

## THE REMOVAL OF PHENOLS FROM WASTEWATER THROUGH SORPTION ON ACTIVATED CARBON

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### Abstract

In the presented study sorption potential of activated carbon to removal of phenolic compounds from municipal wastewater was investigated. The structural property of carbon was characterized by nitrogen adsorption – desorption isotherms. The sorption experiments were carried out in batch system for raw and biologically treated wastewater, namely influent and effluent respectively. The effectiveness of phenols removal was determined by measurement of phenolic index and was in the range 20.7-60.5%; 49.6-94% for influent and effluent respectively. Lower removal of phenols from influent resulted from higher competition with another pollutants for the sorption sites than in effluent. The experimental data fitted slightly better Freundlich model than Langmuir which indicates favorable adsorption and heterogeneity of the sorbent adsorption sites.

### Streszczenie

Celem naukowym prezentowanych badań było określenie możliwości sorpcyjnych węgla aktywnego w stosunku do związków fenolowych zawartych w ściekach komunalnych.

W pracy scharakteryzowano również właściwości strukturalne badanego węgla za pomocą izoterm sorpcji – desorpcji azotu. Badania sorpcji przeprowadzono w układzie statycznym dla surowych i oczyszczonych ścieków komunalnych. Efektywność usuwania fenoli została określona na podstawie pomiaru indeksu fenolowego i była w zakresie 20.7-60.5% i 49.6-94% odpowiednio dla dopływu i odpływu. Niższy stopień usunięcia fenoli ze ścieków surowych wynikał z większej konkurencji o centra adsorpcyjne na powierzchni sorbentu spowodowanej większą liczbą zanieczyszczeń w ściekach surowych niż oczyszczonych. Dane eksperymentalne lepiej opisywał model Freundlicha niż Langmuira, co wskazuje na heterogeniczność energetyczną powierzchni sorbentu.

Keywords: Adsorption; Activated Carbon; Wastewater; Phenols.

## 1. INTRODUCTION

The growing population, industrial development and urbanization contributes to the deterioration of the environment. In recent years, due to the poor condition of surface waters particular attention is paid to

the quality of the aquatic environment. Serious threat to the quality and purity of water constitute micropollutants (anthropogenic origin) which include phenols and its derivatives. These substances and the products of incomplete oxidation, already at low concentrations discharged along with the purified wastewater into

surface waters impair their quality. This creates a serious threat to aquatic ecosystems. The main sources of phenols in environment are production of drugs and several pesticides in particular: phenoxy-herbicides and phenolic biocides like pentachlorophenol, dinoseb or diaryl-ether pesticides [2]. Phenols and their derivatives are released into the environment through municipal/industrial sewage, and landfill leachate [1]. The presence of phenolic compounds have been documented in different mediums such as sewage sludge, influent and effluent of wastewater, river water and soil [3-6]. Pocerull et al. showed concentrations of nitrophenols (2-nitrophenol, 4-nitrophenol and 2,4-dinitrophenol) in Ebro river (Spain) ranging from 0.1 to 5.0 µg/l [6]. The other results indicated concentration of phenol over 40mg/l in river water, which was receiver of wastewater from petrol industry [7]. Moreover, in the area fertilized by municipal sewage sludge, the concentration of 4-nonylphenol was 2.7 mg/kg of soil [8]. Phenols are also included in The List of Priority Pollutants by the US Environmental Protection Agency (EPA) [2]. They are also highly toxic which is very important due to ecological aspects [9]. Chronic toxicity of phenols in humans results in: headache, vomiting, difficulty in swallowing, liver injury, fainting and etc. [10]. Therefore, due to the environmental and ecological safety it is advisable to clean municipal and industrial wastewater of toxic organic micropollutants, to the level excluding their negative impact on the natural environment and surroundings.

Among the methods used to phenols removal, adsorption is one of the simplest and widely applied method. Examination of wastewater treatment containing phenolic compounds, have shown that adsorption on activated carbon is considered as a most potential treatment technique [9,10,11]. US EPA also considers adsorption on activated carbon as one of the best available environmental control technologies.

The aim of the study was: (1) determination of structural property of studied activated carbon, (2) to assess the effectiveness of phenols removal from raw and biologically treated wastewater using activated carbon, (3) fit adsorption models to the experimental data.

## 2. METHODS

### 2.1. Characterization of wastewater

The wastewater used in this work was influent and effluent from Wastewater Treatment Plant located in urban and industrial zone of Silesia. The characteristic of wastewater is presented in Tab. 1. After sampling, wastewater was filtered instantly in the laboratory with paper filter then with glass fibre filters. All samples were stored at 4°C and utilized for the batch experiments within 2 days.

**Table 1.**  
Characteristics of wastewater

Parameter	Influent	Effluent
<b>COD (mgO<sub>2</sub>/l)</b>	886	46
<b>BOD<sub>5</sub> (mgO<sub>2</sub>/l)</b>	399	9.3
<b>Chlorides (mgCl<sup>-</sup>/l)</b>	347	294
<b>Sulfates (mgSO<sub>4</sub><sup>2-</sup>/l)</b>	185	155
<b>N-NH<sub>4</sub> (mgN-NH<sub>4</sub>/l)</b>	57.3	1.86
<b>N-NO<sub>2</sub> (mgN-NO<sub>2</sub>/l)</b>	0.11	0.13
<b>N-NO<sub>3</sub> (mgN-NO<sub>3</sub>/l)</b>	0.64	2.80
<b>N<sub>TOT</sub> (mgN/l)</b>	97.70	8.10
<b>P-PO<sub>4</sub> (mgP-PO<sub>4</sub>/l)</b>	35.50	1.21
<b>Phenolic index (mg/l)</b>	0.54	0.27

COD - Chemical Oxygen Demand,  
BOD<sub>5</sub> – Biochemical Oxygen Demand,  
N<sub>TOT</sub> – Total Nitrogen

### 2.2. Characteristics of carbon

The activated carbon AKPA-22 was purchased from GRYFSKAND (Poland). The particle size was less than 0.12 mm. The carbon was characterized by N<sub>2</sub>/77 K adsorption-desorption isotherms using ASAP 2010 analyzer (Micrometrics, USA). The studied carbon did not undergo any extra treatment in order to repeat its application in commercial water treatment processes.

### 2.3. Batch adsorption studies

Sorption experiments were carried out by means of shaking out various mass of activated carbon with 100 ml of wastewater with initial phenol concentration in ambient conditions. The time required to reach

**Table 2.**  
Structural property of AKPA-22

Structure parameter	BET Surface Area [m <sup>2</sup> /g]	Total Area in Pores [m <sup>2</sup> /g]	Total Pore Volume [cm <sup>3</sup> /g]
AKPA-22	900.4	693.7	0.3652

adsorption equilibrium was determined in earlier kinetics studies and equalled 4 hours. The pH of influent and effluent samples was adjusted to the value 7.5 by means of NaOH and HCl solutions. After reaching equilibrium, carbon was separated from wastewater and filtrates were analyzed. The concentration of phenols in all samples was determined using phenol test (photometric method). Simultaneously blank determination was performed according to the same instruction, excluding dosage of carbon. Above operation was carried out to verify phenols potential accumulation on the glass or filters, which could provide erroneous experimental data. The amount of phenols absorbed onto activated carbon was calculated according to the equation 1:

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

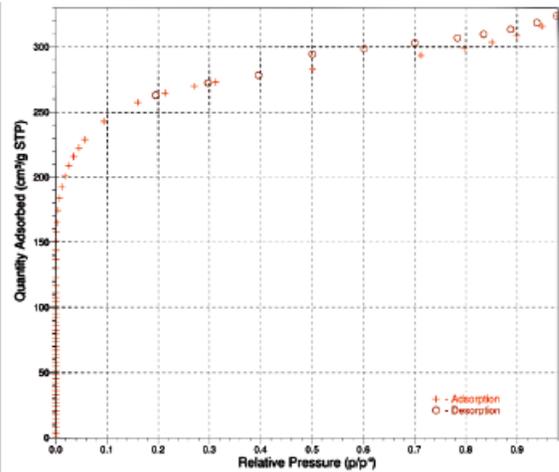
where  $q_e$  (mg/g) is the equilibrium amount of phenols absorbed onto AKPA-22,  $C_0$  (mg/l) is the initial concentration of phenols in wastewater and  $C_e$  (mg/l) equilibrium concentration of phenols,  $v$  (l) is the volume of wastewater,  $m$  (g) is the mass of sorbent.

### 3. RESULT AND DISCUSSION

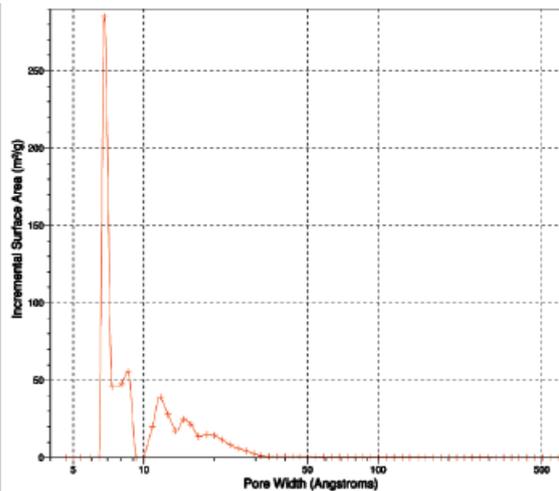
#### 3.1. Textural characteristics of carbon

Carbon AKPA-22 showed type I isotherm according to the IUPAC (International Union of Pure and Applied Chemistry) categorization what indicated occurrence of micropores (Fig. 1). The lack of significant increase of adsorption at higher values of relative pressure resulted from presence of very narrow pores, that it could not contain more adsorbate than single monolayer. Type I isotherm is characterized for chemisorption although several cases of physisorption such as, for very microporous activated carbon could also belong to type I isotherm. The nitrogen adsorption mensuration was used to calculate several parameters such as: the specific surface area, total area in pores, total pore volume and pore size distribution (PSD), listed in Tab 2. The specific surface area of carbon was determined by the standard BET method. The PSD of carbon (Fig. 2) was calcu-

lated according to method of Density Functional Theory (DFT), which is based on a molecular model for adsorption of nitrogen in porous solids. Porous structure of AKPA-22 is bidispersion, in majority consists of micropores and average fraction of mesopores, macropores do not occur.



**Figure 1.**  
Nitrogen adsorption-desorption isotherms of AKPA-22



**Figure 2.**  
Pore size distributions of AKPA-22

### 3.2. Removal efficiency of phenols

Figure 3 illustrates relation between dose of carbon and effectiveness of phenols removal from influent and effluent. This is obvious that dose of carbon had an important role on treatment effects. The application of increasing carbon doses to constant phenol initial amount in wastewater resulted in obtaining additional adsorption sites for phenols, therefore their reduction was improved. It was also found that the efficiency of phenols reduction was higher for effluent than influent and ranged 20.7-60.6% and 49.6-94% respectively for influent and effluent. Observed effect could be explained by presence of more kinds and amount of pollutants in influent than effluent. Probably these pollutants competed with phenols on the adsorption sites, therefore smaller amount of phenols uptake. Sufficient carbon concentration to remove most of phenols from effluent equaled 10 mg/l. Obtained results indicated that activated carbon AKPA-22 has ideal performance for removal of phenols from wastewater even in low dose.

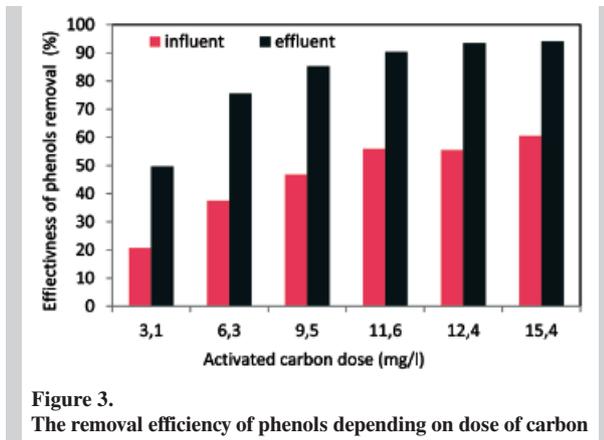


Figure 3. The removal efficiency of phenols depending on dose of carbon

### 3.3. Adsorption isotherms

The equilibrium adsorption isotherms were shown for both influent and effluent in Fig. 4. The experimental data were fitted to Freundlich and Langmuir models, according to equation 2, 3 respectively.

$$q_e = K_f C_e^{1/n} \quad (2)$$

$$q_e = \frac{a b C_e}{1 + b C_e} \quad (3)$$

Where  $q_e$  is the equilibrium amount absorbed in mg per gram of sorbent (mg/g),  $K_f$  is the Freundlich

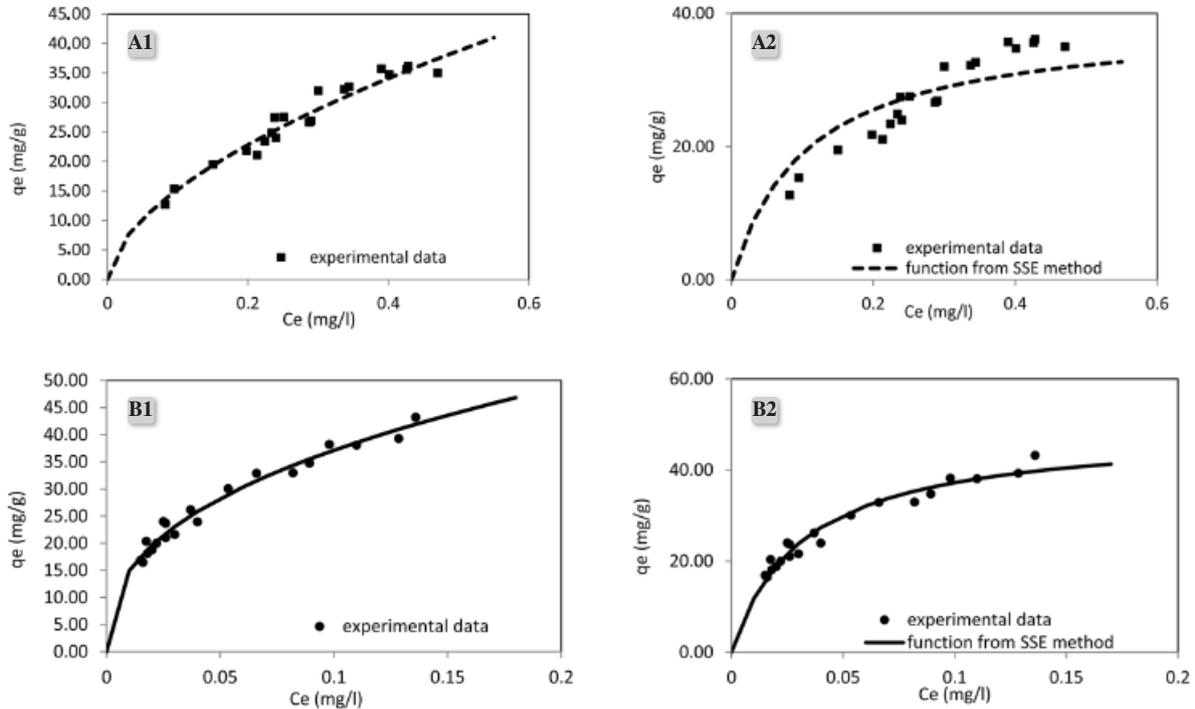
adsorption coefficient ((mg/g)(L/mg)<sup>n</sup>),  $C_e$  is the equilibrium concentration (mg/L),  $n$  is the number which describes surface heterogeneity and sorption intensity,  $a$  is the maximum adsorption capacity (mg/g), and  $b$  is the Langmuir fitting parameter (L/mg).

A trial and error procedure was used for the non-linear method using the solver add-in with spreadsheet, Microsoft Excel. The equation parameters were obtained by means of minimization of the sum of squared errors (SSE) and listed in Tab. 3. Fitting experimental data to sorption models provides information about type of sorption (chemisorption, physisorption). The Langmuir theory is based on the assumption of monolayer adsorption, where molecules interact only with the surface of sorbent. Moreover, it is assumed that the surface is completely smooth and homogeneous, and there is no interaction between adsorbate molecules on adjacent sites. However, Freundlich theory is empirical and describes heterogeneous surface energy system. On the basis of  $R^2$  value it was found that Freundlich model slightly better describes adsorption of phenols onto AKPA-22 both for influent and effluent, which indicates multilayer coverage. This result in connection with earlier outcomes concerning I-type of nitrogen adsorption-desorption isotherms indicates case of physisorption on microporous carbon. Moreover, in this case, I-type of isotherm did not fit to Langmuir equation due to false assumption, that the surface containing the absorbing sites is perfectly flat plane and energetic homogenous are rare and difficult to obtain [12]. Based on the  $n$  value smaller than 10 it was found that adsorption process is favorable and heterogeneity of the sorbent adsorption sites.

Batch studies indicated that phenols were better adsorbed onto AKPA-22 from effluent than influent. This is because of the fact that, in influent phenols were in more competition with another pollutants for the sorption sites than in effluent. A comparison of the maximum phenols uptake ( $a$ ) between influent and effluent also confirmed thesis about competition. Moreover as shown in Tab. 3. the values of  $K_f$ , and  $b$  are lower for influent than effluent which also indicate for more phenols uptake for effluent than influent.

**Table 3.**  
Freundlich and Langmuir fitting parameters obtained from non-linear regression

Wastewater type	Freundlich model			Langmuir model		
	$K_f$ ((mg/g)(L/mg) <sup>n</sup> )	n	R <sup>2</sup>	b [L/mg]	a [mg/g]	R <sup>2</sup>
Influent	57.9	1.728	0.9455	9.5	39.00	0.9043
Effluent	92.2	2.531	0.9727	31.6	49.00	0.9580



**Figure 4.**  
Adsorption isotherms for phenols onto AKPA-22. Influent: Freundlich isotherm (A1) and Langmuir isotherm (A2); Effluent: Freundlich isotherm (B1) and Langmuir isotherm (B2)

#### 4. CONCLUSION

Characterization of AKPA-22 by nitrogen adsorption-desorption isotherms proves bidispersion structure with the greatest amount of micropores and average fraction of mesopores, macropores do not occur. The BET surface area equals 900.4 m<sup>2</sup>/g. Overall, this study demonstrates that the capacity of AKPA-22 enables the removal of phenols from wastewater which proves that it is low-cost method. The removal efficiencies of phenols were higher for effluent than influent due to smaller competition with another pollutants for the sorption sites. The experimental data fitted slightly better the Freundlich model than Langmuir which indicates favorable adsorption and heterogeneity of the sorbent adsorption sites.

#### ACKNOWLEDGE

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