Supplementary research of clinoptilolite-rich tuff composites after adsorption trials using the XPS technique

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Abstract: The paper deals with fabrication of carbonized and hydrophobized clinoptilolite-rich tuff using organic carbon rich substances, here particularly starch and waste vegetable residues, which were pyrolytically combusted and covered the external zeolite surface. Hydrophobization of the zeolite external surface was accomplished by octadecylammonium surfactant. Both surface modified clinoptilolite-rich tuffs were tested and compared with each other with regard to removal of organic (phenol) and inorganic (chromate, arsenate) pollutants from aqueous solutions. These elaborated composites with surface adsorbed pollutant species were analysed by X-ray photoelectron spectroscopy (XPS).

Keywords: Clinoptilolite-rich tuff, hydrophobization, carbonization, chromate and arsenate oxyanion and phenol adsorption, XPS

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1 Introduction

Inorganic arsenic and chromium are documented human carcinogens. Primary natural sources include mineral deposits, hydrogeothermal activity and volcanism. Major anthropogenic sources of arsenic include wood preservatives, pesticides, mining and smelting [1, 2]. Arsenic appears predominantly in natural air saturated aquifiers in the form of an As(V) anion. Sulfidic ore drainage caused enhanced As concentrations in some Artesian wells of Slovakia. Hexavalent chromium comes into water bodies from tanneries, chemical, energy and ceramics industries [3]. The industrial water treatment processes employed so far for the removal of both oxyanions are enhanced coagulation and precipitation, ion exchange, adsorption on iron oxide coated sand or costly membrane technologies.

Sources of phenolic waste waters are the herbicide, phenolic resin, plastics and fiberglass manufacturing industries, petroleum refineries, stocking factories and others. The conventional treatment methods for phenolic waste waters are adsorption, solvent extraction, biological and chemical oxidation [2].

The toxicity of phenols may be summarized as follows: Toxic to fish at levels above 2 mg/l; causing a taste in fish flesh at concentrations far below this level; toxic to aquatic life after exposure of several days due to the high oxygen demand and through the presence of chlorine in disinfected drinking waters (carcinogenic intermediate production) [2].

Active charcoal applied in water treatment mostly as batch-type or flow-through bed-type reactor offers several adsorption mechanisms, e.g. simple physical Van der Waals attractions, electrostatic forces induced by charged functional groups and high energy interactive chemisorption.

Generally, active charcoal is designed mostly for removal of industrial organic pollutants, however several surface reaction mechanisms may effect removal even of some other accompanying pollutants depending upon the base material used for the industrial manufacturing process [4, 5].

Therefore the objective of our current study is focused on the fabrication and characterization of the advanced clinoptilolite-rich tuff composites based on their external surface carbonization, utilizing the various carbon-rich substances (here specifically waste vegetable residues and starch), which due to their above surface C-coating improve or upgrade the clinoptilolite-matrix properties with respect to non-polar organic species, in this case to phenol.

Simultaneously, using the other treatment method, the zeolite surface was surfactant hydrophobized by octadecylammonium acetate (ODA) to enhance its efficiency in specific water pollution control, i.e. for chromate and arsenate removal, in particular.

Both surface modified clinoptilolite-rich tuffs were tested and compared to each other with regard to removal of the above organic and inorganic pollutants from aqueous solutions. These elaborated composites with surface adsorbed pollutant species were analysed by X-ray photoelectron spectroscopy (XPS).
2 Experimental

2.1 Materials

The natural clinoptilolite dominated zeolite, crushed and ground into a 0.4 - 1 mm (35-16 mesh) fraction, was supplied for lab-experiments by ZEOCEM, Share Holding Company, mining at the East-Slovakian repository Nižný Hrabovec. The mineralogical and chemical compositions of the raw zeolite were published elsewhere [5].

2.2 Methods

The specific C-rich waste substratum carbonization inside a high temperature pilot combustion chamber installed at the laboratory used direct heating by exhaust gas flow in an oxygen free atmosphere. The process had many similarities with biomass pyrolysis. During carbonization inside an oven at lower temperatures (∼350 °C) the main process was cracking, producing liquid hydrocarbons and tars. About 650 °C, hydrogen was formed, and finally at about 700 °C, carbon char was produced instead of ash. The heat from the process was recuperated [4] - see the principal sketch of the oven used for carbonization (Scheme 1)

Scheme 1 The principal sketch of the oven used for carbonization.

Hydrophobization of clinoptilolite with ODA-surfactant, to enable chromate and arsenate removal was thoroughly described in paper [3].

Equilibrium adsorption and isotherm measurements at the laboratory were performed with aqueous model solutions of phenol, arsenate or chromate salts, including surface modified (hydrophobized, carbonized) vs.natural clinoptilolite with the solid-to-liquid ra-
tio 1g/100 ml, at $T = 23 \pm 0.1 \, ^\circ\text{C}$. All experiments were run in triplicate, keeping the suspensions equilibrated up to 7 hrs.

2.3 Analytical procedure

Aqueous phenolic solutions were analysed by means of a Hewlett Packard 8452A (USA) Diode Array Spectrophotometer at 286 nm against the calibration curve, measured under analogous conditions by the distilled water pH-value.

Chromate and arsenate concentrations in aqueous solutions were analysed by atomic absorption spectrometry (AAS) with flame atomization on a Perkin-Elmer (USA) apparatus, Model 1100.

X-ray photoelectron spectral (XPS) measurements were carried out on the Specs Phoibos-100 hemispherical analyser operating at constant analyser energy mode. The measurements were performed at room temperature using 100W (wide scans) and 250W (narrow scans) of the Mg anode. The base pressure in the UHV chamber was below $2 \times 10^{-10}$ mbar. The spectrometer energy scale was calibrated using Au 4f$_7/2$ and Cu 2p$_3/2$. Sample charging was compensated by an electron flood at 0.5 mA current and 0.1 ± 0.01 eV energy. The detection angle was normal to the surface. The samples as a powder in the as received state were pressed into a molybdenum sample holder. The C1s peak of the contamination carbon, at 284.6 eV was taken as reference in calculating BEs and accounting effects. The spectra were collected and processed by SpecsLab software. Experimental peaks were decomposed into components (75 % Gaussian, 25 % Lorenzian) using a nonlinear, least squares fitting algorithm and a Shirley baseline.

3 Results and discussion

The simplified principles of both anionic and non ionic species bonded onto the surfaces of hydrophobized or carbonized clinoptilolite dominated zeolite were thoroughly discussed in the scientific papers [3–5]. While below the critical micelle concentration (CMC) of octadecylammonium (ODA)-surfactant in aqueous solution monolayer or hemimicelle formation appears, above the CMC of the surfactant in suspension, association of hydrophobic tails into a bilayer or admicelle takes place. The latter phenomenon is responsible for an enhanced anionic solute uptake due to the upward oriented, positively charged ammonium head groups.

No such efficiency of dissolved anion uptake was achieved with surface carbonized zeolite, as a consequence of its similarity to active charcoal, which is mostly encountered for organic substance removal.

Many laboratory bench-scale trials designed for adsorption-desorption characterization exhibited a higher efficiency of inorganic oxyanion removal from aqueous solutions with ODA hydrophobized zeolite, in which the anionic species remained irreversibly adsorbed, than for those using the carbonized zeolite (Figs. 1, 2, 3).

Nevertheless, a satisfying abatement of phenol concentration by means of the car-
Fig. 1 Chromate adsorption on ODA-clinoptilolite-rich tuff.

Fig. 2 Arsenate adsorption on ODA-clinoptilolite-rich tuff.

Fig. 3 Phenol adsorption on carbonized clinoptilolite-rich tuff.
bonized clinoptilolite-rich tuff with respect to the active charcoal (Slovak industrial product trademark HYS-N) has been achieved on the laboratory scale, by testing numerous aqueous model solutions in static and dynamic arrangements. Obviously, no adsorption of phenol was observed when using an untreated clinoptilolite dominated zeolite.

The adsorption data analysed according to the Freundlich, Langmuir and BET models of isotherms are tabulated (Table 1). The isotherm constants were calculated using linear regression methods. As the published correlation coefficients and standard deviations indicate, the straight lines fitted very well to the experimental points. No such high fit for the BET equation was achieved for the adsorption of inorganic oxyanions onto ODA-clinoptilolites. On the other hand, the mathematical process description using the BET equation for phenol adsorption onto carbonized clinoptilolite, displays a calculated correlation coefficient that may be considered as satisfactory.

| Species                                | Freundlich isotherm | Langmuir isotherm | BET isotherm |
|----------------------------------------|---------------------|-------------------|--------------|
| carbonized clinoptilolite vs phenol solution | $a = 0.0836 \cdot c^{\frac{1}{1.42}}$ | $\frac{1}{a} = \frac{1}{0.0165} \cdot \frac{1}{c} + \frac{1}{10.3}$ | $a = \frac{c(s)}{0.0885 \cdot [c(s) - c]}$ |
| R (correlation coefficient)            | 0.8757              | 0.9644            | 0.678        |
| SD (standard deviation)                | 0.2817              | 0.3386            | 0.00042      |
| ODA - clinoptilolite vs. chromate solution | $a = 0.46 \cdot c^{\frac{1}{1.87}}$ | $a = \frac{0.04545 \cdot c}{(1+0.0009 \cdot c)}$ | —            |
| R                                      | 0.9216              | 0.8745            | —            |
| SD                                     | 1.7198              | 0.9282            | —            |
| ODA - clinoptilolite vs. arsenate solution | $a = 0.16 \cdot c^{\frac{1}{1.44}}$ | $a = \frac{0.0377 \cdot c}{(1+0.0004 \cdot c)}$ | —            |
| R                                      | 0.9894              | 0.9969            | —            |
| SD                                     | 0.3947              | 0.8726            | —            |

Table 1 Adsorption isotherm data for the systems studied: aqueous phenol solution vs. carbonised clinoptilolite and aqueous arsenate or chromate solutions vs. ODA hydrophobized clinoptilolite.

Raw clinoptilolite coated with carbonaceous substances resembled active charcoal and, moreover, proved to have a higher attrition resistance, than the conventional charcoal due to the zeolite content [7, 8]. XRD measurements have not recorded any clinoptilolite matrix destruction so far. SEM analysis supported the amorphous character of carbon coated on the adsorbent surface, the morphology of which was evidently enriched with
meso- and macroporous-sized holes. Finally, Raman spectra confirmed also that the carbon, after its immobilization on the external zeolite surface using the carbonization process described above, was crystallographically disordered [6].

Currently, surface composition and sorption complexes of above mentioned samples were studied using a very powerful XPS (alternatively ESCA - electron spectrometry for chemical analysis) technique. This surface analytical and thin film technique enables the investigation not only of the quantitative elemental composition of solid surfaces, including surface Si/Al and bulk Si/Al ratios that are important in zeolite chemistry, but also various diffusion, oxidation and other processes and reactions on zeolite composites, concentration and distribution profiles of host species, microstructural irregularities, surface interfaces and binding energies. The method offers simultaneously high lateral and deep resolution sensitivities up to several atomic layers, without any destruction forces.

Studies on zeolite surface phenomena and their surface microtopography by means of this ultra high vacuum technique have become well established in recent years.

Binding energies (BEs) shown in Figs. 4, 5, 6 are element specific, and contain chemical information, due to dependence of the core electron energy levels on the chemical state of the element. Usually, the BE increases with increasing oxidation state or with the elevated electronegativity of the ligands.

![Cr 2p$_{3/2}$ spectra of ODA-clinoptilolite with adsorbed chromate.](image)

In accordance with this rule, the highest BEs were observed for the elements chromium and oxygen. Among the studied metals, a higher binding energy component was assigned to tetrahedrally coordinated Cr(VI) than that for the similarly coordinated As(V) on the ODA-clinoptilolite.

Some traces of arsenic in the oxidation state As(III) and some of Cr(III) were also detected, due to an in vacuo reduction process, the effect of surrounding CO or to X-ray irradiation in the XPS system.

Since the deconvoluted N 1s XPS spectra for all the samples regularly showed about a 2:3 concentration ratio for the ODA-nitrogen bonds, this permitted the identification
Fig. 5 XPS As 2p spectra of ODA-clinoptilolite with adsorbed arsenate.

Fig. 6 The XPS N 1s core level of ODA (a), ODA-clinoptilolite (b), ODA-clinoptilolite with adsorbed chromate (c), ODA-clinoptilolite with adsorbed arsenate (d).

of two types of bond. The lower energy peak is probably the ODA interaction with the aluminosilicate skeleton, while the higher energy one represents the interaction of the
ODA with the metal oxyanions that are attached on the outer layer (Fig. 6). According to this figure spectrum (a) for the pure ODA demonstrates very clearly this deconvolution into C-N and N-H bonds.

As Table 2 indicates, the surface Si/Al ratios of both the AODAC and CHODAC samples are determined to be 3.5, which corresponds only approximately with the bulk stoichiometric ratios published for clinoptilolites (i.e., 2.7–5.6) [5]. The reason might be in a difference of Si/Al ratio in the surface and that in the bulk, and also in sample inhomogeneity.

Furthermore, the XPS method confirmed that the whole surface of ODA-modified zeolite was covered with carbon, without differentiation as to whether surface or bulk carbon is present. There was no evidence for, or only traces of C-O or C=O bonds.

Regarding C-element contents of zeolite samples studied by XPS vs. theoretically calculated C-contents of \((\text{ODA})_2\text{CrO}_4\) and \((\text{ODA})_3\text{AsO}_4\) complexes, the values are more or less comparable (Table 2).

On the other hand, chromium and arsenic contents on the ODA-modified zeolites differ considerably from the theoretically predicted values. On the basis of the predominantly mesoporous nature of the structure of Slovakian clinoptilolite, the positively charged ammonium groups of the ODA chains may insert and so be able to shift the electrostatically attached arsenate or chromate much deeper into the mesoporous clinoptilolite than that which allows the XPS surface analysis [6]. The lowering of the above metal concentrations in comparison with the theoretically predicted values also may be caused by some clustered sorption pattern, i.e. by the agglomerations of the surfactant molecules with the adsorbed chromate or arsenate anions, so far confirmed by SEM, TEM and UV-VIS analyses [3, 4].

Consequently, the XPS measurements suggest a larger agglomeration of chromium and arsenic complexes on the zeolite surface than the values obtained from the 10-20 nm thickness of the outer layer detection.

A higher concentration of oxygen on the zeolite composite was found up to 3.5 times relative to its content in the oxyanions complexes, probably due to oxygen presence in the composite matrix, i.e. in the \(\text{AlO}_4^{5-}\) and \(\text{SiO}_4^{4-}\) structural skeleton.

The XPS spectra in Figs. 7, 8 indicate mostly C-element occurrence (71.4 %) in addition to oxygen (20.8 %), nitrogen (5.8 %) and silicon (2 %) appeared on the carbonized zeolite surface (Table 2).

The carbonized surface of zeolite (carbon char) had the character of active charcoal. In the case of each combusted material (currently combusted waste starch and vegetable residues), the char retained its texture from the original material.

IR absorption spectroscopy using the KBr pellet technique confirmed clearly the differences in the presence of mineral components and clarified how the carbon intercalates with those mineral components arising from the used substratum were developed [4]. The polysaccharides and vegetable residues are usually enriched with some residual chlorophyll (C-N bonds) and their derivatives that also contain the elements N, P or S. The XPS C1s core levels of the ODA- and carbonized clinoptilolite-rich tuffs, show broader peaks, and
Fig. 7 The XPS survey scans of ODA-clinoptilolite with adsorbed chromate (a) and arsenate (b), and of carbonized clinoptilolite (c).

thus a higher variety of C- bonded species are present in the carbonized surface than that in the ODA-hydrophobized sample. In particular, alcoholic, aldehydic and ketonic oxygen probably contributed to about 20 % content in the carbonized clinoptilolite sample (Table 2).

| Element/Sample | C   | N   | O   | Al | Si | Cr | As |
|----------------|-----|-----|-----|----|----|----|----|
| Arsenate on ODA-clinoptilolite (AODAC) | 51.2 | 1.5 | 29.9 | 3.7 | 13.2 | - | 0.4 |
| Chromate on ODA-clinoptilolite (CHODAC) | 48.5 | 1.5 | 31.6 | 4.0 | 14.1 | 0.2 | - |
| \((\text{ODA})_2\text{CrO}_4\) | 65.7 | 4.3 | 9.7 | - | - | 7.9 | - |
| \((\text{ODA})_3\text{AsO}_4\) | 68.1 | 4.4 | 6.7 | - | - | - | 7.9 |
| Carbonized clinoptilolite (CACL) | 71.4 | 5.8 | 20.8 | - | 2 | - | - |

Table 2 Surface composition of elements in the studied samples determined by XPS, and calculated values for compounds according to their theoretical formulas (in %).

4 Conclusion

In recent decades the modern material properties have been improved by fabrication of new multiphase systems, i.e. composites which usually multiply the appropriate proper-
Fig. 8 The XPS C 1s core level of ODA-clinoptilolite with adsorbed chromate (a) and arsenate (b), and of carbonized clinoptilolite (c).

ties of the native components and thus the final products are prepared with synergetic effects. Surface engineered material chemistry is currently one of the most developing sciences and the surface coverings with some protective films or thin layers of less than 1 μm thickness are starting to play a key role in electrotechnical, biomedical, optical, construction industries as well as in environmental protection.

The results of the presented research clarify some aspects of the adsorption phenomena on such zeolite based composite materials, in this case targeting water pollution control.

Currently surface engineered, hydrophobized and carbonized clinoptilolite-rich tuffs have been confirmed to operate in accordance with the hypothesis of enhanced water pollutant removal so far, a purpose for which the native clinoptilolite was inactive.

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