Adsorption of Halogenophenols from Aqueous Solutions on Activated Carbon

Krzysztof Kuśmierek*, Katarzyna Bieniek*, Lidia Dąbek**, Andrzej Świątkowski*

*Military University of Technology, Warsaw
**Kielce University of Technology

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 coef-
ficients \((R^2)\) 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical structure</th>
<th>Molecular weight</th>
<th>Solubility in water at 20°C (mg/L)</th>
<th>pK(_a)</th>
<th>logK(_{ow})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-fluorophenol</td>
<td>F–OH</td>
<td>112.10</td>
<td>12.5</td>
<td>9.91</td>
<td>1.77</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>Cl–OH</td>
<td>128.56</td>
<td>24.0</td>
<td>9.30</td>
<td>2.39</td>
</tr>
<tr>
<td>4-bromophenol</td>
<td>Br–OH</td>
<td>173.01</td>
<td>14.0</td>
<td>9.17</td>
<td>2.59</td>
</tr>
</tbody>
</table>

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:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]  

(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:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  

(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](image_url)

**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:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]  

(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:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]  

(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:
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

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>pseudo-first order</th>
<th>pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (1/min)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>4-FP</td>
<td>0.028</td>
<td>0.901</td>
</tr>
<tr>
<td>4-CP</td>
<td>0.025</td>
<td>0.892</td>
</tr>
<tr>
<td>4-BP</td>
<td>0.017</td>
<td>0.911</td>
</tr>
</tbody>
</table>

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:

$$q_t = k_i t^{0.5} + C_i$$

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).
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.

The Freundlich isotherm is described by the formula:

\[ q_e = K_F C_e^{1/n} \]  

which can be converted to a linear form:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

where \( K_F \) \((\text{mmol/g}) (\text{L/mmol})^{1/n}\) 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:

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  

after conversion to a linear form the Eq. 10 becomes:
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 (\( \geq 0.998 \)) 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**

| Adsorbate | Freundlich | | | Langmuir | | |
|-----------|------------|--------------------------|-------------|--------------------------|-------------|
|           | \( K_F \) (mmol/g) (L/mmol)^{-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 ($S_{\text{BET}} = 710 \text{ m}^2/\text{g}$), activated carbon slurry waste ($S_{\text{BET}} = 380 \text{ m}^2/\text{g}$), activated blast furnace sludge ($S_{\text{BET}} = 28 \text{ m}^2/\text{g}$) and activated blast furnace dust ($S_{\text{BET}} = 13 \text{ m}^2/\text{g}$). 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 ($S_{\text{BET}} = 738.8 \text{ m}^2/\text{g}$) 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

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

![Graph showing the influence of pH on adsorption of phenols on Norit SX2 activated carbon](image)

Fig. 5. The influence of the pH on the adsorption of phenols on the Norit SX2 activated carbon

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\text{PZC} = 7.15), while at a pH greater than pH\text{PZC}, the surface had a net negative charge. The pK\text{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\text{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 sur-
face 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 acti-
vated 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 pow-
dered activated carbon. The adsorption kinetics was better represented by
the pseudo-second order model. The adsorption rate increased in the or-
der: 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 signifi-
cantly at basic conditions.

References

Anbia, M., Amirmahmoodi, S. (2011). Adsorption of phenolic compounds from
aqueous solutions using functionalized SBA-15 as a nano-sorbent. Scientia
Iranica C, 18(3), 446-452.
dawnictwo Naukowo-Techniczne.
Dąbek, L., Kuśmierek, K., Świątkowski, A. (2016). Adsorpcja fenoli z roztwo-
rów wodnych na pylistych węglach aktywnych. Inżynieria i Ochrona Śro-
dowiska, 19(2), 217-226.
of phenolic compounds by activated carbon-a critical review. Chemo-
sphere, 58, 1049-1070.
Freundlich, H.M.F. (1906). Über die adsorption in lösungen. Zeitschrift für
Physikalische Chemie, 57, 385-470.
Hamdaoui, O., Naffrechoux, E. (2007). Modeling of adsorption isotherms of
phenol and chlorophenols onto granular activated carbon. Part I. Two-
parameter models and equations allowing determination of thermodynamic


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 wewnętrzчастkowej. 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 R². Obliczona wartości pojemności adsorpcyjnych qₘₐₓ 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