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Sorption of Chlorinated Solvents on Pine and Oak Sawdust

Marek Tobiszewski

Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology (GUT), ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland

Abstract. The article presents assessment of pine and oak sawdusts as sorbents for removal of chlorinated solvents from water. Sawdusts as potential sorbents were characterized with elemental analysis and BET analyses. Sorption capacity was determined for both pine and oak sawdust towards 1,1,2-trichloroethane, tetrachloroethene and 1,1,1,2-tetrachloroethane.

Pine sawdust was able to adsorb greater amounts of chlorinated solvents compared to oak sawdust. Pine sawdust was characterized by larger surface area and its surface was less polar, what promotes sorption. The less polar compounds were sorbed on sawdust surface in greater amounts. Sawdust is weak but cheap sorbent for the removal of chlorinated solvents from water. Its sorption properties could be possibly improved by chemical or physical modification of its surface.

Keywords: Natural sorbents, biosorbents, chlorinated solvents, water treatment.

1. Introduction

Sorption is assumed to be a useful and economical treatment method for removing pollutants, and the most effective conventional sorbent is assumed to be activated carbon. However, its notably high operating cost prohibits the treatment of large amounts of wastewater. Thus, innovative alternatives have been developed by the use of low-cost natural organic solid residue from agricultural and wood industrial activities [1].

Although 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) apparently is not produced or used commercially in large quantities, it may be formed incidentally during the manufacture of other chlorinated ethanes and released into the environment as air emissions or in wastewater**.** An increased incidence of hepatocellular adenomas was observed in mice of each sex and of hepatocellular carcinomas in females. No international guideline for 1,1,1,2-TeCA in drinking-water has been established.

Tetrachloroethene (PCE) is a manufactured chemical that is widely used in the dry-cleaning of fabrics, including clothes. It is also used for degreasing metal parts and in manufacturing other chemicals [2]. PCE is found in consumer products, including some paint and spot removers, water repellents, brake and wood cleaners, glues, and suede protectors.

People are exposed to PCE present in air, water, and food. People may be exposed if they drink the contaminated water. They may also be exposed if PCE evaporates from contaminated drinking water into indoor air during cooking and washing. In humans and animals, the major effects of PCE exposure are on the central nervous system, kidney, liver, and possibly the reproductive system. These effects vary with the level and length of exposure.

1,1,2-Trichloroethane (1,1,2-TCA) is primarily used as a chemical intermediate in the production of 1,1-dichloroethene. It is also used as a solvent for chlorinated rubbers, fats, oils, waxes, and resins. No information is available on the acute, chronic, developmental, reproductive, or carcinogenic effects of 1,1,2-trichloroethane in humans. The effect that has been noted in humans is stinging and burning sensations of the skin upon dermal exposure to the chemical. Acute toxicity animal studies have reported effects on the liver, kidney, and central nervous system (CNS) from inhalation and oral exposure to 1,1,2-trichloroethane, while chronic animal studies have reported effects on the liver and immune system from oral exposure.

The chlorinated solvent can be removed from water by air stripping, catalytic photodegradation [3], advanced oxidation processes [4] or sorption processes [5]. The natural sorbent gain attention for purification processes. The natural sorbents used for purification are straw, peat, tree bark and other agricultural and forest industry wastes.

The aim of this study is to assess pine and oak sawdust as natural sorbent for removal of chlorinated solvents from water.

2. Materials & Methods

Model solutions were prepared by dissolving pure chlorinated solvents (Merck, Germany) in ultrapure water. The sorbent was exactly weighted and put into vial. Then model solution was introduced into vial containing sorbent. After two hours (time needed for sorption determined experimentally) 2 μL of sample was taken from vial with microsyringe and introduced into chromatograph with cold on-column injector. The column applied was Zb-624 60 m of length, 0.32 mm of internal diameter and 1.8 μm of stationary film thickness. The nitrogen was used as carrier gas at the pressure of 130 kPa. The temperature program was started at 102 ℃ and raised to 160 ℃ at rate 10 ℃/min. Electron capture detector was applied.

To perform quantitative analysis external calibration curve was prepared. Five point calibration curve was prepared by analysis of standard solutions of each analyte (Merck, Germany) diluted in water.

The surface area was measured with low temperature (-195 ℃) nitrogen adsorption. Before the measurement the sawdust samples were degassed in 100 ℃ under vacuum. The surface area was calculated by the equation:

$$S_{BET} = a_m \omega N_A$$

where:

a_m – the capacity of monolayer,

ω – surface accupied with single molecule in monolayer (for nitrogen 0,162 nm^2),

N_A –Avogadro number.

The macroelemental composition was measured with Elemental analyzer flash 2000 from Thermo Scientific. Carbon, oxygen, nitrogen and hydrogen content was measured.

The sorption capacity (Q) and partitioning coefficient (Kd) were calculated according to the formulas:

$$Q = (C - C_e) * V/m$$
$$K_d = Q / C_e$$

where:

C – initial concentration of sorbate in model solution [mg L^{-1}]

C_e – concentration of sorbate in water at equilibrium [mg L^{-1}]

V – volume of model solution [L]

m – mass sorbent [g]

3. Results & Discussion

In the Table 1 results of BET and elemental composition analyses are presented. Pine sawdust is characterized by larger surface area (1.8 m^2 g^{-1}) compared to oak sawdust (1.1 m^2 g^{-1}). The atomic ratios [(N+O) / C] and [O/C] give information about polaricity of the surface of the material. The higher the value of atomic ratio the more polar is the material. The atomic ratio [H/C] gives information about aromacity of the material. The higher the value of this atomic ratio the less aromatic material is. The results of elemental analysis show that both sawdusts are similar in terms of aromacity. Pine sawdust is less polar compared to oak sawdust.

In the Table 2 the sorption capacities of each sorbent for each sorbate are presented. Twelve repetitions of each experiment were done. Relatively high values standard deviation can suggest that both sawdusts are materials with low homogenicity. Pine wood sawdust is characterized by larger sorption capacity than oak wood sawdust, towards all three investigated chlorinated solvents. The larger sorption capacity of pine sawdust might be due to:

- larger surface area, what results in higher number of active sites for the adsorption process.
- less polar character of the surface of pine sawdust, what leads to higher affinity of nonpolar molecules of chlorinated solvents towards sorbent.

Table 1: The results of elemental composition and BET analyses of the sorbents

parameter	oak sawdust	pine sawdust
Surface area $m^2 g^{-1}$	1.1	1.8
nitrogen [% w/w]	0.3	0.4
carbon [% w/w]	47.7	50.6
hydrogen [% w/w]	6.3	6.7
oxygen [% w/w]	43.2	40.4
atomic ratio [(N+O) / C]	0.91	0.81
atomic ratio [O/C]	0.91	0.80
atomic ratio [H/C]	0.132	0.132

The three chlorinated solvents are sorbed on the sawdust in different amounts. 1,1,2-TCA is sorbed to less extend probably because of lower octanol – water partitioning coefficient (log Kow = 2.2) compared to 1,1,1,2-TeCA (log Kow = 3) and PCE (log Kow = 3.4). 1,1,1,2-TeCA is the compound sorbed in the greatest amounts on both sawdusts.

For comparison, the sorption capacities of different organic mulches towards PCE varied between 1.3 and 2.2 mg g^{-1}, as determined in other study [6]. The sorption capacity of neem leaf powder towards Congo Red dye was 72 mg g^{-1}, which is much higher compared to the capacity of plant residue with regards to the removal of chlorinated solvents [7]. In the case of Malachite Green sorbed on the plane tree leaves, the measured sorption capacity was 80 mg g^{-1} [8]. The sorption capacity for methylene blue sorbed on jackfruit leaves was 260 mg g^{-1} [9]. In all three aforementioned studies, the sorbents surfaces were prepared in much more extensive manner prior to sorption experiments, what may be the reason for higher sorption capacity.

Table 2: The determined sorption capacities for different systems of sorbent and sorbate.

	Q [mg g^{-1}]	
	Oak	Pine
1,1,1,2-TeCA	0.027 ±0.016	0.032 ±0.013
PCE	0.0203 ±0.0027	0.0278 ±0.0056
1,1,2-TCA	0.019 ±0.011	0.020 ±0.014

The results of calculation of partitioning coefficients are presented in the table 3. For comparison The values of K_d for PCE sorbed on clayey tills ranged from 0.84 to 2.45 L kg^{-1}, while those for PCE sorbed on sandy material varied between 0.22 and 0.72 L kg^{-1} [10].

Table 3: The determined partitioning coefficients for different systems of sorbent and sorbate.

	Kd [L kg^{-1}]	
	Oak	Pine
1,1,1,2-TeCA	29.2 ±8.4	39 ±23
PCE	29.9 ±9.9	59 ±23
1,1,2-TCA	14.3 ±5.7	15.0 ±7.9

4. Conclusions

The sawdust in non-modified form is weak sorbent for removal of chlorinated solvents from water. Its main advantages are low cost and being ready to use. The pine sawdust is characterised by better sorptive properties for chlorinated solvents than oak sawdust. It is connected with its polarity and surface area.

The future research should focus on modification of sorbent surface to obtain better sorptive properties. This could be done by thermal modification or treatment with acidic or alkaline solutions.

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6. References

[1] Ahmad, M., *et al.* Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere (2013), http://dx.doi.org/10.1016/j.chemosphere.2013.10.071

[2] S. Dae Yim, K.-H. Chang, D. J. Koh, I.-S. Nam, Y. G. Kim, Catalytic removal of perchloroethylene (PCE) over supported chromium oxide catalysts. Catalysis Today, 63, 215-222 (2000).

[3] S. Malato Rodríguez, J. Blanco Gálvez, Manuel I. Maldonado Rubio, P. Fernández Ibáñez, W. Gernjak, I. Oller Alberola, Treatment of chlorinated solvents by TiO_2 photocatalysis and photo-Fenton: influence of operating conditions in a solar pilot plant. Chemosphere, 58, 391-398 (2005).

[4] N. N. Mahamuni, Y. G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation. Ultrasonics Sonochem. 17, 990-1003 (2010).

[5] C. Lu, P.L. Bjerg, Fengjun Zhang, Mette M. Broholm, Sorption of chlorinated solvents and degradation products on natural clayey tills. Chemosphere 83, 1467-1474 (2011).

[6] Z. Wei, Y. Seo, Trichloroethylene (TCE) adsorption using sustainable organic mulch. J. Hazard. Mater. 181, 147–153 (2010).

[7] K.G. Bhattacharyya, A. Sharma, Azadirachta indica leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo Red solutions. J. Environ. Manag. 71, 217–229 (2004).

[8] O. Hamdaoui, F. Saoudi, M. Chiha, E. Naffrechoux, Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling. Chem. Engin. J. 143, 73–84 (2008).

[9] M. Tamez Uddin, M. Rukanuzzaman, M. Maksudur Rahman Khan, M. Akhtarul Islam, Adsorption of methylene blue from aqueous solution by jackfruit (Artocarpus heteropyllus) leaf powder: A fixed-bed column study. J. Environ. Manag. 90, 3443–3450 (2009).

[10] C. Ma, Y. Wu, C. Sun, L. Lee, Adsorption characteristics of perchloroethylene in natural sandy materials with low organic carbon content. Environ. Geol., 52, 1511–1519 (2007).