-	CPB - modified Clinoptilolite	88.6	2-24	7.1-3.0	16-82	[248]
P	La- modified synthetic zeolite from natural	0.5	0.8		99.5	[249]
P	NaP1 from CFA, pretreated by 0.9M H_2SO_4	up to10	10		>98	[165]
P	NaP1 from CFA, pretreated by 0.1M H_2SO_4	100	10		>90	[135]
P	Na-zeolite obtained from CFA	50	7.5	2.9 (9.9)		[135]
P	Ca-zeolite obtained from CFA	50	7.5	19.1 (15.5)		[135]
P	Mg-zeolite obtained from CFA	50	7.5	2.9 (7.2)		[135]
P	Al-zeolite obtained from CFA	50	7.5	13.7 (17.1)		[135]
P	Fe-zeolite obtained from CFA	50	7.5	11.8 (16.5)		[135]
P	Zeolite from CFA with high Ca content	1000	18.8		>98	[136]
P	Zeolite from CFA with medium Ca content	1000	18.8		>98	[136]
P	Zeolite from CFA with low Ca content	1000	18.8		>90	[136]
$Sb(OH)_6^-$	HDTMA-modified Clinoptilolite	20	50		42	[250]

* Some values are recalculated and/or rounded. **Arsenate and arsenite anions are marked as Ar(V) and Ar(III), respectively, since the prevailing ion form of As in the solution (i.e. AsO_4^{3-} , $HAsO_4^{2-}$ or $H_2AsO_4^-$ for As(V)) depends on the pH. The same is valid for phosphate and chromate ions, which are therefore marked as P and Cr(VI), respectively.

Arsenic is widely distributed throughout the Earth's crust, most often as arsenic sulfide or as metal arsenates and arsenides. Arsenicals are used commercially and industrially, primarily as alloying agents in the manufacture of transistors, lasers and semiconductors. Arsenic is introduced into drinking-water sources primarily through the dissolution of naturally occurring minerals and ores. There are a number of regions where arsenic may be present in drinking-water sources, particularly groundwater, at elevated concentrations [151]. Arsenic is considered to be a high-priority substance for screening in drinking-water sources, as is a recognized carcinogen for human and other living organisms [151]. The inorganic arsenic is more toxic than organic arsenic [239]. The inorganic arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}), referred to a As(V) and As(III), are most common in natural waters [239]. Maximum contaminant level standard for arsenic in drinking water, recommended by the WHO is 0.01 mg l^{-1}. Conventional precipitation methods for arsenic removals using iron and aluminum salts have not been successful to meet drinking and effluent standards for As due to limitation of solubility of the resultant product [129]. As an alternative, adsorption was found to be one of the promising methods for removal of arsenic from water [129]. A comprehensive review on arsenic removal from (waste)water using adsorbents, including some zeolites [233,234,251-253] was published by Mohan and Pittman [254].

Elizalde-Gonzalez et al. [233,234] investigated arsenic sorption on natural zeolites (from Mexico and Hungary), containing mainly clinoptilolite. The results showed that in the concentration range of 0.1- 4 mg l^{-1} all studied zeolites removed more effectively AsO_4^{3-} than AsO_3^{3-} at equivalent As concentrations, which is in agreement with the results obtained for natural chabasite [251]. The sorption capacities of clinoptilolite, calculated using Langmure model, varied in the ranges 0.002-0.017 mg g^{-1} for AsO_3^{3-} and 0.006-0.1 mg g^{-1} for AsO_4^{3-}. It was demonstrated that both the arsenite and the arsenate content could be lowered from 200 to 10 g l^{-1} using Mexican zeolite [255]. The Hungarian zeolite removed up to 75% of the As(V).

Li et al. [235] studied the removal of arsenic from water using Fe^{3+}-exchanged clinoptilolite. It was demonstrated that arsenic sorption on the Fe-exchanged zeolite could reach up to 0.1 mg g^{-1}. Columns packed with this zeolite were tested for arsenic removal from water collected from AMD and Chia-Nan Plain groundwater. With an initial concentration of 147 g l^{-1} in the AMD water, a complete As removal was achieved up to 40 pore volumes. However, the Fe-modified clinoptilolite was not effective to remove As from the groundwater due to its high initial As concentration (511 g l^{-1}), high amounts of natural organic matter, as well as its low oxidation–reduction potential, under which the As was in reduced As(III) form. Habuda-Stanic et al. [256] studied arsenic adsorption on Fe^{3+} saturated clinoptilolite from solutions prepared from processed groundwater. Results showed that the zeolite had arsenic sorption capacity of 0.055 mg g^{-1} for As(III) and 0.036 mg g^{-1} for As(V). Similar values were reported by Macedo-Miranda and Olguin [257] who investigated As(V) sorption on Mexican clinoptilolite-heulandite natural zeolite modified with iron, lanthanum, and HDTMA. According to Langmuir isotherms obtained, La-modified zeolite possessed highest arsenate sorption capacity of 0.075 mg g^{-1} at pH=3, followed by Fe-modified with 0.054 mg g^{-1} at pH=6. For HDTMA-modified zeolite as low arsenic sorption capacity as 0.004 mg g^{-1} was obtained. Dousova et al. [258] studied the sorption of As (V) from aqueous solution on untreated and Fe^{2+}-modified metakaoline, clinoptilolite, and synthetic zeolite. The results showed that arsenate sorption capacity of Fe^{2+}- treated sorbents was increased significantly from about 0.5 to above 20 mg g^{-1}. Vaclavikova et al. [237] prepared magnetic zeolite by co-precipitation of Fe(II) and Fe(III) in the presence of NaOH and clinoptilolite. The new material combined the good sorption affinity for oxyanions of iron oxides with the high CEC, typical, for zeolites. It was testes under batch conditions for the removal of As(V) from model solutions and demonstrated high sorption capacity- up to 28 mg g^{-1}. The kinetics study showed fast initial removal in the first 60 min and slower subsequent removal up to equilibrium, which was achieved after 7 hours.

The test of Xu et al. [252] on the adsorption of AsO_4^{3-} from drinking water by an Al-loaded natural zeolite indicated a slight pH dependency of the process in a wide range of initial pH (3–10). Competiting arsenite, chloride, nitrate, sulfate, chromate, and acetate ions had little affect but phosphate greatly interfered with the adsorption. The authors supposed a ligand-exchange mechanism between AsO_4^{3-} and surface OH^- groups on Al-zeolite. Shevade et al. [238] investigated the performance of 6 synthetic zeolites: ammonium forms of Y (Si/Al = 6), ZSM-5 and Ferierrite, and hydrogen forms of Y (two samples having Si/Al = 40 and Si/Al = 6) and zeolite Beta, for the removal of arsenate from aqueous solutionsat initial concentration of 5 ppm. It was found that zeolites Beta and Y (Si/Al = 6), were very effective for As(V) removal. The reaction was completed within 15 min for these zeolites. The different arsenic removal capacities obtained for different zeolites Y indicated that the structure, including Si/Al ratio, played an important role in the arsenic removal process. The results showed that Si/Al ratio affects aresenate uptake capacity and CEC in similar way, i.e. high alumina zeolites had higher arsenate sorption capacity, which could be explained with the higher concentration of terminal Al-OH species, which leaded to a greater capacity for a ligand exchange reaction [238]. At initial arsenic concentrations of 1 and 0.5 ppm the treatment with zeolite NH_4-Y (Si/Al = 6) decreased the concentration below 0.002 ppm within 15 min. Mexican CFA-derived zeolites, particularly high aluminium zeolite Y (Si/Al=4) in ammonium form, zeolite W in ammonium form, and aluminum sulfate-modified zeolite W (Si/Al=3.5) were tested for the removal of arsenate from aqueous solution containing 740 ppb As (V) [128]. NaY zeolite demonstrated poor As(V) removal under the studied conditions, while the modification of NaY zeolite with NH_4Cl by ion exchange increased the arsenate removal. In contrast, NH_4-W zeolite obtained by the same procedure demonstrated no significant changes in its sorption behaviour upon ion exchange, due to the increase in pH during the adsorption process, which indicated that surface sites are being hydrolyzed and zeolite particles were becoming negatively charged, which reduced arsenic adsorption rates [128]. The best performance was demonstrated by the Al-modified zeolite W, which reached arsenic removal efficincy of 99%.

Qiu et al. [130] synthesized cancrinite type zeolitic material from CFA by molten-salt method. The product was further modified by loading it with various amounts of alumina via a wet-impregnation method (mass of Al impregnated /mass of zeolite = 10, 30, 50 and 80). The arsenate adsorption capacities of the products were studied and compared with those of activated carbon, silica gel, commercial zeolites 5A, and NaY. Activated alumina was also used as a reference adsorbent. It was found that adsorption capacity decreased in the order CFA-derived cancrinite>5A>activated carbon>NaY>silica gel. However, the adsorption capacities of zeolites were generally lower than that of activated alumina (16.6 mg g^{-1}), which was ascribed to the small pores in zeolite frameworks. The modification with Al significantly improved the As(V) sorption. The modified cancrinite with the optimum alumina loading (mass of Al impregnated/mass of zeolite = 50) showed an adsorption capacity 2.1 times higher than activated alumina. The adsorption kinetics study showed that the adsorption for 10 mg l^{-1} arsenate solution was completed within 1 h at ambient condition using 1.0 g l^{-1} of the Al-modified zeolite. Leachability tests proved that both Al-modified and unmodified spent zeolites were safe to dispose.

Haron et al. [129] prepared Ce(III)-exchanged zeolite P from RHA-derived NaP, and tested it for As(V) removal from aqueous solutions. Maximum sorption of As(V) by Ce-P occurred at pH range 3-10. In addition, the sorption capacity increased with increasing initial As(V) concentrations. The sorption followed Langmuir model with maximum sorption capacity of 8.72 mg g^{-1} at 25◦C and 23.42 mg g^{-1} at 90 ◦C, indicating an endothermic process. The mechanism of the sorption was thus likely to be the formation of surface complex via interaction between negative arsenate ion and positively charge Ce(III) metal ion on the zeolite. The arsenic sorption by Ce-P was not affected by the present of nitrate, chloride, sulphate, carbonate and bromide but was reduced significantly in the presence of phosphate. This result was in compliance with the results obtained by Xu et al. [252] for AsO_4^{3-} removal Al-loaded natural zeolite. The Ce-P was found to be effective in removal of arsenic ion from sample of real wastewater samples from wood treatment industry.

Chutia et al. [239] investigated the adsorption of arsenic from aqueous solution on synthetic zeolites H-MFI-24 and H-MFI-90 at room temperature applying batch equilibrium techniques. It was found that the adsorption of arsenic followed the first-order kinetics and equilibrium time was about 100 min for both the adsorbents. Adsorption performance of H-MFI-90 was higher compared to H-MFI-24 due to its highly mesoporous nature, which in turn accelerated the diffusion. As(V) sorption capacity derived from Langmuir isotherm for H-MFI-24 and H-MFI-90 were 35.8 and 34.8 mg g^{-1}, respectively. The regeneration experiments performed in acidic (0.1N HCl) and alkaline medium (0.1N NaOH) showed that under acidic conditions arsenic removal capacity of the regenerate material was almost same with the fresh material, but the degree of arsenic recovery were low, while in base regeneration tests As recovery increased significantly at the cost of decrease of arsenic removal capacity.

Antimony is suspected to be carcinogenic and similarly toxic as arsenic, thus WHO recommends for potable water as low limit as 0.02 mg l^{-1} [151]. Concentrations of Sb in groundwater and surface water normally range from 0.1 to 0.2 μg l^{-1}, however higher concentrations of Sb in drinking water could appear as a result of dissolution from metal plumbing and fittings [151]. Wingenfelder et al. [250] investigated the sorption of antimonate from aqueous solutions by HDTMA-modified zeolite in sodium form. The results showed that $Sb(OH)_6^-$ binding was most effective when the zeolite was treated with HDTMA solutions exceeding the zeolites external CEC. SMZ suspension (50 g l^{-1}) sorbed up to 42% of antimonate from solutions containing from 0.09 to 2.15 mmol.l^{-1}Sb.

Industrial wastewater from textile, leather tanning and dyes often contain carcinogenic hexavalent chromium in form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) oxyanions, which are soluble in aqueous systems and are readily transported in ground water. The limit for chromium in drinking water recommended by WHO is very low (0.05 mg. l^{-1} total Cr) [151], thus the development of methods for effective removal of chromates from aqueous solution is of permanent interest. Several studies on application of surfactant-modified zeolites for cromate removal were recently published.

Synthetic zeolite ZSM-5 and clinoptilolite, modified by HDTMA bromide and CPD bromide were tested for the removal of chromate from aqueous solution [25]. The highest chromate adsorption capacity of about 15 mmol.kg^{-1} was obtained for CPD modified clinoptilolite, and, generally, zeolites modified by CPD showed higher adsorption capacities than those modified by HDTMABr. For ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios, it was found that the higher the SiO_2/Al_2O_3 ratio, the greater the chromate adsorption capacity was achieved. Good results were obtained for cromate sorption from aqueous solutions by HDTMABr-modified nanozeolite A in batch tests performed at room temperature [242]. Adsorption isotherms were studied under different conditions (pH, adsorbent dose, Cr(VI) concentration and interaction time). At room temperature and pH=3.0 the Langmuir monolayer Cr(VI) adsorption capacity was 14.16 mg g^{-1}. Chromate adsorption on surface modified nanozeolite A was found to be inversely proportional to the pH. The presence of competitive sulfate ions in concentrations up to 1000 mg l^{-1} did not affect chromate adsorption. Results of examinations on a polluted natural sample showed that HDTMA-nanozeolite A could reduce Cr (VI) concentration to acceptable level. Li et al. [241] performed column tests to study the effect of particle size on the chromate adsorption by natural and HDTMABr modified clinoptilolite. At an input concentration of 11-15 mg l^{-1}, unmodified zeolite did not retard chromate transport for all three particle size ranges studied, while for the modified zeolite, smaller particle size resulted in a higher amount of surfactant, and respectively in a higher retardation factor for chromate transport. Desorption of bromide accompanying chromate sorption confirmed that anion exchange is the mechanism for chromate retention by SMZ.

Barquist et al. [240] prepared zeolite Y/maghemite (γ-Fe_2O_3) composites, which were subsequently functionalized with 3-aminopropyltriethoxysilane to form bifunctional zeolite composites. The adsorption capacity determined from the fit to the Langmuir isotherm was 0.849 mmol g^{-1}. Chromate adsorption on the composite material was attributed to external surface adsorption through an electrostatic interaction between the positively charged amine groups and the negatively charged chromate anions.

Fluoride in the environment occurs through its natural presence in the earth's crust and some industrial activities, such as electroplating, aluminum, glass, steel, and fertilizer production. According to the recommendation of the WHO the fluoride content in drinking water should no exceed 1.5 mg l^{-1}. Two recently published studies reported effective water defluorination by modified natural zeolites [244,259]. Zhang et al. [259] used Ca-modified natural zeolite for removal of F^- from aqueous solution. Batch adsorption experiments were conducted to examine the influence adsorbent dosage, contact time, pH, presence of co-ions, and initial fluoride concentration. The fluoride removal efficiency increased from 13.3% to 94.3% with increase in adsorbent dose from 5 to 100 g l^{-1}, while it was only 5.2% to 9.6% for unmodified zeolite. Maximum fluoride adsorption capacity of $CaCl_2$ modified-zeolite was 1.766 mg g^{-1} at an initial fluoride concentration of 100 mg l^{-1}. High fluoride removal efficiency was achieved in a wide range of pH (5-7). The decline of above 30% in the F^- removal at pH>8 was explained with the competition of F^- with OH^- ions. Kinetic study reveals that the fluoride adsorption by Ca-modified zeolite follows both pseudo-second order kinetic and intra-particle diffusion models. Thermodynamic values suggest that the fluoride adsorption process is spontaneous and endothermic. It was observed that Cl^- and SO_4^{2-} ions at all the concentrations studied did not affect the fluoride removal efficiency of zeolite, while the presence of CO_3^{2-} ion caused significant drop in the fluoride removal efficiency. Similar observarions for the effect of HCO_3^- were reported by Karthikeyan et al. [260]. The fluoride removal efficiency of zeolite in aluminum industry wastewater treatment was found to be slightly lower than that in synthetic water probably, due to the presence of competing ions.

Sun et al. [244] tested Fe(III)-modified natural stilbite for fluoride removal from synthetic water. The adsorption of F^- was studied as a function of contact time, adsorbent dose, initial concentration, pH and coexisting ions. It was demonstrated that fluoride concentration could be reduced down to level below 1 mg l^{-1} under the optimum condition (adsorbent dosage 10 g l^{-1} and the contact time of 2 h and pH 6.94) when initial fluoride concentration of 10 mg l^{-1} is employed. The fluoride adsorption on Fe(III)-stilbite was well described by the Langmuir model, according to which the maximum F^- adsorption capacity is 2.31 mg g^{-1}. The percentage of fluoride removal was almost unchanged when the coexisting ion concentration was below 300 mg l^{-1}, and decreased dramatically in the presence of over 500 mg l^{-1} competitive anions.

Nitrate and nitrite are naturally occurring ions that are part of the nitrogen cycle. The nitrate concentration in groundwater and surface water is normally low but agricultural and industrial wastewaters are often characterized by excessive nitrate concentrations, which could cause human health problems and eutrophication. Nitrate content in drinking water should not exceed 50 mg l^{-1} according to the WHO's guidelines [151]. The process of nitrate uptake by SMZ has been investigated is a few studies [245-248].

Masukume et al. [246] tested HDTMABr-modified clinoptilolite for the uptake of nitrate contaminated synthetic water. They tested the effect of modifier loading in SMZ, adsorbent mass (from 2 to 30 g l^{-1}), and temperature (20ºC, 45ºC and 60ºC). The results clearly demonstrated that unmodified zeolite had quite low efficiency in NO_3^- removal (<10%), while at the same conditions SMZ replaced up to 92 % of the nitrate ions. The best results were obtained when clinoptilolite were modified using a solution of 3 g l^{-1} HDTMABr (at solid:liquid ratio 1:100). Total nitrate removal was achieved at the maximum zeolite dosage (30 g l^{-1}). Experimental data showed that adsorption of nitrate onto SMZ was exothermic process and thus, the adsorption is enhanced at lower temperatures. pH was found to have a negligible effect on nitrate adsorption onto zeolite. Column study and breakthrough analysis were carried out to evaluate the effects of inlet flow rate, adsorbent mass, initial concentration and column diameter on the adsorption of nitrates onto surfactant modified natural clinoptilolite in a fixed bed column. As it was expected, the decrease in zeolite mass and flow velocity and the increase in initial nitrate concentration resulted in a reduction of breakthrough time. Column diameter had negligible effect on the adsorption of nitrates on SMZ in a fixed bed column. Schick et al. [247] also performed fixed-bed column experiments for nitrate removal by HDTMA-modified clinoptilolite. The influence of the initial nitrate concentration

(0.32–2.42 mmol.l^{-1}), the flow rate or flux (1.6–47.2 cm.min^{-1}) and the presence of competing anions Cl^-, SO_4^{2-} and HCO_3^- (with concentrations of 1.61 meq.l^{-1}), was examined. At the beginning of each experiment, removal rates were very high (>95%), and then decreased progressively. With an initial nitrate concentration of 100 g l^{-1}, the nitrate removal was kept equal or above 50% up to a filtered volume corresponding to 1.1 l filtered on 40 g of SMZ, allowing thus to meet the European standard for potable water, even with the very short residence time of about 1 min. The longer residence time of 36 min improved the performance and removal reached values above 90% for the same filtered volume. For higher initial nitrate ion concentration of 150 g l^{-1} and residence time of 3.5 min, nitrate removal value was >66% when up to a volume of approximately 0.4 l. The full breakthrough occurred when about 60% of the available adsorption sites had been exchanged. In the presence of competing anions, the nitrate uptake performances were variously affected, being significantly reduced by SO_4^{2-} and slightly reduced in case of HCO_3^-. Cl^- had practically no influence on the nitrate removal. It was demonstrated the nitrate-loaded SMZ could be complete regenerated by treatment with 1M NaBr solution.

Guan et al. [245] examined the nitrate sorbtion by HDTMABr-modified natural zeolites (mainly clinoptilolite) from selected locations in the USA, Croatia, China, and Australia. It was found that nitrate sorption capacity decreased in the following order: SMZ-USA (56 mmol.kg^{-1}) > SMZ-Croatia (45 mmol.kg^{-1}) > SMZ-Australia = SMZ-China (24 mmol.kg^{-1}) > raw Chinese clinoptilolite (3 mmol.kg^{-1}). The different SMZ nitrate removal performance was explained by the varying amounts of the bi-layer surfactant loadins. It was demonstrated that thermo-gravimetric analyses (TGA) could be used to distinguish between a HDTMA bi-layer and a HDTMA mono-layer on the SMZ surface, which had not been previously reported in the literature.

Zhan et al. [248] investigated the removal of nitrate from aqueous solution using CPD bromide - modified natural zeolite. It was found that SMZ with monolayer CPD coverage (<150 mmol.kg^{-1} zeolite) had negligible affinity for nitrate, while samples with patchy bilayer or bilayer CPD coverage were much more efficient. The amount of adsorbed nitrate increased quickly (from 3.8 to 6.1 mg g^{-1}) in the first 10 min and reached the equilibrium value of 6.55 mg g^{-1} after 1.5 h. The process was well described by the pseudo-second order kinetic model. The amount of adsorbed nitrate increased from about 5.5 to 8.5 mg g^{-1} with the increase of the nitrate concentration from 20 to 100 mg l^{-1}, and decreased with the increase of temperature, indicating an exothermal nature of the process. The removal efficiency of nitrate increased from 16% to 82% with the increase of the adsorbent dosage from 2 to 24 g l^{-1}. The presence of competing anions Cl^-, SO_4^{2-} and HCO_3^- slightly reduced the nitrate adsorption. Anionic exchange and electrostatic interaction were proven to be the main mechanisms that govern the adsorption of nitrate on SMZ.

Phosphates, along with ammonia, are the primary nutrients responsible for the eutrophication of aqueous systems, leading to short and long term environmental problems. The two most common methods for phosphate removal from wastewater are chemical precipitation and biological treatment, however complete removal of phosphates is still unattainable by these methods, due to thermodynamic and kinetic limitations [249]. In phosphate removal by zeolites good results have been obtained with the use CFA-derived zeolites.

Chen et al. [136] subjected to HT zeolitization fifteen Chinese CFA and obtained zeolites having from 1.2 to 7.6 times higher phosphate immobilization capacity than initialmaterials. The results indicated that Ca and Fe components were mainly involved in phosphate immobilization. Since their there was no significant change of Ca and Fe content following the conversion of CFA to zeolite, it was supposed that the enhanced phosphate uptake resulted from the increase in dissociated Fe_2O_3 and specific surface area of zeolites compared with corresponding CFA. The greatest removal of phosphate occurred within the pH range of 3.5-9 for zeolite synthesized from high calcium CFA, and in the range of 3.5-5.5 for zeolites, synthesized from medium and low calcium fly ash. This behaviour was explained by the reaction of phosphate with calcium and iron components. Authors concluded that the mechanism of phosphate removal by CFA-derived zeolite was the formation of calcium phosphate precipitate and the sorption through ligand exchange with Fe-related component. Guan et al. [135] examined the influence of seawater electrolytes on removal of phosphate by zeolite (type P1) synthesized from CFA. A low-calcium zeolite was initially saturated with Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, and Fe^{3+}. Al- and Fe-zeolites showed nearly complete removal of phosphate regardless of the major seawater electrolytes, pH, and salinity. This result was explained primarily on the basis of the adsorption mechanism through the formation of inner-sphere complexes. The remaining zeolites showed lower phosphate removal (mostly by precipitation), in general with the order of Ca-zeolite>Mg-zeolite>Na-zeolite. The individual presence of major seawater electrolytes all facilitated the retention of phosphate, with $CaCl_2$ being the most effective. In Table 12, the phosphate sorption values obtained for simulated seawater are given in brakes.

Zhang et al. [165] investigated the simultaneous removal of ammonia and phosphate by acid-pretreated zeolite NaP1, obtained from CFA. At low initial concentrations of phosphate, zeolite treated with 0.9M and 1.8M H_2SO_4 showed the greatest affinity for phosphate. This was explained by the fact that the adsorption mechanism of phosphate was primarily associated with Fe and Al through ligand exchange at acidic pH levels. However, the removal efficiency quickly declined as the initial phosphate concentration increased due to the limited immobilization capacity. At all initial phosphate concentrations, zeolite treated with 0.01M and 0.1M H_2SO_4 showed notably higher removal efficiency than the untreated one, which was explained by the fact that acid treatment caused transformation of $CaCO_3$ into more soluble calcium sulphates, thus favoring the dissolution of Ca^{2+} and precipitation of calcium phosphate.

Ning et al. [249] synthesized a novel La(III)-modified zeolite adsorbent for selective removal of phosphate in the presence of competitive anions like sulfates, bicarbonates, and chlorides. Batch tests showed that this adsorbent was quite effective for removal phosphates in low concentrations. At phosphate concentration of 1.5 mg l^{-1}, a complete removal was achieved at zeolite dosage of 1.2 g l^{-1}. It was proved that the La-modified zeolite had high selectivity to phosphates. The adsorption superiority order of anions followed the order: $PO_4^{3-}>CO_3^{2-}>SO_4^{2-}>Cl^-$ and the presence of competing anions in the effluent from sewage treatment plant did not affect the phosphate adsorption. Regeneration tests were also performed. In the seven regeneration experiments, adsorption capacity of regenerated zeolite was never lower than 90% of that of the fresh one.

3.2.6. Organic compounds removal

Organic contaminants are important pollutants in water and their removal in an economic way remains a significant problem, although various methods have been developed [9]. Owing to their native negative surface charge, zeolites are able to capture organic cations by ion exchange. However, both natural and synthetic zeolites exhibit little adsorption of organics in aqueous solution due to their surface hydrophilics. The modification of zeolite by suitable surfactant can change the surface functionality by adding hydrophobic groups and thus to enhance the adsorption of various organics, including non-polar species. In the last decade SMZ was extensively researched as sorbents of benzene, toluene, ethylbenzene, xylenes, phenols, pesticides, herbicides, dyes, humic acids, etc. from aqueous solutions. The application of natural SMZ for organic matter removal from wastewaters was recently reviewed by Apreutesei et al. [123] and by Wang and Peng [9].

3.2.6.1. Dyes removal

Dyes in wastewater originate mainly from textile, printing, food and leather industries. In aqueous ecosystems dyes reduce sunlight penetration and thus affect photosynthesis. Some dyes, in addition, are toxic or carcinogenic [261]. The most important types of water-soluble dyes are acid, basic (cationic), direct (anionic), and reactive dyes. The application of different adsorbents for dye removal from wastewaters was reviewed by Gupta and Suhas [262]. The adsorption dyes by natural and modified clinoptilolites was recently reviewed in [9]. Table 13 presents selected data for the performance of some natural and modified zeolites for the removal of various dyes.

Table 13. Dyes adsorption on some natural and synthetic zeolites

Dye	Zeolite	Dye concentration	Zeolite dosage, g l^{-1}	Dye sorption	Dye removal, %	Refe-rence*
Thionine	Zeolite products, obtained from CFA	5.10^{-6} mol.l^{-1}	10	$3.5\text{-}3.7\text{x}10^{-6}$ mol.g^{-1}		[263]
Safranine T	Zeolite products, obtained from CFA	5.10^{-6} mol.l^{-1}	10	$1.3\text{-}2.37\text{x}10^{-6}$ mol.g^{-1}		[263]
Rhodamine B	Clinoptilolite + mordenite from Australia	$10^{-6}\text{-}10^{-5}$ mol.l^{-1}	0.25	2.58 x10^{-5} mol.g^{-1}		[18]
Methylene blue	Clinoptilolite + mordenite from Australia	$10^{-6}\text{-}10^{-5}$ mol.l^{-1}	0.25	6.3 x10^{-5} mol.g^{-1}		[18]
Methylene blue	Clinoptilolite + mordenite from Australia	$2.7\text{x}10^{-5}$ mol.l^{-1}	0.1	5 x10^{-5} mol.g^{-1}		[264]
Methylene blue	CMC-22	$2.7\text{x}10^{-5}$ mol.l^{-1}	0.1	$1.7\text{x}10^{-4}$ mol.g^{-1}		[264]
Methylene blue	Clinoptilolite + mordenite from Chile	100 mg l^{-1}		27.0 mg g^{-1}		[47]
Methylene blue	Zeolite A, obtained from CFA	50 mg l^{-1}	1	37.8 mg g^{-1}	80	[265]
Methylene blue	Zeolite X, obtained from CFA	50 mg l^{-1}	1	43.0 mg g^{-1}	90	[265]
Methylene blue	Hydroxisodalite obtained from CFA	0.5 mmol.l^{-1}	10	0.28 mmol.g^{-1}		[266]
Methylene blue	Ti-modified zeolite A, obtained from RHA, as a photodegradation catalyst	10 mg l^{-1}	0.7		92	[267]
Derma blue IDB	Cu−NaY as a catalyst for oxidation with H_2O_2 (175 mmol.l^{-1})	50 mg l^{-1}	0.3		100	[268]
Reactive Brilliant Blue KN-R	Fe-modified zeolite ZSM-5 as a catalyst for oxidation with H_2O_2 (50mmol.l^{-1})	250 mg l^{-1}	4		>95	[269]
Acid red1	Fe-modified zeolite Y as a catalyst for oxidation with H_2O_2 (16 mmol.l^{-1})	50 mg l^{-1}	2.5		>99	[270]
Blend of 6 printing inks	H-ZSM-5 (Si/Al=40)	5 g l^{-1} TOC-1052 mg l^{-1}	10		59	[271]
Blend of 6 printing inks	H-ZSM-5 (Si/Al=25)	5 g l^{-1} TOC-1052 mg l^{-1}	10		60	[271]
Blend of 6 printing inks	NH_4-ZSM-5	5 g l^{-1} TOC-1052 mg l^{-1}	10		62	[271]
Blend of 6 printing inks	NH_4-beta	5 g l^{-1} TOC-1052 mg l^{-1}	10		67	[271]
Blend of 6 printing inks	NH_4-mordenite	5 g l^{-1} TOC-1052 mg l^{-1}	10		46	[271]
Blend of 6 printing inks	H-Y	5 g l^{-1} TOC-1052 mg l^{-1}	10		55	[271]
Blend of 6 printing inks	NaY	5 g l^{-1} TOC-1052 mg l^{-1}	10		29	[271]

Blend of 6 printing inks	13X	5 g l^{-1} TOC-1052 mg l^{-1}	10	12	[271]

* Some values are recalculated and/or rounded. **TOC-total organic carbon.

Basic (cationic) dyes are used for coloring of paper, polyacrylonitrile, silk, wool, cotton, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate, etc. [262]. In aqueous solutions basic dyes yield coloured cations, which could be captured on zeolites by cation ion exchange [263-265,272,273], if the geometry of zeolite pores allows their sorption.

Australian natural zeolite, composed of clinoptilolite and mordenite was tested for basic dyes adsorption in aqueous solution [18]. The results showed that the natural zeolite presents higher adsorption capacity for methylene blue (MB) than for rhodamine B. The maximal adsorption capacities were 2.8x10^{-5} and 7.9x10^{-5} mol.g^{-1} at 50 ◦C, respectively. Thermodynamic and kinetic calculations indicated that the adsorption was endothermic reaction with two-step diffusion process. The adsorption kinetics could be described by the pseudo second-order model. Both Langmuir and Freundlich models fitted well the adsorption isotherm. Wang et al. [264] compared MB adsorption by the same natural zeolite and by synthetic zeolite MCM-22. Two methods, Fenton oxidation and high temperature combustion, have been tested for regeneration of used materials. It was found that MCM-22 exhibits much higher dye adsorption than the natural zeolite. Increase of solution pH from 3 to 9 increased the adsorption capacity twice. Physical regeneration by high temperature (540ºC) calcination recovered more than 88% of MCM-22 adsorption capacity, while chemical regeneration by Fenton oxidation - only 60%. For the natural zeolite, the regeneration tests showed that both techniques were able to restore only 60% of the adsorption capacity on the fresht adsorbent. Tsai et al. [274] studied synthetic zeolite type P2 as an adsorbent for removal of MB and bisphenol-A (4,4-isopropylidenediphenol), which had similar molecular sizes, but quite different chemical properties. The results indicated that the zeolite P2 exhibited significantly higher adsorption capacity for MB than that for bisphenol-A, due to the difference in molecular properties. The adsorption kinetics of MB onto the zeolite was well described by pseudo-second-order model. Wang et al. [265] performed kinetic and equilibrium studies on the adsorption of MB from wastewater by zeolites A and X, synthesized from CFA. Batch method was used to study influence of initial pH value of the solution (3-11), temperature (20-50°C), and adsorbents dosage (0.1-0.3mg.), on the adsorption process. Generally, the removal efficiency of MB increased with a rise of these three factors. The experimental data well fitted to Ho'pseudo-second-order model and liquid film diffusion model. The Langmuir model was found to describe accurately the sorption isoterms. In all the experiments, the adsorption capacity of zeolite X was higher than that of zeolite A. The greatest adsorption capacity value obtained for zeolite X and A, were respectively 31.9 mg g^{-1} and 23.2 mg g^{-1} at 20°C, and 51.2 mg g^{-1} and 43.8 mg g^{-1} at 40°C. Woolard et al. [266] investigated the sorption of MB and alizarin sulfonate (anionic dye) by CFA-derived hydroxysodalite. The CEC of the modified ash was significantly increased over that of the raw CFA (188 vs 2 mg g^{-1}). Adsorption experiments showed that hydroxysodalite adsorbed the cationic dye to a much greater extent than the anionic one. Since the adsorption capacity of MB on the zeolitized CFA was much lower than the CEC, the adsorption of MB was ascribed to be a surface effect rather than involving incorporation into the channels of the hydroxysodalite structure. Atun et al. [263] investigated the adsorption characteristics of two basic dyes, thionine and safranine T, onto CFA, and three zeolitized products prepared from CFA at different HT treatment conditions. Typical two-step isotherms were observed for thionine adsorption onto four adsorbents, whereas the isotherms of the larger safranine T molecules were S-shaped. The adsorption capacities of the zeolitized fly ash estimated from the first plateau region of the thionine isotherms was nearly twice the CFA capacity. The capacities increased by up to five times in the second plateau region. The safranine T adsorption capacities of CFA and zeolites were lower than those found for thionine. The equilibrium results were well described by the Freundlich isotherm model. Petkowicz et al. [267] investigated the photodegradation of MB by in-situ generated titania supported on a NaA zeolite, which were obtained by using alternative silicon sources, namely rice husk and chrysotile. The highest catalyst activity was reached with samples having 10 wt.% Ti. Catalyst activity was shown to be comparable to that exhibited by commercial P-25 after 1 h of UV light exposition. Experiments, carried out in natural sunlight reached 92% MB decomposition.

Acid dyes (used for nylon, wool, silk, modified acrylics, paper, leather, ink-jet printing, food, and cosmetics), direct dyes (used for cotton and rayon, paper, leather, and nylon) and reactive dyes (used for cotton and other celluloses, wool and nylon) [262] are among the most widely used types of water-soluble anionic dyes. Several researchers have investigated the process of oxidation of acid, direct, and reactive dyes using zeolite-based catalysts [268-270].

Copper(II) complex of NN’−ethylene bis(salicylidene-aminato) encapsulated in zeolite Y was tested as a catalysts for wet hydrogen peroxide oxidation of an anionic dye (Derma blue IDB, Clariant) [268]. The effects of various parameters such as pH, catalyst and hydrogen peroxide concentration onthe oxidation of dye were studied. Complete removal of color was obtained after treatmnt for less than 1 h at 60 ºC, 0.175M H_2O_2, and 0.3 g l^{-1} catalyst. Dye removal from commercial tannery dye effluent was also experimented in order to assess the efficiency of the catalyst to oxidize the dye in the presence of other chemicals used in leather processing. Above 95% dye removal efficiency for the commercial effluent was attained. COD removal of 85% was observed after the treatment. The catalyst was reused more than 10 times without any significant change in the catalytic property. Chen et al. [269] examined the decolorization of an anthraquinone dye (Reactive Brilliant Blue KN-R) by H_2O_2 using Fe-containing Y and ZSM-5 zeolites as heterogeneous catalysts. Catalysts were prepared by ion exchange and co-precipitation methods, and calcined at different temperatures. The influence of dye concentration, catalyst dosage, and solution pH was evaluated. The results showed that both zeolites exhibited similar or better catalytic efficiency compared to homogeneous Fenton reagent, with Fe-containing ZSM-5 being more efficient. Fe-containing ZSM-5, which was prepared by coprecipitation and calcination at 450◦C, displayed the greatest decolorization capacity. Under the conditions of initial pH 2.5, 30 mmol.l^{-1} H_2O_2 and 4.0 g l^{-1} catalyst, 250 mg l^{-1} KN-R was decolorized over 90% within 20 min. A resent investigation on the oxidative decolorization of Acid Red 1 solutions by Fe–loaded zeolite Y catalyst [270] showed that at the optimal reacting conditions (initial pH 2.5, 16 mmol.l^{-1} H_2O_2 and 2.5 g l^{-1} catalyst, 50 mg l^{-1} dye, at 30 °C) 99% decolorization efficiency could be achieved within 60 min of reaction time. Karadag et al. [276] studied raw and SMZ for adsorption of Basic Red 46 and Reactive yellow 176 dyes from aqueous solutions. They compared the effect of different surfactants, CTAB and HTDMA, on dye adsorption and established that the increase in ionic strength caused a decrease in adsorption of basic and an increase in adsorption of the reactive dye. Adsorption of the cationic dye on natural zeolite was more favourable than Reactive Yellow 176 on the CTAB and HTDMA modified zeolites. Another study on the removal of reactive dyes by CTAB-modified natural zeolite [277] demonstrated that the adsorption capacity for Reactive Red 239 was almost twice higher than that of Reactive Blue 5, due to the hydrophilicity of the dye molecules. Benkli et al. [278] also investigated HDTMA-Br modified clinoptilolite for removal of reactive dyes, (Reactive Black 5, Reactive Red 239 and Reactive Yellow 176), in a fixed bed column. The results indicated the order of dye removal by SMZ was the following: Black >Yellow>Red. However, the results obtained by Armagan et al. [279] for the sorption of the same dyes by HTDMA-modified zeolite showed that maximum adsorption capacities of decreased in the order Red (111 mg g^{-1})>Yellow (89 mg g^{-1}) > Black (61 mg g^{-1}).

Ozdemir et al. [280] investigated the ability of SMZ to remove color from real textile dyeing wastewater, containing blend of reactive dyes and auxiliary chemicals. Tests were performed in a fixed-bed column reactor and the surface of natural zeolite was modified with HDTMA-Br. Effects of wastewater color intensity, flow rates and bed heights were also studied. Wastewater was diluted several times in the ratios of 25%, 50% and 75% in order to assess the influence of wastewater strength. The breakthrough curves of the original and diluted wastewaters were dispersed due to the fact that breakthrough color intensities and saturation of the bed appeared faster at higher color intensities. The column had a 3-cm diameter and four bed heights from 12.5 to 50 cm, which treated from 5.25, to 51 l original textile wastewater, respectively, at the breakthrough time at a flow rate of 0.025 l min^{-1}. The various design parameters obtained from fixed-bed experimental studies showed good correlation with corresponding theoretical values, under different bed heights.

Metes et al. [271] investigated the unselective adsorption of residual organic pollutants from flocculated printing ink wastewater onto eight synthetic zeolites as a finishing method for additional reduction of total organic content (TOC) in this effluent. Simulated wastewater was obtained by combining six single wastewaters of a specific printing ink, each at a concentration of 5.0 g l^{-1}. The initial TOC of wastewater at pH 7.5-7.8 was 1052 mg l^{-1}. The amount of adsorbed organics was largest for ZSM-5 and NH_4-Beta while the other zeolites studied showed lower efficiency, suggesting that adsorption was independent of pore structure. All the zeolites tested, except NaY and 13X were found to have a higher organic capacity in comparison to that obtained with powdered activated carbon. The adsorption rates of organic pollutants were fast as well. The 88% reduction of TOC obtained with a single flocculation treatment was improved with the combination of flocculation and adsorption with ZSM-5, which resulted in the overall TOC efficiency of 95%. It was concluded that flocculation followed by adsorption with zeolites is an effective treatment method for this kind of wastewater.

3.2.6.2. Humic substances removal

Humic substances (including humic acid, fulvic acid, and humin) make up about 80% of soil organic matters in dark soils [9]. Their presence in surface and ground water may produce toxic chemicals during disinfection processes and thus should be reduced. Some important studies on humic substances adsorption by natural zeolites were summarized by Wang and Peng [9].

Capasso et al. [281] investigated the adsorption of humic acid on raw Neapolitan yellow natural zeolitic tuff (containing phillipsite and chabazite), and Li^+, Na^+, K^+, NH_4^+, Ca^{2+} or Ba^{2+} - enriched samples. The raw zeolite showed humic acid sorption capacity of about 8.5 mg g^{-1}. It was demonstrated that the enrichment of tuff by monovalent cations slightly reduced the adsorption (down to 6.5-7.0 mg g^{-1}), whereas the enrichment by divalent cations significantly enhanced humic acid sorption. Ca and Mg - enriched samples, yielded the best results - 21.5 and 22 mg g^{-1}, respectively. Compared to the Neapolitan tuff, natural clinoptilolite, even in Ca-exchanged form, was found to be much more ineffective [282] with humic acid adsorption capacity of 2.6 mg g^{-1}. Remarkably, high humic acid adsorption of 68 mg g^{-1} was achieved for Australian natural zeolite tuff [283] at 30ºC and pH=5.

HDTMA-modified natural and synthetic zeolites have been also investigated for humic substances removal. Li et al. [286] recently reported an investigation on the performance of HDTMA-modified zeolites, obtained from CFA, for adsorption of humic acid from water. Two zeolite samples were synthesized from high-Ca and low-Ca CFA and then modified with HDTMA as described in [287]. The performance of modified and unmodified samples was examined in a batch tests. The experiments were performed with adsorbent dosage of 5 g l^{-1}, humic acid initial concentrations ranging from 50 to 900 mg l^{-1}, at room temperature, and 24 h treatment time. The results showed that, although CFA-derived zeolites had little affinity for humic acid, the adsorption by SMZ was high. The maximum adsorption capacities calculated from the Langmuir model for low-Ca and high-Ca SMZ was respectively 31.6 mg g^{-1} and 126.6 mg g^{-1}, which values were comparable or higher than those for activated carbons and clays previously reported. It was observed that the uptake of humic acid on SMZ was substantially increased under acidic pH conditions and that the removal efficiency of low-Ca SMZ was more pH sensitive than that of high-Ca sample. For high-Ca SMZ removal efficiency of nearly 100% was reached at pH<9, while for low-Ca SMZ the same results were achieved at pH $\leq$ 5. The uptake of humic acid was improved in the presence of electrolyte (NaCl).

3.2.6.3. Removal of other organics

Phenols are toxic compound coming from a variety of industrial sources, such as pesticides, dyes, and paper industries, coke and resin manufacturing, textile, plastic, rubber, pharmaceutical, and petroleum production. Wu et al. [286] examined the adsorption of bisphenol A by two zeolite samples, synthesized from CFA, and modified with HDTMA. The SMZ showed greatly enhanced adsorption capacity than the parent zeolite. Bisphenol A uptake increased at alkaline pH conditions, which enabled the formation of bisphenolate anion [286]. The SMZ having higher BET surface area and higher amount of loaded HDTMA showed greater retention for bisphenol A. The uptake of bisphenol A was improved slightly in the presence of NaCl, and was enhanced at a low temperature. The authors proposed that the anions interact strongly with the positively charged heads of HDTMA, with the two hydrophobic benzene rings of bisphenol A pointing to the inside of HDTMA bilayers, while the adsorption of uncharged bisphenol A probably involved hydrophobic partitioning into HDTMA bilayers and the coordination of the oxygen atoms of bisphenol A with positively charged heads of HDTMA. Tsai et al. [287] obtained very good results for the sorption of bisphenol-A by zeolite Y (up to 120 mg g^{-1}) and negligible sorption (<0.5 mg g^{-1}) for zeolite type P2 [274], although the specific surface area of the zeolites were similar - 500 m^2 g^{-1} and 400 m^2 g^{-1}, respectively. These results were explained with the repulsive interaction between the hydrophilic surface of the zeolite P2 (having low Si/Al ratio) and, conversely, the attracting interaction between the bisphenol-A and hydrophobic surface of high-silica zeolite [274]. Kuleyin [288] investigated the adsorption of phenol and 4-chlorophenol on HDTMA- and BDTDA-modified natural zeolite. At initial concentration of 50 mg l^{-1} the phenol removal efficiencies reached up to 71% and 73% for HDTMA-zeolite and BDTDA-zeolite, and the 4-chlorophenol removal efficiencies reached up to 81% and 89% for HDTMA-zeolite and BDTDA-zeolite. The maximum capacities of surfactant-modified zeolite for phenol and 4-chlorophenol have been calculated in the range of 0.7647–1.2977 mg $g^{-1}$and 6.4102–12.7065 mg g^{-1}, respectively. Lopez [289] studied the adsorption of paranitrophenol in a packed bed adsorption reactor filled with dealuminated Y (Si/Al=20) zeolite and granulated active carbon. The maximum amount of paranitrophenol adsorption on the zeolite was found to be as high as 330 mg g^{-1}.

Benzene, toluene, ethylbenzene, and xylene (abbreviated as BTEX) are volatile aromatic compounds, typically found in petroleum products, such as gasoline and diesel fuel. BTEX are carcinogenic and have harmful effects on the central nervous system. BTEX are notorious due to the contamination of groundwater and soil that typically occurs near petroleum and natural gas production sites, and petrol stations and other areas with storage tanks containing gasoline or other petroleum-related products. Ranck et al. [290] investigated the effectiveness of HDTMA-modified zeolite in BTEX removal along with changes in sorption properties with long-term use. The results showed that SMZ completely removes BTEX from produced water up to a compound-specific capacity, and that SMZ can be regenerated via air sparging without loss of sorption capacity. The most soluble compound, benzene, began to elute first - at 8 pore volumes (PV), while the least soluble compounds, ethylbenzene and xylenes, began to elute at 50 PV, which was in agreement with the BTEX behaviour previously reported by Bowman [122]. The field-scale system was also tested at a natural gas produced-water treatment facility. In the field column, initial benzene breakthrough occurred at 10 PV and toluene breakthrough began at 15 PV and no breakthrough of ethylbenzene or xylenes occurred throughout the 80 PV experiment. Altare et al. [291] performed column tests to estimate applicability of HDTMA-modified clinoptilolite for the removal of BTEX from produced water generated as a byproduct of oil and gas recovery. The results showed that BTEX removal was controlled by the total number of PV that passed through the SMZ bed, and to a minor degree by flow rate, suggesting only minor kinetic effects on regeneration. BTEX sorption and SMZ regeneration profiles varied little over 50 sorption/regeneration cycles. Each cycle consisted of BTEX sorption from 100 PV of produced water followed by regeneration with approximately 2000 PV of air. Only a small loss in sorption affinity after 50 cycles was detected. Ghiaci et al. [292] investigated the adsorption of benzene, toluene and phenol by CPD- and HDTMA- modified ZSM-5-31, ZSM-5-88, and clinoptilolite besides as-synthesized MCM-41 molecular sieve. They found that the increase in contaminant concentration or initial concentrations of surfactants resulted in an increase in the adsorption. At equal concentration, CPD modified zeolite showed higher adsorption than that of the corresponding HDTMA-modified zeolite. Sorption capacity of the organics onto the as-synthesized MCM-41 and modified zeolites were in the order of MCM-41> SMZclinoptilolite >ZMZ ZSM-5-88> SMZ ZSM-5-31. Benzene and toluene showed almost similar sorption capacity, whereas phenol showed the lowest sorption capacity among them.

Ersoy and Celik [293] examined the adsorption of aniline and nitrobenzene on raw and HDTMA-modified natural zeolite. In batch tests the adsorption capacity of aniline and nitrobenzene onto natural zeolite surface was negligible, while that onto SMZ was significant. In the column tests, adsorption capacity of two compounds on SMZ from the breakthrough curves was determined as 2.36 and 3.25 mg g^{-1} for aniline and nitrobenzene, respectively.

Atrazine is a widely used herbicide, which use is controversial, due to widespread contamination in drinking water and its associations with birth defects, and other health problems. Although it has been banned in the EU, it is still one of the most widely used herbicides in the world. Grcic et al. [294] studied the application of different types of synthetic zeolites (CuZSM-5, FeZSM-5, HZSM-5, NH_4ZSM-5 and HY) as adsorbents for atrazine removal from wastewater. After two hours of treatment the highest removal efficiency was demonstrated by CuZSM-5 (54.3%), while the protonated form of ZSM succeeded to remove only 5.1% of the initial pollutant. The application of a combination of advanced oxidation technologies and adsorption resulted in complete removal of atrazine from model wastewater and significant decrease in TOC value. Lemic et al. [295] performed systematic adsorption tests in order to determine the efficiency of SDBAC-modified zeolite for removal of pesticides, atrazine, lindane and diazinone from water. The effects of adsorbent particle size and dosage, and the initial organic compaound concentration in the solutions were investigated. The adsorption capacities, calculated by Langmuir–Freundlich equation, were 2.0 μmol.g^{-1} (atrazine), 4.4 μmol.g^{-1} (diazinone), and 3.4 μmol.g^{-1} (lindan).

Bai et al. [296] investigated the removal of pyridine and quinoline from synthetic and coking wastewater by bio-zeolite composed of mixed degrading bacteria and modified clinoptilolite. The modified zeolite was made of clinoptilolite, white cement, natural zeolite gizzard, amylum, and coal powder with the proportion of 24:6:30:5:3 (v/v). After the addition of 7% carboxylic methyl cellulose solution, the mixture was extruded and then burned at 650 ◦C for 2 h. The experimental results indicated that the mixed bacteria could degrade pyridine and quinoline simultaneously, while zeolite could remove the NH_4^+-N transformed from pyridine and quinoline.

Some results for the performance of natural and synthetic SMZ for organic species removal are presented in Table 14.

Table 14. Performance of some SMZ for separation of different organic contaminants

Organic compound	Zeolite	Organic compound concentration, mg l^{-1}	Zeolite dosage, g l^{-1}	Organics sorption	Removal efficiency, %	Refe-rence*
Bisphenol-A	NaY (Si/Al=100)	30	0.5	120 mg g^{-1}		[287]
Bisphenol-A	NaP2 (Si/Al=5)	20	0.5	<0.5 mg g^{-1}		[274]
Bisphenol-A	NaP1 L	100	0.5	42 mg g^{-1}		[286]
Bisphenol-A	Hydroxisodalite and NaP1	100	0.5	100 mg g^{-1}		[286]
Naphthalene	HTDMA-clinoptilolite	20	6-120	2 μmol C. g^{-1}		[124]
Phenol	HTDMA-clinoptilolite	50			71	[288]
Phenol	BDTDA-clinoptilolite	50			81	[288]
4-chlorophenol	HTDMA-clinoptilolite	50			73	[288]
4-chlorophenol	BDTDA-clinoptilolite	50			89	[288]
O-xylene	HTDMA-clinoptilolite	30	6-120	3 μmol C. g^{-1}		[124]
Atrazine	H-ZSM-5	1	0.5		5	[294]
Atrazine	NH_4-ZSM-5	1	0.5		39	[294]
Atrazine	Cu-ZSM-5	1	0.5		54	[294]
Atrazine	Fe-ZSM-5	1	0.5		46	[294]
Atrazine	H-Y	1	0.5		45	[294]
Atrazine	SDBAC-natural zeolite	1.8	0.5	0.45 μmol g^{-1}		[295]
Diazinone	SDBAC natural zeolite	3.9	0.5	1.8 μmol.g^{-1}		[295]

* Some values are recalculated and/or rounded.

Another perspective application of zeolites exploiting their absorption and molecular sieving properties is for the productions of supported polycrystalline zeolite membranes (ZM). ZM can be prepared by different methods: in-situ HT synthesis, chemical vapor phase method, spray seed coating [228] on the supporting material (e.g. sintered alumina), but regardless to the method of preparation, ZM have several important advantages when compared to conventional polymeric membranes, namely chemical, mechanical, and thermal resistance that allow ZM to be used at strong solvent environments, and at high temperatures and pressures [178]. ZM have been extensively researched for separation of organic contaminants from (waste)water, since most of organic pollutants damage the polymeric membranes [228]. Selected results from zeolitic membrane separation of different organic contaminants are presented in Table 15.

Table 15. Zeolitic membrane separation of different organic contaminants

Organic compound	Conc. of solution, %	Zeolite membrane	Membrane thickness	Water flux	Organic rejection, %	Refe-rence*
Isopropanol	90	NaA on α-Al_2O_3	10 μm	1.2 kg.m^{-2} h^{-1}	>98	[225]
Pentanoic acid	0.01	MFI on α-Al_2O_3	1.2 μm	0.03 kg.m^{-2} h^{-1}	96.5	[297]
Toluene	0.1	MFI on α	1.2 μm	0.33 kg.m^{-2} h^{-1}	99.5	[297]
Etanol	0.1	MFI on α	1.2 μm	0.31 kg.m^{-2} h^{-1}	17.0	[297]
Oil	0.1	NaA on α-Al_2O_3		60 l.m^{-2} h^{-1}	98.8	[298]

* Some values are recalculated and/or rounded.

Oil contaminated water is commonly discharged by large steel mills and related industries and is a major pollution problem because of the difficulty in treating oily wastewater. Cui et al. [298] investigated the application of zeolite/ceramic microfiltration membranes for treatment of oil-contaminated water. NaA ZM with different average inter-particle pore sizes of 1.2 μm and 0.4 μm were prepared on α-Al_2O_3 tube by in situ HT method. The filtration decreased the oil content in the emulsions from 100–500 mg. l^{-1} down to < 3 mg. l^{-1} at moderate to high flux. Consistent membrane performance was maintained by a regeneration regime consisting of frequent backwash with hot water and alkali solution.

MFI silicate ZM was synthesized on the inner surface of tubular α-alumina substrates [297]. The obtained membrane was tested for separation of pentanoic acid, toluene and ethanol from aqueous solutions. The results indicate that ZM have great potential for separation of dissolved organics from wastewater. At initial concentrations of 100 ppm ZM rejected 96.0% of pentanoic acid and 99.5% of toluene in the solutions. It was observed that organic rejection and water flux were affected by the organic concentration. As pentanoic acid concentration increased from 100 ppm to 500 ppm, both organic rejection and water flux decreased slightly.

3.2.6.4. Micro-organisms capturing

The large surface area of the zeolites is accessible for adhering microorganisms. This makes zeolites a suitable material for biofilter for removal of pathogen microorganisms [125], or for cultivation of bacteria, employed in active sludge at wastewater treatment plants [8]. The main advantage of zeolites in comparison with clay adsorbents is that zeolite has better hydraulic properties [122]. The main drawback of the use of zeolites is the slow rate of bacteria uptake from wastewater (when zeolite is used for bacteria removal) or the slow rate of formation of the bacteria layer on the zeolite surface (when zeolite is used as bacteria carrier) [8].

Garcia et al. [300] conducted a research on removal of bacteria indicators of pollution (total coliforms, faecal coliforms and faecal streptococci) and organic matter (evaluated as COD and BOD) from wastewater from the water treatment plant at Santa Cruz de Tenerife city (Canary Islands) using natural phillipsite. The tests were performed in a percolation reactor at a constant solution flow rate. Faecal coliform and faecal streptococci were totally removed at the 10th and 17th day, respectively. 75% COD retention at the 25th day and 100% BOD in the 90th day were achieved. Escherichia Coli, poliovirus, coxsackie virus and bacterophages from drinking water was effectively removed from drinking water using $Al_2(SO_4)_3$ coagulant and clinoptilolite [230]. The microorganisms were captured by the formation of microorganism-clinoptilolite-coagulant complexes. Research on the potential of clinoptilolite for removal of coliform bacteria, total bacteria, phyto-and zooplankton from drinking water showed that the physiochemical and mechanical properties of the zeolite were kept unaltered after 3 years of usage and gave a stable decrease in the content of microorganisms [230].

The modification of zeolites by cation active polyelectrolytes accelerates the interaction between the bacteria and the zeolite surface, thus increases the sludge activity [243]. The SMZ show better ability to bind pathogen microrganisms, as well [122,301,302]. The investigation of Nikashina and Myasoedov [302] demonstrated that Escherichia coli could be totally removed from drinking water by treatment with clinotsid, an organozeolite, prepared by modifying natural clinoptilolite with amine groups-polyhexamethylene guanidine chloride linked with epichlorohydrine. Bowman [122] studied HDTMA-modifyed clinoptilolite from St. Cloud, New Mexico, as adsorbent for removal of Escherichia coli and bacteriophage MS2 from sewage-contaminated water. Results indicated the complete removal of Escherichia coli by the SMZ. Based on laboratory and field results, SMZ performed very well in removing viruses from groundwater. The only concern is the non-selectivity of SMZ, e.g. the removal of both viruses and negatively charged ions such as bromide, which may limit the applicability of SMZ in high-salinity waters and in long-term applications. Most of the virus removal by SMZ was attributed to sorption. It was observed that a minor amount of the surfactant coating dissolved into the water and thus probably removed a significant percentage of the viruses in the field test. Escherichia coli was completely removed by SMZ during the field tests. Author commented that although HDTMA was bactericidal in aqueous solution, the adsorbed

Escherichia Coli might remain viable for a period of time, because the toxicity of HDTMA to the organisms is greatly reduced when surfactant was bound to zeolite. Finally, laboratory experiments showed that toluene-degrading organisms could be effectively cultured on SMZ.

3.2.7. Permeable reactive barriers (PRB)

The leakage of municipal, industrial, and radioactive waste disposal sites may cause distribution of contaminants in the surrounding environment. PRB have been developed and successfully used for in-situ treatment of contaminated ground water [124,303]. The barriers are filled with reactive material, which captures or modifies the contaminants, thus improving the ground water quality. The high sorption capacity, plasticity, chemical stability, mechanical strength, and thermal conductivity make the raw and modified zeolitic materials, along with the clays, suitable for utilization as liners prohibiting the spreading of the contaminants [8]. The use of SMZ as a PRB sorbent offers several advantages when dealing with mixed contaminant plumes [122]. Bowman [122] evaluated HDTMA-modified natural clinoptilolite in a permeable reactive barrier for the removal of contaminants from sub-surface water. A 15-week pilot test showed barrier retardation factors of 44 and 39 for chromate and PCE, respectively, similar to the values predicted from laboratory experiments. SMZ was also tested for removal of organics from oilfield wastewaters. The results showed that the higher solubility species benzene and toluene appeared first in the effluent and reach influent concentrations relatively rapidly, followed by the more hydrophobic, more strongly retained ethylbenzene and xylenes. At influent concentration of 13-15 mg l^{-1} the total mass of BTEX retained by the SMZ-filled column is 65.3 mg for benzene, 148 mg for toluene, 628 mg for methylbenzene, 698 mg for m-, p-xylene, and 657mg for o-xylene, respectively. Total removal of bacteria and viruses from sewage effluent, was also reported (see 3.2.7). Northcott et al. [124] synthesized hydrophobic zeolite and characterized its suitability as a PRB material for treatment of hydrocarbons in groundwater. Batch sorption tests were performed along with a number of standard characterization techniques. High and low ionic strength and pH tests were also conducted to determine their impact on hydrocarbon uptake. Further ion exchange tests were carried out to evaluate the potential of zeolite to act as both a hydrocarbon capture material and nutrient a delivery system for bioremediation. The natural zeolite was coated with octadecyltrichlorosilane to change its surface properties. The results of the surface characterization tests showed that the underlying zeolite structure was largely unaffected by the coating. TGA measurements showed a reactive carbon content of 1–2%. O-xylene and naphthalene sorption isotherms results compared well with the behaviour of similar materials investigated by other researchers. Ionic strength and pH had little effect on hydrocarbon sorption and the treated zeolite had an ion exchange capacity of 0.3 meq g^{-1}, indicating it could be utilized as a nutrient source in PRB. Recycle tests indicated that the zeolite could be re-used at least three times without significant reduction in treatment effectiveness. Hornig et al. [304] tested several sorbent materials (MYCELX coated sand, granular activated carbon and HDTMA-modified clinoptilolite) for treatment of hydrocarbon-contaminated ground water in cold regions. Batch sorption tests at 20 °C and 4 °C were performed with using toluene, o-xylene and naphthalene. The results of the surface characterization tests showed that the quality of the MYCELX coating on the sand was highly variable, thus leading to unreliable adsorption results. Activated carbon proved to be the best sorbent material at high and low temperatures on a mass basis, while on a surface area basis, SMZ performed better. High ionic strength and high and low pH had little effect for hydrocarbon sorption. Both materials exhibited reduced adsorption efficiency at 4 °C compared to 20 °C. For SMZ the decrease of temperature caused about 40% the reduction of the distribution coefficient for all hydrocarbons. A study [305] on the application of clinoptilolite in PRB for the treatment of heavy metal contaminated waters in Antarctic also indicated that the performance of the zeolite was significantly reduced at low temperatures.

3.2.8. Sea water desalination

A number of seawater desalination technologies were developed during the last several decades to augment the supply of water in arid regions of the world. Two of the most commercially important technologies are based on the multi-stage flash distillation and reverse osmosis (RO) processes [306]. In the RO process, the osmotic pressure is overcome by applying external pressure. Thus, water flows in the reverse direction to the natural flow across the membrane, leaving the dissolved salts behind [306]. The reverse osmosis membrane materials for desalination have been recently reviewed by Lee at al. [307]. A molecular dynamic simulation has shown that some ZM are theoretically suitable for ion removal from aqueous solutions by RO [228]. For instance, MFI ZM was expected to reject 100% Na^+ through size exclusion of hydrated ions, which have kinetic sizes larger than the aperture of zeolite. The sizes of some hydrated ions are presented in Table 16 [309].

Table 16. Size of hydrated ions

Ion	Hydrated diameter, nm
H_2O	0.26
Li^+	0.76
Na^+	0.72
K^+	0.66
Mg^{2+}	0.86
Ca^{2+}	0.82
OH^-	0.60
Cl^-	0.66
NO_3^-	0.68

According to this mechanism, MFI zeolite, which has an effective intracrystal nanopore diameter of 0.51 nm, is supposed to be suitable for separating the small water molecules (0.26 nm) from larger ions like Na^+ and Cl^- having hydrated sizes of 0.72 and 0.66 nm, respectively [309]. However, the first experimental attempt for RO of a NaCl solution using a MFI silicalite-1 ZM showed only 77% salt rejection and a water flux as low as $0.003 m^3 m^{-2} day^{-1}$ at 21 bar [310]. It was also reported that rejection of bivalent cations was higher than for monovalent ions, in a test using a feed containing mixed ion species. These results showed that the filtration mechanism was not only dependent on size exclusion, but also on Donnan exclusion, due to the charged double layer induced by adsorbed ions on the pore or the intercrystalline walls. Although the first RO test with a ZM was unsuccessful, subsequent work was conducted to improve both salt rejection and water flux by modifying the zeolite structure. The Si/Al ratio, which dominates the wettability and membrane surface charge, was optimised to give improved flux. Duce et al. [311] developed silicalite and ZSM-5 ZM and tested desalination using the thermally based pervaporation, and RO operation modes. ZM were synthesized by template-free secondary growth technique with varying Si/Al ratios. In pervaporation with 3.8 wt% sea salts feed, zeolites containing alumina actively rejected ions, displaying equivalent rejections exceeding 99%. Flux typically decreased after introduction of seawater, but the membrane with Si/Al ratio of 100 (ZSM100) uniquely showed a 30% increase in flux, which could only be explained by an ion exchange/interaction mechanism, which opened the zeolite structure to permeation. Optimal temperature for pervaporation was found to be 80°C, where high rejections persisted, and flux increased to $0.72 kg.m^{-2}.h^{-1}$. In RO at the consistent conditions of room temperature operation and 0.5 wt% sea salts fed at 700 kPa, strikingly different results for both flux and rejection for the different membranes were observed. In terms of flux, ZSM100 showed 3-fold greater flux than silicate and ZSM020 (Si/Al ratio of 20). Li et al. [312] investigated RO of 0.1M solutions of alkali metal chlorides, including LiCl, NaCl, KCl, RbCl, and CsCl on MFI-type ZM synthesized from an aluminum-free precursor. The MFI zeolite membrane exhibited high rejection rates (>95%) for all alkali metal ions at an applied pressure of 2.75 MPa. The rejection rates of Li^+ and Na^+ declined slightly, while the ion flux increased more dramatically than did the water flux with moderately raising the temperature. Increasing the hydraulic pressure difference across the membrane resulted in significant enhancements in both the water flux and the ion rejection rates but with much less influence on the ion flux. The ion flux increased monotonically with the crystallographic ion size from Li^+ to Cs^+ while the dependence of the water flux on ion size exhibited a maximum for the 0.1M KCl solution.

Kazemimoghadam [309] synthesized hydrothermally hydroxysodalite ZM (pore diameter 0.4 nm) and tested its performance using an experimental pervaporation setup. Effects of temperature, rate and pressure on the membrane structure and performance were investigated for hydroxysodalite ZM grown onto seeded mullite supports. Increasing pressure, feed rate and temperature increases the flux linearly. Water flux of about 4 $kg.m^{-2}.h^{-1}$ was achieved at 3 bar, 3 $l.min^{-1}$ and 60°C. Khajavi et al. [313] synthesized hydroxysodalite ZM and tested it pervaporative desalination of North Sea water and aqueous salt solutions for more than 100 h over a temperature range of 303–473 at 2.2 MPa. In all cases the membrane showed salt rejection better than 99.99%, the collected permeate was ultra pure water with a resistance of 0.1 μS/cm at 25 ◦C. Flux through the membrane in seawater desalination showed a steep increase with feed temperature, exceeding the flux values obtained for pure water. Increasing the salt concentration of NaCl in the feed led to an increase in the water flux, whereas the opposite trend was observed for $NaNO_3$ solutions. It was speculated that under the applied HT conditions, hydroxide groups in the sodalite cages were exchanged with chloride anions of the solution, resulting in higher water mobility. The bulkier nitrate could not do so, and a decrease in water flux was attributed to the decrease in water activity in combination with a blocking effect by the nitrate anion.

Cho et al. [314] investigated the pervaporative seawater desalination characteristics of the NaA ZM having upper limit of the non-zeolitic pore diameter 0.8 nm. ZM showed excellent (> 99.9%) salt rejections for all of the ions in the seawater (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, SO_4^{2-}, PO_4^{3-}, NO_3^-, F^-, Cl^-, Br^-), and up to 79.2% rejection for boron. The high rejections were attributed to a joint size exclusion/charge exclusion/surface evaporation mechanism. High water flux in the seawater (1.9 $kg.m^{-2}.h^{-1}$at 69◦C) also was manifested, and was much higher than that in pure water at temperatures below 100°C. Moreover, the apparent activation energy of the water permeation in seawater was always lower than that in pure water. The higher water flux and low activation energy were explained by the reduced electrostatic interaction between the positive surface charge and the polar water. The positive surface charge was induced by the charge reversal that was incurred by the adsorption of metal species on the zeolite surface. The water flux in the NaOH, NaCl, $NaNO_3$ and Na_2SO_4 solutions also was investigated, and could be understood as a function of the surface charge. The excellent salts rejection and water flux data indicated that the pervaporation process incorporating the NaA ZM was a promising candidate for seawater desalination applications.

In addition to ZM, zeolite nano-particles was used to prepare polymer-zeolite nanocomposite membranes, which were expected to combine the advantages of both materials. Jeong et al. [315] prepared zeolite NaA/polymer membrane. For this aim, NaA type nanopartices in the size range of 50–150 nm with a Si/Al ratio of 1.5 were first synthesized and then dissolved into a cross-linking agent solution before the interfacial polycondensation reaction. A homogeneous dispersion of zeolite particles was achieved using ultrasonication. RO membranes with various zeolite loadings were prepared. The membrane with increased zeolite loading was found to be smoother, more hydrophilic and more negatively charged. The membrane exhibited 90% of flux and a slight improvement in salt rejection relative to the polymer membrane without zeolite nano-particles. Fathizadeh et al. [316] studied the effect of added NaX nano-zeolite into polyamide as a top thin layer of membrane on water flux and salt rejection in a RO process. The thin film nanocomposite of polyamide and nano-NaX (40–150 nm) membranes was coated via interfacial polymerization of trimesoyl chloride and m-phenylenediamine monomers over porous polyethersulfone ultrafiltartion support. Different types of nanocomposite films were synthesized using two levels of monomer concentrations and nanozeolite loading into the polyamide film. The prepared nanocomposite membranes had higher thermal stability and more water permeability than the pure polyamide membranes. The results showed that addition of nano-NaX to the polyamide membrane led to improvement of surface properties such as RMS roughness, contact angle and solid–liquid interfacial free energy, a decrease in film thickness and an increase in pore size and water flux. Excellent membrane performance was observed for the nanocomposite membrane containing about 0.2% nano-NaX zeolite, 0.1% trimesoyl chloride and 2% m-phenylenediamine.

4. CONCLUSION

On the base of the reviewed publications, it could be concluded that, due to their unique properties, zeolites have a great potential as effective sorbent materials for a large number of water treatment applications, such as water softening (for boilers and drinking), ammonia removal (from municipal sewage, animal farms, fertilizer factory wastewaters, fish breeding ponds, swimming pools), removal of heavy metals (from natural waters, acid mine drainages, industrial wastewater), phosphates removal, removal of dissolved organic compounds and dyes, oil spillages treatment, separation of solid impurities, radioactive wastewater purification, seawater desalination, PRB, and many others.

Synthetic zeolites obtained by reprocessing of industrial, municipal or agricultural waste materials, especially CFA and RHA, have huge potential as a cost-effective, environmental-friendly solution that can improve the efficiency of (waste)water treatment. The low price and the additional ecological benefit (reduced raw materials mining and solid wastes disposal) of the production of zeolites from wastes increase their popularity and inspire growing interest among zeolite researchers and manufacturers worldwide.

5. REFERENCES

1. Querol, X.; Moreno, N.; Umaña, J. C.; Alastuey, A.; Hernández, E.; López-Soler, A.; Plana, F. *Int. J. Coal Geol.* **2002**, *50(1-4)*, 413-423.
2. Mumpton, F. A. *Proc. Natl. Acad. Sci. USA* (*Colloquium Paper)* **1999**, *96,* 3463-3470.
3. Anuwattana, R.; Khummongkol, P. *J. Hazard. Mater.* **2009**, *166,* 227-232.
4. International Zeolite Association, Index of Natural Zeolites Datasheets. *Available online at http://www.iza-online.org/natural/index.htm (last accessed 2011).*
5. International Zeolite Association, Database of Zeolite Structures. *Available online at http://www.iza-structure.org/databases (last accessed 2011).*
6. Qiu, W.; Zheng, Y. *Chem. Eng. J.* **2009***, 145*, 483–488.
7. Kalló, D. *Reviews in Miner. Geochem.* **2001**, *45*, 519-550.
8. Misaelides, P. *Microporous Mesoporous Mater.* **2011**, *144(1),* 15-18.
9. Wang, S.; Peng, Y. *Chem. Eng. J.* **2010**, *156,* 11-24.
10. Booker, N. A.; Cooney, E. L.; Priestley, A. J. *Water Sci. Technol.* **1996**, *34(9),* 17-24.
11. Rozic, M.; Cerjan-Stefanovic, S.; Kurajica, S.; Vancina, V.; Hodzic, E. *Water Res.* **2000**, *34(14),* 3675-3681.
12. Ouki, S.; Kavannagh, M. *Water Sci. Technol.* **1999**, *39(10-11)*, 115-122.

13. Motsi, T.; Rowson, N. A.; Simmons, M. J. H. *Int. J. Miner. Process.* **2009**, *92,* 42-48.
14. Ames, L. L. Removal of cesium by sorption from aqueous solutions. U.S. Patent No. 30,017,242, January 16, 1962.
15. Borai, E. H.; Harjula, R.; Malinen, L.; Paajanen, A. *J. Hazard. Mater.* **2009**, *172,* 416-422.
16. Osmanlioglu, A. E. *J. Hazard. Mater.* **2006**, *B137*, 332-335.
17. Virta, R. L. Zeolites (Natural), U.S. Geological Survey, Mineral Commodity Summaries, **2011**. *Available online at: http://minerals.usgs.gov/minerals/pubs/commodity/zeolites/mcs-2011-zeoli.pdf (last accessed 2011).*
18. Wang, S.; Zhu, Z. H. *J. Hazard. Mater.* **2006**, *B136,* 946-952.
19. Lihareva, N.; Dimova, L.; Petrov, O.; Tzvetanova, Y. *Microporous Mesoporous Mater.* **2010**, *130,* 32-37.
20. Englert, A. H.; Rubio, J. *Int. J. Miner. Process.* **2005**, *75,* 21-29.
21. Du, Q.; Liu, S.; Cao, Z.; Wang Y. *Sep. Purif. Technol.* **2005**, *44,* 229-234.
22. White, D. A.; Bussey, R. L. *Sep. Purif. Technol.* **1997**, *11,* 137-141.
23. Li, M.; Zhu, X; Zhu, F.; Ren, G.; Cao, G.; Song, L. *Desalination* **2011**, *271,* 295-300.
24. Farkas, A.; Rozic, M.; Barbaric-Mikocevic, Z. *Croatia, J. Hazard. Mater.* **2005**, *117,* 25-33.
25. Ghiaci, M.; Kia, R.; Abbaspur, A.; Seyedeyn-Azad, F. *Sep. Purif. Technol.* ***2004****, 40, 285-295.*
26. Petrus, R.; Warchol, J. *Microporous Mesoporous Mater.* **2003**, *61(1-3)* 137-146.
27. Alpat, S. K.; Özbayrak, Ö.; Alpat, S.; Akcay, H. *J. Hazard. Mater.* **2008**, *151,* 213-230.
28. Capasso, S.; Coppola, E.; Iovino, P.; Salvestrini, S.; Colella, C. *Microporous Mesoporous Mater.* **2007**, *105,* 324-328.
29. Sarioglu, M. *Sep. Purif. Technol.* **2005**, *41,* 1-11.
30. Sprynskyy, M.; Lebedynets, M.; Terzyk, A. P.; Kowalczyk, P.; Namiesnik, J.; Buszewski, B. *J. Colloid Interface Sci.* **2005**, *284,* 408-415.
31. Barrer, R. M., *J. Chem. Soc.* **1948**, 127-132.
32. Milton, R. M. Molecular sieve adsorbents. US Patent 2882243, 1959.
33. Cundy, C. S.; Cox, P. A. *Microporous Mesoporous Mater.* **2005**, *82*, 1-78.
34. Marui, Y.; Irie, R.; Takiyama, H.; Uchida, H.; Matsuoka, M. *J. Cryst. Growth* **2002**, *237-239,* 2148-2152.
35. Koroglu, H. J.; Sarioglan, A.; Tatlier, M.; Erdem-Senatalar, A.;. Savasci, O. T. *J. Cryst. Growth* **2002**, *241,* 481-488.
36. Kosanovic, C.; Jelic, T. A.; Bronic, J.; Kralj, D.; Subotic, B. *Microporous Mesoporous Mater.* **2011**, *137,* 72-78.
37. Basaldella, E. I.; Tara, J. C. *Zeolites* **1995**, *11*, 243-248.
38. Ríos, C. A.; Williams, C. D.; Fullen, M. A. *Appl. Clay Sci.* **2009,** *42*, 446-454.
39. Akolekar, D.; Chaffee, A.; Howe, R. F. *Zeolites* **1997**, *19*, 359-365.
40. Murat, M.; Amokrane, A.; Bastide, J. P.; Montanaro, L. *Clay Miner.* **1992**, *27(1)*, 119-130.
41. Meftah, M.; Oueslati, B.; Ben Haj Amara, A. *Physics Procedia,* **2009**, *2,* 1081-1086.
42. Mezni, M.; Hamzaoui, A.; Hamdi, N.; Srasra, E. *Appl. Clay Sci.* **2011**, *52(3),* 209-218.
43. Abdmeziem, K.; Siffert, B. *Appl. Clay Sci.* **1994**, *8(6),* 437-447.
44. Abdmeziem, K.; Siffert, B. *Appl. Clay Sci.* **1989**, *4*, 1-9.
45. Baccouche, A.; Srasra, E.; Maaoui, M. E. *Appl. Clay Sci.* **1998**, *13*, 255-273.
46. Cañizares, P.; Durán, A.; Dorado, F.; Carmona, M. *Appl. Clay Sci.* **2000**, *16*, 273-287.
47. Mackinnon, I. D. R.; Millar, G. J.; Stolz, W. *Appl. Clay Sci.* **2010**, *48,* 622-630.
48. Ruiz, R.; Blanco, C.; Pesquera, C.; Gonzalez, F.; Benito, I.; Lopez, J. L. *Appl. Clay Sci.* **1997**,

12, 73-83.
49. Faghihian, H.; Godazandeha, N. *J. Porous Mater.* **2009**, *16*, 331-335.
50. Barth-Wirshing, U.; Holler, H.; Klammer, D.; Konrad, B. *Mineral. Petrol.* **1993**, *48,* 275-294.
51. Christidis, G. E.; Paspaliaris, I.; Kontopoulos, A. *Appl. Clay Sci.* **1999**, *15,* 305-324.
52. Kang, S. J.; Egashira, K.; Yoshida, A. *Appl. Clay Sci.* **1998**, *13(2)*, 117-135.
53. Covarrubias, C.; Garcıa, R.; Arriagada, R.; Yanez, J.; Garland, M. T. *Microporous Mesoporous Mater***.** **2006**, *88*, 220-231.
54. Ibrahim, H. S.; Jamil, T. S., Hegazy, E. Z. *J. Hazard. Mater.* **2010**, *182,* 842-847.
55. Colina, F.G.; Llorens, J. *Microporous Mesoporous Mater.* **2007**, *100,* 302-311.
56. Chandrasekhar, S.; Pramada, P. N. *J. Porous Mater.* **1999,** *6*, 283-297.
57. Georgiev, D.; Bogdanov, B.; Angelova, K.; Markovska, I.; Hristov, Y. Synthetic zeolites – structure, classification, current trends in zeolite synthesis: Review. In *Proc. Int. Sci. Conf. "Economics and society development on the base of knowledge"*, Stara Zagora, Bulgaria 2009, Vol. 7, pp. 1-5.
58. Du, Y.; Shi, S., Dai, H. *Particuology* **2011**, *9(2)*, 174-178.
59. Chaisena, A.; Rangsriwatananon, K. *Mater. Lett.* **2005**, *59,* 1474- 1479.
60. Ghosh, B.; Agrawal, D. C.; Bhatia, S. *Ind. Eng. Chem. Res.* **1994**, *33*, 2107-2110.
61. Novembre, D.; Di Sabatino, B.; Gimeno, D.; Garcia-Valles, M.; Martınez-Manent, S. *Microporous Mesoporous Mater.* **2004**, *75,* 1-11.
62. Zhao, Y.; Zhang, B.; Zhang, X.; Wang, J.; Liu, J.; Chen R. *J. Hazard. Mater.* **2010**, *178,* 658-664.
63. Kim, D. J.; Chung, H. S. *Appl. Clay Sci.* **2003**, *24*, 69-77.
64. Tounsi, H.; Mseddi, S.; Djemel, S. Preparation and characterization of Na-LTA zeolite from Tunisian sand and aluminum scrap. In *Proc. JMSM 2008 Conf., Physics Procedia 2,* **2008**, 1065-1074.
65. Ahmaruzzaman, M. *Prog. Energy Combust. Sci.* **2010**, *36(3)*, 327-363.
66. Höller, H.; Barth-Wirsching, U. *Fortschritte der Miner.* **1985**, *63*,. 21-43
67. Ríos, C. A. R.; Williams, C. D.; Roberts, C. L. *Fuel* **2009**, *88*, 1403-1416.
68. Garcia-Martiez, J.; Cazorla-Amoros, D.; Linares-Solano, A. Zeolite synthesis from conformed fly ash derived from coal. In *PROGRESS Workshop on Novel Products from Combustion Residues*, Spain, 2001, pp. 125-130.
69. Murayama, N.; Yamamoto, H.; Shibata, J. *Int. J. Miner. Process.* **2002,** *64*, 1-17.
70. Mimura, H.; Yokota, K.; Akiba, K.; Onodera, Y. *J. Nucl. Sci. Technol.* **2001,** *38*, 766-772.
71. Querol, X.; Alastuey, A.; Fernandez-Turiel, J. L.; Lopez-Soler, A. *Fuel* **1995,** *74*, 1226-1231.
72. Querol, X.; Umana, J. C.; Plana, F.; Alastuey, A.; Lopez-Soler, A.; Medinaceli, A.; Valero, A.; Domingo, M. J.; Garcia-Rojo, E. *Fuel* **2001,** *80*, 857-865.
73. Moreno, N.; Querol, X.; Ayora, C. *Environ. Sci. Technol.* **2001,** *35*, 3526- 3534.
74. Belardi, G.; Massimilla, S.; Piga, L. *Resour., Conserv. Recycl.*, **1998,** *24*, 167-181.
75. Nam, S. S.; Lee, M. W.; Kim, S. B.; Lee, K. W.; Ko, M. K. *Environ. Eng. Res.* **2000**, *5*, 35-40**.**
76. Wang, C. F.; Li, J. S.; Wang, L. J.; Sun, X. Y. *J. Hazard. Mater.* **2008**, *155,* 58-64.
77. Shoumkova, A.; Stoyanova, V.; Tsacheva, Ts. *Proc. Bulg. Acad. Sci.* **2011**, *64(7),* 937-944.
78. Steenbruggen, G.; Hollman, G. *J. Geochem. Explor.* **1998**, *62(1-3)*, 305-309.
79. Yaping, Y.; Xiaoqiang, Z.; Weilan, Q.; Mingwen, W. *Fuel* **2008**, *87,* 1880-1886.
80. Hui, K. S.; Chao, C. Y. H.; Kot, S. C. *J. Hazard. Mater.* **2005**, *B127,* 89-101.
81. Wang, C.; Li, J.; Sun, X.; Wang, L.; Sun, X. *J. Environ. Sci.* **2009**, *21,* 127-136.

82. Koukouzas, N.; Vasilatos, C.; Itskos, G.; Mitsis, I. I.; Moutsatsou, A. *J. Hazard. Mater.* **2010**, *173,* 581-588.
83. El-Naggar, M. R.; El-Kamash, A. M.; El-Dessouky, M. I.; Ghonaim, A. K. *J. Hazard. Mater.* **2008**, *154,* 963-972.
84. Derkowski, A.; Franus, W.; Nowicka, H.; Czímerová, A. *Int. J. Miner. Process.* **2007**, *82,* 57-68.
85. Rungsuk, D.; Apiratikul, R.; Pavarajarn, V.; Pavasant, P. Zeolite synthesis from fly ash from coal-fired power plant by fusion method. In *Proc. 2nd Joint Int. Conf. Sustainable Energy and Environment Bangkok, Thailand,* ***2006.*** *Available online at: http://www.jgsee.kmutt.ac.th/see1/cd/file/E-042.pdf (last accessed 2010).*
86. Zhang, M.; Zhang, H.; Xu, D.; Han, L.; Niu, D.; Tian, B.; Zhang, J.; Zhang, L.; Wu, W. *Desalination* **2011**, *271,* 111-121.
87. Sallam, M. Zeolite synthesis from municipal solid waste ash using fusion and hydrothermal treatment. Ph.D. Thesis, University of South Florida, **2006.** *Available online at http://scholarcommons.usf.edu/etd/2688 (last accessed 2011).*
88. Fan, Y.; Zhang, F. S.; Zhua, J.; Liu, Z. *J. Hazard. Mater.* **2008**, *153*, 382-388.
89. Yao, Z.; Tamura, C.; Matsuda, M.; Miyake, M. *J. Mater. Res.* **1999**, *14,* 4437-4442.
90. Miyake, M.; Tamura, C.; Matsuda, M. *J. Am. Ceram. Soc.* **2002**, *85(7),* 1873-1875.
91. Yang, G. C. C.; Yang, T. Y. *J. Hazard. Mater.* **1998**, *62,* 75-89.
92. Penilla, R. P.; Bustos, G.; Elizalde, G. *J. Am. Ceram. Soc.* **2003**, *86*, 1527-1533.
93. Shawabkeh, R.; Al-Harahsheh, A.; Hami, M.; Khlaifat, A. *Fuel* **2004**, *83,* 981-985.
94. Machado, N. R. C. F.; Miotto, D. M. M. *Fuel* **2005**, *84,* 2289-2294.
95. Shawabkeh, R. A. *Micropor Mesopor Mater* **2004**; *75*, 107-114.
96. Nur, H. *Indones. J. Agricult. Sci.* **2001**, *1*, 40-45.
97. Azizi, S. N.; Yousefpour, M. *J. Mater. Sci.* **2010**, *45*, 5692-5697.
98. Yusof, A. M.; Nizam, N. A.; Rashid, N. A. A. *J. Porous Mater.* **2010**, *17*, 39-47.
99. Bhavornthayod, C.; Rungrojchaipon, P. *Materials and Minerals* **2009**, *19(2),* 79-83.
100. Folletto, E. L.; Castoldi, M. M.; Oliveira, L. H.; Hoffmann, R.; Jahn, S. L. *Lat. Am. Appl. Res.* **2009**, *39*, 75-78.
101. Ghasemi, Z.; Younesi, H. *J. Nanomater.* **2011**, Article ID 858961. *Available online at: http://www.hindawi.com/journals/jnm/2011/858961/cta/ (last accessed 2011).*
102. Petkowicz, D. I.; Rigo, R. T.; Radtke, C.; Pergher, S. B.; dos Santos, J. H. Z. *Microporous Mesoporous Mater.* **2008**, *116,* 548-554.
103. Wajima, T.; Kiguchi, O.; Sugawara, K.; Sugawara, T. *J. Chem. Eng. Jpn.* **2009**, *42(1)*, 61-66.
104. Katsuki, H.; Komarneni, S. *J. Solid State Chem.* **2009**, *182,* 1749-1753.
105. Khemthong, P.; Prayoonpokarach, S.; Jatuporn Wittayakun; J. *Suranaree J. Sci. Technol.* **2007**, *14(4),* 367-379.
106. Rahman, M. M.; Hasnida, N.; Wan Nik, W. B. *J. Sci. Res.* **2009**, *1(2)*, 285-291.
107. Yusof, A. M.; Keat, L. K.;; Ibrahim, Z.; Majid, Z. A.; Nizam, N. A. *J. Hazard. Mater.* **2010**, *174,* 380-385.
108. Wittayakun, J.; Khemthong, P.; Prayoonpokarach,S. *Korean J. Chem. Eng.* **2008**, *25,* 861-864.
109. Chareonpanich, M.; Namto, T.; Kongkachuichay, P.; Limtrakul, J. *Fuel Proc. Tech.* **2004**, *85,* 1623-1634.
110. Katsuki, H.; Furuta, S.; Watari, T.; Komarneni, S. *Microporous Mesoporous Mater.* **2005**, *86,* 145-151.

111. Kordatos, K.; Gavela, S.; Ntziouni, A.; Pistiolas, K. N.; Kyritsi, A.; Kasselouri-Rigopoulou, V. *Microporous Mesoporous Mater.* **2008**, *115,* 189-196.
112. Mohamed, M. M.; Zidan, F. I.; Thabet, M. *Microporous Mesoporous Mater.* **2008**, *108,* 193-203.
113. Panpa, W.; Jinawath, S. *Appl. Catal.* **2009**, *B 90,* 389-394.
114. Wang, P. H.; Lin, K. S.; Huang, Y. J.; Li, M. C.; Tsaur, L. K. *J. Hazard. Mater.* **1998**, *58,* 147-152.
115. Prasetyoko, D.; Ramli, Z.; Salasiah Endud, S.; Halimaton, H.; Sulikowski, B. *Waste Manage.* **2006**, *26,* 1173-1179.
116. Loiha, S.; Prayoonpokarach, S.; Songsiriritthigun, P.; Wittayakun, J. *Mater. Chem. Phys.* **2009**, *115,* 637-640.
117. Wajima, T.; Haga, M.; Kuzawa, K.; Ishimoto, H.; Tamada, O.; Ito, K.; Nishiyama, T.; Downs, R. T.; Rakovan, J. F. *J. Hazard. Mater.* **2006**, *B132,* 244-252.
118. Wajima, T.; Ikegami, Y. *Ceram. Int.* **2009**, *35,* 2983-2986.
119. Anuwattana, R.; Bulkus Jr., K. J.; Asavapisit, S.; Khummongkol, P. *Micropor. Mesopor. Mater.* **2008**, *111, 260-266.*
120. Misaelides, P.; Nikashina, V. A.; Godelitsas, A.; Gembitskii, P. A.; Kats, E.M. *J. Radioanal. Nucl. Chem.* **1998**, *227*, 183-186.
121. Basaldella, E. I.; Torres Sánchez, R. M.; Conconi, M. S. *Appl. Clay Sci.* **2009**, *42,* 611-614.
122. Basaldella, E. I.; Paladino, J. C.; Solari, M.; Valle, G. M. *Appl. Catal. B* **2006**, *66,* 186-191.
123. Bowman, R. S. *Microporous Mesoporous Mater.* **2003**, *61,* 43-56.
124. Apreutesei, R. E.; Catrinescu, C.; Teodosiu, C. *Environ. Eng. Manage. J.* ***2008***, *7(2),* 149-161.
125. Northcott, K. A.; Bacus, J.; Taya, N.; Komatsu, Y.; Perera, J. M.; Stevens, G. W. *J. Hazard. Mater.* **2010**, *183,* 434-440.
126. Widiastuti, N.; Wu, H.; Ang, M.; Zhang, D. *Desalination* **2008**, *218,* 271-280.
127. Richards, M. D.; Pope, C. G. *J. Chem. Soc. Faraday Trans.* **1996**; *92*, 317-23.
128. Medina, A.; Gamero, P.; Almanza, J. M.; Vargas, A.; Montoya, A.; Vargas, G.; Izquierdo, M. *J. Hazard. Mater.* **2010**, *181,* 91-104.
129. Haron, M. J.; Rahim, F. A.; Abdullah, A.H.; Hussein, M. Z.; Kassim, A. *Mater. Sci. Eng.* **2008**, *B 149,* 204-208.
130. Wei Qiu W., Zheng Y. *J. Hazard. Mater.* **2007**, *148,* 721-726.
131. Henkel, Persil., http://snurl.com/1kmpeo, (last accessed 2011).
132. Anon, *J. Am. Oil Chem. Soc.* **1980**, *57*, 228A.
133. Yangxin, Y.; Zhao, J. Z., Bayly, A. E. *Chin. J. Chem. Eng.* **2008**, *16(4),* 517-527.
134. Maki, A. W.; Macek, K. J. *Environ. Sci. Techn.*, **1978**, *12,* 573-580.
135. Guan, Q.; Hu, X.; Wu, D.; Shang, X.; Ye, C.; Kong, H. *Fuel* **2009**, *88,* 1643-1649.
136. Chen, J.; Kong, H.; Wu, D.; Hu, Z.; Wang, Z.; Wang, Y. *J. Colloid Interface Sci.* **2006**, *300,* 491-497.
137. Karapinar, N. *J. Hazard. Mater.* **2009**, *170,* 1186-1191.
138. Loiola, A. R.; Andrade, J. C. R. A.; Sasaki, J. M.; da Silva, L. R. D. *J. Colloid Interface Sci.* **2010**, doi: 10.1016/j.jcis.2010.11.026, *Available online at: http://www.sciencedirect.com/science/article/pii/S0021979710013044 (last accessed 2011).*
139. Zeodet-Association of Detergent Zeolite Producers, Zeolite for detergents - as Nature Intended, Brussels. Ziirn, M. (**1998**), *Available online at:*

http://www.zeodet.org/downloads/Zeolites.pdf (last accessed 2011).

140. Nieuwenhuizen, M. S.; Ebaid, A. H. E. F.; van Duin, M.; Kieboom, A. P. G.; van Bekkum, H. *Tenside Surfact*. *Det*. **1984**, *21,* 221-225.

141. Le VanMao, R.; Thanh Vu, N.; Xiao, S.; Ramsaran, A. *J. Mater. Chem.* **1994**, *4,* 1143-1147.

142. Arrigo, I.; Catalfamo, P.; Cavallari, L.; Di Pasquale, S. *J. Hazard. Mater.* **2007**, *147,* 513-517.

143. Hauthal, H. G. *SÖFW-Journal* **1996**, *122(13),* 899-911.

144. de Lucas, A.; Uguina, M. A.; Covian, I.; Rodriguez, L. *Ind. Eng. Chem. Res.* **1992**, *32*, 2134-2140.

145. Culfaz, M.; Saracoglu, N. E. *J. Environ. Sci. Health.* **1999**, *A34,* 1619-1626.

146. Culfaz, M.; Saracoglu, N.; Ozdilek, O. *J. Chem. Tech. Biotechnol.* **1996**, *65,* 265-271.

147. Zatta, A. et al., "Zeolite AX - A New Zeolite Builder for Detergents", *XXVII. Journadas del Comite Español de la Detergencia,* 1997, p. 71.

148. Hui, K. S.; Chao, C. Y. H. *J. Hazard. Mater.* **2006**, *B137,* 401-409.

149. Kurzendörfer, C. P.; Kuhm, P.; Steber, J. Zeolites in theEnvironment, In *Detergents in the Environment*, Schwuger, M. J., Ed.; Marcel Dekker, New York 1997, p. 127.

150. Krings, P.; Smulders, E. J. *Journal of the 45th SEPAWA-Congress*, Bad Durkheim **1998**, p. 70.

151. World Health Organization, Guidelines for drinking-water quality: incorporating first addendum, vol. 1, Recommendations, 3rd ed. (ISBN 92 4 154696 4), **2006**.

152. Fux, C.; Boehler, M.; Huber, P.; Brunner, I.; Siegrist, H. *J. Biotechnol.* **2002**, *99,* 295-306.

153. Kurniawan, T. A.; Lo, W. H.; Chan, G. Y. S. *J. Hazard. Mater.* **2006**, *129,* 80-100.

154. Kurama, H.; Karaguzel, C.; Mergan, T.; Celik, M. S. *Desalination* **2010,** *253* 147-152.

155. Hedstrom, A., *J. Environ. Eng. - ASCE* **2001**, *127(8)*, 673–681.

156. Weatherley, L. R.; Miladinovic, N. D. *Water Res.* **2004**, *38,* 4305-4312.

157. Malekian, R.; Abedi-Koupai, J.; Eslamian, S. S.; Mousavi, S. F.; Abbaspour, K. C.; Afyuni, M. *Appl. Clay Sci.* **2011**, *51,* 323-329.

158. Wang, Y.; Lin, F.; Pang W. *J. Hazard. Mater.* **2008**, *160,* 371-375.

159. Luna, Y.; Otal, E.; Vilches, L. F.; Vale, J.; Querol, X.; Fernandez-Pereira, C. *Waste Manage.* **2007**, *27,* 1877-1883.

160. Wang, Y. F.; Lin, F.; Pang, W. Q. *J. Hazard. Mater.* **2007**, *142,* 160-164.

161. Shih, W. H.; Chang, H. L. *Mater. Lett.* **1996**, *28,* 263-268.

162. Otal, E.; Vilches; L. F.; Moreno, N.; Querol, X.; Vale, J.; Fernandez-Pereira, C. *Fuel* **2005**, *84,* 1440-1446.

163. Liang, Z.; Ni, J. *J. Hazard. Mater.* **2009**, *166,* 52-60.

164. Saltali, K.; Ahmet Sari, A.; Aydın, M. *J. Hazard. Mater.* **2007**, *141,* 258-263.

165. Zhang, B. H.; Wu, D. Y.; Wang, C.; He, S. B.; Zhang, Z. J.; Kong, H. N. *J. Environ. Sci.* **2007**, *19,* 540-545.

166. Zhang, M.; Zhang, H.; Xu, D.; Han, L.; Niu, D.; Zhang, L.; Wu, W.; Tian, B. *Desalination* **2011**, *277(1-3)*, 46-53.

167. Huang, H. M.; Xiao, X.; Yan, B.; Yang L. *J. Hazard. Mater.* **2010**, *175,* 247-252.

168. Halim, A. A.; Aziz, H. A.; Johari, M. A. M.; Ariffin, K. S. *Desalination* **2010**, *262,* 31-35.

169. Guo, X.; Zeng, L.; Li, X.; Park, H.-S.*J. Hazard. Mater.* **2008**, *151,* 125-133.

170. Halim, A. A.; Aziz, H. A.; Johari, M. A. M.; Ariffin, K. S. *Desalination* **2010**, *262,* 31-35.

171. Querol, X.; Moreno, N.; Umana, J.; Juan, R.; Hernandez, S.; Fernandez-Pereira, C.; Ayora, C.; Janssen, M.; Garcia, J.; Linares, A.; Cazorla, D. Fly ash zeolitization products applied to waste water and gas decontamination. In *Proc. Int. Ash Utilization Symp.,* Center for Appl. Energy Res., Univ. Kentucky, Paper No 29, 2001, *Available online at http://www.flyash.info/2001/envben1/29querol.pdf (last accessed 2010).*

172. Cooney, E. L.; Booker, N. A.; Shallcross, D. C.; Stevens, G. W. *Sep. Sci. Technol.* **1999**, *43,* 2307-2327.

173. Vaughan, D. E. W. Properties of natural zeolites. In: *Natural Zeolites, Occurrence, Properties, Use,* Sand, L. B.; Mumpton F. A., Eds.; Pergamon Press, New York, 1978, pp**.** 353-371.

174. Demir, A.; Gunay, A.; Debik, E. *Water S. A.* **2002**, *28(3),* 329-336.

175. Rahmani A. R.; Mahvi, A. H. *Global NEST J.* **2006**, *8(2),* 146-150.

176. Lei, X.; Li, M.; Zhang, Z.; Feng, C.; Baid, W.; Sugiura, N. *J. Hazard. Mater.* **2009**, *169,* 746-750.

177. Barakat, M. A. New trends in removing heavy metals from industrial wastewater, *Arabian J. Chem.* **2010**, *Available online at: http://www.sciencedirect.com/science/article/pii/S1878535210001334 (last accessed 2011).*

178. Ahmadun, F. R.; Pendashteh, A.; Abdullah, L. C.; Biak, D. R. A.; Madaeni, S. S.; Abidin, Z. Z. *J. Hazard. Mater.* **2009**, *170,* 530-551.

179. Dal Bosco, S. M.; Jimenez, R. S.; Carvalho, W.A. *J. Colloid Interface Sci.* **2005**, *281,* 424-431.

180. Bosso, S. T.; Enzweiler, J. *Water Res.* **2002**, *36,* 4795-4800.

181. Curkovic, L.; Stefanovic, C.; Filipan, T. *War. Res.* **1997,** *31(6),* 1379-1382**.**

182. Alvarez-Ayuso, E.; Garcia-Sanchez, A.; Querol, X. *Water Res.* **2003**, *37,* 4855-4862.

183. Pitcher, S. K.; Slade, R. C. T.; Ward, N. I. *Sci. Total Environ.* **2004**, *334-335,* 161-166.

184. Lee, M. G.; Yi, G.; Ahn, B.J.; Roddick, F. *Korean Z Chem. Eng.,* **2000**, *17(3),* 325-331.

185. Purna Chandra Rao, G.; Satyaveni, S.; Ramesh, A.; Seshaiah, K.; Murthy, K. S. N.; Choudary, N. V. *J. Env. Manag.* **2006**, *81*, 265-270.

186. Pena, R.; Guerrero, A.; Goni, S. *J. Hazard. Mater.* **2006**, *B129*, 151–157.

187. Jha, V. K.; Matsuda, M.; Miyake, M. *J. Hazard. Mater.* **2008**, *160,* 148–153.

188. Erdem, E.; Karapinar, N.; Donat, R. *J. Colloid Interface Sci.* **2004**, *280,* 309-314.

189. Panayotova, M. I. *Waste management* **2001,** *21,* 671-676**.**

190. Calvo, B.; Canoira, L.; Morante, F.; Martínez-Bedia, J. M.; Vinagre, C.; García-González, J. E.; Elsen, J.; Alcantara, R. *J. Hazard. Mater.* **2009**, *166,* 619-627.

191. Abdel Salam, O. E.; Reiad, N. A.; ElShafei, M. M. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents *J. Adv. Res.* **2011**, *Available online at: linkinghub.elsevier.com/retrieve/pii/S2090123211000269 (last accessed 2011).*

192. Endres, J. C. T.; Ferret, L. S.; Fernandes, I. D.; Hofmeister, L. C. The Removal of Fe, Zn, Cu, and Pb from Wastewaters Using Chabazite Zeolites Produced from Southern Brazilian Coal Ashes, International Ash Utilization Symposium, Kentucky, 2001, Paper No 20, *Available online at: http://www.flyash.info/2001/envben1/20endress.pdf (last accessed 2011).*

193. Al-Anber, M.; Zaid, A.; Al-Anber, Z. *Desalination* **2008**, *225,* 70-81.

194. Somerset, V.; Petrik, L.; Iwuoha, E. *J. Env. Manage.* **2008**, *87,* 125–131.

195. Dimirkou, A.; Doula, M. K. *Desalination* **2008**, *224*, 280-292.

196. Rajic, N.; Stojakovic, D.; Jevtic, S.; Logar, N. Z.; Kovac, J.; Kaucic, V. *J. Hazard. Mater.* **2009**, *172,* 1450-1457.

197. Taffarel, S. R.; Rubio, J. *Miner. Eng.* **2009**, *22*, 336-343.

198. Taffarel, S. R.; Rubio, *J. Miner. Eng.* **2010**, *23,* 1131-1138.

199. Rajic, N.; Stojakovic, D.; Mina Jovanovic, M.; Logar, N. Z.; Mazaj, M.; Kaucic, V. *Appl. Surf.*

Sci. **2010**, *257,* 1524-1532.
200. Inglezakis, V. J.; Stylianou, M. A.; Gkantzou, D.; Loizidou, M. D. *Desalination* **2007**, *210,* 248-256.
201. Woolard, C. D.; Petrus, K.; van der Horst, M., *Water SA* **2000**, *26(4*), *Available online at: http://www.wrc.org.za (last accessed 2011).*
202. Stylianou, M. A.; Hadjiconstantinou, M. P.; Inglezakis, V. J.; Moustakas, K. G.; Loizidou, M. D. *J. Hazard. Mater.* **2007**, *143,* 575-581.
203. Inglezakis, V.,J.; Grigoropoulou, H. P. *J. Hazard. Mater.* **2004**, *B 112,* 37-43.
204. Oter, O.; Akcay, H. *Water Environ. Res.* **2007**, *79,* 329-335.
205. Cincotti, A.; Mameli, A.; Locci, A. M.; Orru, R.; Cao, G. *Industrial & Eng. Chem. Res.* **2006**, *45,* 1074-1084.
206. Caputo, D.; Pepe, F. *Microporous Mesoporous Mater.* **2007**, *105,* 222-231.
207. Gallant. J.; Prakash, A.; Removal of Selected Radionuclides and Metal Contaminants by Natural Zeolites from Liquid Effluents, prepared for Canadian Nuclear Society 30th Annual CNS Conference and 33rd CNS/CAN Student Conference, **2009**, *Available online at: http://www.zoxtsx.de/download/0123456.doc (last accessed 2011).*
208. Ahmed, S.; Chughtai, S.; Keane, M. A. *Sep. Purif. Technol.* **1998**, *13*, 57-64.
209. Rios, C. A.; Williams, C. D.; Roberts, C. L. *J. Hazard. Mater.* **2008**, *156,* 23-35.
210. Bektas, N.; Kara, S. *Sep. Purif. Technol.* **2004**, *39,* 189-200.
211. Wang, S. G.; Gong, W. X.; Liu, X. W.; Gao, B. Y.; Yue, Q. Y. *Sep. Purif. Technol.* **2006**, *51,* 367-373.
212. Coruh, S. *Desalination* **2008**, *225,* 41-57.
213. Panayotova, M. *Fresenius Environ. Bull.* **2001**, *10,* 267-272.
214. Panayotova, M. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2000**, *35,* 1591-1601.
215. Panayotova, M.; Velikov, B. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2002**, *37,* 139-147.
216. Panayotova, M.; Velikov, B. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2003**, *38,* 545-554.
217. Doula, M. K. *Water Res.* **2006**, *40,* 3167-3176.
218. Dimirkou, A. *Water Res.* **2007**, *41,* 2763-2773.
219. Katsou, E.; Malamis, S.; Tzanoudaki, M.; Haralambous, K. J.; Loizidou, M. *J. Hazard. Mater.* **2011**, *189,* 773-786.
220. Keane, M. A. *Colloids Surf., A* **1998**, *138,* 11–20.
221. Jamil, T. S.; Ibrahim, H. S.; Abd El-Maksoud, I. H.; El-Wakee, S. T. *Desalination* **2010**, *258,* 34-40.
222. Jha, V. K.; Nagae, M.; Matsuda, M.; Miyake, M. *J. Env. Manage.* **2009**, *90,* 2507–2514.
223. Misaelides, P.; Godelitsas, A.; Filippidis, A.; Charistos, D.; Anousis, I. *The Sci. Total Envir.* **1995**, *173/174,* 237-246.
224. Nilchi, A.; Maalek, B.; Khanchi, A.; Ghanadi Maragheh, M.; Bagheri, A.; Savoji, K. *Appl. Radiat. Isot.* **2006**, *64,* 138-143.
225. Malekpour, A.; Millani, M. R.; Kheirkhah, M. *Desalination* **2008**, *225,* 199-208.
226. Garcia-Sosa, I.; Solache-Ríos, M. *J. Radioanal. Nucl. Chem.* **2001**, *250(1),* 205-206.
227. Dyer, A.; Abou-Jamous, J. K. *J. Radioanal. Nucl. Chem.* **1994,** *183(2),* 225-233.

228. Kazemimoghadam, M.; Mohammadi, T. *Desalination* **2007**, *206,* 547-553.

229. Bosch, P.; Bulbulian, S. *Revista Mexicana de Física* **1992**, *38(1),* 237-241.

230. Applications of Natural Zeolites in Water and Wastewater Treatment, Kallo, D.; Ming, W., Eds., Mineralogical Society of America: Washington, USA. 2001, p. 654.

231. Chelishchev, N. F. Use of natural zeolites at Chernobyl. In *Natural Zeolites '93,* Mumpton, D.W., Ming F.A., Eds., Int. Committee on Natural Zeolites, 1993, pp 525-532.

232. Vintró, L. L.; Smith, K. J.; Lucey, J. A.; Mitchell, P. I. The environmental impact of the Sellafield discharges, *Available online at http://homepage.eircom.net/'radphys/scope.pdf (last accessed 2011).*

233. Elizalde-Gonzalez, M. P.; Mattusch, J.; Einicke, W.-D.; Wennrich, R. *Chem. Eng. J.* **2001**, *81(1-3),* 187-195.

234. Elizalde-Gonzalez, M. P.; Mattusch, J.; Wennrich, R.; Morgenstern, P. *Micropor. Mesopor. Mater.* **2001**, *46(2-3),* 277-286.

235. Li, Z.; Jean J. S; Jiang, W. T., Chang, P. H.; Chen, C. J.; Liao, L. *J. Hazard. Mater.* **2011**, *187(1-3),* 318-323.

236. Davila-Jimenez, M. M.; Elizalde-Gonzalez, M. P.; Mattusch, J.; Morgenstern, P.; Perez-Cruz, M. A.; Reyes-Ortega, Y.; Wennrich, R.; Yee-Madeira, H. *J. Colloid Interface Sci.* **2008**, *322,* 527-536.

237. Vaclavikova, M.; Stefusova, K.; Ivanicova, N.; Jakabsky, S.; Gallios, G. P. Magnetic zeolite as arsenic sorbent. In *Water treatmnet technologies for the removal of high toxiti pollutants.* NATO Science for Peace and Security Series-C, Springer, Dordrecht, 2010, 51-59.

238. Shevade, S.; Ford, R. G. *Water Res.* **2004**, *38,* 3197-3204.

239. Chutia, P.; Kato, S.; Kojima, T.; Satokawą, S. *J. Hazard. Mater.* **2009**, *162,* 440-447.

240. Barquist, K.; Larsen, S.C. *Microporous Mesoporous Mater.* **2010**, *130,* 197-202.

241. Li, Z.; Hong, H. *J. Hazard. Mater.* **2009**, *162,* 1487-1493.

242. Tashauoei, H. R.; Movahedian Attar, H.; Kamali, M.; Amin, M. M.; Nikaeen, M. *Int. J. Environ. Res.,* **2010,** *4(3),* 491-500**.**

243. Princz, P.; Olah, J.; Smith, S. E.; Hatfield, K.; Litrico, M. E. Wastewater treatment using modified natural zeolites. In: *Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice,* Perminova, I. V.; Hatfield, K.; Hertkorn, N., Eds.; Springer, 2005, pp. 267-282.

244. Sun, Y.; Fang, Q.; Dong, J.; Cheng, X.; Xu, J. *Desalination* **2011,** *277 (1-3),* 121-127.

245. Guan, H.; Bestland, E.; Zhu, C.; Zhu, H.; Albertsdottir, D.; Hutson, J.; Simmons, C. T.; Ginic-Markovic, M.; Tao, X.; Ellis, A. V. *J. Hazard. Mater.* **2010**, *183,* 616-621.

246. Masukume, M.; Onyango, M. S.; Aoyi, O.; Otieno, F. Nitrate removal from groundwater using modified natural zeolite, *Available online at: http://www.ewisa.co.za/literature/files/144_97%20Masukume.pdf (last accessed 2011).*

247. Barquist, K.; Larsen, S.C. *Microporous Mesoporous Mater.* **2010**, *130,* 197-202.

248. Zhan, Y.; Lin, J.; Zhu, Z. *J. Hazard. Mater.* **2011**, *186,* 1972-1978.

249. Ning, P.; Bart, H. J.; Li, B.; Lu, X.; Zhang, Y. *J. Environ. Sci.* **2008**, *20,* 670-674.

250. Wingenfelder, U.; Furrer, G.; Schulin, R. *Microporous Mesoporous Mater.* **2006**, *95*, 265-271.

251. Payne, K. B.; Abdel-Fattah, T. M. *J. Environ. Sci. Health* **2005**, *A40(4),* 723-749.

252. Xu, Y. H.; Nakajima, T.; Ohki, A. *J. Hazard. Mater.* **2002**, *B92,* 275-287.

253. Onyango, M. S.; Matsuda, H.; Ogada, T. *J. Chem. Eng. Jpn.* **2003**, *36(4),* 477-485.

254. Mohan, D.; Pittman, C. U. Jr. *J. Hazard. Mater.* **2007**, *142,* 1-53.

255. Elizalde-Gonzalez, M. P.; Mattusch, J.; Wennrich, R. *J. Environ. Monit. 3* **2001**, 22-26.
256. Habuda-Stanic, M.; Kules, M.; Kalajdzic, B.; Romic, Z. *Desalination* **2007**, *210,* 157-162.
257. Macedo-Miranda, M. G.; Olguin, M. T. *J. Inclusion Phenom. Macrocyclic Chem.* **2007**, *59,* 131-142.
258. Dousova, B.; Grygar, T.; Martaus, A.; Fuitova, L.; Kolousek, D.; Machovic, V. *J. Colloid Interface Sci.* **2006**, *302,* 424-431.
259. Zhang, Z.; Tan, Y.; Zhong, M. *Desalination* **2011** *276* (1-3), 246-252.
260. Mohan, D.; Pittman, C. U. Jr. *J. Hazard. Mater.* **2007**, *142,* 1-53.
261. Wang, S. B.; Boyjoo, Y.; Choueib, A.; Zhu, Z. H. *Water Res.* **2005**, *39,* 129-138.
262. Gupta, V. K.; Suhas *J. Environ. Manage.* **2009**, *90,* 2313-2342.
263. Atuṇ, G̃.; Hisarlı, G.; Kurtoglu, A. E.; Ayar, N. *J. Hazard. Mater.* **2011**, *187,* 562-573.
264. Wang, S.; Li, H.; Xie, S.; Liu, S.; Xu, L. *Chemosphere* **2006**, *65,* 82-87.
265. Wang, C.; Li, J.; Wang, L.; Sun, X.; Huang J. *Chin. J. Chem. Eng.* **2009**, *17(3)*, 513-521.
266. Woolard, C. D.; Strong, J.; Erasmus, C. R. *Appl. Geochem.* **2002**, *17,* 1159-1164.
267. Petkowicz, D. I.; Brambilla, R.; Radtke, C.; da Silva, C. D. S.; da Rocha, Z. N.; Pergher, S. B. C.; dos Santos, J. H. Z. *Appl. Catal.* **2009**, *A 357,* 125-134.
268. Fathima, N. N.; Aravindhan, R.; Rao, J. R.; Nair, B. U. *Chemosphere* **2008**, *70,* 1146-1151.
269. Chen, A.; Ma, X.; Sun, H. *J. Hazard. Mater.* **2008**, *156,* 568-575.
270. Hassan, H.; Hameed, B. H. *Desalination* **2011**, *276(1-3),* 45-52.
271. Metes, A.; Kovacevic, D.; Vujevic, D.; Papic, S. *Water Res.* **2004**, *38,* 3373-3381.
272. Richards, M. D.; Pope, C. G. *J. Chem. Soc. Faraday Trans.* **1996**; *92*, 317-23.
273. Huddersman, K.; Patruno, V.; Blacke, G. J.; Dahm, R. H. *J. Soc. Dyers Colourists* **1998**, *114,* 155-159.
274. Tsai, W. T.; Hsien, K. J.; Hsu; H. C. *J. Hazard. Mater.* **2009**, *166,* 635-641.
275. Meshko, V.; Markovska, L.; Mincheva, M.; Rodrigues, A. E. *Water Res.* **2001**, *35,* 3357-3366.
276. Karadag, D.; Akgul, E.; Tok, S.; Erturk, F.; Kaya, M. A.; Turan, M. *J. Chem. Eng. Data* **2007**, *52*, 2436-2441.
277. Karadag, D.; Turan, M.; Akgul, E.; Tok, S.; Faki, A. *J. Chem. Eng. Data* **2007**, *52***,** 1615-1620.
278. Benkli, Y. E.; Can, M. F.; Turan, M.; Celik, M. S. *Water Res.* **2005**, *39,* 487-493.
279. Armagan, B.; Ozdemir, O.; Turan, M.; Celik, M. S. *J. Chem. Technol. Biotechnol.* **2003**, *78,* 725-732.
280. Ozdemir O.; Turan M.; Turan, A. Z.; Faki, A.; Engin, A. B. *J. Hazard. Mater.* **2009**, *166,* 647-654.
281. Capasso, S.; Salvestrini, S.; Coppola, E.; Buondonno, A.; Colella, C. *Appl. Clay Sci.* **2005**, *28,* 159-165.
282. Capasso, S.; Coppola, E.; Iovino, P.; Salvestrini, S.; Colella, C. *Microporous Mesoporous Mater.* **2007**, *105,* 324-328.
283. Wang, S.; Terdkiatburana, T.; Tadé, M. O. *Sep. Purif. Technol.* **2008**, *62***,** 64-70.
284. Wang, S. G.; Gong, W. X.; Liu, X. W.; Gao, B. Y.; Yue, Q. Y. *Sep. Purif. Technol.* **2006**, *51,* 367-373.
285. Li, C.; Dong, Y.; Wu, D.; Peng, L.; Kong, H. *Appl. Clay Sci.* **2011**, *52,* 353-357.
286. Dong, Y.; Wu, D.; Chen, X.; Lin, Y. *J. Colloid Interface Sci.* **2010**, *348,* 585-590.
287. Tsai, W. T.; Hsu, H. C.; Su, T. Y.; Lin, K. Y.; Lin, C. M. *J. Colloid Interface Sci.* **2006**, *299***,** 513-519.

288. Kuleyin, A. *J. Hazard. Mater.* **2007**, *144,* 307-315.
289. Muñiz-Lopez, C.; Duconge, J.; Roque-Malherbe, R. *J. Colloid Interface Sci.* **2009**, *329,* 11-16.
290. Ranck, J. M.; Bowman, R. S.; Weeber, J. L.; Katz, L. E.; Sullivan, E. J. *J. Envir. Eng.* **2005**, *131,* 434-442.
291. Altare, C. R.; Bowman, R. S.; Katz, L. E.; Kinney, K. A.; Sullivan, E. J. *Microporous Mesoporous Mater.* **2007**, *105,* 305-316.
292. Ghiaci, M.; Abbaspur, A.; Kia, R.; Seyedeyn-Azad, F. *Sep. Purif. Technol.* **2004**, *40*, 217-229.
293. Ersoy, B.; Celik, M. S. *Environ. Technol.* **2004**, *25*, 341-348.
294. Lemic, J.; Kovacevic, D.; Tomasevic-Canovic, M.; Kovacevic, D.; Stanic, T.; Pfend, R. *Water Res.* **2006**, *40,* 1079-1085.
295. Lemic, J.; Kovacevic, D.; Tomasevic-Canovic, M.; Kovacevic, D.; Stanic, T.; Pfend, R. *Water Res.* **2006**, *40,* 1079-1085.
296. Bai, Y.; Sun, O.; Xing, R.; Weṇ, D̃.; Tang, X. *J. Hazard. Mater.* **2010**, *181,* 916-922.
297. Cui, J.; Zhang, X.; Liu, H.; Liu, S.; Yeung, K. L. *J. Membr. Sci.* **2008**, *325,* 420-426.
298. Collins, E. D. The three mile island accident and post-accident recovery – What did we learn? Chem. Technol. Division, Oak Ridge Natl. Lab., Conf. Report CONF-820559-1, 1982.
299. Cui, J.; Zhang, X.; Liu, H.; Liu, S.; Yeung, K. L. *J. Membr. Sci.* **2008**, *325,* 420-426.
300. Garcia, J. E.; Gonzalez, M. M.; Notario, J. S. *Appl. Clay Sci.* **1992**, *7(4),* 323-333.
301. Schulze- Makuch, D.; Bowman, R. S.; Pillay, S. Removal of biological pathogens using surfactant-modified zeolite. U.S. Patent No. 7,311,839, December 25, 2007.
302. Nikashina, V. A.; Myaosedov, B. F. Environmental applications of modified natural zeolites, P. Misaelides, Ed.; Natural Microporous Materials in Environmental Technology, Kluwer Academic Publishers, The Netherlands, 1999, pp. 335-343.
303. Naftz, D.; Morrison, S.; Fuller, C.; Davis, J. Handbook of Groundwater Remediation using Permeable Reactive Barriers, Elsevier, Amsterdam, 2002. pp. 544.
304. Hornig, G.; Northcott, K.; Snape, I.; Stevens, G. *Cold Reg. Sci. Technol.* **2008**, *53,* 83-91.
305. Woinarski, A. Z.; Stevens, G. W.; Snape, I. *Proc. Safety Environ. Protect.* **2006**, *84*, 109-116.
306. Akili, D.; Khawaji, A. D.; Kutubkhanah, I. K.; Wie, J. M. *Desalination* **2008**, *221,* 47-69.
307. Lee, K.P.; Arnot, T. C.; Mattia, D. *J. Membr. Sci.* **2011**, *370*, 1–22.
308. Costa, E.; Lucas, A.; Uguina, M. A.; Ruiz, J. C. *Ind. Eng. Chem. Res.* **1988**, *27,* 1291-1296.
309. Kazemimoghadam, M. *Desalination* **2010,** *251,* 176–180.
310. Li, L.; Dong, J.; Nenoff, T. M.; Lee, R. *J. Membr. Sci.* **2004**, *243*, 401–404.
311. Duke, M.C.; O'Brien-Abraham, J.; Milne, N.; Zhu, B.; Lin, J. Y. S.; Diniz da Costa, J. C. *Sep. Purif. Technol.* **2009**, *68*, 343–350.
312. Li, L.; Dong, J.; Nenoff, T. M. *Sep. Purif. Technol.* **2007**, *53*, 42–48.
313. Khajavi, S.; Jansen, J. C.; Kapteijn, F., *J. Membr. Sci.* **2010**, *356*, 52–57.
314. Cho, C̃. H.; Oh, K. Y.; Kim, S. K.; Yeo, J. G.; Sharma, P. *J. Membr. Sci.* **2011**, *371,* 226-238.
315. Ciobanu, G.; Carja, G.; Ciobanu, O. *Mater. Sci. Eng.* **2007**, *C27*, 1138–1140.
316. Fathizadeh, M.; Aroujalian, A.; Raisi, A. *J. Membr. Sci.* **2011**, *375*, 88–95.