ADSORPTION OF 4-CHLORPHENOL BY BROWN COAL ACTIVATED BY POTASSIUM HYDROXIDE

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The purpose of the work is to evaluate the 4-chlorophenol (CP) adsorption capacity of brown coal activated carbons (ACs) prepared at different temperature of KOH activation. ACs were obtained in three stages: 1) impregnation of coal with a KOH solution, 2) heating (4 deg/min) in argon to a given temperature t (400-800°C) and exposure for 1 h, 3) cooling, washing from KOH, drying. The samples are designated as AC(t). Based on the N_2 adsorption-desorption isotherms, the ACs total pore volume (V_t, cm^3/g) and specific surface area (S, m^2/g) were determined. The ACs adsorption capacities were measured at 25°C, CP concentration ≤700 mg/L, AC dosage – 1 g/L. The alkaline activation temperature was found to be a key factor in forming porosity of ACs and ability to adsorb CP. The CP maximum capacity ($A_{CP(m)}$, mg/g) increases 6.6 times up to 307 mg/g for AC(800) having S=1142 m^2/g. The specific adsorption capacity ($A_{CP(S)} = A_{CP(m)}/S$, mg/m^2) sharply decreases in a sample range from AC(400) to AC(550) and weakly depends on temperature at 550-800°C. The kinetics of CP adsorption is best described by a pseudo-second order model. The rate determining stage is the interaction of CP molecules with AC surface. The CP adsorption isotherms are best described by the Langmuir model. The dependence of the $A_{CP(m)}$ from S can be approximated by three linear equations that probably correspond to the three regions of forming surface adsorbtion centers (AdCs). The first (S≤370 m^2/g) is characterized by a small adsorption capacity increment (k_S=0.103 mg/m^2), but a significant (16.4 times) decrease in the specific capacity $A_{CP(S)}$. In the second region (S=370-770 m^2/g, t=550-750°C), capacity increment is 10 times more (k_S=0.985 mg/m^2) and in the third region (S≥770 m^2/g, t≥750°C) the increase in CP capacity is the smallest (k_S=0.067 mg/m^2). The thermoinitiated formation of AdCs is assumed to be not proportional to the increase in surface area, and their chemical structure and reactivity is determined by the alkaline activation temperature.

Keywords: *activated carbon, adsorption, alkaline activation, brown coal, porous structure, 4-chlorophenol*

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1. Introduction

Chlorophenols are widely used as intermediates to produce organic compounds (pesticides, biocides, dyes) and are potential pollutants of the natural environment (Czaplicka, 2004). The main sources of its release are wastewaters from petrochemical plants, pharmaceutical companies, coal gasification sites and municipal solid waste incineration plants (Czaplicka, 2004; Peng et al., 2016). The disinfection of drinking water with chlorine may also produce chlorophenols in case the water resource is contaminated by phenol (Ding et al., 2016).

These compounds are ecotoxicants because of its high toxicity, strong odor emission and persistence in the environment, and suspected carcinogenity and mutagenity to living organisms (Czaplicka, 2004; Ahmed & Theydan, 2013; Chen, Geng & Huang, 2017).

Judging by the LD_{50} parameter (Peng et al., 2016), pentachlorophenol

(LD_{50}=50 mg/kg) and 4-chlorophenol (LD_{50}=261 mg/kg) are the most toxic. The upper permissible limit of chlorophenols in publicly supplied water is 0.5 mg/L (Ahmed & Theydan, 2013), and their concentration as high as 0.1 mg/L in drinking water causes unpleasant taste and odor (Ding et al., 2016). So, the effective removal of chlorophenols from industrial effluents is of great practical significance for environmental protection.

A widespread method of aqueous media purification from organic pollutants is adsorption due to the relative simplicity of the process, and effective adsorbents for the removal of chlorophenols are activated carbons (ACs) (Ahmed & Theydan, 2013; Lin & Juang, 2009).

To capture 4-chlorophenol (hereinafter CP) use a variety of adsorbents, which differ significantly in the values of the maximum adsorption capacity $A_{CP(m)}$. According to (Chen, Geng & Huang, 2017), this parameter varies from $A_{CP(m)}$=43 mg/g (nanotubes) to $A_{CP(m)}$=323 mg/g (AC Prolabo).

A special group of ACs consists of materials prepared by activation with potassium hydroxide. They are characterized by a high specific surface area (≤2000 m^2/g) and a significant adsorption capacity for 4-chlorophenol.

Samples of ACs from different types of biomass activated by KOH show the values of $A_{CP(m)}$ = 72.8-663.5 mg/g depending on the AC dosage (0.5-5.0 g/L) in a solution of CP (Ahmed & Theydan, 2013). Organic sewage sludge activated by KOH (1.0-3.0 g/g, 750°C, 0.5 h) forms ACs with $A_{CP(m)}$ = 233-363 mg/g (Monsalvo, Mohedano & Rodriguez, 2011). Higher capacity ($A_{CP(m)}$ = 610-711 mg/g) is shown by adsorbents obtained by alkaline activation (KOH, 2.5-3.5 g/g, 780°C, 1 h) of corncobs pre-carbonized (290°C, 2 h) in the presence of H_2SO_4 (25%) (Wu, et al., 2011). Most likely, the greatest value of capacity ($A_{CP(m)} \leq$ 723 mg/g at an initial concentration of ≤84 mg/L) was obtained for ACs from fossil coal activated by KOH (2-4 g/g, 780°C, 1 h) (Wu et al., 2010). These examples do not cover all published data, but only illustrate the variety of carbon materials tested in the capture of 4-chlorophenol from aqueous media.

Promising materials are carbon adsorbents, which are obtained by alkaline (KOH) activation of fossil coal at a low weight ratio of KOH/coal (1 g/g) (Kucherenko et al., 2010). Such materials are able to adsorb heavy metal ions (Simonova et al., 2012) and organic compounds from aqueous media (Fedorova, Manina & Ismagilov, 2015; Tamarkina et al., 2020) and can be effective in water purification processes from multicomponent contaminants. It was previously found that alkali-activated brown coal forms ACs (yield 30±2%) with a specific surface area S=1100±100 m^2/g (Kucherenko, Tamarkina & Rayenko, 2017) and a significant adsorption capacity for phenol (240 mg/g), dye methylene blue (197 mg/g) and elemental iodine (963 mg/g) (Tamarkina et al., 2020).

The purpose of this work is to quantify the adsorption capacity of brown coal-based ACs in relation to 4-chlorophenol and influence of the ACs preparation temperature on its adsorption properties.

2. Materials and Methods

A brown coal of 0.5-1.0 mm particle sizes from the Alexandria deposit was used; a detailed description is given in (Kucherenko, Tamarkina & Rayenko, 2017). Preparation of

ACs was carried out by alkaline activation, which includes the following stages: 1) impregnation of dry coal with an aqueous solution of KOH (Chemapol) (weight ratio KOH/coal R_{KOH} 1.0 g/g) followed by drying (120±10°C, ≥2 h), 2) thermoprogrammed (4 deg/min) heating the sample (~40 g) in an argon atmosphere to a given temperature (t) varied in the range t=400-800°C) and holding for 1 h, 3), cooling, washing from KOH, drying. The obtained samples are marked as AC(t), where t is the activation temperature. The AC yield is marked as Y_{AC}. The AC particle sizes are 25-130 μm mostly (99%), that is evaluated by Winner 2000 Lazer Particle Size Analyzer, Jinan Winner Instrument Co., Ltd (China).

The characteristics of ACs pore structure was quantified using isotherms of low-temperature (77 K) adsorption-desorption of nitrogen (ASAP 2020, Micromeritics, USA). Before the tests, the samples were degassed for 20 h at 200°C. The total pore volume V_t (cm^3/g) was calculated by the amount of nitrogen adsorbed at a relative pressure p/p_0 ~1.0. The micropore volume (V_{mi}, cm^3/g) and the pore size distribution were measured using the integral and differential dependences of the above characteristics on the average pore width (W, nm) calculated by the 2D-NLDFT method (Jagiello & Olivier, 2013). The total volume of meso- and macropores was calculated as the difference $V_{me+ma} = V_t - V_{mi}$. The specific surface area S (m^2/g), the specific surface area of micropores (S_{mi}) and the total surface area of meso- and macropores (S_{me+ma}) were calculated similarly.

The CP adsorption capacity (A_{CP}, mg/g) was determined as follows. The AC sample (0.100 g) dried at 120±10°C was mixed with a CP solution (100 mL) of a given initial concentration ($C_{CP(0)} \leq 700$ mg/L) in a conical flask, and shaken at 25°C (200 rpm, bath shaker MAXTURDY-45, Daihan Scientific Co, China). In all experiments, the AC content in the CP solution was constant (1 g/L). After a specified time, the mixture was filtered and the optical density of the solution was measured using a Perkin-Elmer Lambda 20 spectrophotometer at a wavelength of 280 nm. The CP concentration was determined by comparing the optical density OD with a calibration graph or by the correlation equation $C_{CP} = 86.723 \cdot OD - 0.3721$ ($R^2 = 0.9999$). The amount of adsorbed CP was determined as $A_{CP} = (C_{CP(0)} - C_{CP}) \times V/m$, where $C_{CP(0)}$ and C_{CP} are the initial and final concentrations of CP, V is the volume of solution (100 mL), m is is the mass of dried AC (100 mg).

The final concentration C_{CP} is the current concentration at a given time τ (when registering the adsorption kinetics) or equilibrium $C_{CP(e)}$ (when registering the adsorption isotherm). The specific adsorption capacity $A_{CP(S)}$ (mg/m^2) was determined as $A_{CP(S)} = A_{CP}/S$. The value of this parameter is proportional to the concentration of adsorption centers (AdCs) on the carbon surface. Additionally, the degree of coverage (DC) of the AC surface with adsorbate molecules was calculated as $DC = A_S \cdot 10^{-3} \times N_A \times S_{CP}$, where N_A is Avogadro's constant, S_{CP} is the projection area of the adsorbed CP molecule, which is taken as 0.482 nm^2 (Lorenc-Grabowska, Gryglewicz & Machnikowski, 2010) or 0.487 nm^2 (Wu et al., 2011; Wu, Tseng & Hu, 2005). For these calculations, it was assumed that the adsorbate molecules are embedded tightly to each other, and $S_{CP} = 0.487$ nm^2.

3. Results and Discussion

Under accepted conditions of alkaline activation, the yield of AC decreases with increasing temperature (Table 1). Sample AC(400) is characterized by low values of V_t and S. With increasing temperature, the porous structure develops significantly, which leads to an increase in pore volume by 5.1 times, and the specific surface area by ~90 times. The micropore volume increases most significantly: its portion (V_{mi}/V_t) increases by almost two orders of magnitude (from 0.0074 to 0.75).

Table 1. *The yield and characteristics of ACs obtained at different activation temperatures*

Sample	**Y_{AC}, %**	**Pore volume, cm^3/g**			**Pore surface area, m^2/g**		
		V_t	**V_{mi}**	**V_{me+ma}**	**S**	**S_{mi}**	**S_{me+ma}**
AC(400)	71	0.095	0.0007	0.094	12.8	<2	10.8
AC(450)	57	0.109	0.013	0.096	73.3	60.2	13.1
AC(500)	54	0.281	0.086	0.172	273	244	29
AC(550)	52	0.262	0.133	0.106	370	339	31
AC(600)	50	0.384	0.160	0.235	450	407	43
AC(650)	47	0.392	0.199	0.160	555	518	37
AC(700)	41	0.496	0.249	0.267	695	652	43
AC(750)	35	0.476	0.280	0.207	773	738	35
AC(785)	30	0.483	0.362	0.121	1113	989	24
AC(800)	29	0.487	0.367	0.120	1142	1120	22

Accordingly, the portion of the specific surface area of micropores increases up to (S_{mi}/S) = 0.98, i.e. the total surface area of AC(800) consists almost entirely of the micropores surface.

Such formation of porous structure is a distinctive feature of alkaline activation being thermolysis of fossil coal impregnated with alkali metal hydroxides. This is the result of thermoinitiated reactions of KOH with structural fragments of coal framework, in particular, dealkylation of polyarenes and heterolysis of C-O and C-C bonds (Tamarkina, Kucherenko & Shendrik, 2014).

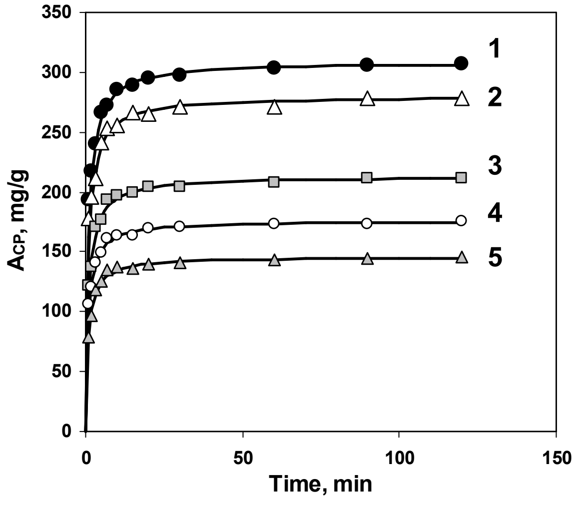

Fig. 1. *Kinetics of 4-chlorophenol adsorption by AC(800) at initial concentrations of 600 mg/L (1), 400 mg/L (2), 250 mg/L (3), 200 mg/L (4), and 150 mg/L (5); solid line – the pseudo-second order model*

For AC(800) sample having the most developed porous structure, the kinetics of CP adsorption were studied in detail. With increasing time, the CP adsorption capacity increases (Fig. 1) and within about 2 h reaches the maximum values for all initial concentration varied in the range of $C_{CP(0)}$ = 150-700 mg/L.

The same time is required for reported adsorption equilibrium by ACs from other starting materials (Ahmed & Theydan, 2013; Wu et al., 2011; Li et al., 2009; Termoul et al., 2006; Hameed, Chin & Rengaraj, 2008). The kinetic curves of Fig. 1 are poorly approximated by the pseudo-first order equation ($R^2 \leq 0.8$).

For the AC samples obtained in this work, the pseudo-second order model $A_{CP} = k_2 \cdot A^2_{CP(m)} \cdot \tau / (1 + k_2 \cdot A_{CP(m)} \cdot \tau)$ is well applicable, where k_2 is a pseudo-second order constant. This model postulates that the adsorption rate is limited by the interaction of adsorbate molecules with adsorption centers on the surface of the carbon material (Ho & McKay, 1999), and not by diffusion into the particles of the adsorbent. The prefix "pseudo" is used in the world scientific literature (Ho & McKay, 1999; Simonin, 2016; Moussout et al., 2018; Khamizov, 2020) in order to distinguish kinetic equations using adsorption capacities from ordinary first- and second-order equations using the concentration of adsorbate in aqueous solution.

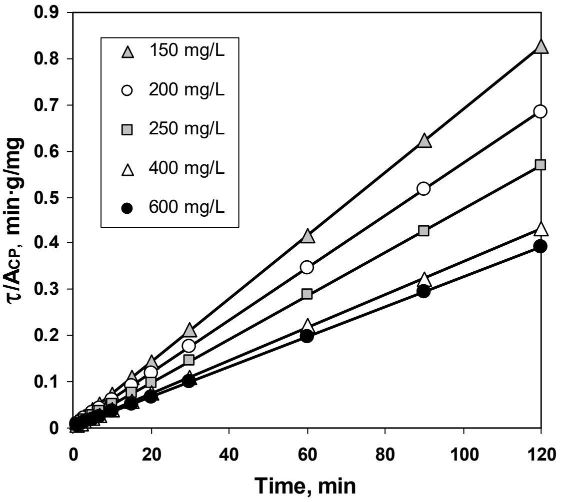

Fig. 2. *Linearizations of adsorption kinetics curves by pseudo-second order model at 4-chlorophenol initial concentrations of 150-600 mg/L*

Table 2. *Parameters of pseudo-second order model and intraparticle diffusion model for the adsorption of 4-chlorophenol by the AC(800) sample*

Parameters	**Initial concentration $C_{CP(0)}$, mg/L**						
	150	200	250	300	400	500	600
Pseudo-second order model							
$A_{CP(m)}$, mg/g (exp)	145	175	211	234	279	297	307
$A_{X\Phi(m)}$, mg/g (calc)	146.0	176.0	213.1	235.9	280.2	296.3	308.6
$k_2 \times 10^3$, mg/g·min	7.89	6.80	5.00	4.90	3.95	3.40	3.61
Intraparticle diffusion model							
k_{d1}, mg/g^{-1}·min$^{-0,5}$	33.6	32.9	44.0	40.5	48.3	52.5	50.0
k_{d2}, mg/g^{-1}·min$^{-0,5}$	1.15	1.45	1.79	1.95	2.46	2.47	2.69
C_{d1}, mg/g	50.2	76.4	80.7	107.9	128.9	129.7	147.6
C_{d2}, mg/g	133.5	160.6	193.5	215.1	253.6	268.8	279.9
R^2_{d1}	0.927	0.958	0.930	0.979	0.991	0.942	0.965
R^2_{d2}	0.891	0.824	0.914	0.772	0.834	0.890	0.912

This equation can be represented as $\left(\tau / A_{CP}\right) = \left(1 / k_2 \cdot A^2_{CP(m)}\right) + \tau / A_{CP(m)}$ then kinetic curves are linearized in "$(\tau/A_{CP}) - \tau$"coordinates (Fig. 2). This allows to calculate the maximum capacities $A_{CP(m)}$ and the k_2 constants. These parameters of AC(800) sample at different initial concentrations of CP are summarized in Table 2.

With increasing the initial concentration of CP, the k_2 values decrease (Fig. 3, line 1). Similar relationships were described for the adsorption of CP on other types of ACs obtained by alkaline activation. For example, a decrease in the k_2 value from $3.7\cdot10^{-3}$ g/mg·min to $0.9\cdot10^{-3}$ g/mg·min with an increase in the CP initial concentration from 50 mg/L to 250 mg/L was defined for AC having $S = 1677$ m^2/g and $V_t = 0.527$ cm^3/g (Ahmed & Theydan, 2013). Adsorption of CP by another AC sample ($S = 1083$ m^2/g and $V_t = 0.644$ cm^3/g) is characterized by a decrease in k_2 values from $49.4\cdot10^{-3}$ g/mg·min to $1.0\cdot10^{-3}$ g/mg·min with increasing $S_{CP(0)}$ from 27 mg/L to 191 mg/L (Hameed, Chin & Rengaraj, 2008). The constant of the same order ($k_2=7.5\cdot10^{-3}$ g/mg·min) was determined for the CP adsorption by single-layer nanotubes ($S = 625$ m^2/g) (Ding et al., 2016).

Kinetic data on Fig. 1 show that the main amount of CP is adsorbed for the short initial period. To characterize this property, we can use the parameter $A_{CP(1)}$ – the amount of CP (mg/g) adsorbed in the first minute of the process. It was introduced in (Wu et al., 2011) for comparative estimation of mass transfer intensity in “AC-CP-H_2O” systems and can be useful for engineering calculations.

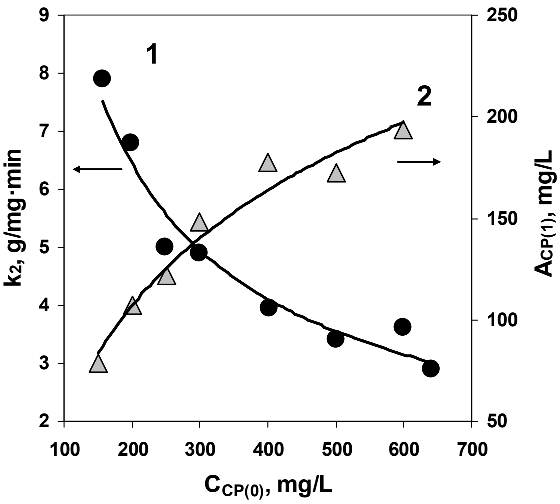

Fig. 3. *Pseudo-second order constants (1) and $A_{CP(1)}$ parameter (2) as functions of the initial concentration of 4-chlorophenol*

For the studied AC(800) sample, the $A_{CP(1)}$ value are quite large and increase with increasing initial concentration of CP (Fig. 3, line 2). But under the same conditions, the degree of CP extraction from the aqueous phase for the first minute little depends on the $C_{CP(0)}$ value and varies between 54.3-63.8%.

Approximation of kinetic data by pseudo-second order equation is supplemented in almost all works by the application of the intraparticle diffusion model $A_{CP} = k_d\cdot\tau^{0.5} + C_d$, where k_d is the diffusion constant; C_d is a constant proportional to the thickness of the boundary layer (Ahmed & Theydan, 2013; Chen, Geng & Huang, 2017; Tamarkina et al., 2020; Hameed, Chin & Rengaraj, 2008). This model assumes the following. The dependence of the adsorption capacity on $\tau^{0.5}$ is a straight line passing through the origin of coordinates if diffusion into the AC particles is the rate-determining stage. The presence of several linear sections indicates that the adsorption rate in different periods of the adsorbtion process is controlled by different factors.

For the AC(800) sample, the dependences of the A_{CP} on $\tau^{0.5}$ show two linear sections (Fig. 4) with significantly different values of k_d and C_d (Table 2). The first linear portion with a steep slope appears to be the fast surface adsorption attributed to the boundary layer effect caused by the diffusion of CP from solution to the surface of AC. The second linear portion with a much smaller slope can be attributed to diffusion into micropores. In comparison with the k_{d1} values, the constants k_{d2} are 18-29 times lower (Table 2), which may be a consequence of the gradual attainment of adsorption equilibrium due to intra-particle diffusion of the adsorbates within ACs.

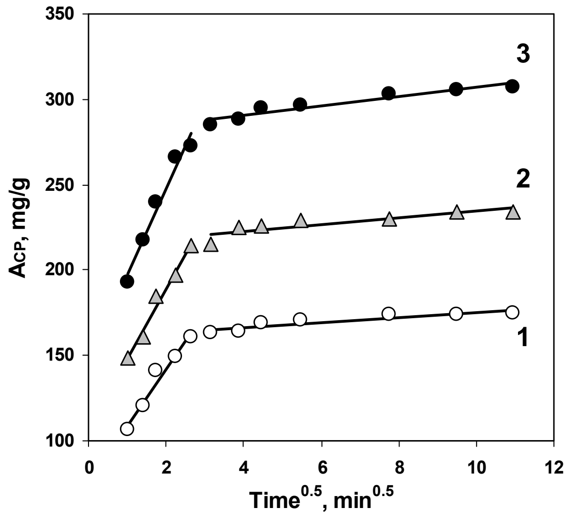

Fig. 4. *Fitting of the AC(800) adsorption rate data to the intraparticle diffusion model for initial concentrations of 200 mg/L (1), 300 mg/L (2), and 600 mg/L (3)*

Thus, the application of the two models to the same system "AC-CP-H_2O" leads to two different conclusions. The equation of intra-particle diffusion makes it possible to postulate the limiting role of the transport of CP molecules to the AC surface. The good applicability of the pseudo-second order model (Fig. 2) indicates that the rate-determining stage is the adsorption of CP molecules as their interaction with adsorbtion centers on the surface.

At the same time, it is believed [Khamizov, 2020] that the applicability of the pseudo-second order model does not depend on the mechanisms determining the adsorption rate. In any case, the chemical reaction of CP with structural fragments of the AC spatial framework can affect the overall rate of the process. It is rather difficult to separate the contributions of the mass transfer and the chemical stage based on using only formal equations (Khamizov, 2020).

To assess the diffusion effect, the adsorption of CP was compared with the adsorption of phenol (Ph) having much smaller molecular size. The idea of this comparison is as follows: if diffusion is the rate-determining stage, the rate of phenol adsorption will be higher, as the size of its molecule is smaller and the phenol diffusion into the porous system will be less difficult.

During kinetic measurements performed under strictly identical conditions (C (0) = 5 mmol L, AC dosage – 1 g/L, 25°C, time ≤120 min), three experimental facts were established: 1) large (1.43 times for τ=120 min) the amount of adsorbed CP in comparison with phenol (2.40 mmol/g *vs* 1.62 mmol/g); 2) the rate of CP absorption in the first minute of the process is much higher (~5 times): $A_{CP(1)}$ = 1.149 mmol/g *vs* $A_{Ph(1)}$ = 0.244 mmol/g; 3) larger value of the pseudo-second order constant for CP (k_2=37.4·10^{-2} g/mmol·min) compared to k_2 value for phenol (k_2=37.4·10^{-2} g/mmol·min).

Thus, in comparison with the adsorption of phenol, the rate of CP adsorption is higher, although the sizes of CP molecules are larger. Therefore, the rate-determining stage can be assumed to be the interaction of adsorbate molecules with surface adsorption centers.

Isotherms of CP adsorption were obtained for the AC(650) and AC(800) samples (Fig. 5). These data were fitted with the same models used for the adsorption of methylene blue dye and iodine on AC samples from fossil coal (Tamarkina et al., 2020). Only the Langmuir model turned out to be well acceptable $A_{CP(e)} = A_{CP(L)} \cdot k_L C_{CP(e)} / \left(1 + k_{CP(L)} \cdot C_{CP(e)}\right)$, where $A_{CP(L)}$·is the adsorption capacity corresponding to the saturated monolayer of adsorbate; $k_{CP(L)}$·is the Langmuir constant. For AC(800) and AC(650) samples, it is represented by solid lines in Fig. 5. This model is reported to be most suitable for describing CP uptake by other types of adsorbents (Chen, Geng & Huang, 2017; Monsalvo, Mohedano & Rodriguez, 2011; Wu et al., 2011; Wu et al., 2010, Lorenc-Grabowska, Gryglewicz & Machnikowski, 2010; Li et al., 2009).

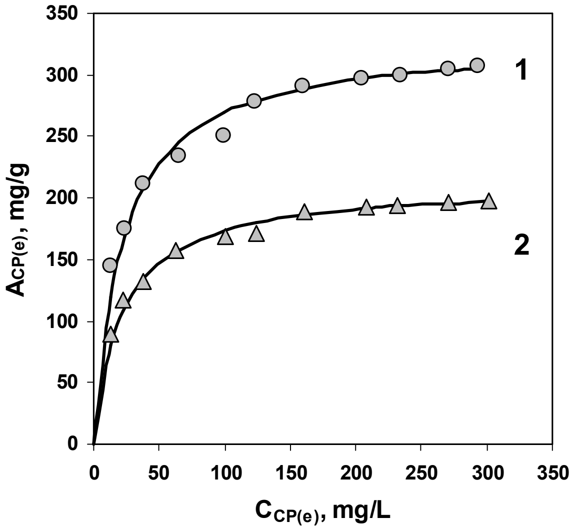

Fig. 5. *Adsorption isotherms of 4-chlorophenol by AC(800) (1) and AC(650) (2); the solid curves were calculated by the Langmuir equation*

The adsorption isotherms were linearized in the "($C_{CP(e)}$ / $A_{CP(e)}$) – $C_{CP(e)}$" coordinates; the Langmuir equation coefficients were calculated: $A_{X\Phi(L)} = 211.4$ mg/g and $k_{X\Phi(L)} = 0.0459$ L/mg for AC(650); $A_{X\Phi(L)} = 328.95$ mg/g and $k_{X\Phi(L)} = 0.0450$ L/mg for AC(800). Thus, the Langmuir constants are almost the same, although the specific surface area of the AC samples differs by ~2 times (Table 1).

The values of $k_{CP(L)}$ reported are within a fairly wide range. For ACs of different nature with specific surface areas S = 560-1968 m^2/g, the $k_{CP(L)}$ values differ by a factor of 12 and are in the range $k_{CP(L)}$ = 0.0282-0.338 L/mg (Wu et al., 2011). Adsorbents synthesized by alkaline (KOH) activation show the following values: $k_{CP(L)}$ = 0.0747-0.0995 L/mg (AC samples from fossil coals; S = 670-1520 m^2/g) (Wu et al., 2010) and $k_{CP(L)}$ = 0.32 L/mg (wood-derived AC; S = 1083 m^2/g) (Hameed, Chin & Rengaraj 2008). Two AC samples (with S = 950 m^2/g and S = 1832 m^2/g) from biomass activated with KOH show the same constant ($k_{CP(L)}$ = 0.0115 L/mg (Monsalvo, Mohedano & Rodriguez, 2011)) as the AC(650) and AC(800) samples. As it turned out, the constant $k_{CP(L)}$ is very sensitive to the method of AC preparation, but does not directly depend on the specific surface area.

For other ACs in this work, the maximum adsorption capacities of CP ($A_{CP(m)}$) were obtained under the same conditions: $C_{CP(0)}$ = 600 mg/g, AC dosage – 1 g/L, 25°C, time – 2 hours. The $A_{CP(m)}$ values are proportional to the surface concentration of adsorption centers and increase with increasing temperature by 6.6 times (Table 3), although the specific surface area increases in 90 times (Table 1).

The temperature dependence of $A_{CP(m)}$ can be approximated by by two linear relationships (Fig. 6, line 1). The first corresponds to the correlation equation $A_{CP(m)} = 0.263 \cdot t - 60.55$ ($R^2 = 0.963$) and corresponds to the temperature range of 400-550°C. The second relationship for the 550-800°C interval is fitted with the equation $A_{CP(m)} = 0.922 \cdot t - 416.42$ ($R^2 = 0.982$).

***Table 3**. Adsorption properties of ACs from brown coal*

Parameter	**Temperature of AC preparation, °C**									
	400	450	500	550	600	650	700	750	785	800
$A_{CP(m)}$, mg/g	46.2	53.7	74.5	83.1	127	198	243	283	303	307
$A_{CP(S)}$, mg/m^2	3.609	0.733	0.273	0.225	0.282	0.357	0.350	0.366	0.299	0.269
DC	8.15	1.66	0.62	0.51	0.64	0.81	0.79	0.83	0.68	0.61

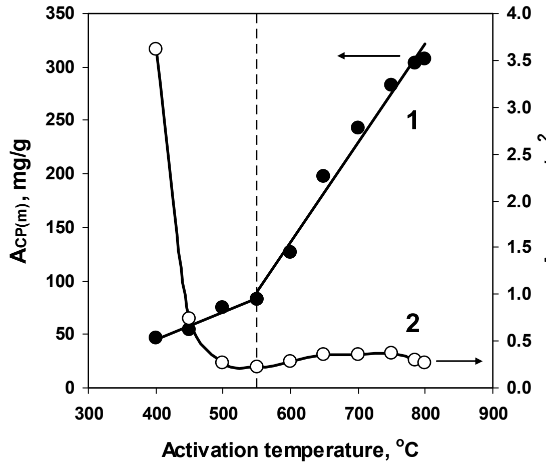

Fig. 6. The maximum capacity $A_{CP(m)}$ (1) and the specific capacity $A_{CP(S)}$ (2) of 4-chlorophenol as functions of the alkaline activation temperature

The specific adsorption capacity $A_{CP(S)}$ shows a completely different picture (Fig. 6, line 2). The $A_{CP(S)}$ parameter decreases sharply 16.4 times (from 3.61 mg/m^2 to 0.23 mg/m^2) with increasing temperature up to 550°C and is almost independent of temperature in the range of 550-800°C. For a number of samples from AC(550) to AC(800), all $A_{CP(S)}$ values are in the range of $A_{CP(S)}$ = 0.225-0.366 mg/m^2 (Table 3). These values are typical for carbon materials with a developed porous structure.

For example, the values of $A_{CP(S)}$ = 0.227-0.249 mg/m^2 were reported for AC with S = 879-933 m^2/g and $A_{CP(m)}$ = 212-221 mg/g, and $A_{CP(S)}$ = 0.276-0.347 mg/m^2 for AC with S = 929 m^2/g and $A_{CP(m)}$ = 256-323 mg/g (Chen, Geng & Huang, 2017).

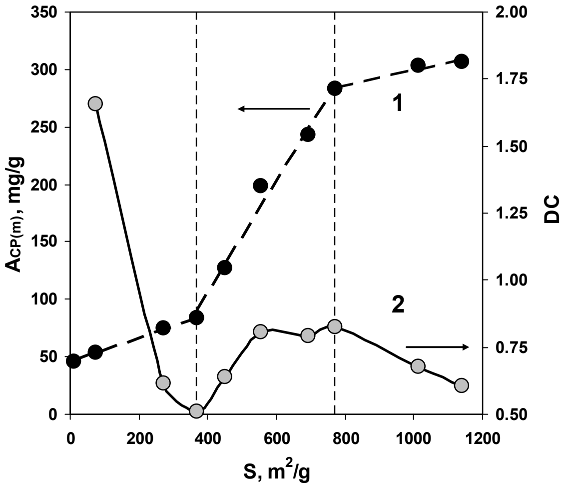

***Fig. 7**. The maximum capacity $A_{CP(m)}$ (1) and the degree of coverage DC (2) of 4-chlorophenol as functions of the AC specific surface area*

Changes in $A_{CP(m)}$ values are symbate with changes in the specific surface area of AC samples (Table 1). The "$A_{CP(m)} – S$" dependence is not linear, similar to S-shape curve (Fig.7, line 1) and can be approximated by three linear dependences shown by dashed lines. They conditionally correspond to three regions of the formation of surface adsorbtion centers with increasing temperature of alkaline activation.

The first region ($S \leq 370\ m^2/g$) is characterized by a small increase in the adsorption capacity (4-chlorophenol capacity growth factor $k_S = 0.103\ mg/m^2$), but a significant decrease (16 times) in the $A_{CP(S)}$ specific capacity (Fig. 6). The second region ($S = 370\text{-}770\ m^2/g$) shows the greater increase in CP capacity ($k_S = 0.985\ mg/m^2$) and this happens with increasing temperature from 550°C to 750°C. The third region ($S \geq 770\ m^2/g$) shows the smallest increase in capacity ($k_S = 0.067\ mg/m^2$): an additional increase in $A_{CP(m)}$ is ~8% (from 283 mg/g to 307 mg/g).

In comparison with the "$A_{CP(m)} – S$" dependence, the degree of surface coverage changes differently (Fig. 7, line 2). The sample AC(400) shows DC = 8.15 (Table 3, not shown in Fig. 7), i.e. more than eight adsorption layers are formally formed. With increasing surface area to $370\ m^2/g$, the DC magnitude decreases to the minimum value of DC = 0.51. For other ACs, the degree of surface coverage changes with increasing temperature along the curve with a maximum (DC = 0.81 ± 0.02) for AC samples with specific surface area varied within $S = 370\text{-}1142\ m^2/g$ (Fig. 7).

Note, these DC values are common for CP adsorption by porous carbon materials obtained using various activators (NaOH, KOH, H_2O-vapor, CO_2) (Wu et al., 2011). An increase in the DC value to a maximum (DC = 0.83) corresponds to an increase in the specific surface area to $770\ m^2/g$ (Fig. 7). For AC samples with $S \geq 770\ m^2/g$, the DC value decreases against the background of an increase in the specific surface area. This indicates a decrease in the surface concentration of active adsorption sites.

Changes in the adsorption properties of ACs with increasing temperature can be explained as follows. Low-temperature alkaline activation at 400°C partially destroys structural fragments of brown coal, in particular, quinoid and OH-groups and heterocycles containing O-atoms. In addition, KOH cleaves the C–C and C–O bonds of the carbon framework to form oxygen functional groups (Tamarkina, Kucherenko & Shendrik 2014).

Because of this, the AC(400) sample contains a sufficiently large number of reaction centers that can interact with CP to form complexes or even new chemical compounds. In addition, the spatial framework of AC(400) is not rigid three-dimensionally one and allows steric mobility of its individual structural fragments. For this reason, the AC(400) can absorb CP due to its diffusion into the swellable framework. The contribution of the chemical reaction to the CP adsorption by the AC(400) sample is dominant and looks like multilayer adsorption (DC = 8.15).

With increasing temperature from 400°C to 550°C, the contribution of the chemical reactions decreases and is manifested in a sharp 16-fold decrease in the specific capacity and degree of surface coverage (Fig. 6 and 7). The contribution of the adsorption itself is still small due to the small development of the surface and the low concentration of adsorbtion centers. A break point is observed at 550°C (Fig. 6) and formally corresponds to ending the region of the main thermal destruction of coal, when most of the polyarene substituents are cleaved off and leave the reaction medium as volatile products.

The spatial framework of the AC(550) has no reaction centers for chemical binding of CP, and the uptake of adsorbate is determined only by adsorption. In the temperature range (550-750°C), ACs are formed with increasing specific surface area (from 370 m^2/g to 773 m^2/g) and increasing surface concentration of adsorption centers. This leads to increasing the values of the specific capacity up to $A_{CP(S)} = 0.366$ mg/m^2 and the degree of surface coverage up to DC = 0.83.

An increase in temperature to 800°C further develops the AC surface, but the concentration of surface adsorption centers decreases and causes a decrease in the $A_{CP(S)}$ and DC values. Obviously, the thermoinitiated formation of adsorption centers, which chemically or adsorptively interact with 4-chlorophenol molecules, is not strictly proportional to the specific surface area. It is also undoubted that the chemical structure and, as a consequence, the reactivity of the AC is determined by the temperature of alkaline activation.

4. Conclusions

1. The temperature of alkaline (KOH) activation of brown coal is a key factor in the porosity formation of activated carbons and their ability to adsorb 4-chlorophenol from aqueous media.

2. The kinetics of 4-chlorophenol adsorption (25°C) by the most microporous AC sample obtained at 800°C is described by a pseudo-second order model ($R^2 \geq 0.998$). The rate-determining stage stage is interaction of adsorbate molecules with surface adsorption centers, that is, physical sorption and chemisorption.

3. Adsorption isotherms are best described by the Langmuir model. For ACs prepared at 650°C and 800°C, the Langmuir constants are the same (0.0459 L/mg and 0.0450 L/mg) although the specific surface area differs by ~ 2 times (555 m^2/g and 1142 m^2/g).

4. The maximum 4-chlorophenol capacity is proportional to the surface concentration of adsorption centers and grows from 46.2 mg/g (400°C) to 307 mg/g (800°C) with increasing temperature, i.e. 6.6 times with an increase in the surface area 90 times. The specific adsorption capacity of ACs sharply decreases (16.4 times) in the range 400-550°C and weakly depends on the temperature at 550-800°C.

5. The dependence of the CP maximum capacitance on AC specific surface is similar to the S-shaped curve and can be approximated by three linear dependences corresponding to the three regions of surface adsorbtion centers formation with increasing alkaline activation temperature.

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АДСОРБЦІЯ 4-ХЛОРФЕНОЛУ БУРИМ ВУГІЛЛЯМ, АКТИВОВАНИМ ГІДРОКСИДОМ КАЛІЮ

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Мета даної роботи – оцінити адсорбційну здатність буровугільного активованого вугілля (АВ), отриманого при різних температурах лужної активації з КОН по відношенню до 4-хлорфенолу (ХФ). Зразки АВ отримували в три стадії: 1) імпрегнування вугілля водним розчином КОН, 2) нагрівання (4 град/хв) в аргоні до заданої температури t (400-800°С) та витримка 1 год, 3) охолодження, відмивка від КОН, сушка. Зразки позначено як АВ(t). На основі ізотерм адсорбції-десорбції азоту визначено об'єм пор АВ (V_t, см^3/г) та їх питому поверхню (S, м^2/г). Адсорбційні ємності за 4-хлорфенолом (ХФ) зразків АВ отримано при 25°С, початковій концентрації $C_{ХФ(0)} \leq 700$ мг/л, вмісті АВ – 1 г/л.

Встановлено, що температура лужної активації є ключовим фактором формування пористості АВ та його здатності адсорбувати ХФ. Максимальна ємність за ХФ ($A_{СР(m)}$, мг/г) збільшується у 6.6 разів до 307 мг/г у АВ(800) з питомою поверхнею 1142 м^2/г. Питома адсорбційна ємність ($A_{ХФ(S)} = A_{ХФ(m)}/S$, мг/м^2) різко зменшується для зразків від АВ(400) до АВ(550) та слабо залежить від температури інтервалі t=550-800°С. Кінетика адсорбції ХФ найкраще описується моделлю псевдо-другого порядку. Швидкість визначальною стадією є взаємодія молекул адсорбата з поверхнею АВ. Ізотерми адсорбції ХФ найкраще описуються моделлю Ленгмюра.

Залежність максимальної ємності АВ від їх питомої поверхні може бути апроксимована трьома лінійними рівняннями, які відповідають трьом областям формування поверхневих адсорбційних центрів. Перша ($S \leq 370$ м^2/г) характеризується невеликим коефіцієнтом приросту адсорбційної ємності ($k_S = 0.103$ мг/м^2), але значним (в 16.4 разів) зниженням питомої ємності. У другій області (S = 370-770 м^2/г) приріст ємності в 10 разів більший ($k_S = 0.985$ мг/м^2), і в третій області ($S \geq 770$ м^2/г, $t \geq 750$°С) приріст ємності найменший ($k_S = 0.067$ мг/м^2). Припущено, що термоініційоване утворення адсорбційних центрів не є пропорційним збільшенню питомої поверхні, а їх хімічна будова і реакційна здатність по відношенню до ХФ визначається температурою лужної активації.

Ключові слова: *адсорбція, активоване вугілля, буре вугілля, лужна активація, пориста структура, 4-хлорфенол*