# “Green” adsorbents in the wastewater treatment service

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*In this study, the adsorption of acetic acid on the so-called "green" adsorbents was studied. Waste materials, i.e. eggshells and coffee grounds were used as adsorbents. In addition, activated carbon was used to compare the adsorption efficiency with "green" adsorbents. The obtained results showed that the equilibrium time of all studied adsorbents is achieved in 30 minutes. By comparing the adsorption efficiency of acetic acid on the tested adsorbents, it was shown that their use as cheap adsorbents under the tested conditions is possible. The coffee grounds showed a relatively high adsorption efficiency, very similar to the adsorption efficiency obtained when using the commercial and most commonly used adsorbent, i.e. activated carbon.*
***Keywords:*** *adsorption, "green" adsorbents, acetic acid*

## 1. Introduction

Urbanization, as well as the increasing modernization of industry, in addition to significant benefits, leads to water, air and soil pollution. One of the consequences of pollution is the appearance of increasing amounts of wastewater that is loaded with organic and inorganic pollutants. Among other, these are heavy metals or organic substances such as dyes, acids, phenols, etc. Acetic acid is one of the frequent pollutants. It is present in oil, but also in wastewater from the pharmaceutical, chemical and food industries [1].

A large number of countries have prescribed strict legal regulations related to the discharge of wastewater into natural recipients, which also means the obligation to treat wastewater [2].
Today, a whole series of different methods are known for wastewater treatment, such as precipitation, coagulation, ion exchange, reverse osmosis, etc., which are applied as independent methods or in combination [3]. However, as the demands of the market increase, efforts are also being done on the modernization of already existing methods. A very well-known, efficient and often used method for wastewater treatment is adsorption [4]. It is most often carried out with the use of activated carbon, which is known as an excellent adsorbent with high adsorption capacity, available and easy to use, but a relatively high price is a limiting factor [5]. Therefore, in recent times, significant efforts have been made to find new, cheaper, and equally efficient adsorbents. Most often, these are non-hazardous waste materials that are available in very large quantities, have a low price, high adsorption ability, but also the possibility of regeneration. By using waste materials, it is possible to remove pollution from waste water, but at the same time, their amount in landfills is reduced and the problem of their disposal is at least partially solved [6].
Waste materials, also known as "green" adsorbents that are usually researched, and some are already used, are wastes from different industries: wood (bark, sawdust),

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food (citrus peels, nut shells, fruit seeds, bones), metallurgical (slag, waste moulding mixture, blast furnace sludge), etc. [7-9].
This study is focused on acetic acid adsorption on the so-called "green" adsorbents, i.e. egg shells and coffee grounds. In addition, the tested adsorbents were compared with the most commonly used, activated carbon.

## 2. Experimental

Two so-called "green adsorbents": egg shells and coffee grounds were studied. In addition to green adsorbents, adsorption was also performed on commercial activated carbon, the most efficient and most commonly used. Acetic acid was used as adsorbate. The experiment was carried out in such a way that 0.5 g of adsorbent was placed in contact with 25 ml of 0.5 mol/L acetic acid for 5, 15, 30 and 60 minutes. After the contact time, filtering was carried out through Whatman filter paper (blue ribbon). In the filtrates, the concentration of acetic acid after adsorption was determined by titration with 0.1 mol/L sodium hydroxide. Phenolphthalein was used as an indicator. From the values for the initial and final concentration of acetic acid and from the data for the mass of the adsorbent and the volume of the adsorbate, the adsorption capacity, eq. (1) was calculated for each individual adsorbent/adsorbate contact time in order to obtain data on the equilibrium establishment time:

$$q_t = \frac{c_0 - c_e}{m} \times V \qquad (1)$$

where is:
$q_t$ – adsorption capacity in time $t$, mg/g,
$c_0$ - initial concentration of acetic acid, mol/L,
$c_t$ - concentration of acetic acid in time t, mol/L,
$m$ - mass of adsorbent, g,
$V$ - volume of acetic acid, L.

In addition, from the data on the initial and final concentration of acetic acid as well as the data on the adsorbent mass, the adsorption efficiency was calculated for each individual adsorbent/adsorbate system, eq. (2):

$$E = \frac{c_0 - c_e}{c_0} \cdot 100 \qquad (2)$$

where is:
$E$ – adsorption efficiency, %,
$c_0$ - initial concentration of acetic acid, mol/L,
$c_e$ - equilibrium concentration of acetic acid, mol/L,
$m$ - mass of adsorbent, g,
$V$ - volume of acetic acid, L

## 3. Results and Discussion

The dependence of adsorption capacity on time for all tested systems is shown in Fig.1.
Fig.1 shows that the adsorption of acetic acid on the tested adsorbents depends on the adsorbent/adsorbate contact time. The adsorption capacity increases signifycantly already after 5 minutes of contact, which indicates very fast adsorption [10]. At the very beginning of adsorption, all sites on the surface of the adsorbent are unfilled, which are quickly filled by acetic acid molecules. With further adsorbent/adsorbate contact, adsorption follows a linear curve, the speed is somewhat slower, but acetic acid molecules still bind to the surface of the adsorbent. The equilibrium capacity is reached after 30 minutes for all tested systems. After that, there is stagnation (in the case of adsorption on coffee grounds) or a decrease in adsorption capacity (in the case of adsorption on eggshells and activated carbon). The stagnation of the adsorption capacity probably occurs due to the fact that all free places on the adsorbent are filled, but also due to the possibility that the adsorption is of a chemical nature, i.e. that the acetic acid molecules are chemically bound to the surface of the adsorbent, which does not allow the simultaneous release and adsorption of acetic acid molecules to the surface adsorbent. A decrease in the adsorption capacity after the establishment of equilibrium may indicate the simultaneous adsorption and desorption that occurs in the case of physical adsorption.

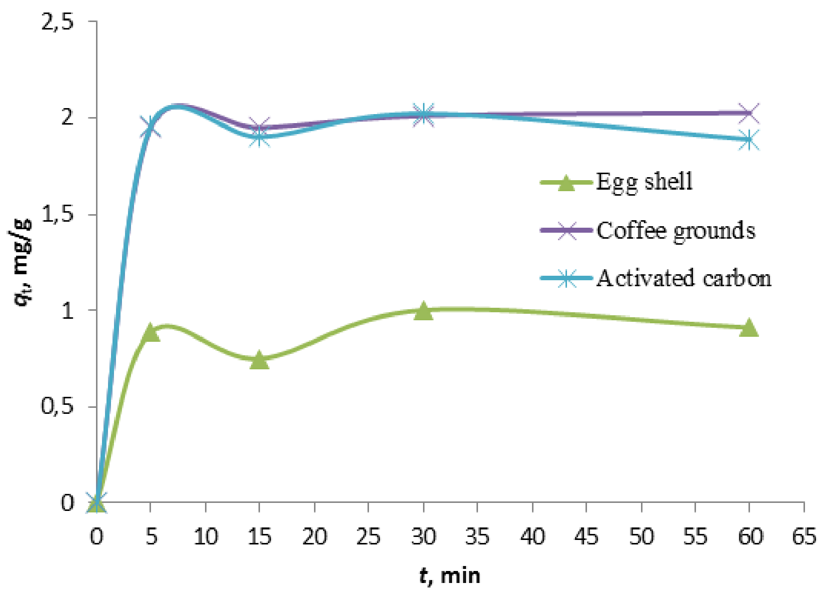


Fig.1 Dependence of adsorption capacity on time

Adsorption and desorption occur in such a way that there is no equal adsorption and desorption of acetic acid molecules [11]. In this case, desorption is more likely to be faster, resulting in a reduction in adsorption capacity. The obtained results are in accordance with the research of other researchers [12, 13]. By comparing the data obtained for the efficiency of acetic acid removal using the mentioned adsorbents (Fig.2), it can be seen that the efficiency of acetic acid removal using activated carbon is 67.44%, using coffee grounds is 67.04%, and using eggshells is 33.40%.

The obtained results indicate that the best adsorbent is activated carbon (E = 67.44%), which is expected. Since it is known that activated carbon shows great efficiency and as such it is used the most, in this research it is taken as a reference material on the basis of which the efficiency of the tested adsorbents can be compared.

It can be seen from Fig.2 that the efficiency of coffee grounds is also very high and amounts to 67.04%, which is close to the efficiency of activated carbon, while the efficiency of removing acetic acid using eggshells is the lowest and amounts to 33.40%. By comparing the efficiency of the so-called of the "green" adsorbents examined in this research with activated carbon, it can be considered that both adsorbents, coffee grounds and eggshells are suitable for the adsorption of acetic acid. It is assumed that it is possible to use a more economically acceptable "green" adsorbent, ie. coffee grounds as a substitute for relatively expensive activated carbon, which certainly needs to be confirmed by additional tests.

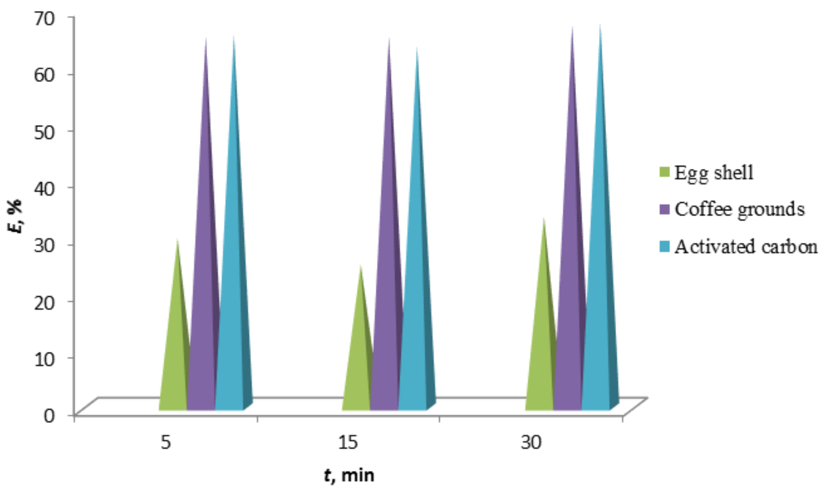


Fig.2 Comparison of the efficiency of acetic acid removal using "green" adsorbents and commercial activated carbon

## 4. Conclusion

The results of testing the waste materials as potential "green" adsorbents indicate that their application in the removal of acetic acid from an aqueous solution is possible. Equilibrium in the tested systems is relatively fast and is achieved in 30 minutes. Adsorption takes place in two steps, the first is fast and the second is somewhat slower. Such kinetics of adsorption probably depends on the number of available active sites on the adsorbent itself as well as the method of binding adsorbent/ adsorbate. A comparison of the efficiency of potential "green" adsorbents and commercial activated carbon indicates that both tested adsorbents - coffee grounds and eggshells - are suitable for use as adsorbents for removing acetic acid from aqueous solutions. Coffee grounds showed significantly higher removal efficiency than eggshells, which is very similar to the efficiency of commercial activated carbon.

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