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REMOVAL OF SELECTED ORGANIC COMPOUNDS ON MODIFIED ACTIVATED CARBONS

The presented work attempted to modify activated carbons with ultrasonic field and evaluate the efficiency of sorption of organic compounds on the obtained modified activated carbons. The results showed that the applied procedure had a positive effect on the removal of the investigated substance. In the case of removal of benzoic and phthalic acids, the highest sorption capacities were obtained for activated carbons modified with ultrasonic waves with the amplitude of 100% and the exposure time of 5 min. The removal efficiency for both acids was approximately 80% at the initial pH and 65% at pH = 8.0. Sorption of imidazole on modified activated carbons showed that lower final concentration was obtained for activated carbons modified with ultrasounds at the amplitude of 100%. The time of exposure to ultrasounds did not have a significant effect on reducing final concentrations. The average removal degree was approximately 45%. Sorption of phenol showed that the average degree of removal was approximately 80% for the solution of the initial pH whereas for higher pH the average removal degree was close to 65%.

1. INTRODUCTION

Activated carbons, due to their large specific surface area, high degree of surface reactivity, as well as well-developed porous structure, are regarded as potential sorbents for the removal of organic compounds from wastewater. Adsorption on activated carbons is an effective process for the removal of numerous contaminants from water, however, it is mainly used for the elimination of dissolved organic compounds. The most essential parameters determining removal of organic compounds from water by adsorption include the properties and size of organic compound molecules, chemical and porous structure of carbon, as well as pH of water solution. In the case of binding separate organic substances from diluted water solutions on activated carbons, the

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amount of adsorbed species is calculated as a function of the following properties of an organic compound: the type of functional groups, molecular weight, geometrical size and shape, polarity and solubility [1].

The size of specific surface area of the adsorbent plays the most important role in physical absorption of adsorbate. Oxidation of activated carbon decreases sorption of low-polar and non-polar substances. Adsorption of more polar compounds is increased at the presence of acid functional groups. This process can also be intensified along with the growth of molecular weight, whereas it decreases upon increasing volume of particles characterised by increased solubility and polarity [2, 3].

Adsorbents containing surface functional groups are used for the removal of polar organic compounds from water solutions while carbons without such groups are used for removal of non-polar organic compounds. Furthermore, for the adsorption of large organic compounds the carbons with high percentage of mesopores and macropores ought to be applied [4–6].

Many different methods exist for modification of activated carbons and depending on their implementation procedure, they can be divided into chemical and thermal methods [7–12].

In order to assess the influence of methods used for modification of activated carbons, organic compounds of various particle size and chemical nature were applied as test substances. Benzoic acid is used in food industry. Phthalic acids are intermediate products for polyester fibres industry, dyes, drugs as well as in the synthesis of other organic compounds. Many of the imidazole derivatives find practical application in industries and technologies. Phenol, for example is found in coke wastewater [13,14].

2. EXPERIMENTAL

The ROW 08 Supra activated carbon was used in the research. This carbon, obtained from peat, is manufactured by means of vapour-gas method by NORIT, the Dutch company. Its advantages like large volume of pores and significant size of grains makes it a commonly applied carbon for potable water treatment aiming at improving the taste of water and removing smell, ozone, chlorine and micro-contaminants (for example, dissolved organic substances or pesticides).

Selected technical parameters of ROW 08 carbon, provided by the manufacturer, are presented in the Table 1.

Before starting the research the process of ash removal from carbon was conducted in order to eliminate the impact of alkaline water from activated carbons on changes in reactions of tested solutions. Then the carbon was washed out with 10% solution of hydrochloric acid and distilled water and subsequently dried to constant mass in the temperature of 140 °C. This carbon was used as a control sample.

Table 1

Physicochemical properties
of granulated ROW 08 Supra carbon

Coefficient	Value
Bulk density, g/dm ³	381
Water absorability, cm ³ /g	0.97
pH (after ash removal)	7.0
Mechanical strength, %	98
Ash content, %	5.94
Methylene number, LM	30
Iod adsorption, mg/g	1098
Specific surface, m ² /g	805

The activated carbons modified by ultrasonic wave were also used for the research. The sonication of ROW 08 Supra carbon in UP 400S ultrasonic generator was conducted at various amplitudes and times. The sonication parameters of activated carbon are presented in Table 2.

Table 2

Sonication parameters
of ROW 08 Supra granulated carbon

Assay of ROW 08 Supra modified carbon	Time [min]	Amplitude [%]	Acoustic power density [W/cm ²]
A	5	50 (30 μm)	42.5
B	10		42.5
C	15		42.5
D	5	100 (60 μm)	85.0
E	10		85.0
F	15		85.0
G	20		85.0

Some of the physicochemical properties of ROW 08 Supra carbon were changed under the influence of ultrasonic field, the results are presented in Table 3.

Table 3

Physicochemical properties of ROW 08 Supra modified carbon

Coefficient	A	B	C	D	E	F	G
Bulk density, g/dm ³	405.03	409.03	409.67	407.27	415.63	417.37	428.97
Iod adsorption, mg/g	750	770	790	840	820	810	800
Methylene number, LM	35	34	33	40	37	35	33
Ash content, %	5.5	6.0	6.5	5.0	5.5	5.5	6.5

The adsorption process on activated carbons was conducted from single-component model solutions based on benzoic acid, phthalic acid, phenol or imidazole, at the initial concentrations of 1, 1.5 and 2 mmol/dm³. According to pH in the solution, these compounds are found in dissociated form (benzoic acid, phthalic acid and phenol – anions) or in undissociated form (imidazole – cation, Table 4).

Table 4

Characteristics of investigated organic compounds [3]

Compound	p <i>K</i>	Molecular weight [g/mol]
Benzoic acid	4.19	122.12
Phthalic acid	2.89 (1) 5.43 (2)	166.14
Imidazole	7.0	68.08
Phenol	9.89	94.11

The tests were conducted for the solutions at initial pH values and at pH = 8.0. The measurements of acid sorption were done at the initial pH = 3.5 for benzoic acid and equal to 3.0 for phthalic acid. The other series of measurements was carried out at pH = 8.0, providing full ionization of the acids. Sorption of imidazole was conducted at initial pH = 7.5 and at pH = 3.0, that is at full ionization. Finally, measurements for phenol were taken at the initial pH = 7.0 and at pH = 11.5 when full ionization took place. At the same time tests were carried out on the control sample with the application of non-modified carbon.

Adsorption processes of selected test substances were conducted in static conditions from solutions of the volume of 0.250 dm³ with 1 g of activated carbon. Then, samples were mechanically shaken for 2 h and stored after shaking for 22 h. After 24 h, the final concentration of solution was determined with a Helios α spectrophotometer at the wavelengths of: $\lambda = 272$ nm for benzoic acid, $\lambda = 280$ nm for phthalic acid, $\lambda = 220$ nm for imidazole and $\lambda = 270$ nm for phenol.

3. RESULTS AND THEIR OVERVIEWS

3.1. ADSORPTION OF BENZOIC ACID

In order to verify the influence of carbon modification on its adsorption capability, the isotherms of adsorption of benzoic acid were determined for both initial pH (Fig. 1) and pH = 8.0 (Fig. 2).

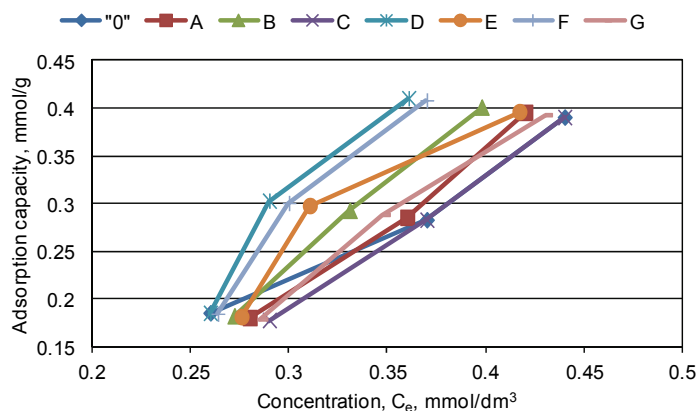


Fig. 1. Adsorption isotherms of benzoic acid at the initial pH (pH = 3.0)

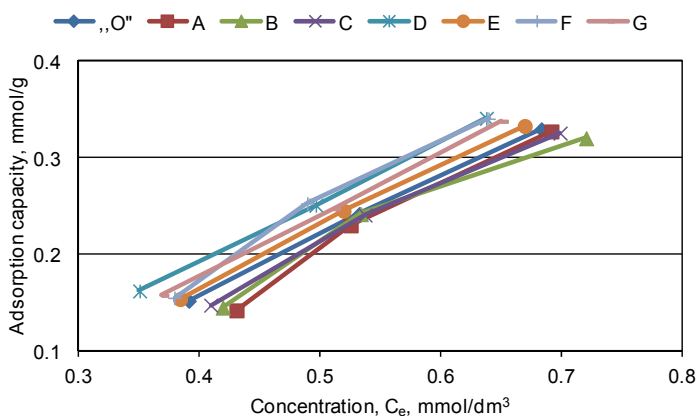


Fig. 2. Adsorption isotherms of benzoic acid at the pH = 8.0

Modification of the ROW 08 Supra carbon by its sonication caused an increase in its adsorption capacity in solutions at initial pHs. The highest effectiveness of adsorption of benzoic acid was noted for amplitude of 100% and for 5 and 15 min sonication, whereas the lowest – for amplitude of 50% and 15 min. For samples with NaOH solution added, the degree of removal of a given organic substance increased by several per cent in comparison with the initial carbon, however only for amplitude of 100%. The activated carbons modified by ultrasonic field with the amplitude of 50% removed benzoic acid in a lesser degree than the control carbon.

3.2. ADSORPTION OF PHTHALIC ACID

Next, adsorption isotherms for phthalic acid from water solutions of the initial pH and pH = 8.0 were determined. The process was efficient for carbon sonicated for 5

and 10 min, with the amplitude of 100% (at initial pH). For such modified carbons, the final concentration of phthalic acid was lower than for the initial carbon. On the other hand, in the case of sorption from the solution of pH = 8.0, most of the modified activated carbons removed phthalic acid better than the control carbon. The lowest final concentration was obtained for carbons modified for 5 and 10 min with the ultrasonic waves of the amplitude of 100%, just like in the case of sorption from the solution at the initial pH (Figs. 3, 4).

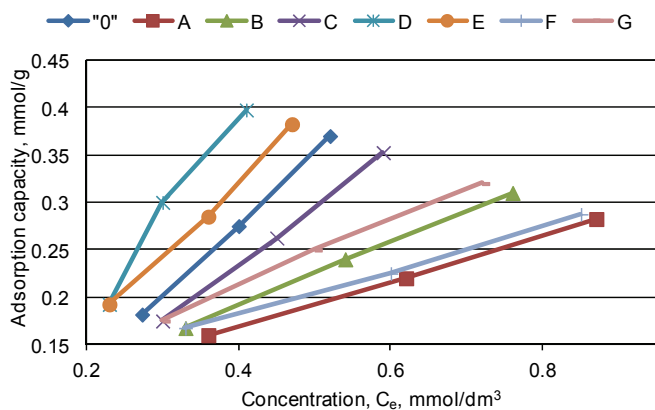


Fig. 3. Adsorption isotherms of phthalic acid at the initial pH (pH = 3.0)

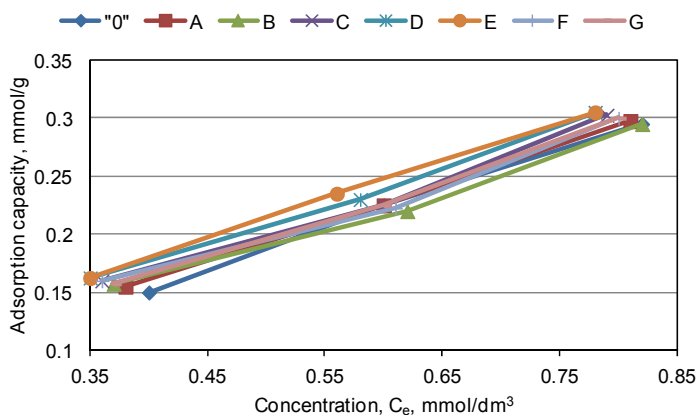


Fig. 4. Adsorption isotherms of phthalic acid at the pH = 8.0

3.3. IMIDAZOLE ADSORPTION

The imidazole isotherms from water solutions at initial pH and pH = 3.0 are presented in Figs. 5 and 6, respectively. It was found that carbons modified with ultrasonic field of the amplitude of 100% enabled one to obtain sorption capacities higher

than in the case of non-modified carbon. Such dependences were obtained during the process of sorption for both pH values of the solutions tested.

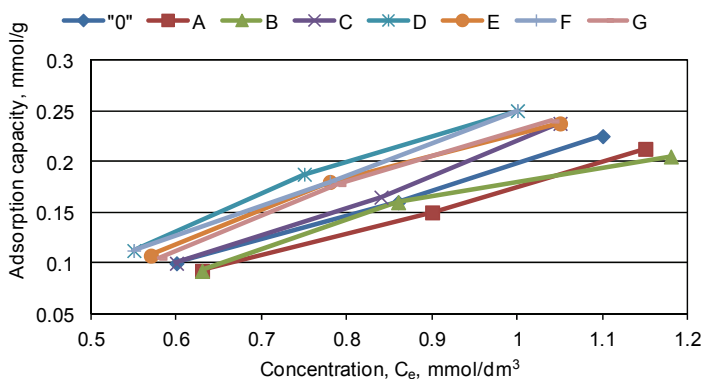


Fig. 5. Adsorption isotherms of imidazole at the initial pH (pH = 7.5)

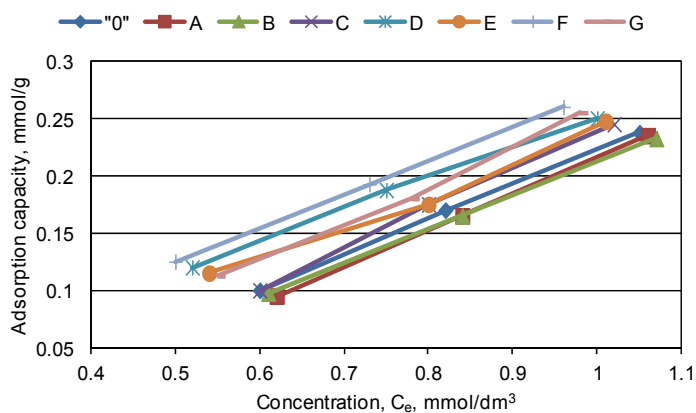


Fig. 6. Adsorption isotherms of imidazole at the pH = 3.0

3.4. PHENOL ADSORPTION

Adsorption isotherms at the initial pH and pH = 11.5 are presented in Figs. 7 and 8. The results obtained from the tests proved, that the highest sorption capacity towards phenol was observed for the solution of the concentration of 2 mmol/dm³ for both the initial pH and pH = 11.5. The lowest sorption capacity was observed for the solution of the concentration of 1 mmol/dm³, for both pH. In the case of sorption from the solution at pH = 11.5, the highest sorption capacities were obtained for D carbon (sonication time equal to 5 min, amplitude of 100%) whereas in the case of

the solution of the initial pH for the activated F carbon (sonication time equal to 15 min, amplitude of 100%).

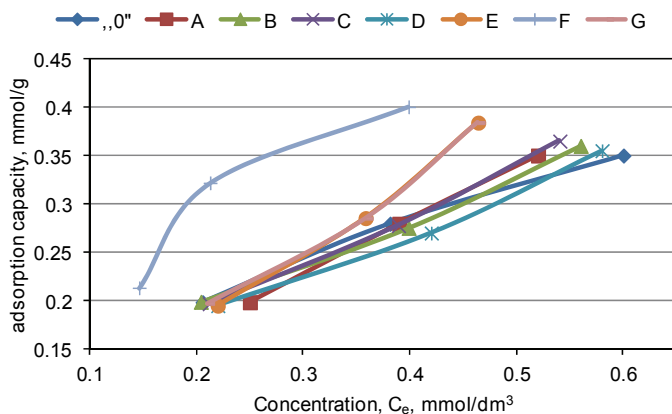


Fig. 7. Adsorption isotherms of phenol at the initial pH (pH = 7.0)

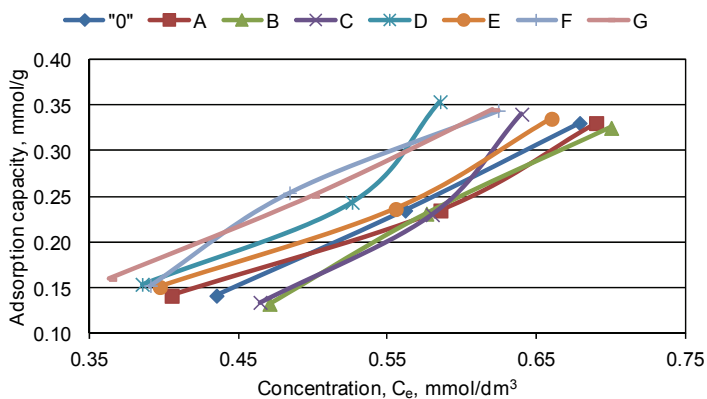


Fig. 8. Adsorption isotherms of phenol at the pH = 11.5

4. DISCUSSION

An important parameter in the sorption process of organic compounds on activated carbons is pH of the initial pH of the solution. The tests were conducted for the solutions at the initial pH (pH \approx 3.0 for phthalic and benzoic acids, pH = 7.5 for imidazole and pH = 7.0 for phenol) at which the acid was undissociated, and at pH = 8.0, 3.0 and 11.5 at which the organic compounds were fully dissociated. Dissociation significantly influences adsorption. Undissociated organic particles are bound during adsorption by van der Waals forces and that is the reason for the adsorption being

related with the specific surface area. In the case of dissociated particles, the dominant adsorption mechanism is ion exchange. Since the activated carbons are characterized by small number of alkali groups capable of ion exchange, sorption of dissociated particles is usually smaller. All conducted experiments proved, that the increase in pH caused reduction in effectiveness of sorption of a given organic substance, which is consistent with literature studies [3]. At lower pH of a solution, the particles of tested organic compounds occur in unionized form. As pH of a solution increases, the adsorption capacity decreases. Sonication of ROW 08 Supra carbon had a positive impact on the sorption effectiveness. Such modification caused an increase in the removal of substances from solutions of the initial pH values by several per cent. The highest sorption capacities were obtained for activated carbons modified with ultrasonic waves of 100% amplitude for 5 and 10 min. The carbons sonicated in the field of the 50% amplitude showed similar results in removing tested organic substances as the initial carbon.

The increase of adsorption effectiveness of tested compounds may be connected with the change of chemical character of carbon surface. During ultrasonic modification of activated carbon, its surface is treated by cavitation. The intensity of cavitation in water is about 1 W/cm^2 . The increase of intensity of ultrasonic field resulted in intensification of this effect. Thus under the experimental conditions (the intensity above 40 W/cm^2), the influence of ultrasonic modification probably had a great importance. The sharp thermodynamic conditions (500 atm, 5000 K) during cavitation generated considerable force power and caused emission of hydroxyl radicals $\cdot\text{OH}$. Hydrogen peroxide might also be formatted. As the phenomena of physicochemical nature occur mainly on the border of phase, the carbon surface in terms of its structure, is particularly exhibited to the ultrasonic effects. Modification of surface properties of activated carbon may be reached by oxidizing of hydroxyl oxygen groups. Mechanical reactions accompanying ultrasonic cavitation may also influence the changes of carbon surface. The effectiveness of physicochemical modification of the activated carbon depends on the ultrasonic field applied, being higher at the maximum value of ultrasound intensity.

5. CONCLUSIONS

- The activated carbons modified by ultrasonic field remove organic compounds better than the carbons before modification. The activated carbons treated by ultrasonic waves of the amplitude of 100% display larger sorption capacities towards organic compounds.
- pH of the solution from which the sorption is carried out influences the process of sorption. Lower final concentration was obtained at lower pH of the solution where

the particles of tested organic compounds occurred in unionized form. As pH of the solution increases, the adsorption capacity decreases.

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