



# XPS (X-Ray Photoelectron Spectroscopy) Study of Removing Iron Ions from Water by Zeolite and Bentonite

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## Abstract

Zeolites as a member of family of hydrated aluminosilicate minerals contains alkali and alkaline-earth metals. They are noted for their lability toward ion-exchange and reversible dehydration. Their framework structure encloses interconnected cavities occupied by large metal cations and water molecules. Bentonites are clays generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. They present strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid. The special properties of bentonite (hydration, swelling, water absorption, viscosity, thixotropy) make it a valuable material for a wide range of uses and applications. The purpose of this paper is to document an ability of a zeolite and bentonite to remove iron ions and various other pollutants from water. The surface analysis of zeolite and bentonite was performed by the very sensitive analytical device – XPS (X-ray photoelectron spectroscopy).

**Keywords:** XPS, bentonite, zeolite, iron, adsorption

## Introduction

With increasing rate of urbanization is hand in hand increasing a rate of the environmental pollution. Today, a world is facing a water crisis. It is necessary to reduce negative impacts of human industrialization on environment and develop such technologies, which will be more ecological and will be helpful in environmental cleaning processes. A huge quantity of wastewater has been produced from industrial processes and was discharged into soils and water systems. Contained pollutants such as cationic and anionic ions, oil and organics have poisonous and toxic effects on the whole ecosystem.

For the removal of these contaminants, a variety of techniques, such as chemical precipitation, electro-flotation, membrane separation, reverse osmosis, electro dialysis and others, have been developed. 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. Application of natural zeolites for water and wastewater treatment is a promising technique in environmental recovery processes.

## Zeolites

Zeolites as crystalline aluminosilicates have a microporous structure with elevated thermal stability and high chemical resistance. Due to their thermal stability, high exchange capacity, easy modification and selectivity, zeolites are considered to be excellent adsorbents, which have large adsorption capacity with good cationic exchange properties [1].

In chemical industry they are usually used for purifications and separations. Their ion exchange capacity is associated with amount of Al and makes them suitable for their application in detergents, metals removal, and recovery industries, among others [2].

They consist of honeycomb structure with pores. The structure of zeolite is shown in Fig.1.

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. Substitution of Si<sup>4+</sup> by Al<sup>3+</sup> 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.

The ion-exchange behaviour of natural zeolite depends on several factors, such as the framework structure, ion size and shape, charge density of the anionic framework, ionic charge and concentration of the external electrolyte solution. The adsorption characteristics of any zeolite depends on 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].

The sorption of metal ion by zeolite is significantly affected by the pH. The lower metal uptake in more acidic conditions is probably attributed to competition between the metal ions and the hydrogen ions. It is documented, that the most optimal pH is 7. It was also observed, that the adsorption capacity has a correlation with the mass of sorbent [4].

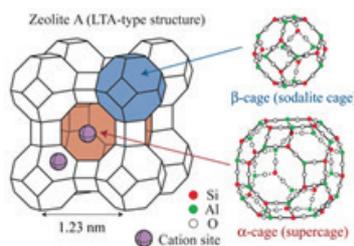


Fig. 1. The structure of zeolite [5]

Rys. 1. Struktura zeolitu [5]

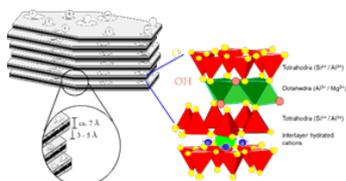


Fig. 2. The structure of bentonite [6]

Rys. 2. Struktura bentonitu [6]

## Bentonites

The main clay mineral of bentonite is montmorillonite, which is a good sorbent because it has high cation exchange capacity and a large specific surface area. Raw montmorillonite can sorb cations, but not anions, because of the negative charges on the crystal lattice. Therefore, several methods have been investigated in order to sorb anionic pollutants by montmorillonite [7].

Montmorillonite is a layered, dual-dimensional mineral. It consists of hydrated aluminium silicate [8] [9]. The crystal unit of montmorillonite is Tetrahedral-Octahedral-Tetrahedral (TOT) layer structure, which is assembled by two silicon-oxygen tetrahedral sheets fused to one edge-shared aluminium-oxygen octahedral sheet. The structure of bentonite is shown in Fig. 2. The cations in the interlayer space of montmorillonite can be exchanged which is the cation exchange property of bentonite [8] [9] [10] [11].

It is used to line the base of landfills to prevent migration of leachate, for quarantining metal pollutants of groundwater, and for the sealing of subsurface disposal systems for spent nuclear fuel. Similar uses include making slurry walls, waterproofing of below-grade walls, and forming other impermeable barriers, e.g., to seal off the annulus of a water well, to plug old wells [12].

Sodium bentonites absorb large quantities of water, swelling to many times their original volume. They have been used for building a seal dams, in portland cements and concrete, ceramics, emulsions, insecticides, soaps, pharmaceuticals, and paints, in the manufacture of paper they are using for clarifying water and as a water softener to remove calcium from hard water.

## Materials and methods

X-ray photoelectron spectroscopy is a sensitive and non-destructive method for analysing the surface of materials, based on the binding energy of chemical species, providing information about the chemical composition and the electron structure of the surface to the depth of 10 nm.

The XPS measurements were conducted using PHOIBOS 100 SCD model of XPS instrument that was equipped with a non-monochromatic X-ray source. The survey spectra were measured at the transition energy of 70 eV and the core spectra

at 30 eV at room temperature. All spectra were obtained at a basic pressure of  $2 \times 10^{-8}$  mbar with the AlK $\alpha$  excitation at 10 kV (150 W) and were corrected with the reference to aliphatic carbon at 285 eV. XPS data were processed using the CASA XPS software.

The samples were derived using distilled water, ferric sulfate non-hydrate  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and sorbents consisted of Bentonite Brown, Bentonite Blue (from Kramost a.s. company of Braňany), zeolite Zeocem M-20 and Zeocem M-50 ((klinikoptilolite) from Zeocem a.s. company Bystré of Nižný Hrabovec). The mass of 1g of each sorbent was placed into the PET bottles with 10 ml of distilled water. Calibration mixture of ferric sulfate was prepared by using 100 and 2000 mg/l of ferric sulfate non-hydrate. The corresponding mass of the ferric sulfate non-hydrate and 100 ml of distilled water were placed into the beakers, of which 10 ml was taken out. The rest of the solution was decanted to the PET bottles with the sorbents. The filter apparatus with the filter papers isolated the adsorbents with the ferric sulfate from distilled water and un-adsorbed residues. The samples were dried, homogenized in achate mortar and subjected to XPS analyse.

## Results and discussion

As shown on Fig. 3, with the iron concentration of 100 mg/l by using bentonite brown – Ca, Al, Fe species are bonded on the adsorbent, while Si species were desorbed. With the iron concentration of 2000 mg/l, the opposite effect occurred. Fig. 4 illustrates the desorption process of the Al, Si and Ca species with the iron concentration of 100 mg/g by using bentonite blue. Only amount of Fe increased. With the iron concentration of 2000 mg/l, the amount of Si and Al species were increasing together with the Fe species, as well. The decrease of the Ca species is visible for both cases.

In case of adsorption on zeolite M-20 (Fig.5) it is visible, that with the iron concentration of 100 and 2000 mg/l, the amount of the Al and K species is decreasing. On the other hand, with the different iron concentrations we can see the differences in amount of Si and Ca species. Their quantity is decreasing with the iron concentration of 100 mg/l, while increasing with the iron concentration of 2000 mg/l.

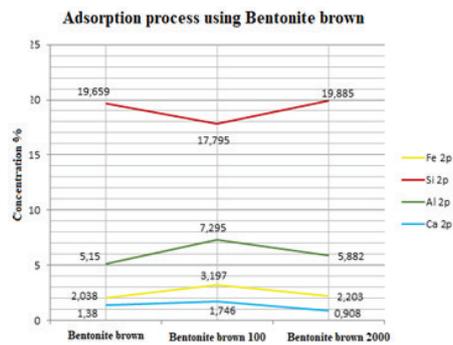


Fig. 3. Bentonite brown  
Rys. 3. Bentonit brązowy

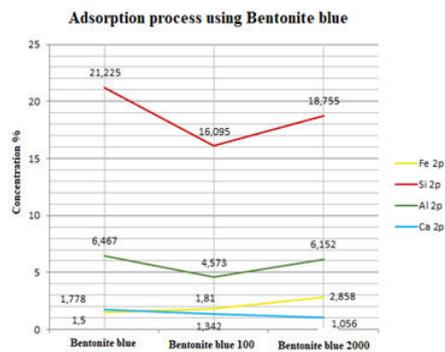


Fig. 4. Bentonite blue  
Rys. 4. Bentonit niebieski

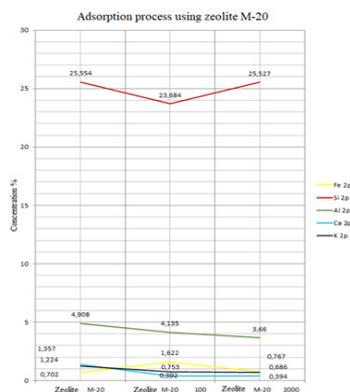


Fig. 5. Zeolite M-20  
Rys. 5. Zeolit M-20

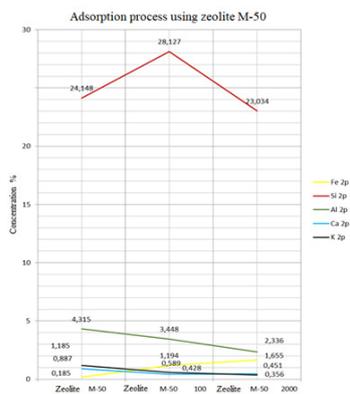


Fig. 6. Zeolite M-50  
Fig. 6. Zeolite M-50

Fe species are behaving in the opposite way. The highest adsorption is occurring with the lower concentration of iron ions.

As we can see on the Fig. 6, after the adding 100 mg/l of iron ions into the zeolite M-50, it is documented increase of the Fe and Si species, but only Fe species are still increasing even in iron concentrations of 2000 mg/l. In both cases, the quantity of Al and K species is decreasing. Calcium species are decreasing at first (100 mg/l of iron ions added), but then increasing (2000 mg/l of iron ions added).

## Conclusion

The results showed, that the best adsorption process occurred by using bentonite blue with the iron concentration of 2000 mg/l. In the primary structure of bentonite blue is

amount of Fe 1.5%. After the adsorption we measured 2,858%. In case of zeolites, the best results were shown by zeolite M-50 with the iron concentration of 2000 mg/l. In basic structure of zeolite M-50 is amount of Fe 0,185%. After the adsorption was this amount increased to value 1,655%.

## Acknowledgements

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## *Badanie z użyciem XPS (roentgenowskiej spektroskopii fotoelektronowej) usuwania jonów z wody za pomocą zeolitów i bentonitów*

*Zeolity należą do rodziny uwodnionych minerałów glinowokrzemianowych, zawierających metale alkaliczne oraz alkaliczno-ziemne. Są zauważane ze względu na ich zdolność wymiany jonowej oraz odwrotnej dehydratacji. Ich struktura zawiera wewnątrz połączona wgłębienia zajęte przez duże kationy metali oraz cząsteczki wody. Bentonity to ily tworzone często poprzez alterację popiołu wulkanicznego, zawierające głównie minerały smektytu a zazwyczaj montmorillonitu. Wykazują silne właściwości koloidalne a ich objętość wzrasta kilkukrotnie podczas wejścia w kontakt z wodą, tworząc w ten sposób galaretowatą i lepłą ciecz. Specjalne właściwości bentonitu (hydratacja, puchnięcie, absorpcja wody, lepkość, tiksotropia) powodują, że jest to cenny materiał dla szerokiej gamy zastosowań. Celem tego artykułu jest udokumentowanie zdolności zeolitów oraz bentonitów do usuwania jonów żelaza oraz różnych innych zanieczyszczeń z wody. Analiza powierzchni zeolitu i bentonitu została wykonana za pomocą bardzo czułego urządzenia analitycznego – XPS (roentgenowska spektroskopia fotoelektronowa)*

**Słowa kluczowe:** XPS, bentonit, zeolit, żelazo, adsorpcja XPS, bentonit, zeolit, żelazo, adsorpcja