

ADSORPTION OF PHENOL COMPOUNDS BY ACTIVATED CARBON FORMED DURING CARBONIZATION OF BROWN COAL WITH POTASSIUM HYDROXIDE

© Ju.V. Tamarkina, PhD in Chemical Sciences, I.B. Frolova, PhD in Chemical Sciences, O.O. Velichko, V.O. Kucherenko, Doctor of Chemical Sciences (L.M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry of the National Academy of Sciences of Ukraine, 02160, Kyiv, Kharkiv Highway St., 50, Ukraine)

The aim of the work is to evaluate the adsorption capacity of activated carbons (ACs) from brown coal in relation to phenol (Ph) and 4-chlorophenol (CPh) and the influence of the ACs formation temperature under carbonization with potassium hydroxide on capacities.

The samples of ACs were prepared by heating with KOH (1 g/g, 1 h) at a given temperature in the range of $t=400-800^{\circ}\text{C}$ and marked as AC(t). The ACs porosity characteristics were determined by low-temperature (77 K) adsorption – desorption nitrogen isotherms (Micromeritics ASAP 2020) calculated by the 2D-NLDFT method. They are as follows: total pore volume V_t (cm^3/g), specific surface area S (m^2/g), volume (V_{mi}) and surface (S_{mi}) of micropores, volume (V_{1nm}) and surface (S_{1nm}) of subnanopores, the total surface of meso- and macropores S_{me+ma} . The adsorption of phenol and 4-chlorophenol was determined at equilibrium concentrations in aqueous solutions ≤ 5 mmol/l (25°C).

The alkaline carbonization temperature of brown coal was found to be a key factor in the formation of micro- and subnanopores, the growth of the AC specific surface area (from 12.8 m^2/g to 1142 m^2/g) and adsorption activity against phenolic compounds. Its increase to 800°C causes an exponential increase in the AC adsorption capacity in 8.7 times (Ph) and 6.7 times (CPh), which is proportional to the concentration of surface adsorption centers (AdCs). The values of the effective activation energy of forming AdCs being active in relation to adsorbates were determined as 29.5 kJ/mol (Ph) and 31.5 kJ/mol (CPh). The kinetics of Ph and CPh absorption was found to obey the pseudo-second-order model, and the adsorption rate is limited by the interaction of the adsorbate molecules with the AdCs. Adsorption isotherms at equilibrium concentrations ≤ 5 mmol/l are approximated by the Langmuir model ($R_2 \geq 0.994$). Compared with Ph, the degree of CPh extraction is much higher, which is a consequence of its stronger connection with the AC surface. The specific adsorption capacity for Ph and CPh shows a sharp decrease (10-16 times) with increasing carbonization temperature from 400°C to 550°C and a weak temperature dependence at $550-800^{\circ}\text{C}$. In this range, ACs are formed with similar concentrations of AdCs, but different for various phenolic compounds. Adsorption on brown coal ACs was postulated to include π - π interaction, formation of electron-donor-acceptor complexes and formation of hydrogen bonds, but their contributions depend on adsorbate nature and they change while increasing alkaline carbonization temperature.

Keywords: brown coal, alkaline carbonization, activated carbon, porosity, adsorption, phenol, 4-chlorophenol.

Corresponding author Tamarkina Ju.V., e-mail: Tamarkina@nas.gov.ua