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Adsorption of Halogenophenols from Aqueous Solutions on Activated Carbon

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1. Introduction

The increase in industrial activity has led to the production of environmental impurities which are dangerous to the ecosystem and human health. Phenol and its derivatives are common water contaminants, which are generated by coal conversion, petrochemical, pharmaceutical, paper and pesticide producing industries. The toxicity and environmental impact of these compounds can vary depending upon the number, type and position of substituent groups on the phenol ring. Phenolic compounds impart an unpleasant taste and odor to drinking water. Many of them are not only toxic at lower concentrations but are also suspected carcinogens and endocrine disrupting chemicals (Michałowicz and Duda, 2007). Therefore, the removal of these compounds from an environment is necessary. Several methods are currently used for the removal of phenolic compounds from aqueous solutions. These methods have been classified in two principal categories: non-destructive processes e.g. adsorption, and destructive processes such as biodegradation, oxidation by Advanced Oxidation Processes, photochemical oxidation, photocatalytic oxidation (Pera-Titus et al., 2004) as well as catalytic hydrodechlorination (HDC) of chlorophenols based on the reductive cleavage of a C–Cl bond by highly reactive atomic hydrogen (Xia et al., 2009; Witońska et al., 2014).

The destructive methods, however, are often relatively expensive or do not provide complete mineralization. They can also generate toxic decomposition intermediates, often more dangerous than the starting compound. The adsorption process by solid adsorbents is one of the most efficient methods for the removal of organic contaminants from water (Dąbrowski et al., 2005; Bansal and Goyal, 2009). Adsorption is attractive for its relative flexibility and simplicity of design, low cost, ease of operation as well as the no or low generation of toxic substances. Activated carbons are now the most commonly used adsorbents of proven adsorption efficiency for organic pollutants.

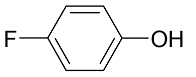
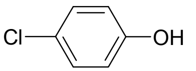
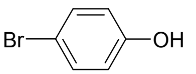
In this study, the adsorption of halogenated phenols including 4-fluorophenol (4-FP), 4-chlorophenol (4-CP) and 4-bromophenol (4-BP) from aqueous solution on powdered activated carbon was investigated. The kinetic studies and adsorption isotherms were studied and the results were analyzed by applying conventional theoretical models. The effect of solution pH on the adsorption was also investigated.

2. Materials and methods

The 4-fluorophenol (4-FP) was from PCR Incorporated (Gainesville, USA), 4-chlorophenol (4-CP) was from Sigma-Aldrich (St. Louis, USA) and 4-bromophenol (4-BP) was from Alfa Aesar (Karlsruhe, Germany). The physicochemical properties and molecular structures of the selected compounds are given in Table 1. The hydrochloric acid and sodium hydroxide were obtained from Avantor Performance Materials (Gliwice, Poland). As adsorbent the powdered activated carbon SX2 (Norit, The Netherlands) was chosen. Prior to use, the activated carbon was dried in an oven at 130°C to constant weight and stored in a desiccator until use. The BET surface area of the activated carbon was obtained on the basis determined low-temperature adsorption-desorption isotherms (ASAP 2020, Micromeritics, Norcross, USA).

The adsorption experiments were carried out in an Erlenmeyer flasks. For each time 0.02 g of the activated carbon and 0.04 L of 4-FP, 4-CP or 4-BP solutions were mixed and then shaken (200 rpm). After an appropriate time the solutions were filtered and concentration of the adsorbates was measured using a UV-Vis spectrophotometer (Carry 3E, Varian, USA) at the wavelengths of 270, 274 and 276 nm, which correspond to the maximum absorption peaks of the 4-FP, 4-CP or 4-BP, respectively. The calibration curves for the phenolic compounds were linear in the studied ranges (from 0.05 to 1.5 mmol/L) with correlation coefficients (R^2) better than 0.998. The equations for the regression line (n = 3) were: $y = 1.977x + 0.080$ for 4-fluorophenol, $y = 1.362x + 0.032$ for 4-chlorophenol and $y = 1.262x + 0.010$ for 4-bromophenol (where y is the absorbance and x is the concentration of the adsorbate).

Table 1. Physicochemical properties of the halogenophenols
Tabela 1. Właściwości fizykochemiczne halogenofenoli

Compound	Chemical structure	Molecular weight	Solubility in water at 20°C (mg/L)	pK_a	$\log K_{ow}$
4-fluorophenol		112.10	12.5	9.91	1.77
4-chlorophenol		128.56	24.0	9.30	2.39
4-bromophenol		173.01	14.0	9.17	2.59

The kinetic studies were conducted for initial concentration of the phenols 1.0 mmol/L. The amount of adsorption at time t, q_t (mmol/g), was calculated by the equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t are the initial concentration and adsorbate concentration at time t (mmol/L), m is the mass of the adsorbent (g) and V is the volume of the solution (L).

In adsorption isotherm studies, the solutions of adsorbates with different initial concentrations (from 0.5 to 2.0 mmol/L) were added to an Erlenmeyer flasks containing 0.02 g of the activated carbon and shaken for 6 hours. The uptake of the adsorbates at equilibrium, q_e (mmol/g), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where: C_e is equilibrium concentration of adsorbates (mmol/L) in solution.

The effect of pH on the adsorption of halogenated phenols onto activated carbon was studied by varying the initial pH of the solutions from pH 2 to 11. The pH was adjusted (prior to the addition of the adsorbent) using 0.1 mol/L HCl or 0.1 mol/L NaOH and was measured using pH meter. The initial concentration of 4-FP, 4-CP and 4-BP was fixed at 1.0 mmol/L.

All of the experiments were carried out in duplicate, and the average values were used for further calculations. The experimental error being around 5% (mean value).

3. Results and discussion

3.1. Adsorbents characterization

Fig. 1 shows the adsorption-desorption isotherm of nitrogen at 77.4 K on the SX2 activated carbon. The specific surface area was calculated from the Brunauer-Emmett-Teller equation and was found to be 890 m^2/g. The micropore volume V_{mi} and mesopore volume V_{me} were 0.370 and 0.242 cm^3/g, respectively. The point of zero charge (pH_{PZC}) of the activated carbon was measured elsewhere (Dąbek et al., 2016) and was found to be 7.15.

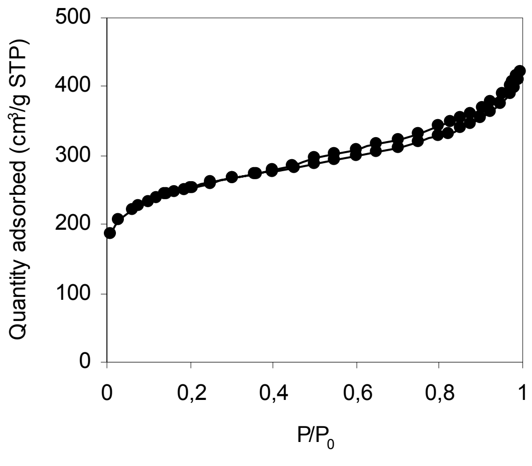


Fig. 1. Nitrogen adsorption-desorption isotherm of Norit SX2 activated carbons at 77.4 K
Rys. 1. Izoterma adsorpcji-desorpcji azotu na węglu aktywnym Norit SX2 w temperaturze 77,4 K

3.2. Kinetic studies

The adsorption kinetic curves of the 4-FP, 4-CP and 4-BP are shown in Fig. 2. As can be seen, the adsorption equilibriums were achieved after about 60 min.

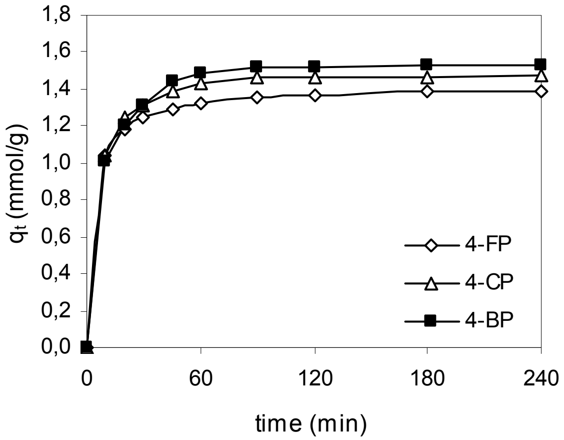


Fig. 2. Adsorption kinetics of the halogenated phenols on Norit SX2 activated carbon
Rys. 2. Kinetyka adsorpcji halogenofenoli na węglu aktywnym Norit SX2

For the description of the experimental data the pseudo-first order (Lagergren, 1898) and pseudo-second order (Ho and McKay, 1999) kinetic models were used. The pseudo-first order equation has the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where k_1 is the pseudo-first order rate constant (1/min).

After integration and applying the initial conditions the integrated form of the Eq. 3 becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

The values of k_1 were obtained from the intercept and the slope of the linear plot of $\log(q_e - q_t)$ versus t.

The pseudo-second order kinetic model is expressed in the form:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (5)$$

where k_2 is the pseudo-second order rate constant (g/mmol·min).

Integrating the Eq. 5 and applying the initial conditions we have:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

The rate constants of the pseudo-second order adsorption (k_2) were calculated from the straight line plots of t/q_t vs. t.

The kinetic parameters for the adsorption of the phenolic compounds on the SX2 activated carbon are presented in Table 2. As can be seen, the correlation coefficients for the pseudo-first order kinetic model are relatively low, whereas the R^2 values for the pseudo-second order kinetic model are higher than 0.997. This indicates that the adsorption system belongs to the pseudo-second order kinetic model. The k_2 values were 0.202, 0.186 and 0.153 g/mmol·min, for 4-FP, 4-CP and 4-BP, respectively. The adsorption rate followed the sequence: 4-bromophenol < 4-chlorophenol < 4-fluorophenol.

Table 2. The pseudo-first order and pseudo-second order kinetic parameters for 4-FP, 4-CP and 4-BP adsorption on the activated carbon
Tabela 2. Parametry kinetyczne równań pseudo 1. i pseudo 2. rzędu opisujące kinetykę adsorpcji 4-FP, 4-CP i 4-BP na węglu aktywnym

Adsorbate	pseudo-first order		pseudo-second order	
	k_1 (1/min)	R^2	k_2 (g/mmol·min)	R^2
4-FP	0.028	0.901	0.202	0.999
4-CP	0.025	0.892	0.186	0.998
4-BP	0.017	0.911	0.153	0.998

In order to investigate the mechanism of the adsorption, the intra-particle diffusion model (Weber and Morris, 1963) was used. The intra-particle diffusion equation is described as:

$$q_t = k_i t^{0.5} + C_i \qquad (7)$$

where: k_i is the intra-particle diffusion rate constant (mmol/g·min$^{-0.5}$) and C_i is the thickness of the boundary layer (mmol/g). Both constants were determined experimentally from the slope and intercept of plot q_t versus $t^{0.5}$ (Fig. 3).

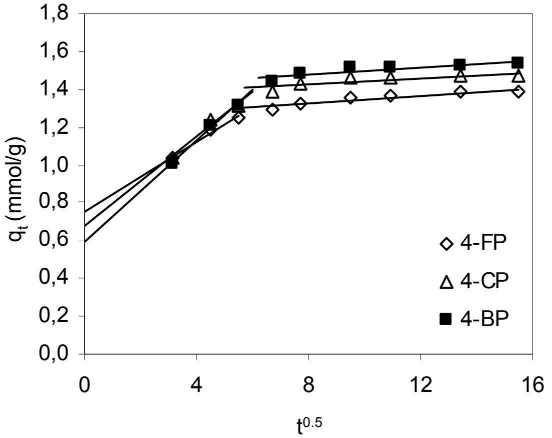


Fig. 3. Intra-particle diffusion kinetics for adsorption of phenols from aqueous solutions
Rys. 3. Kinetyka dyfuzji wewnątrzcząstkowej opisująca adsorpcję fenoli z roztworów wodnych

If the plot of q_t vs. $t^{0.5}$ passes through the origin, then the rate limiting process is only due to the intra-particle diffusion. If the plot is linear, then the diffusion is involved in the entire adsorption process (Lorenc-Grabowska et al., 2013). As shown in Fig. 3, none of the lines passed through the origin. This indicates that the intra-particle diffusion was not the only rate-controlling step. Moreover, the plots were not linear over the whole time range, suggesting that more than one process affected the adsorption. Similar adsorption mechanism of 4-chlorophenol was observed on the multi-walled carbon nanotubes (Kuśmierek & Świątkowski, 2015a; Kuśmierek et al., 2015; Strachowski & Bystrzejewski, 2015), carbon-encapsulated iron nanoparticles (Strachowski & Bystrzejewski, 2015), carbon black (Kuśmierek et al., 2015) and various activated carbons including Filtrasorb 400 (Kuśmierek and Świątkowski, 2015a), L2S Ceca (Kuśmierek et al., 2015), Sigma-Aldrich AC (Strachowski & Bystrzejewski, 2015), Norit ROW 0.8 Supra (Reczek et al., 2017) and modified granular activated carbon Norit R3ex (Kuśmierek et al., 2015).

3.3. Equilibrium studies

The adsorption isotherms of the 4-FP, 4-CP and 4-BP on the SX2 activated carbon are shown in Fig. 4. Two isotherm models (Freundlich, 1906 and Langmuir, 1916) were used to test the fitting of the experimental data. The Freundlich isotherm is widely applied for sorption surfaces with nonuniform energy distribution while the Langmuir isotherm is employed to monolayer adsorption.

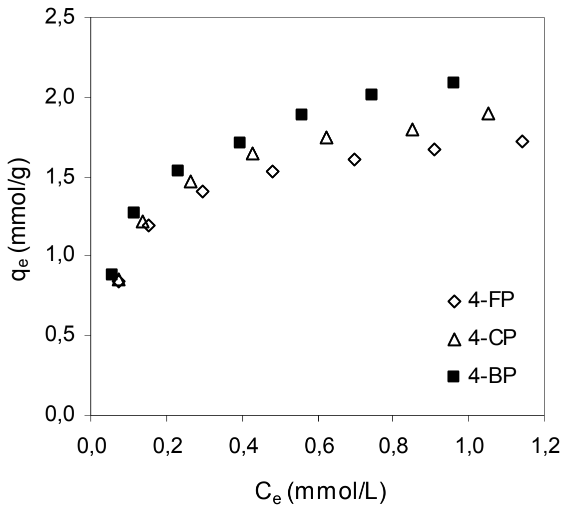


Fig. 4. Adsorption isotherms of halogenated phenols on Norit SX2 activated carbon
Rys. 4. Izotermy adsorpcji halogenofenoli na węglu aktywnym Norit SX2

The Freundlich isotherm is described by the formula:

$$q_e = K_F C_e^{1/n} \tag{8}$$

which can be converted to a linear form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

where K_F ((mmol/g) (L/mmol)$^{1/n}$) and n are the Freundlich equation constants which relate to adsorption capacity and adsorption intensity of the adsorbent. These constants were calculated from the intercept and slope of $\ln q_e$ vs. $\ln C_e$ plot.

The Langmuir isotherm is expressed as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{10}$$

after conversion to a linear form the Eq. 10 becomes:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \tag{11}$$

where q_m (mmol/g) is a monolayer adsorption capacity, and b (L/mmol) is the equilibrium adsorption constant. The values of the q_m and b were calculated from the intercept and slope of C_e/q_e vs. C_e plot.

The Freundlich and Langmuir adsorption isotherm model parameters as well as the correlation coefficients R^2 for the adsorption of the halogenated phenols on the activated carbon are listed in Table 3. The linear regression correlation coefficient values show that the equilibrium data obtained for all of the adsorbents were well represented by both models, nevertheless, a higher R^2 values (≥ 0.998) were observed for the Langmuir equation. The values of the Langmuir maximum adsorption capacity (q_m) as well as the Freundlich constant K_F increased in the order: 4-FP < 4-CP < 4-BP. The adsorption efficiency increased with respective increase in the molecular weight and octanol-water partition coefficient of the phenols.

Table 3. Parameters of the Freundlich and Langmuir adsorption isotherm models for the halogenated phenols
Tabela 3. Parametry równań izoterm Freundlicha i Langmuira opisujące adsorpcję halogenofenoli

Adsorbate	Freundlich			Langmuir		
	K_F (mmol/g) (L/mmol)$^{1/n}$	n	R^2	q_m (mmol/g)	b (L/mmol)	R^2
4-FP	1.493	0.188	0.986	1.603	12.04	0,998
4-CP	1.847	0.234	0.978	1.834	12.68	0.999
4-BP	1.927	0.261	0.968	2.004	10.51	0.999

The adsorption of the 4-CP on activated carbon was investigated by many authors. The Langmuir adsorption capacity (q_m) for the adsorption of 4-CP onto various activated carbons are presented in Table 4. As can be seen, the adsorption capacity of the SX2 activated carbon is more or less comparable with other adsorbents. Only a few papers describe the adsorption of 4-bromophenol and 4-fluorophenol. Bhatnagar (2007) studied the adsorption of 4-bromophenol from water on the activated carbon obtained from Merck (S_{BET} = 710 m^2/g), activated carbon slurry waste (S_{BET} = 380 m^2/g), activated blast furnace sludge (S_{BET} = 28 m^2/g) and activated blast furnace dust (S_{BET} = 13 m^2/g). The maximum adsorption of the 4-BP was 0.502, 0.235, 0.073 and 0.055 mmol/g, respectively. Anbia and Amirmahmoodi (2011) investigated the adsorption of 4-bromophenol and 4-chlorophenol on untreated (SBA-15) and amino functionalized (NH_2-SBA-15) mesoporous silica materials. They found that the uptake of 4-chlorophenol was higher than 4-bromophenol. The Langmuir adsorption constants for adsorption of 4-CP and 4-BP were 0.447 and 0.185 mmol/g for SBA-15, and 1.633 and 0.647 mmol/g for NH_2-SBA-15, respectively. Recently, Oh and Seo (2016) studied the adsorption of pharmaceuticals and halogenated phenols including 4-FP, 4-CP and 4-BP on graphite powder (Aldrich), charcoal-based granular activated carbon (DC Chemical) and five types of biochar. The maximum adsorption capacity of the activated carbon (S_{BET} = 738.8 m^2/g) was found to be 1.133 mmol/g for 4-FP, 1.580 mmol/g for 4-CP and 0.988 mmol/g for 4-BP (4-BP < 4-FP < 4-CP).

Table 4. Comparison of 4-chlorophenol adsorption on various activated carbons
Tabela 4. Porównanie adsorpcji 4-chlorofenolu na różnych węglach aktywnych

Activated carbon	S_{BET} (m^2/g)	Adsorption capacity, q_m (mmol/g)	Reference
Norit SX2	890	1.834	this study
modified Norit R3ex	1530	3.004	Kuśmierek et al., 2015
Gryfskand CXZ 2	977	2.505	Lorenc-Grabowska et al., 2010
Sigma-Aldrich AC	1187	2.178	Strachowski and Bystrzejewski, 2015
Prolabo AC	929	1.980	Hamdaoui and Naffrechoux, 2007
L2S Ceca	925	1.981	Kuśmierek et al., 2015
DC Chemical AC	739	1.580	Oh and Seo, 2016
F-400	997	1.537	Kuśmierek and Świątkowski, 2015a
AC from rattan sawdust	1083	1.468	Hameed et al., 2008

3.4. Influence of solution pH

The pH of the solution is an important parameter as it strongly affects the surface charge of the adsorbent as well as the degree of ionization and speciation of adsorbate. The effect of the initial solution pH on the adsorption equilibrium of the halogenated phenols was studied in the range of 2 to 11 and the results are presented in Fig. 5.

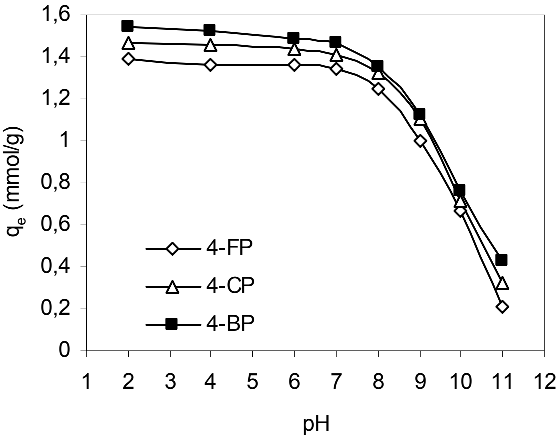


Fig. 5. The influence of the pH on the adsorption of phenols on the Norit SX2 activated carbon
Rys. 5. Wpływ pH na adsorpcję fenoli na węglu aktywnym Norit SX2

The data indicate that the adsorption behavior of the adsorbates on the activated carbon was similar. The adsorption of the phenols was almost constant at acidic pH range from 2 to 7 and decreased with the further increasing in the pH (from pH 7 to 11). In the pH range of 2-7, the surface of the activated carbon was positively charged (pH_{PZC} = 7.15), while at a pH greater than pH_{PZC}, the surface had a net negative charge. The pK_a of 4-FP, 4-CP and 4-BP is 9.91, 9.30 and 9.17, respectively. At a pH greater than the pK_a value, the adsorbates existed predominantly in anionic forms as negatively charged phenoxide ions. The results presented in Fig. 5 suggested that the non-dissociated forms of the phenols were preferred by the positively charged surface of the adsorbent. The large reduction in the adsorption at highly basic conditions can be attributed to the electrostatic repulsion between the negatively charged adsorbent surface and the dissociated molecules of the adsorbates. A similar results were reported for the adsorption of 4-CP onto activated carbon prepared from rattan sawdust (Hameed et al., 2008) and Norit R3-ex granular activated carbon (Kuśmierek and Świątkowski, 2015b).

4. Conclusions

This study investigated the adsorption of 4-fluorophenol, 4-chlorophenol and 4-bromophenol from aqueous solutions on the powdered activated carbon. The adsorption kinetics was better represented by the pseudo-second order model. The adsorption rate increased in the order: 4-BP < 4-CP < 4-FP. The adsorption isotherms of the phenols were analyzed using the Freundlich and Langmuir models. The experimental data received were found to be well described by the Langmuir isotherm equation. The adsorption efficiency increased in the order: 4-FP < 4-CP < 4-BP. The adsorption was strongly pH dependent. The adsorption of the phenols was almost constant at acidic environment and decreased significantly at basic conditions.

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Adsorpcja halogenofenoli z roztworów wodnych na węglu aktywnym

Streszczenie

Zbadano adsorpcję *para*-halogenopochodnych fenolu – 4-fluorofenolu (4-FP), 4-chlorofenolu (4-CP) oraz 4-bromofenolu (4-BP), z roztworów wodnych na pylistym węglu aktywnym Norit SX2. Zbadano kinetykę adsorpcji, adsorpcję w warunkach równowagowych oraz wpływ pH roztworu. Do opisu kinetyki adsorpcji zastosowano równania pseudo 1. rzędu, pseudo 2. rzędu oraz model dyfuzji wewnątrzcząstkowej. Stwierdzono, że kinetyka adsorpcji była najlepiej opisana równaniem pseudo 2. rzędu; najszybciej adsorbował się 4-fluorofenol, a najwolniej 4-bromofenol (4-FP > 4-CP > 4-BP). Do opisu adsorpcji w warunkach równowagowych zastosowano równania Freundlicha i Langmuira. Adsorpcję badanych fenoli najlepiej opisywał model izotermy Langmuira, dla którego uzyskano najwyższe wartości współczynników korelacji R^2. Obliczone wartości pojemności adsorpcyjnych q_m zwiększały się w kolejności 4-FP < 4-CP < 4-BP. Skuteczność adsorpcji fenoli była silnie zależna od pH roztworu.

Abstract

The adsorption of p-substituted halogenophenols – 4-fluorophenol (4-FP), 4-chlorophenol (4-CP) and 4-bromophenol (4-BP) from aqueous solutions on Norit SX2 powdered activated carbon was investigated. The adsorption kinetics, adsorption equilibrium as well as the effect of the solution pH were studied. The kinetic data were evaluated in terms of the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. The adsorption kinetics was better represented by the pseudo-second order model. The adsorption rate decreased in the order: 4-FP > 4-CP > 4-BP. To describe the adsorption isotherms, the Freundlich and Langmuir equations were applied. The Langmuir model provides the better correlation of the experimental data with higher R^2 values in comparison to the Freundlich equation. The values of the Langmuir maximum adsorption capacity (q_m) increased in the order: 4-FP < 4-CP < 4-BP. The results showed that the adsorption of the phenols was strongly pH dependent.

Słowa kluczowe:
adsorpcja, węgiel aktywny, 4-fluorofenol, 4-chlorofenol, 4-bromofenol

Keywords:
adsorption, activated carbon, 4-fluorophenol, 4-chlorophenol, 4-bromophenol