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Adsorption of alachlor and pentachlorbenzene on biochar and hydrochar originating from Miscanthus giganteus and sugar beet shreds

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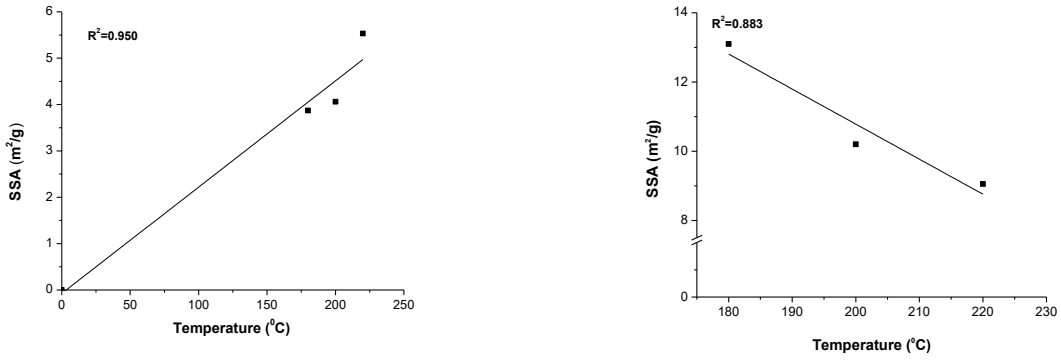
In this work we studied the adsorption of two structurally different organic compounds (pentachlorobenzene and alachlor) on biochar and hydrochar obtained during different thermal carbonization processes. As biomass we used energy crop*Miscanthus*×giganteus and sugar beet shreds. Both types of hydrochar were obtained at three different HTC temperatures (180, 200 and 220ºC), while the biochar was obtained during a slow pyrolysis process at 400ºC.

Characterization of the investigated adsorbents included multi-point BET specific surface area (SSA), pore volume and elemental analysis. The multi-point BET (Brunauer-Emmett-Teller) SSA and pore volume of the adsorbents was determined by nitrogen adsorption at 77 K using an AutosorbiQ Surface Area Analyzer (Quantochrome Instruments, USA). Elemental analysis (C, H, N, and S) was conducted using a Vario EL III CHNS Analyzer. The SSA for all investigated adsorbents ranged from 3.87 to 260 m^2/g. Both of the biochars had a significantly higher SSA than the hydrochar. It is interesting to note thatthe SSA of the hydrochars obtained from sugar beetshredsincreased with increasing temperature of the hydrothermal carbonization process (Fig. 2a), while in the case of the hydrochars obtained from *Miscanthus,*increasing the reaction temperature reduced the resulting specific surface area (Fig. 2b).



A) B)

Figure 1: Relationship of SSA and reaction temperature during formation of hydrochars from A) sugar beet shreds and B) *Miscanthus*

The mesopore contents of the biochars were expressed as BJH total pore volume (cm^3/g),and for the biochars obtained from sugar beet shreds and *Miscanthus* were 0.016 and 0.023 cm^3/g, respectively. The obtained mesopore volumes were lower compared to the hydrochars, which shows that the porosity of the material decreased during pyrolysis at higher temperatures. The biochars originating from sugar beet shreds and *Miscanthus*had micropore volumes of 0.086 and 0.1042 cm^3/g, respectively. All the investigated hydrochars originating from *Miscanthus*had higher pore volumes (micro- meso and total pore volume) than those obtained for hydrochars of sugar beet shreds. Additionally, it can be noticed that the volume of micro- meso- and total pore volume for all the investigated hydrochars increases with increasing temperature from 180°C to 220°C.

The results of the elemental analysis show that the H/C atomic ratiodecreases with increasing temperature of the HTC processto values close to 1, indicating an increase in the aromatic structure as the temperature of the process increases. In addition, (N+O)/C ratio, expressed as the polarity index, decreases as the temperature of the process rises, which indicates the formation of less polar structures with increasing temperature.

In order to investigate the adsorption characteristics of the adsorbents, experiments were performed in conventional batch adsorption experiments. The background solution was 0.01 M $CaCl_2$ in doubly distilled water with 100 mg/l NaN_3 as a biocide.The amount of adsorbent in each experiment corresponded to a sample/solution ratio that resulted in 20-80% uptake of the given organic compounds. The procedure was as follows: flasks containing premeasured adsorbent and background solution and a certain volume of methanol organic compoundstock solution was spiked and equilibrated at room temperature by continuous shaking for 72 h. Samples of clear supernatant were then removed for gas-chromatographic determination of the organic compound equilibrium concentrations.

All adsorption isotherms well fitted the Freundlich model. The nonlinearity of all the isotherms ranged from 0.450 to 0.986, except for alachlor on sugar beet shreds hydrochar at200ºC, where the value of n was 1.180. Adsorption coefficients (K_F) were in the range 0.053 to 243 (µg/g)/(µg/l)^n for both compounds and all adsorbents. However, direct comparison of adsorption affinities could not be made because of their different units as a result of the nonlinearity of the adsorption isotherms. Therefore, distribution coefficients (K_d) were calculated for three equilibrium concentrations (C_e = 0.01S_W, 0.1S_W and 0.5S_W). Generally, in the case of both compounds, theK_d values increased in the range: hydrochar of sugar beet shreds<hydrochar of *Miscanthus*<biochars of sugar beet shreds and *Miscanthus*. The highest adsorption affinities were obtained for biochars for both investigated compounds. The reason for the higher adsorption affinity for both compounds on the investigated biochars may be due to higher specific surface areas.It is known that slow pyrolysis produces biocharswith higher specific surface area, as well as a higher content of aromatic structures in relation to the hydrochar produced by hydrothermal conversion process, which can affect the formation of additional adsorption sites on the surface as well as increase the hydrophobicity of the adsorbent (Fig. 2).

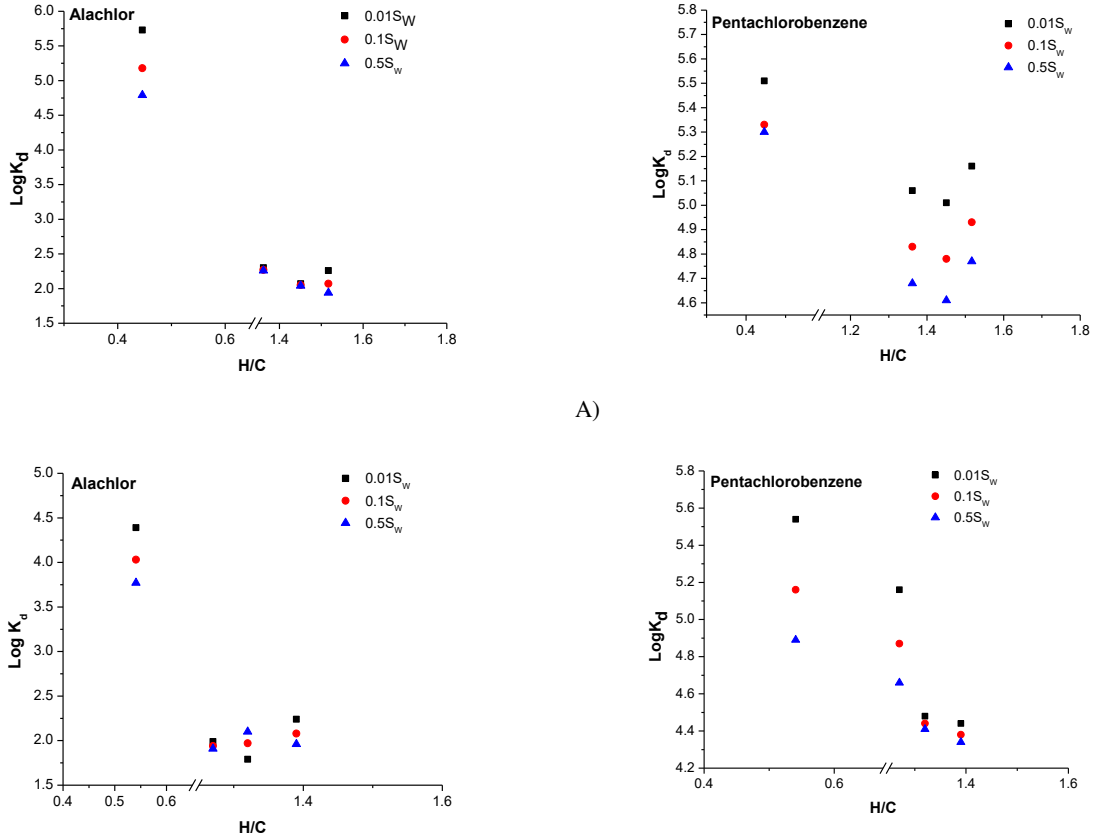


Figure 2: Relationship between adsorption affinity and H/C ratio obtained for the adsorbents from A) sugar beet shreds and B) *Miscanthus*

To support this fact, the logK_d values obtained for the adsorbents were correlated with the atomic H/C ratios, whereby a positive trend was observed between the aromaticity and the affinity for adsorption in the case of both investigated compounds (Fig. 2). Generally, adsorption affinity increased with increasing aromatic structure in the adsorbents. In addition, it can be noticed that changes in logK_d with the change in the atomic H/C ratio were particularly pronounced at the low equilibrium concentrations, indicating the importance of specific interactions such as π-π interactions in the overall adsorption mechanism.

Based on the obtained results, it can be concluded that the adsorption efficiency is significantly dependent on the physico-chemical characteristics of the investigated adsorbents, which arestrongly affected by the process and conditions during adsorbents synthesis. In addition,both investigated adsorbents could be used for the purpose of remediationof water or sediment polluted with organic compounds.

Keywords: biochar, hydrochar, adsorption, organic compounds

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