Pentachlorobenzene sequestration in sediment by carbon rich amendment

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Abstract
Organic pollutants in sediments are a worldwide problem because sediments act as sinks for hydrophobic, toxic, persistent and bioaccumulative hazardous compoundssuch as penta-chlorobenzene (PeCB). PeCB can be involved in adsorption, desorption and transformation processes and can be made available to benthic organisms through the sediment–water interface. In order to reduce the risk, this study investigates effects of the dose and contact time between sediment and carbon-rich amendments (activated carbon (AC), biochar (BC) and hummus (HC)) on the effectiveness of detoxification. Four doses of carbon-rich amendments (0.5-10 %) and four equilibrations contact times (14 - 180 days) were investigated. The present research highlights the need for further examination and process optimization of different carbon-rich materials used for contaminant removal. Results have shown that the smallest dose (0.5 %) of investigated sorbents was sufficient to reduce the bioavailable fraction of PeCB below 5 %, and the ageing process after 14 days for AC and 30 days for HM and BC negligibly influenced the bioavailable fraction.

Keywords: *sequestration, bioavailability, sediment, remediation, pentachlorobenzene*

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1. INTRODUCTION

Hydrophobic contaminants, such as persistent organic pollutants (POPs), have the ability to associate with fine-grained, organic-rich, sediment material. This association results in contamination of water/sediment system and if conditions in these systems are changed, POPs can be released and become available for uptake by benthic organisms. The term bioavailability represents the amount of a chemical pollutant available for biotransformation and toxicity. This concept is difficult to simplify and numerous scientists tried to define and redefine it [1-7]. Conventional environmental dredging techniques are invasive, expensive and often ineffective, so the management and clean-up of contaminated sediment is a challenging problem [8]. On the other hand, in situ techniques have the ability to isolate contaminants and reduce their maximal flux thus delaying their release to the open water. Active in situ techniques, based on binding, and not eliminating the bioavailable and mobile fraction of organic pollutants (like pentachlorobenzene), currently attract a great interest in the area of sediment quality [8-10].

Pentachlorobenzene (PeCB) has been proposed for inclusion in the Stockholm Convention and in the POPs protocol of the long-range transport of atmospheric pollutants (LRTAP) Convention of the United Nations Economic Community for Europe (UNECE). It was used as a representative chlorinated aromatic because it is frequently detected in sediments[11].

In some earlier studies, researchers observed that POPs may be associated with coal-derived and char particles, in which the compounds are strongly bound and therefore less bioavailable [8]. Addition of carbonaceous materials (such as activated carbons (AC) or biochars (BC)) or hummus (HM) and compost have been shown to significantly reduce pollutant concentrations and risks by binding organic chemicals present in the system sediment/water[12-15]. It is already proven that AC has a great potential for POPs removal. Carbon-rich materials like biochar and hummus have received increased attention in this respect during the past few decades. However, studies are mostly at a lab scale,

focusing on sorption of one or two targeted organic pollutants, while in different natural water/sediment systems coexist organic and inorganic pollutants and there is a competition among them for sorption sites on carbon-rich materials surfaces. Though BC has shown potentials for POPs removal from sediments, its production cost is still the main constraint for field application. Making it cost-effective is a key factor for biochar application in ex situ remediation.

This study is aimed to develop sustainable remediation strategies for sediments contaminated with POPs and to further investigate impacts of different sorbent addition. The more specific objectives of this study were: 1) to review characteristics of activated carbon, biochar and hummus to better understand their efficiency in organic sorption, (2) to investigate effects on sediment geochemistry by amending sediment with hummus, biochar and activated carbon in order to stabilize and sequester the contaminants; 3) to investigate the long-term effects of applied sediment amendments on PeCB bioavailability and 4) to identify problems and suggest directions for future research. Changes in bioavailability of PeCB were measured by using XAD4 Amberlate uptake.

2. MATERIALS AND METHODS

2. 1. Chemicals

Following chemicals were used in the experiment: amberlite XAD4 resin (Fluka, France), silika gel (Fluka, Switzerland), calcium-chloride (Sigma, Germany), potassium-carbonate (Merck, Germany) and mercury (II)-chloride (Centrochem, Serbia). Organic solvents: acetone (Honeywell, Germany), hexane (Panreac, Germany), penta-chlorbenzene (Sigma, Germany) pentane and dichloromethane (Prochem, Germany) were at least of analytical grade. Carbon-rich amendments used in this study were active carbon (Norit, USA), biochar (Maxigrill, Serbia) and humus (Savacoop, Serbia).

2. 2. Sediment preparation

Sediment was collected from Jegrička river site in Autonomous Province of Vojvodina (Republic of Serbia). Sediment was air dried in the dark at room temperature, ground, sieved through a2 mm sieve, spiked with PeCB and left to age 2 years in dark before the experiment. The final concentration of PeCB in the sediment after the two year period was $3340\pm20.5\,\mu g\ kg^{-1}$.

2. 3. Methods for analysis and characterization

Sediment and sorbents characterization. Methods ISO 11277:2009 (wet sieving method)[16] and ISO 8245:1999 (loss of ignition at 550 °C)[17] were used for determination of the particle size distribution and total organic content in sediment, respectively. The surface carbon content in sediment and all investigated sorbents was analyzed by scanning electron microscope (SEM, Hitachi TM3030, Japan) with an energy-dispersive spectrometer (EDS, Bruker Quantax 70 X-ray detector system, Bruker, Germany), while the multi-point BET specific surface area was determined by nitrogen adsorption at 77 K by AutosorbiQ Surface Area Analyzer (Quantachrome Instruments, USA). Mesopore volumes (V_{mes}) were derived from desorption isotherms using the BJH (Barrett–Joyner–Halenda) model. Micropore volumes of sorbents were calculated by t-test and Horwath-Kawazoe (HK) method.

The total amount of PeCB. The total amount of PeCB in the sediment and XAD4 resin were determined according to EPA3550B [18]. Elemental sulfur was removed with copper powder according to the EPA3660B method [19]. The samples were fractionated according to the procedure 3620B [20]. PeCB was analyzed using gas chromatography according to the EPA method 8270C [21].

2. 4 Sediment amendment with carbon rich sorbents

Sediment was treated by the amendment with a certain amount of appropriate sorbent (activated carbon (AC), biochar (BC) and hummus (HC)). For this purpose, 1 g of the spiked sediment was placed in 40 mL glass vials and AC, BC or HC were added in the next doses: 0.1; 0,5; 1; 5 and 10 wt% with respect to the carbon content in the sorbents given in Table 1. All experiments were done in triplicates. In order to prevent microbiological degradation of organic compounds during the experiment, 20 mL of a 300 mg L^{-1} HgCl$_2$ solution was added in the glass vials. Mixtures were thoroughly mixed and left to age for 14, 30, 90 and 180 days in the dark with daily mixing, in order to investigate short-term and the long-term effects of the amended sediments. The efficacy of sorbent amendment, with respect to the dose and aging time, was assessed by the bioavailability test using a desorption experiment with the XAD4 resin.

2.5 Desorption experiments

Preparation of the resin [22, 23]: the XAD4 resin was purified by Soxhlet extraction with ultra-pure water; methanol; mixture of hexane/acetone 1:1; methanol and finally ultra-pure water. Each extraction took 6 h. After that, 0.2 g of XAD4 beads and CaCl$_2$ anhydrous powder (to achieve the amount of 5 mmol CaCl$_2$) were added to each prepared

amended sediment mixture in 40 mL glass vials. The vials were shaken horizontally on an oscillator at 180 rpm for 2, 4, 6, 24, 48, 96 and 144 h (25 °C). In order to facilitate separation of the resin, at selected times 0.8 g of K_2CO_3 powder was added into the vials to increase density of the aqueous phase. The XAD4 beads were refreshed, rinsed 2 times with deionized water, and subjected to ultrasonic extraction 3 times with 10 mL of hexane/acetone (1:1, v/v). The combined extracts were then cleaned and concentrated to 1mL for analysis of PeCB.

A two compartments model was used to describe a two-stage process of desorption of PeCB [24]:

$$\frac{S_t}{S_0} = F_{fast}e^{-k_{fast}t} + F_{slow}e^{-k_{slow}t}$$

$F_{fast} + F_{slow} = 1$

where, S_t and S_o represent the amount of sediment-sorbed contaminant at time *t* and time zero, respectively. The F_{fast} and F_{slow} are fractions of the chemical compound in the rapid and slow desorbing phases at time zero, and k_{fast}, and k_{slow} are the corresponding desorption rate constants, respectively. It is important to note that these compartments are operationally defined and that in reality desorption rates represent a continuum of values. For desorption modeling, the software Origin Lab (free version, OriginLab Corp., MA) was used.

3. RESULTS AND DISCUSSION

3. 1. Sediment and sorbents characterization

The sediment used in this study had 31.6 % of clay, 11.9 % of silt and 15.6 % of coarse sand determined by the wet sieving method ISO 11277:2009. The total pore volume was 0.77 $cm^3 g^{-1}$ and pH value 7.26. The obtained TOC and BET specific surface area values were 2.90 % and 20.3 $m^2 g^{-1}$ respectively, while SEM analyses showed that the examined sediment had 39.7 wt% O, 7.24 wt% C and 53.06 wt% other compounds (Fig. 1a).

The structural and surface characterization of the investigated sorbent materials (AC, BC and HC) is shown in Table 1. As it can be expected, the highest TOC and carbon surface content values had AC. In addition, BET and porosity decreased from AC (690 $m^2 g^{-1}$ and 0.25 $cm^3 g^{-1}$, respectively), HC (2.06 $m^2 g^{-1}$ and 0.014 $cm^3 g^{-1}$, respectively) to BC (0.897 $m^2 g^{-1}$ and 0.007 $cm^3 g^{-1}$, respectively).Characterization of BC and HC using the t-test method showed absence of micropores, while for AC the micropore volume was 0.18 $cm^3 g^{-1}$.However, the HK method showed the presence of micropores in all investigated sorbent materials (Table 1). Based on the obtained results, AC has a microporous structure, while HC and BC consist mainly of mesopores. Besides that, additional information on the surface chemistry of all investigated sorbents is shown in SEM images in Figure 1 (b,c,d).

Table 1. Physical characterization of investigated sorbents

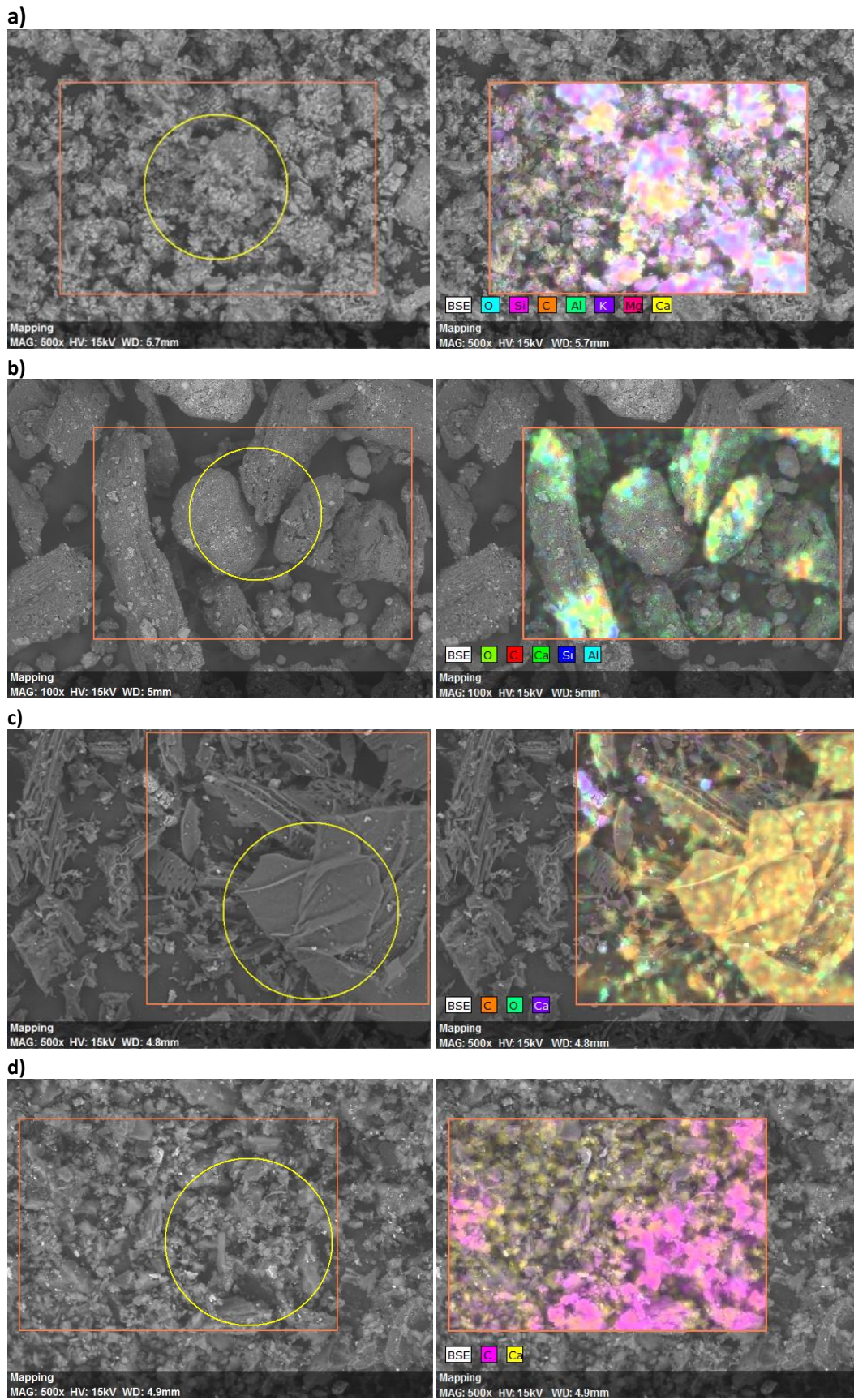|	**AC**	**BC**	**HC**
TOC, %	83.3	75.4	18.5
Content of O, wt%	10.6	18.4	44.0
Content of C, wt%	83.4	81.0	43.3
Content of other elements, wt%	6.00	0.63	12.7
BET specific surface areas, m^2g^{-1}	690	0.897	2.06
BJH pore volume, $cm^3 g^{-1}$	0.25	0.007	0.014
Micropore volume - t test, $cm^3 g^{-1}$	0.18	0	0
Micropore volume - HK method, $cm^3 g^{-1}$	0.20	0.0003	0.0007
Total pore volume, cm^3g^{-1}	0.52	0.006688	0.01
Average pore radius, nm	1.52	149	13.9

Figure 1. The structural and surface characterization of sediment (a), humus (b), biochar (c) and activated carbon (d) (*MAG = magnification)

3.2. Pentachlorobenzene desorption from the unamended sediment

The total amount of the desorbed PeCB from sediment by XAD4 beads was 3333±20.7 µg kg^{-1}, which represents 99.8 % of the total PeCB quantity (Fig. 2). The obtained desorption results were modelled according to the two compartments model using the OriginLab software, where F_{fast} is generally considered as a readily bioavailable fraction [22-27]. Hua *et al.*[25] reported that the XAD beads have a large sorption capacity for POPs. Obtained results in the present study indicate that, even though the sediment aged for two years, almost all present content of PeCB can be released from the sediment and become bioavailable for uptake through the food chain. As it is stated earlier, it is extremely important to evaluate the available fraction of a pollutant. Estimation of bioavailability is traditionally performed by using biodegradation and accumulation in organism tissues. However, these methods have some limits and the need arises for developing rapid, accurate, compound specific, cheap and environmental-friendly methods such as chemical tests [7]. The desorption test of PeCB in the unamended sediment showed that equilibrium was quickly achieved within 1 day with 38.2 % of PeCB in the fast desorbing domain of organic matter (F_{fast}) (Fig. 2).

3. 3. Effects of AC, BC and HC amendments on PeCB desorption from sediment

The reduced PeCB availability in AC, BC or HC amended sediments is manifested in the XAD4beads uptake data [28-30]. Addition of all three sorbents individually reduces the ecological risk of PeCB that was present in the examined sediment, which is a crucial issue in the process of remediation[29-32]. Figure 3 shows that the extracted amount of PeCB decreased in all sediment/AC, sediment/BC and sediment/HC treatments after 180 days. At the lowest dose of AC, potentially bioavailable PeCB concentration was 49.1±2.45 µg kg^{-1}. Increasing the doses from 0.5 wt%, to 1, 5 and 10 wt% the potentially bioavailable amount is reduced to 36.9±1.84, 9.76±0.49 and 2.69±0.134 µg kg^{-1}, respectively. In the sediment/HC treatments, as well as in the BC treatments, increasing the sorbent doses did not lead to the reduction of PeCB uptake by XAD4. The desorbed amount was about 135 µg kg^{-1} for all used doses. Generally, all three sorbents have been shown as good materials for capping the examined pollutant at the concentration 0.5 wt%, although the AC treatment gave the best results with the dose of 10 wt%. Some authors reported that sorption capacity for reduction of HOCs in sediment was determined mainly by the surface area and content of organic carbon[33,34], while others claim that decreasing the surface area does not lead to a decrease in the sorption performance [35-37].
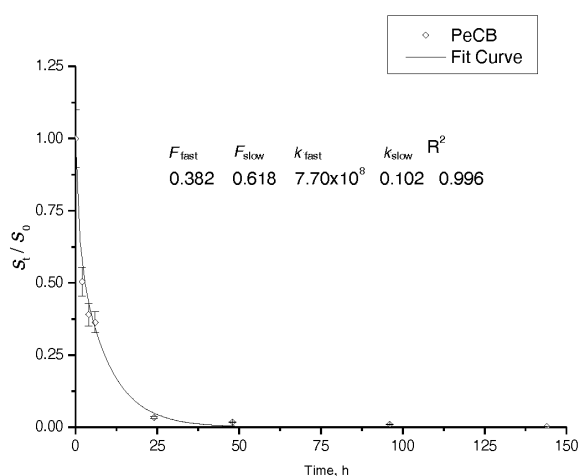

Figure 2. Desorption kinetic modeling by the two-compartment modelfor the unamended sediment: experimental data (symbols) and model predictions (line) (the units for kinetic rate constants are h^{-1})
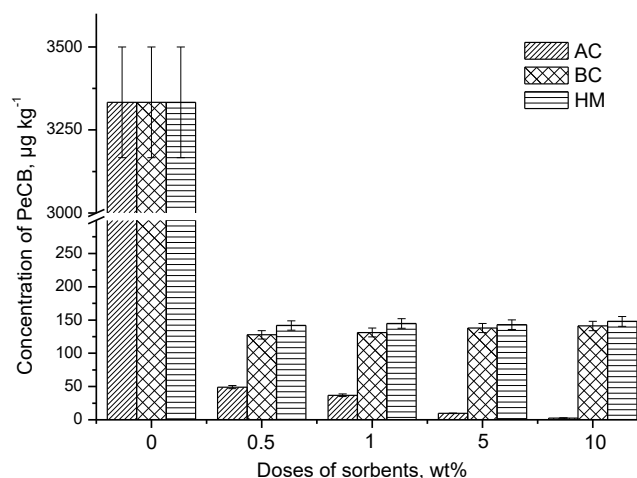

Figure 3. Amounts of PeCB uptaken by XAD4 from sediments without and with sorbent addition

3. 4. Effects of contact time between sorbents and sediment on potentially bioavailable PeCB fraction

Assuming that aging of the sediment with AC, BC and HM affects the bioavailability, it was expected that the increase in the adsorbent dose and time will result in reduction of the bioavailable fraction (Fig. 4). A good correlation was observed for all three sorbents that were used. Addition of AC in the dose of 0.5 wt%, after 30 days reduced the potentially bioavailable fraction up to almost 200 µg kg^{-1} (compared to the 14 days treatment). After that time, the bioavailable fraction was not further significantly reduced. The same observation can be made for addition of 1 wt% AC. For treatments with 5 and 10 wt% AC it can be conclude that after 14 days the XAD4 uptake is already reduced. After that time, the pollutant stayed sorbed onto AC. Regarding the sediment/BC and sediment/HC treatments, after 30days the XAD4 uptake was not further reduced so that it can be concluded that the pollutant stayed sorbed (Fig. 4). Some

previous studies have shown that regardless the carbon type, an increase in the contact time between the sorbent and sediment caused a further reduction of the bioavailable fraction, as compared to the untreated sediment [25]. However, in the present study after 14 and/or 30 days in all treatments, sorbents achieved their maximum and prolonging the time did not lead to further sorption or desorption. These results are in agreement with some previous studies [38-42].
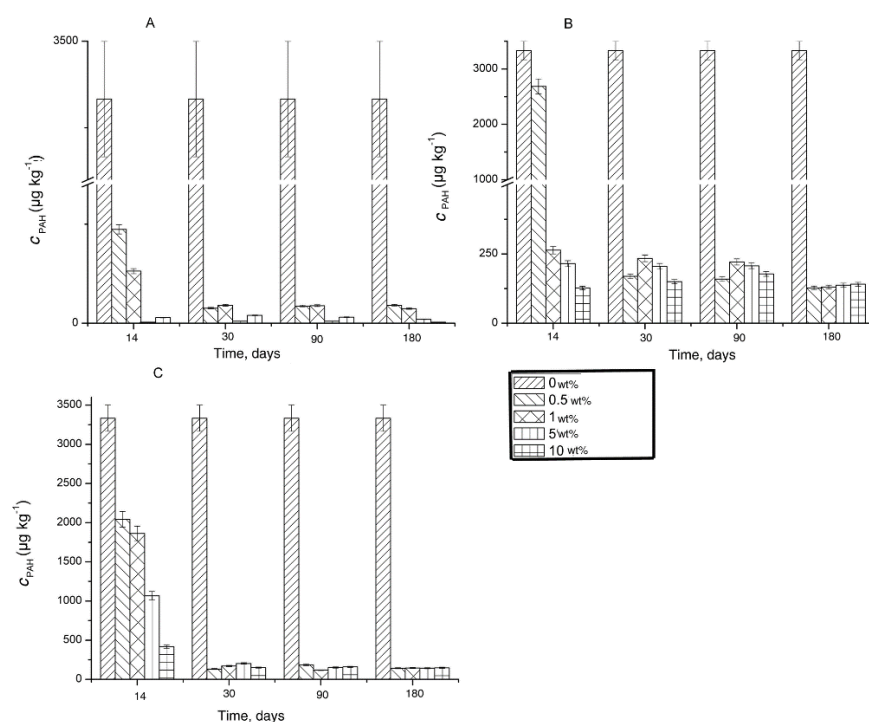

Figure 4. Amounts of PeCB uptaken by XAD4 at different time periods from sediments treated with AC (A), BC (B) and HC (graph C) (0 wt% (without sorbents) was measured only once, in the beginning of the experiment)

The mechanism itself is explained in several research and review papers[13,43-45]. The most probable mechanism of PeCB binding to nanopores of carbonaceous materials is by π-π bonds with its graphene surface, which results in an irreversible binding of PeCB to the sorbents and reduction of the extractable fraction. These results are consistent with the mechanism of sorption of highly hydrophobic, persistent organic pollutants with planar structures by soot and soot-like carbon particles [14,45-48].

4. CONCLUSION

The present research highlights the need for further examination and process optimization of different carbon-rich materials used for contaminant removal. The smallest dose (0.5 wt%) of investigated sorbents was sufficient to reduce the bioavailable fraction of PeCB below 5 wt%, and the ageing process after 14 days for AC and 30 days for HM and BC did not affect significantly the bioavailable fraction. By observing the sorbent prices, it can be concluded that satisfactory results can be obtained by BC or HM, which are available in wholesale for acceptable price. Without a doubt the effect of addition of different sorbents to sediments requires further research. However, before direct application, properties and impact of these materials on sediment characteristics and long-term effects on microbial ecology should be investigated. This might be worth proving under field conditions, aiming to evaluate the process efficiency in a real system.

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SAŽETAK

Sekvestracija pentahlorbenzena u sedimentu primenom sorbenata bogatih ugljenikom

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(Stručni rad)

Prisustvo organskih polunatanata, kao što je pentahlorbenzen (PeCB) predstvalja problem širom sveta. Sediment se ponaša kao rezervoar za hidrofobne, toksične, perzistentne i bioakumulativne organske komponente. PeCB može da podlegne procesima sorpcije, desorpcije, kao i transformacionim procesima, te može postati biodostupan vodenim organizmima. U cilju smanjenja rizika, ova studija imala je za cilj procenu efikasnosti doze i kontaktnog vremena između sedimenta i nekoliko sorbenata bogatih ugljenikom(aktivni ugalj (AC), biougalj (BC) i humus (HM)) na proces detoksifikacije sedimenta. Ispitivane su četiri doze sorbenata (0.5-10 %) i četiri vremena (14-180 dana). Dobijeni rezultati su pokazali da je pri najmanjoj dozi od 0.5 % za sve upotrebljene sorbente biodostupna frakcija smanjena ispod 5 % i da se procesom starenja nakon 14 dana za AC i 30 dana za HM i BC biodostupna količina PeCB ne povećava.

Ključne reči: starenje, biodostupnost, sediment, remedijacija, pentahlor-benzen