Triazine Herbicides Removal from Water with Granular Activated Carbon

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Abstract. The general characteristics of triazine herbicides and their negative effect on environments and human health are described in this article. Triazine herbicides currently account for more than half of all pesticide formulations. They 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 herbicides 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 1 to 2 years. 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 the two granular activated carbons Filtrasorb 400 and Norit 1240 W. Model solution of the pesticides, with concentration of approximately 1 µg/L, was prepared by mixing 50 mL of the pesticide’s standards with approximately 5 L of drinking water. The pH of drinking water was neutral, and this solution was then properly mixed and was used in the experiments. The experiments were performed in the glass bottles with the volume of 200 mL pesticide solution. On the analytical scales weighed out 200 mg granular activated carbon was used and then it was 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 thiosulfate for preservation. After the experiments, these vials were sent to the analytical laboratory, which performed the analysis of the concentration of pesticides. The performed analytical methods were consistent with US EPA 535 and US EPA 1694. Concentration was determined by liquid chromatography using an internal standard method. The triazine herbicides detection analysis results after adsorption process in drinking water spiked with standard of pesticides shows, that the efficiency of selected triazines 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.

1. Introduction
Pesticides are chemicals of inorganic or organic type, used to destroy plant and animal pests as preparations for the protection of plants. They are categorised as insecticides, fungicides and herbicides on the basis of their intended purpose. Insecticides are used against insects which damage agricultural
plants, fungicides against harmful parasitic fungi and herbicides against weeds. Other groups include acaricides (against mites), nematicides (against nematodes), molluscicides (against molluscs) and rodenticides (against rodents).

The global consumption of pesticides is around 2 million tonnes a year, of which 24% is consumed in the USA, 45% in Europe and 25% in the rest of the world. Pesticides are currently in use on 25% of cultivated land.

Preparations for the protection of plants are among those products most strictly regulated in the European Union. In 2009, 1,223 active substances were registered, of these 814 were not approved and 350 were certified. Presently, 1,361 active preparations for the plant protection are registered in the EU pesticide database; of these 832 are not approved for use in the EU and 489 are approved.

![Figure 1. Pesticide consumption in Slovakia in 1993, 2000–2015 in tonnes according to preparation category (environmental, ÚKSUP)](image)

The lists of monitored substances are updated in the individual European countries by the substances in current use. At present, 250 active substances are authorised in the Slovak Republic. Compared with 1997, when a maximum of 385 authorised substances was achieved, this represents a 35% reduction in the number of pesticide substances used.

There are four main ways by which agricultural pesticides can enter waters:
- directly during spraying in the form of aerosols – mainly during aerial spraying,
- by penetration or seepage through the soil,
- by soil out-wash,
- by accidental or intentional release into the environment (e.g. during manipulation, cleaning, storage, etc.).

Important factors determining the pesticide’s potential for water pollution are as follows: solubility of the pesticide, distance of application from a body of water or watercourse, type of soil, gradient, presence, density of crop, agrochemical application method and technique.

1.1. Triazine herbicides
At present, triazine-based herbicides represent more than half of all pesticide preparations. They are used intensively for the protection of field crops, orchards and vineyards; however, they also find application in the removal of undesirable vegetation on non-agricultural land (railway embankments, sports grounds, handling areas, etc.), in water management (for the treatment of coastal zones, destruction of growths in irrigation channels), in forestry and similar.
The content of herbicides in the aquatic environment and agricultural products increases as a result of regular applications. Their occurrence in water is quite frequent and is a consequence of these substances being used in large quantities. Residues from these substances can remain in the soil for as long as 1 to 2 years. As they are readily soluble in water, they are easily transported into the aquifers.

S-triazines are six-membered heterocyclic compounds with three atoms of nitrogen and three substituents bound in a triazine ring at the 2, 4 and 6 carbon positions. The substituted s-triazine ring is highly stable, which is reflected in the stability post-application. S-triazine herbicide derivatives are divided into three main groups: chloro-, methoxy- and methyl-thiotriazines.

As it is not possible nowadays to avoid the application of herbicides (their use forms a part of crop-growing technology), it is necessary to proceed in such a way so as to minimise the health risk of triazine residues and degradation products for the general population.

Due to groundwater contamination by atrazine, simazine and their metabolites, these were removed from the List of Active Substances (i.e. those which may be applied) by Commission Decisions 2004/248/EC and 2004/247/EC. Cyanazine, prometrine, propazine and terbutylazine were also excluded from the List of Active Substances, by Commission Regulation 2076/2002/EC and Commission Decision 2008/934/EC. The major problem presented by triazines is their low biodegradability and lengthy persistence in the aquatic environment – of the parent substances as well as their metabolites (approx. 2 years).

Currently, six villages on Žitný ostrov have had their drinking water supply cut off, due to atrazine being identified as present; this has long been included in the list of banned substances and is classified as a potential carcinogen by the International Agency for Research on Cancer (IARC).

Pesticides and herbicides are harmful for life due to their toxicity and carcinogenic and mutagenic properties [1-3]. Hence, due to the toxicity of pesticides and of the products formed in their degradation, these chemical substances carry a potential risk of contamination of the environment, the aquatic ecosystem and human health. The contamination of groundwater, surface water and soil by pesticides and herbicides currently represents a serious problem.

The concentration of pesticides in drinking water is regulated by the Decree of the Ministry of Health of the Slovak Republic No. 247/2017. A maximum limit value of 0.1 µg/l is determined for each defined pesticide; at the same time, a maximum limit value of 0.5 µg/l is stipulated for the sum of pesticides, whereby the limit value represents the sum of concentrations of all pesticides in the analysed sample. A limit value of 0.03 µg/l applies to aldrin, dieldrin, heptachlor and heptachlor epoxide. Pesticides comprised: organic insecticides, herbicides, fungicides, nematicides, acaricides, algicides, rodenticides, slimicides, related products (e.g. growth regulators) and their relevant metabolites. Only those pesticides are determined that might be anticipated as present in drinking water.

The analytical determination of triazines depends on the possibilities of the workplace (equipment available, availability of chemicals and standards), purpose of the analysis, type of sample and overall level of their content in the sample. Currently, chromatographic methods, high-performance liquid chromatography (HPLC) and gas chromatography (GC) in association with mass spectrometry (MS) are used most frequently. Current analytical methods enable determination of the concentration at the level of ng/l [4,5].

1.2. Removal of pesticides from water
A range of methods, for instance, coagulation, filtration with coagulation, precipitation, ozonisation, adsorption, ion exchange, nanofiltration, reverse osmosis and advanced oxidation processes can be used
to remove pesticides from water. Their efficiency varies considerably and depends largely on the chemical nature of the pesticide to be removed [6-8].

Activated carbon (powdered, granular, extruded, surface-treated) is the best-known sorption material for the removal of organic pollution (pesticides, micro-pollutants). Activated carbon is a highly porous carbon with a large inner surface. It is a set of graphite platelets wherein the mutual distance creates micropores (diameter < 2 nm), where the adsorption of pollutants on the surface of the activated carbon takes place (micropores constitute 90 to 95 % of the adsorbent’s total surface), mesopores (with a diameter of 2 to 50 nm) which secure the transport of the pollutant molecules into the internal area of carbon towards the micropores, and which also have a small adsorption capacity, and transport pores (macropores) with a diameter > 50 nm, which enable access of the adsorbate molecules to the adsorbent’s inner space; they have no adsorption properties. The quantity of micropores and transport pores determines the properties of the activated carbon and its suitability for the treatment of drinking water. The material the activated carbon is produced from is decisive for the “correct” micropores to transport pores ratio – black coal, coconut shells, wood, lignin, brown coal and others. Activated carbon made from black coal usually possesses a suitable ratio of micropores to transport pores, while in activated carbon made from coconut shells micropores predominate, and in activated carbon made from wood macropores predominate. The pore size, specific surface, and chemical reactivity of the surface determine the adsorption properties.

Activated carbon used in a powdered form is applied in the first water treatment stages, especially in surface waters when an emergency deterioration of the quality of the treated water may occur. Powdered activated carbon (PAC) is used only in emergency cases (prior to flocculation). Its disadvantage entails the adsorption also of substances which can be removed by coagulation, hence its adsorption capacity is more readily exhausted.

Granular activated carbon (GAC) is usually used in filters at the end of the water treatment process as the filtration medium of open or pressure filters with a grain size of 0.5–2 mm. Open filters are designed for a filtration rate of 5 to 10 m/h, pressure filters for up to 20 m/h. The activated carbon layer in open filters is 0.6 to 1.0 m, in closed filters 1 to 2 m, depending on the filtration rate. Activated carbon is layered in open and closed filters on a sand layer base of 30 to 40 cm. The activated carbon grain size should be 4 to 5 times the size of the efficient sand grain [9,10].

Filters filled with activated carbon are washed in the same way as conventional sand filters, i.e. by backflow of air and water. The shortest filtration cycle is approximately 14 days. About 5 to 10 % of the original volume of activated carbon is consumed during the washing (by abrasion, washing out, chemical reaction). The capacity of the activated carbon is exhausted over the course of 1 to 3 years of continuous operation, depending on the quality of the water treated (Table 1).

Table 1. Contact time and life cycle of activated carbon for various applications

| Application                                  | Contact time [min] | Life cycle [years] |
|----------------------------------------------|--------------------|--------------------|
| Improvement of sensoric properties            | 6-12               | 2-4                |
| Removal of pesticides                         | 10-15              | 1-3                |
| Removal of humic substances and THM           | 15-30              | 1.5-3              |
| Removal of halogenated hydrocarbons           | 10-20              | 0.5-1.5            |
| Dechlorination                               | 4-8                | 1.2                |

Regeneration is performed by thermal processes at a temperature of 900 – 1,000 °C or by chemical processes. Reactivation provides the exhausted material with properties that are very similar to the original activated carbon. The regeneration process is performed by the manufacturer.
2. Material and Methods
The experiments sought to compare the efficiency of the removal of selected pesticides from water by means of granular activated carbon from two manufacturers (Cabot Corporation, Calgon Carbon). Filtrasorb F400 was supplied by Jako, s.r.o., Norit by Vulcascot Austria. The basic properties of the materials used are given in Table 2.

Table 2. Properties of filtration materials Norit 1240 and Filtrasorb F400

| Property                      | Norit 1240 | Filtrasorb F400 |
|-------------------------------|------------|-----------------|
| Iodine number [mg/g]          | min. 1020  | min. 1050       |
| Methylene blue [mg/g]         | min. 230   | min. 260        |
| Particle size [mm]            | 0.85-2.0   | 0.42-1.68       |
| Hardness                      | 97         | 95              |
| Operating density [g/cm³]     | 0.480      | 0.425           |
| Specific surface area (BET) [m²/g] | 1150      | 1100           |
| Uniformity coefficient        | 1.6        | 1.7             |

The model water was prepared by adding a mixture of standards into 5 litres of drinking water (without treating the pH) with a resulting pesticide concentration of approx. 1 µg/l. For each experiment, 200 ml of model water and 0.2 g of granular activated carbon (Norit 1240, Filtrasorb F400) were used. The samples were regularly mixed manually, whereby 40 ml of water was taken in the set time intervals and transferred to glass vials with added thiosulphate which acted to preserve the sample. The individual samples were taken at the following times: 0, 30, 60, 90, 120, 180, 240 and 360 min. Directly after the samples were taken, the vials were stored in a refrigerator and subsequently transferred to the ALS laboratory for analysis. Pesticides were determined using the HPLC method with direct sample injection and the inner standard method.

3. Results and discussions
The efficiency of pesticide removal from water by means of the sorption materials used was monitored at pH 7.6, at ambient temperature (22-23 ºC) and with an input pesticide concentration of 0.8-0.95 µg/l and a water – sorbent contact time of 30 to 360 minutes. The results of static tests are given in Tables 3 and 4.

The adsorption efficiency (in %) and immediate adsorption capacity (in µg/g) of activated carbon were calculated for the individual triazine herbicides depending on the water – material contact time on the base of the measured concentrations of the individual triazine herbicides.

Based on the defined values, the efficiency of herbicides removal η [%] and immediate adsorption capacity of selected sorption materials – \( a_t [\mu g/g] \) were calculated.

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

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

where \( a_t \) is the immediate adsorption capacity in µg/g, η is the adsorption efficiency [%], c₀ is the concentration of s-triazines before the adsorption, cₘ is the concentration of s-triazines after the adsorption at the time \( t [\mu g/L] \), 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 of the adsorption capacity for sorption materials Norit 1240 and Filtrasorb F400 at the concentration of s-triazines of 0.8-0.95 µg/l are shown in figure 2 and 3.
Comparison of efficiency of removal of atrazine and terbutylazine on activated carbon from water are shown in figure 4.

According to the calculated values, the efficiency of Norit 1240 ranged from 6 to 32 %, the adsorption capacity from 54 to 280 µg/g, depending on the contact time. As regards Filtrasorb F400, the values were considerably higher – the efficiency ranged from 12 to 59 % and adsorption capacity from 120 to 420 µg/g.

Table 3. Pesticide concentration in water depending on adsorption time

| Pesticide      | Norit 1240 | Filtrasorb F400 |
|----------------|------------|-----------------|
|                | 0  | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
| Simazine       | 0.892 | 0.836 | 0.801 | 0.772 | 0.756 | 0.739 | 0.726 | 0.719 |
| Atrazine       | 0.948 | 0.854 | 0.807 | 0.773 | 0.750 | 0.721 | 0.710 | 0.692 |
| Propazine      | 0.873 | 0.813 | 0.774 | 0.746 | 0.730 | 0.713 | 0.704 | 0.689 |
| Terbutylazine  | 0.910 | 0.798 | 0.755 | 0.712 | 0.671 | 0.621 | 0.603 | 0.588 |

Table 4. Pesticide concentration in water depending on adsorption time

| Pesticide      | Norit 1240 | Filtrasorb F400 |
|----------------|------------|-----------------|
|                | 0  | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
| Simazine       | 0.892 | 0.778 | 0.740 | 0.707 | 0.686 | 0.661 | 0.648 | 0.624 |
| Atrazine       | 0.948 | 0.778 | 0.740 | 0.707 | 0.686 | 0.661 | 0.648 | 0.624 |
| Propazine      | 0.873 | 0.699 | 0.672 | 0.649 | 0.634 | 0.614 | 0.597 | 0.577 |
| Terbutylazine  | 0.910 | 0.714 | 0.691 | 0.670 | 0.652 | 0.630 | 0.623 | 0.618 |

Figure 2. Efficiency of removal of selected herbicides on activated carbon
Conclusions
The experiment was aimed at observing the efficiency of selected sorption (filtration) materials at the removal of triazine herbicides from the drinking water under laboratory conditions. Based on the static tests, the adsorption efficiency of particular materials observed was compared, and their adsorption capacity was calculated.

The adsorption efficiency and adsorption capacity of the granular activated carbons used differed considerably. Filtrasorb F400 proved to be a better sorption material than Norit 1240. The efficiency of this material ranged from 12 to 59%; by contrast, the efficiency of Norit 1240 was markedly lower (from 6 to 32 %). The adsorption capacity for Filtrasorb F400 and Norit 1240 was from 6 to 285 µg/g or from 120 to 420 µg/g, respectively. The adsorption capacity (µg/g) for the individual triazine herbicides depending on the quality of the water, contact time and concentrations of the individual triazine herbicides in water.

Figure 3. The adsorption capacity of removal of selected herbicides on activated carbon

Figure 4. Comparison of efficiency of removal of selected herbicides on activated carbon
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