Removal of selected pesticides from water using granular activated carbon

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Abstract. Pesticides are intensively used for the protection of field crops, orchards and vineyards, but they are also used in the removal of undesirable stands on non-agricultural land (railway embankments, playgrounds, handling areas, etc.), in water management (in coastal management, destruction of growths in irrigation canals), in forestry, etc. Regular application of pesticides increases their content in the aquatic environment and agricultural products. Their occurrence in water is relatively common and it follows that these substances are used in large quantities. Residues of these substances can persist in soils for 2 to 12 weeks. Due to their good solubility in water, they are easily transported from the soil to aquifers. Several methods can be used to remove pesticides from water, e.g., coagulation, filtration, precipitation, ozonation, adsorption, ion exchange, nanofiltration, reverse osmosis and advanced oxidation processes. Their effectiveness varies considerably and depends mainly on the chemical nature of the pesticide being removed.

This article studies adsorption on two granular activated carbons Filtrasorb 400 and Norit 1240. Mixture of the pesticide standards (acetochlor, alachlor, dimethachlor, propachlor, metazachlor and metolachlor) was added to drinking water with concentration of approximately 1 µg/L. The experiments were performed in the glass bottles with the volume of 200 mL of water. The granular activated carbons (200 mg) were added to the bottles. Subsequently these bottles were regularly stirred, and the samples were taken out at times 0, 30, 60, 90, 120, 180, 240 and 360 minutes. Samples were taken by pipette into the 40 ml glass vials with added thiosulphate for preservation. Analyses of target pesticides were performed in laboratories of ALS Czech Republic in Prague. LC-MS using the internal standard method was used to determine chlorinated pesticides in water samples. The adsorption efficiency of pesticides removal and the adsorption capacity of granular activated carbon depends on the time of contact of water with the material. The results showed that the efficiency of selected pesticides removal and adsorption capacity for two granular activated carbons used varied. Filtrasorb F400 proved to be a better sorption material than Norit 1240. The efficiency of this material ranged from 18 to 60%, while the efficiency of Norit 1240 was significantly lower.

Adsorption capacity of activated carbons for selected pesticides and reaction kinetics of 0th, 1st, 2nd and 3rd order was also studied.

1. Introduction

In the last decade, traces of micropollutants (pharmaceuticals, drugs, pesticides and their metabolites, microplastics, etc.) typically at levels in the nanograms to micrograms per litre range, have been reported in the water cycle, including surface waters, wastewater, groundwater and, to a lesser extent, drinking water. Advances in analytical technology have been a key factor driving their increased detection.
Pesticide substances are one of the major pollutants of water. They are among the undesirable substances that have a negative effect on human health. The behaviour of pesticides after their application to the environment and the possible presence of their residues in groundwater and surface water depends on the physicochemical properties of the particular ‘substance active’ as well as on the whole product itself, the way of application (dose, time of period) and on the agroclimatic conditions. Metabolites of these pesticides are relevant and irrelevant while their relevance is considered within the approval process of the ‘substance active’ [1].

Pesticides are preparations for plant health protection that are used to eliminate the plant and animal pests. They can be categorized by the purpose of their use as insecticides, fungicides and herbicides. Insecticides are aimed against insects that act towards the agricultural crops, fungicides against the damaging parasitic fungi and herbicides are aimed against weed species. There are other categories the pesticides can be assorted in, such as acaricides (against mites), nematocides (eel), molluscocides (molluscs) and rodenticides (against rodents).

The limit for pesticides in water in Slovakia is laid down by the Decree of the Ministry of Health of the Slovak Republic No. 247/2010 Col., which provides the detailed requirements on drinking water quality, drinking water control, monitoring programme and risk management related to drinking water supply. Annex 1 and 2 provide the drinking water quality parameters, their limits, and range and frequency of analyses for the minimal and for the complete analysis. Within the meaning of Annex 1 and Annex 2, complete analysis involves the examination of water parameters, particular pesticides and pesticides together. Limit value for each particular pesticide is set to 0,10 μg/l with the exception for aldrin, dieldrin, heptachlorine and heptachlorinepoxide with the limit concentration of 50 μg/l. These limits are the highest limit values and their exceedance classifies the water as unusable for human consumption. Organic insecticides, herbicides, fungicides, nematocides, acaricides, algicides, rodenticides, slimicides and similar products (growth regulators) are considered pesticides and their relevant metabolites. Only those pesticides are a matter of laboratory determination and evaluation whose presence can be presupposed [2].

The subjected Decree No. 247/2017 Col. does not set the criteria for relevance of metabolites of certain pesticides and does not set the limits for irrelevant metabolites of pesticide substances. Requirements of the decree are in line with the current EU Council Directive 98/83/EC from 3rd November 1998 on the quality of water intended for human consumption, which does not cover the issue in much detail, either. There are about 1300 ‘active substances’ recorded within the European Union – the pesticides for plant health protection. Among this total number, 350 of the active substances are listed as admitted active substances (which represents 28,6%) and their use in the EU is allowed. Other 59 substances are under ongoing evaluation (4,8%) in order to place them on the list of admitted substances and 814 substances are not listed and their use in the EU is not allowed (66,6%). About 250 pesticides have been registered for plant health protection in the Slovak Republic [3].

Regarding the human health, the chlorinated pesticides are the most used and most dangerous pesticides due to their toxicity, carcinogenicity and mutagenicity. Chlorinated pesticides have a high persistence in the environment. They accumulate mainly in the fat tissue, liver, kidneys, muscles, brain and in the heart as well. Acute intoxication is usually manifested in loss of weight and paralysis of the central nervous system afterwards. Apepsy, headache, hyperphonia and total exhaustion occur in relation with the chronic intoxications while the nervous and mental defects occur later on. Those are the reasons why the use of them has been prohibited in many countries or permitted only in exceptional cases [4].

The content of pesticides in water environment and agricultural products increases by their regular application. Their presence in water is quite frequent and that means these substances are used in large quantities. The great issue related to pesticides is represented by their low biodegradability and their long persistence in water environment – as the original substances, as their metabolites (approx.. 1-2 years). Having good solubility, they can be easily transported in the water or from soil into the watered horizons [5].

Important factors that have an impact on pesticide potential to cause pollution of water are the following: pesticide solubility, distance of application from the expanse of water or a flow, weather, type of soil,
down-sloping, presence and density of cultivated crops, method and technique of application of agrochemicals.

Continual monitoring of these substances is not real due to the difficulty and cost of the analyses. Increased attention is paid to the pesticide monitoring in Slovakia as well as the EU as a result of potential risk, and also due to the proven pollution caused by the pesticides. In regard of the duty to monitor the relevant pesticides in drinking water since 1st January 2019, which was imposed by the new legislation, the need to make the new and current list of relevant pesticides for ground water used for drinking purposes in Slovakia emerged.

Analytic determination of pesticides depends on the capability of facility (measurement equipment, availability of chemicals and standards), purpose of analysis, type of the sample and total level of their content in the sample. Chromatographic methods are currently the most used, including the high performance liquid chromatography (HPLC) and gas chromatography (GP) combined with the mass spectrophotometry (MS). The current analytic methods make possible to determine the concentration at the level of ng/l [6,7].

Several methods can be used for removing the pesticides from the water, e.g. coagulation, precipitation filtration combined with coagulation, biodegradation, ozonisation, adsorption, ion exchange, nanofiltration, reverse osmosis and advanced oxidative processes. Their efficiency varies significantly and depends mainly on the chemical nature of the pesticide to be removed [8-10].

The most used sorption material to remove the organic pollution (pesticides, micropollutants) from water is activated carbon (powder, granules, extruded, with a treated surface). There are many publications within which the efficiency of removal of various pesticides and their metabolites from the water using activated carbon was examined [11-15].

Pesticides are a diverse group of chemicals, with varying physical and chemical properties. Treatment efficacy depends on these physical and chemical characteristics (e.g. hydrophobicity, molecular weight, polarity, volatility, chemical nature), their reactivity towards different treatment processes and process control, such as solids retention time, temperature, pH value, and hydraulic retention time. Treatment processes can therefore achieve some level of removal.

1.1. Pesticides used in this research

Organochlorine compounds used in this research (acetochlor, alachlor, dimethachlor, propachlor, metolachlor, metazachlor) are known as chloroacetanilides. They play a role as an environmental contaminant, xenobiotic and herbicide.

Invented in 1960s, chloroacetanilide class of herbicides constitutes one of the major classes of herbicides to be used worldwide in the agricultural sector for the control of broadleaf weeds and annual grasses. These are primarily the N-alkoxyalkyl-N-chloroacetyl- substituted derivatives of aniline. Available studies reported that a sharp increase in the usage of the chloroacetanilide herbicides has been observed in the recent past, where about 90 million kg of the herbicide belonging to this class had been used in US alone for the year 2012 [16].

Chloroacetanilide herbicides are commonly used for the crops like corn, cotton, rice, soybean, sugar cane, beetroot, sunflower, etc. These herbicides are relatively high water-soluble and are persistent in nature. Hence, their residues and their metabolites are often detected in soil as well as in surface and groundwater. The most commonly used chloroacetanilide herbicides are acetochlor, alachlor, butachlor, metolachlor, metazachlor, propachlor, and propisochlor. These herbicides are listed as B2, L2 and C classes of carcinogens by the USEPA and reported to have moderate to high chronic toxicity. Ecotoxicological studies suggested that these herbicides are the causal agents for DNA damage and tumour induction in rats, fishes and human cells, as revealed during in-vitro studies [17,18]. Therefore, much attention has been paid to the fate and removal of these herbicides from the environment.

2. Experimental part

The aim of these experiments was to compare the efficiency of removal of selected pesticides from the water by using the granulated activated carbon made by two producers (Cabot Corporation, Calgon
Carbon). Filtrasorb F 400 was submitted by Jako Ltd. and Norit 1240 by Vulcascot Austria. Basic properties of used materials are introduced in the table 1.

| Table 1. Properties of filtration materials Norit 1240 and Filtrasorb 400 [19,20]. |
|---------------------------------------------------------------|
| Norit 1240 | F400 |
| Iodine number [mg/g] | min. 1020 | min. 1050 |
| Methylene blue [mg/g] | min. 230 | min. 260 |
| Grain size [mm] | 0.85-2.0 | 0.42-1.68 |
| Operational density [g/cm³] | 0.480 | 0.425 |
| Specific surface (BET) [m²/g] | 1150 | 1100 |
| Abrasion [%] | 75 | 75 |
| Coefficient of same granularity | 1.6 | 1.7 |

Model water was prepared by the addition of mixture of standards into the 5 litres of water (without pH being adjusted) with the final concentration of pesticides approx. 1 μg/l. There was used 200 ml of model water and 0.2 g of granulated activated carbon (Norit 1240, Filtrasorb F400) in each single experiment. Samples were regularly manually stirred and 40 ml of water was taken into the glass vials with thiosulphate (for preservation) in a predetermined time intervals. Individual samples were taken at the following times: 0, 30, 60, 90, 120, 180, 240, 360 min. After the samples were taken the vials were kept in a fridge and delivered to the ALS laboratory for analysis afterwards. The determination of pesticides was done by the HPLC method (US EPA 535 and 1694) with a direct inject of sample and by the method of internal standard. Analyses of target pesticides were performed in laboratories of ALS Czech Republic in Prague.

3. Results and discussions

The efficiency of pesticides removal from the water by using the sorption materials was observed at the pH 7.6; laboratory temperature (22-23°C) and initial concentration of pesticides ranging between 0,8-0,95 μg/l. The time of the contact of water with the sorbent was 30 – 360 minutes. The results of static tests are given in tables 2 and 3. In these tables you can see the concentration of each organochlorine pesticides before and after sorption with granular activated carbon depending of the contact time.

| Table 2. Concentration of pesticides [μg/L] before and after filtration with Norit 1240. |
|---------------------------------------------------------------|
| Compounds | 0 | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
| Acetochlor | 0.837 | 0.680 | 0.655 | 0.635 | 0.619 | 0.596 | 0.582 | 0.572 |
| Alachlor | 0.754 | 0.629 | 0.606 | 0.591 | 0.578 | 0.560 | 0.546 | 0.539 |
| Dimethachlor | 0.671 | 0.632 | 0.621 | 0.611 | 0.608 | 0.598 | 0.588 | 0.581 |
| Propachlor | 0.571 | 0.535 | 0.525 | 0.513 | 0.503 | 0.490 | 0.482 | 0.471 |
| Metazachlor | 0.834 | 0.789 | 0.765 | 0.746 | 0.728 | 0.705 | 0.695 | 0.686 |
| Metolachlor | 0.934 | 0.861 | 0.821 | 0.790 | 0.767 | 0.741 | 0.728 | 0.722 |

| Table 3. Concentration of pesticides [μg/L] before and after filtration with F400. |
|---------------------------------------------------------------|
| Compound | 0 | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
| Acetochlor | 0.837 | 0.462 | 0.414 | 0.374 | 0.345 | 0.319 | 0.307 | 0.299 |
| Alachlor | 0.754 | 0.407 | 0.390 | 0.369 | 0.350 | 0.334 | 0.326 | 0.316 |
| Dimethachlor | 0.671 | 0.544 | 0.532 | 0.521 | 0.506 | 0.492 | 0.485 | 0.467 |
| Propachlor | 0.571 | 0.501 | 0.487 | 0.474 | 0.462 | 0.446 | 0.438 | 0.424 |
The adsorption efficiency (in %) and immediate adsorption capacity (in µg/g) of activated carbons Norit 1240W and F400 were calculated for the individual chlorinated pesticides depending on the water – material contact time on the base of the measured concentrations of the individual organic compounds. Based on the defined values, the efficiency of chlorinated pesticides removal $\eta$ [%] and immediate adsorption capacity of selected sorption materials -- at [µg/g] were calculated.

$$a_t = \frac{(c_0 - c_m)V}{m} \quad [\mu g/g]$$  \hspace{1cm} (1)

$$\eta = \frac{(c_0 - c_m) \cdot 100}{c_0} \quad [%]$$  \hspace{1cm} (2)

where $a_t$ is the immediate adsorption capacity in µg/g, $\eta$ is the adsorption efficiency [%], $c_0$ is the concentration of pesticides before the adsorption, $c_m$ is the concentration of pesticides after the adsorption at the time $t$ [µg/L], $V$ is the volume of water solution of 0.2 litre, $m$ is the weight of sorption material, 0.2 g.

Results of the adsorption efficiency and the immediate adsorption capacity for sorption materials Norit 1240W and Filtrasorb F400 are shown in figures 1 and 2.

|          | Norit 1240 | Filtrasorb F400 |
|----------|------------|-----------------|
| Metazachlor | 0.834 0.678 0.660 0.641 0.623 0.600 0.587 0.577 |
| Metolachlor | 0.934 0.612 0.562 0.510 0.477 0.438 0.426 0.420 |

**Figure 1.** Adsorption efficiency [%] of activated carbon for chlorinated pesticides removal from the water in relation with the contact time.
The calculated results showed that the efficiency of Norit 1240 ranged between 5-32% and its adsorption capacity was between 26 to 285 µg/g. Results provided the values for Filtrasorb F400 were significantly higher as the efficiency ranged between 12-64% and adsorption capacity between 50 to 560 µg/g, depending on the contact time of water with the material.

Reaction kinetics was also studied for the adsorption of these chloroacetanilides. Reaction kinetics of 0th, 1st, 2nd and 3rd order were studied. Table 4 shows basic characteristics for kinetic equations, where \( c_A \) is concentration at time, \( c_{A0} \) equilibrium concentration, \( k_0, k_1, k_2, k_3 \) are rate constants and \( t \) is time reaction.

**Table 4.** Kinetic rate equations.

| Kinetic model | General formula | Grafical Plot | Rate Law | Half live |
|---------------|-----------------|---------------|----------|-----------|
| Zero order    | \( c_A = c_{A0} + k_0t \) | \( c_A \) vs \( t \) | rate = \( k_0 \) | \( T_{1/2} = \frac{c_{A0}}{2k_0} \) |
| First order   | \( \ln c_A = \ln c_{A0} + k_1t \) | \( \ln c_A \) vs \( t \) | rate = \( k_1 \cdot c_A \) | \( T_{1/2} = \ln \frac{2}{k_1} \) |
| Second order  | \( \frac{1}{c_A} = \frac{1}{c_{A0}} + k_2t \) | \( \frac{1}{c_A} \) vs \( t \) | rate = \( k_2 \cdot c_A^2 \) | \( T_{1/2} = \frac{1}{k_2 c_{A0}} \) |
| Third order   | \( \frac{1}{c_A^2} = \frac{1}{c_{A0}^2} + k_3t \) | \( \frac{1}{c_A^2} \) vs \( t \) | rate = \( k_3 \cdot c_A^3 \) | \( T_{1/2} = \frac{3}{2k_3 c_{A0}^2} \) |

In figures 3 to 6 are illustrated calculated values of kinetic reactions in linearised shape (\( y = a \cdot x + b \)) and constants a, b and \( R^2 \) are showed in table 5 to 8.
Figure 3. Reaction kinetics of zero order for selected pesticides.

Table 5. Kinetic model for zero order reaction for two different granular activated carbons.

| Pesticides    | Regression equation \((y = ax + b)\) | \(a\)      | \(b\)      | \(R^2\) | \(a\)      | \(b\)      | \(R^2\) |
|---------------|--------------------------------------|------------|------------|---------|------------|------------|---------|
|               |                                       | Norit 1240 | Filtrasorb 400 |
| Acetachlor    |                                       | -0.0003    | 0.6723     | 0.8287  | -0.0004    | 0.4294     | 0.7380  |
| Alachlor      |                                       | -0.0003    | 0.6217     | 0.9250  | -0.0003    | 0.3981     | 0.8386  |
| Dimethachlor  |                                       | -0.0001    | 0.6287     | 0.9109  | -0.0002    | 0.5407     | 0.8983  |
| Propachlor    |                                       | -0.0002    | 0.5324     | 0.9163  | -0.0002    | 0.4966     | 0.9166  |
| Metazachlor   |                                       | -0.0003    | 0.7762     | 0.8125  | -0.0003    | 0.6722     | 0.8733  |
| Metolachlor   |                                       | -0.0004    | 0.8320     | 0.7238  | -0.0005    | 0.5711     | 0.6952  |

Figure 4. Reaction kinetics of first order for selected pesticides.
Table 6. Kinetic model for first order reaction for two different granular activated carbons.

| Pesticides      | Norit 1240 | Filtrasorb 400 |
|-----------------|------------|----------------|
|                 | a  b  R²   | a  b  R²       |
| Acetachlor      | -0.0005 -0.3957 0.8411 | -0.0012 -0.8423 0.7760 |
| Alachlor        | -0.0005 -0.4735 0.9388 | -0.0008 -0.9182 0.8590 |
| Dimethachlor    | -0.0002 -0.4637 0.9174 | -0.0006 -0.6135 0.9096 |
| Propachlor      | -0.0004 -0.6292 0.9254 | -0.0005 -0.6983 0.9284 |
| Metazachlor     | -0.0004 -0.2527 0.8225 | -0.0005 -0.3957 0.8848 |
| Metolachlor     | -0.0005 -0.1836 0.7396 | -0.0011 0.5593 0.7248 |

Figure 5. Reaction kinetics of second order for selected pesticides.

Table 7. Kinetic model for second order reaction for two different granular activated carbons.

| Pesticides      | Norit 1240 | Filtrasorb 400 |
|-----------------|------------|----------------|
|                 | a  b  R²   | a  b  R²       |
| Acetachlor      | 0.0009 1.4829 0.8531 | 0.0033 2.3097 0.8104 |
| Alachlor        | 0.0009 1.6021 0.9512 | 0.0022 2.4956 0.8783 |
| Dimethachlor    | 0.0004 1.5891 0.9237 | 0.0009 1.8438 0.9203 |
| Propachlor      | 0.0008 1.8738 0.9340 | 0.0011 2.0061 0.9394 |
| Metazachlor     | 0.0005 1.2866 0.8321 | 0.0008 1.4828 0.8957 |
| Metolachlor     | 0.0006 1.2011 0.7549 | 0.0022 1.7461 0.7530 |
Figure 6. Reaction kinetics of third order for selected pesticides.

Table 8. Kinetic model for third order reaction for two different granular activated carbons

| Pesticides     | Regression equation (y = a.x + b) | Norit 1240 | Filtrasorb 400 | R²   |
|----------------|-----------------------------------|------------|----------------|------|
| Acetachlor     | a = 0.0028, b = 2.1904             | 0.8644     | 0.0186         | 0.8403 |
| Alachlor       | a = 0.0030, b = 2.5537             | 0.9622     | 0.0123         | 0.8962 |
| Dimethachlor   | a = 0.0014, b = 2.5228             | 0.9296     | 0.0036         | 0.9304 |
| Propachlor     | a = 0.0031, b = 3.5017             | 0.9422     | 0.0047         | 0.9495 |
| Metazachlor    | a = 0.0015, b = 1.6525             | 0.8413     | 0.0026         | 0.9060 |
| Metolachlor    | a = 0.0016, b = 1.4411             | 0.7697     | 0.0091         | 0.7796 |

As the tables 5 to 8 present, third order kinetics has been shown to best describe adsorption process for adsorbent Norit 1240 and Filtrasorb F400. R² factor represents how accurate and precise kinetic equation is. The closer the number is to 1, the better kinetic equation describes the process. These equations are acquired by linearization of the kinetic equations.

4. Conclusions
The chloroacetanilides are among the most commonly used herbicides worldwide, which contaminate aquatic environments. This article studies adsorption of chloroacetanilides from water on the two granular activated carbons Filtrasorb 400 and Norit 1240. The efficiency and adsorption capacity of the adsorption materials used was different. Filtrasorb F400 proved to be a better sorption material than Norit 1240, the efficiency ranged between 12-64% and adsorption capacity between 50 to 560 µg/g, the efficiency of Norit 1240 ranged between 5-32% and its adsorption capacity was between od 26 to 285 µg/g, depending on the contact time of water with the material.

The adsorption efficiency (%) and immediate adsorption capacity (µg/g) for the individual pharmaceuticals depending on the water – material contact time, pH value of water, and concentrations of the individual pharmaceuticals in water.

Kinetic equations were used to find the best values fitting experimental data with simulation results. Third order kinetics has been shown to best describe adsorption process for adsorbent Norit 1240 and Filtrasorb F400.
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