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# Pesticide removal and efficiency of different types of granular activated carbon

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ABSTRACT

Pesticides as one of the micro-pollutants present a great problem and threat to the environment and human health. They can infiltrate the sources of drinking water by application on the agricultural fields. This article is focused on Atrazine, Terbuthylazine and their metabolites. It is their complex structure that makes them hard to degrade naturally and, thus, water needs to be treated before safe using. Therefore, this article studies adsorption on the two granular activated carbons Filtrasorb 400 and Norit 1240 W. For the determination of the concentration liquid chromatography was used. In this article it is presented that Filtrasorb 400 efficiency (26–40% and 33–45% for atrazine and terbuthylazine respectively) is better than the efficiency of Norit 1240 W (9–27% and 10–24% for atrazine and terbuthylazine respectively).

KEYWORDS

micro-pollutants, pesticides, adsorption, activated carbon, chromatography

## 1. INTRODUCTION

The term micro-pollutants can refer to a variety of substances and molecules. It usually includes chemicals from industries, pharmaceuticals and personal care products, pesticides, hormones, endocrine disruptors, fragrances and drugs. These compounds are mostly complex in their structure and therefore are persistent in the environment, which causes number of problems for living organisms [1]. In this article some pesticides will be presented, which were specifically chosen for their occasional presence in the drinking water in Slovakia. Application of these pesticides was already banned in Slovakia, but there can still be detected their presence in some sources of drinking water. Because of their complex chemical structure, it is very difficult to remove them from drinking water by traditional water treatment technologies [2]. More advanced technologies are necessary for their removal. Pesticides presented in this paper are already banned from usage in Slovakia. They belong to the group of pesticides called herbicides. They target mostly plants and weed [3]. Pesticides are usually composed of two types of chemicals. The first one is called active agent, which is basically a chemical compound, which destroys targeted group of plants. The other part is made of inert chemicals; they provide an environment for the pesticide and ensure their correct application. But sometimes these inert compounds are more toxic than the active agent and therefore it is necessary to remove them from water [4]. Adsorption is a process of attachment or adhesion of atoms, molecules or ions from gaseous, liquid or solution onto the surface of an adsorbent. This process can be carried out by two types of an adsorption. Physical adsorption is accomplished by the formation of London dispersion forces (Van der Waals forces) between the adsorbent and adsorbate. This type of forces is relatively easy to break by comparison to other types of bonds. Chemisorption is another type of adsorption, where the creation of chemical bonds occurs. Chemical bond is much more difficult to break than physical bond [5]. This process is quite widely used in many different types of industry e.g. food, beverages, purification of gasses and liquids, water treatment technologies, mining, in pharmaceutical industry and many others [6]. In the process of adsorption the right

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material to adsorb specific compounds and molecules is needed. A variety of adsorbents is used for the adsorption processes like zeolites, iron-based adsorbents, different types of clay materials, activated carbon and others [7]. The selection of the right material depends on variety of requirements e.g., pollution, temperature, chemical structure and the amount of the pollution, which plays a very big role in the selection of adsorbent. Even the economical price of the adsorbent has a high priority [8]. Activated carbon is a kind of an adsorbent, which is very commonly used as adsorbent material. It is due to its properties and price over the other adsorbents. Activated carbon is made from raw materials as peat, coconut shells, wood, coal and many others. Different type of raw material creates different type and quality of activated carbon [9]. Activated carbon is carbon, which has been activated by physical or chemical process. Physical activation of a carbon is accomplished by high temperature and steam. High temperature and steam create cracks, crannies and crevices in the molecular structure of the carbon, which creates bigger adsorption surface. Chemical activation is provided by implementing chemicals, which activate carbon in a similar way. After the activation process, carbon needs to be cleaned and then it can be used for adsorption [10]. There are three types of activated carbon. First is Powdered Activated Carbon (PAC), which has small fine particles and resembles powder. It is mostly used for the adsorption of unwanted smell and taste from water. This activated carbon has one disadvantage, which is its inability to be regenerated. Granular Activated Carbon (GAC) has particles in the range of 0.2–5 mm. GAC can be regenerated and for this reason it is used more often. This type of activated carbon can be used in either column flow reactor or batch reactor. And third kind of the activated carbon is extruded activated carbon with the shape of small pellets [11]. Areerachakul et al. [12] experimented with GAC (Calgon carbon). Columns packed with GAC at different bed depths were operated at different filtration rates over a period of several weeks. Removal of Metsulfuron-Methyl (MM) was performed via adsorption using GAC fixed beds of 5, 10 and 15 cm depths. The best results were achieved with bed depth of 15 cm and the least efficient was bed depth of 5 cm. Efficiency of the removal was between 20 and 60% for the bed depths of 5–15 cm. Salman J. M. and Hameed B. H. [13] performed adsorption of 2.4-Dichlorophenoxyacetic acid (2.4-D) and Carbofuran on GAC F300. The initial sample volume was set to 200 mL with concentration ranging between 50 and 300 mg/L. Dosage of GAC F300 was 0.2 g and the solution was agitated at 120 rpm with temperature of 30 °C. Adsorption capacity of the GAC 400 was determined to be 181.82 and 96.15 mg/g for 2.4-D and Carbofuran respectively. This experiment proved that GAC F300 is suitable and efficient in removing these pesticides from water.

## 2. MATERIALS AND METHODS

The pesticide standards were purchased from a company ALS Czech Republic, which also provided the sample vials and analysis of pesticides in samples. Pesticides monitored for this study were atrazine, terbuthylazine and their metabolites. GAC Norit 1240 W was purchased from Cabot Corporation and Filtrasorb 400 was purchased from Chemviron Carbon. The characteristics of this GAC are presented in Table 1. The selection of these adsorbents was based on previous experiments carried out for heavy metal adsorption [14].

*Table 1.* Characteristics of granular activated carbons Norit 1240 W and Filtrasorb 400

| | Norit 1240 W | Filtrasorb 400 |
|---|---|---|
| Iodine number [–] | 975 | 1,000 |
| Particle size >0.17 [mass%] | 10% | 5% |
| Particle size <0.425 [mass%] | 5% | 4% |
| Total surface area B.E.T. [$m^2/g$] | 1,100 | 1,050 |
| Apparent density [$kg/m^3$] | 470 | 450 |
| Effective size $D_{10}$ [mm] | 0.6–0.7 | 0.6–0.7 |
| Uniformity coefficient [–] | 1.7 | 1.7 |

Stock 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 stock pesticide solution. On the analytical scales weighed out 200 mg GAC 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 min. 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 [15] and US EPA 1694 [16]. Concentration was determined by liquid chromatography using an internal standard method.

## 3. RESULTS AND DISCUSSION

The pesticide detection analysis results after adsorption process in drinking water spiked with pesticides are shown below. It is important to highlight that these experiments were conducted in the same conditions (room temperature of 24 °C, neutral range of pH level and equivalent dosage of activated carbon). The goal of this study was to examine and determine the adsorption efficiency of different types of GAC. The decrease in pesticide concentration for GAC Norit 1240 W and Filtrasorb 400 is shown in Tables 2–5. In these tables the efficiency of each GAC can be observed and the comparison main pesticides and their metabolites.

As it is obvious from the results presented in the tables, metabolites are little harder to adsorb on the surface of GAC. This fact can be explained by the absence of functional group, which has better adsorption capabilities than others. In the tables it can be observed that main pesticide has

*Table 2.* Pesticides concentration [μg/L] over time for GAC Norit 1240 W

| Time [min] | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
|---|---|---|---|---|---|---|---|
| Atrazine | 0.854 | 0.807 | 0.773 | 0.754 | 0.721 | 0.710 | 0.692 |
| Atrazine-2-hydroxy | 0.960 | 0.944 | 0.933 | 0.919 | 0.904 | 0.893 | 0.878 |
| Atrazine-desethyl | 0.892 | 0.874 | 0.852 | 0.834 | 0.820 | 0.806 | 0.785 |
| Atrazine-desisopropyl | 0.898 | 0.873 | 0.845 | 0.818 | 0.798 | 0.783 | 0.768 |

*Table 3.* Pesticides concentration [μg/L] over time for GAC Filtrasorb 400

| Time [min] | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
|---|---|---|---|---|---|---|---|
| Atrazine | 0.699 | 0.675 | 0.643 | 0.634 | 0.620 | 0.597 | 0.565 |
| Atrazine-2-hydroxy | 0.889 | 0.871 | 0.852 | 0.833 | 0.817 | 0.795 | 0.785 |
| Atrazine-desethyl | 0.853 | 0.838 | 0.809 | 0.788 | 0.760 | 0.736 | 0.714 |
| Atrazine-desisopropyl | 0.825 | 0.806 | 0.783 | 0.764 | 0.754 | 0.731 | 0.706 |

*Table 4.* Pesticides concentration [μg/L] over time for GAC Norit 1240 W

| Time [min] | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
|---|---|---|---|---|---|---|---|
| Terbuthylazine | 0.813 | 0.784 | 0.746 | 0.730 | 0.713 | 0.704 | 0.689 |
| Terbuthylazine-desethyl | 0.861 | 0.847 | 0.822 | 0.809 | 0.797 | 0.782 | 0.756 |
| Terbuthylazine-desethyl-2-hydroxy | 0.932 | 0.907 | 0.883 | 0.865 | 0.853 | 0.838 | 0.831 |
| Terbuthylazine-hydroxy | 0.939 | 0.902 | 0.869 | 0.838 | 0.828 | 0.813 | 0.804 |

*Table 5.* Pesticides concentration [μg/L] over time for GAC Filtrasorb 400

| Time [min] | 30 | 60 | 90 | 120 | 180 | 240 | 360 |
|---|---|---|---|---|---|---|---|
| Terbuthylazine | 0.602 | 0.584 | 0.557 | 0.535 | 0.527 | 0.513 | 0.499 |
| Terbuthylazine-desethyl | 0.788 | 0.772 | 0.753 | 0.726 | 0.715 | 0.707 | 0.692 |
| Terbuthylazine-desethyl-2-hydroxy | 0.843 | 0.816 | 0.792 | 0.779 | 0.769 | 0.755 | 0.752 |
| Terbuthylazine-hydroxy | 0.754 | 0.727 | 0.694 | 0.658 | 0.645 | 0.636 | 0.628 |

higher adsorption efficiency than its metabolites. This fact is obvious in both main pesticides and their metabolites. The comparison of Norit 1240 W and Filtrasorb 400 is presented in the figures below, where you can observe the difference in the adsorption efficiency.

Atrazine and Terbuthylazine both belong to the triazine group of pesticide. They both possess triazine group, amino group and chlorine. The GAC Norit 1240 W is less efficient than Filtrasorb 400, as it can be observed in Figs 1–4.

In Figs 1 and 2 the efficiency of the adsorption capacity of the pesticide Atrazine and its metabolites are presented. Atrazine showed far better adsorption characteristics than its metabolites. In terms of adsorption onto GAC, Filtrasorb 400 demonstrated better efficiency than Norit 1240 W. Adsorption efficiency for Filtrasorb 400 was in range of 26–40%, compared to that of Norit 1240 W in range 9–27%.

Terbuthylazine and its metabolites demonstrated similar characteristics in terms of adsorption efficiency (Figs 3 and 4), and again Filtrasorb 400 showed better characteristics than Norit 1240 W.

Adsorption efficiency for Norit 1240 W ranged from 10 to 24%, which compared to Filtrasorb 400 in range 33–45%, is less efficient. Adsorption capacity, considering contact time of material with water, for Norit 1240 W and Filtrasorb 400 was considerably different. Adsorption materials showed slightly higher adsorption capacity for Terbuthylazine (and its metabolites) than for Atrazine (and its metabolites). The adsorption capacity was calculated from the difference between the concentration of the stock and the final solution, multiplied by the proportion of sample volume and weight of activated carbon. Due to the volume of the sample and the weight of the activated carbon, this formula is simplified only by the difference in concentration. Adsorption capacity for Norit 1240 W ranges from 0.094 to 0.256 μg/g, 0.05 to 0.180 μg/g, 0.097 to 0.221 μg/g and 0.041 to 0.146 μg/g for Atrazine, Atrazine metabolites, Terbuthylazine and Terbuthylazine metabolites respectively. Adsorption capacity for Filtrasorb 400 ranges from 0.249 to 0.383 μg/g, 0.091 to 0.230 μg/g, 0.308 to 0.411 μg/g and 0.114 to 0.210 μg/g for Atrazine, Atrazine metabolites, Terbuthylazine and Terbuthylazine metabolites respectively (Tables for adsorption capacity is not shown in this article). The adsorption of the pesticide metabolites is less efficient than the main pesticide. This fact can be explained by the absence of the specific functional groups. These groups, when present, provide better adsorption onto the surface of

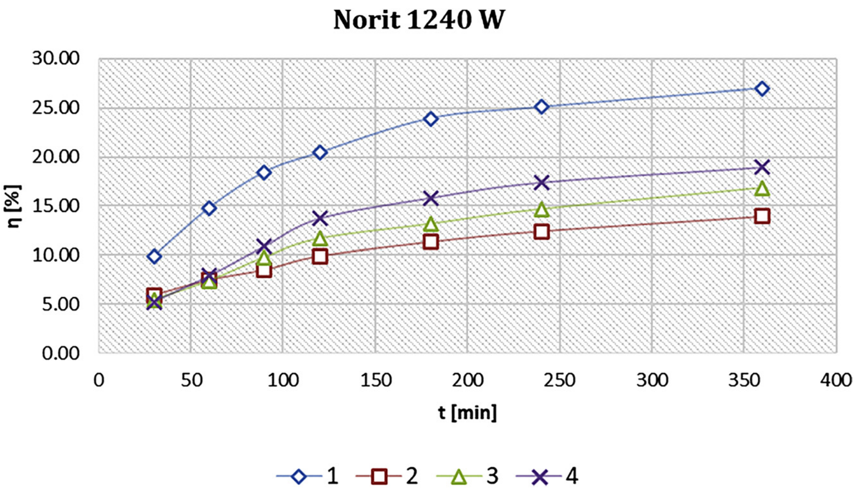


*Fig. 1.* The adsorption efficiency of GAC Norit 1240 W for the time reaction in the range 30–360 min (1 – Atrazine, 2 – Atrazine-2-hydroxy, 3 – Atrazine-desethyl, 4 – Atrazine-desisopropyl)

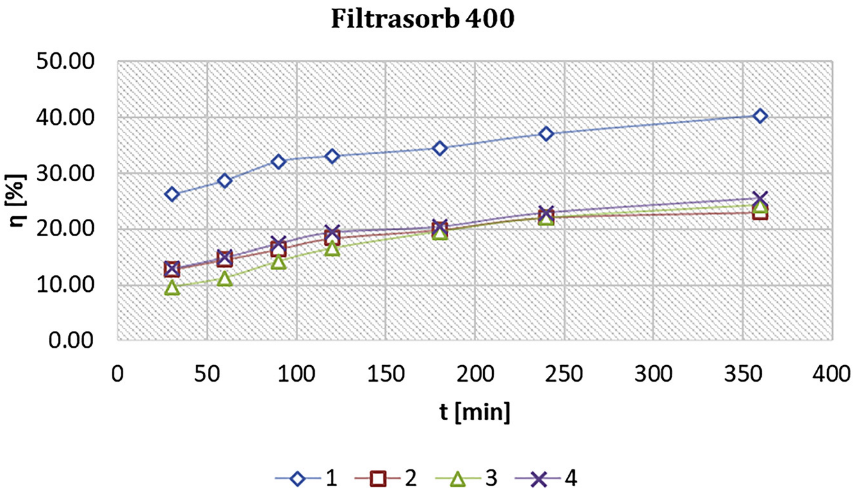


*Fig. 2.* The adsorption efficiency of GAC Filtrasorb 400 for the time reaction in the range 30–360 min (1 – Atrazine, 2 – Atrazine-2-hydroxy, 3 – Atrazine-desethyl, 4 – Atrazine-desisopropyl)

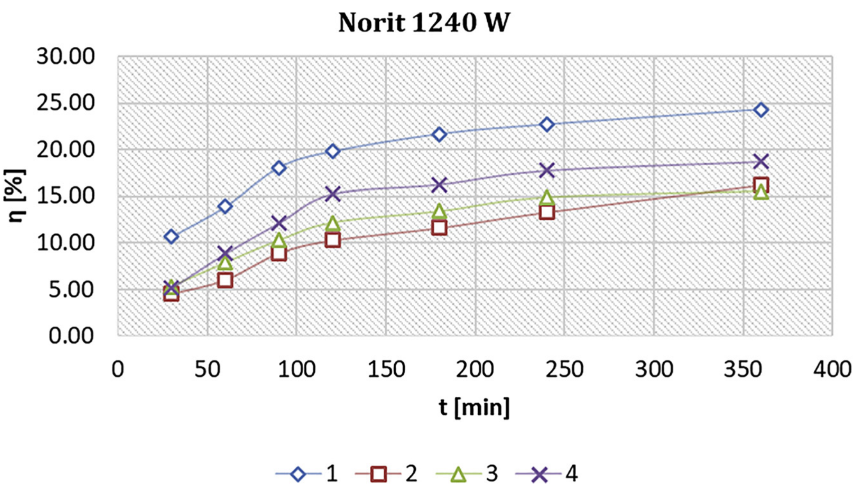


*Fig. 3.* The adsorption efficiency of GAC Norit 1240 W for the time reaction in the range 30–360 min (1 – Terbuthylazine, 2 – Terbuthylazine-desethyl, 3 – Terbuthylazine-desethyl-2-hydroxy, 4 – Terbuthylazine-hydroxy)

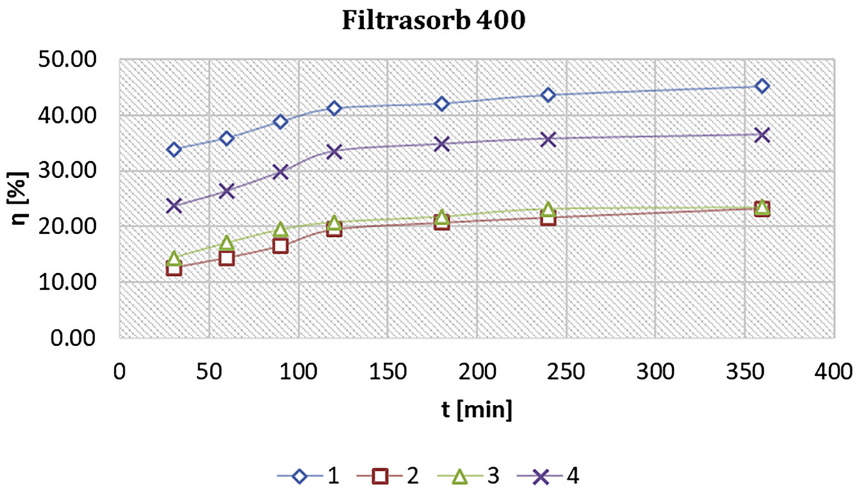


*Fig. 4.* The adsorption efficiency of GAC Filtrasorb 400 for the time reaction in the range 30–360 min (1 – Terbuthylazine, 2 – Terbuthylazine-desethyl, 3 – Terbuthylazine-desethyl-2-hydroxy, 4 – Terbuthylazine-hydroxy)

activated carbon. When the functional group is missing, adsorption still occurs but with limitations. For Atrazine, the metabolite with hydroxy group is not as well adsorbed as Terbuthylazine, whose adsorption efficiency is better than of other metabolites. But in both cases the adsorption efficiency is far better with chlorine than without. Chlorine with its seven valence electrons can easily form a bond onto the surface of activated carbon, where on the other hand, oxygen has fewer free valence electrons and hydroxyl group with bonded. Hydrogen has less space left for the creation of Van der Waals bonds.

This treatment process needs to be examined more, because the concentration of the pesticides was not low enough. Concentration of used pesticides after the experiment ranged from 0.5 to 0.78 μg/L. In order to consider the water safe for drinking purposes, the concentration needs to be less than or equal to 0.1 μg/L. To achieve this concentration, higher quantity of GAC or longer period of adsorption time is required.

## 4. CONCLUSIONS

As it is presented in this article, the adsorption efficiency of the two studied GACs, Filtrasorb 400 proved to be more efficient than Norit 1240 W and fulfilled the expectations. Norit 1240 W, on the other hand, showed a bit disappointing results with low adsorption efficiency. The adsorption of the pesticide metabolites showed to be more difficult and less efficient than the main pesticide. This fact is explained by the missing functional groups, which provide better adsorption onto the surface of the activated carbon.

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