



<sup>1</sup>Sabolč PAP, <sup>1</sup>Veselin BEŽANOVIĆ, <sup>1</sup>Mladenka NOVAKOVIĆ,  
<sup>1</sup>Dragan ADAMOVIĆ, <sup>1</sup>Ivana MIHAJLOVIĆ, <sup>1</sup>Maja ĐOGO, <sup>1</sup>Anica BABIĆ,  
<sup>1</sup>Sanja ŠARIĆ, <sup>1</sup>Jelena RADONIĆ, <sup>1</sup>Maja Turk SEKULIĆ

## **ADSORPTION OF PHOSPHATE AND ORGANIC MATTER FROM MEAT INDUSTRY WASTEWATER BY ACTIVATED CARBONS NORIT SA2, HYDRODARCO AND ZEOLITE ZSM-5**

<sup>1</sup> University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, Trg Dositeja Obradovića 6, 21 000 Novi Sad, SERBIA

**Abstract:** This paper presents the ability of new and not previously studied commercial activated carbons Norit SA2, Hydrodarco C and Zeolite ZSM-5 to remove phosphate ions and reduce the organic load, after the secondary treatment of the meat industry wastewater. The influence of pH, contact time and initial concentrations are studied. Adsorbent Hydrodarco C shows substantial capacity to adsorb phosphate ions, as well as organic matter from meat industry wastewater (removal efficiencies of 81.20% and 84.92%, respectively). The best fit of the experimental results with theoretical models was obtained for the Langmuir and Freundlich's equilibrium models, while the kinetics was the best described by the pseudo second-order model. This study proved the effectiveness of commercial activated carbons for removal of phosphate ions and organic matter and their possibility to be used for tertiary treatment of meat industry wastewater.

**Keywords:** phosphate, organic matter, meat industry wastewater, adsorption kinetics, commercial adsorbents

### **INTRODUCTION**

The wastewaters of meat industry are characterized by large organic load and high content of phosphorus and nitrogen as dominant pollutants that cause the degradation of water bodies of rivers and lakes [1-4]. The discharge of untreated or insufficiently treated wastewater with high concentration of phosphorous stimulates the growth of algae and other photosynthetic organisms in recipients and coastal areas and leads to eutrophication and disturbance of the natural balance of water bodies due to the reduction of dissolved oxygen [5, 6].

Increasingly stricter directives and regulations in the field of environmental protection require a lower concentration of phosphorus and organic load in wastewater streams, where their removal by conventional wastewater treatment systems represents a problem that has not been fully resolved. Quite often, the primary and secondary treatment processes in the wastewater treatment are not sufficient, therefore tertiary treatment of municipal and industrial

wastewater treatment has become a necessity which can meet the requirements that are in accordance with the stringent regulations on the issue of environmental protection [5].

The process of adsorption is one of the most effective methods for the treatment of wastewaters. The benefits of adsorption technology are reflected in high efficiency, easy operation, availability and cost-effectiveness of various adsorbents [2]. Activated carbon, natural and modified clays are used as adsorbents for the removal of pollutants from wastewater [7-12]. Natural clay has proven as a good adsorbent for the removal processes of cations of different metals and organic compounds [8, 13, 14].

Despite the large number of cited studies that describe adsorption processes on various adsorbents as a possible way of treating the municipal and industrial wastewaters [15, 16], studies on using commercial activated carbons as adsorbents for the removal of phosphorus compounds and reduction of organic load in the real samples have not been conducted in large

numbers. Therefore, it is necessary to conduct a research on adsorption capacity and characteristics of commercial activated carbons, as well as the possibilities of their use in tertiary treatment of meat industry wastewater.

The aim of this study was to assess the ability of commercial active carbons Norit SA2, Hydrodarco C and Zeolite Socony Mobil-5 (ZSM-5) to remove phosphate ions and reduce the organic load expressed as the chemical oxygen demand, after the secondary treatment of purification of the meat industry wastewater. During experimental research, the kinetics and adsorption equilibrium of commercial activated carbons in real samples in the pH range from 2 to 11 have been examined. In defining the adsorption equilibrium, Langmuir, Freundlich and Temkin equations have been used. Kinetics has been quantitatively determined by using models of pseudo-first- and pseudo-second-order.

## MATERIALS AND METHODS

### Adsorbents

Commercial activated carbons Norit SA2, Hydrodarco C and Zeolite ZSM-5 (manufacturer Acros Organics, Geel, Belgium) were used as adsorbents.

Activated carbon Hydrodarco C is a powdered activated charcoal with mesh pore structure and 1-150  $\mu\text{m}$  particle size. It is obtained from lignite, after activation by water vapor. It is used for the removal of organic substances from industrial and municipal wastewaters. Activated carbon Norit SA2 is produced from peat rich in organic carbon. It contains neither substances that can be harmful to the environment, nor compounds susceptible to bioaccumulation. Activated carbon Norit SA2 is not soluble in water (Table 1).

Table 1. Norit SA-2 and Hydrodarco C general characteristics

Property	Norit SA-2	Hydrodarco C
Methylene blue adsorption (g/100g)	15	9,3
Iodine number	850	550
Total surface area (BET) ( $\text{m}^2/\text{g}$ )	950	545
Apparent density (tamped) ( $\text{kg}/\text{m}^3$ )	460	388
Particle size $D_{10}$ ( $\mu\text{m}$ )	3	2
Particle size $D_{50}$ ( $\mu\text{m}$ )	20	13
Particle size $D_{90}$ ( $\mu\text{m}$ )	140	165
Ash content (mass %)	9	17.7
Moisture (as packed) (mass %)	2	5

Zeolite ZSM-5 is a type of a "high-silica"-Zeolite, which is responsible for most of its special properties. Zeolite ZSM-5 can be moderately hydrophilic to highly hydrophobic (depending on the Si/Al ratio). Zeolite ZSM-5 has a very high temperature and acid stability ( $>1000^\circ\text{C}$  and down to  $\text{pH}=3$ , respectively). It is

synthesized at high temperatures and pressures in an autoclave coated with Teflon and is characterized by low water solubility (Table 2).

Table 2. Zeolite ZSM-5 general characteristics

Property	Zeolite ZSM-5
Si/Al	37
$S_{\text{meso}}$ ( $\text{m}^2/\text{g}$ )	40
Total surface area (BET) ( $\text{m}^2/\text{g}$ )	390
Apparent density (tamped) ( $\text{kg}/\text{m}^3$ )	250
Particle size $D_{10}$ ( $\mu\text{m}$ )	4.5
$V_{\text{micro}}$ ( $\text{cm}^3/\text{g}$ )	0.17
$V_{\text{meso}}$ ( $\text{cm}^3/\text{g}$ )	0.09

### Wastewater samples

In four sampling campaigns during the spring, summer and autumn 2013 and the winter 2014 wastewater samples from the meat processing plants in the Province of Vojvodina, Republic of Serbia, were collected. Determination of their physico-chemical characteristics was conducted in order to get deeper insight into the current quality issues and to evaluate the efficacy of the applied treatment methods [1]. Only one of the selected meat processing industries has installed wastewater treatment plant. Hence, the meat industry wastewater collected after the secondary treatment of purification at a slaughterhouse in Vojvodina (Serbia) was used for adsorption experiments in our study.

The slaughterhouse has a modern system of wastewater treatment (Figure 1). The equipment installed in the purification system facilitates the treatment of the wastewater generated by the washing of slaughterhouses, meat processing plants, laboratories and vehicles for the transport of livestock and meat. The plant capacity is about 300  $\text{m}^3$  of wastewater per day. Pretreatment of wastewater in the plant involves the removal of burly material with coarse grid and the leveling of flow and composition of wastewater in the equalization tank (D and I). After the burly content removal, wastewater is transferred from the equalization tank to the flotation device by pumps (A and B). During the flotation process, suspended and floating particles are removed from the wastewater (oils, greases, emulsions). At the output of the flotation device, moderately purified water is separated from the waste sludge (F). Separated foam is removed from the surface of the flotation device by skimmers and is then transported to the waste sludge tank, while the incompletely purified water is transferred to the next tank for further treatment (G). The next step of the process is the biological treatment of wastewater (E and E1). During the biological treatment nitrification occurs. Nitrification is the biological oxidation of ammonia nitrogen to nitrite, followed by the oxidation of the nitrite to nitrate. After nitrification, the denitrification process follows, i.e. the biological reduction of nitrate to



molecular nitrogen (C). After the biological treatment, the disinfection of the effluent is carried out.

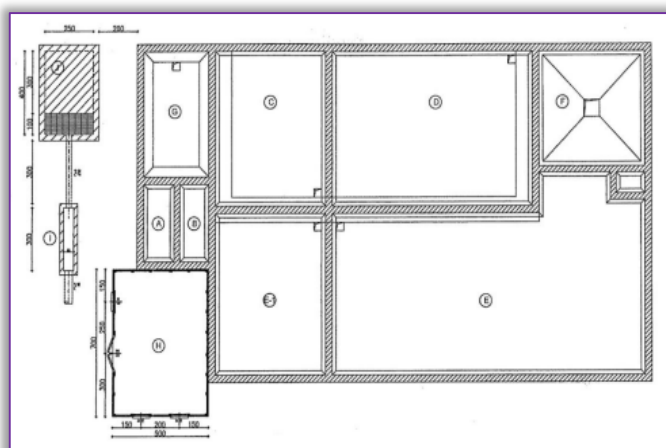


Figure 1. Scheme of the system for wastewater treatment – A – Balancing tank, B – Flotation tank, C – Denitrification, D – Flow equalization tank, E and E1 – Biological oxidation, F – Sedimentation tank, G – Sludge processing, H – Technical premises, I – Grid with channel, J – Pumping station

#### Reagents and adsorbates

For the purposes of the experiment, standard solutions of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and ADDISTA LCA 703 (Hach Lange GMBH, Dusseldorf, Germany) standards have been used. The initial concentrations of phosphate ions and organic load were 10 and 50  $\text{mg L}^{-1}$ , respectively. All solutions were prepared by diluting with a real sample of the meat industry wastewater collected after the secondary treatment of purification. Adjustment of pH value, before the start of and during the experiment was carried out by adding small volumes of 0.1 M NaOH or 0.1 M HCl with a micropipette.

All parameters were determined by using the standard Environmental Protection Agency (EPA) methods (EPA 365.3 for phosphate anions and EPA 410.4 for COD). The concentrations of phosphate ions and Chemical Oxygen Demand (COD) values were measured by Ultraviolet-Visible (UV-Vis) spectrophotometer DR 5000 (Hach Lange, Germany).

#### The influence of pH value

The pH of the solution affects the total surface charge of activated carbon and Zeolite. In the acidic solution, the area is protonated and therefore positively charged. In an alkaline solution protons are removed from the surface, and therefore it becomes negatively charged. Hence, it is very important to investigate the effect of pH on removal efficiency of selected contaminants typical for the wastewater pollution.

Multiparameter device, Multi 340i (WTW Germany), was used for measuring the initial pH value of suspension obtained by adding 0.2 g of the adsorbent, in the form of commercial activated charcoal, in 50 mL of experimental samples, additionally spiked with  $\text{KH}_2\text{PO}_4$  and ADDISTA LCA 703 to obtain final concentrations of

10  $\text{mgL}^{-1}$  and 40  $\text{mgL}^{-1}$ , respectively. The initial pH values of suspensions spiked with phosphate ions and organic matter were: 8.30, 8.48 and 8.21, respectively. In order to examine the characteristics of adsorbents in acidic, basic and neutral media, pH value was adjusted by titration using hydrochloric acid or sodium hydroxide. During examining the adsorption characteristics of adsorbents in relation to phosphate ions, pH value was set at the following levels: pH=2, pH=4, pH=7, pH=9 and pH=11. In the case of testing of the reduction of organic load, pH value was adjusted by titration to levels: pH=3, pH=5, pH=7 and pH=9.

#### Kinetics of adsorption

The adsorption kinetics of organic matter was evaluated for the initial concentration of 40  $\text{mgL}^{-1}$ . In neutral conditions (pH = 7), 0.2 g of commercial activated carbons (Norit SA2 and Hydrodarco C) was used in different contact time. The phosphate ions adsorption kinetics was studied for activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM-5. Wastewater from the meat processing industry was spiked with standard solution of  $\text{KH}_2\text{PO}_4$ , to a concentration of 10  $\text{mg L}^{-1}$ , 0.2 g of the adsorbent was added, and the pH value was adjusted to 9.

The mixing procedure was carried out at a Heidolph shaker Unimax 1010 with fixed speed (140 rpm) for the periods of 5, 10, 20, 30 and 40 minutes. Adsorbed amount,  $q_e$  ( $\text{mg g}^{-1}$ ), was calculated via the equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$C_0$  - the initial concentration of adsorbate,  
 $C_e$  - the residual concentration of adsorbate,  
 V - the volume of solution,  
 m - the mass of adsorbent.

The removal efficiency is defined by the equation:

$$R_e (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

In order to determine the kinetics and mechanism of adsorption, different initial concentrations of organic matter (5-50  $\text{mg L}^{-1}$ ) and phosphate ions (1-20  $\text{mg L}^{-1}$ ) were used. Two kinetic models were tested: pseudo first-order model and pseudo second-order model. Kinetic models of pseudo-first- and pseudo second-order together can provide a simple and satisfactory explanation of the adsorption process. Linearized forms of the equations of pseudo first- and pseudo second-order kinetic models can be used to calculate the values of characteristic kinetic parameters. Pseudo first-order model is the oldest model which describes the speed of adsorption based on the adsorption capacity. This model in a real system corresponds mainly to the adsorption at low adsorbate concentrations and it is presented by the equation:

$$\log (q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (3)$$





where  $K_1$  ( $\text{mg g}^{-1}$ ) presents adsorption constant of pseudo first-order kinetic model and can be determined by the graph  $\log(q_e - q_t)$  as a function of  $t$ .

Pseudo second-order model is based on the assumption that the adsorption could be explained by the second order chemisorption processes:

$$t / q_t = 1 / (K_2 q_e^2) + t / q_e \quad (4)$$

from graph  $t/q_t$  versus  $t$ .

#### Adsorption equilibrium

The data on the influence of different initial concentrations of pollutants on the residual concentrations in a solution is the basis for obtaining the data on the adsorption equilibrium. In the experiments, 0.2 g activated carbon samples were mixed for 30 min with 50 mL solutions of various organic matter and phosphate ion concentrations ranging from 5 mg/L to 50 mg/L. Langmuir, Freundlich and Temkin adsorption isotherms were used in this paper to define the adsorption equilibrium. The parameters were obtained by linear regression.

The linear form of the Langmuir isotherm is represented by the equation:

$$C_e / q_e = C_e / q_{\max} + (1 / K_L q_{\max}) \quad (5)$$

where  $C_e$  is the equilibrium concentration of adsorbate ( $\text{mg L}^{-1}$ ),  $q_e$  equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_L$  the Langmuir constant ( $\text{L mol}^{-1}$ ) related to the free energy of adsorption and  $q_{\max}$  ( $\text{mg g}^{-1}$ ) theoretical monolayer saturation capacity.

Freundlich's isotherm model is empirical and based on the existence of heterogeneous energy adsorption centers on the surface of the adsorbent. The linear form of this isotherm is represented by the equation:

$$\log q_e = \log K_f + (1 / n) \log C_e \quad (6)$$

where  $K_f$  ( $\text{L g}^{-1}$ ) presents Freundlich's constant, and  $n$  is Freundlich's exponent which shows how adsorption is favored. The linear form of Freundlich isotherm and its graphical representation  $\log q_e$  to  $\log C_e$  are needed to determine the values of  $K_f$  and  $n$ . Ratio of  $1 / n$  ranges from 0 to 1 and the intensity of adsorption is greater when this value is lower.

Linear form of Temkin isotherm is represented by the equation:

$$q_e = B \ln A_T + B \ln C_e \quad (7)$$

where  $A$  and  $B$  are constants which could be determined by graphical presentation of isotherm.

## RESULTS AND DISCUSSION

Applied pre-, primary and secondary treatment of wastewater within the meat processing plant improved the quality of water by reducing COD and  $\text{BOD}_5$  (Biochemical Oxygen Demand 5-day test) values from 96% to 98.6%, while phosphorus concentrations were only partially removed from 15.29% to 68.48%. Even after treatment, concentration levels of phosphorus

were eight times higher than the maximum allowed value prescribed by the Regulation of the Republic of Serbia (No. 67/2011) [17]. Therefore, special attention was focused on removal efficiency of phosphate anions from meat industry wastewater effluent.

#### Effect of pH

Influence of pH on removal efficiency of organic matter and phosphate ions by adsorption on commercial activated carbons Norit SA2, Hydrodarco C and Zeolite ZSM-5 were presented in Figure 2 and 3.

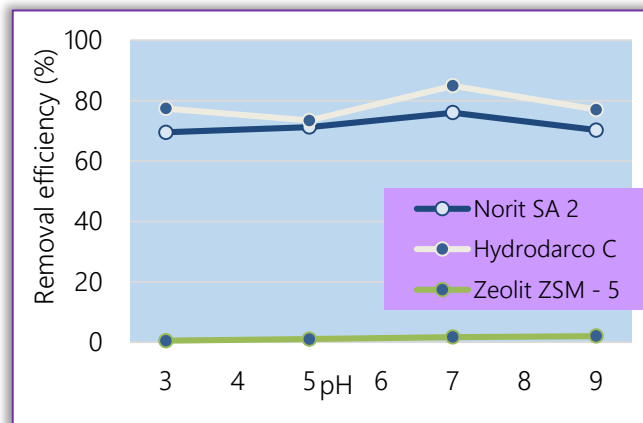


Figure 2. Effect of pH on removal efficiency of organic matter adsorption on different types of activated carbons and Zeolite

The results presented in Figure 2 indicate that the removal efficiency of organic matter was 69.50% and 84.92% for commercial activated carbon Norit SA 2 and Hydrodarco C, respectively. pH value didn't influence significant changes in adsorption capacity. However, the adsorption was most favored in neutral solution with the efficiency of adsorption 76.00% and 84.92% for Norit SA2 and Hydrodarco C, respectively. Therefore, the further studies of organic matter adsorption were performed at  $\text{pH}=7$ . During the adsorption process, the pH should be constant. In the practical use, it would be necessary to pay special attention on setting the pH value of the suspension.

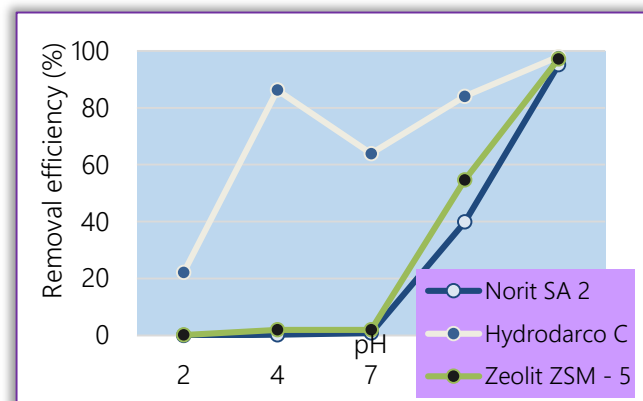


Figure 3. Effect of pH on removal efficiency of phosphate anions by adsorption on different types of activated carbons and Zeolite





Organic matter removal on Zeolite ZSM-5 was 2%, which indicates that ZSM-5 cannot be applied for the reduction of organic matter from aqueous solutions.

The highest removal efficiency of phosphate anions was achieved on pH = 11 for adsorbents Norit SA 2, Hydrodarco C and ZSM-5 (Figure 2).

However, due to cost effectiveness and commercial viability of adsorption process, pH = 9 was used for further adsorption studies. In basic solution (pH=9), removal efficiency of phosphate anions was 39.90%, 84.00% and 54.70%, respectively for above mentioned adsorbents. The results indicated that Hydrodarco C was the most efficient adsorbent for phosphate anions removal from meat industry wastewater. High specific surface area, wide range of different sizes pore distribution and a hydrophobic surface of activated carbon are the main features that make this adsorbent more efficient than Zeolite for removing phosphate anions from water.

#### Adsorption kinetics of organic matter

The organic matter adsorption results (Figure 4 and Figure S11 - appendix) showed that a rapid uptake takes place on activated carbon Norit SA 2 within the first 30 min. After this time, the rate of organic matter uptake was reduced as the equilibrium approached. The removal efficiency of organic matter amounts to 80.80% on activated carbon Norit SA2 and 81.68% on activated carbon Hydrodarco C.

The data presented in supplementary (see Figure S1 and S2) were used to determine kinetic parameters in the kinetic models tested (Table 2).

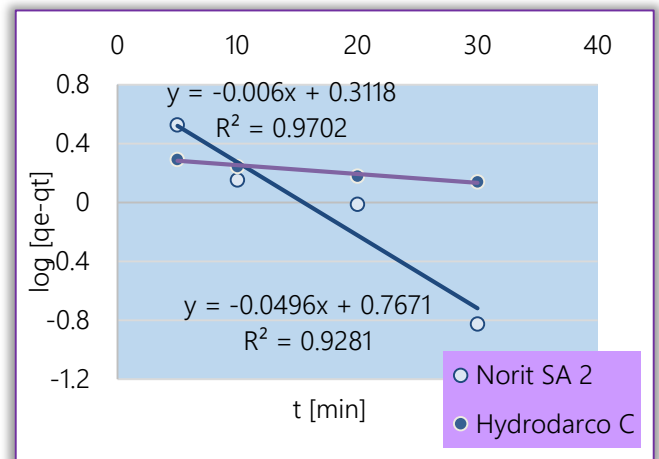


Figure S1. Kinetic pseudo – first order model for adsorption of organic matter on different types of activated carbons

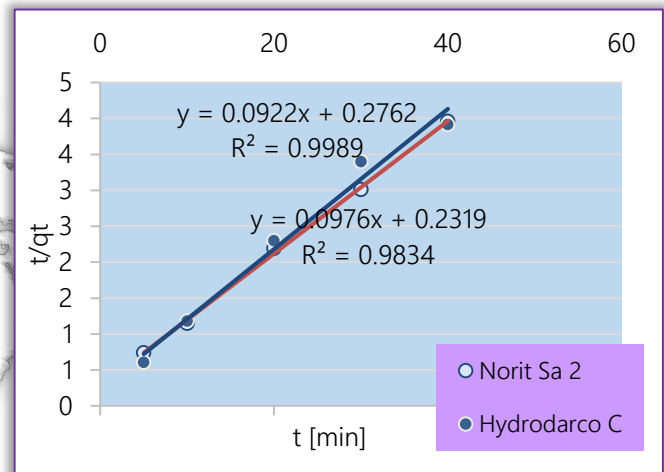


Figure S2. Kinetic pseudo – second order model for adsorption of organic matter on different types of activated carbons

Based on the values of the kinetic parameters shown in Table 3, it can be concluded that the adsorption kinetics of organic matter on activated carbons Norit SA 2 and Hidrydarco C could be better explained by the pseudo second-order kinetic model.

It is confirmed by the excellent agreement between experimental values obtained for the adsorption capacity ( $q_e=10.100 \text{ mg g}^{-1}$ ) with a calculated maximum adsorption capacity for pseudo second-order model ( $q_e=10.845 \text{ mg g}^{-1}$ ).

#### Adsorption kinetics of phosphate anions

The phosphate adsorption results showed that within the first 30 min a rapid uptake of phosphate ions takes place (Figure 5 and Figure S12 - appendix). The same conclusion was obtained by Benyoucef and Amrani (2011).

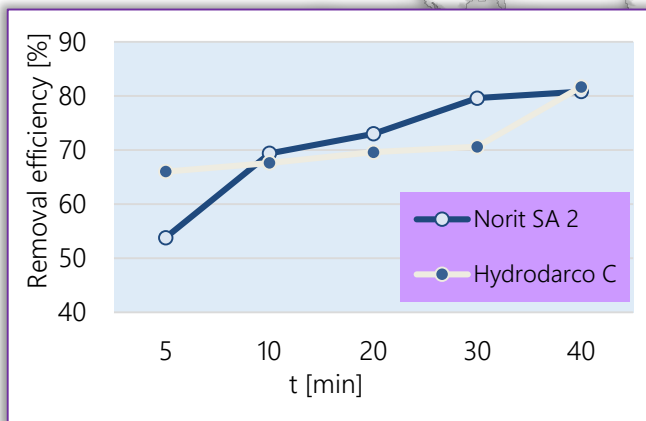


Figure 4. Effect of contact time on removal efficiency of organic matter by adsorption on activated carbons Norit SA 2 i Hydrodarco C

Table 3. The kinetic parameters of organic matter adsorption on activated carbons Norit SA 2 and Hydrodarco C

Pseudo first-order model			
Activated carbon type	R <sup>2</sup>	k <sub>1</sub> [gmg <sup>-1</sup> min <sup>-1</sup> ]	q <sub>e</sub> [mg g <sup>-1</sup> ]
Norit SA2	0.9281	0.1142	5.8492
Hydrodarco C	0.9702	-0.0138	2.0500
Pseudo second-order model			
Activated carbon type	R <sup>2</sup>	k <sub>2</sub> [gmg <sup>-1</sup> min <sup>-1</sup> ]	q <sub>e</sub> [mg g <sup>-1</sup> ]
Norit SA2	0.9989	32.4940	10.8450
Hydrodarco C	0.9834	24.3400	10.2450



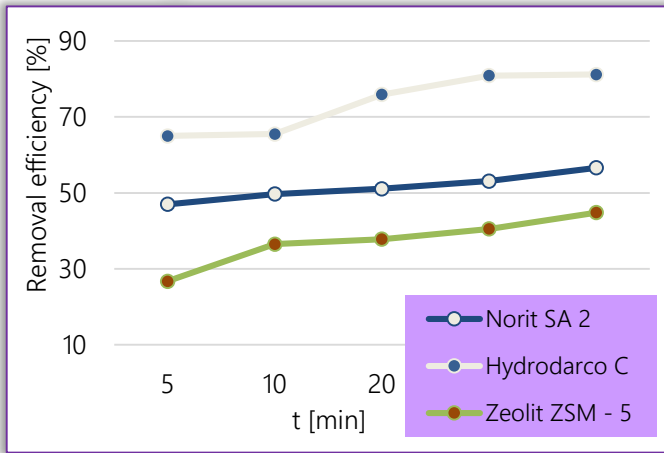


Figure 5. Effect of contact time on removal efficiency of phosphate anions by adsorption on activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM-5

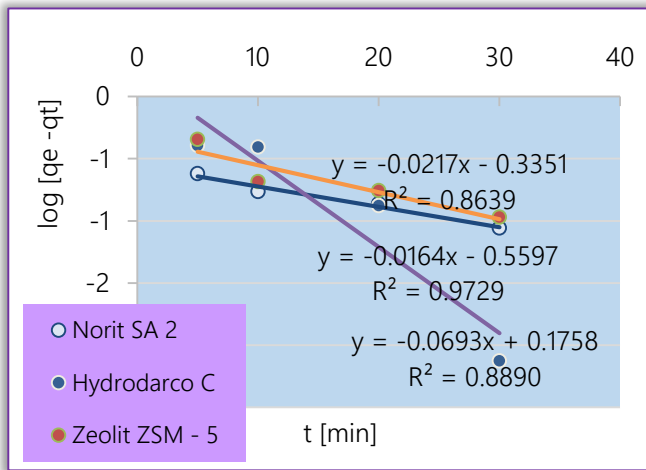


Figure S3. Kinetic pseudo – first order model for adsorption of phosphate anions on activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM - 5

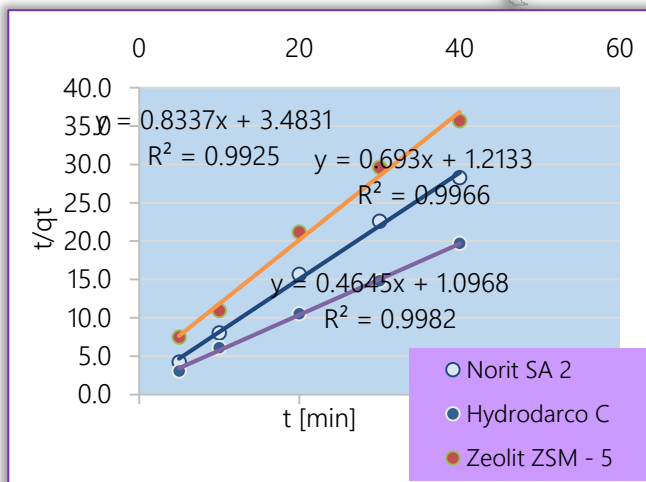


Figure S4. Kinetic pseudo – second order model for adsorption of phosphate anions on activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM - 5

The highest degree of phosphate ions reduction was achieved for activated carbon Hydrodarco C, and amounted to 81.20% after the equilibrium was achieved. The removal efficiency of phosphate ions in the case of

Norit SA2 slightly raised during time, and amounted to 56.60% after 40 min. Adsorption of phosphate ions on Zeolite ZSM-5 showed the lowest removal efficiency, and amounted to 44.80%.

According to the data shown in supplementary (see Figure S3 and S4), kinetic parameters were calculated and presented in Table 4.

Table 4. The kinetic parameters of phosphate anions adsorption on activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM-5

Pseudo first-order model			
Adsorbent type	R <sup>2</sup>	k <sub>1</sub> [gmg <sup>-1</sup> min <sup>-1</sup> ]	q <sub>e</sub> [mg g <sup>-1</sup> ]
Norit SA 2	0.9729	-0.0377	0.2756
Hydrodarco C	0.8890	-0.1596	1.4990
Zeolite ZSM-5	0.8639	-0.0500	0.4623
Pseudo second-order model			
Adsorbent type	R <sup>2</sup>	k <sub>2</sub> [gmg <sup>-1</sup> min <sup>-1</sup> ]	q <sub>e</sub> [mg g <sup>-1</sup> ]
Norit SA 2	0.9966	0.3958	1.4431
Hydrodarco C	0.9982	0.1968	2.1526
Zeolite ZSM-5	0.9925	0.1996	1.1994

Correlation coefficients presented in Table 3 confirmed that adsorption kinetics of phosphate anions on activated carbons Norit SA 2, Hidrydarco C and Zeolite ZSM-5 fit to the pseudo second-order model, indicating that binding of the adsorbate to the adsorbent surface occurs by chemical bonding.

#### Adsorption isotherms of organic matter on activated carbons Norit SA 2 and Hydrodarco C

Removal efficiency and q<sub>e</sub> of organic matter on the activated carbons Norit SA2 and Hydrodarco C for different initial concentrations of organic matter at pH =7 is presented on Figure 6 and Figure S13 (appendix).

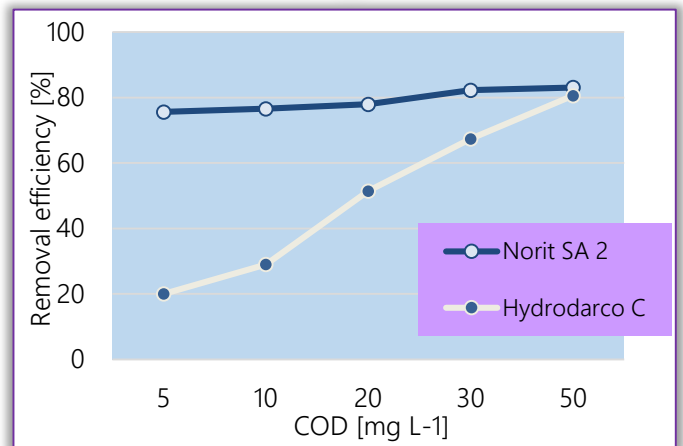


Figure 6. Effect of initial concentration of organic matter on its removal efficiency by adsorption on activated carbons Norit SA 2 and Hydrodarco C

Increase of initial concentration of adsorbate caused better removal efficiency on activated carbon Hydrodarco C, while removal efficiency remained constant (about 80%) for whole range of organic matter initial concentrations on activated carbon Norit SA2.



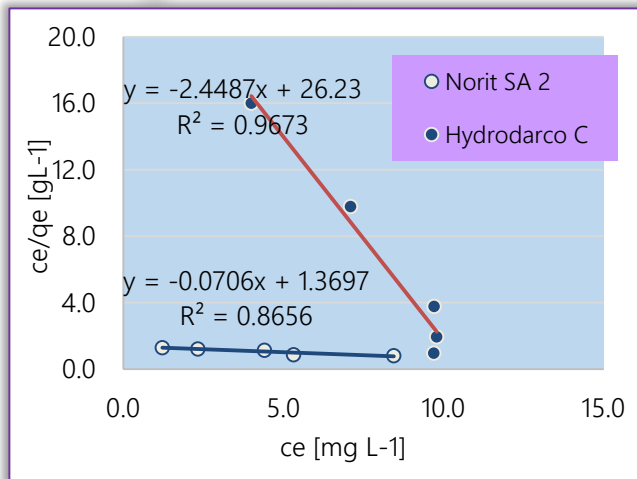


Figure S5. Langmuir isotherm of organic matter adsorption on activated carbons Norit SA 2 and Hydrodarco C

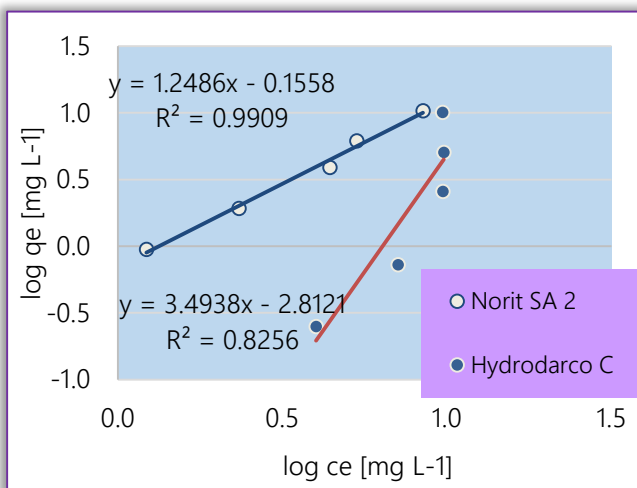


Figure S6. Freundlich isotherm of organic matter adsorption on activated carbons Norit SA 2 and Hydrodarco C

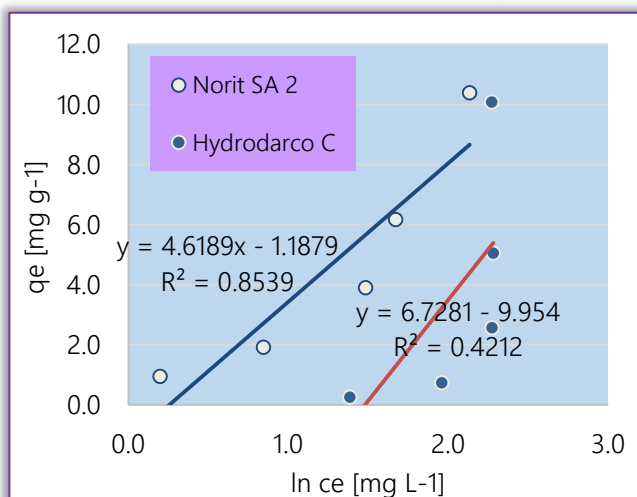


Figure S7. Temkin isotherm of organic matter adsorption on activated carbons Norit SA 2 and Hydrodarco C  
Linear forms of Langmuir, Freundlich and Temkin equations are presented in supplementary data (see Figure S5-S7). Correlation coefficients are calculated and presented in Table 5.

Table 5. Isotherms used for description of organic matter adsorption onto Norit SA 2 and Hydrodarco C, including the calculated correlation coefficients

Langmuir	Activated carbon type	$K_L$ [L mol <sup>-1</sup> ]	$q_0$ [mg g <sup>-1</sup> ]	$R^2$ [-]
	Norit SA 2	0.730	14.17	0.865
Hydrodarco C	0.038	0.410	0.967	
Freundlich	Activated carbon type	$K_F$ [L g <sup>-1</sup> ]	$n$ [-]	$R^2$ [-]
	Norit SA 2	0.699	10.373	0.991
Hydrodarco C	0.002	1.840	0.826	
Temkin	Activated carbon type	A [L g <sup>-1</sup> ]	B [Lg <sup>-1</sup> ]	$R^2$ [-]
	Norit SA 2	-1.187	4.618	0.854
Hydrodarco C	-9.954	6.728	0.421	

Adsorption of organic matter on activated carbon Norit SA 2 is the best explained by Freundlich equilibrium model ( $R^2=0.991$ ). High correlation coefficient indicates that the physical adsorption predominates in the total adsorption of organic substances on activated carbon Norit SA 2. Freundlich exponent  $n$  is 10.73, which indicates the energy heterogeneous surface. As  $n > 1$ , with increasing concentration of adsorbate, free energy for further adsorption increases, proving physical adsorption as dominant process.

Adsorption of organic substances on activated carbon Hydrodarco C best fit to the Langmuir isotherm ( $R^2=0.967$ ). The relatively high value of the correlation coefficient indicates that the Langmuir model provides relatively good agreement with the experimental data and therefore it can be concluded that the chemisorption is dominant process.

#### Adsorption isotherms of phosphate ions on activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM-5

Removal efficiency and  $q_e$  of phosphate ions for different initial concentrations and pH=9 is presented on Figure 7 and Figure S14 (appendix).

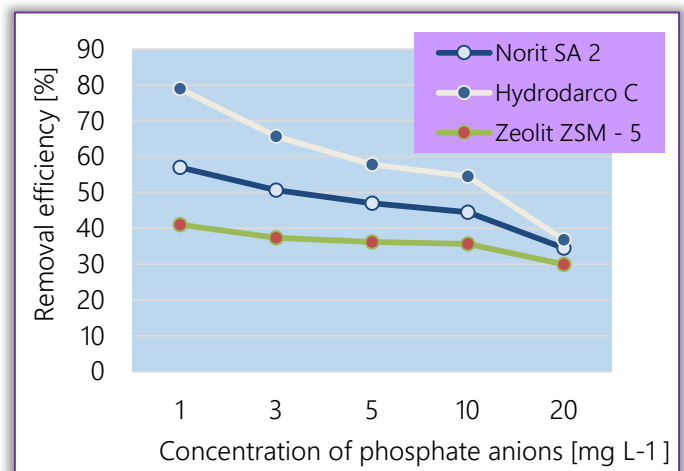


Figure 7. Effect of initial concentration of phosphate ions on their removal efficiency by adsorption on activated carbons Norit SA 2, Hydrodarco C and Zeolite ZSM-5



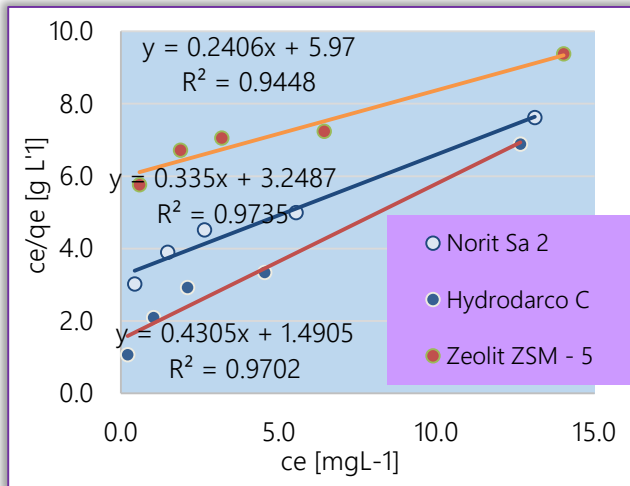


Figure S8. Langmuir isotherm of phosphate ions adsorption on activated carbons Norit SA 2, Hydrodarco C and zeolite ZSM-5

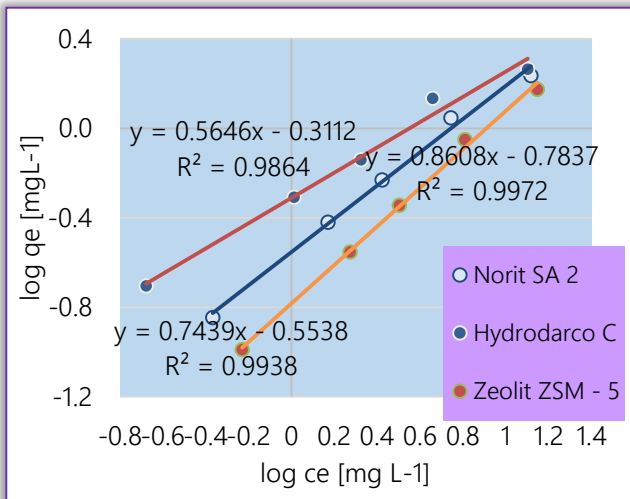


Figure S9. Freundlich isotherm of phosphate ions adsorption on activated carbons Norit SA 2, Hydrodarco C and zeolite ZSM-5

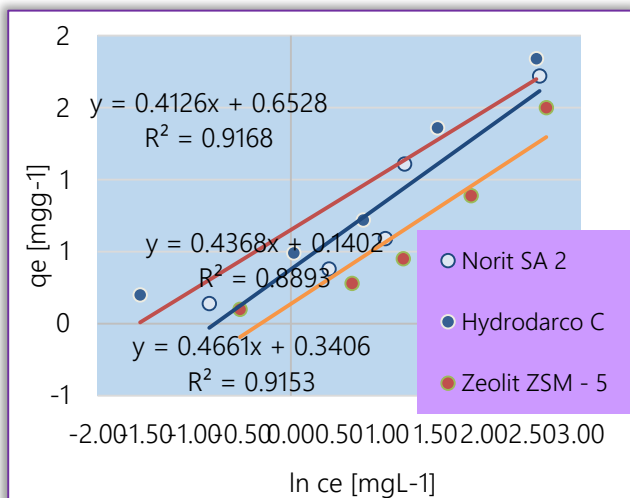


Figure S10. Temkin isotherm of phosphate ions adsorption on activated carbons Norit SA 2, Hydrodarco C and zeolite ZSM-5

The efficiency of phosphate ions removal decreases with the increase of their initial concentrations in all cases. The highest reduction was obtained for adsorption on Hydrodarco C and it ranges from 37% to 79%, while the lowest removal was achieved for Zeolite ZSM-5 in the range from 30% to 41%.

Linear forms of Langmuir, Freundlich and Temkin equations are presented in supplementary data (Figure S8-S10). Correlation coefficients are calculated and presented in Table 6.

Table 6. Isotherms used for description of phosphate ions adsorption onto Norit SA 2, Hydrodarco C and Zeolite ZSM-5, including the calculated correlation coefficients

Langmuir	Adsorbent type	$K_L$ [L mol <sup>-1</sup> ]	$q_0$ [mg g <sup>-1</sup> ]	$R^2$ [-]
	Norit SA 2	0.308	2.98	0.973
	Hydrodarco C	0.671	2.32	0.970
Zeolite ZSM-5	0.168	4.16	0.944	
Freundlich	Adsorbent type	$K_F$ [L g <sup>-1</sup> ]	$n$ [-]	$R^2$ [-]
	Norit SA 2	0.279	1.344	0.994
	Hydrodarco C	0.488	1.771	0.986
Zeolite ZSM-5	0.165	1.162	0.997	
Temkin	Adsorbent type	A [L g <sup>-1</sup> ]	B [L g <sup>-1</sup> ]	$R^2$ [-]
	Norit SA 2	0.341	0.466	0.915
	Hydrodarco C	0.653	0.413	0.917
Zeolite ZSM-5	0.140	0.437	0.889	

Adsorption of phosphate ions could be explained the best by Freundlich equilibrium model for all adsorbents. Similar results have been reported for the adsorption of phosphate by modified sawdust [18, 19]. High correlation coefficients indicate that the physical adsorption predominates in the phosphate ions adsorption on activated carbons and Zeolite ZSM-5.

### CONCLUSIONS

This study showed that commercial activated carbons Norit SA2 and Hydrodarco C can be used for organic matter removal from real samples of waste water from the meat industry after the secondary treatment.

High removal efficiency of organic matter is achieved in neutral conditions (pH = 7) for activated carbons Hydrodarco C (84.92%) and Norit SA2 (76.00%). Extremely low level of organic matter separation on the Zeolite ZSM-5 in acidic, neutral and alkaline conditions indicates that aforementioned adsorbent can not be applied for the separation of organic matter from real aqueous solutions.

The kinetic modeling studies show that adsorption kinetics of organic matter follow pseudo second-order model. The equilibrium studies proved that Freundlich isotherm model best describes the adsorption of organic matter on the activated carbon Norit SA2, while the adsorption equilibrium of organic matter on activated carbon Hydrodarco C could be best described by the Langmuir isotherm model.







Adsorbent Hydrodarco C proved to be very effective in the reduction of phosphate ions from meat industry wastewater (removal efficiency of 81.20%). The effectiveness of adsorption process decreased with increasing initial concentration of phosphate ions. The kinetic modeling studies showed that kinetics of phosphate ions on Norit SA2, Hydrodarco C and the Zeolite ZSM-5 follow the model of pseudo - second order. Freundlich isotherm model the best describes the equilibrium of phosphate ions adsorption on above mentioned adsorbents.

Our study proved the effectiveness of commercial activated carbons for removal of phosphate ions and organic matter and their possibility to be used for tertiary treatment of meat industry wastewater.

#### APPENDIX

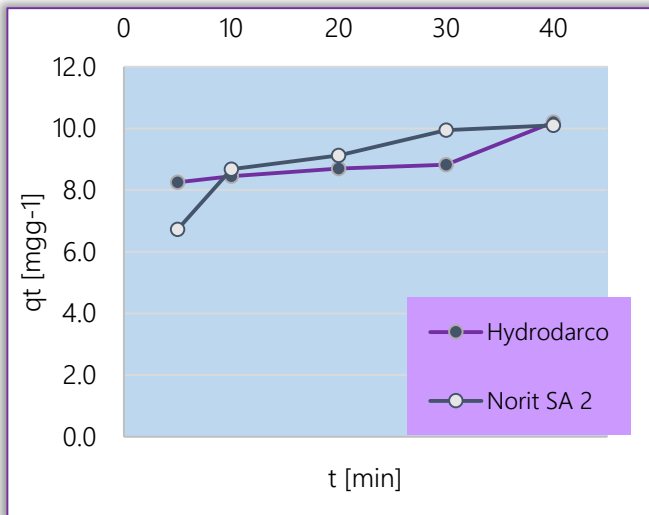


Figure S11. The kinetic data for organic matter adsorption on activated carbons Norit SA 2 and Hydrodarco C

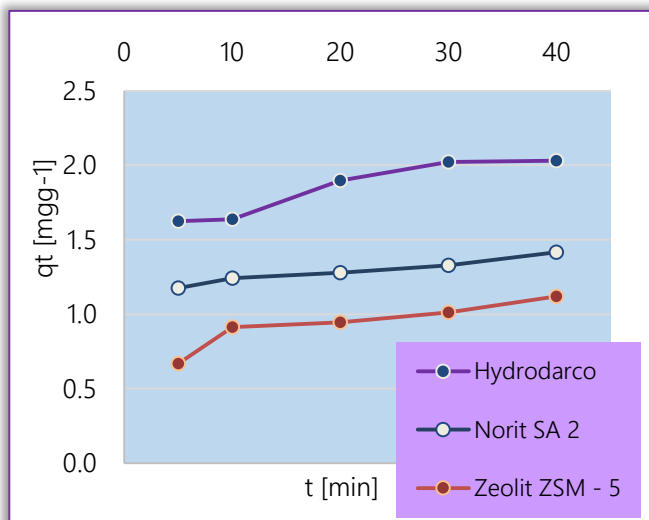


Figure S12. The kinetic data for phosphate ions adsorption on activated carbons Norit SA 2, Hydrodarco C and zeolite ZSM-5

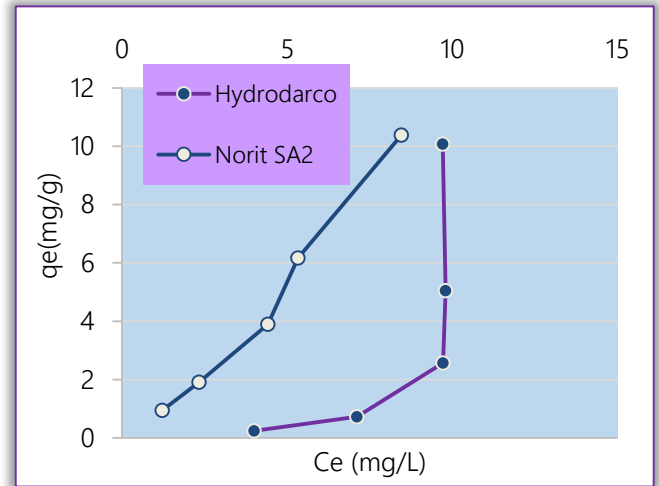


Figure S13. Adsorption isotherms for organic matter adsorption on activated carbons Norit SA 2 and Hydrodarco C

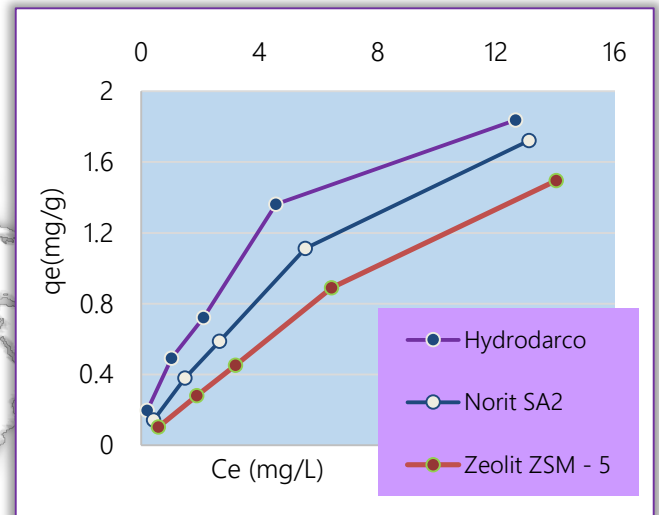


Figure S14. Adsorption isotherms for phosphate ions adsorption on activated carbons Norit SA 2, Hydrodarco C and zeolite ZSM-5

#### Acknowledgement

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University POLITEHNICA Timisoara,  
Faculty of Engineering Hunedoara,  
5, Revolutiei, 331128, Hunedoara, ROMANIA  
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