

COMPARATIVE STUDY OF ADSORPTION ACTIVITY OF ACTIVATED CHAR-COAL AND SILICA GEL IN CASE OF WATER/TOLUENE MIXTURES

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Abstract: Efficiency of the liquid phase adsorption of toluene has been investigated for two common and widely used adsorbents: activated charcoal and silica gel. The adsorption values were determined using the UV-photometry method, where the solution's absorbance has been measured at the wavelength, which corresponds to the characteristic "benzene" peak of the adsorptive. It has been found that charcoal is a highly effective adsorbent for toluene, while silica gel reveals almost no adsorption activity towards this substance no matter if it is used raw or after desiccation. This conclusion can be used in the development of various adsorbents designed to decontaminate water or wastewaters from toluene and its homologues. Such adsorbents should be based mostly on activated charcoal as the most active substrate for the benzene-series hydrocarbons.

Keywords: adsorption, liquid phase, toluene, activated charcoal, silica gel.

1. Introduction

Toluene and other benzene-series compounds are present, among other contamination agents, in many kinds of municipal, industrial wastewaters and, consequently, can be found in contaminated natural water bodies. Aromatic compounds are known as highly toxic and persistent pollutants [1-3]. Therefore, a problem of effective extraction and decontamination from these pollutants is important and topical for many fields of technology, industry and environment protection. Basically, various solutions can be employed in this context: biological cleaning, chemical destruction, physical destruction and adsorption. However, efficiency of many of them remains insufficient, which complicates fast, effective and comparatively inexpensive decontamination of liquids from the benzene homologies.

Indeed, even nonnuclear aromatic hydrocarbons are typical xenobiotics and the rate of their aerobic or anaerobic biodegradation is comparatively low [4, 5]. Remediation and biodegradation of many aliphatic pollutants usually occur much faster [6-8]. It should be noticed that phenol and its homologues are especially persistent and their biodegradation takes the longest time [8]. On the other hand, this method remains the only option for remediation of contaminated soils, water bodies or other similar objects.

Low reactivity of aromatic compounds decelerates their chemical decomposition and requires quite strong oxidizing agents. Apart from low efficiency and apparent high cost of this option, its applicability is seriously restricted by potential danger of formation of the secondary pollution agents, which may be more toxic and dangerous than the primary pollutants. For instance, oxidative decomposition of phenols, halogen phenols and some other aromatic compounds may result in formation of highly toxic dioxins [9, 10].

Physical destruction of aromatic pollutants can be performed, for instance, by UV irradiation solely or in combination with some chemical oxidizing agents (such as H_2O_2) [11]. This method is comparatively safe, effective and competitive.

Various substrates can be used for adsorption removal of aromatic compounds from water. In this context it is important to pay attention to adsorption efficiency (1) and post-adsorption utilization of adsorbent (2). Second issue assumes both remediation and recycling of adsorbent (in this case the pollutant is collected and reused, buried or utilized otherwise) and direct utilization of the adsorbent without any remediation (by burning the activated carbon together with captured contamination).

Both adsorption efficiency and adsorbent usability should be considered for the first issue. In this context, silica gel seems interesting since this material is very cheap, stable, and easy to handle with and can be separated from the liquid systems by very simple technological operations.

On the other hand, it is highly hydrophilic and expectable adsorption efficiency for aromatic compounds to be captured from aqueous solution is arguable.

The main aim of this work was to investigate adsorption efficiency of silica gel in respect to toluene to be captured from its aqueous solution.

2. Experimental

All experimental investigations have been performed using toluene\distilled water mixtures with the solute concentration 0.2 ml/l. Changes in concentration of toluene were measured by determination of absorbance at the wavelength 258 nm corresponding to the 'benzene' peak for this compound [12, 13]. Since absorbance is in the direct dependence on the optically active component molarity, this parameter can be used in further analysis directly instead of the concentration. Further details of the experimental procedures can be found in [13-15].

Two kinds of adsorbents were used in our work: the medicinal activated charcoal in the form of regular detoxification pills (0.5 g each) available at drugstores and regular commercial silica gel balls. The charcoal was used directly while silica gel was divided into two experimental series. In one series we used raw material while in another one we used desiccated silica gel after preliminary thermo treatment at 185 °C during 48 hours. The weight of the latter silica gel samples was controlled repeatedly after the treatment and cooling in the desiccators box and, in case the constant weight value was reached, the balls were considered desiccated and ready for adsorption. No grinding was applied to both adsorbents because the adsorbent dispersion can only influence the rate of adsorption, not its value [13, 15, 16].

The dummy experiments were carried out preliminary with a system containing water and silica gel or charcoal without toluene. No changes in absorbance were registered in that series, which indicates no optical activity in the dummy systems without toluene. Therefore, this experimental method can be applied to the system under investigation.

Then, 1 liter of distilled water was mixed with 0.2 ml of toluene, stirred thoroughly and placed in an inert and closed plastic container for 24 hours to reach stabilization of the solute's concentration. Afterwards, the absorbance was measured using LOMO SF-46 spectrophotometer (5 times for each sample) and an averaged value was taken as the initial point.

Then some amounts of different adsorbents (silica gel and activated charcoal) were

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added to the liquid and temporal changes in the absorbance were measured during 2-3 hours. At last, the final absorbance values were measured after next 24 hours for each system.

3. Results and discussion

A dynamics of temporal changes in absorbance for the system with the thermotreated silica gel is represented in Fig. 1. It can be seen that adsorption activity of silica gel towards toluene remains very insignificant. It changes within 5-8 % from its initial value that does not even go beyond experimental error range.

No adsorption activity has been registered for the raw silica gel and temporal dependencies in this case remained almost horizontal with some very insignificant scattering of the data because of unavoidable experimental errors.

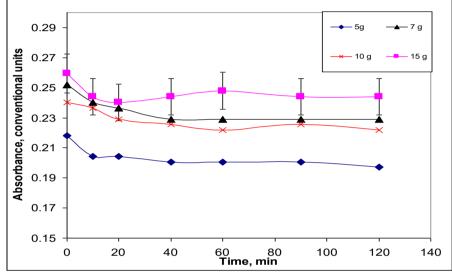


Fig. 1. Temporal changes in absorbance (conventional units) for the systems toluene/water with different samples of silica gel. An approximate experimental error range (5%) is shown for one of the series

Therefore, these changes in absorbance cannot be considered as a reliable mark of active adsorption capturing of toluene by silica gel within the indicated time frame.

In contrary to the above, the activated charcoal shows quite active adsorption of toluene (see Fig. 2). As seen in this case, the changes in absorbance go far beyond the experimental errors range ensuring reliability of the data that proves toluene adsorption on activated charcoal within time frame of the experiment.

Another proof can be obtained from comparison between the initial and final adsorption values for two adsorbents (Table 1).

The data of Table 1 prove that the thermo treated silica gel does not show appropriate adsorption efficiency towards toluene to be adsorbed from aqueous solutions. Amount of the captured adsorptive is very low and it stays beyond accuracy of our experimental investigation. In contrary, adsorption efficiency of untreated medicinal activated charcoal is much higher and it is capable to retain up to 50-60 % of toluene extracted from the 0.2 ml/l aqueous solution.

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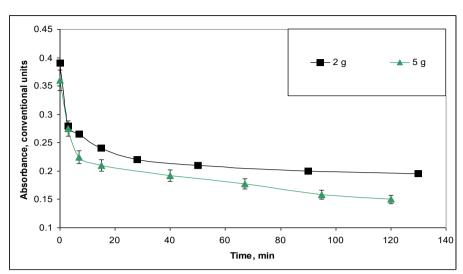


Fig. 2. Temporal changes in absorbance for the systems toluene/water with different samples of activated charcoal. An approximate experimental error range (5%) is shown for one of the series

Relative amounts of the solute retained on the adsorbent's surface for the silica gel and activated charcoal samples Table 1.

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Adsorbent mass, g	Initial absorbance I_{θ} , c. u.	Final absorbance <i>I_f</i> , c.u.	Amount of adsorbed solute (*), %
	Silica gel (the	rmally treated)	
5	0.218	0.206	5.5
7	0.255	0.234	8.2
10	0.242	0.229	5.4
15	0.261	0.246	5.7
	Activated	d charcoal	
2	0.391	0.168	57.0
5	0.369	0.127	65.6

(*) - Any amount of the solute retained by the substrate was calculated as a ratio $\frac{I_0 - I_f}{I_0} * 100\%$, which can be taken as a rela-

tive amount of the solute (in percent) captured by the adsorbent

4. Conclusions

Lower cost, higher durability and handling characteristics of silica gel do not compensate its low adsorption efficiency in toluene/water systems. This substrate cannot be any alternative for usage of activated charcoal in various water/wastewater treatment solutions and other environmental protection technologies.

5. References

[1]. KIM K. H., JAHAN S.A., KABI E., BROWN R.J.C., A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects, *Environment International*, 60: 71-80, (2013).

[2]. SCWARZENBACH R.P., et all, Environmental organic chemistry, Chapter 7, *John Wiley & Sons Inc.*, 213-386, (2013).

[3]. WANG L., ASIMAKOPOULOS A.G., KAN-NAN K., Accumulation of 19 environmental phenolic and xenobiotic heterocyclic aromatic compounds in human adipose tissues, *Environment International*, 78: 45-50, (2015).
[4]. DIAZ E., JIMÉNEZ J.I., NOGALES J., Aero-

bic degradation of aromatic compounds, *Current Opinion in Biotechnology*, 24(3): 431-442, (2012). [5]. BOLL M., LÖFFLER C., MORRIS B.E., KUNG J.W., Anaerobic degradation of homocyclic aromatic compounds via arylcarboxyl-coenzyme A esters: organisms, strategies and key enzymes, *Environmental Microbiology*, 16(3): 612-627, (2014). [6]. LASIECKI P., Biodegradation of diesel/biodiesel blends in saturated sand microcosms. *Fuel*, 116(1): 321-327, (2014).

Igor WINKLER, Kateryna BODNARYUK, *Comparative study of adsorption activity of activated charcoal and silica gel in case of water/toluene mixtures*, Food and Environment Safety, Volume XVI, Issue 3 – 2017, pag. 135 – 139

[7]. VARJANI S.J., Microbial degradation of petroleum hydrocarbons, *Bioresource Technology*, 223(1): 277-286, (2017).

[8]. KRASTANOV A., Microbial degradation of phenol and phenolic derivatives, *Engineering in Life Sciences*, 13(1): 76-87, (2013).

[9]. SHI X., ZHANG R., ZHANG H., XU F., ZHANG Q., WANG W., Influence of water on the homogeneous gas-phase formation mechanism of polyhalogenated dioxins/furans from chlorinated/brominated phenols as precursors, *Chemosphere*, 137: 142-148, (2015).

[10]. FERNANDEZ-CASTRO P., ROMÁN M.F.S., ORTIZ I., Theoretical and experimental formation of low chlorinated dibenzo-*p*-dioxins and dibenzofurans in the Fenton oxidation of chlorophenol solutions, *Chemosphere*, 161: 136-144, (2016).

[11]. BAHNMULLER S., LOI C.H., LINGE K.L., VON GUNTENA U., CANONI S., Degradation rates of benzotriazoles and benzothiazoles under UV-C irradiation and the advanced oxidation process UV/H₂O₂, *Water Research*, 74: 143-154, (2015).

[12]. ARDYUKOVA T., et all, *Aromatic and Hheterocyclic Spectra Atlas. Vol. 7*, Nauka, Novosibirsk, (1973) (In Russian).

[13]. WINKLER I., AGAPOVA N., Determination of water pollution by the oil products through UV photometry, *Environmental Monitoring and Assessment*, 168: 115-119, (2010).

[14]. WINKLER I., DIYCHUK V., Adsorption of toluene from the mixed water-toluene system on medicinal activated carbon, *Canadian J. Chem.*, 92(5): 392-396, (2014).

[15]. WINKLER I., SAVIUC A., Adsorption and electroadsorption of toluene on some graphite/clay materials, *Revue Roumaine de Chimie*, 61(10): 773-778, (2016).

[16]. WINKLER I., KUVILA I., Decontamination of toluene pollution in water using raw walnuts shells, *Food and Environment Safety*, 14(3): 241-244, (2015).