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STUDY OF ADSORPTION PHENOMENA ONGOING ONTO CLINOPTILOLITE WITH THE IMMOBILIZED INTERFACES

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The development of innovative clean-up technologies remains a challenge as current procedures have many limitations, such as being expensive, concentration or pollutant specific, and many others. Natural zeolite of clinoptilolite type was beneficiated with surfactant octadecylammonium and alginate biopolymers using the sol–gel method. Carbonization process in pyrolysis chamber combusted organic waste materials and reaching the maximum temperature of 700°C was used for the surface carbonization, respectively.

Resulted zeolite based products were analyzed by FTIR, TG, DTA and examined on the selected aqueous pollutants removal using the conventional laboratory adsorption experiments. The ability of ODA and alginate linked zeolite of clinoptilolite type to form complexes with anions (such as nitrate, sulphate, chloride and phosphate) and to remove them from contaminated waters was validated. Carbon deposition onto clinoptilolite surface originated from the pyrolytic carbon-rich waste combustion simulated the new zeolite based hybrid to active coke, adsorption efficiency of which towards phenol was approved. Thermogravimetric analyses of the advanced zeolite-based adsorbents were accomplished to find out how temperature resistant are the novel zeolite based materials in respect to the original, untreated one. While the native clinoptilolite indicated according to DTA analysis one broad endothermic response around 100–130°C, resulted from the loss of adsorbed water, by the ODA–modified clinoptilolite was except this DTA peak, the broad exothermic response started from 370 up to 560°C observed. This DTA profile is assumed to record a slowly breakdown of attached ODA surfactant and sequential loss of mass due to continual heating of sample under elevated temperature.

Keywords: *alginate immobilization, carbonization, clinoptilolite type of natural zeolite, hydrophobization, surface tayloring for pollutants removal, thermal behaviours*

Introduction

An organic inorganic composite adsorbent termed as a hybrid material too, may be defined hereto as a combination of a polymerous substance immobilized onto surface of the inorganic e.g. zeolite carrier to avail advantages of both zeolitic and polymerous constituents as well. Accordingly, hybridization can be used to modify organic or inorganic materials and hybrids should therefore be considered as the new generation of composites that may encompass a wide variety of applications [1–6].

The conversion of inorganic ion exchange materials into hybrid fibrous or nanoscale ion exchangers is considered to be the latest development of the discipline. These nanomaterials are drawing a great attention as they exhibit a high efficiency and rate of sorption with short diffusion path towards environmental pollutants. Advances in nanoscale science and engineering are providing unprecedent opportunities to develop more cost effective and environmentally acceptable water purification processes, respectively [7–10]. For the water purification, besides the metal-containing nanoparticles, carbonaceous materials and dendrimers, also the zeolites are being evaluated as the most progressive functional and nanosized materials of the millenium. A progress in marketing natural zeolites is encouraging, given that natural zeolites are being considered to be a commodity of great potential since the industry's beginning in the late 1960s. Zeolite unique market position is providing by continued development of their ion exchange and adsorption properties and especially trough their surface treatment [10–14].

Active surface induced removal of aqueous Mn(II) and Fe(II) pollutants onto silicious sand or gravel coated with catalytically affecting high valency manganese sesquioxides is in water purification process applied for decades. The scope of present study was to investigate and highlight the principles of linkage between immobilized interfaces, i.e. octadecylammonium (hereafter denoted as ODA) chains, alginates or by carbonization process resulted mostly disordered carbons on the one site and the external surface of clinoptilolite on the another due to improved adsorption performance of such a clinoptilolite-based hybrid even towards anions.

The Slovakian natural clinoptilolite was chosen as the interface carrier on the base of its huge abundance in the country, price easily accessibility and feasibility, cost effectiveness and due to its sufficiently large surface area, rigidity and surface functionality.

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The intent was to taylor such macromolecular organic components immobilized onto zeolite rock, which enable or even synergy the water purification and flocculation effectiveness, acquiring thus the necessary adhesion and aggregation forces towards the colloidal and other ionic water impurities [15–18].

TG and DTA analyses have been used to describe the new hybridized zeoadsorbent properties, which efficiently testified an enhanced sulphate, chloride, nitrate and phenol removal from model aqueous solutions so far [9, 10]. The bounding nature of the immobilized carbon-rich substances with the zeolite surface was studied by FTIR spectroscopy, furthermore.

Experimental

Materials

The principal rock constituent of the volcanic–sedimentary zeolite deposit in Eastern Slovakia at Nižný Hrabovec is clinoptilolite. This species was used for all experiments accomplished in this study. The Zeocem Company mining and processing natural zeolite in this locality is leader and substantial producer of zeolite products not only in the Slovak Republic but also for many European countries.

Detailed mineralogical and chemical analyses of zeolitic rock and the procedures of hydrophobization, carbonization and alginate immobilization are published elsewhere [15, 16].

Analytical measurements

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a DuPont 990 (TGA 951) derivatograph heating 100 mg of sample at 10°C min^{-1} in the temperature range 30–1000°C.

Infrared spectra of the samples were accomplished on the FTIR Spectrometer 781 (Perkin Elmer) using the KBr disc technique.

Aqueous model solutions of chosen pollutants examined in adsorption experiments have been analysed by means of Diode Array Spectrophotometer HP 8452A and by Isotachophoresis on the Analyser ZKI 02 (Villa Labeco).

Results and discussion

A development of new hybrid organic inorganic materials is one of the principal direction of modern materials science. Usually, the inorganic component of such hybrids provides mechanical, thermal or structural stability of new product (adsorbent) and the organic component functionalizes the adsorbent´s surface. This was the key or dominant objective for our new adsorbent fabrication [16].

According to our published SIMS results [18] dealing with the depth profile measurements of the prepared ODA hydrophobized and carbonized clinoptilolites, the predominantly amorphous carbon deposition onto zeolite surface (from biomass pyrolysis i.e. carbonization process) was neither by chemical composition nor by produced thickness of such extent homogenous than the ODA surface coating. Carbonization process enriched the clinoptilolite surface with about 5 μm thick external layers, approximately one order of magnitude higher than the thickness of ODA–surfactant layers was. Other applied, biobased polymers like alginate, have the potential for use in disposable products which can be collected, processed and reused for animal feed or left in the nature to degrade releasing components non toxic or compatible with environment. Based on above facts the alginate immobilized clinoptilolite using the conventional sol–gel method was prepared, respectively.

All the prepared clinoptilolite composed adsorbents were analysed and the characteristic zeolite matrix *vs.* immobilized interfaces interactions verified by the FTIR spectroscopy. As the Fig. 1 shows, especially the alginate and ODA–clinoptilolites present profoundly the adsorption bands at 2917–2921 and 2848 cm^{-1} corresponding to the assigned intense vibrations of the surface attached ODA and alginate groups. It is assumed that octadecylammonium chains are bounded onto zeolite $(\text{SiO}_4)^{4-}$–$(\text{AlO}_4)^{5-}$ skeleton electrostatically and alginate by means of surface accessible Ca^{2+} ions covalently. Carbon deposition from

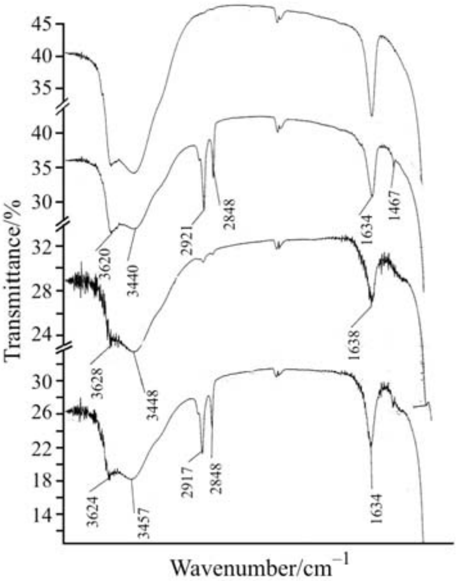

Fig. 1 FTIR spectra of natural and surface modified zeolites (downwards): natural, ODA–modified, carbonized, alginate immobilized zeolites

biomass pyrolysis did not prove with zeolite support almost any IR signals, by the other words, this deposition was only of physical nature. Carbon may be dispersed or fulfiled in various surface interstitial spaces of host zeolite rock.

Figure 2 depicts adsorption performance of selected natural aluminosilicate towards phosphate ions. Commercial product Slovakite decodes an adsorbent, manufactured from domestic dolomite, bentonite, diatomic clays, alginite and zeolite, justified only with clinker and final pressurizing. As Fig. 2 indicates, also a natural zeolite on the base of surface accessible and exchangeable Ca^{2+} ions, removes the PO$_4^{3-}$ from aqueous solution efficiently (pKs of calcium phosphate equals 26), more or less comparable with the adsorption performance of ODA–clinoptilolite, when the contact time was reaching nearly 250–300 min. This result evolves a finding, that the density of the specific sorption sites of both adsorbents may be comparable.

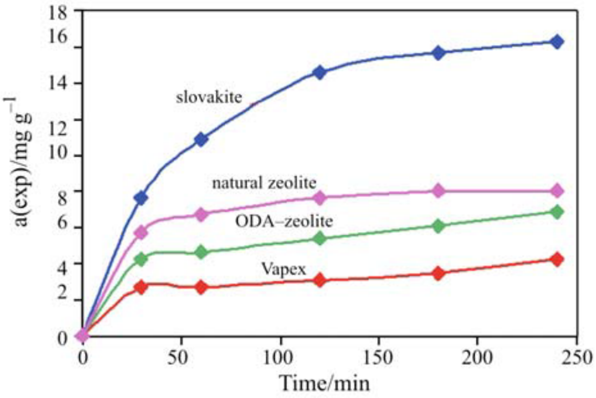

Fig. 2 Kinetics of phosphate adsorption on the surface of some aluminosilicates studied

Moreover, the verified desorption experiments with the equilibrated PO$_4^{3-}$ attached adsorbents confirmed a very strong bounding force of Slovakite, which is derived and explained on the base of the mentioned alkalic components presence in the manufactured product, however not such a case by a natural zeolite was attained. Some minor PO$_4^{3-}$ elution into the tap water after about 2 h reciprocate mixing clarified an easy of ion exchange principle and function of aluminosilicate matrix with a small, but the entire compound of Ca$_3$(PO$_4$)$_2$ release out of external surface. Vapex, expanded perlite, as the other tested domestic aluminosilicate (thermally treated by producer Ceramic Works Košice) did not exhibit a profound adsorption performance towards the examined PO$_4^{3-}$ anions (Fig. 2).

Figure 3 presents except the nitrates, chloride and sulphate adsorption onto ODA–clinoptilolite some adsorption results obtained by alginate clinoptilolite *vs*. nitrate and carbonized clinoptilolite *vs*. phenol, respectively. Due to basically active coke imitation, the carbonized clinoptilolite was examined for organic pollutant like phenol, that means for such chosen pollutant which used to be removed with typical carbonaceous adsorbents.

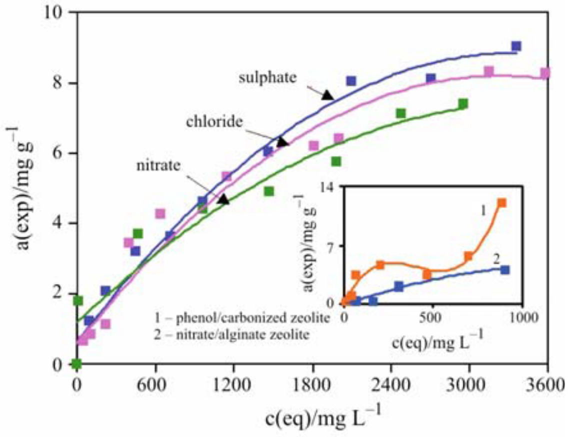

Fig. 3 Adsorption isotherms of the systems studied (downwards): sulphate *vs*. ODA–zeolite, chloride *vs*. ODA–zeolite, nitrate *vs*. ODA–zeolite, phenol *vs*. carbonized zeolite and nitrate *vs*. alginate immobilized zeolite

The last i.e. thermogravimetric analyses of the advanced zeolite based adsorbents were accomplished to find out how temperature resistant are the novel zeolite based materials in respect to the original, untreated one. While the native clinoptilolite indicated according to DTA analysis one broad endothermic response around 100–130°C, resulted from the loss of adsorbed water (Fig. 4), by the ODA–modified clinoptilolite was except this DTA peak, the broad exothermic response started from 370 up to 560°C observed (Fig. 5). This DTA profile is assumed to record a slowly breakdown of attached ODA surfactant and sequential loss of mass due to continual heating of sample under elevated temperature. While pure ODA mass *vs*. temperature profiling according to DTA curve involves the first endothermic minimum at about 60°C, the second one just before approximately 500°C indicates probably total pyrolytic decomposition of this chemical (Fig. 6). By DTA curve of ODA–zeolite composed material was

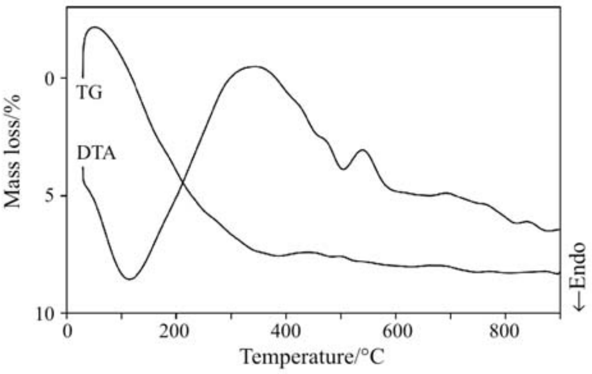

Fig. 4 TG and DTA curves of natural zeolite of clinoptilolite type

that response shifted to lower temperature of about 440°C and expressed with not such a sharp slope as in the individual ODA curve. This phenomenon was probably related with gradual release of intermediate and higher energy bounded surfactant molecules out of the zeolitic carrier.

Some similar course of shape in the DTA curve concerns also the alginate immobilized zeolite. Surface accessible Ca cations of the external zeolite structure caused an alginate gel development responsible for interchain ionic bounds and cross-linked network building at the surface with alginate solidification and internal gelation, respectively. According to Fig. 7 pure alginate polysaccharide degrades gradually by fragmentation of the original carbohydrate polymers into particular open block monomers and further residual associates, leaving at the DTA record several sharp endothermic responses at about 130, 300, 610 and 630°C. Any profound degradation behaving of the examined substance was detected in the temperature range from 400 up to 600°C. No such multifractional breakdown of the polymer attached on the zeolite support in the derivative curve was observed (Fig. 8). It can be assumed that on the base of energetically stronger bounding forces of alginate with surface accessible Ca-ions, the second endothermic response appeared at about 470°C, that means later than by ODA–modified zeolite, where the surfactant was supposed surface attached only with electrostatic bounds. The results are in coincidence with FTIR measurements.

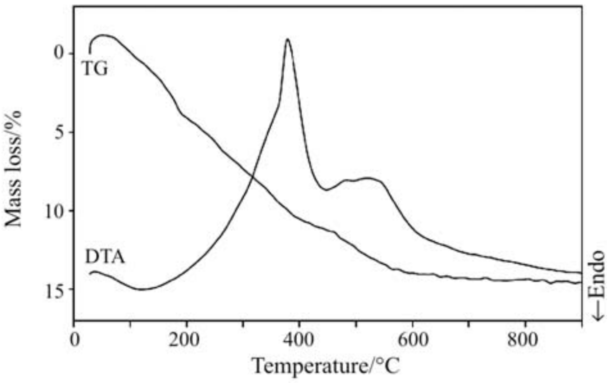

Fig. 5 TG and DTA curves of ODA–zeolite

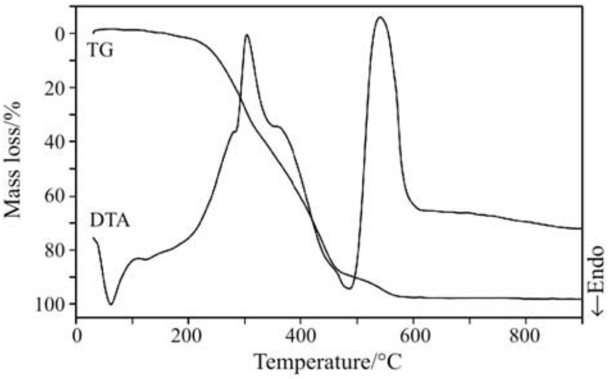

Fig. 6 TG and DTA curves of ODA surfactant

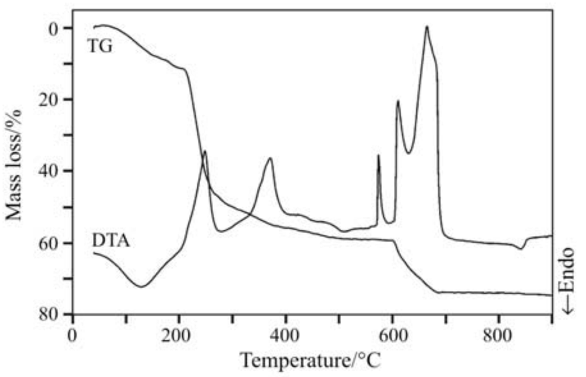

Fig. 7 TG and DTA curves of pure alginate

Totally different thermogravimetric properties presents organic carbon-rich substance at DTA (Fig. 9) used for surface covering of grained zeolite during pyrolytic combustion. A mass loss curve corresponds clearly with derivative curve at the major slope change of thermic characterization (about 450°C), i.e. a tem-

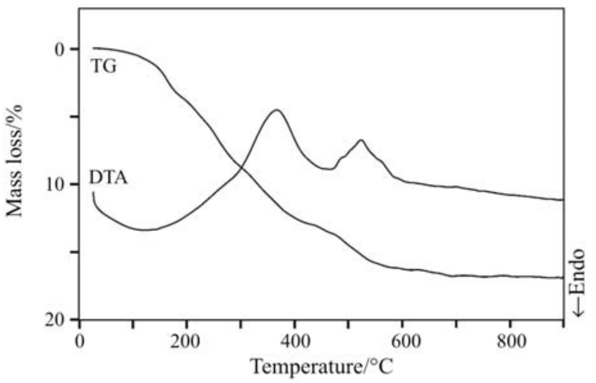

Fig. 8 TG and DTA curves of alginate immobilized zeolite

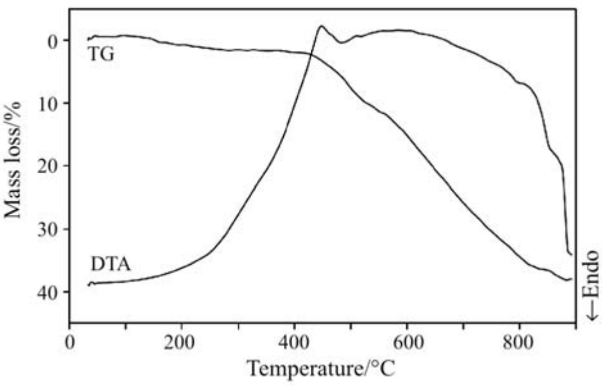

Fig. 9 TG and DTA curves of carbon rich substance used in pyrolytic combustion and deposition onto zeolite surface

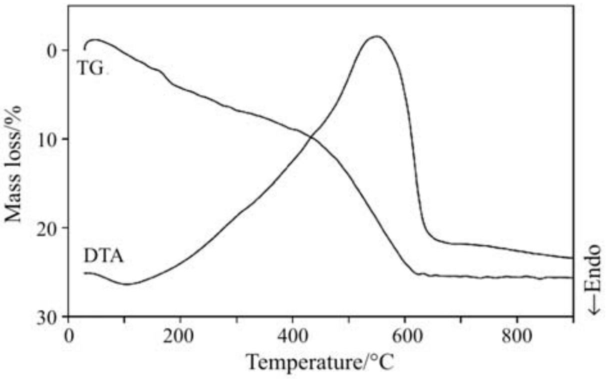

Fig. 10 TG and DTA curves of carbonized zeolite

perature from which a gradual removal of carbon residual mass up to 900°C proceeds. Nevertheless, still about one fifths of the initial carbon sample remained as not combustible residue (ash). At the carbonized zeolite DTA curve was this characteristic peak shifted towards higher temperature (about 550°C) what supports an argumentation, that various carbon clusters, hydrocarbon associates and pyrolysis fragments were hard accessible till higher temperature attack, due to their deeper impregnation and fulfilling of numerous interstitial spaces of used zeolite support.

The simple comparison of both, rather similar DTA curves, the native *vs.* carbonized zeolite, let us believe that the higher temperature resistance of carbon covered zeolite was testified (verified insulating abilities). Some small DTA peak upon heating the carbonized zeolite sample by about 110°C indicated water desorption process, respectively (Fig. 10).

Conclusions

The ability of ODA and alginate linked zeolite of clinoptilolite type to form complexes with anions (such as nitrate, sulphate, chloride and phosphate) and to remove them from contaminated waters was validated. Carbon deposition onto clinoptilolite surface originated from the pyrolytic carbon-rich waste combustion simulated the new zeolite based hybrid to active coke, adsorption efficiency of which towards phenol was approved.

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References

1 S. C. Mojumdar, K. G. Varshney and A. Agrawal, Res. J. Chem. Env., 10 (2006) 89.
2 G. Crini, Prog. Polymer. Sci., 30 (2005) 38.
3 E. M. Araújo, R. Barbosa, C. R. S. Morais, L. E. B. Soledade and A. G. Souza, J. Therm. Anal. Cal., 90 (2007) 841.
4 M. Drábik, S. C. Mojumdar and R. C. T. Slade, Ceramics-Silikaty, 46 (2002) 68.
5 K. G. Varsheny and P. Gupta, Ind. J. Chem., 42A (2003) 2974.
6 S. C. Mojumdar and L. Raki, Ceramic Transact. (Ceramic Nanomat. Nanotech. IV), 172 (2006) 11.
7 E. Jóna, M. Kubranová, S. C. Mojumdar and M. Kopcová, Chem. Pap., 56 (2002) 295.
8 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 721.
9 S. C. Mojumdar, K. Mazanec and M. Drabik, J. Therm. Anal. Cal., 83 (2006) 135.
10 G. Crini and M. Morcellet, J. Sep. Sci., 25 (2002) 789.
11 G. J. Yu, J. L. Gong, D. Z. Zhu and S. X. He, Diamond Relat. Mater., 15 (2006) 1261.
12 N. Savage and M. S. Diallo, J. Nanopart. Res., 7 (2005) 331.
13 R. L. Virta, US Geological Survay, 2005 Minerals Yearbook, Zeolites, June 2006.
14 (Zeocem, a.s., 0904 34 Bystré 282, Slovakia), www.zeocom.sk.
15 E. Chmielewská, K. Jesenák and K. Gáplovská, Collect. Czech. Chem. Commun., 68 (2003) 823.
16 E. Chmielewská and K. Pilchowski, Chem. Pap., 60 (2006) 98.
17 M. Morvová, I. Morva, M. Janda, F. Hanic and P. Lukač, Int. J. Mass. Spectrom., 223 (2003) 613.
18 E. Chmielewská, D. Velič and M. Aranyosiova, X. Ukrainian Polish Symp. Lviv 2006, Book of Abstracts.

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