HDTMA-modified carbon-zeolite composites as adsorbents of 2,4-D and MCPA pesticides

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Since the latter half of the nineteenth century, extensive agricultural use of plant protection products, which are commonly referred to as "pesticides", has been observed to pose a serious impact on soil, air, and water. The global demand for increased food production has not only led to significant deterioration of food quality, resulting in severe consequences on the environment, but also caused public health issues due to overuse or misuse of pesticides (Ahmad et al., 2010). Over 98% of the sprayed insecticides and 95% of herbicides reach nontarget species, as well as air, water, and soil. Traces of these products are frequently detected in surface water, and more importantly, groundwater, which is a major source of drinking water around the world (Loos et al., 2009). The presence of many types of pesticides and their derivatives in water is of great concern to the public and authorities, due to increased adverse health effects associated with these compounds even at very low concentrations (pg/L to ng/L) (Skinner et al., 1997). Thus, the removal of pesticides and their derivatives from water is one of the major environmental concerns. Physical remediation, based on the process of adsorption, is one of the most frequently applied methods for water purification because of its efficiency, capacity, and applicability on a large scale. Among many effective adsorbents of pesticides, activated carbons, modified and unmodified clays, fly ashes, zeolites, zeolite–mineral composites, metal–organic frameworks (MOFs), mesoporous silica materials, are frequently used.

In this study three composites of active carbon and zeolites with faujasite (NaX-C), LTA (NaA-C), and gismondite (NaP1-C) structures were investigated. The composites were synthesized by the hydrothermal method from High Carbon Fly-ash (HCF), derived from the combustion of hard coal. All composites were further modified with cationic surfactant HDTMA-Br (hexadecethyltrimethylammonium bromide) in the amount of 1.0 ECEC (external cation exchange capacity). The samples were prepared by mixing 10 g of each composite with 500 g of the HDTMA solution at a concentration of 1.0 ECEC (Tab.1). After 24 h of stirring at 80°C, the samples were centrifuged for 10 min at 14,000 rpm, washed with distilled water, and dried at 80°C for 24 h. The effectiveness of the modification differs from the established and is presented in Tab. 1. The differences between established and obtained effectiveness of modification are a result of the modification method. The properties were studied by elemental analysis CHNS, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The adsorption of 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (2-methyl-4-chlorophenoxyacetic acid) were tested under static conditions. 20 mg of each adsorbent were mixed with 7 ml of 2,4-D or MCPA solutions at concentrations of 4 mg/L and pH 4. The samples were shaken 24 h, then centrifuged and filtered. The concentration of pesticides in the remaining solutions was determined by direct injection to a high-performance liquid chromatograph (HPLC) with a UV-Vis detector. All experiments were carried out at room temperature.

Table 1. The results of elemental analysis CHNS of zeolite-carbon composites.

	NaA-C	NaX-C	NaP1-C
ECEC [meq/100 g]	20.2	34.2	49.5
Effectiveness of modification	0.95 ECEC	0.91 ECEC	0.93 ECEC

The phase composition of the tested sorbents was obtained during XRD analysis. The diffraction patterns of individual materials show reflections characteristic of NaA, NaX, and NaP1 zeolites. Moreover, the mineral phases of such minerals as mullite, hematite, and quartz were detected in all composites. All materials exhibit a characteristic baseline elevation, indicating the presence of an amorphous phase in the range of 20-30 °2θ.

FTIR spectra of zeolite-carbon composites allow identifying the characteristic bands originating from the secondary building units (SBU) present in the zeolite structures. SBUs of NaA zeolite, which is a component of NaA-C composite, are built from double 4-membered rings (D4R), which bands are visible at ~ 560 cm^{-1} and ~ 460 cm^{-1}. Six-membered rings (S6R) can also be recognized in the skeletal structure, and their characteristic band is probably at ~ 560 cm^{-1}. For NaX zeolite (in NaX-C composite) the main SBU is the D6R double 6-membered rings with bands at ~ 560 cm^{-1} and ~ 450 cm^{-1}. The structure also includes single 12-membered rings, single 6-membered rings, and single 4-membered rings. The structure of the NaP1 zeolite consists of single 4-

membered rings (S4R), that are combined into single 8-membered rings (S8R). The characteristic bands are ~ 740 cm^{-1}, ~ 590 cm^{-1} and ~ 450 cm^{-1}. All these bands are visible on the FTIR spectra of zeolite-carbon composites and are a confirmation that analysed composites consist of different types of zeolites. Modification of composites with HDTMA resulted in the formation of new bands corresponding to the bonds between atoms in surfactants molecules and between composite surface and surfactant.

SEM images of zeolite carbon composites show that zeolites crystallized in the intermolecular spaces and on the carbon surface. The shape of zeolites depends on the zeolite type. However, for composites those zeolite structures are not perfectly preserved - crystals take spherical and isometric shapes of 1-3 μm. The modification resulted in the loss of the existing structure since the amount of HDTMA used was to form single layer of surfactant on the surface of zeolite-carbon composites.

Experiments of 2,4-D and MCPA adsorption revealed that modification of zeolite-carbon composites with cationic surfactant significantly increase adsorption efficiency (Fig. 1). 2,4-D and MCPA the most commonly used herbicides in agriculture and the home/garden market sector are phenoxy herbicides. In aqueous solutions they occur in anionic form. Since the surface of zeolites is negatively charged it is not surprising, that adsorption efficiency of zeolite-carbon composites is not high. Modification of composites with cationic surfactants enhance adsorption of 2,4-D and MCPA. Introduction of cations onto the surface of adsorbents create new active centres that can interact with pesticides in anionic form. Although both pesticides are very similar in structure, MCPA appears to be slightly better immobilized by modified composites. Adsorption of MCPA is rather high (around 80%), and do not depend on the type of zeolite in the composite. On the other hand, 2,4-D seems to be more sensitive on the type of zeolite - modified NaX-C composite was able to remove almost 100% of 2,4-D while adsorption onto NaA-C and NaP1-C do not exceed 60%.

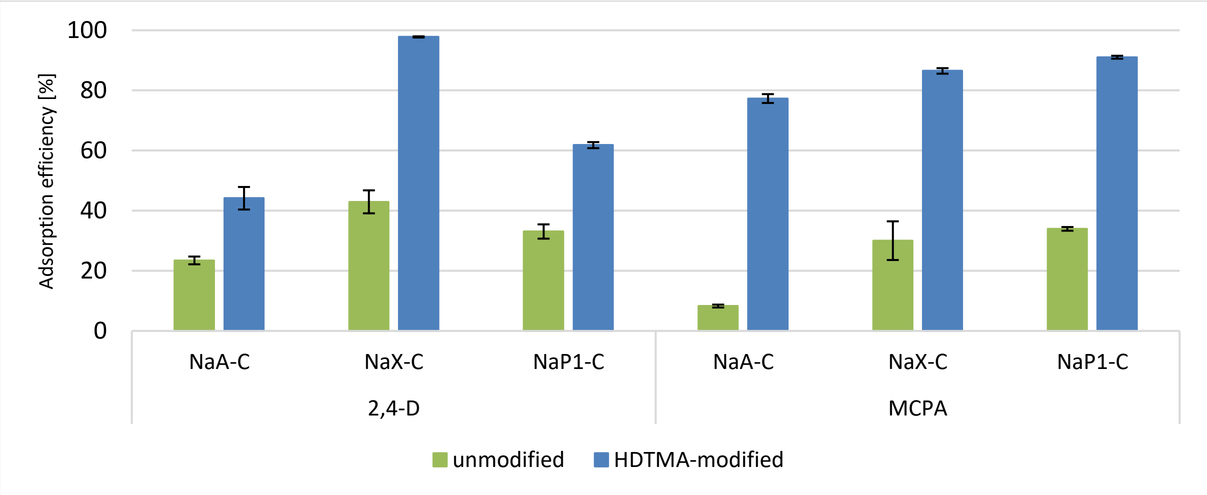

Figure 1. Adsorption of 2,4-D and MCPA onto unmodified and HDTMA-modified zeolite-carbon composites.

The zeolite carbon composites NaX-C, NaA-C, and NaP1-C are characterized by good sorption abilities towards 2,4-D and MCPA. Modification of the surface of composites with HDTMA enhances their adsorption properties. Moreover, adsorption efficiency depends on the type of pesticide, which suggests that the structure of molecules plays an important role in mechanisms of removal. Further experiments are required to fully understand the potential of unmodified and modified zeolite-carbon composites as adsorbents of pesticides.

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