Iwona Lupul **28.06.2017**

Removal of selected toxic compounds from water by adsorption on activated carbon from agricultural by-products

ABSTRACT

The performance of hemp stem-based ACs and palm kernel shell-based ACs have been investigated for the adsorption of organic pollutants from a pesticides group (atrazine) and dyes group (methylene blue, Congo red, cyanocobalamin) and an inorganic contaminant (hexavalent chromium) from aqueous solutions. A series of hemp stem-based ACs was produced by physical activation of hemp stem with steam and carbon dioxide and chemical activation with potassium hydroxide and phosphoric acid. A series of palm kernel shell-based ACs was prepared by physical activation of palm kernel shell with steam and chemical activation with potassium hydroxide. The properties of the resultant ACs depended on the precursor, the activation method (physical and chemical), the type of activating agent and the process conditions (temperature, soaking time, impregnation ratio). The resultant ACs were characterized by a wide porosity spectrum, ranging from microporous to mesoporous. Palm kernel shells as precursor, which contain more lignin in their structure, yielded the AC with better developed porous structure than cellulose-rich hemp stems.

The selected hemp stem and palm kernel shell-based ACs were subjected to oxidative treatments with HNO_3 and H_2O_2, ammination and high temperature treatment under nitrogen and hydrogen flows in order to modify their surface chemistry and to improve target pollutants removal. The ACs oxidized with HNO_3 had a strong acidic character due to high contribution of carboxyl groups on the carbon surface. The high temperature treatment in nitrogen and hydrogen atmospheres resulted in a decrease of carbon acidity due to the removal of oxygen-containing surface groups. Aminated activated carbons showed a basic surface character due to an enhanced nitrogen content mostly as pyridinic structures.

The surface chemical character of the KOH activated hemp stem-based ACs had a significant impact on the adsorption of atrazine. The AC annealed in a nitrogen atmosphere with a highly basic surface but free of heteroatom-containing surface functional groups was the most favorable for the removal of atrazine from an aqueous solution at pH 6. π-π dispersion interactions were mainly responsible for atrazine adsorption on the modified hemp stem-based ACs.

The mesoporous hemp stem-based AC prepared by H_3PO_4 activation followed by annealing in hydrogen atmosphere was used for the adsorption of three high molecular

contaminants of different structure, molecule size and ionic state, such as cationic methylene blue dye, anionic Congo red dye and non-ionic cyanocobalamin. The adsorption capacity of AC was determined by the volume of pores with a width sufficiently larger than the molecular size and by the molecular structure of adsorbate which determines the interactions with the carbon surface. The fastest adsorption kinetics of the studied dyes was revealed for methylene blue due to its smallest molecule dimension. Adsorption of Congo red was the slowest due to its largest molecular size. The rate of adsorption of cyanocobalamin, which occurs in non-dissociated form in an aqueous solution, was high and comparable to the adsorption rate of methylene blue. The hydrogen bonding interaction between amino groups of cyanocobalamin and carboxyl, carbonyl or phenol groups present on the carbon surface was the most probable mechanism of cyanocobalamin adsorption.

The study of the influence of textural parameters of H_3PO_4 activated hemp stem-based mesoporous ACs on the adsorption kinetics has proven that the higher the developed mesoporosity, the shorter the time to achieve the equilibrium stage for methylene blue adsorption. Adsorption of methylene blue dye was also studied for ACs prepared by H_3PO_4 activation of hemp stem followed by annealing in nitrogen and hydrogen atmospheres in order to evaluate the influence of carbon surface chemistry. The highest adsorption capacity was obtained for the heat treated AC under nitrogen which contained more surface oxygen functionalities. The oxygen groups enforced the electrostatic interactions, resulting in an enhancement of methylene blue adsorption.

The adsorption of a series of microporous palm kernel shell-based ACs (steam treated and subsequent modified by oxidative treatments with HNO_3, H_2O_2 and ammination) towards hexavalent chromium was found to be strongly dependent on the solution pH and the carbon surface chemistry. The optimum pH for the removal was 2. Adsorption-coupled reduction was the leading mechanism for Cr(VI) removal by palm kernel shell-based ACs. The basic surface character of the ammonia treated palm kernel shell-based AC enhanced its removal capacity towards Cr(VI) compared with the other ACs.

This work emphasizes the importance the porosity development of AC in combination with its surface chemistry in the removal efficiency of organic and inorganic contaminants from water. A significant enhancement of AC adsorption kinetics and capacity can be achieved by a suitable modification of the carbon surface.