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DECONTAMINATION OF TOLUENE POLLUTION IN WATER USING RAW WALNUTS SHELLS

***Igor WINKLER[1,2], Ivan KUVILA[1]**

[1]*Institute of Biology, Chemistry and Bioresources, Yu Fedkovych National University of Chernivtsi, 2 Kotsyubynsky Str., Chernivtsi, 58012, Ukraine*
[2]*Medical Chemistry Department, Bukovyna Medical University,2 Thetralna Sq., Chernivtsi, 58002, Ukraine*
i.winkler@chnu.edu.ua
*Corresponding Author
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Abstract: *Raw untreated walnut shells were tested as an adsorbent for the extraction of toluene pollution from water systems, and high cleaning efficiency (up to 28 % of the specific toluene extraction) was determined by the direct UV-photometry measurement of the residue toluene concentration. The adsorption efficiency of the shells is higher than that of some widely distributed carbon-based adsorbents.*
Extended use of shells is recommended since this material is very cheap and easily available as waste in some food processing factories. Further utilization of the used shells through burning is proposed as an environment friendly solution.

Keywords:toluene; walnut shells; UV-photometry; wastewater decontamination

1. Introduction

Decontamination of water and wastewater is still a very topical problem since billions tons of insufficiently treated and untreated effluents are discharged systematically and washed-off into various water bodies [1, 2]. Many kinds of water treatment technologies can be used in order to decontaminate water and remove toxicants from effluents: mechanical treatment methods, biotreatment, oxidation decomposition, adsorption, evaporation, etc. It is well known that the organic pollutants, especially aromatic compounds, are considered as quite persistent pollution agents, which are very difficult to remove, extract or decompose [3-6]. On one hand, this problem is grounded on a wide variety of various aromatic compounds used in many fields of the everyday activities. They are used extensively as engine oils and grease components, in various mixtures for construction and so on. On the other hand, oxidation and/or decomposition of most aromatic compounds are a very slow process while their biodecomposition is also low effective. Finally, it should be mentioned that the majority of the aromatic compounds are considered very highly toxic agents with a distinct ability to cumulate along the trophic chains. That is why rather strict limitations are set for their content in wastewater to be discharged while development of new effective solutions for the extraction of the organic compounds remains a topical issue.

Various porous materials of plant nature become more and more popular as possible adsorbents for such class of pollution agents because such materials are quite cheap, easily available and can exhibit

rather high efficiency. It has been reported [7] that the oil products content in water can be decreased under its maximum permissible level using the carbonized walnut shells after their preliminary thermotreatment at 450-600 ^{0}C in the air or at 550-600 ^{0}C in nitrogen. Such carbonized material represents mostly mineralized and highly porous substrate containing 5-10 wt % of SiO_2 and 80-90 wt % of carbon.
Modification of the carbonized shells using acids is another way to increase their porosity [8]. It should be emphasized that carbon is the main adsorption substrate for most organic, especially aromatic compounds and, therefore, the content of carbon in the water cleaning material is the key factor and it should be kept high. It should also be mentioned that the air bubbles can be fixed firmly on the carbon surface during its contact with wastewater, which results in the total or partial deactivation of the adsorbent surface [9]. That is why deaeration of water is a required pretreatment stage in the adsorptive extraction of the oil products.
The aim of our investigation was to assess the efficiency of removing toluene from water by the raw untreated walnut shells. This material is also easily available and does not require any additional treatment, which keeps its potential cost very low. Practically, in many cases this material can be obtained for free. On the other hand, potential utilization of the used shells after oil products adsorption is also very simple since this material is combustible and it can be burned directly in any solid fuel equipment independently or as an admixture to the main fuel (coal, wood, etc.). High combustion temperature would ensure complete decomposition of the adsorbed aromatic compounds to environmentally safe combustion products.

2. Materials and methods

All model water/toluene systems were made using the distilled water and pure toluene with concentration 0.2 ml/l. Then some amount of the preliminary dried and roughly ground shells (to the particles size 2-5 mm) was added to the system and the toluene adsorption was determined as a ratio between its initial and final concentration in the system. The contact time was of 24 hours.
The concentrations of toluene in water were determined using the modified UV-photometry method [10], which implies the measuring of the light absorbance of the system at the wave length of 258 nm. The method has to be modified since our preliminary investigation proved that some unidentified and optically active substance is released to water from the shells. As a result, the shell itself results in some decrease in the absorbance of the system at 258 nm even without toluene. A series of the blank experiments was carried out in order to take this effect into account and the absorbance decrease values in the blank experiments are shown in Table 1.
Then the calibration diagram was built on the basis of data of Table 1 and the 'blank' values were subtracted from the corresponding results obtained in further measurements where the toluene-consisting systems were used.

Table 1.
Decrease in the absorbance for the water/walnut shells without toluene (blank experiments)

Walnut sample weight, g	Absorbance (*)			Average absorbance for all three series
	Series 1	Series 2	Series 3	
0.49	0.075	0.08	0.072	0.0757
0.98	0.139	0.142	0.136	0.139
1.52	0.162	0.163	0.167	0.164
3.02	0.28	0.27	0.279	0.276

(*) - absorbance of the clear distilled water was taken as the reference point.

It should be emphasized that the absorbance values can be used in our experiments instead of the toluene concentrations because these parameters are in linear dependence and we can consider the relative decrease in the toluene concentrations instead of finding their absolute values. In other words. in the framework of our investigation it is sufficient to determine that the concentration of toluene has decreased for instance by 50 % instead of finding its initial and final values (for instance. 0.18 and 0.09 ml/l).

3. Results and discussion

The initial absorbance of the water/toluene systems and the final absorbance after the addition of some amount of shells to the system are shown in Table 2. Additionally. the percent of the absorbance decrease is shown in the right column of the table.

As seen from Table 2. walnut shells is a quite effective adsorbent. which is capable to adsorb (in terms of 1 g of the adsorbent) up to 27 % of toluene (0.5 g of the shells); 28 % (1 g); 18.7 % (1.5 g) and 11.3 % (3 g). Therefore. the highest specific adsorption of toluene has been determined for the system containing 1 g of the shells. It should be noted that this adsorption performance value can be considered as quite high since it is better than the efficiency of various carbon-clay compositions and comparable with the efficiency of the widely used activated carbon [11].

Taking into account the data of this experiment. we can conclude that the walnut shells exhibit good adsorption properties and can be effective for decontamination of water and wastewater system through extraction of toluene and other aromatic toxicants.

Besides. it was found that in case of activated carbon. low amount of adsorbent can cause an adverse effect of 'bridging' the toluene into the aqueous phase [11. 12]. which results in an unexpected raise in the pollutant's concentration. The shells do not exhibit such an effect. which makes this adsorbent safer than the activated carbon. Even an insufficient amount of shells would not cause any unwanted increase in the pollutant's concentration in water.

4. Conclusion

Walnut shells can be used as an inexpensive and easily available material for adsorption removal of the organic aromatic pollutants in water or wastewater.

Table 2.
Absorbance of the experimental water/toluene systems with various walnut shells samples

Sample weigh. g	Initial absorbance	Final absorbance (*)	Percent of absorbance decrease (**)
(1)	(2)	(3)	(4)
0.5	0.228	0.197	13.5
1.0	0.235	0.170	28.0
1.5	0.196	0.142	28.1
3.0	0.217	0.144	33.9

(*) – all values here are calculated as a result of subtraction of the experimental absorbance from the corresponding value of the blank experiment (see Table 1);

(**) – all values here are calculated by the formula $\frac{value(2) - value(3)}{value(2)} * 100\%$

Within the framework of this investigation. this material has shown the highest specific adsorption performance - 28 % of the initial toluene has been extracted from the system containing 0.2 ml/l of the substance. Higher amounts of the adsorbent provided higher total extraction of toluene. but the specific adsorption efficiency of the shells was lower for the systems with more than 1 g of the shells per liter. It is expected that the most effective adsorbent amount will vary depending on the initial concentration of toluene in water.

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