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SORPTION OF SELECTED CHLORINATED SOLVENTS ON PLANT DEBRIS COLLECTED IN A CITY PARK

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Abstract

Debris from deciduous trees in the form of park green waste was investigated as a potential biosorbent for the removal of chlorinated solvents from water. The sorption properties of beech leaves and cupules, oak leaves and acorns, birch leaves and lime leaves (all tree species common for a moderate climate) in a non-modified form were investigated with regard to the removal of perchloroethylene, 1,1,2-trichloroethane and 1,1,1,2-tetrachlorothane. The preliminary results showed that these biosorbents are characterized by very similar sorption properties as well as the surface area and elemental composition. Therefore the sorption capacities and rate constants were determined in the mixture of debris sampled from park green waste. The values of sorption capacity and partitioning coefficient of biosorbent mixture varied from 22.4 to 70 µg g^{-1}, and from 28 to 173 L kg^{-1} respectively. The pseudo-first order reaction kinetics model was fitted to the experimental data, yielding rate constants in the range 0.0187-0.0223 min^{-1}. Due to the lowest polarity, perchloroethylene was a sorbate with the highest affinity for sorbent surface. The results show that chlorinated solvents can be sorbed on park green waste. Although park green waste displays weak sorption capacity, it might be still an attractive sorbent due to good availability and low cost.

Key words: biosorbents, chlorinated solvents, low-cost adsorbent, sorption

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1. Introduction

Chlorinated solvents are environmental pollutants frequently determined in surface and groundwater. Perchloroethylene (PCE), 1,1,1,2-tertachloroethane (1,1,1,2-TeCA) and 1,1,2-trichloroethane (1,1,2-TCA) are used as degreasing agents in the production of plastics and resins, and as extraction agents of wide application (Cheng and Wu, 2011). Their utilization is widespread, while their application involves accidental or intentional releases leading to contamination of surface and groundwater. Due to their toxicity (Bale et al., 2011), chlorinated solvents cause harm to aquatic organisms as well as to humans who drink contaminated water. The U.S. Environmental Protection Agency (U.S. EPA) set the maximum allowable concentrations of 1,1,2-TCA and PCE to 5 µg L^{-1}. Once released to the environment chlorinated solvents can undergo several processes. Because of high density and low solubility in water they tend to percolate to the ground forming dense non-aqueous phase liquids (DNAPL) at the bottom of aquifers (Hartog et al., 2010). Chlorinated solvents are slowly released from DNAPL, which can act as a source of water pollution for even decades (Yang and McCarty, 2000). Apart from dissolution and dispersion, chlorinated solvents may undergo slow biological (Pant and Pant, 2010) or abiotic degradation (Tobiszewski and Namieśnik, 2012).

Considering the processes that chlorinated solvents can undergo, sorption on organic and inorganic matter is often underestimated. Chlorinated solvents can be weakly sorbed on mineral surfaces such as, stylolites (Langer et al., 1999), zeolites (Pasti

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et al., 2012) sand (Ma et al., 2007) and clayey tills (Lu et al., 2011). The most common artificial sorbent is activated carbon (Plagentz et al., 2006) that can be used to remove pollutants or be support for biodegradation on its surface (Nakano et al., 2000). Chlorinated solvents can also be sorbed on organic surfaces such as mulch (Wei and Seo, 2010) or humin (Cunha et al., 2010). Zhang et al. (2008) investigated chemisorption of trichloroethylene (TCE) on iron surfaces. The study demonstrated that sorption on iron plays an important role in reductive dechlorination by increasing the rates of TCE degradation which results in chloroacetylene formation as a by-product. Sorption on plant roots determines both toxicity of chlorinated solvents to plant and applicability of plant organisms to phytoremediation (phytovolatilization) (Ma and Wang, 2009). Various aspects of sorption of organic pollutants on biosorbents have been summarised in the comprehensive review (Aksu, 2005).

Deciduous plant debris is ubiquitous in the environment and may be in contact with chlorinated solvents that are present in surface water or water present in soil. Fallen leaves have also been investigated as potential sorbents for the removal of organic compounds, mainly dyes, from water. Jackfruit leaf powder (Tamez Uddin et al., 2009) and guava leaf powder (Ponnusami et al., 2008) both display sorptive properties in regard to methylene blue, with COOH, CO and OH groups acting as active sites for dye molecules. The Neem tree (*Azadirachta Indica*) leaf powder was found to be a good sorbent for Congo Red dye (Bhattacharyya and Sharma, 2004). PAHs present in water can be sorbed on bamboo leaves, although bamboo leaves are weaker sorbents than pine needles, orange peel or wooden chips (Chen et al., 2011). Fallen leaves have been found to be a substrate for the production of carbonaceous porous material, which can be used as sorbent (Dmitruk et al., 2007).

The aim of the study was to investigate the sorptive properties of deciduous tree debris with regard to PCE, 1,1,2-TCA and 1,1,1,2-TeCA. The study results will help to better understand the environmental fate of chlorinated solvents. The applicability of fallen tree leaves as sorbents in the water remediation systems will also be assessed.

2. Experimental

2.1. Sorbents and sorbates

The materials used in this study as sorbents had been collected in the local park. Samples were rinsed with ultrapure water to remove any impurities and dried in a warm (~27 °C) place for 4 months. Then samples were ground with a mechanical grinder (1 mm sieve size) and stored in plastic bags until analysis. In order to compare sorptive properties of different plant material, tests were performed with granulated activated carbon. The characteristics of granulated activated carbon (Merck, Germany) were as follows: molar mass = 12.01 g mol^{-1}; bulk density 0.4 – 0.5 g cm^{-3}; particle size 0.3 – 0.5 mm. The surface area is 1600 m^3 g^{-1} and the pore volume is 2 cm^3 g^{-1}.

The sorbates, i.e. 1,1,2-trichloroethane (1,1,2-TCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) and tetrachloroethylene (PCE) were of >99% purity (Sigma-Aldrich, Germany). The test solutions were prepared by dissolving the exact volume of solvent in ultrapure water to obtain the desired concentration of solvent in water. The physicochemical properties of sorbates are summarized in Table 1 (Mackay et al., 2006).

Table 1. Physicochemical constants of 1,1,2-TCA; 1,1,1,2-TeCA and PCE

	1,1,2-TCA	***1,1,1,2-TeCA***	***PCE***
Molar mass [g mol^{-1}]	133.4	167.85	165.83
Density [g mL^{-1}]	1.44	1.54	1.62
Boiling point [°C]	113.8	130.2	121.3
Solubility in water at 25 °C [mg L^{-1}]	4390	1100	200
log K_{OW} at 25 °C	2.2	3	3.4

2.2. Chromatographic analysis

The chromatographic analysis was performed by using a gas chromatograph equipped with GC 8000Top electron capture detector (Carlo Erba Instruments, Italy) and cold on-column injection system which allows for direct injection of aqueous samples. A Zb-624 chromatographic column (Zebron, USA; 60 m × 0.32 mm i.d. × 1.8 μm film thickness) was used, while guard capillary columns were installed as pre-column and post-column. Hydrogen was used as a carrier gas. The temperature program started at 102°C, which was held for 1 minute and then raised to 180°C at 10°C/min. The detector temperature was 330°C, and nitrogen was applied as a make-up gas.

In order to calibrate the instrument, a five-point calibration curve was plotted. Standard solutions were prepared by diluting an appropriate volume of stock solution of 1,1,2-TCA, 1,1,1,2-TeCA and PCE (Sigma Aldrich, Germany) with ultrapure water.

2.3. BET analysis

In order to construct the BET adsorption isotherm, 0.3 mg of sorbent was added to each test tube, and the samples were introduced into a Micromeritics Flow Prep 060. The sorbents were heated at 200°C for 2 hours to remove the air, water, and gases present. The next step was to perform the BET analysis by using a Micromeritics Gemini V surface area analyzer.

2.4. Elemental analysis

The elemental analysis (C, O, N and S) was performed with a Flash 2000 analyzer (Thermo Scientific, USA).

2.5. Sorption tests

The sorption tests were performed in 60-mL amber glass bottles. The exact mass of sorbent (0.1 g for single sorbent tests, 0.2; 0.5 or 1 g for mixed sorbent tests) and a 3-mm magnetic stirrer were put into a bottle which was filled with the test solution without leaving any headspace volume. The filling of bottle with the test solution (C_0= 1 mg L^{-1}) was noted as T = 0 min, and the sample was mixed at 200 rpm. The bottle was periodically opened to remove a 2-µL subsample with a microsyringe, and the drawn volume was injected into a chromatograph. The procedural blank had shown that the losses of organic solvent were much lower than the precision of the method therefore they were negligible. Based on the test results, the values of removal efficiency (*RE*) (Eq. 1), sorbed amount (*Q*) (Eq. 2) and partition coefficient (K_d) (Eq. 3) were calculated. These parameters were calculated from the Eqs. (1-3):

$$RE = (C_0 - C_{eq})/\ C_{in} \times 100\%\ [\%] \qquad (1)$$

$$Q = (C_0 - C_{eq}) \times V/m\ [\mu g\ g^{-1}] \qquad (2)$$

$$K_d = Q\ /\ C_{eq}\ [L\ kg^{-1}] \qquad (3)$$

where C_0 is the initial concentration of sorbate; C_{eq} is the concentration of sorbate at equilibrium with sorbent; *V* is the volume of sorbate solution; and *m* is the mass of sorbent.

The kinetics of sorption process is usually described by the pseudo-first order reaction model (Bhattacharyya and Sharma, 2004). The constants of pseudo-first order reaction were determined using Eq. (4):

$$dq_t/dt = k(q_e - q_t) \qquad (4)$$

where q_t is amount sorbed in time *t*, and q_e is amount sorbed at equilibrium. The plot of $log(q_e - q_t)$ versus *t* is a linear function from which the rate constant *k* can be obtained.

3. Results and discussion

3.1. Single sorbent tests

Table 2 contains the information about physicochemical properties of the six investigated sorbents. The elemental composition of the sorbents did not differ much. The range values for the contents of oxygen, carbon, hydrogen and nitrogen were 37.1-42.76, 43.27-48.29, 5.77-6.89, and 0.59-2.61%, respectively. For each sorbent, the mass remaining after the elemental analysis was considered to be ash content.

Apart from macroelemental content, the ratios of H/C and (N + O)/C were calculated for each material. The ratio of H/C gives some information about the structure of material in terms of its aromaticity and the presence of unsaturated carbon-carbon bonds. The higher the value of H/C ratio, the lower the content of aromatic rings and unsaturated bonds. The (N + O)/C ratio gives information about the polarity of material, with high values indicating high content of polar groups in the material structure (Wang et al., 2007). The investigated sorbents did not differ in terms of aromaticity as all the values of H/C ratio fell within the narrow range of 0.13-0.14. The values of (N + O)/C ratio showed that beech cupules, oak acorns and lime leaves were more polar in structure than the leaves of other tree species. The values of carbon content, (O + N)/C ratio and surface area obtained in this study are comparable with those determined by Wei and Seo (2010). The BET analysis demonstrated that the surface areas of beech cupules and oak acorns were much smaller (0.19 - 0.26 m^2 g^{-1}) than those of tree leaves (2.47 - 5.39 m^2 g^{-1}).

Fig. 1 presents the sorption kinetics of three chlorinated solvents in reaction with granulated activated carbon and six tree-based biosorbents. In the case of biosorbents, the equilibrium concentration was reached in less than 1 h for all solvents. In the case of sorption on activated carbon, the time necessary to reach the equilibrium was more variable, i.e. 70, 50 and 20 min for 1,1,2-TCA; 1,1,1,2-TeCA; and PCE, respectively. The efficiency of 1,1,2-TCA removal per 0.1 g of each investigated biosorbent varied between 2.0 and 8.5%. When 0.1 g of granulated activated carbon was used, the removal efficiency reached 96.6%. Oak acorns were the best biosorbent for the removal of 1,1,2-TCA from water, while lime leaves were the least efficient. The differences in the values of removal efficiency were not large. The efficiency of 1,1,1,2-TeCA removal per 0.1 of each investigated biosorbent varied between 5.6 and 11.9%; the efficiency reached 96.9% when 0.1 g of granulated activated carbon was applied.

Table 2. The properties of sorbents determined by elemental and BET analysis

	Beech cupules	***Oak acorns***	***Beech leaves***	***Oak leaves***	***Birch leaves***	***Lime leaves***
O [%]	42.76	40.81	38.81	38.06	37.1	38.12
N [%]	0.59	2.61	1.08	1.27	1.22	1.38
C [%]	46.28	48.29	46.06	47.55	48.06	43.27
H [%]	5.89	6.89	5.82	6.47	6.36	5.77
Ash [%]	4.48	1.41	8.22	6.66	7.27	11.46
(N + O)/C	0.94	0.9	0.87	0.83	0.8	0.91
H/C	0.13	0.14	0.13	0.14	0.13	0.13
Surface area [m^2 g^{-1}]	0.26	0.19	2.47	2.82	2.94	5.39

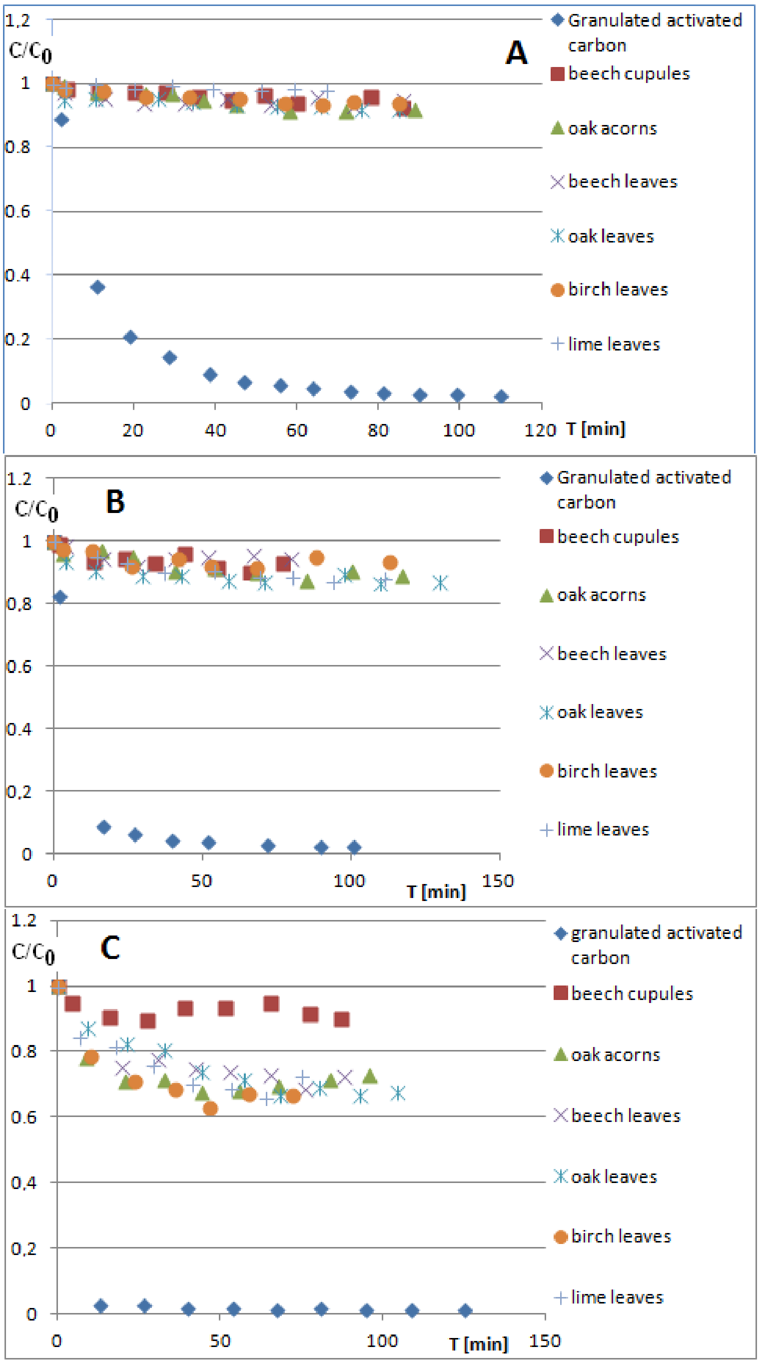

Fig. 1. Sorption of a) 1,1,2-TCA;b) 1,1,1,2-TeCA; and c) PCE on 0.1 g of granulated activated carbon, beech cupules, oak acorns, beech leaves, oak leaves, birch leaves and lime leaves.

In the case of biosorbents, tetrachloroethylene was removed with the efficiency ranging from 26.3 to 32.6%, with the exception of beech cupules which yielded the value of RE = 8.1 %. The application of granulated activated carbon resulted in the efficiency of tetrachloroethylene removal of 98.5%. Beech cupules were the weakest sorbent for the removal of chlorinated solvents from water, which may be related to their highest polarity and low surface area compared to other investigated sorbents. Another sorbent displaying lower sorptive properties was beech leaves. Similarly, to beech cupules, beech leaves are characterized by low content of nitrogen and hydrogen, but they are less polar than the cupules. Since the differences in sorptive properties of the investigated materials are not significant and these materials are often found together in the environment, the next part of the study deals with testing sorbent mixtures, consisting of equal parts of the sorbents.

3.2. Tests on sorbent mixtures

Sorption curves for 1 mg L^{-1} solutions of 1,1,2-TCA; 1,1,1,2-TeCA and PCE plotted against the amount of sorbent are presented in Fig. 2. The removal efficiencies of 1,1,2-TCA were 8, 18.6 and 34.7% per

0.2, 0.5 and 1.0 g of sorbent mixture, respectively. The corresponding values for 1,1,1,2-TeCA solutions were 24.9, 34.2 and 47.7%. PCE was removed with the efficiency of 29.8, 62.5 and 76.1% per 0.2, 0.5 and 1g of sorbent mixture, respectively.

The pseudo-first order rate constants, determined in sorbent mixtures, equaled 0.0187 ± 0.0012, 0.0197 ± 0.0034 and 0.0223 ± 0.0045 min^{-1} for 1,1,2-TCA, 1,1,1,2-TeCA and PCE, respectively. The value of pseudo-first order rate constants for sorption of Congo Red on neem leaf powder, reported by Bhattacharyya and Sharma (2004), was 0.0124 min^{-1}, which is similar to the values for tree-based sorbents obtained in this study. Taking into consideration sorption of chlorinated solvents, Akyol et al. (2011) determined that the sorption constant k for the process of trichloroethylene sorption on caliche soil was equal 0.03 – 0.046 min^{-1}. In this case, the initial amount of trichloroethylene did not greatly influence the sorption constant.

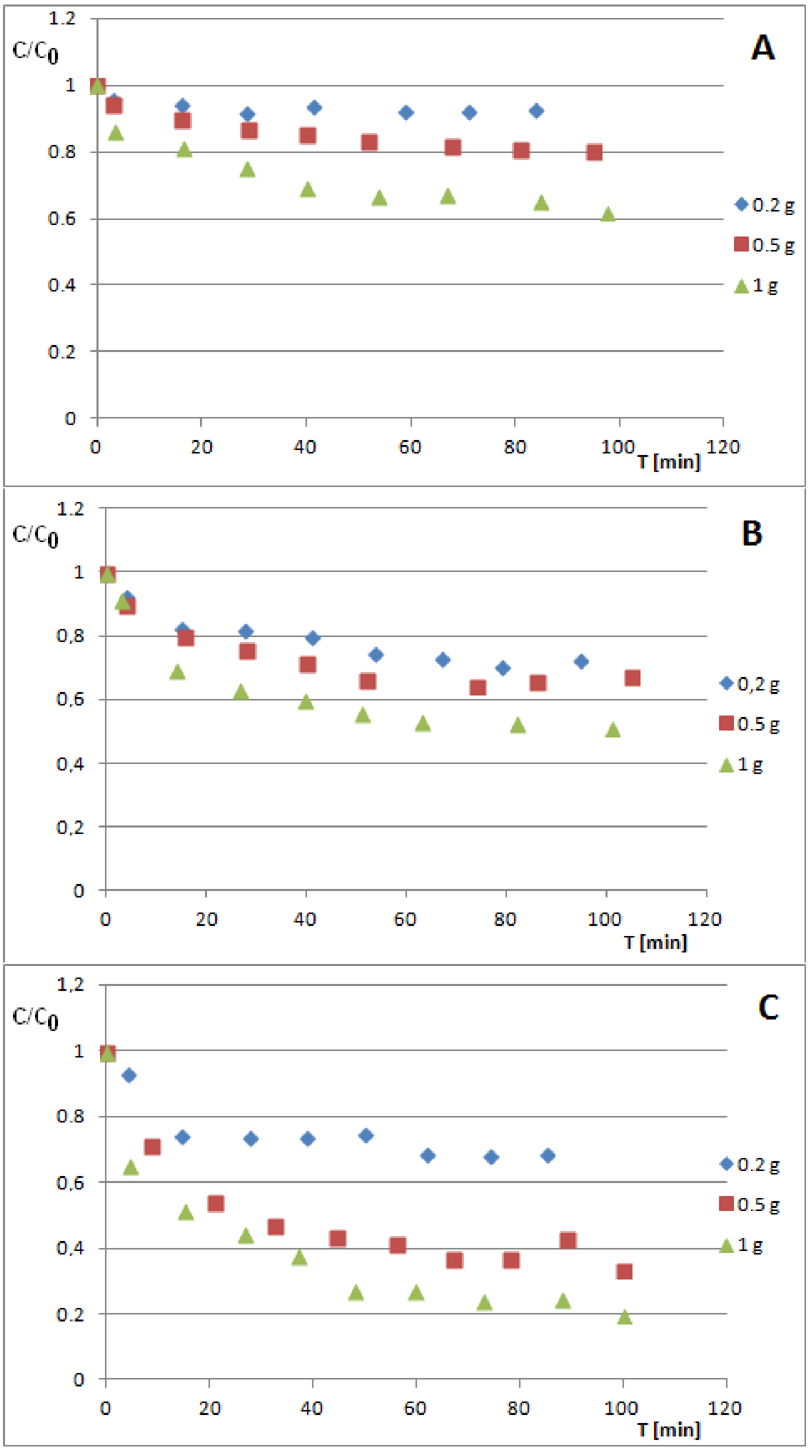

Fig. 2. Sorption of a) 1,1,2,-TCA; b) 1,1,1,2-TeCA; and c) PCE on different masses of mixtures prepared from equal parts (by weight) of beech cupules, oak acorns, beech leaves, oak leaves, birch leaves and lime leaves

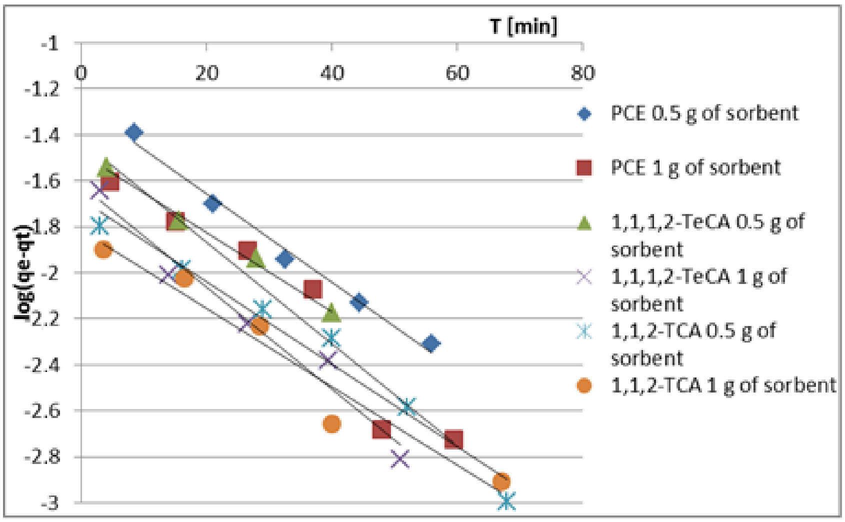

Fig. 3. Plots of pseudo-first order reaction for sorption of 1,1,2-TCA; 1,1,1,2-TeCA and PCE on the mixture of sorbents

The calculated sorption capacity of sorbent mixtures was 22.4 ± 1.6 μg g^{-1} for 1,1,2-TCA, 48 ± 23 μg g^{-1} for 1,1,1,2-TeCA, and 70 ± 22 μg g^{-1} for PCE. The reported sorption capacity of neem leaf powder in relation to Congo Red dye was 72 mg g^{-1}, which is much higher than the capacity of plant residue with regard to the removal of chlorinated solvents (Bhattacharyya and Sharma, 2004). In the case of Malachite Green sorbed on the plane tree leaves, the measured sorption capacity was 80 mg g^{-1} (Hamdaoui et al., 2008). Even higher values of sorption capacity were measured for methylene blue sorbed on jackfruit leaves, i.e. 260 mg g^{-1} (Tamez Uddin et al., 2009). In all three studies, a more extensive sorbent preparation was applied prior to sorption experiments.

The calculated partition coefficients equaled 28 ± 3, 64 ± 23, and 173 ± 39L kg^{-1} for 1,1,2-TCA; 1,1,1,2-TeCA; and PCE, respectively. The partition coefficients for PAHs in a water-bamboo leaves system are in the range from 179 to 15430 L kg^{-1}, with higher coefficients for high-molecular-weight PAHs (Chen et al., 2011). The partition coefficient for naphthalene (179 L kg^{-1}) is similar to the partition coefficient for PCE obtained in this study. The log K_{OW} for naphthalene is 3.3, while that for PCE is 3.4. This seems to confirm the similarity of sorption coefficients determined in leaves (assuming city park waste and bamboo leaves are similar sorbents). The values of K_d for PCE sorbed on clayey tills ranged from 0.84 to 2.45 L kg^{-1} (Lu et al., 2011), while those for PCE sorbed on sandy material varied between 0.22 and 0.72 L kg^{-1} (Ma et al., 2007). The aforementioned coefficients are much lower than those obtained in the present study because the carbon fraction in clayey tills is only 0.02-0.08%, and in sandy material, 0.08-0.54%.

The obtained values of sorption capacity indicate that the investigated plant material, although capable of sorbing chlorinated solvents, is a rather weak sorbent. The application of park green waste as a sorbent of organic compounds has some advantages, e.g. low price, good availability, and no need for processing of biosorbent before application. The presented approach has the disadvantage of the need to treat the sorbent after sorption as it can be considered hazardous. Such problematic waste can be incinerated or dried and chlorinated solvents can be photocatalytically treated in the gaseous phase. More research is necessary to investigate the possible modification of sorbent surface in order to enhance the efficiency of sorption process. This study demonstrates that sorption of chlorinated solvents on plant debris should be considered when modelling the environmental fate of these compounds.

4. Conclusions

Deciduous tree debris was found to be a weak for the removal of chlorinated solvents from water. All the investigated biosorbents were characterized by very similar sorptive properties.

The sorption capacities obtained for park green waste ranged between 22.3 and 70 μg g^{-1}, and depend on the polarity of sorbate, with higher capacity values being associated with nonpolar compounds.

The constants of pseudo-first order reaction ranged from 0.0187 to 0.0223 min^{-1}, while sorption equilibrium was reached in less than 1 hour.

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