Naturally Engineered Analcime for Water Treatment Process and its Calorimetric Properties

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Abstract: *Analcime ($NaAlSi_2O_6.H_2O$) is a natural zeolite and one of the most common rock-forming zeolites. It forms in a wide range of geologic environments that span a range of temperature and pressure from ambient to magmatic conditions. Due to its Gibbs free energy, it has a wide variety applications in water filtration and cleaning process. In analcime, the presence of at least two distinct states of short range Si/Al disorder [low (less disordered) and high (more disordered) analcime], and that configurational entropy associated short-range Si-Al disorder within each of these states increases regularly with increasing Si content. XRD technique was used to determine the entropy of analcime (Si-Al disorder). Enthalpies of formation from the element at $25°C$ (ΔH_f) for the samples fall on a linear trend, except for a sample of analcime for which ΔH_f was about 6.1 ± 3.0 kJ. The entropy derived from XRD technique were in turn used to derive Gibbs Free energy of analcime whose compositions are bounded by an aluminous end member and a siliceous end member $NaAlSi_2O_6.H_2O$. These relationships between Debye temperature, d-spacing between planes of analcime molecule, entropy were used to retrieve thermodynamic property Gibbs free energy from x- ray diffraction analysis carried out on analcime. Retrieved values of entropy $S°$, Gibbs free energy are in excellent agreement with the calorimetric results of this study. So, due to its calorimetric properties it is a naturally engineered material which can be used for water treatment process in industries.*

Keywords: Analcime, XRD analysis, Debye Waller Temperature, Entropy, Gibbs free energy, water treatment process.

1. Introduction

Natural zeolites are environmentally and economically acceptable hydrated aluminosilicate materials with exceptional ion-exchange and sorption properties. Their effectiveness in different technological processes depends on their physical-chemical properties that are tightly connected to their geological deposits. The unique tree dimensional porous structure gives natural zeolites various application possibilities. Because of the excess of the negative charge on the surface of zeolite, which results from isomorphic replacement of silicon by aluminum in the primary structural units, natural zeolites belong to the group of cationic exchangers. Numerous studies so far have confirmed their excellent performance on the removal of metal cations from wastewaters. However, zeolites can be chemically modified by inorganic salts or organic surfactants, which are adsorbed on the surface and lead to the generation of positively charged oxihydroxides or surfactant micelles, and which enables the zeolite to bind also anions, like arsenates or chromates, in stable or less stable complexes. Natural zeolites have advantages over other cation exchange materials such as commonly used organic resins, because they are cheap, they exhibit excellent selectivity for different cations at low temperatures, which is accompanied with a release of non-toxic exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) to the environment, they are compact in size and they allow simple and cheap maintenance in the full-scale applications. The efficiency of water treatment by using natural and modified zeolites depends on the type and quantity of the used zeolite, the size distribution of zeolite particles, the initial concentration of contaminants (cation/anion), pH value of solution, ionic strength of solution, temperature, pressure, contact time of system zeolite/solution and the presence of other organic compounds and anions. For water treatment with natural zeolites, standard procedures are used, usually a procedure in column or batch process. Ion exchange and adsorption properties of natural zeolites in comparison with other chemical and biological processes have the advantage of removing impurities also at relatively low concentrations and allows conservation of water chemistry, if the treatment is carried out in the column process[1]. Subject of further academic and industrial research should be to improve the chemical and physical stability of modified zeolites and to explore their catalytic properties, which would allow their use in catalytic degradation of organic pollutants. More careful consideration of their superb metal removal properties and awareness of possible regeneration or further use of contaminant/metal-loaded forms can considerably increase their environmental application possibilities, with a focus the reduction of high concentrations of cations and anions in drinking water and wastewater, for surface, underground and public municipal water treatment independently or in combination with others physical -chemical methods [2].

Analcime is a zeolite (and feldspathoid) having a complex aluminosilicate framework that is common to all leucite-type feldspathoids. The framework is based on corner sharing $(Al,Si)O_4$ tetrahedra, arranged in fourfold, sixfold and eightfold rings. The sixfold rings are arranged axially, forming structural channels parallel to 111. Such a channel arrangement shows many possibilities for structural modification, including framework distortion, channel collapse, and ionic mobility. Due to the similarities in structure, analcime can serve as a precursor for the synthesis of leucite. The latter might become an essential component of composite dental materials designed to exhibit high fracture toughness [3].

Results of analcime synthesis are presented of in this paper. Usually analcime is attributed to zeolites, though in natural conditions it is often discovered together with feldspatoids. Some properties of analcime are similar to those of feldspatoids, that is why it is called feldspatoid too. The idealized formula of this cubic syngony mineral is $NaAlSi_2O_6.H_2O$, But in nature it makes an isomorphic row of solid solutions up to wairacite (zeolite of Ca cationic form). Besides, its chemical composition is rich in potassium. The Si/Al ratio varies from 1.8 to 2.8 in the natural mineral and the content of water can increase, if the amount of SiO_2 grows in its lattices.

Natural analcime is found in cavities of basalt, serpentinite, dacite, riolites, and tiff rocks, in associations with other zeolites. Neither natural nor synthetic analcime is used as a molecular sieve or catalyst, because the channels of its crystal lattice (internal cavities of the analcime lattice) are relatively narrow. It couldn't be used as a molecular sieve because of a high density of the mineral (2.25….2.30g/cm³). The crystal structure of analcime was one of the first zeolites to be determined. Its ideal crystal structure is composed of 16 formula units in a cubic unit cell (space group I$a3d$), with a random distribution of 16 Al and 32 Si atoms on the 48 tetrahedral positions and a random distribution of 16 Na atoms on the 24 channel positions. Framework O atoms are in 96 general positions, and the O atoms of the H_2O molecules are in 16 channel positions. Framework O atoms are shared between linked (Si, Al) tetrahedral to form an aluminosilicate framework composed of rings of six and four tetrahedral. Sodium is coordinated inside these channels by 4 framework oxygen atoms and two water molecules. Water is found in the centre of the largest pore cages. Upon dehydration, the sodium cations become less stable due to a lower coordination number and begin to move into the position that were initially occupied by the water molecules. It is possible that the sodium migration coupled with changing unit cell dimension blocks the external water vapour from reaching some of the framework oxygen sites. This prevents the bulk isotopic composition of analcime from reaching the expected equilibrium value. As the silica content increases, the sodium content decreases, and there is a concurrent linear increase in the number of H_2O molecules. This structure is similar to that of leucite ($KAlSi_2O_6$), which is tetragonal .The only difference is that the larger K atoms in leucite occupy the H_2O 16 positions of analcime, instead of the Na 24 position. Barrer in 1971 reported diffusion coefficients for heulandite, chabazite, melinite and various sieve zeolites of the order of 100 thousand to 100 million times greater than that for analcime. Other zeolites can be expected to be greater in water content and internal surface area. Analcime has the densest structure of any zeolite.

The water content of analcime varies linearly with the silica content. As the silica content increases, the cation population decreases and there is a concurrent increase in the number of water molecules. The Na+ ions can be exchanged by alkali metal cations (Li^+, K^+), NH_4^+, Ag^+ and divalent ions (Ca^{2+}, Mg^{2+}) at high temperatures (225^oC). If the ions are too large, they occupy the water positions. For example, replacement of the Na^+ in analcime by K^+ or Cs^+ removes H_2O molecules due to occupancy of the water sites by the alkali metal ion.

Therefore, the degree of hydration varies with the degree of ion exchange.

The activation energy of analcime crystallization determined by kinetic study was 11.2 kcalmol⁻¹ corresponding to the dehydration of the silicate and aluminate ions in solution. The Avrami exponent (n) ranged from 3.4 to 6.4 indicating crystallization of the amorphous phase took place in the autocatalytic stage of the crystallization process. The diffusion exchange of Cu^{2+}, Ni^{2+}, $Pb^{2+}$and Zn^{2+} with Na^+ in the synthetic analcime was investigated in the temperature range 25-60 ^oC. The diffusion coefficients (D) were calculated from the BBK (Barrer, Barri and Klinowski) equation. Thermodynamic results indicating activation energy (E_a), entropy (ΔS^*) and free energy (ΔG^*) showed that all the channel sites were involved in the diffusion processes. Finally the ion exchange of Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} with Na^+ in the synthetic analcime was studied at 25-60 ^oC. The selectivity sequence for those ions entering analcime, indicated by the values of free energy (ΔG^o) was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. The results also indicated that the selectivity could be determined by enthalpy of hydration of cation. Standard entropy (ΔS^o) values were related to changes in water content and the exchange processes were endothermic.

Natural and synthesized zeolites are in focus of interests of ceramic industry in the last decades. Zeolites are used as a non plastic material or peptizing agent of ceramics masses, as a raw material for faience majolica and other products. The mineral is often found in alkalis activated and polluted by clay siliceous mixes after their autoclave treatment, it occurs in the concrete (mortar) articles modified with kaolin as a secondary component of the steam cured concrete binder with glass fibers and so on.

Some natural or synthesized zeolites are easily modified by the ion exchange method, therefore the minerals could be used as raw materials suitable for burning at lower temperatures in comparison with ordinary raw material. This is the way to obtain ceramics. Leucite and analcime often formed in the same natural conditions or are substituted by each other in the rocks. Thus the synthesis of analcime has the practical value[4].

In this paper we report on the characterization of analcime by XRD analysis. Special attention was paid to the investigation of calculation of the reaction parameters like Debye temperature, entropy and Gibbs free energy.

2. Interpretation of Debye temperature (A function of vibrational temperature)

Analcime is having a complex aluminosilicate framework that is common to all leucite-type feldspathoids. The maximum topological symmetry of analcime is cubic, $Ia3d$. However, deviations from cubic symmetry are well known. Regarding the genetic conditions, analcimes have been divided into five groups: primary igneous analcimes (called P-type); those formed by cation exchange from leucite (L-type or X-type); hydrothermal analcimes (H-type); sedimentary analcimes (S-type); and metamorphic analcimes (Mtype). X-type analcimes are typically cubic, whereas H

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type analcimes have tetragonal, rhombohedral, or orthorhombic symmetry. Dehydration of analcime is a one step process, as evidenced by the DTA and TG curves that show only one maximum at roughly 620 K; this corresponds to the loss of H2O molecules in the sole symmetry-independent site in the cubic structure. Kim and Burley in 1971 and in 1980 suggested that a structural phase transition occurs upon dehydration, which leads to a stable high-temperature dehydrated phase (high-analcime) with a unit-cell volume smaller than that of low-analcime. The kinetics of the dehydration process in *H*-type (hydrothermal) and X-type (cation exchange from leucite) cubic analcimes studied by DTA methods show apparent activation energies for the H-type analcimes that are four times greater than for X-type analcimes. Cubic analcime has recently been the subject of a series of papers, given its similarity to the structure of leucite that has displacive phase transitions currently of great interest. Putnis in 1993 reported that cubic analcime transformed to tetragonal upon heating at a temperature of about 600 K, depending on the atmosphere, mainly due to the *c* axis contraction. After dehydration, the unit cell became cubic again, due to the increase of the *c* axis, and it remained cubic until analcime turned to amorphous. Line in 1995 found no displacive phase transition associated to the high-temperature dehydration process of cubic analcime. Line in 1996 also studied the lowtemperature behavior of analcime by high-resolution neutron powder diffraction in the range 30–300 K, and found no sign of any phase transition[5].

The mineral analcime has attracted a lot of interest recently for a number of reasons. In part some of the interest has arisen because of the similarities of its structure to leucite, and the displacive phase transitions in the leucite and related materials are themselves a topic of current research[6]. One of the issues in the study of leucite has been the role of Al/Si ordering. In the cubic phase of leucite or analcime, there can be no long range ordering that is consistent with the *Ia3d* space group. The issue of short- range Al/Si ordering in analcime has therefore received some recent attention [6][7].

The low temperature behavior of analcime, focusing on the behavior associated with the water molecules. The study of rotational dynamics of water molecules is important. The structure of a synthetic sample of analcime has been determined as a function of temperature between 30-300K by high- resolution neutron powder diffraction[8].

3. Interpretation of entropy as a function of Debye temperature (vibrational temperature)

Since 1952, when Latimer published the second edition of his classic"Oxidation Potentials," sufficient free energy data on compounds and ions have been easily available to calculate equilibrium relations for many low temperature-low pressure systems of geologic interest. Although these data are strictly applicable only at 25°C and 1 atmosphere total pressure, the error in applying them to natural environments at or near the earth's surface is usually small.

Eh-pH diagrams utilizing such data were first used by Pourbaix (1949) as a convenient and provocative method of

showing interrelation between solids and dissolved ionic species with special reference to problems of metallic corrosion. Since then, similar diagrams have been used to depict approximate equilibrium relations between minerals and the ions in equilibrium with them in aqueous solution, and the results have been compared to natural relations, especially in problems of atmospheric oxidation of ores, and those of primary chemical precipitation.

When such diagrams were first constructed, it was with hope that they would bear a faint resemblance to nature, and conceivably might be used like an "ideal gas" or "ideal solution"-as hypothetical models useful in showing how far complex natural relations departed from simple systems involving chemical compounds instead of minerals, and containing only those ions or other dissolved species for which thermo chemical information happened to be available.

It has been a surprise to find that these naive chemical analogs of nature are directly useful in many instances. That is to say that numerous calculated solubilites fit those deduced from geologic relations, predicted assemblages of chemical compounds are reflected by identical assemblages of their nearest mineral analogs, and the environment of their occurrence, expressed on a pH-potential grid, corresponds to that found in the field. In fact, natural systems reflect the diagrams much better than most experimental ones!

The reasons for this agreement seem to be:

(1) There is sufficient time available for achievement of near-equilibrium in many natural low temperature aqueous environments. Even though the low temperature activation energies for transformations of silicate structures, for example, are high, and experimental work is well-nigh impossible, the months and years during which natural systems fluctuate through a small range of conditions permit a close approach to equilibrium.

(2) The amount of interaction in natural systems is less than might be anticipated from their complexity. For example, the error in calculating the free energy of formation of calcite from solubility data on sea water is small if all the currently known interactions are considered.

(3) The effect of biological activity is to add complexity on the one hand, and to catalyze reaction on the other. The net effect seems to be one of increasing reaction rates of well-established reactions, and hence of helping rather than hindering the investigator.

(4) In a considerable number of instances, the difference in free energy between a pure synthetic compound and its mineral analog is not large (although the difference may be extremely important for some processes.

Because of the close correspondence between natural relations and those calculated from free energy data-that is, from experiments carefully designed to approach equilibrium, the interesting possibility arose of obtaining free energy data directly from observations on natural systems[8].

4. Thermodynamic, compressibility and thermal expansion properties of analcime

If you are using *Word,* use either the Microsoft Equation Analcime ($NaAlSi_2O_6.H_2O$) is one of the most common rock-forming zeolites. It forms in a wide range of geologic environments that span a range of temperature and pressure from ambient to magmatic conditions. Enthalpy ΔH_f of formation at 25°C analcime was about $6.1 + 3.0$ kJ. The Gibbs energy of disordering at 298.15 K, 1 bar consistent with the retrieval calculations is ~ 6 kJ/mol[10][11].

From the single-crystal moduli the aggregate bulk moduli k_T is neary 720 kbar[9]. The bulk and shear moduli of both zeolites are relatively low compared with those of densely packed aluminosilicates[9]. The thermal expansion of analcime is $5x10^{-6}$ K^{-1}[12].

5. Objectives

5.1 Interpreting Diffraction Data with the Debye Theory

In 1914, Debye worked out the effect of the vibrational motion on the diffraction patterns of crystals. He showed that the intensity of a diffraction peak is proportional to an exponentially decreasing factor, now known as the Debye-Waller factor, which is given by

$$I \alpha e^{-8\pi^2 \langle u^2 \rangle / d^2} \quad (1)$$

The negative exponent is proportional to $<u^2>$, implying that the intensities decrease with increasing temperature as seen in the powder diffraction data. Moreover, the exponent is inversely proportional to d^2, which means that the attenuation due to vibrational motion is very strongly enhanced at short d-spacings.

If the interatomic forces behave like harmonic springs, as they do in the Debye model, the very general equipartition law requires that each vibrational mode have $(K_B T)/2$ of energy, which means that $<u^2>$ increases linearly with temperature at high enough temperatures:

$$\langle u^2 \rangle = \frac{K_B T}{\beta_{spring}} \quad (2)$$

A materials constant that appears in this equation is Θ_{DW}, which as mentioned earlier, is a direct measure of the atomic spring constant β_{spring} of the material. The relationship between Θ_{DW} and β_{spring} is given by the following equation [13]:

$$\beta_{spring} = \frac{mK_B^2 \Theta_{DW}^2}{3\hbar^2} \quad (3)$$

Crystals are often used to isolate individual spectral lines from a diode source. They are used in plasma diagnostics as components of a spectrograph. The crystal reflectivity follows the Bragg law for the location of the maximum reflection as a function of X-ray energy

$$n\left(\frac{12398.425}{E}\right) = 2d \sin\theta \quad (4)$$

n= an integer equal to the diffraction order
E= X-ray energy, eV
d= distance between the X-ray beam and the crystal
θ= angle between the X-ray beam and the crystal plane

For n=1 and a given θ, only the X-rays having the energy E given by the Bragg law will be reflected. For a monochromatic plane wave the Bragg reflection curve has a finite width[14].

From equation 1,2,3

$$\Theta_{DW}^2 = \frac{24\pi\hbar^2 T}{d^2 mK_B} \ln \frac{I}{I_o} \quad (5)$$

As intensity is directly proportional to the energy, so equation 5 can be modified as

$$\Theta_{DW}^2 = \frac{24\pi\hbar^2 T}{d^2 mK_B} \ln \frac{12398.425}{2d \sin\theta} \quad (6)$$

5.2 Formulation of Gibbs free energy

The relation between Gibbs free energy, Enthalpy and entropy is as follows:

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Enthalpy ΔH of any reaction is given by

$$\Delta H = \Delta H_{products} - \Delta H_{reactants} \quad (8)$$

Change in entropy of the system is given by

$$\Delta S = \Delta S_{products} - \Delta S_{reactants} \quad (9)$$

Entropy of a system is given by

$$S = \int \frac{C_p}{T} dT \quad (10)$$

Kieffer (1979, 1980) has developed a model based on lattice dynamics that allows calculation of heat capacity (C_V), entropy (S), and the Helmholz free energy (F) from vibrational frequencies and acoustic velocities. Calculated C_V can be compared to calorimetric measurements of C'' by using the anharmonic correction of [15].

$$C_p = C_V + T\alpha^2 k_T V$$

Which is modified to

$$C_p = C_V + \frac{T\alpha^2 k_T V}{D} \quad (11)$$

Where α is coefficient of thermal expansion, D is the specific density ,V is molar volume and k_T is the bulk modulus of substance. The above equation is further modified to

$$\alpha = \frac{dV}{VdT} \quad (12)$$

From 5 & 6

$$C_P = C_V + \frac{T\alpha^2 K_T V^2}{D \ln \alpha VT} \quad (13)$$

$$C_V = \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_{vib}}\right)^3 \quad (14)$$

$$\Theta_{vib} = \frac{h\nu}{K_B} \qquad (15)$$

Where Θ_{Vib} is the vibrational temperature and ν is the frequency of the substance. Therefore, the entropy for material
Entropy

$$S = \frac{12\pi^4 R}{15}\left(\frac{T}{\Theta_{vib}}\right)^3 + \frac{T\alpha^2 k_T V^2}{D\ln(\alpha VT)} \qquad (16)$$

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6. X-ray Diffraction analysis of Analcime sample

The x-ray diffraction analysis was carried out on x- ray diffractometer. The synthesized analcime sample, which was analyzed on XRD, consisted of x-ray tube with Cu K-Alpha. The chart which depicted peaks ran from 4° to 99° consuming current of 30mA and voltage of 40 kV at temperature 25°C. The XRD chart was given numbers coinciding the numbering of the sample peaks.

XRD analysis of analcime:

Table 1: Peak List

PEAK NO.	POS [2TH]	d-spacing	Rel intensity[%]
4	12.90	6.86235	2
10	21.90	4.18098	2
11	25.86	3.44647	100
13	30.75	2.92753	50
18	40.55	2.22462	40
21	47.70	1.90662	14
22	49.90	1.82750	2
24	52.85	1.73223	20
25	53.70	1.70680	6
26	54.65	1.67936	2
27	55.05	1.66810	2
30	57.90	1.59259	6
33	64.10	1.45270	2

Molar thermodynamic properties (units: kJ, K, kbar) . ΔG_c is the calculated Gibbs free energy of the formation from the elements, ΔG_m is the actual Gibbs free energy, ΔS_c is calculated entropy and ΔS_m is actual entropy of the substance, ΔH is the enthalpy of formation, V is the molar volume, α is the coefficient of thermal expansion, k_T is the bulk modulus, Θ_{Vib} is the debye temperature, D is the specific density [12].

Table 2: For calculation of Debye Temperature and Entropy for analcime

Parameters	Values
D	2.23
Θ_{vib} (K) (actual)	30-300
Θ_{vib} (K) (cal)	137
k_T (kbar)	730
V(Jbar⁻¹)	9.7

α (10⁻⁶ K⁻¹)	5.0
ΔS_c (JK⁻¹)	271.4
ΔS_m (JK⁻¹)	232.0

Table 3: For calculation of Gibbs free energy from calculated entropy

Parameters	Values
ΔH (KJ)(actual)	-3309.9
ΔS_c (JK⁻¹)	271.4
ΔG_c (KJ)	3390.97
ΔG_m (KJ)	3090.77

7. Results

The XRD patterns of the as-prepared analcime in the range of 2θ=12°-65° are shown in peak list. All evident peaks could be indexed as the analcime structure. Lattice parameters such as the values of d, the distance between adjacent planes in the Miller indices (hkl) are calculated from the Bragg equation, λ=2dsinθ . The calculated Debye temperature, entropy and Gibbs free energy are summarized in Table 1 and 2.

8. Analysis of XRD data and Gibbs free energy

Statistical theory, XRD data, combined with theoretical considerations of the energetic consequences of solid analcime were used in this study to derive thermodynamic properties for analcime that are in excellent agreement with not only the experimental observations, but also geologic observations of analcime stability and composition, support the presence of at least two distinct states of Si-Al disorder in natural and synthetic analcimes.

The results of the present study bear directly on the next order-disorder transition in analcime, that from low analcime to high analcime. The Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the disordering transition between low and high analcime at 298.15 K, 1 bar are related through:

ΔG=ΔH –TΔS

The properties of disordering in equation are dependent on the composition of analcime, and in the discussion below we consider only the properties of this transition for the composition of analcime.

It is clear that further investigation on the energetics of analcimes, along with experimental equilibrium observations and determination of the energetics of dehydration in low and high analcimes, are necessary in order to predict the conditions associated with a potential order-disorder transition in this material and to evaluate the stability of analcime in high temperature geologic environments. This investigation is particularly relevant to understanding the stability of analcime with respect to isostructural phases such as leucite, pollucite, and wairakite. Due to these calorimetric

results for analcime in nature it can be used in applications like water treatment process in industries.

9. Applications of Zeolites

9.1. Water treatment using natural zeolites

9.1.1 Wastewater treatment

The use of natural zeolites in waste water treatment is one of the oldest and the most perspective areas of their application. The presence of heavy metals (Zn, Cr, Pb, Cd, Cu, Mn, Fe, etc.) in wastewater is a serious environmental problem and their removal by natural zeolites have been extensively studied along with other technologies, including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation flocculation, flotation and electrochemical method. Recent investigations of natural zeolites as adsorbents in water and wastewater treatment, their properties and possible modification of natural zeolites have been a subject of many studies. Various natural zeolites around the world have shown good ion-exchange capacities for cations, such as ammonium and heavy metal ions. Modification of natural zeolites can be performed by several methods, such as acid treatment, ion exchange, and surfactant functionalization. The modified zeolites can show high adsorption capacity also for organic matter and anions.

9.1.2 Surface waters, ground and underground water treatment

The applicability of natural zeolites for the simultaneous removal of ammonia and humic acid, two of the most encountered current contaminants, from the surface waters was also investigated. Their removal depends on pH value, initial concentrations of humic acid and ammonia, temperature and contact time. The obtained results indicated that zeolite showed best performance for simultaneous removal of ammonia and humic acid at the pH close to that of natural waters. The use of natural and modified zeolites has been further investigated for the simultaneous removal of Fe and Mn ions from underground water samples. In particular, Fe and Mn removal levels are between 22-90% and 61-100% for natural zeolite - clinoptilolite. The development of new and cost effective methods to remove As from ground water and drinking water also becomes one of the research priorities. The occurrence of arsenic in natural ground waters is due to geological composition of soil.

9.1.3. Drinking and grey water treatment

Several conventional methods are used for the removal of pollutants from drinking water, such as coagulation followed by filtration, membrane processes and ion exchange. Adsorption methods proved to be effective, economically efficient, easy to perform and construct. Some experiments were conducted to study the efficiency of natural zeolite clinoptilolite and of the clinoptilolite-Fe system in removal of Cu, Mn, Zn, which are simultaneously found in water samples. A very unique property of natural zeolites is their selectivity towards cationic. The excellent results of adsorption experiments, especially for the modified forms along with the fact that the clinoptilolite–Fe system is inexpensive, easily synthesized and regenerated, harmless for human beings, as well as for the environment, we can consider it as a very promising selective metal adsorbent. Using iron/aluminum hydroxide to remove arsenic from water is a proven technology. An alternative method to enhance the performance is to use coarse-grained sorbents to increase the flow rate and throughput of the process. The removal of arsenic from drinking water was studied by using modified adsorbents (natural zeolite) prepared by the use of different iron solutions. The arsenic sorption on the Fe-exchanged zeolite could reach up to 100 mg/kg. The high surface area of modified natural zeolite (clinoptilolite)-iron oxide system in strongly basic conditions, can also enhance the removal of cations, like Cu from drinking water. The specific surface area of modified clinoptilolite increased up to 5-times (from 30 to 151m2 /g) and the maximum amount of adsorbed Cu ions was 13.6 mg/g zeolite for natural clinoptilolite and 37.5 mg/g for modified clinoptilolite. In spite of many scientific evidences of the effectiveness of zeolites in anion removal, not many of them are used on larger scales up to date. High concentrations of fluoride ions in groundwater up to more than 30 mg/L, occur widely, notably in the United States of America, Africa and Asia. More than 260 million people worldwide consume drinking water with a fluoride content of >1.0 mg/L. The available techniques for the removal of F- -anions from drinking water are membrane techniques, dialysis, electro-dialysis and finally adsorption techniques. Clinoptilolite-type natural zeolite was pre-conditioned with nitric acid solution before loading with Al3+, La3+ or ZrO2+. Aluminium-loaded low-silica zeolites as adsorbents for fluorides showed that modified zeolites were able to defluoridate water to below WHO's maximum allowable concentration (MAC) of 1.5 mg/L. The maximum fluoride adsorption was in the pH range of 4–8. High nitrate concentrations in drinking water sources can lead to a potential risk to environment and public health. Removal efficiency of NO3- ions can be increased by treatment of the clinoptilolite samples with HDTM+ (hexadecyltrimethylammonium cation) or cetylpyridinium bromide (CPB). Grey water is wastewater originated from bathroom and laundry in households. Ammonium is one of the most significant grey water contaminants. Natural and modified zeolites are used for their purification and they shows good performance with up to 97% of ammonium removal depending on contact time, zeolite loading, initial ammonium concentration and pH value. The desorption–regeneration studies demonstrated that the desorption of ammonium on the zeolite is sufficiently high.

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