# The influence of ozonation on the activated carbon adsorption of phenol and humic acid

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To study the influence of ozonation on the activated carbon adsorption, a model solution containing approximately 8 mg/dm$^3$ of humic acid and approximately 1 mg/dm$^3$ of phenol has been ozonated, and then adsorption kintetics and adsorption isotherm experiments have been performed. The applied ozone doses ranged from 1 to 3 mg O$_3$/dm$^3$, and a contact time was 1 min. In the adsorption experiments, the commercial activated carbon CWZ-30 (Gryfskand Sp. z o.o., Hajnówka, Poland) has been used. Phenol adsorption under equilibrium conditions was determined by the Freundlich isotherm equation, and the modified Freudlich isotherm equation has been employed for the determination of humic acid equilibrium adsorption. The applied oxidation conditions resulted in color, chemical oxygen demand (COD), total organic carbon (TOC) and UV$_{254}$ absorbance removal, by 4 – 13%, 3 – 6%, 3 – 7%, respectively. After ozonation, phenol concentration decreased by 6 – 23%. These changes in the model solution did not affect the humic acid adsorption, however, they deteriorated phenol adsorption.

## INTRODUCTION

Both ozonation and the activated carbon adsorption have been commonly introduced to water treatment plants for over 30 years. These processes are applied to remove the organic matter to a high extent. At present in Poland, ozone is the most commonly used oxidant and has been applied in about 60% water treatment plants. It is due to its very high oxidation and disinfection potentials. Ozone in water treatment systems can be applied in preoxidation and before sand or carbon adsorption. In preoxidaton, small ozone doses and short contact times are used. The use of this oxidant allows the reduction of the amount of chlorine disinfectants at the final stage of a water treatment system. In water treatment systems, activated carbon is usually used in the granular form as column fillings. However, powdered activated carbon can be applied during coagulation and in this case it acts not only as adsorbent but also as a floc ballast. Powdered activated carbon is usually applied when a water source feeding a treatment plant is contaminated with additional pollutants, compared to average composition, or the contaminants are present at higher concentration. Ozonation of organic matter usually produces the lower molecular weight and more polar compounds. Smaller molecules can be more easily adsorbed in micropores of the activated carbon, which is advantageous as most of the currently produced activated carbons have large surfaces that are characterized by the microporous structure. On the other hand, due to solvation by water, polar molecules stay in water more eagerly, and are less adsorbable. For this reason, the influence of ozonation on the activated carbon adsorption was studied in this research. In this study, phenol and humic acid have been chosen as the compounds that do not compete in the adsorption process[1]. Humic acid has been chosen as the representative of humic substances, which is the main component of natural organic matter and phenol has been chosen as the representative of micropollutants. For these contaminants, both adsorption kinetics and adsorption isotherms under equilibrium conditions have been investigated.

## MATERIALS AND METHODS

The model solution was freshly prepared daily in a 5-dm$^3$ glass bottle, by the dilution of stock solutions with the distilled water. The stock solutions contained approximately 100 mg of phenol and 80 – 100 mg of commercial humic acid (Fluka), respectively, and were refrigerated. The concentrations of phenol and humic acid in the stock solutions were analysed every month by the bromite-bromate titration method and by the TOC (total organic carbon) measurement, respectively. The model solution containing a mixture of humic acid (the concentration of approximately 8 mg/dm$^3$) and phenol (the concentration of approximately 1 mg/dm$^3$) has been used. These low contaminant concentrations are recommended for adsorption studies on drinking waters[3]. To study both adsorption kinetics and isotherms, a bottle point method has been employed. In this method, every point of a graph is obtained by shaking the model solution with a sample of activated carbon. For phenol adsorption isotherms, phenol concentration data under equilibrium conditions have been used. For humic acid adsorption isotherms, the TOC data have been used, because the majority of TOC in the model solution originated from humic acid. Due to a very fast decrease in phenol concentration in all adsorption experiments, the correction factors for TOC originating from phenol (TOC up to 0.05 mg/dm$^3$ in all adsorption isotherm experiments) were not taken into consideration for the humic acid adsorption isotherm calculations. The surface characteristics of CWZ 30 was performed by Mozia et al.[4] and is presented in Table 1.

**Table 1.** Surface characteristics of CWZ 30 [4]

| | |
|---|---|
| BET, m$^2$/g | 982 |
| Total pore volume, cm$^3$/h | 0.22 |
| Micropore volume, cm$^3$/g | |
| < 2 nm | 0.18 |
| Percent | 82 |
| Mesopore volume, cm$^3$/g | |
| small (2-10 nm) | 0.018 |
| large (10-50 nm) | 0.022 |
| Percent | 18 |
| Average pore diameter, nm | 2.1 |

The ozonation set-up has been shown and described in detail elsewhere[5]. The ozomatic LAB 802 ozone generator (Wedeco, Germany) was used in the experiments. The amounts of ozone generated were controlled by the oxygen flow regulation. The ozonation processes were performed in a 5-dm[3] glass bottle, equipped with a parched plate, for gas dispersion. Ozone contents in the inlet and outlet gases were determined by the iodometric procedure and in water by the o-tolidyne method[6]. After the ozonation nitrogen gas was passed through the model solution within 1 min so no residual ozone was present in the model solution during the adsorption experiments. Both before and after the oznation, the following parameters in the model solution have been measured: phenol concentration, TOC, $UV_{254}$ absorbance and COD (chemical oxygen demand). Phenol concentration was analysed by the 4-amino-antipyrine-ferricyanide photometric method[2]. TOC concentration was measured with Multi N/C Analyzer (Analytik Jena, Germany) with a detection limit of 0.02 mg/dm^{3}. COD, and $UV_{254}$ absorbance (the organic compounds content measured as absorbance at 254 nm) were analysed according to Polish Standards[7, 8]. All absorbance measurements were performed with a V-530 spectrophotometer (Jasco, Japan) in the 1-cm path length quartz cuvettes.

## RESULTS AND DISCUSSION

The changes of the organic matter concentration in the model solution after ozonation are provided in Figure 1.
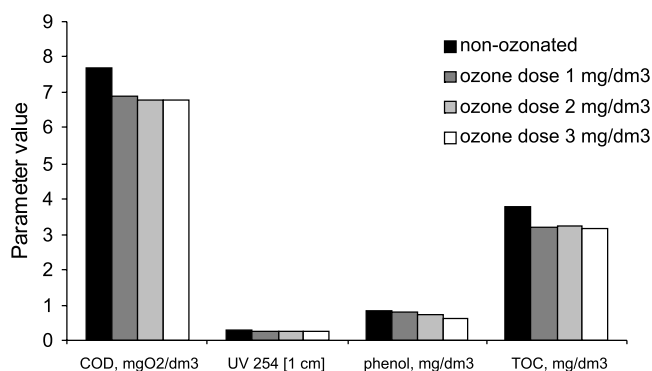


**Figure 1.** The parameters of the model solution before and after ozonation

The applied oxidation conditions resulted in the decrease of phenol concentration by 6 – 23%. The removals of chemical oxygen demand, TOC and $UV_{254}$ absorbance were 10 – 12%, 14 – 17%, and 4 – 12%, respectively. That means that partial decomposition of phenol and possibly humic acid molecules took place, and a part of them were mineralized. The pH of the model solution has changed very little, from 6.40 before the ozonation to 6.27 – 6.40 after the ozonation. The kinetics study (Figure 2) indicated that for all the studied activated carbons, adsorption equilibrium for phenol was achieved within 72 hours (Figure 2). Likewise, the adsorption kinetics of the organic matter, measured by $UV_{254}$ absorbance and TOC, showed that humic adsorption equilibrium was obtained within 72 hours as well (Figure 3).

For phenol adsorption kinetics the following equation has been matched:

$$y = \frac{a}{x} + b,$$

where $y$ is a phenol concentration, $x$ is contact time, $a$ and $b$ are the calculated parameters. The calculated values of
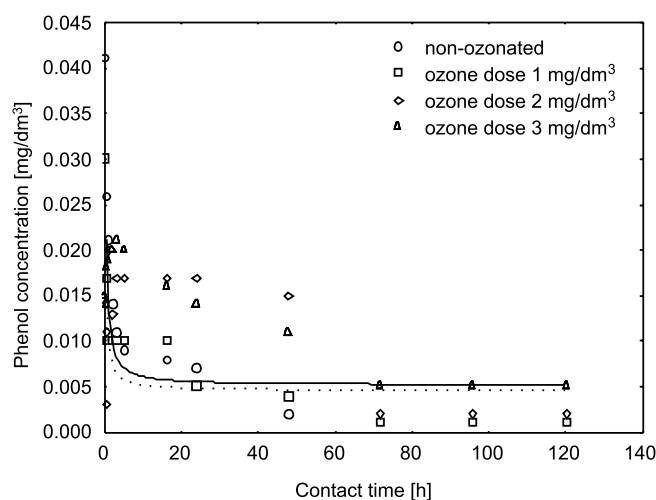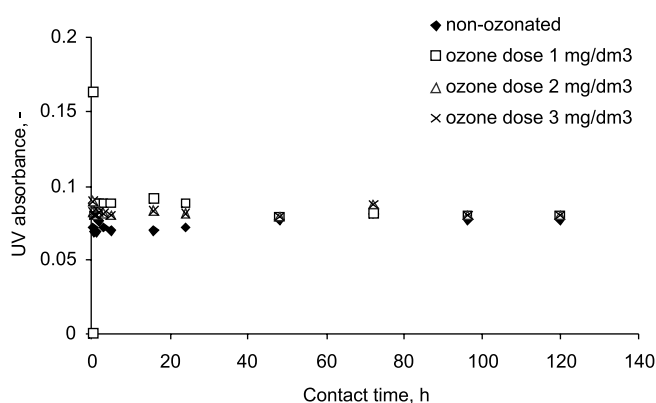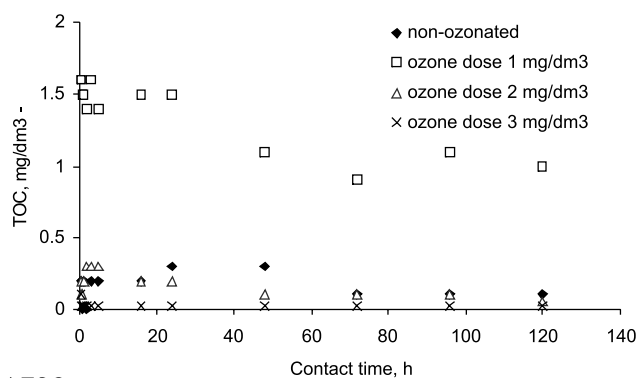


**Figure 2.** Adsorption kinetics. Changes in phenol concentration as a function of time



a) $UV_{254}$ absorbanc



b) TOC

**Figure 3.** The adsorption kinetics. Changes in organic carbon concentration as a function of time

$a$ and $b$, and $R^2$ were 0.010, 0.005 and 0.95 for the non-ozonated model solution, and 0.006, 0.005 and 0.92 for the solution ozonated with 1 mg $O_3$/mg TOC. The curves plotted according to these parameters are shown in Figure 2. For the two model solutions oxidized with higher ozone doses, the $R_2$ values were less than 0.85, therefore they have not been plotted. Likewise, for TOC and $UV_{254}$ – the absorbance adsorption kinetics of the non-ozonated and all the ozonated model solutions, the $R_2$ values were less than 0.85 and they have not been shown in the adsorption kinetics graphs (Figure 3). For the ozonated model solution, competitive adsorption of the ozonated and the non-ozonated molecules might have taken place. The molecules might be both adsorbed and desorbed from carbon surface, therefore their concentration in water might decrease or increase, respectively.
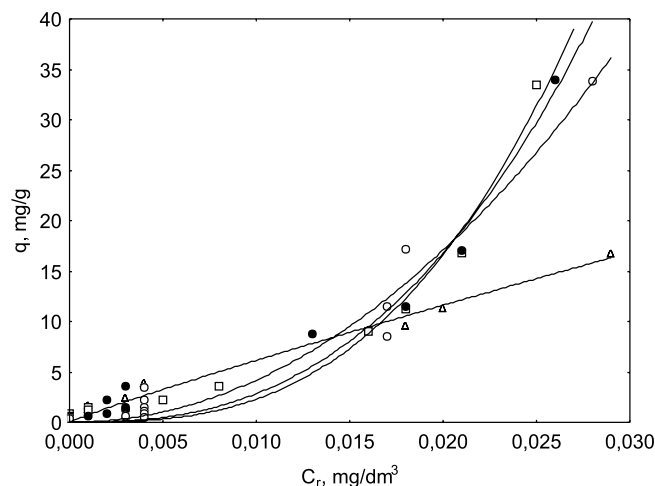
**Table 2.** Phenol adsorption. The coefficients of the Freundlich, Langmuir and Freundlich-Langmuir equations

| Model solution/ ozone dose mg $O_3$/dm$^3$ | Freundlich equation $q = K_F \cdot c_r^n$ | | | Langmuir equation $q = q_m \cdot \dfrac{K_L \cdot c_r}{1 + K_L \cdot c_r}$ | | | Freundlich-Langmuir equation $q = q_m \cdot \dfrac{K_{F-L} \cdot c_r^n}{1 + K_{F-L} \cdot c_r^n}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $K_F$ | $N$ | $R^2$ | $K_L$ | $q_m$ | $R^2$ | $K_F$ | $q_m$ | $n$ | $R^2$ |
| Non-ozonated | 419 | 0.92 | 0.99 | 1.91 | 30 | 0.99 | 0.35 | 1261 | 0.93 | 0.99 |
| Ozone dose 1 | 3845340 | 3.17 | 0.99 | 0.13 | 7118 | 0.90 | 24 | 163232 | 3.17 | 0.98 |
| Ozone dose 2 | 376712 | 2.6 | 0.98 | 0.11 | 8477 | 0.92 | 2,5 | 150421 | 2,6 | 0.98 |
| Ozone dose 3 | 46694 | 2.02 | 0.98 | 0.14 | 6707 | 0.93 | 0,73 | 64423 | 2.02 | 0.98 |

Where: $q$ – real adsorption capacity, mg/g, $q_m$ – adsorption capacity related to a monolayer coverage, mg/g, $K_F$, $K_L$, $K_{F-L}$ – empirical Freundlich, Langmuir and Freundlich-Langmuir constants, -, $c_r$ – equilibrium concentration, mg/dm$^3$, $n$ – exponent, -.

The adsorption equilibrium isotherms were determined for a 72-hour contact time of the model solution with activated carbon. The obtained results of phenol adsorption equilibrium have been determined by the Freundlich, Freundlich-Langmuir and Langmuir equations. For the Freundlich and Freundlich-Langmuir models, high correlation coefficients have been obtained both for the non-ozonated and the three ozonated model solutions (Table 2).

The phenol adsorption isotherms according to the Freundlich equation have been plotted in Figure 4.



**Figure 4.** Phenol adsorption isotherms according to the Freundlich equation

For the Freundlich equation, the $K_F$ coefficient might be used as an indirect value of adsorption capability. However, the exponent $n$ has greater impact on the isotherm shape. The shape of the isotherm (convex, linear, concave) indicates how susceptible to adsorption the contaminant is. A good adsorption is characterized by a convex isotherm, and a weak adsorption by a concave isotherm. Moreover, the shape of an isotherm might change for different concentration ranges. For the studied isotherms, the exponent $n$ is close to 1, only for the non-ozonated model solution, so for this solution the Freundlich isotherm is almost linear. For the three ozonated model solutions, the isotherms are concave which indicated that phenol was more easily adsorbed from the non-ozonated model solution. No significant influence of the applied ozone doses on phenol adsorption has been found. Apparently, the difference in the used oxidant doses was too little to observe a significant difference, which is in agreement with the results obtained by Cipparone et al.[9] .

To determine the humic acid adsorption isotherms, TOC contents have been used, because 83% of TOC in the non-ozonated model solution originated from humic acid. To determine humic acid equilibrium adsorption, the modified Freudlich isotherm equation has been employed[10]. The coefficients of the modified Freundlich equation and the isotherm have been shown in Table 3 and Figure 5, respectively. The curve shapes of phenol adsorption isotherms might have been caused by the slower adsorption of phenol from the ozonated solutions, which resulted in greater adsorption capacity for this compound. Apparently, the presence of the oxidized compounds influenced the course of phenol adsorption on the activated carbon. It might have been due to the mechanism described by Coughlin and Ezra[11]. This mechanism defines adsorption selective to a molecule orientation. The molecules oriented to fast adsorption might decrease the adsorption capacity of the activated carbon. This is due to pore clogging, resulting from the faster but less ordered adsorption.

**Table 3.** Humic acid adsorption. The coefficients of the modified Freundlich equation

| Model solution/ ozone dose mg $O_3$/dm$^3$ | Modified Freundlich equation $q = K_F \cdot \left( \dfrac{c_r}{D} \right)^n$ | | |
|---|---|---|---|
| | $K_F$ | $n$ | $R^2$ |
| Non-ozonated | 8.30 | 0.41 | 0.96 |
| Ozone dose 1 | 5.10 | 0.54 | 0.99 |
| Ozone dose 2 | 6.98 | 0.48 | 0.99 |
| Ozone dose 3 | 6.46 | 0.54 | 0.99 |

Where: $q$ – adsorption capacity, mg/g; $K_F$ – Freundlich unit capacity factor, - ; $c_r$ – equilibrium solution-phase constant, mg/dm$^3$; $D$ – adsorption dose or concentration, g/dm$^3$; $n$ – Freundlich exponent, -.
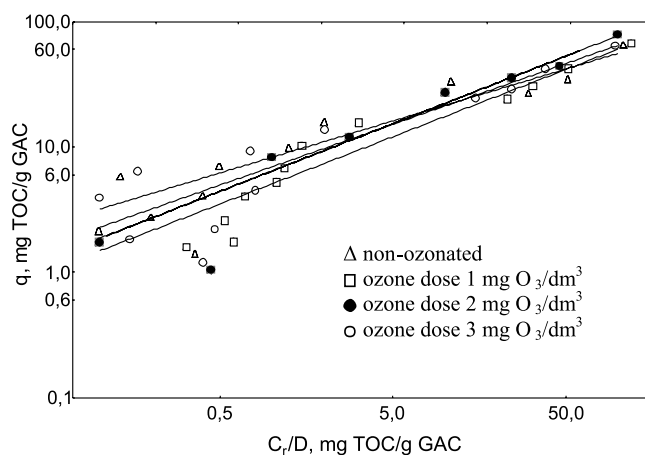


**Figure 5.** The organic carbon adsorption isotherms according to the modified Freundlich equation

The data provided in Table 3 showed that the employed modified Freundlich isotherm equation was highly correlated with the results obtained for the non-ozonated as well as all the ozonated model solutions ($R^2$ in range of 0.96 – 0.99). The $K_F$ content for the non-ozonated solution is higher than for all the ozonated solutions. However, for the suggested for this isotherm graphs logarithmic scale, the courses of the isotherm curves were very similar. The modified Freundlich adsorption isotherm equation has been proposed for the mixtures of organic substances. The obtained results showed that, in the studied range of ozone dose, this equation turns out to be a good approximation of the course of the ozonated humic acid adsorption. Apparently, it was caused by the fact that the applied ozonation conditions did not affect humic acid molecules and the adsorption isotherms for the ozonated and non-ozonated model solutions were very similar.

## CONCLUSIONS

The applied oxidation conditions (1-min contact time and ozone dose ranging from 1 to 3 mg $O_3/dm^3$) resulted in partial decomposition of phenol and humic acid molecules. These changes in the model solution did not affect humic acid adsorption on the PAC, however, they deteriorated phenol adsorption.

### Acknowledgements

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