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Review

Natural zeolites as effective adsorbents in water and wastewater treatment

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ABSTRACT

Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past decades. In this paper, we review the recent development of natural zeolites as adsorbents in water and wastewater treatment. The properties and modification of natural zeolite are discussed. Various natural zeolites around the world have shown varying ion-exchange capacity for cations such as ammonium and heavy metal ions. Some zeolites also show adsorption of anions and organics from aqueous solution. Modification of natural zeolites can be done in several methods such as acid treatment, ion exchange, and surfactant functionalisation, making the modified zeolites achieving higher adsorption capacity for organics and anions.

1. Introduction

Nowadays, the world is facing water crisis due to lacking of clean drinking water. With the fast development of various industries, a huge quantity of wastewater has been produced from industrial processes and was discharged into soils and water systems. Wastewater usually contains many pollutants such as cationic and anionic ions, oil and organics, which have poisonous and toxic effects on ecosystems. Removal of these contaminants requires cost effective technologies and a variety of techniques have been developed in the past decades in dealing with wastewater treatment. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent. Activated carbon [1], clay minerals [2,3], biomaterials [4], zeolites [5,6], and some industrial solid wastes [7,8] have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment.

Since the original discovery of zeolitic minerals in a volcanogenic sedimentary rock, zeolitic tuffs have been found in many areas of the world. In the past decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy [9,10]. It has been estimated that the world natural zeolite consumption is 3.98 Mt and will reach 5.5 Mt in 2010 [11].

Natural zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption. The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Application of natural zeolites for water and wastewater treatment has been realised and is still a promising technique in environmental cleaning processes. In the past decades, utilisation of natural zeolites has been focussed on ammonium and heavy metal removal due to the nature of ion exchange and some review papers have been appeared [6,12,13]. Apart from the presence of cations in water, anions and organic compounds are widely presented in wastewater. In recent years, natural zeolite and its modified forms have also been reported for removal of anions and organics from water systems. However, no such a review has been found. In this paper, we will update the recent research in cation adsorption using natural zeolites as well as their modified forms for removal of anions and organic compounds in water and wastewater treatment.

2. Properties of natural zeolite

There are many natural zeolites identified in the world. Clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and laumontite are very common forms whereas offretite, paulingite, barrerite and mazzite, are much rarer. Among the zeolites, clinoptilolite is the most abundant natural zeolite and is widely used in the world. In zeolite structure, three relatively independent components are found: the aluminosilicate framework, exchangeable

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Table 1
Structural properties of some natural zeolites.

Zeolite	Chemical formula	Structure type	Symmetry, space group
Clinoptilolite	$(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72}\cdot 21H_2O$	HEU	Monoclinic, C2/m
Mordenite	$(Na_2, Ca)_4Al_8Si_{40}O_{96}\cdot 28H_2O$	MOR	Orthorhombic, Cmcm
Chabazite	$(Ca, Na_2, K_2)_2Al_4Si_8O_{24}\cdot 12H_2O$	CHA	Rhombohedral or triclinic P1
Phillipsite	$K_2(Ca, Na_2)_2Al_8Si_{10}O_{32}\cdot 12H_2O$	PHI	Monoclinic, $P2_1/m$
Scolecite	$Ca_4Al_8Si_{12}O_{40}\cdot 12H_2O$	NAT	Monoclinic,Cc
Stilbite	$Na_2Ca_4Al_{10}Si_{26}O_{72}\cdot 30H_2O$	STI	Monoclinic, C2/m
Analcime	$Na_{16}Al_{16}Si_{32}O_{96}\cdot 16H_2O$	ANA	Cubic Ia3d
Laumontite	$Ca_4Al_8S_{16}O_{48}\cdot 16H_2O$	LAU	Monoclinic, C2/m
Erionite	$(Na_2K_2MgCa_{1.5})_4Al_8Si_{28}O_{72}\cdot 28H_2O$	ERI	Hexagonal $P6_3/mmc$
Ferrierite	$(Na_2, K_2, Ca, Mg)_3Al_6Si_{30}O_{72}\cdot 20H_2O$	FER	Orthorhombic, Immm Monoclinic, $P2_1/n$

cations, and zeolitic water. The general chemical formula of zeolites is $M_{x/n}[Al_xSi_yO_{2(x+y)}]\cdot pH_2O$ where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1–6$, $p/x = 1–4$.

The primary building block of zeolite framework is the tetrahedron, the centre of which is occupied by a silicon or aluminium atom, with four atoms of oxygen at the vertices. Substitution of Si^{4+} by Al^{3+} defines the negative charge of the framework, which is compensated by monovalent or divalent cations located together with water. The aluminosilicate framework is the most conserved and stable component and defines the structure type. The water molecules can be present in voids of large cavities and bonded between framework ions and exchangeable ions via aqueous bridges. The water can also serve as bridges between exchangeable cations. Table 1 presents the chemical formula and structure of some important natural zeolites.

Zeolites are capable of exchanging ions with external medium, which is the significant characteristic of zeolite. Ion exchange proceeds in an isomorphous fashion. The equilibrium ion exchange is expressed by the following equation

$$z_B A^{z_A^+} + z_A BL_{z_B} \Leftrightarrow z_A B^{z_B^+} + z_B AL_{z_A} \quad (1)$$

where z_A^+ and z_B^+ are the valences of the respective cations, and L is defined as a portion of zeolite framework holding unit negative charge.

The ion-exchange behaviour of natural zeolite depends on several factors, including the framework structure, ion size and shape, charge density of the anionic framework, ionic charge and concentration of the external electrolyte solution [9,14]. Due to the formation environment, natural zeolite has varying chemical composition and cation-exchange capacity (CEC). Table 2 shows the chemical composition and cation-exchange capacity of various natural zeolites from the world. It is seen that the CEC is between 0.6 and 2.3 meq/g.

3. Modification of natural zeolite

The adsorption characteristics of any zeolite are dependent upon the detailed chemical/structural makeup of the adsorbent. The Si/Al ratio, cation type, number and location are particularly influential in adsorption. These properties can be changed by several chemical treatments to improve separation efficiency of raw natural zeolite. Acid/base treatment and surfactant impregnation by ion exchange are commonly employed to change the hydrophilic/hydrophobic properties for adsorption of various ions or organics.

3.1. Acid/base treatment

In general, acid washing of natural zeolite may remove impurities that block the pores, progressively eliminate cations to change into H-form and finally dealuminate the structure. There are two main types of modification procedure, which can be used to form proton exchanged zeolite; ammonium exchange followed by calcination and direct ion exchange with dilute acid solution. Ammonium exchange can maintain the stable structure while acid

Table 2
Chemical composition and CEC of natural zeoltes in the world.

Zeolite	Chemical composition (%)								CEC (meq/g)	Reference
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2		
Turkey clinoptilolite	70.90	12.40	1.21	2.54	0.83	0.28	4.46	0.089	1.6–1.8	[15]
Iranian clinoptilolite	70.00	10.46	0.46	0.2	–	2.86	4.92	0.02	–	[16]
Cuba clinoptilolite	62.36	13.14	1.63	2.72	1.22	3.99	1.20	–	–	[17]
Brazil mordenite	67.82	14.96	0.42	1.87	0.18	0.32	4.47	0.07	2.29	[18]
Italy phillipsite + chabazite	56.42	15.8	4.08	2.42	0.86	2.35	8.14	0.004	2.12	[19]
Turkey clinoptilolite	69.72	11.74	1.21	2.30	0.31	0.76	4.14	–	1.84	[20]
Chinese clinoptilolite	65.52	9.89	1.04	3.17	0.61	2.31	0.88	0.21	1.03	[21]
Chilean clinoptilolite + mordenite	67.00	13.00	2.00	3.20	0.69	2.60	0.45	0.20	2.05	[22]
Turkey clinoptilolite	69.31	13.11	1.31	2.07	1.13	0.52	2.83	–	–	[23]
Croatia clinoptilolite	64.93	13.39	2.07	2.00	1.08	2.40	1.30	–	1.45	[24]
Iranian clinoptilolite + mordenite	66.5	11.81	1.3	3.11	0.72	2.01	3.12	0.21	1.20	[25]
Turkey clinoptilolite	64.99	9.99	3.99	3.51	1.01	0.18	1.95	–		[26]
Chinese clinoptilolite	68.27	7.48	1.95	2.61	1.87	0.68	1.69	–	–	[27]
Turkey clinoptilolite	70.00	14.00	0.75	2.50	1.15	0.20	2.30	0.05		[28]
Chinese clinoptilolite	69.5	11.05	0.08	2.95	0.13	2.95	1.13	0.14	–	[29]
Ukrainian clinoptilolite	67.29	12.32	1.26	3.01	0.29	0.66	2.76	0.26	–	[30]
Ukrainian mordenite	64.56	12.02	0.95	3.58	0.68	0.94	2.03	0.23	–	[30]
Slovakian clinoptilolite	67.16	12.30	2.30	2.91	1.10	0.66	2.28	0.17	–	[31]
Croatian clinoptilolite	55.80	13.32	1.30	5.75	0.70	3.90	2.35	–		[32]
Ukraine clinoptilolite	66.7	12.3	1.05	2.10	1.07	2.06	2.96	–	0.64	[33]
Australian clinoptilolite	68.26	12.99	1.37	2.09	0.83	0.64	4.11	0.23	1.20	[34]

treatment generally results in dealumination and reduction of thermal stability.

Kurama et al. [35] investigated the conversion of a natural Turkish clinoptilolite to hydrogen form by the two ways, ammonium exchange followed by calcination and direct treatment with HCl. They found that the ion exchange with H^+ has a great influence on the effective pore volume and surface area of clinoptilolite. The pore volume and surface area are increased from 0.13 to 0.25 mL/g and from 35 to 315 m^2/g, respectively. Cakicioglu-Ozkan and Ulku [36] reported a study of acid treatment of a Bigadic clinoptilolite using HCl solution at varying concentrations (0.032, 0.16, 0.32, 1.6 or 5 M) and temperatures (25, 40, 75 and 100 °C). They found that super-micropore volume was not very sensitive to acid treatment but the Langmuir surface area and ultra-micropore volume depend on the degree of the removal of aluminium from the structure.

A natural zeolite, stilbite, from China was treated in hot HCl solution. The modification leads to the variation in framework dealumination, resulting in the modified zeolites with different thermal stabilities and adsorption property. High silica H-STI zeolites prepared with NH_4^+ exchange and followed by calcination in fluid air exhibit thermal stability up to 1000 °C with open and perfect channel systems. The H-form STI zeolite possesses high ion-exchange capacity of Ag^+ [37].

The stability and effective ion-exchange capacity (E_{fCEC}) of a Mexican clinoptilolite were also investigated upon treatment by acid phosphate solutions. The results show that the pH of the phosphate solutions influences the stability and E_{fCEC} of the clinoptilolite-rich tuff. At pH 0, the dealumination of the clinoptilolite takes place, it loses crystallinity and its E_{fCEC} diminishes. When the pH is increased to 4 or 6, changes in the crystallinity are not observed and the amount of aluminium is similar to clinoptilolite-rich tuff without treatment, but the E_{fCEC} is slightly increased [38].

Three zeolites from Armenia, Georgia and Greece were treated with dilute KOH and subsequently either reacted with HCl or heated at 700 °C. KOH treatment increased slightly specific surface area and microporosity due to dissolution of amorphous material. Acid treatment increases significantly both the specific surface area and microporosity and decreases the cation-exchange capacity due to partial dissolution of both Si-tetrahedra and free linkages, which yields secondary micropores and destroys specific exchange sites of the zeolites. Heating decreases both specific surface area and microporosity [39].

Therefore, it is deduced that acid treatment will reduce the cation-exchange capacity due to dealumination but it can improve capacity and Si/Al ratio offering advantages for the adsorption/separation of non-polar molecules from water or gas flows.

3.2. *Surfactant modification*

Due to the net negative charge on the framework, raw natural zeolites usually have little or no affinity for anions and exhibit low adsorption for organics in aqueous solution. To change the surface properties, one modification method widely employed is to use organic surfactants. In the past, many investigations have been conducted on modification of natural zeolite with cationic surfactants and then use to remove multiple types of contaminants from water. The surfactants are tetramethylammonium [40,41], cetyltrimethylammonium (CTMA)[42,43], hexadecyltrimethylammonium (HDTMA)[40,44–49], octadecyldimethylbenzyl ammonium (ODMBA)[42,50–52], n-cetylpyridinium(CPD) [53], benzyltetradecyl ammonium (BDTDA) [49], stearyldimethylbenzylammonium (SDBAC)[54,55], N,N,N,N′,N′,N′-hexamethyl-1,9-nonanediammonium [56], and polyhexamethylene-guanidine[57].

It has been found that surfactant modification depends on the degree of surfactant adsorption on zeolite. A general model of sorption of ionic surfactants on a solid surface is the formation of a monolayer or "hemimicelle" at the solid–aqueous interface via strong Coulombic (ionic) bonds at surfactant concentrations at or below its critical micelle concentration (CMC). If the surfactant concentration in solution exceeds the CMC, then the hydrophobic tails of the surfactant molecules associate to form a bilayer or "admicelle" as shown in Fig. 1 [48]. Thus, surfactant-modified zeolite can have a complex functional groups for positively charged exchange sites formed by the positive groups $-NR^+$ of the surfactant directed towards the surrounding solution in the bilayer.

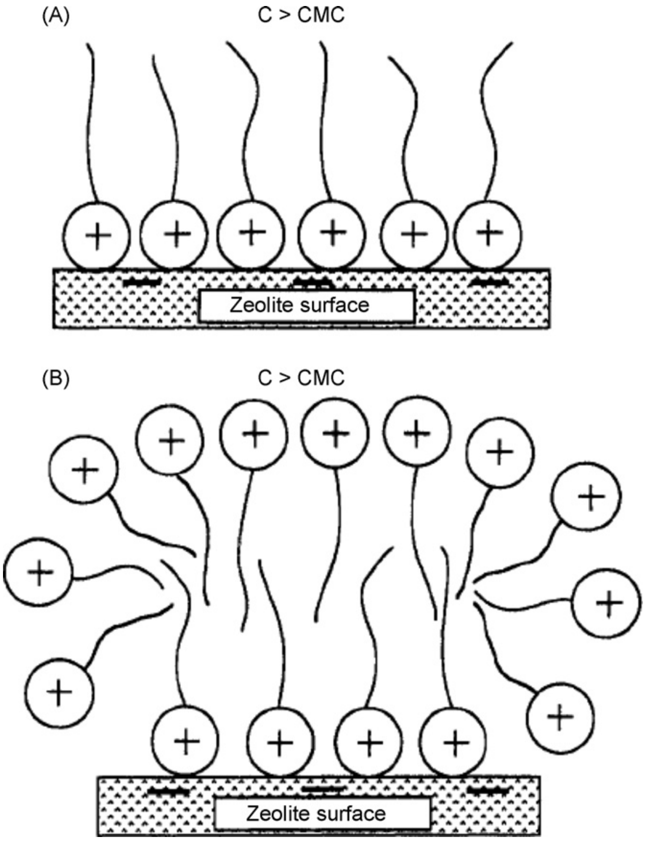

Fig. 1. Hemimicelle (A) and admicelle (B) formation by cationic surfactants on zeolite surface [48].

4. Application for water treatment

Surface water, ground water, and industrial or household wastewater contains many different types of pollutants. These pollutants include inorganic and organic compounds and are more or less hazardous to human being, animals and plants. In the following sections, more recent applications of natural zeolites and their modified forms for removal of various pollutants from water are discussed in detail.

4.1. *Ammonium*

Ammonium is an important nitrogen ion form in aqueous solution. Its pollution mainly comes from municipal sewage, fertiliser factory wastewater and agricultural wastes. Ammonia nitrogen contributes to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving waters. Higher concentration of ammonium will cause a sharp decrease of dissolved oxygen and obvious toxicity on aquatic organisms. In the past decades, various methods of ammoniacal nitrogen removal from waters have been developed; biological treatments and adsorption are the widely used methods. Natural zeolite from

Table 3
Ammonium adsorption on natural zeolite.

Material	Capacity (mg/g)	Temperature (°C)	Reference
New Zealand clinoptilolite	7.1–8.6	–	[59]
NaOH–clinoptilolite	7.3–8.4	–	[59]
$NaHCO_3$–clinoptilolite	8.1–9.3	–	[59]
HCl–clinoptilolite	13.4–16.8	–	[59]
New Zealand clinoptilolite	8.5	–	[68]
New Zealand mordenite	12.2	–	[68]
Croatian clinoptilolite	13.6	–	[32]
Croatian clinoptilolite	7.7–17.6	–	[24]
Chinese clinoptilolite	2.7–3.2	20	[65]
Chinese clinoptilolite	18.5	–	[21]
Chinese Ca–clinoptilolite	20.2–26.3	20–60	[27]
Chinese clinoptilolite	11.2	–	[69]
Chinese Na–clinoptilolite	22.6	–	[69]
Chinese clinoptilolite	12.3–12.9	25	[66]
Biofilm–clinoptilolite	9.6–13.2	25	[66]
Chinese zeolite-microwave	30.6	25	[29]
Turkish clinoptilolite	5.2–8.1	25–55	[64]
Turkey clinoptilolite	5.7–7.7	30	[28]
Turkey clinoptilolite	14.5–15.4	23–70	[26]
Canada clinoptilolite	18.4–22.9	20	[70]
USA clinoptilolite	18.5	20–21	[71]
Na–clinoptilolite	20.5	20–21	[71]
Ukraine–clinoptilolite	6.6–21.5	–	[33]
Chilean natural zeolite	11.4–14.8	–	[22]
Iranian clinoptilolite	17.8	28	[16]

various sources was explored as an effective adsorbent. Table 3 summarises NH_4^+ adsorption capacity on various sourced natural zeolites. Based on the table, it is seen that ammonium adsorption on natural zeolite is 2.7–30.6 mg/g.

Cooney et al. [58] undertook a laboratory study of a natural Australian zeolite, clinoptilolite, to remove ammonium from water. They investigated the equilibria and kinetic characteristics of ammonium exchange in the zeolite under binary and multi-component conditions. The results revealed that the highest ammonium removal efficiency was achieved when the zeolite's exchange sites were converted to the sodium form. For a multi-component system there was a competitive effect between ammonium 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. Rozic et al. [32] investigated the removal of ammonium ion from aqueous solutions using a Croatian clinoptilolite and bentonite. The highest removal efficiency for N–NH_4^+(61.1 wt%) was achieved with the natural zeolite at the lowest initial concentration, i.e. 100 mg N–NH_4^+/L. With the increase of the initial concentration of ammoniacal nitrogen, the removal efficiency quickly decreased. For the clay, the ammoniacal nitrogen removal efficiency was higher in a liquid colloidal state and the acid modification of the clay decreased the efficiency of ammoniacal nitrogen removal.

A clinoptilolite from New Zealand was treated with alkali solutions and evaluated to remove NH_4^+ ions from a fellmongery wastewater stream [59]. It was found that after treatment the cation-exchange capacity of the natural zeolite was increased by up to 74% and the zeolite could hold a potential maximum of 18.7–20.1 mg NH_4^+/g. The presence of other cations in the fellmongery wastewater apparently interfered with NH_4^+ ion adsorption, resulting in only a small fraction of the CEC getting occupied by the NH_4^+ ions. The cation-loaded zeolite could be regenerated for NH_4^+ ion adsorption by leaching with 0.5 M HCl, and NH_4^+ adsorption remained unaffected after 12 regeneration cycles.

Lebedynets et al. [60] carried out a study of NH_4^+ sorption from synthetic aqueous solutions by a Ukraine clinoptilolite. NH_4^+ sorption by the zeolite would be completed within 24 h for all fraction sizes, initial NH_4^+ ion concentrations and adsorbate volumes. The amounts of NH_4^+ ions sorbed increased with increasing initial NH_4^+ concentration and decreasing adsorbate volumes, with the maximum sorption capacity of 11.5 mg/g. Sprynskyy et al. [33] investigated NH_4^+ uptake from synthetic aqueous solutions onto raw and pretreated forms of the same clinoptilolite under dynamic conditions. NH_4^+ uptake onto the zeolite occurred by exchange with Na^+, Ca^{2+}, and K^+ ions. Although Na^+ ions were observed to be more easily exchanged for both hydrogen and ammonium ions, the role of Ca^{2+} ions increased with zeolite saturation by NH_4^+ ions. The maximum sorption capacity of the clinoptilolite towards NH_4^+ ions, estimated under dynamic conditions, was significantly higher than that measured under static conditions. A recycling study confirmed the importance of external diffusion for ammonium sorption by the clinoptilolite. Preliminary treatment of the sorbent by heat, acid, and NaCl confirmed the predominant importance of the ion-exchange mechanism. NaCl treatment of the clinoptilolite showed an improvement of ammonium removal over other treatments.

Englert and Rubio [22] used a Chilean natural zeolite as an adsorbent for ammonia removal from aqueous solutions. The tests showed the particles were negatively charged over a broad pH range with 18.4 mg NH_4^+/g cation-exchange capacity. The ammonia removal appeared to proceed through rapid kinetics at neutral pH value, with removal capacities up to 0.68 meq NH_4^+/g. Watanabe et al. [61] carried out a modification of Japanese natural zeolites under hydrothermal conditions to improve the effectiveness of the uptake of ammonium ions. The samples were treated with 0.1, 0.3, 1.0 and 3.0 M NaOH solutions at temperatures from 25 to 150 °C under autogenous pressure for 7 days. After the hydrothermal treatment, the transformation of the zeolites to phillipsite, hydroxyl-sodalite and analcime was observed. The treated products, containing mainly phillipsite, took up twice the amount of ammonium ions as the starting materials. The maximum uptake of ammonium ions was 34.6 mg/g. Farkas et al. [24] studied the adsorption of ammonium ions and organic pollutants on a natural clinoptilolite in the treatment of 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. After pretreated by activated carbon, the exchange of ammonium ions on the zeolite was increased to 5.7 mg NH_4^+/g. In the ammonium solution, the exchange was 17.70 mg NH_4^+/g, suggesting that organic pollutants and K^+ and Ca^{2+} ions in leakage water prevented the exchange of NH_4^+ ions.

Jorgensen and Weatherley [62] investigated three cationic exchangers including natural clinoptilolite, a gel resin (Dowex 50w-x8), and a macronet resin (Purolite MN-500) for the removal of ammonia from wastewaters after secondary biological treatment. The results showed that the presence of organic compounds had variable effects on ammonium ion uptake. For the clinoptilolite a very significant increase in column breakthrough performance was observed after cycles of exhaustion and regeneration. Regenerated clinoptilolite showed a maximum breakthrough capacity of 450 bed volumes.

The kinetic and equilibrium of ammonium ion uptake from aqueous solutions using a Romanian zeolite tuff and synthetic zeolites (5A, 13X and ZSM-5) was reported by Maranon et al. [63]. The influences of contact time, pH, ammonium concentration, presence of other cations and anion species were investigated. Adsorption capacities of 19 mg NH_4^+/g were obtained in multi-component solutions (containing NH_4^+, Zn^{2+}, Cd^{2+}, Ca^{2+}, Na^+). The presence of Zn and Cd at low concentrations did not affect the ammonium adsorption capacity. Comparison between natural and synthetic zeolites, the removal efficiencies of ammonium by zeolite tuff were similar to those of zeolites 5A and 13X at low initial ammonium concentration, and much higher than those of zeolite ZSM-5. A study of kinetics and equilibrium isotherms of ammonium ion on a natural Turkish clinoptilolite was also conducted using a batch experimental technique [64]. The effects of relevant parameters, such as temperature, contact time, and initial ammonium concentration were examined. The Langmuir and Freundlich models were applied to describe the equilibrium isotherms for ammonium uptake and the Langmuir model agreed very well with experimental data. Thermodynamic parameters showed that the exchange of ammonium ion by the clinoptilolite is spontaneous and exothermic process.

Some natural Chinese clinoptilolites were also tested for ammonia removal. Wang et al. [65] assessed the application for ammonia removal from the leachate solution of sewage sludge in batch study. The effects of relevant parameters, such as contact time, initial ammonia concentration, and particle size of clinoptilolite, were examined, respectively. The results show that the Langmuir isotherms reflect more reasonable for ammonium ion uptake onto the clinoptilolite with the maximum adsorption capacity of 1.74 mg NH_4–N/g. Wen et al. [66] studied the sorption kinetics of ammonium onto three types of zeolite, natural zeolite, natural zeolite covered by biofilm, and ammonium-bearing zeolite covered by biofilm. Ion exchange between NH_4^+ and cations in the zeolite increased with decreasing particle size of the zeolite. Biofilm covered on the zeolite did not affect the ion exchange for the smaller particle size but decreased the ion-exchange capacity by 22% for the larger particle size. Bioregeneration could recover 78.0 and 63.9% ion-exchange capacity for the smaller and larger particle size of zeolite, respectively. Equilibrium studies showed that the adsorption system was well fitted by the Freundlich isotherm [67]. Lei et al. [29] compared the effect of pre-treatment method of a natural Chinese zeolite on ammonium adsorption. Adsorption kinetics, adsorption equilibrium isotherms and the effects of the individual presence of other cations and humic acid on the removal of ammonium were investigated. The zeolite treated under microwave irradiation had the highest ammonium adsorption capacity value, followed by the zeolite obtained by thermal process and the untreated zeolite. Five isotherm models were used to describe the isotherm data and the three-parameter isotherm models (Redlich–Peterson and Langmuir–Freundlich) provided much better fitting to isotherm data than two-parameter isotherm models (Freundlich, Temkin and Langmuir). The presence of Na^+, K^+, Ca^{2+} and Mg^{2+} could reduce the uptake of ammonium onto the zeolite treated under microwave irradiation and the order of ammonium ion over other cations was $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$, while the presence of humic acid increased the uptake of ammonium.

A natural Bigadic clinoptilolite was evaluated for NH_4^+ adsorption [26]. Thermodynamic investigation indicated that ammonium removal by the clinoptilolite was favourable at lower temperatures and exothermic in nature. Different isotherm models were evaluated for fitting the equilibrium data and Khan's model had better performance for modelling the equilibrium data. Recently, Hedstrom and Amofah [72] performed column experiments to estimate the ammonium adsorption capacity of clinoptilolite. Results showed the ammonium adsorption capacity increased with decreasing grain size, and the highest experimental adsorption capacity was 2.7 mg NH_4–N/g. The breakthrough occurred immediately due to a too high loading rate. About 23% of adsorbed ammonium could be desorbed by tap water and desorption was more pronounced during saturated conditions. An Iranian natural clinoptilolite for ammonia removal from aqueous solutions has also been thoroughly studied by Ashrafizadeh et al. [16]. Both batch and column experiments were carried out. Through the batch experiments, it was found that ammonia removal occurred rapidly within the first 15 min of contact time. An adsorption capacity about 17.8 mg NH_4^+/g at feed ammonia concentration of 50 mg/L was obtained and the optimum range for pH was about 5.5–7.6. The adsorption capacity of clinoptilolite in the continuous mode was about 15.16 and 15.36 mg NH_4^+/g for the original and regenerated types of clinoptilolite, respectively. The presence of cations such as Ca^{2+}, Mg^{2+} and Na^+ in the feed solution reduced the clinoptilolite adsorption capacity to about 11.68 mg NH_4^+/g.

It has been shown that the main mechanism that accounts for the adsorption of ammonium ion onto natural zeolites is ion exchange. The results in Table 3 have demonstrated that adsorption capacity of clinoptilolite is 2–30 mg NH_4^+/g. Some treatments of clinoptilolite zeolite could increase adsorption capacity, especially after Na^+ exchange due to high affinity of NH_4^+ over Na^+. For other types of natural zeolite, ion exchange with NH_4^+ is similar to clinoptilolite. The ion-exchange order of zeolite for alkali metal, alkaline earth metal and NH_4^+ ions is $Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Na^+ > Ca^{2+} > Li^+$. However, other components in solution such as heavy metal ions and organics will reduce ammonium exchange capacity due to competitive adsorption. Natural zeolite after ammonium adsorption can be regenerated by Na or K ion exchange or by heat treatment for NH_3 devolatilisation.

4.2. *Heavy metal ions*

Contamination of heavy metals in water supplies has steadily increased over the last decades as a result of over population and expansion of industrial activities. The presence of heavy metals in the environment is a major concern due to their toxicity. It has been found that many heavy metal ions produce strong health problem and damage to plants and animals. Most of these heavy metals present in polluted waters include Hg, Pb, Ag, Cu, Cd, Cr, Zn, Ni, Co and Mn. In the past, many investigations have been conducted using natural zeolite for metal ion adsorption and several review works have been appeared [12,14]. However, these investigations focussed on single metal ion and the affinity to zeolite. While for real wastewater systems, there are different types of contaminants and may contain a mixture of metal ions. In recent years, more investigations have concentrated in this area. Table 4 presents the adsorption capacity of various metal ions on different natural zeolites.

Panayotova [73] conducted a series of experiments using a Bulgarian natural zeolite and modified forms for removal of several metal ions such as Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}. In Ni^{2+} adsorption, natural and NaOH-, NaCl-, HCl-, and CH_3COONa-modified zeolites have been tested in a batch process. For raw zeolite, the uptake process obeys the first-order irreversible kinetics. The uptake equilibrium is best described by the Langmuir adsorption isotherm. Zeolite modification with CH_3COONa and NaCl can increase Ni^{2+} adsorption by 25–30%. The raw and modified zeolites will be easily regenerated in 2 M NaCl solution. For Cu^{2+} removal, 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+} does not significantly influence the uptake of Cu^{2+} [74]. The uptake equilibrium is best described by the Langmuir adsorption isotherm with maximum adsorption of 6.74 mg/g. The zeolites modified by NaCl, CH_3COONa and NaOH exhibit higher uptake ability. Kinetics and thermodynamics of uptake of Cd^{2+} by natural and modified zeolites have shown the second-order irreversible reactions and the equilibrium data obtained were best fit to Freundlich adsorption isotherm [75]. But uptake of Cd^{2+} was considerably decreased in the presence of Ca^{2+} and Mg^{2+} and the zeolite treated with NaCl and CH_3COONa showed the highest uptake ability.

Panayotova and Velikov [76] further studied the kinetics of the uptake of cadmium, lead, copper, nickel and zinc ions from single ion solutions and from their mixture by the Bulgarian zeolitic rock. It was found that lead ions were strongly immobilised by the zeolite, in single ion and mixed solutions, as well as soft and hard water. Further investigation indicated that pre-treatment of zeolite with NaCl leads to increased rate of heavy metal ions' immobilisation, as

Table 4
Adsorption of heavy metal ions on various natural zeolites.

Material	Metal	Adsorption (meq/g)	Reference
Sardinian clinoptilolite	Cu^{2+}	0.34	[78]
	Cd^{2+}	0.05–0.19	
	Pb^{2+}	0.27–1.2	
	Zn^{2+}	0.1	
Turkish clinoptilolite	Pb^{2+}	0.299–0.730	[82]
	Zn^{2+}	0.108–0.251	
	Cu^{2+}	0.022–0.227	
	Ni^{2+}	0.017–0.173	
Natural phillipsite	Pb^{2+}	0.234–0.345	[81]
Natural clinoptilolite	Cr^{3+}	0.237	[95]
	Ni^{2+}	0.068	
	Zn^{2+}	0.106	
	Cu^{2+}	0.186	
	Cd^{2+}	0.082	
Clinoptilolite	Cd^{2+}	0.12–0.18	[87]
Scolecite	Pb^{2+}	0.056	[94]
	Cu^{2+}	0.130	
	Zn^{2+}	0.064	
	Ni^{2+}, Co^{2+}	0.031	
	Cd^{2+}	0.0078	
		0.0032	
Bigadic clinoptilolite	Pb^{2+}	0.222	[85]
	Zn^{2+}	0.734	
	Cd^{2+}	0.0053	
Mexican clinoptilolite	Pb^{2+}	1.4	[80]
Ukraine clinoptilolite	Pb^{2+}	0.134	[84]
	Cu^{2+}	0.405	
	Ni^{2+}	0.222	
	Cd^{2+}	0.0375	
Turkish clinoptilolite	Co^{2+}	0.448	[23]
	Cu^{2+}	0.282	
	Zn^{2+}	0.268	
	Mn^{2+}	0.153	
Brazilian scolecite	Cr^{3+}	5.81	[97]
	Ni^{2+}	2.08	
	Cd^{2+}	1.78	
	Mn^{2+}	4.00	

well as to increased distribution coefficients. However, zeolite pretreatment with NaCl practically does not change zeolite selectivity sequence for the ions in multi-component solutions [77]. Cincotti et al. [78] examined Sardinian natural clinoptilolites for removal of heavy metals, i.e., lead, cadmium, copper, and zinc in as-received and sodium homoionic forms. A selectivity scale Pb > Cu > Cd ∼ Zn was found based on maximum metal removal.

Inglezakis et al. [79] presented a study of using natural clinoptilolite and bentonite to remove Pb^{2+} from aqueous solutions. Bentonite was found to be more effective for the removal of Pb^{2+} than clinoptilolite under the experimental conditions used. The removal of Pb^{2+} using bentonite reached 100% at ambient temperature and mild agitation (100 rpm) while the highest removal level reached by clinoptilolite was 55%. Clinoptilolite dust is found to be more efficient than granular clinoptilolite. Agitation and temperature affected the uptake of Pb^{2+}, especially in the case of granular clinoptilolite (2.5–5.0 mm). The adsorption of lead increased with an increase in pH of the solution from 1 to 4.

The retention of lead by a Mexican clinoptilolite-rich tuff was evaluated by Llanes-Monter et al. [80]. The maximum Pb^{2+} exchange capacity of the Mexican clinoptilolite-rich tuff was 1.4 meq/g at pH 3. The chemical lead speciation, the pH, as well as the characteristics of the clinoptilolite-rich tuff are important factors to be considered on the lead sorption process by natural zeolites. Al-Haj-Ali and Al-Hunaidi [81] studied Pb^{2+} on a natural phillipsite in a laboratory-scale packed-bed column. Bed depth-service time (BDST) model was applied and parameters for column design were determined for lead ions at 5% breakthrough yielding BDST sorption capacity of 24.3–35.7 mg/g.

A natural clinoptilolite from Turkey for the uptake of Pb^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in single and mixed ion solutions was evaluated by Oter and Akcay [82]. Contact time, initial solution pH, solid-to-liquid ratio and initial metal cation concentration were determined as single ion sorption parameters. The maximum adsorption capacity was found as 0.730, 0.251, 0.227 and 0.173 meq/g for Pb^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, respectively. However, the values from the mixed ion solutions were significantly reduced to 0.299, 0.108, 0.022 and 0.017 meq/g for Pb^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} ions, respectively. The clinoptilolite selectivity in both single and mixed ion solution is $Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$, which is the similar order to the report of Cincotti et al. [78].

Payne and Abdel-Fattah [83] conducted batch kinetic and isotherm studies to compare and evaluate different types of adsorbents such as activated carbon and naturally occurring zeolites (clinoptilolite and chabazite) and synthesised zeolites Faujasite (13X) and Linde type A (5A) for Pb^{2+} removal. The relative rate for lead ion adsorption was: 13X > chabazite > clinoptilolite > 5A > activated carbon. Adsorption isotherm of chabazite and clinoptilolite could be best fit with the Freundlich isotherm. Applications of chabazite and clinoptilolite would require pH values between 4 and 11 and ionic competition reduced lead ion removal by the zeolites. Increasing temperature improved adsorption performance for the zeolites.

Sprynskyy et al. [84] carried out a study on the sorption of heavy metals (Ni^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+}) under static conditions from single- and multi-component aqueous solutions by raw and pretreated clinoptilolites. Fig. 2 presents kinetic adsorption of Ni^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+} in single- and multi-component systems. They found the sorption to be an ion-exchange process and consisted of three stages, i.e., the adsorption on the surface of microcrystals, the inversion stage, and the moderate adsorption in the interior of the microcrystal. The finer clinoptilolite fractions adsorbed higher amounts of the metals due to relative enriching by the zeolite proper and higher cleavage. For Cu^{2+}, Pb^{2+} and Cd^{2+}, no difference was observed in single- and multi-component systems. The decrease of nickel adsorption from multi-component solutions was probably caused by the propinquity of its sorption forms to the other metals and by competition. The maximum sorption capacity of Cd^{2+} is determined as 4.22 mg/g at an initial concentration of 80 mg/L and 27.7, 25.76 and 13.03 mg/g at 800 mg/L for Pb^{2+}, Cu^{2+} and Ni^{2+}.

Turkman et al. [85] studied removal of heavy metals (Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}) in synthetic and real wastewaters using activated and non-activated natural clinoptilolite. Gordes and Bigadic zeolites in Turkey were used for Cd^{2+} and Ni^{2+} removal and their efficiencies were compared with that of natural zeolites from other different areas. Although Cd^{2+} was not removed effectively by Bigadic zeolite, while 46% removal efficiency was achieved on Gordes zeolite after 90 min of contact in batch tests. Column studies were also performed for the removal of Pb^{2+}, Cd^{2+} and Zn^{2+} from a lead–zinc mining process raw wastewater. The clinoptilolite exhibited about 100, 98, and 96% removal efficiency for Pb^{2+}, Zn^{2+} and Cd^{2+}, respectively. The overall adsorption capacities for Bigadic clinoptilolite were around 23 mg Pb^{2+}/g, 24 mg Zn^{2+}/g and 0.6 mg Cd^{2+}/g. Oren and Kaya [86] also compared Zn^{2+} adsorption characteristics of Gordes and Bigadic zeolites. The results showed the removal efficiency of Gordes zeolite is two times higher than that of Bigadic zeolite, similar to the above Turkman results. Gedik and Imamoglu [87] also investigated Cd^{2+} removal from aqueous solutions using as-received and NaCl-pretreated forms of Gordes and Bigadic zeolites. The maximum sorption capacities for as-

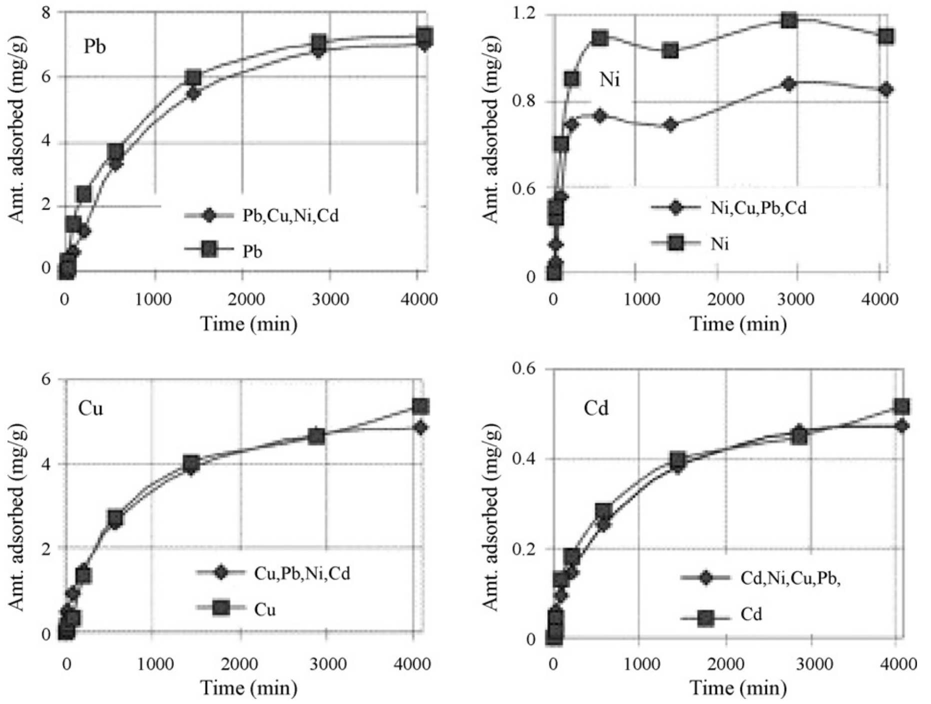

Fig. 2. Kinetics of metal sorption from single- and multi-component (Cu^{2+}, Pb^{2+}, Ni^{2+}, and Cd^{2+}) solutions under static conditions (0.5 g zeolite, fraction 0.71–0.50 mm, 200 mL solution, C_0 = 20 mg/L for Cu^{2+}, Ni^{2+}, and Pb^{2+} and C_0 = 2 mg/L for Cd^{2+}, pH 6.2).[84].

received samples were determined as 0.18 and 0.12 meq/g for Gordes and Bigadic zeolites, whereas 0.72 and 0.41 meq Cd/g were determined for their pretreated forms, respectively.

Wingenfelder et al. [88] investigated the removal of Fe, Pb, Cd, and Zn from synthetic mine waters by a natural zeolite. Pb was removed efficiently from neutral as well as from acidic solutions, whereas the uptake of Zn and Cd decreased with low pH and high iron concentrations. With increasing Ca concentrations in solution, elimination of Zn and Cd became poorer while removal of Pb remained virtually unchanged. The zeolite was stable in acidic solutions. Disintegration was only observed below pH 2.0.

A natural clinoptilolite was modified to a clinoptilolite–iron oxide system (Clin–Fe) for the removal of Mn^{2+} [89], Zn^{2+} [90] and Cu^{2+} [91] ions from drinking water samples. Under experimental conditions, the adsorbed maximum amount of Mn for clinoptilolite was 7.69 mg/g whereas that for the Clin–Fe system was 27.1 mg/g. The respective values for the adsorption of Zn were 71.3 and 94.8 mg/g and the maximum adsorbed Cu amount on clinoptilolite was 13.6 mg/g whereas on the Clin–Fe system was 37.5 mg/g. These results indicated an improvement of metal adsorption with iron exchanger.

Stefanovic et al. [92] investigated the effect of pre-treatment of clinoptilolite tuff from Serbia by using NaCl or $CaCl_2$ on Zn^{2+} adsorption. Pre-treatment of zeolite tuff affects the sorption capacity and local structure of Zn^{2+}. Pre-treatment of clinoptilolite tuff by using NaCl or $CaCl_2$ solutions resulted in a higher zinc uptake comparing to the untreated zeolite sample, i.e. up to 4 wt% of zinc in the clinoptilolite crystals in Na-pretreated form and up to 1.5 or 0.6 wt% of zinc in Ca-pretreated and in untreated zeolite form, respectively. Trgo et al. [93] investigated the kinetics of zinc and lead ions removal by NaCl-modified clinoptilolite. The rate of the ion-exchange process for lead ions is faster than for zinc ions. The ion-exchange capacity of zeolite of lead ions is doubly higher than that of zinc ions. Bosso and Enzweiler [94] evaluated a scolecite for heavy metal removal (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+}) from aqueous solutions. The results indicated an affinity order of scolecite for Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+} with a retention value of 130, 64, 56, 31, 7.8 and 3.2 μeq/g, respectively.

Alvarez-Ayuso et al. [95] studied the sorption behaviour of natural clinoptilolite and synthetic NaP1 zeolites for Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in purification of metal finishing wastewaters. The synthetic zeolite exhibited about 10 times greater sorption capacities than natural zeolite. The adsorption capacity of natural clinoptilolite is 0.079 mmol/g for Cr, 0.034 mmol/g for Ni, 0.053 mmol/g for Zn, 0.093 mmol/g for Cu and 0.041 mmol/g for Cd, respectively. This mineral showed the same high sorption capacity values when used in the purification of metal electroplating wastewaters.

Table 5
Cation-exchange selectivity of heavy metal ions on natural zeolites.

Zeolite	Selectivity	Si/Al	Reference
Clinoptilolite	$Pb^{2+} > Ag^{+} > Cd^{2+} \sim Zn^{2+} > Cu^{2+}$	2.7–5.3	[12]
Clinoptilolite	$Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$	4.9	[82]
Clinoptilolite	$Pb^{2+} > Cd^{2+} > Zn^{2+} \sim Cu^{2}$	4.2	[13]
Clinoptilolite	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$	–	[14]
Clinoptilolite	$Pb^{2+} > Fe^{3+} > Cu^{2+} > Zn^{2+} \sim Cd^{2+} \sim Co^{2+} > Ni^{2+} > Mn^{2+} > Cr^{3+}$	–	[14]
Phillipsite	$Pb^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+}$	2.4–2.7	[13]
Mordenite	$Mn^{2+} > Cu^{2+} > Co^{2+} \sim Zn^{2+} > Ni^{2+}$	4.4–5.5	[12]
Scolecite	$Cu^{2+} > Zn^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$	1.56	[94]
Chabazite	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+}$	2.2–2.6	[13]

Table 6
Kinetic parameters for adsorption of heavy metal ions on natural zeolites.

Zeolite	Metal ion	Reaction order	First-order rate constant (min^{-1})	Second-order rate constant (g/mg h)	Reference
Clinoptilolite	Cd^{2+}	Firs-order	0.0137		[76]
	Pb^{2+}		0.0532		
	Ni^{2+}		0.0158		
	Cu^{2+}		0.0200		
	Zn^{2+}		0.0210		
Clinoptilolite	Pb^{2+}	First-order	2.9×10^{-4}		[83]
Chabazite	Pb^{2+}	First-order	4.3×10^{-4}		[83]
Clinoptilolite	Pb^{2+}	First-order	0.0053		[84]
	Ni^{2+}		0.1419		
Clinoptilolite	Pb^{2+}	First-order	3.5×10^{-4}		[98]
Scolecite	Mn^{2+}	Second-order		0.0155	[97]
	Cr^{3+}			0.0365	
	Ni^{2+}			0.0248	
	Cd^{2+}			0.0503	
Clinoptilolite	Cu^{2+}	Second-order		0.00113	[84]
	Cd^{2+}			0.0226	

Akgul et al. [96] have recently investigated the removal of silver ions from aqueous solution using a natural clinoptilolite. They carried out batch experiments to examine the effects of various parameters such as pH, adsorption time, metal ion concentration and the acidic treatment on the adsorption process. They found that acid treatment has a substantial effect on the metal uptake. Adsorption phenomena appeared to follow the Langmuir and Freundlich isotherms and Ag^+ maximum adsorption capacity was 33.23 mg Ag^+/g.

For ion exchange with various heavy metals in wastewater systems, cation selectivity of zeolite is important for selective ion removal. Table 5 shows cation-exchange selectivity of important heavy metal ions on several natural zeolites. As seen that Pb has the higher affinity for ion exchange for most of zeolites. Other metal ions show varying order depending on the type of zeolite. It is noted that ion-exchange selectivity also depends on the ion concentration and solution pH. Therefore, these factors should be taken into consideration in real wastewater treatment.

For zeolite application in heavy metal adsorption, ion-exchange kinetics is also important. Previous investigations have showed that adsorption of heavy metal ions generally follow two kinetic models, pseudo-first-order or pseudo-second-order. Table 6 gives some results of previous investigations. It is seen that the kinetics of heavy metal depends on zeolite type and metal ions.

4.3. Inorganic anions

Inorganic anions contain several acid ions and some metalloid and metal anions. The acid ions such as NO_3^-, SO_4^{2-}, PO_4^{3-}, F^-, ClO_4^-, CN^- are largely present in wastewater. These ions can cause pollution at high content. Other important inorganic anions include Cr(V) with CrO_4^{2-}, $Cr_2O_7^{2-}$ forms, and As(V) with $H_2AsO_4^{2-}$, $HAsO_4^-$, and As(III), which are strong toxic species in water system. Currently, removal of anions using natural zeolites can be achieved on ion-exchanged zeolite and surfactant-modified forms.

For acid anions, natural zeolite has been tested for F^- and CN^- adsorption. Diaz-Nava et al. [99] evaluated the sorption of fluoride ions on a natural Mexican heulandite–clinoptilolite. In their work, the effects of sodium, calcium, lanthanum, and europium in the crystalline network as well as the effects of pH and particle size of the zeolite on the fluoride sorption were investigated. They found that retention of fluoride was similar for the untreated material and treated samples with sodium, calcium, lanthanum, and europium. The fluoride retention was proposed as occlusion and adsorption of fluoride on zeolite. Samatya et al. [100] also prepared metal ion (Al^{3+}, La^{3+} and ZrO^{2+}) exchanged zeolites for fluoride removal from water on a Turkish clinoptilolite. The natural zeolite samples were pre-conditioned with HNO_3 (ZEO-1), $NaNO_3$ (ZEO-2), and deionised water (ZEO-3) before loading Al^{3+}, La^{3+} and ZrO^{2+}. They found that ZEO-1 type zeolite had a higher capacity than ZEO-2 and ZEO-3 type zeolites. Equilibrium isotherms fitted well to the Langmuir and Freundlich models. Percent removal of fluoride from aqueous solution containing 2.5 mg F/L was 94% using metal loaded zeolite (ZEO-1) at an adsorbent concentration of 6.00 g/L. For Al^{3+}, La^{3+} and ZrO^{2+} exchanged zeolites, fluoride adsorption capacity follows the order of Zr-Zeo > La-Zeo > Al-Zeo.

Faghihian [101] described the preparation and evaluation of various modified metal forms of clinoptilolite for removal of cyanide from aqueous solutions. The cobalt form of the zeolite showed the highest uptake of 1.95 meq/g-zeolite whereas the uptake on natural forms is 0.070 meq/g.

It has been known that metal chromium is a highly toxic metal. Its presence in water is generally in Cr^{3+} and Cr(VI). Compared with Cr^{3+}, Cr(VI) state is of particular concern due to its higher toxicity. Since earlier work of Haggerty and Bowman [48] using surfactant to modify surface charge of zeolite for anion adsorption, a lot of investigations have been carried out. Ghiaci et al. [25] compared the performance of synthetic and natural zeolites modified by surfactant HDTMA and CPB as well as MCM-41 molecular sieve for removal of chromate from aqueous solution. HDTMA- and CPC-clinoptilolite exhibit higher adsorption than ZSM-5 based adsorbents, but less than MCM-41. The maximum chromate adsorption on HDTMA- and CPC-clinoptilolite is dependent on surfactant loading in a range of 4.4–16.6 and 3.9–21.4 mmol/kg, respectively. Campos et al. [18] investigated the modified-natural mordenite using HDTMA and ethylhexadecyldimethylammonium (EHDDMA) as adsorbents for the removal of Cr (VI) from aqueous solution. The results showed that the HDTMA-HSO_4 modified zeolite exhibited higher adsorption for Cr(VI) than EHDDMA-modified zeolite. The sorption of chromate on HDTMA-zeolite resulted from a combination of entropic, coulombic, hydrophobic effects, and HDTMA counterion. Cordoves et al. [102] also reported a study of a surfactant-modified clinoptilolite (SMZ) in the removal of Cr(VI) and Cr^{3+}. The cation and anion exchange capacities of each zeolite were obtained. It has been demonstrated that the affinity distribution analysis combined with the Freundlich binding model allows the characterization of the SMZ binding properties for Cr(VI). In comparison to other surfactant-modified clinoptilolites, this activated zeolite proved to have improved properties for Cr(VI) adsorption, providing a method for separation of Cr(VI) from Cr^{3+}.

Wingenfelder et al. [103] employed HDTMA-modified zeolite for sorption of antimonate. During the modification, the zeolite sorbed more than 94% of HDTMA. Desorption of HDTMA from the zeolite was less than 15% in total after threefold washing with distilled water. Antimonate binding was most effective on the zeolite treated with HDTMA solutions exceeding the zeolites external cation-exchange capacity. Antimonate sorption on modified zeolite was best described by the Langmuir isotherms. HDTMA-zeolite in aqueous suspension (50 g/L) sorbed up to 42% of antimonate from solutions containing from 0.09 to 2.15 mmol Sb/L.

Elizalde-Gonzalez et al. [104] investigated arsenic sorption on clinoptilolites from Mexico and Hungary. Both clinoptilolites are able to decrease the initial arsenic concentration of 200 μg/L by more than 75% in deionised, drinking, ground and surface waters. In the case of the Mexican zeolite, both the arsenite and the arsenate concentrations (200 μg/L) can be lowered from 200 to 10 μg/L. It was found that the presence of cations and anions in the natural waters did not reduce the efficiency of the selected zeolites. The Hungarian zeolite removed 75% of the arsenate and only 50% when the sample was first acidified. This zeolite totally desorbed the fixed arsenic into a water volume. Dousova et al. [105] studied the sorption of arsenate from aqueous solution on three adsorbents, metakaoline, clinoptilolite-rich tuff, and synthetic zeolite, in both untreated and Fe^{2+}-treated forms. It was found that the sorption capacity of Fe^{2+}-treated sorbents increased significantly from about 0.5 to >20.0 mg/g, which represented more than 95% of the total As removal.

Habuda-Stanic et al. [106] compared different modified adsorbents (zeolite–clinoptilolite, manganese greensand and cationic exchange resin) for arsenic removal from contaminated drinking water. Adsorbents were chemically modified and saturated with Fe^{3+} ions, while the arsenic solutions were prepared by processed groundwater. Adsorption tests show that Fe^{3+} saturated zeolite is effective for arsenic removal with capacity of 55.3 μg/g for As(III) and 36.4 μg/g for As(V).

Macedo-Miranda and Olguin [107] reported arsenic sorption onto Mexico clinoptilolite-heulandite rich tuffs modified with lanthanum, hexadecyltrimethylammonium or iron. The Langmuir isotherm presented the arsenic (V) sorption capacity of the zeolites as 75.4 μg As/g at pH 3, 3.9 μg As/g at pH 5 and 53.6 μg As/g at pH 6, for the lanthanum, HDTMA and iron modified clinoptilolite-heulandite rich tuff, respectively. In general, the results suggested that the arsenic retention depends on the precedence of zeolitic material, the nature of arsenic chemical species, pH as well as the characteristics of modified-natural zeolites.

Davila-Jimenez et al. [108] introduced iron species into a clinoptilolite-rich zeolitic tuff using different organic and inorganic iron salts after pre-treatment with NaCl. The introduced iron corresponded to four coordinated species with tetrahedral geometry, primarily low spin ferric iron adsorbing almost 12 μg/g arsenite (99% removal) from a 360 μg(As(III))/L and 6 μg/g arsenate from a 230 μg(As(V))/L. Adsorption of arsenite and arsenate reached practically a plateau at Fe/Si = 0.1 in the series of exchanged tuffs. The oxidation of arsenite to arsenate in the solution in contact with iron modified tuff during adsorption was observed by speciation.

4.4. Organics

Organic contaminants are important pollutants in water. The removal of dyes and organics in an economic way remains an important problem although a number of systems have been developed with adsorption techniques. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.

Table 7
Dye adsorption on natural zeolite.

Material	Dye	Adsorption (mg/g)	Reference
Clinoptilolite	Methylene blue	19.9	[34]
Clinoptilolite	Rhodamine B	12.4	[34]
Clinoptilolite	Malachite green	19.7	[98]
HTAB-clinoptilolite	Reactive black 5	60.6	[112]
HTAB-clinoptilolite	Reactive red 239	111.1	[112]
HTAB-clinoptilolite	Reactive yellow 176	88.5	[112]
CTAB-clinoptilolite	Reactive black 5	12.1–12.9	[43]
CTAB-clinoptilolite	Reactive red 239	11.0–15.9	[43]
Clinoptilolite	Basic red 46	8.6	[42]
HTAB-clinoptilolite	Reactive yellow 176	13.2	[42]
CTAB-clinoptilolite	Reactive yellow 176	5.5	[42]
Clinoptilolite	Toluidine blue O	33.0–58.7	[15]

4.4.1. Dye adsorption

Dyes are important pollutants in wastewater, which are mainly discharged from textile, printing, food and leather industries. Various types of dyes including basic, acidic, reactive, and dispersive dyes are widely used. Dyes in waters affect the nature of the water, inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction. Some dyes are also toxic and even carcinogenic [109]. In the past years, some investigations using natural zeolites for dye adsorption have been reported and Table 7 presents the adsorption capacities of various dyes on natural zeolites.

Meshko et al. [110] investigated the adsorption of two basic dyes, MG-300 and MG-400 with components of (2-[[(4-methoxyphenyl)methylhydrazono]methyl]-1,3,3-trimethylindolium methosulfat and 2-[[4-[ethyl(2-hydroxyethyl) amino]phenyl]azo]-6-methoxy-3-methylbenzothiazoliumchloride), onto granular activated carbon and natural clinoptiolite. The influences of agitation, initial dye concentration and adsorbent mass were studied using batch reactor. The equilibrium studies showed that both dyes have higher adsorption capacity for the granular activated carbon than for the natural zeolite. Homogeneous diffusion model combined with external mass transfer resistance was proposed for the kinetic investigation. The adsorption capacities of two dyes on natural zeolite are 55.9 and 14.9 mg/g, respectively.

Armagan et al. [111–115] conducted a comprehensive study on a Turkey clinoptillolite for adsorption of three reactive azo dyes (reactive black 5, reactive red 239, and reactive yellow 176) and compared the adsorption with a clay sample, sepiolite. The adsorption results indicated that both natural sepiolite and zeolite have limited adsorption capacities of the reactive dyes. After modification with quaternary amines (hexadecyltrimethylammonium bromide. HTAB), the adsorption was significantly improved. An electrostatic adsorption mechanism involving the formation of a bilayer of amine molecules on the clinoptilolite surface onto which anionic dye molecules adsorb was proposed. The adsorption data were fitted to the Langmuir isotherm and the modified zeolite produced adsorption capacities of 111, 89, and 61 mg/g for reactive red, yellow and black, respectively.

Benkli et al. [44] also investigated HTAB-modified clinoptilolite for removal of reactive azo dyes, reactive black 5, red 239 and yellow 176, in a fixed bed. The results indicated the order of dye removal by modified zeolite in the following manner: black > yellow > red. Calculations of the HTAB coverage on zeolite surface indicate that a bilayer formation is the most viable packing that enables maximum removal of the dyes.

Karadag et al. [42] also studied raw zeolite and surfactant-modified zeolite for adsorption of basic red 46 (BR46) and reactive yellow 176 (RY176) and compared the effect of different surfactants of cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HTAB) on dye adsorption. BR46 adsorption onto natural zeolite increased to minor extent with increasing pH, whereas pH did not significantly affect RY176 adsorption. The increase in ionic strength caused a decrease in adsorption of BR46 and an increase in adsorption of RY176. Adsorption of BR46 on natural zeolite is more favourable than RY176 on the CTAB and HTAB modified zeolites. They [43] further investigated CTAB modified-natural zeolite for other reactive dye adsorption. The adsorption capacity of Reactive Red 239 was found to be two times higher than Reactive Blue 5 due to the hydrophilicity of the dye molecules. The pseudo-second-order model provided a very good fitting for the two anionic dyes. The calculated maximum adsorption capacity increased with increasing initial dye concentration, but there is no linear relationship with pH and temperature.

Alpat et al. [15] also used the Turkish clinoptilolite for the adsorption of toluidine blue O (TBO). Kinetic studies showed that adsorption of TBO on the clinoptilolite was fitted to the second-order adsorption model with two-step diffusion process. The activation energies for TBO adsorption on clinoptilolite for the first and second diffusion processes were 8.72 and 19.02 kJ/mol, respectively. The adsorption isotherm was well fitted to both the Langmuir and Freundlich models. The maximum adsorption capacity of clinoptilolite for TBO was 2.1×10^{-4} mol/g at solution pH of 11.0.

An Australian natural clinoptiloite was tested for basic dye adsorption [34]. The natural zeolite presented maximal adsorption capacity of 2.8×10^{-5} and 7.9×10^{-5} mol/g at 50 °C for Rhodamine B and methylene blue, respectively. Kinetic studies indicated that the adsorption followed the pseudo-second-order kinetics and could be described as two-stage diffusion process. It has also found that the regenerated zeolites by high-temperature calcination and Fenton oxidation showed similar adsorption capacity but lower than the fresh sample. Only 60% capacity could be recovered by the two regeneration techniques [116]. Wang and Ariyanto [98] also investigated the competitive adsorption of malachite green and Pb^{2+} ions from aqueous solution on the Australian natural zeolite. For single system, malachite green adsorption isotherm follows the Langmuir model and the adsorption capacity is 5×10^{-5} mol/g. In the binary system, malachite green and Pb^{2+} exhibit competitive adsorption on the natural zeolite. The adsorption is reduced to 90 and 80% of single component of Pb^{2+} and malachite green, respectively. However, the total adsorption is higher. In the binary system, Pb^{2+} exhibits relative higher affinity and selectivity to be adsorbed on zeolite. The dynamic adsorption of malachite green and Pb^{2+} still follows the first-order kinetics.

Han et al. [117] studied methylene blue adsorption on a Chinese natural zeolite in column tests under different flow rates and initial concentrations and estimated the kinetic parameters. The results showed that natural zeolite was efficient to remove methylene blue from solution. The breakthrough data were fitted to Thomas model equations.

From the above investigations, it is found that natural zeolites are effective for cationic dye adsorption due to the cation-exchange characteristic while they exhibits low capacity in anionic dyes. After surfactant modification, natural zeolites will be good adsorbents for anionic dye adsorption.

4.4.2. Humic substances

Humic substances make up about 80% of soil organic matters in dark soils. Most humic substances are resulted from the natural process of plant matter decay. Humic substances have been designated as either humic acid, fulvic acid or humin. The presence of humic substance in surface and ground water will produce toxic chemicals during disinfection processes and thus should be removed. Many techniques have been developed for removal of humic substance. Some investigators have also employed natural zeolite for removal of humic substance by adsorption. Table 8 presents a summary of previous investigation results.

Table 8
HA adsorption on natural zeolites.

Adsorbent	Capacity (mg/g)	Temperature (°C)	pH	Reference
NYT	8.51	30	–	[19]
Na-NYT	6.70	30	–	[19]
K-NYT	6.58	30	–	[19]
NH4-NYT	7.02	30	–	[19]
Ca-NYT	21.5	30	–	[19]
Mg-NYT	22.0	30	–	[19]
Ba-NYT	11.3	30	–	[19]
CLT	2.35	RT	7.2	[20]
Ca-CLT	2.60	RT	7.2	[20]
NYT	17.1	RT	7.2	[20]
Ca-NYT	22.5	RT	7.2	[20]
Australian	68	30	5.0	[120]

Wang et al. [118] reported an investigation of modification of clinoptilolite surface (SMZ) with HDTMA to improve the removal efficiency of fulvic acids (FA). They investigated the effects of relevant parameters such as HDTMA loading levels, FA flow rate and effluent concentration in a fixed bed. FA adsorption on SMZ surfaces is largely due to the hydrophobic interaction and hydrogen bonding. Optimisation studies showed that the SMZ bed with HDTMA loading of 120% of ECEC at a flow rate of 5 BV/h had the best performance and the volume of 23 BV of 30 vol% ethanol solution with the feed flow rate of 5 BV/h was sufficient for complete regeneration of the SMZ.

Capasso et al. [19] studied the interaction of humic acid (HA) with zeolitic (phillipsite + chabazite) Neapolitan yellow tuff (NYT). HA sorption isotherms were carried out on untreated as well as on Li^+-, Na^+-, K^+-, $NH_4{}^+$-, Ca^{2+}- or Ba^{2+}-enriched samples. They obtained maximum HA sorbable amount and the affinity constant between sorbate and the sorbent. Fig. 3 shows the adsorption isotherms of humic acid on various zeolites. The results demonstrated that enrichment by divalent cations enhances the ability of NYT to take up humic acid, whereas enrichment by monovalent cations reduces the adsorption. The results also showed that humic acid sorption on tuff must be regarded as a complex phenomenon, occurring as a compromise between the ability of the cations to form stable bridges with the organic matter and, on the other hand, their specific selective sorption by the ruff. They [119] further tested the ability of NYT enriched with calcium ions to remove humic acids from water by batch and column experiments. The sorption capacity increased with the ionic strength and has the highest value at pH 7.4. They [20] also compared the sorption of humic acids (HA) on Ca-enriched NYT and a clinoptilolite-rich tuff from Turkey (CLT). NYT sorption capacity was higher than that of CLT. HA sorption by Ca-enriched NYT readily attained a pseudo steady-state, after which the tuff/HA-solution system evolved in a few months to a final equilibrium state characterized by a much higher sorption capability. Desorption experiments at high pH levels resulted in a HA recovery >80%.

Wang et al. [120] studied the adsorption of humic acid (HA) on an Australian natural zeolite tuff. The adsorption capacity of humic acid at 30 °C with pH 5 was found as 68 mg/g. Solution pH influenced humic acid adsorption. In Pb^{2+}/HA system, Pb^{2+} exhibits competitive adsorption with humic acid on the natural zeolite, resulting in reduced adsorption of both Pb^{2+} and humic acid. However, in Cu^{2+}/HA system, competitive adsorption and complexation between Cu^{2+} and humic acid influence the adsorption, resulting in decreased adsorption of humic acid but increased adsorption of Cu^{2+}. The complexation structure of Pb–HA/zeolite and Cu–HA/zeolite in three-component system was proposed as S–Pb–HA and S–HA–Cu, respectively.

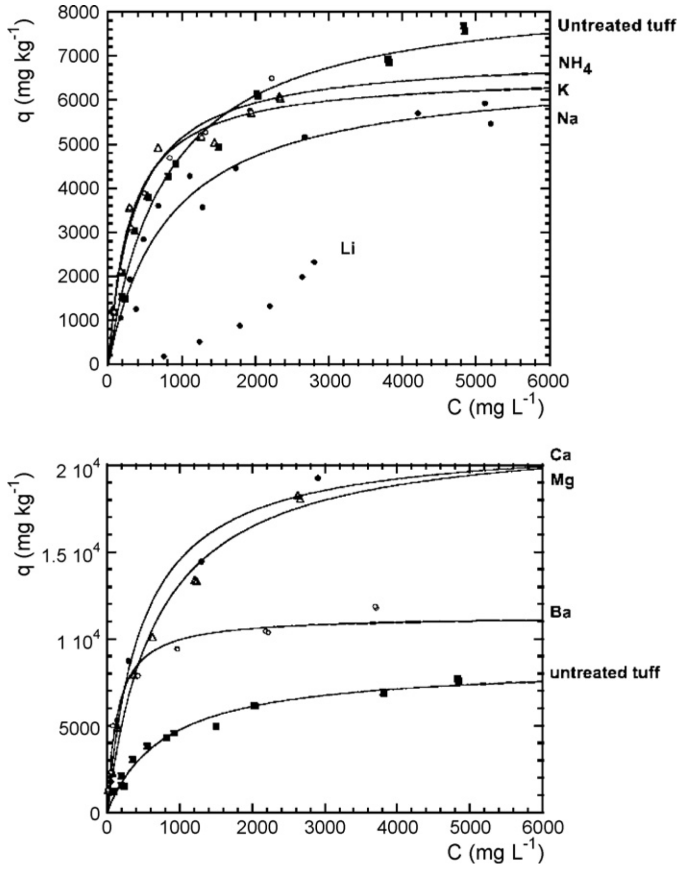

Fig. 3. Humic acid adsorption on untreated zeolite tuff and on various cation-enriched tuff samples [19].

Therefore, it is seen that natural zeolite can also be used as an adsorbent for humic substance adsorption. However, the adsorption capacity depends on the structure and chemical composition of natural zeolite.

4.4.3. Other organics

Apart from dyes and natural organic matter, wastewater usually contains other organic compounds, such as phenolic compounds, petroleum, surfactants, pesticides, and pharmaceuticals, which are from various industrial sources. These organics are generally more toxic than dyes and humic substance and removal of these organic compounds is more important in water and wastewater treatment. However, removal of organics from water using natural zeolite is usually involved of surfactant modification of zeolite.

Li and Bowman [121] investigated the sorption of a non-polar organics, perchloroethylene (PCE), on HDTMA-modified zeolite (SMZ). Below monolayer coverage by the surfactant, the PCE sorption coefficient on SMZ was proportional to the fractional organic carbon content. Above monolayer coverage, increasing fractional organic carbon content resulted in minimal further increase in the PCE sorption coefficient. They also determined the sorption of ionisable organic solutes, benzene, phenol and aniline on SMZ [122]. The sorption was affected by solution pH. Phenol sorption by SMZ treated to bilayer coverage increased with the pH and hence fraction of anionic phenolate increased. The counterion balance indicated that the increased retention of phenol was due partially to anion exchange of phenolate for bromide, the same mechanism responsible for sorption of inorganic anions by SMZ. In contrast, decreases in pH resulted in reduced aniline sorption due to a lower concentration of the neutral species and repulsion of the positively charged anilinium from SMZ treated to bilayer coverage.

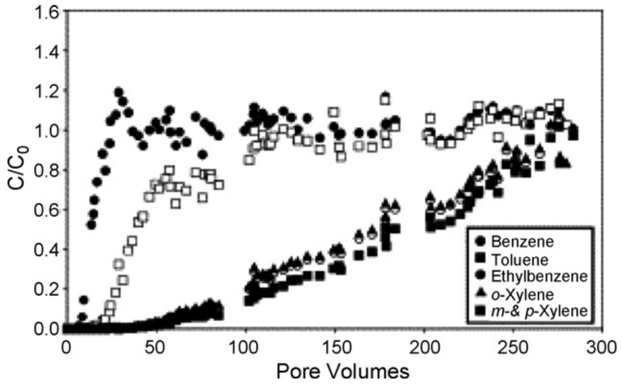

Fig. 4. BTEX breakthrough curves for HDTMA-modified zeolite column saturation, oilfield water experiment [45].

Huttenloch et al. [123] investigated chlorosilanes modified-natural diatomite and zeolite materials for sorption of toluene, o-xylene, and naphthalene from water. Trimethylchlorosilane (TMSCI), tert-butyldimethylchlorosilane (TBDMSCI), dimethyloctadecylchlorosilane (DMODSCI), and diphenyldichlorosilane (DPDSCI) were used. Sorption tests showed enhanced adsorption on the surface modification materials compared to the untreated ones which showed no measurable sorption. Batch sorption experiments showed that the phenyl head groups of DPDSCI have the best affinity for aromatic compounds. Removal from an aqueous solution of 10 mg/L of naphthalene, o-xylene, and toluene was 51, 30, and 16% for modified clinoptilolite, respectively.

Ersoy and Celik [124] investigated the adsorption of aniline and nitrobenzene on natural zeolite and HDTMA-modified zeolite (OZ). In batch tests, the adsorption capacity of aniline and nitrobenzene onto natural zeolite surface is very low or almost nil but becomes significant on OZ. In the column tests, adsorption capacity of two compounds on OZ from the breakthrough curves was determined as 2.36 and 3.25 mg/g for aniline and nitrobenzene, respectively.

Ghiaci et al. [53] prepared organo-zeolites, ZSM-5 and natural zeolites with HDTMA and n-cetylpyridinium bromide (CPB), and tested for adsorption of nonionic organic contaminants (NOCs) such as benzene, toluene, and phenol from contaminated wastewater. They found that the increase in NOCs concentration or initial concentrations of surfactants resulted in an increase in the NOC adsorption. At a certain concentration, CPB modified zeolite showed higher adsorption than that of the corresponding HDTMA-modified zeolite. Organo-natural clinoptilolite exhibits higher sorption capacity of NOCs than organo-ZSM-5.

A study for evaluation of HDTMA-modified zeolite (SMZ) for removal of BTEX from produced water was reported by Ranck et al. [125]. The results showed that SMZ completely removes BTEX and that SMZ can be regenerated via air sparging without loss of sorption capacity. 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.

Bowman [45] evaluated a HDTMA-modified zeolite 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. He also tested the HDTMA-modified zeolite for removal of organics present in oilfield wastewaters. Fig. 4 shows the first BTEX saturation experiment. As expected, the higher solubility species benzene and toluene appear first in the effluent and reach influent concentrations relatively rapidly, followed by the more hydrophobic, more strongly retained ethylbenzene and xylenes which take much longer to reach influent concentrations. 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 657 mg for o-xylene, respectively. Laboratory and field experiments also showed that SMZ removed 99–100% of bacteria and viruses present in sewage effluent.

Systematic adsorption tests were carried out to determine the efficiency of SDBAC-modified zeolite for removal of pesticides, atrazine, lindane and diazinone from water [55]. The effects of adsorbent particle size, solid content in the suspension and the initial pesticide concentration in the solutions were investigated. The adsorption capacities, calculated by fitting the experimental data to the Langmuir–Freundlich equation, were 2.0 μmol/g (atrazine), 4.4 μmol/g (diazinone) and 3.4 μmol/g (lindan). Column experiments showed that at volumetric flow of 6 cm^3/min, the breakthrough points (at $C/C_0 = 0.1$) were 560 bed volume (BV) for lindane and 620 for diazinone.

Dakovic et al. [50] investigated the adsorption of ochratoxin A (OCHRA) on clinoptilolite-heulandite rich tuff modified with ODMBA at different amounts 20, 50 and 100 μmol/g, which were denoted as OZ-2, OZ-5 and OZ-10. They found that adsorption of OCHRA on organo-zeolites is dependent on the amount of organic cation at the surface as well as on their surface concentration-arrangement of alkyl chains at the surface. High surface coverage of ODMBA resulted in higher OCHRA adsorption. At low surface concentration of ODMBA, OCHRA adsorption was pH dependent while at higher concentrations of ODMBA adsorption of both neutral and anionic forms of OCHRA occurred. They also investigated the adsorption of zearalenone (ZEN) [52] and fumonisin B-1 (FB1) [51] on OZ-2, OZ-5, and OZ-10. Results showed that the presence of ODMBA ions at the zeolite surface greatly improved adsorption of ZEN and FB1. The pH significantly influenced ZEN and FB1 adsorption. The estimated maximum FB1 adsorption to OZ-10, based on a Langmuir model, was 10.82 mg/g at pH 3.

Kuleyin [49] investigated the adsorption of phenol and 4-chlorophenol on HDTMA- and BDTDA-modified zeolite. Phenol and 4-chlorophenol removal efficiency by the surfactant-modified zeolite was higher than natural zeolite. 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 at 50 mg/L.

Therefore, natural zeolite exhibits little adsorption of organics in aqueous solution due to its surface hydrophilics. Surfactant modification can change the surface functionality by adding hydrophobic groups and thus enhancing adsorption capacity of various organics. However, the adsorption depends on surfactant loading and coverage on zeolite.

5. Conclusion and future perspectives

Natural zeolites are important low cost materials for water and wastewater treatment. Due to the nature of cation exchange, natural zeolites exhibit high performance in adsorption of cations in aqueous solution such as ammonium and heavy metals. However, zeolites show varying ion selectivity and competitive adsorption for a multi-component system. In addition, these materials are not good adsorbents for adsorption of anionic ions and organics. Surface modification using cationic surfactant can change the surface charge of natural zeolite, making them applicable for adsorption of anions and organics. Modification of natural zeolites using some heavy metals can also make them for inorganic anion adsorption by surface precipitation.

Natural zeolite for cationic ion adsorption has been intensively investigated; however, its modified forms using surfactants for anionic ion adsorption have not been comprehensively carried out. Detailed mechanism of contaminant/surfactant/zeolite interactions is required for better design of surfactant-modified zeolite. In addition, regeneration of spent zeolite using simple methods for adsorbent recycling should also be a focus in future research.

In the past, most tests using natural zeolites were based on batch mode, focussing on their applicability and selectivity. However, once batch conditions, adsorptive capacity and the uptake mechanism are established work should be directed to design and carry out some pilot-plant scale studies to check their feasibility at industrial level. More important, real wastewater should be tested instead of synthetic wastewater.

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