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FOR THE
PROTECTION
OF THE
ENVIRONMENT 4
ENVIROMENTAL SCIENCE RESEARCH

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Preface

The central goal of Chemistry for the Protection of the Environment conference series is to improve technology transfer and scientific dialogue, thereby leading to a better comprehension of and solution to a broad spectrum of environmentally related problems.

The first meeting in the CPE series was organized by Professor Lucjan Pawlowski and Dr. William Lacy in 1976 at the Marie Curie-Sklodowska University in Lublin, Poland. The conference dealt with various physicochemical methodologies for water and wastewater treatment research projects that were jointly sponsored by the United State Environmental Protection Agency (EPA) and Poland.

The great interest expressed by the participants led the organizers to expand the scope of the second conference, which was also held in Poland in September 1979. A third and enlarged symposium was again successfully held in Lublin, Poland in 1981. At that time, the participating scientists and engineers expressed their desire to broaden the coverage as well as the title "Chemistry for the Protection of the Environment." The next meeting, CPE IV, was convened in September 1983 at the Paul Sabatier University in Toulouse, France, and included participants from various government agencies, academia, and the private sector, representing industrialized countries as well as emerging nations from both the East and West, in an independent non-political forum.

CPE V, held in September 1985 at the Catholic University in Leuven, Belgium, covered topics dealing with treatment technologies and phenomena related to hazardous waste and the utilization of fossil fuels. It provided an opportunity for interdisciplinary discussions and encouraged the exchange of ideas among international specialists from diverse fields and backgrounds.
CPE VI was held in 1987 at the University of Turin in Italy, with over 150 scientific papers and posters presented to an audience from 32 nations. This assemblage comprised in equal measure scientists from Europe, the New World, and developing nations.

CPE VII was convened at the Catholic University in Lublin, Poland in 1989. The exchange of information by approximately 200 scientists and engineers made this a memorable scientific meeting. Distinguished participants included Poland’s Minister and Deputy Minister for Environmental Protection, U.S. Scientific Council, Israel’s Deputy Minister of the Environment, presidents and vice presidents of five universities, representatives of the Academies of Sciences for Czechoslovakia, France, Italy, Poland, and the U.S.S.R., as well as many department heads and acclaimed scientists.

In September 1991, CPE VIII was convened in Lublin, Poland. The technical presentations were original and informative, with the major topics being chemical/physical/biological treatment technologies, monitoring, modeling, and risk assessment.

CPE IX, held in September 1993 in Alexandria, Cairo/Luxor, Egypt, was a joint conference with EPA/U.S. AID’s Fourth International Symposium on Industry in the Developing World. This included a workshop on industrial pollution prevention and clean technologies, and other cooperation and institutional issues. Participants were comprised of a multi-disciplined technical group from 27 countries.

CPE X, the 20th anniversary meeting, was held in the city of CPE’s birth, Lublin, Poland. Papers and posters on technology transfer; novel, innovative and alternative treatment processes; and environmental problems facing countries were presented. The meeting was enhanced by the participation of large delegations from both The Peoples Republic of China and the Taiwan Chinese Republic.

CPE XI returned to Cairo, Egypt in 1997, and papers and posters were presented on adsorption, analytical methods, chemical/biological/treatment, groundwater studies, ion exchange, modeling, risk assessment, waste minimization and treatment, and for the first time, ISO 14001, which focuses on environmental management and quality systems.

CPE XII took the conference series to the other side of the world, and was held in Nanjing, China in September 1999. Once again, the conference brought environmental scientists, engineers, and policymakers together to present innovative solutions to environmental problems and to develop collaborations.

CPE XIII, marked the 25th anniversary of CPE and the first time the CPE conference was convened in the United States. Environmental scientists,
engineers, and policymakers from India, Japan, the Philippines, Poland, Germany, the Netherlands, Russia, Slovakia, and the United States gathered to discuss current issues, including new risk assessment methodologies, innovative analytical and waste management techniques, and emerging environmental security policies. Field excursions led by Hilo scientists to the Hawaii Scientific Drilling Project and the Hawaii Volcanoes National Park, and an ecological tour of local rainforests complemented the lectures and promoted interactions among the participants. For the first time, a student poster session was held, and the Tristan J. DLugosz Memorial Award for excellence in student poster presentations was presented to University of Hawaii at Hilo students Mark Albins, Wiley Evans, Megan Flynn and Rachel Horton for their poster “How Does Hilo Bay Function? A Biogeochemical Snapshot of the Waters and Sediments of the Bay.” CPE co-founder and co-president Dr. William J. Lacy was honored with an award commending him for his vision and role in establishing CPE and promoting scientific dialogue and international cooperation among participating environmental scientists and policymakers from around the world. Through his leadership and knowledge, the goals of CPE have become a reality.

Robert Mournighan, CPE XIII Lead Editor
Marjorie Auyong Gonzalez, CPE XIII Chairperson
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STUDY OF THE CLINOPTILOLITE-RICH TUFT-BASED COMPOSITES FOR SOME AQUEOUS ANIONIC SPECIES RECOVERY

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Abstract: Batch and column sorption experiments have been performed to study a significantly enhanced removal of toxic oxyanions, i.e. chromate and arsenate from aqueous effluents on inland clinoptilolite modified by the octadecylammonium acetate (ODA). The arrangements (orientation and length) of the surface-attached organic chains and thus the initial concentration of ODA - modifier by composite preparation have been the important factor for the difference in the adsorption states of the guest species [oxyanions]. Novel nano-structure inorganic - organic composites prepared have been investigated using SEM, thermogravimetry, NMR, IR, HR TEM, UV-VIS DRS and powder XRD spectral analytical methods. Finally, adsorption isotherms for system studied have been expressed. Some approach for regeneration of exhausted surfactant-immobilized clinoptilolite with inorganic salt solutions under dynamic regime has been proposed, respectively.

Key words: Clinoptilolite, ODA-modifier, chromate and arsenate removal, adsorption, isotherm, and breakthrough curve.

1. INTRODUCTION

Both arsenic and chromium are considered to pose risks to public health and, in the inorganic state, especially chromium in hexavalent form, are generally highly toxic to biota. Their toxicity to humans was evidenced by
many acute poisoning episodes in past; e.g., Nippon Chemical Ind. has apparently been employed in construction materials principal source of airborne chromium, therefore the local groundwater was known to be contaminated. Contamination of drinking water by arsenic has been of concern in Taiwan, Argentina and Chile. In Taiwan, an increased incidence of skin cancer has resulted in the local population and isolated cases of Blackfoot disease have also occurred due to this pollution. Arsenic has been associated with poisoning of humans in the USA through the consumption of “moonshine” whisky, respectively.

In former Czechoslovakia, arsenic emissions from a coal-fired plant are considered to have given rise to respiratory problems. Currently, in Slovakia approaching the environmental legislation of European Union, the State Regulatory Authorities implement the increasingly stringent water quality standards. Consequently to arsenic occurrence in some drinking water reservoirs in the region, some treatment methods for removal of arsenic and chromium from waters have been examined using the naturally abundant domestic clinoptilolite. Arsenic appears mostly in natural air-saturated aquifers in the form of As(V)-anions. However, natural occurrence of the element in underground water bodies is rarely, especially sulfuric ore drainage use to cause its enhanced, over-limit concentration in some artesian wells of the country.

Generally, inorganic arsenic can occur in the environment in several forms but in natural waters and thus in drinking water, it is mostly found as trivalent arsenite or pentavalent arsenate. Organic arsenic species, abundant in seafood, are very much less harmful to health and are readily eliminated by the body.

Chromium hexavalent, the more toxic than the tri-valent form, comes in surface waters from anneries, chemical, energetic and ceramic industries. The stable chromate form predominates in alkali, whereas dichromate in acidic waste waters, mostly in deficiency of reductives.

Organo-modified natural zeolites as new tailored natural materials for removal of cations, anions and even organic pollutants may present fairly large potential for water utility companies. The topic of this study was to examine the oxyanions removal from waters by octadecylammonium-enriched inland clinoptilolite. The 18-carbon chain consisting surfactant attached on the clinoptilolite surface, as to the organic acids of living bodies comparable substances, makes the treatment process economic on scale and cost-effective as well.
2. EXPERIMENTAL

2.1 Sample Preparation

Clinoptilolite tuff used in these experiments was supplied by the Mining and Beneficiation Company of natural zeolite in Slovakia Zeocem Bystré (industrial quarry at Nižný Hrabovec). Grain-size fraction of the sample package was (0.3 – 1.0) mm. Cation exchange capacity (CEC) towards ammonium measured according to Kozáč reached 1.4 mmol/g. Physico-chemical and mineralogical specifications of zeolite rock are reported elsewhere.

Since sorption behaviors of organo-modified zeolite is determined by the properties of both the size of organo-modifier and CEC of zeolite, respecting the economy as well, we chose octadecylammonium (ODA) acetate for the organo-inorganic composite preparation. ODA adsorption was reacted with clinoptilolite by adding the weighed adsorbent to an acidified aqueous adsorbate solution (Merck, AR Grade) under continuous stirring for 24 hr at a temperature of 80 °C. Thereafter, the surfactant-loaded sample was filtered, repeatedly washed with distilled water, oven-dried at 105 °C and ground with a mortar and pestle at the laboratory, respectively. Then such a prepared zeolite was screened mechanically to make the selected particle-size distribution of (0.2 – 0.6) mm. To compare chromate and arsenate removal on organically and inorganically modified clinoptilolite as well, we utilize Ag⁺- and Pb²⁺- exchanged forms of natural zeolite, supposing these will create on the zeolite surface chemically bound precipitates of silver or lead arsenates and chromates. The crushed, raw zeolite samples were loaded up with 4% silver nitrate or lead acetate aqueous solutions following an conventional ion exchange procedure, analogous to that reported by many other authors.

2.2 Apparent Equilibrium and Feasibility Studies

A 0.5-gram mass of either the organo-treated or inorganic cation exchanged zeolite and 50 mL of 10 mM/L arsenate or chromate aqueous solutions were placed into Erlenmeyer flasks and mechanically shaken in reciprocating mode to attain equilibrium. Different equilibrium periods for individual zeolite modifications and both aqueous oxyanions species have been established. The adsorption isotherm experiments were conducted using above mass/volume ratio of samples with an initial metal concentrations ranged from 0.5 to 100 mM/L at laboratory temperature. The
amount of anion sorbed to the zeolite was determined from the difference between the metal concentration in solution before and after equilibrium. Batch desorption experiments have been performed respectively to prove how strongly ODA molecules charged to the zeolite and exchanged cation sites on the surface with the examined oxyanions are bound in various ionic strength solutions. Dynamic fixed bed runs have been carried out in laboratory glass columns by altering the hydraulic down flow load in the range from 10 – 25 Bed Volumes per hour (BV/hr). The initial metal concentrations in tested solutions were about 0.5 mM/L. The operation cycle, until zeolite bed saturation, from 6 to 15 hr., depending on feed flow rate. Furthermore, optimization of regeneration for laboratory columns by reverse flow with several 2% aqueous salt solutions (NaCl, NaNO₃, Na₂SO₄, and Na₂CO₃) was undertaken. Chemicals for preparation of stock solutions were of analytical grade.

2.3 Analytical Procedures

The zeolite was characterized by means of powder- XRD (Philips – APD computer controlled Diffractometer equipped with APD analytical software, set-up of parameters: CuKα radiation, voltage 30 kV, intensity 15 mA, Co/Ni-filter, diaphragm 1,1,05, 0.1 step, time 1 sec.) and Electron Probe Microanalyser Jeol-JXA 840A (Japan). Ion sputtering device Jeol JFC-1100 was applied for coating of some well-formed single crystals of zeolite rock fragments with a gold alloy after carbon film coating of the surface by High vacuum Balzers BAE 080 device. The concentration of chromates was analysed by means of Diode Array Spectrophotometer Hewlett Packard 8452A (USA) in UV spectral range at wavelength 372 nm using the statistical Quant I program. Arsenates concentration was analysed by means of Atomic Emission Spectrometer with Inductively Coupled Plasma, sequential Plasmakon S35, Kontron (Germany) and Baird ICP 2070 Spectrometer (USA).

3. RESULTS AND DISCUSSION

X-ray diffraction measurements indicated that the zeolite rock consisted primarily of clinoptilolite (60-70%), volcanic glass (10%), feldspar (10%) and minor quantities of cristobalite, quartz and plagioclase (20%). Fig. 1 represents the XRD pattern of ODA-Clinoptilolite-rich tuff used for arsenate or chromate removal from aqueous solutions.
Figure 1. XRD pattern of ODA-modified clinoptilolite-rich tuff adsorbed with arsenate (chromate)
Figure 2. Photomicrographs of unmodified, raw; ODA-modified and ODA-modified clinoptilolite-rich tuff adsorbed with arsenate (from the left to the right); magnification 3700X

However, the polymerous ODA-surfactant attached on the clinoptilolite surface disabled to appear the characteristic arsenate or chromate peaks at the X-ray diffractogram except the typical clinoptilolite ones according to JC PDF 25-1349.

Photomicrographs of the natural (unmodified) clinoptilolite samples exhibited well-defined, tabular-shaped crystals with excellent crystal edges. As surface coverage with the polymeric compound occurred, smaller, more agglomerated crystals and more poorly defined crystal edges were observed in about 1-μm scale SEM image (Fig. 2). The apparent sharpness of the images decreased with increasing surfactant coverage.
IR spectra were measured by the KBr disc technique using an Infrared Spectrophotometer 781 (Perkin-Elmer). According to the results of infrared spectroscopy of the raw clinoptilolite-rich tuff (CT) and the ODA-modified two forms (CT ODA 2 and CT ODA 5) all three spectra according to Fig. 3 exhibit a strong broad absorption band in the 1200 - 900 cm\(^{-1}\) region, which corresponds to the asymmetric stretching vibrations of the Al-Si-O group. This band changes from a sharp to a broad one, probably when the clinoptilolite-rich tuff becomes amorphous after heating to 900 °C. In the case of CT ODA 2 and CT ODA 5 no significant changes of the absorption band at 1200 - 900 cm\(^{-1}\) were observed, except for a slight broadening and decreasing in CT ODA 2. According to these results the ODA in the both forms is bound on the surface. The presence of water in the unmodified sample and the ODA-modified products was observed by two absorption bands. The first one corresponds to the stretching vibrations (3300 - 3600 cm\(^{-1}\)) and the second one to the bending vibration of water at 1630 cm\(^{-1}\). However, the intensity of these two bands in CT ODA 2 and CT ODA 5 is lower in comparison to the original material. The presence of \(-\text{NH}_3^+\) is to check with difficulties due to the overlapping of the absorption bands corresponding to the \(-\text{NH}_3^+\) and water.
Figure 3. IR spectra of natural clinoptilolite-rich tuff (CT) and the ODA-modified forms (CT ODA 2 and CT ODA 5).
The NMR measurements were carried out at room temperature by using a CW spectrometer constructed at the Department of Physics, Technical University in Kosice with working frequency 10.545 MHz. The attained derivative recordings were averaged out of a few accumulated repetitions and the average was used for the next evaluation of the derivative recordings.

The $^1$H NMR derivative spectra of natural clinoptilolite sample CT and two modified clinoptilolite samples CT ODA 2 and CT ODA 5 are at Fig. 4. The NMR signal arose from hydrogen in OH groups of water that are placed along the clinoptilolite channel walls, from the CH$_3$, CH$_2$ and $-$NH$_3^+$ groups that are in the ODA chains and also from free water molecules that are always present in natural clinoptilolites.

Consequently to the scope of the NMR measurements to find, how the ODA chains are bound with the clinoptilolite and how they influence the shape of NMR lines, it was necessary to compare the lines with each other and to justify which changes in the structure took place.
Figure 4. Derivative 1H NMR spectra of the measured clinoptilolite samples at room temperature. The modulation amplitude was 0.22 G, phase detector time constant 0.1s, speed of the field 6.9 mGs⁻¹. The lines are averaged out of eight accumulated repetitions.

For the evaluation of NMR measurements, there are a few very important parameters: second moment $M_2$ and width of NMR line. They can offer some
kind of information about the surrounding of the resonating nuclei, i.e. hydrogen nuclei in that case. It is because the molecules around the resonating nuclei give rise to the magnetic field also in the resonating nuclei place so that they influence the resonance state of the measured hydrogen atoms. The second moment of the experimental lines of CT, CT ODA 2 and CT ODA 5 was calculated from equation published using a computer program. The calculations resulted in the following values of the second moment: M_2 = 2.02 G^2 for the CT sample, M_2 = 2.82 G^2 for the CT ODA 2 sample and M_2 = 5.79 G^2 for the sample CT ODA 5.

The second moment values can also be calculated from the structure. When the nuclei are tightly arranged, i.e. their thermal motion is negligible, M_2 depends on the sixth power of the surrounding nuclei distances. It means, that it is mainly influenced by the nearest atoms around the resonating nuclei. Thus, when the resonating hydrogen nuclei form groups or when there are more of them bound with an element in the sample, M_2 value is higher.

As for the width of NMR resonance lines, it is inversely proportional to mobility of resonating nuclei. The width calculated from the experimental NMR lines of the three samples is of the highest value for the sample CT ODA 5 and there is only a small difference between the linewidths of CT and CT ODA 2.

The above mentioned second moment values of the three samples and their linewidths indicate that the molecules of ODA in the sample CT ODA 5 are more tightly bound in this sample than in the sample CT ODA 2 and that they are placed closer to each other. As for the kind of bond of the ODA within the samples, there is no direct proof about it in the ^1H NMR measurements
Figure 5. Adsorption isotherms for arsenate (upper line) and chromate (lower line) aqueous solutions with ODA-clinoptilolite, \( T_{\text{const.}} = 23^\circ \text{C} \)

The initial ODA concentration for preparation of surfactant modified clinoptilolite was set up according to Haggerty and Bowman\(^{10}\) to satisfy external CEC of zeolite and to provide a bilayer formation, i.e. attachment of the amine head groups with a permanent 1+ charge to available exchange sites by coulombic interactions and among them upward slipped ODA chains, by hydrophobic organic carbon enriched tail group interactions. Above described surface modification was intended to encourage fairly irreversibly bound octadecylammonium onto zeolite. To attain equilibrium about 30 hr time period was necessary for oxyanions adsorption onto inorganically exchanged zeolite, whereas about 3 days for organomodified zeolite.
Some differences in arsenate and chromate adsorption on ODA-clinooptilolite and Pb-(Ag-clinooptilolites) as well were recorded (Figs. 5 and 6). ODA-clinooptilolite exhibited more efficient arsenate and chromate removal from aqueous solutions than the inorganically exchanged modifications. However, silver exchanged clinoptilolite revealed higher capacity values for both oxyanions uptake than lead exchanged clinoptilolite did. This phenomenon supports preferred silver treated clinoptilolite utilization for specific water purification process even on the base of environmental acceptability.

The rate of adsorption from dilute aqueous solutions by solid adsorbents (zeolites) is a highly significant factor for applications of this process for water quality control.

Generally it can be stated that in rapidly stirred, batch type systems the rate of uptake is controlled primarily by the rate at which adsorbate (solute) is transported from the exterior to the interior sites of the zeolite particles.
The amount of solute adsorbed per unit weight of solid adsorbent, as a function of the concentration of solute remaining in solution at equilibrium and constant temperature is termed an adsorption isotherm.

Predominantly, Freundlich's fitted adsorption isotherms computed by means of simple linear regression were proposed for the mathematical description of the process studied. Unlike the Langmuir equation, the Freundlich model did not reduce to a linear adsorption expression at very low nor very high solute concentrations, as above resulted.

Figure 7. Regeneration of ODA-clinoptilolite columns loaded with chromate by means of 2% NaCl and 2% Na2SO4 aqueous solutions and breakthrough curves for ODA-clinoptilolite in 0.5 mM/L chromate solution by 30 BV/hr and 15 BV/hr in downflow mode (from the left)

By batch description trials Organo- and inorganically- modified zeolite was subjected up to 24 hr in distilled water, tap water and 2% Nalco aqueous solutions in laboratory shaken machine to demonstrate how strongly the examined oxyanions are bound on the modified zeolite. While only slightly chromate desorption in the maximum extent about 20 mg/L was observed, approximately one order higher arsenate desorption was found, corresponding to increased ionic strength in waters. However, in both cases ODA-clinoptilolite exhibited the lowest desorption characteristics. Here, the
desorbed anion concentrations negligible differed for above proposed elution reagents.

Fig. 7 presents partial results of dynamic regime experiments for chromate adsorption and desorption by ODA-clinoptilolite. As shown by breakthrough curves, ODA-clinoptilolite column quantitatively removes chromate species from “simulated waste water”, apparently more efficiently by lower flow rate. Consequently to similar configuration of chromate and sulfate molecules, such loaded column was more efficient to regenerate with Na₂SO₄ than NaCl solution, as elution curves at the Fig. 7 illustrate.

![Regeneration of ODA-clinoptilolite column loaded with arsenate by means of 2% NaCl aqueous solution and breakthrough curves for ODA-clinoptilolite in arsenate solution of co = 25 mg/L; repeated cycle after regeneration, first cycle; breakthrough curve on Pb-clinoptilolite (from the left).](image)

**Figure 8.** Regeneration of ODA-clinoptilolite column loaded with arsenate by means of 2% NaCl aqueous solution and breakthrough curves for ODA-clinoptilolite in arsenate solution of co = 25 mg/L; repeated cycle after regeneration, first cycle; breakthrough curve on Pb-clinoptilolite (from the left).

Arsenate removal by ODA-clinoptilolite proceeded almost analogous as chromate removal did, however the front part of the breakthrough curve is fairly shallow and indicates earlier leakage of pollutant into adsorbate (Fig.