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Adsorption of Phenols on Carbonaceous Materials of Various Origins but of Similar Specific Surface Areas

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Abstract: The adsorption of phenol (Ph), 4-chlorophenol (CP), and 4-cresol (MP) from aqueous solutions on three carbonaceous materials of diverse origins but similar specific surface areas was investigated. Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysis char (AP) were examined as adsorbents. The kinetics and equilibrium adsorption, as well as the influence of pH and ionic strength of each solution on the adsorption process, were studied. The results revealed that the adsorption was pH-dependent and preferred an acidic environment. The presence of an inorganic salt in the solution (ionic strength) did not affect the adsorption processes of the three adsorbates. The pseudo-first- and pseudo-second-order equations, as well as the Weber–Morris and Boyd kinetic models, were used to describe the adsorption kinetics. It was found that equilibrium was reached for all adsorbates after approximately 2–3 h. Adsorption kinetics followed a pseudo-second-order model, and the adsorption rate was determined by film diffusion. The adsorption isotherms were described using the Langmuir and Freundlich equations. The results revealed that the adsorption processes of Ph, CP, and MP on all three adsorbents from the water were better described by the Langmuir model. The adsorption of CP was the most efficient, the adsorption of MP was slightly weaker, and the adsorption of phenol was the least efficient.

Keywords: phenols; adsorption; carbon black; activated coke; activated tire pyrolysis char

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1. Introduction

Phenol and its derivatives (i.e., halogenated and alkyl-phenols) are widely used in many industries. They are used in the production of plastics and epoxy resins, various types of dyes, pharmaceuticals, and pesticides in the automotive, pharmaceutical, and construction industries among others. Unfortunately, such a wide and widespread use of phenolic compounds has its negative consequences; these compounds are easily released into the environment with wastewater and are now serious contaminants of ground and surface water. The presence of phenolic compounds in water is highly undesirable. Phenolic compounds have a very strong and unpleasant odor, and even traces of them in water degrade their organoleptic properties. However, a greater problem is their relatively high toxicity. Phenol and its derivatives, such as chlorophenol or cresol, are suspected to be carcinogenic, mutagenic, or teratogenic [1–3].

For this reason, the presence of phenol and its various derivatives in water and the possibilities of removing them from water are now among the increasingly important problems requiring immediate action. In recent years, a large number of methods have been proposed for the removal of phenols from aqueous solutions [2,4]. These methods are categorized as biological, chemical, and physical, and differ in complexity, overall cost, and efficiency. Adsorption is perhaps the most popular of the available water treatment methods as it is relatively low-cost, easy to operate, and highly efficient, and produces no additional pollutants (intermediates) [3–6]. Adsorption is a very universal water treatment technique and can be successfully used to remove both soluble and insoluble organic

contaminants with an efficiency of approximately 99.9% as reported by Garba et al. [3]. Apart from this, all other methods have relatively high costs and lower removal efficiencies combined with more complex designs than adsorption [3]. For example, biological methods are sensitive to microorganisms and environmental factors, time-consuming, and difficult to control, while chemical methods (e.g., oxidation) require an excess of reagents and produce a low-quality mixture that may contain intermediates that are sometimes more toxic than the compound being removed [3]. The efficiency of the adsorption process is closely related to the physicochemical properties of the adsorbent that is used. Therefore, a priority task that will affect the overall process efficiency is the selection of an appropriate adsorbent for the removal of specific pollutants. Selecting an optimal adsorbent, that is, one with the highest adsorption capacity at the lowest cost, will maximize the efficiency of the water treatment process. The search for new adsorbents is very important and is being studied by many research centers. Various conventional and unconventional materials from different sources (e.g., organic and inorganic materials, agricultural and industrial wastes) have been used as adsorbents [3]. The largest group of adsorbents for the removal of organic compounds, including phenolic compounds, are carbon materials [3,5].

Among the porous carbon materials, activated carbons play an important role. They are used especially as effective adsorbents both for the liquid and gaseous phases [7]. They are produced and used on a large scale. Their specific surface area usually varies between 900–1200 m^2/g. This large specific surface area generally results in a high adsorption capacity. In the case of porous carbon materials with a much lower (e.g., 4 or 5 times) specific surface area, carbon blacks [8] or activated cokes [9] can be mentioned as examples. Although their potential as adsorbents is already partially confirmed, it still requires further research.

Carbon black (CB) is a commercially available solid carbon consisting primarily of pure carbon, typically 98% by weight, with minor additions of oxygen, hydrogen, and nitrogen. It is produced by the tightly controlled thermal decomposition of carbonaceous feedstocks in oxygen-deficient (partial combustion) or oxygen-free (pyrolysis) atmospheres [8]. Carbon blacks are most commonly used in tires and other rubberized components as reinforcing additives and to increase conductivity, viscosity, or UV resistance. They are also widely used in the polymer, coating, and printing industries and in various other specialty applications such as fuel cells, batteries, supercapacitors, photocatalysts, and CO_2 storage processes [8,10].

Activated coke (AC) is a granulated carbonaceous material characterized by high strength, high mechanical strength, and a relatively low specific surface area (150–300 m^2/g). It is widely used as a catalyst and catalyst support and also as an adsorbent, mainly for the purification of gases [9,11,12]. The use of activated coke for flue gas treatment on an industrial scale is a dry and highly efficient process that removes most of the pollutants contained in the flue gas such as hydrogen chloride, hydrogen fluoride, SO_2, heavy metals, and various organic compounds. The AKP-5 activated coke is produced by Gryfskand (Poland) in the form of cylindrical granules approximately 5 mm in diameter and 8 mm long, made from a special type of coal fines and an aqueous solution of a starch binder, which forms granules after drying at 350 °C. The final product (activated coke) is produced by means of the carbonization of the granulate at 900 °C and activation with steam at 800 °C [9].

The purpose of this paper is the evaluation of the effectiveness and suitability of each of three carbonaceous materials—carbon black, activated coke, and activated tire pyrolysis char—as potential alternative adsorbents for the removal of phenolic compounds from water. Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysate (AP) were used as adsorbents in our study. These are therefore unique carbonaceous materials of different origins but with similar specific surface areas (S_{BET}). Although materials such as carbon black and activated coke are well known, widely available, and widely used, they are rarely used as liquid-phase adsorbents. Their adsorption capacity and therefore adsorption potential is not well understood and requires further research. To

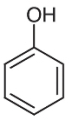
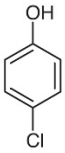
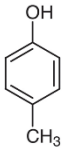
our knowledge, such a comparative study has not yet been described in the literature. The model organic contaminants selected were phenol (Ph), 4-chlorophenol (CP), and 4-cresol (MP). The adsorption kinetics, as well as adsorption under equilibrium conditions, were studied. The effects of pH and ionic strength of the solution on the effectiveness of the adsorption process were also studied.

2. Materials and Methods

2.1. Reagents and Adsorbents

The phenol (99%, Ph) and 4-chlorophenol (≥99%, CP) were obtained from Sigma-Aldrich (St. Louis, MO, USA), while 4-cresol (99%, 4-methylphenol, MP) was purchased from POCh (Gliwice, Poland). The main properties of these compounds, as well as their structural formulas, are given in Table 1. Chempur (Piekary Slaskie, Poland) supplied all other analytical-grade chemicals and reagents.

Table 1. Physicochemical properties of the phenolic compounds [5,6].

Parameter	Phenol (Ph)	4-Chlorophenol (CP)	4-Cresol (MP)
CAS number	108-95-2	106-48-9	106-44-5
Chemical structure			
Molecular weight	94.11	128.56	108.14
Solubility in water * (g/L)	93	27	23
pK_a	10.0	9.4	10.2
Log P	1.46	2.39	1.94

* at 25 °C.

The Vulcan XC72 carbon black (CB) from Cabot Corporation (Boston, MA, USA), AKP-5 activated coke (AC) from Gryfskand (Hajnówka, Poland), and activated tire pyrolysis char (AP) prepared by physical activation with CO_2 for 150 min at 1100 °C as described elsewhere [13] were used as adsorbents. The textural properties of the carbonaceous materials, including their specific surface areas (S_{BET}) and pore size volumes, were determined via the analysis of nitrogen adsorption–desorption at 77.4 K using an ASAP 2020 adsorption analyzer supplied by Micromeritics Instrument Corporation (Norcross, GA, USA). The samples were previously degassed at 300 °C for 10 h at a pressure of 10^{-6} Pa.

2.2. Batch Adsorption Experiments

All adsorption tests were carried out in 100 mL Erlenmeyer flasks into which 20 mL of adsorbate solutions (phenol, 4-chlorophenol, or 4-cresol) of appropriate concentration were introduced, followed by the addition of 0.02 g of adsorbent (carbon black, activated coke, or activated tire pyrolysis char). Samples prepared in this way were agitated at 23 °C at a constant speed of 200 rpm. After reaching equilibrium (or after a suitable time, in the case of kinetic studies), the solutions were filtered through filter paper, and the resulting filtrates were analyzed for phenolic compounds. The following relationships were used to calculate the amounts of Ph, CP, and MP adsorbed at equilibrium (q_e) and after an appropriate time t (q_t):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 is the initial concentration of phenols [mmol/L], C_e is the equilibrium concentration of phenols after adsorption [mmol/L], C_t is the concentration of phenols after time t [mmol/L], V is the volume of solution [L], and m is the mass of carbonaceous materials [g].

Studies on the effects of pH on adsorption were carried out for solutions of phenols with initial concentrations of 0.5 mmol/L and pH values in the range of 2 to 11. Solutions of the appropriate pH were prepared by the addition of small amounts of 0.1 mol/L of NaOH and/or HCl, and the pH of each solution was controlled using a pH meter. After adjusting the solutions to the desired pH, 0.02 g of each adsorbent was added to each solution and agitated for 8 h.

To study the effect of solution ionic strength on adsorption, solutions of phenols with an initial concentration of 0.5 mmol/L were prepared in Erlenmeyer flasks, to which appropriate amounts of sodium sulfate were weighed to obtain solutions with Na_2SO_4 concentrations of 0, 0.01, 0.05, and 0.1 mol/L. Then, 0.02 g of adsorbent was added to each solution, and the whole solution was agitated for 8 h.

The adsorption kinetics of Ph, CP, and MP were studied for their initial concentrations of 0.5 mmol/L (the mass of the adsorbent was 0.02 g and the volume of the solution was 0.02 L). The flasks were then shaken at a constant speed, and after a suitable time (10, 20, 30, 45, 60, 90, 120, 180, and 240 min), the solutions were separated from the adsorbents via filtration and analyzed for residual phenol content in the solutions.

Adsorption isotherms were obtained using a similar procedure. Solutions with different initial concentrations of Ph, CP, or MP (0.25–1.0 mmol/L) were agitated for 8 h. The concentrations of each adsorbate in the solutions were determined via UV-Vis spectrophotometry (Carry 3E UV-Vis spectrophotometer, Palo Alto, CA, USA). Absorbance was measured at the analytical wavelength λ corresponding to the absorption maximum of each compound: 269 nm for Ph, 274 nm for CP, and 270 nm for MP. Calibration curves generated in the concentration range from 0.05 to 1.0 mmol/L were linear ($R^2 \geq 0.997$) and were described by the following equations: $y = 1.342\ x + 0.079$ for Ph, $y = 1.332\ x + 0.142$ for CP, and $y = 1.530\ x + 0.150$ for MP (where y is the absorbance and x is the concentration in mmol/L).

3. Results and Discussion

3.1. Characterization of the Carbonaceous Materials

Figure 1 shows the adsorption–desorption isotherms of N_2 at 77.4 K on the Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysis char (AP). The collected adsorption data allowed the calculation of the structural parameters. The specific surface areas (S_{BET}, m^2/g) were calculated according to the Brunauer–Emmett–Teller method at relative pressure $P/P_0 \approx 0.05$–0.2 and were found to be 235 m^2/g for CB, 265 m^2/g for AC, and 255 m^2/g for AP. Total pore volume (V_t, cm^3/g) was determined from the adsorption isotherm at relative pressure $P/P_0 \approx 0.95$. The micropore volume (V_{mi}, cm^3/g) and mesopore volume (V_{me}, cm^3/g) were also determined using the Barrett–Joyner–Halenda and t-plot methods. The obtained results are shown in Table 2.

Table 2. The values of parameters characterizing the porous structures of Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysis char (AP).

Adsorbent	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)
CB	235	0.289	0.111	0.178
AC	265	0.184	0.162	0.022
AP	255	0.284	0.117	0.167

As can be seen, despite the similar BET-specific surface areas, the porous structures of these three carbon materials differ. While a relatively high similarity can be observed between the porous structures of CB and AP, the porous structure of AC is very different. Micropores represent 38.4% of the total pore volume for CB and 41.2% for AP. AC is a highly

microporous material, with micropores accounting for over 88% of the total pore volume. These differences in pore size distribution are visible in Figure 1, where the different shapes of the nitrogen isotherm for AC can be seen compared to the isotherms obtained for CB and AP. The last two curves (CB and AP) can be classified as Type II adsorption isotherms according to the IUPAC classification [7,14]. In contrast, nitrogen adsorption–desorption isotherm for activated coke can be classified as Type I.

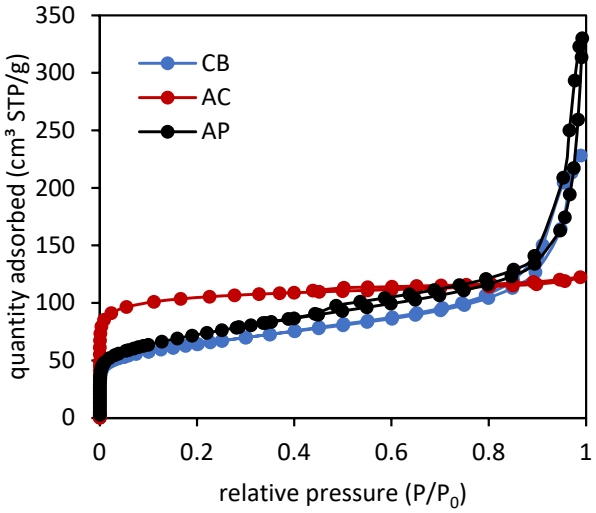


Figure 1. Nitrogen adsorption–desorption isotherms at 77.4 K for Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysis char (AP).

3.2. Adsorption Studies

3.2.1. Effect of Solution pH

The pH of a solution is a factor that affects the adsorption capacity of the entire system. The adsorbent–adsorbate interactions are strongly influenced by the pH of the solution because the solution pH affects both the degrees of dissociation and ionization of the adsorbate molecules as well as the charge that will be present on the surface of the adsorbent. In this study, the adsorption of phenolic compounds on all three adsorbents was investigated from solutions with different initial pHs ranging from 2 to 11, and the results are shown in Figure 2.

As can be seen, the adsorption is most effective in an acidic environment and remains more or less constant in the pH range from 2 to about 6–7. In a slightly alkaline environment, a slow decrease in the adsorption efficiency can be observed, and the lowest adsorption efficiency was found in the most alkaline environment at a pH of 11. Figure 2 shows that all three adsorbates behave very similarly, which is to be expected since they are weak acids with similar physical properties including pK_a values (Table 1). The acid dissociation constant on the logarithmic scale indicates the form in which the molecule of the adsorbate will appear in the solution. Thus, in a solution with a pH below pK_a, the phenol molecule (as well as CP and MP) will exist in a non-dissociated, protonated form, whereas in a solution with a pH > pK_a, the adsorbate will rise in a dissociated form as a negatively charged phenolate ion. As shown in Table 1, the pK_a values for Ph, CP, and MP are 10.0, 9.4, and 10.2, respectively.

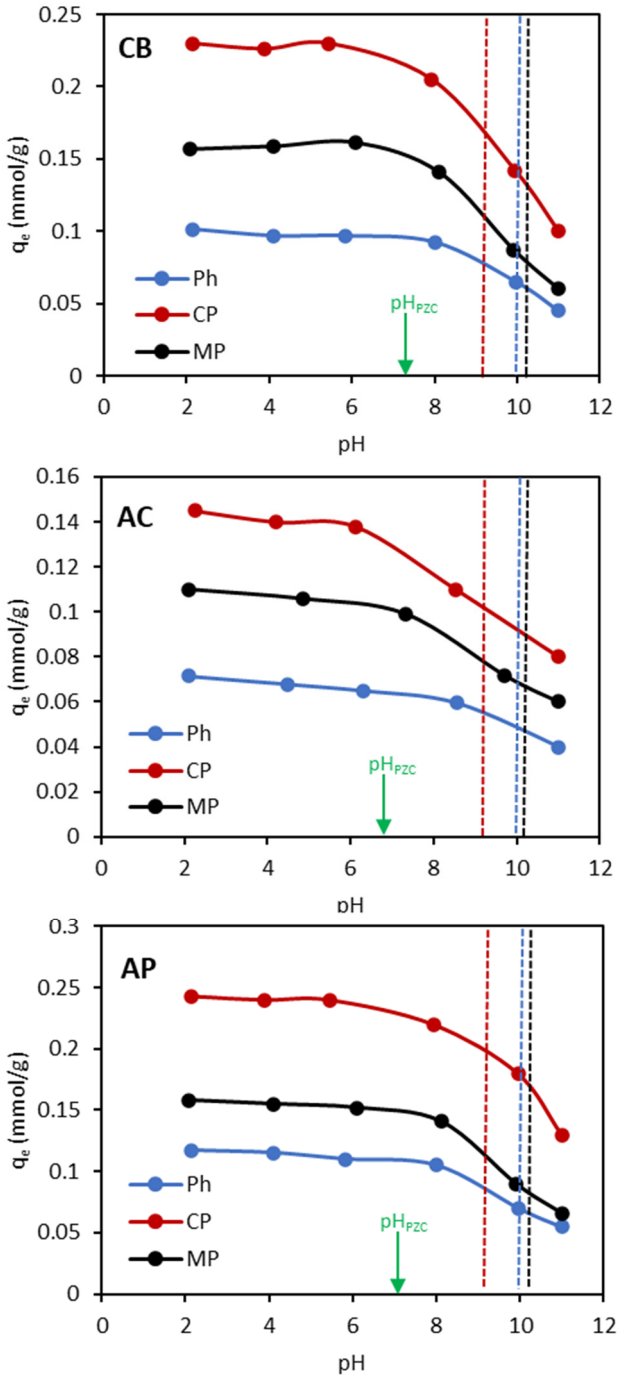


Figure 2. Effects of pH on phenol (Ph), 4-chlorophenol (CP), and 4-cresol (MP) removal on the carbonaceous materials. The dashed horizontal lines indicate the pK_a values for the individual phenolic compounds.

Figure 2 demonstrates similar behaviors not only for all three adsorbates but also for the adsorbents. As mentioned above, the pH of a solution affects the charge on the surface of the adsorbent. This phenomenon is well characterized and described by the point of zero charge (pH_{PZC}), which should be understood as the pH value at which the surface charge is zero. The values of pH_{PZC} for all three carbon materials were experimentally determined according to the method described elsewhere [15]. It was found that the pH_{PZC} for CB, AC, and AP are 7.1, 6.8, and 7.0, respectively. When the adsorbent is in a solution with a pH lower than pH_{PZC}, its surface has a positive charge, and when it is in a solution with a pH

higher than pH_{PZC}, its surface has a negative charge. The obtained values of pH_{PZC} for CB, AC, and AP are very similar and are about 7. This means that the carbon materials under consideration will have positive charges on their surfaces in an acidic environment, while in an alkaline environment (at pH > pH_{PZC}), a negative charge will accumulate on their surfaces. The correlations shown in Figure 2 indicate that adsorption occurs preferentially in an acidic environment, suggesting that the interaction of non-dissociated (protonated) adsorbate molecules with the positively charged surface of each adsorbent is most favorable. The least efficient adsorption takes place in an environment of pH 11, when the phenol molecules are present in the form of phenolate anions and the surface of the carbon materials is negatively charged. Under these conditions, there is repulsion between the negatively charged adsorbate ions and the negatively charged surface of the adsorbent. As a result, the adsorption efficiency is reduced. The adsorption of Ph, CP, and MP on these carbon materials is thus determined by the electrostatic interactions (attractive or repulsive) between the adsorbate and the adsorbent. The results obtained here are generally similar to those reported by other authors [13,15–18]. Similar behavior has been reported for the adsorption of phenol and its chlorinated derivatives on activated tire pyrolysis chars [13], activated carbons from bituminous coal [16], CMK-1 mesoporous carbon material [17], carbonylated hypercrosslinked polymeric adsorbent [18], and pristine lignite [15].

3.2.2. Effect of Ionic Strength

The ionic strength of the solution can, among other things, affect the hydrophobic adsorbent–adsorbate interactions and thus the efficiency of the overall adsorption process. From the experimental data shown in Figure 3, it can be concluded that the presence of inorganic salts has no major effect on the adsorption capacities of the carbonaceous materials.

The observed differences in adsorption are small (the coefficient of variation does not exceed 7%) and appear to be due to measurement errors rather than actual changes in adsorption. Thus, one may conclude that the adsorption of Ph, CP, and MP on all three adsorbents is independent of the ionic strength of the solution in question. Our previous results on the adsorption of 4-chlorophenol [19] showed that the inorganic salts increased the adsorption capacity of the activated carbon and that the adsorption efficiency of the CP increased with the increase in the ionic strength of the solution. On the other hand, it was also observed that increasing the ionic strength of the solution did not affect the adsorption capacity of the carbon nanotubes [19]. Both the adsorption of Ph, CP, and 2,4-dichlorophenol on the activated tire pyrolysis chars [13], as well as the adsorption of phenol on the carbonylated polymeric adsorbent HJ-1 [18], increased slightly with the increasing ionic strength of the solution. The authors explain that this phenomenon is due to a "salting-out" effect, which reduces phenol solubility and thus increases adsorption [13,18,19]. However, in several studies, no effect of ionic strength on the adsorption of phenols was observed. This was the case, for example, in the adsorption of phenolic compounds on lignite [15] or of 4-chlorophenol on Calgon F-400 activated carbon [20].

3.2.3. Adsorption Kinetics

The adsorbed amounts of phenol, 4-chlorophenol, and 4-cresol (q_t) as functions of time are presented in Figure 4. The figure shows that the adsorption equilibrium of phenolic compounds was reached after about 2 h for CB and AP and after about 3 h for activated coke.

Two of the most commonly used kinetic models were used to describe the adsorption kinetics: the pseudo-first-order (PFO, Equation (3)) and pseudo-second-order (PSO, Equation (4)) [21,22] models, shown below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_1 and k_2 are the PFO (1/min) and the PSO (g/mmol·min) rate constants, respectively.

The values of the rate constants k_1 and k_2, the experimental adsorption capacities ($q_{e\,EXP}$), and the adsorption quantities obtained for both models (q_e^1 and q_e^2), as well as the correlation coefficients R^2, were calculated using linear regression. The data are summarized in Table 3.

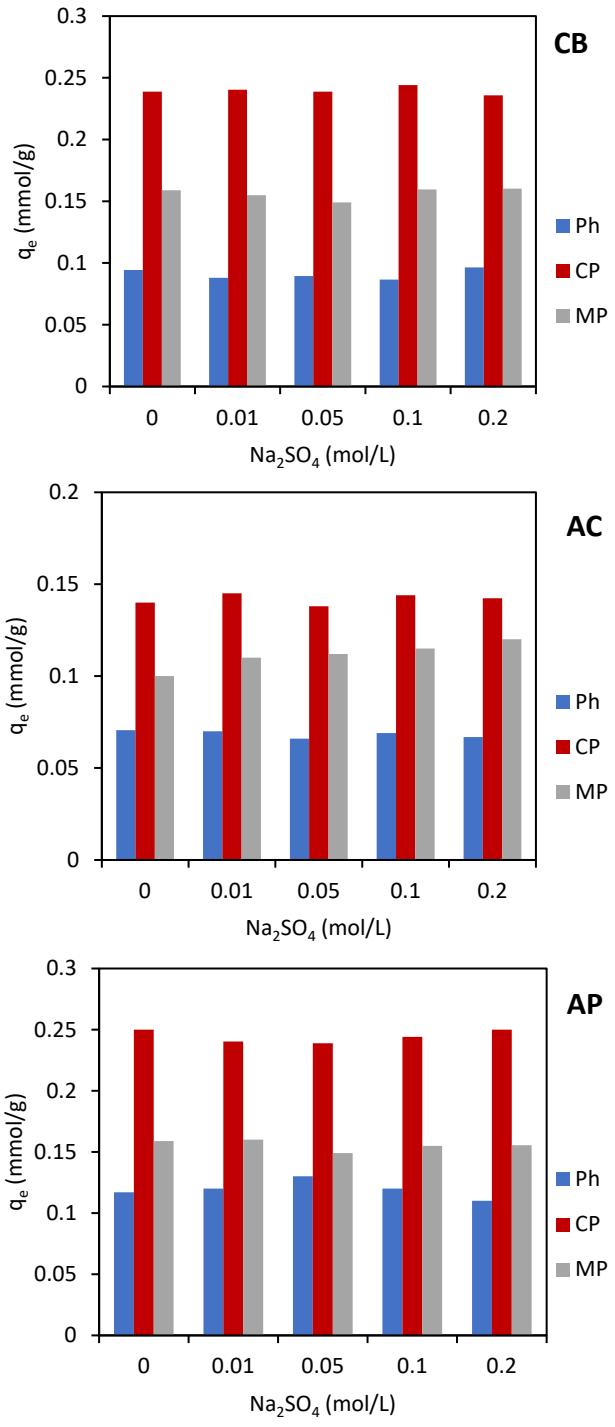


Figure 3. Influence of the ionic strength of the solution on the adsorption of phenolic compounds on carbon materials.

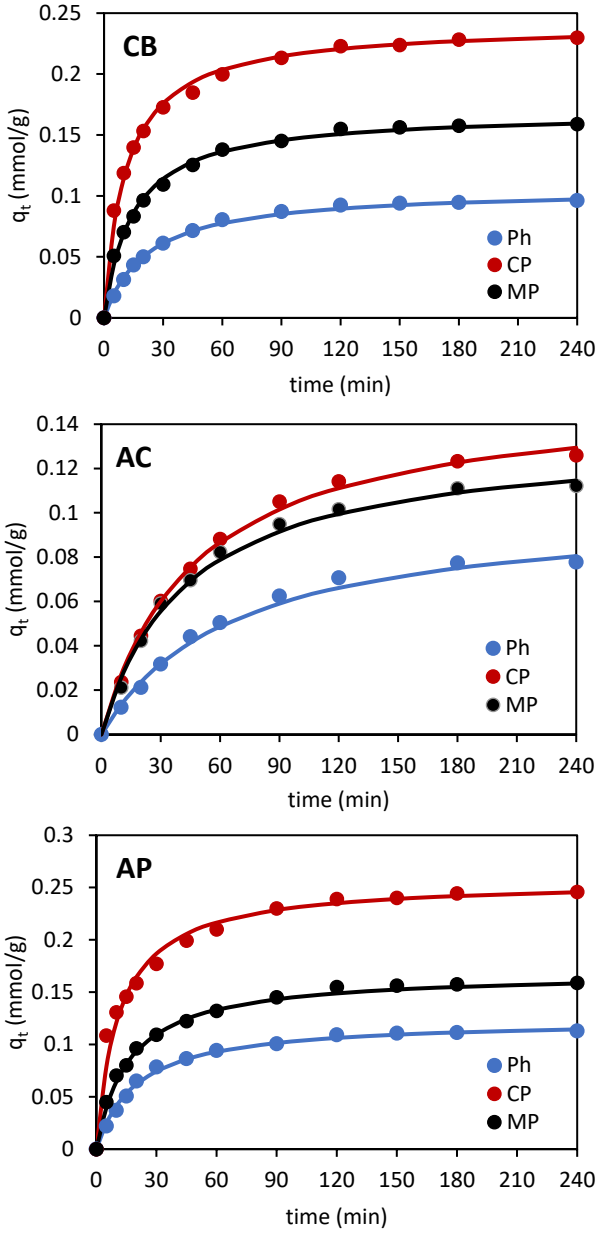


Figure 4. Kinetic curves for the adsorption of phenolic compounds on CB, AC, and AP (line: fitting of the PSO kinetic model).

The fitting results (Table 3) demonstrate that the adsorption values of all phenols on the tested carbonaceous materials obey the PSO equation ($R^2 \geq 0.997$). The R^2 coefficients obtained for the PFO model are low ($\leq$0.990), which indicates that the model is not in agreement with the experimental data. This is also confirmed by the calculated q_e values obtained for the PSO model, which are closer to the experimental q_e values ($q_{e\,EXP}$) than those calculated for the PFO model (Figure 5).

The obtained values of the k_1 rate constants increase in the order: Ph < CP < MP. This suggests that the adsorption of phenol is the slowest on all three carbon materials and that the adsorption of 4-cresol is the fastest. However, these observations are not supported by the results obtained for the PSO model, which is a kinetic model that, as mentioned earlier, better describes the experimental data. The values of the rate constants k_2, which should be considered more reliable, increase in the order CP < MP < Ph for CB and AP and the order CP < Ph < MP for activated coke. Thus, phenol is adsorbed the fastest on CB and AP, and 4-chlorophenol is adsorbed the slowest, while CP is ad-

sorbed the fastest on AC, and MP is adsorbed the slowest. These observations suggest that there is no clear relationship between the chemical structures of adsorbates (e.g., type of aromatic ring substituent) and their adsorption rates on carbon adsorbents. This is in line with the work of other authors, who have found different and sometimes opposite results. The faster adsorption of 4-chlorophenol than Ph was reported on thermally treated Norit R3-ex activated carbon [23], lignite [15], activated tire pyrolysis chars [13], or Fe-, N- and S-multi-doped carbon xerogels [24]. On the other hand, on the commercial activated carbon from Sigma-Aldrich [25] and the unmodified carbon nanotubes [25], the order was reversed (Ph > CP). Phenol was adsorbed faster than 4-cresol on carbonylated polymer adsorbent [18], while on commercial granular activated carbon from Sinopharm Chemical Reagent Co. [26], the adsorption rate increased in the following order: phenol < hydroquinone < 3-cresol < resorcinol < catechol < 2-cresol < 4-cresol.

Table 3. Phenolic compound adsorption kinetic parameters of Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysis char (AP).

Adsorbent	Kinetic Parameter	Adsorbate		
		Ph	CP	MP
CB	$q_{e\,EXP}$ (mmol/g)	0.096	0.230	0.159
	PFO			
	k_1 (1/min)	0.0235	0.0244	0.0258
	q_e^1 (mmol/g)	0.077	0.146	0.116
	R^2	0.989	0.976	0.971
	PSO			
	k_2 (g/mmol·min)	0.428	0.374	0.410
	q_e^2 (mmol/g)	0.106	0.241	0.169
	R^2	0.999	0.999	0.998
AC	$q_{e\,EXP}$ (mmol/g)	0.078	0.126	0.113
	PFO			
	k_1 (1/min)	0.0196	0.0209	0.0242
	q_e^1 (mmol/g)	0.103	0.155	0.135
	R^2	0.990	0.989	0.974
	PSO			
	k_2 (g/mmol·min)	0.145	0.136	0.173
	q_e^2 (mmol/g)	0.081	0.128	0.122
	R^2	0.998	0.997	0.998
AP	$q_{e\,EXP}$ (mmol/g)	0.114	0.243	0.158
	PFO			
	k_1 (1/min)	0.0244	0.0251	0.0260
	q_e^1 (mmol/g)	0.088	0.161	0.121
	R^2	0.983	0.980	0.981
	PSO			
	k_2 (g/mmol·min)	0.403	0.346	0.365
	q_e^2 (mmol/g)	0.124	0.257	0.169
	R^2	0.998	0.999	0.999

A clearer conclusion can be drawn if the individual adsorbents are compared with each other. Both the PFO and PSO parameters (k_1 and k_2) show, in agreement, that all of the phenolic compounds were adsorbed fastest on carbon black, slightly slower on activated tire pyrolysates, and clearly slowest on activated coke (AC < AP < CB). This order can be explained by the porous structures of the adsorbents (Table 2). It is well known that adsorption takes place mainly in the micropores and partly in the mesopores, which act

mainly as transport routes for adsorbate molecules to enter the micropores. In general, the larger the mesopore volume is, the faster the adsorption will take place. The V_{me} values obtained for CB, AP, and AC were 0.178 cm^3/g, 0.163 cm^3/g, and 0.022 cm^3/g, respectively. Thus, it can be concluded that the adsorption rates of Ph, CP, and MP on carbon materials are correlated with their porous structures and increase with increases in mesopore volume.

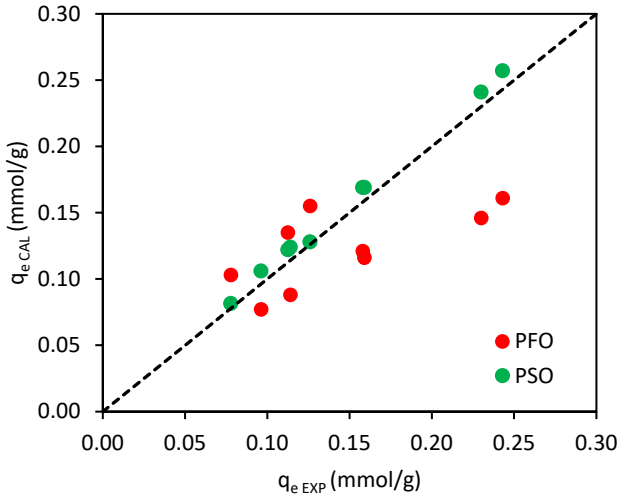


Figure 5. Correlation between the amounts of phenols adsorbed: $q_{e\,EXP}$ (experimental data) and $q_{e\,CAL}$ (calculated using the pseudo-first-order (red) and the pseudo-second-order (green) kinetic models).

The adsorption process involves several steps, including the following: (I)—the migration of the adsorbate from the solution to the adsorbent surface; (II)— the diffusion of the adsorbate through the boundary layer; (III)—intraparticle diffusion; (IV)— the adsorbate binding to the internal adsorbent surface. The rate of adsorption is controlled by its slowest step and, therefore, either by interparticle diffusion or film diffusion, or both at the same time. The diffusion models proposed by Weber–Morris and Boyd [21,22] can help understand the adsorption mechanism and identify the stage that determines the rate of the overall process. The Weber–Morris model, often referred to as the intraparticle diffusion model, is described by the following equation:

$$q_t = k_i t^{0.5} + C_i \tag{5}$$

where k_i is the intraparticle diffusion rate constant ($mmol/g{\cdot}min^{-0.5}$) and C_i is the thickness of the boundary layer.

The Boyd model can be expressed by two equations. The application of these equations depends on the value of the q_t/q_e ratio. Thus, when q_t/q_e is less than 0.85, Equation (6) applies, while when q_t/q_e is greater than 0.85, Equation (7) is appropriate.

$$B_T = \pi\left(1 - \sqrt{1 - \frac{\pi}{3}\frac{q_t}{q_e}}\right)^2 \tag{6}$$

$$B_T = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{7}$$

Here, B_T is a function of $\frac{q_t}{q_e}$.

The Weber–Morris and Boyd models are shown in Figure 6 as plots of q_t vs. $t^{0.5}$ (left column) and as plots of B_T vs. t (right column), respectively.

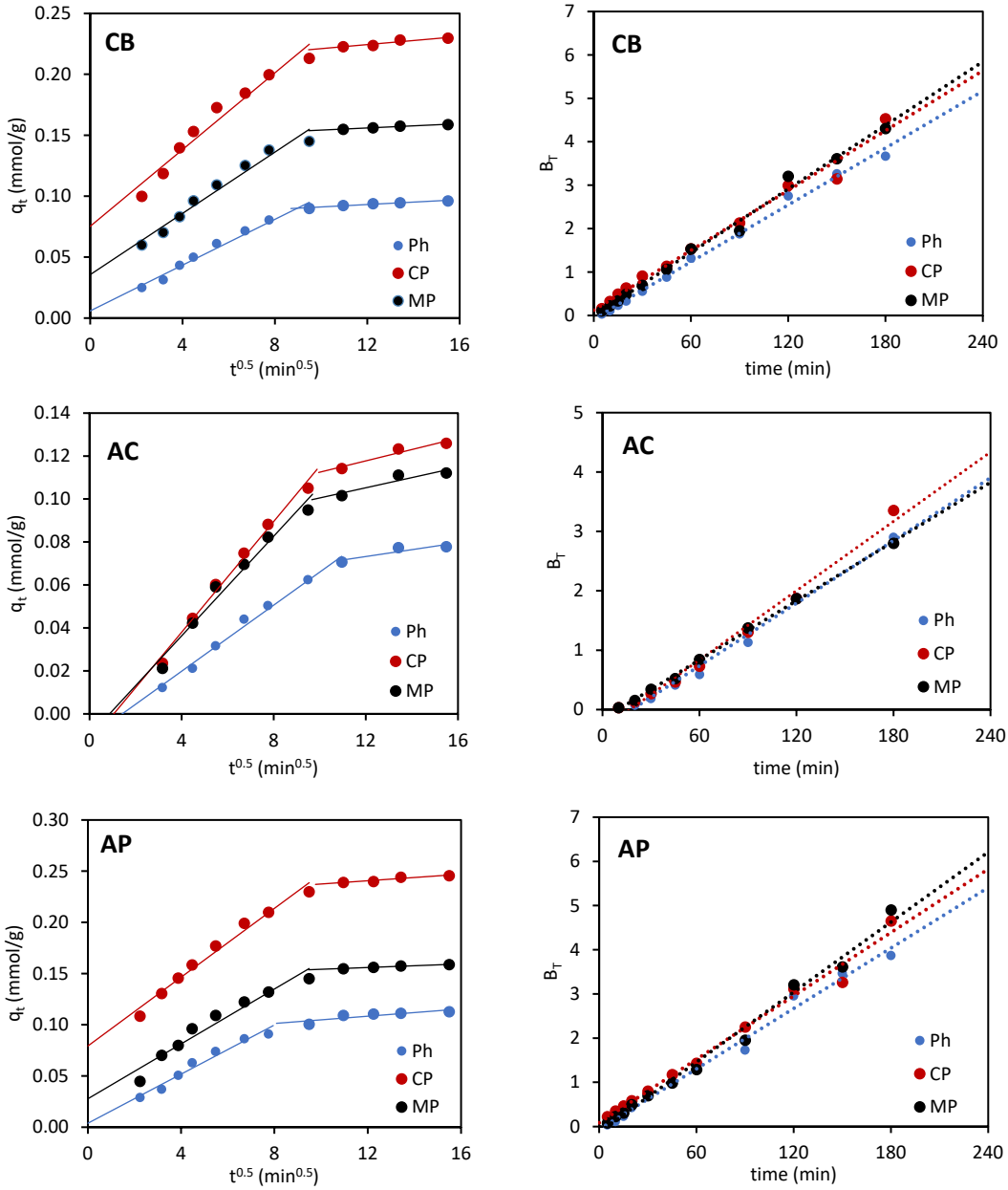


Figure 6. The Weber–Morris model (**left column**) and the plots of the Boyd model (**right column**) for the adsorption of Ph, CP, and MP on the carbonaceous materials.

The curves of the Weber–Morris model are not passing through the origin and are not linear over the entire range, indicating that there are multiple mechanisms controlling the adsorption process and that interparticle diffusion does not play a primary role. This is supported by the results obtained for the Boyd model, showing that the adsorption processes are controlled by film diffusion, as the curves are linear and not passing through the origin (the intercept is different from zero in each case). The results from both models indicate that the adsorptions of Ph, CP, and MP on all three carbon materials are complex processes affected by both external and intraparticle diffusion and that the most important step controlling the rate of the whole adsorption process is film diffusion.

3.2.4. Adsorption Isotherms

Adsorption isotherms of phenol, 4-chlorophenol, and 4-cresol on carbon materials were performed in the concentration range of 0.25 to 1.0 mmol/L and are shown in Figure 7.

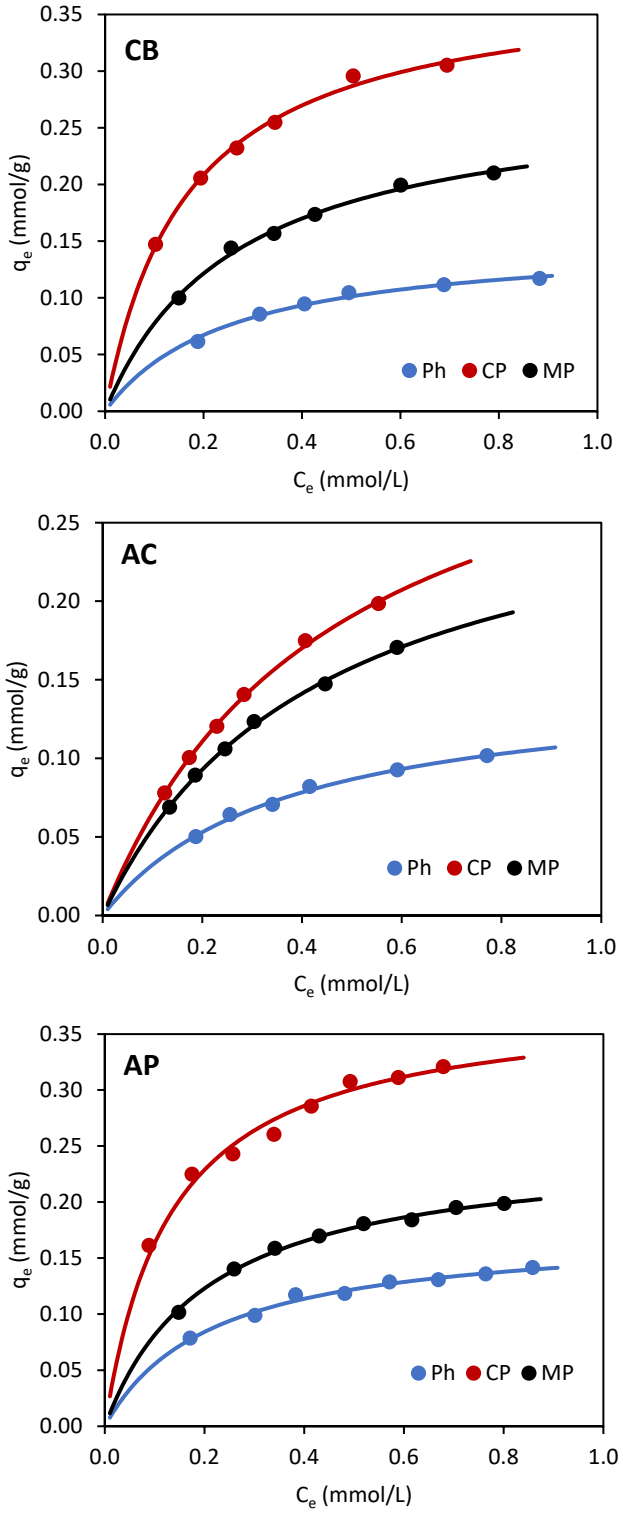


Figure 7. Adsorption isotherms of Ph, CP, and MP on the carbonaceous materials (line: fitting of the Langmuir model).

For the description of the experimental data, the Langmuir and Freundlich isotherm models [27,28] were applied.

The theoretical model of the Langmuir isotherm assumes that the adsorbate molecules interact poorly or not at all with the adsorption sites and that a monolayer of molecules is

formed on the homogeneous surface of the adsorbent [27,28]. The Langmuir equation can be written in general terms as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (8)$$

which, when converted to linear form, has the form:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \quad (9)$$

where q_m is the maximum adsorption capacity (mmol/g), C_e is the equilibrium adsorbate concentration [mmol/L], and b is the Langmuir constant [L/mmol].

The Freundlich model is based on the assumption that adsorbate molecules interact with each other and accumulate on the heterogeneous adsorbent surface in the form of a multilayer [27,28]. The Freundlich equation is expressed by the general formula below:

$$q_e = K_F \, C_e^{1/n} \quad (10)$$

which, when rearranged into a linear form, becomes as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (11)$$

where n and K_F ((mmol/g)(L/mmol)$^{1/n}$) are the Freundlich constants.

The slopes and intercepts of the linear plots of C_e/q_e vs. C_e and ln q_e vs. ln C_e were used to determine the Langmuir and Freundlich adsorption isotherm parameters, respectively. The results are listed in Table 4.

Table 4. Parameters of the Langmuir and Freundlich isotherm models for the adsorption of Ph, CP, and MP onto Vulcan XC72 carbon black (CB), AKP-5 activated coke (AC), and activated tire pyrolysis char (AP).

Adsorbent	Isotherm Parameter	Adsorbate		
		Ph	CP	MP
CB	Langmuir			
	q_m (mmol/g)	0.153	0.332	0.233
	b (L/mmol)	3.922	6.012	3.764
	R^2	0.995	0.998	0.997
	Freundlich			
	K_F ((mmol/g)(L/mmol)$^{1/n}$)	0.131	0.345	0.247
	n	2.431	2.574	2.255
	R^2	0.948	0.971	0.965
AC	Langmuir			
	q_m (mmol/g)	0.130	0.294	0.201
	b (L/mmol)	2.735	2.162	2.298
	R^2	0.995	0.997	0.997
	Freundlich			
	K_F ((mmol/g)(L/mmol)$^{1/n}$)	0.119	0.302	0212
	n	2.050	1.576	1.659
	R^2	0.975	0.981	0.983
AP	Langmuir			
	q_m (mmol/g)	0.175	0.381	0.251
	b (L/mmol)	4.641	7.521	4.808
	R^2	0.996	0.995	0.998
	Freundlich			
	K_F ((mmol/g)(L/mmol)$^{1/n}$)	0.153	0.378	0.267
	n	2.802	3.010	2.597
	R^2	0.965	0.976	0.959

A comparison of the correlation coefficients calculated for both models shows that higher R^2 values were obtained for the Langmuir equation ($\geq$0.995) than for the Freundlich isotherm ($\leq$0.983). Thus, it is the Langmuir model that better describes the experimental data, suggesting that the adsorption of Ph, MP, and CP on all of the tested materials may involve the homogeneous nature of the adsorbents' surfaces as well as the monolayer adsorption without any interactions between the molecules of each adsorbate.

Comparing not only the adsorption capacities obtained from the Langmuir equation (q_m) but also the K_F constants of the Freundlich equation, it can be seen that phenol was the least adsorbed on all three adsorbents, followed by 4-cresol and the best 4-chlorophenol (Ph < MP < CP). For example, the maximum adsorption capacities of CB for Ph, MP, and CP were 0.153, 0.233, and 0.332 mmol/g, respectively. The adsorption of phenolic compounds on carbonaceous materials is the result of various types of interactions, including hydrogen bonding and π-π interactions, as well as hydrophobic interactions between adsorbate molecules and adsorbent surfaces [5,6]. These interactions are most intense for CP, which was adsorbed most efficiently, and weakest for Ph, which was adsorbed least efficiently. Such differences in adsorption are due to the physicochemical properties of these compounds, including their particle sizes and masses or polarities. Many papers [5,6,13,15,23,24,27,29,30] have reported that the adsorption of chlorophenols increases with a corresponding increase in molecular weight and hydrophobicity and a decrease in solubility and pK_a. The presence of chlorine atoms in the benzene ring modifies the physical, chemical, and energetic properties of the molecule, increasing or decreasing the affinity of the molecule for the surface of the adsorbent. Substituting chlorine atoms in the benzene ring reduces its electron density, which reduces its solubility in water by increasing the hydrophobicity of the molecule. The methyl group has a weaker effect on attracting electrons from the ring than the strongly electronegative chlorine atom, and so, the acidic character of cresols is weaker than that of chlorophenols but stronger than that of phenol. In general, compounds that are poorly soluble in water have greater affinities (better adsorption) for the hydrophobic surface of the adsorbent. The hydrophobicity of the compounds is characterized by the octanol–water partition coefficient (Log P), a higher value of which indicates a higher affinity of an adsorbate to the surface of the corresponding adsorbent [6]. Therefore, the obtained differences in adsorption efficiency (Ph < MP < CP) correlate with an increase in the molecular weight of the adsorbents and, in particular, with the increasing Log P values of 1.46 for Ph, 1.94 for MP, and 2.39 for CP, respectively. This is consistent with the results obtained by other researchers. A similar trend, Ph < MP < CP, has also been reported by other authors for the adsorption of these compounds on Charsob CP-1300 activated carbon fibers [31], as well as on Amberlite XAD-4 polymeric adsorbents and its modified derivatives [32–34]. The same adsorption sequence was reported by Mourão et al. [35] for activated carbons prepared from cork by chemical activation with phosphoric acid. On the other hand, in the same work [35], it was found that on activated carbons prepared by physical activation with carbon dioxide, the adsorption capacity increased in the order Ph < CP < MP, while on steam-activated adsorbents, the adsorption increased in the following order: CP < MP < Ph. The adsorption of 4-chlorophenol has been reported to be stronger than that of phenol by many authors [5,6,13,15,23,24,27,29,30]. Strachowski and Bystrzejewski [25] reported the better adsorption of CP than Ph on multi-walled carbon nanotubes and carbon-encapsulated iron nanoparticles but a different relationship (better adsorption of Ph than CP) on Sigma-Aldrich commercial activated carbon. The better adsorption of 4-cresol than Ph was observed on activated carbons from bituminous coal [16] or a carbonylated hypercrosslinked polymeric adsorbent [18], among others. However, there are also some reports of better adsorption of Ph compared to MP. Such a phenomenon was observed on mesoporous carbon materials (CMK-1, CMK-1/PANI) [17] as well as commercial activated carbon from Sinopharm Chemical Reagent Co. [26].

A comparison of all three carbon materials used in the study clearly shows that activated tire pyrolysis char is the best adsorbent. Ph, MP, and CP adsorbed most efficiently on AP and least efficiently on activated coke (AP < CB < AC). It is well known that the

adsorption capacity of a material is determined by its physicochemical properties including its porous structure and surface chemistry (the presence and type of functional groups on the adsorbent surface). In general, better adsorption properties (higher adsorption capacity) result from a more developed porous structure in an adsorbent. Also important is the size of the pores, which according to IUPAC recommendations, are divided into three categories: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Equally important are their type (closed, blind, through, or cross-linked pores) and shape (cylindrical, conical, slit, or bottle-neck pores) [14]. As adsorption mainly takes place in micropores, their large volume (and thus high BET-specific surface area) is generally associated with a high adsorption capacity in an adsorbent. Thus, based on specific surface area alone, one would expect the best adsorbent to be activated coke (S_{BET} 265 m^2/g), the next best to be activated tire pyrolysis char (S_{BET} = 255 m^2/g), and the adsorbent with the lowest adsorption capacity to be carbon black (S_{BET} = 235 m^2/g). However, the results obtained show the opposite trend. The highest adsorption capacity was observed for activated tire pyrolysis char. Activated coke was found to be the worst adsorbent. This was despite it having the highest BET surface area. As mentioned above, adsorption is influenced not only by the sizes (diameter) of the pores but also by their types and shapes. The lower adsorption capacity of AC than CB and AP could be explained by the unsuitable (mismatched) shape of the AC pores (e.g., ink bottle-neck type pores) for the adsorbate molecules. However, this theory is contradicted by the course of the nitrogen adsorption–desorption isotherm shown in Figure 1. AC is a microporous material, and no hysteresis loop is observed on the isotherm. According to the classification of physisorption isotherms and associated hysteresis loops, the adsorption–desorption isotherm of N_2 for AC should be classified as a Type I isotherm [7,14]. If AC did indeed contain ink-bottle pores, the shape of the nitrogen isotherm would be quite different, with a well-developed hysteresis loop characteristic of Type H2 isotherms [14,36].

All this suggests that the adsorption capacity of activated coke is determined by its surface chemistry rather than its textural properties. The lower adsorption capacity of AC may be due to the presence of, for example, oxygen groups on its surface, which are known to negatively affect the adsorption of phenolic compounds on carbonaceous materials [37,38].

Table 5 compares the adsorption capacities of Ph, CP, and MP on the carbon materials used in this work with those of other adsorbents reported in the literature. Langmuir adsorption capacities (q_m) have been used to compare them. The units have been standardized and converted to mmol/g units when necessary.

Table 5. Comparison of phenol, 4-chlorophenol, and 4-cresol adsorption on various materials.

Adsorbent	S_{BET} (m^2/g)	q_m (mmol/g)			Ref.
		Ph	CP	MP	
Vulcan XC72 carbon black (CB)	235	0.153	0.332	0.233	this study
AKP-5 activated coke (AC)	265	0.130	0.294	0.201	this study
Activated tire pyrolysis char (AP)	255	0.175	0.381	0.251	this study
Raw lignite	0.91	0.038	0.099	-	[15]
Carbon-encapsulated iron nanoparticles	36	0.054	0.069	-	[25]
Activated tire pyrolysis char ATPC-1	70	0.135	0.158	-	[13]
Activated tire pyrolysis char ATPC-2	155	0.167	0.242	-	[13]
Multi-walled carbon nanotubes	156	0.251	0.401	-	[25]
MWCNTs	181	-	0.256	-	[19]
N–3Fe carbon xerogel	220	0.296	0.360	-	[24]
Activated CNTs	254	0.681	0.814	-	[25]
Activated tire pyrolysis char ATPC-3	255	0.295	0.409	-	[13]
Carbon-coated monolith	470	0.700	0.894	-	[30]
Norit R3-ex heated at 1800 °C	554	0.668	1.114	-	[23]

Table 5. *Cont.*

Adsorbent	S_{BET} (m^2/g)	q_m (mmol/g)			Ref.
		Ph	CP	MP	
C2/PA/2 activated carbon (H_3PO_4)	618	0.31	0.64	0.56	[35]
bituminous coal activated carbon AP-5	633	1.466	-	1.591	[16]
C8.750-23.CO_2 activated carbon	647	1.54	1.58	1.82	[35]
C8.750-30.H_2O activated carbon	660	2.11	1.94	2.08	[35]
Hypercrosslinked polymeric adsorbent	727	1.783	-	2.166	[18]
CMK-1/PANI	770	5.060	-	2.202	[17]
bituminous coal activated carbon AP-10	828	1.615	-	2.247	[16]
NS–3Fe carbon xerogel	910	1.208	1.509	-	[24]
C8.750-48.CO_2 activated carbon	957	1.99	2.27	2.88	[35]
Norit R3-ex heated at 1500 °C	967	1.637	2.023	-	[23]
F-400 activated carbon	997	-	1.537	-	[19]
Activated carbon fiber (Charsob CP-1300)	1380	1.653	2.046	1.841	[31]
Norit R3-ex activated carbon	1386	2.408	2.976	-	[23]

4. Conclusions

In this paper, the adsorption of phenol (Ph), 4-chlorophenol (CP), and 4-cresol (MP) from water on three different carbon materials with similar BET-specific surface areas was investigated. These materials were carbon black (CB), activated coke (AC), and activated pyrolysate from used tires (AP). The effects of solution pH and ionic strength on the adsorption efficiencies of Ph, CP, and MP were investigated. It was found that the adsorption was pH-dependent and preferred in an acidic environment and that the ionic strength did not affect the adsorption processes of the three adsorbates. Adsorption kinetics was studied and described using both PFO and PSO equations as well as the Weber–Morris and Boyd diffusion models. Equilibrium was reached after about 2–3 h. The adsorption kinetics were best described by the PSO equation. Diffusion models indicate that the adsorption rates of phenolic compounds are mainly determined by film diffusion. The results revealed that the adsorption rates of Ph, CP, and MP on carbon materials were correlated with their porous structures and increased with increases in mesopore volume. Equilibrium adsorption was studied and described using the Langmuir and Freundlich isotherm equations. The isotherm that better described the adsorption process was the Langmuir isotherm. Activated pyrolysate from waste tires had the highest adsorption capacity, carbon black had a lower adsorption capacity, and activated coke had the worst (AP < CB < AC). The results obtained indicate that specific surface area is not a key criterion for predicting the adsorption capacity of a carbon-based material. Phenol had the lowest adsorption capacity on all three adsorbents, followed by 4-cresol and 4-chlorophenol (Ph < MP < CP). The observed differences in adsorption efficiency are correlated with increases in the molecular weight and the hydrophobicity of the adsorbates. The results show that the carbonaceous materials tested in this study, such as carbon black, activated coke, and activated tire pyrolysate, can be used as adsorbents for the removal of phenolic compounds from water despite their relatively low specific surface area. Activated tire pyrolysis char was found to be the best adsorbent, further demonstrating that scrap tires can be relatively good precursors for the production of carbon adsorbents. In addition, this significantly reduces production costs and helps solve the problem of scrap tire management by giving these tires a 'second life'. Carbon black has proven to be an equally effective adsorbent. The high availability of carbon black, which is used on a large scale in the production of car tires, suggests that it could be an interesting alternative material to use as an adsorbent for water treatment. Active coke showed the lowest adsorption efficiency, although it performs better as a gas-phase adsorbent than as a liquid-phase adsorbent.

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