Czech University of Life Sciences Faculty of Environmental Sciences Department of Applied Ecology



Bachelor Thesis Appendices

Experimental comparison of the suitability of filter materials for the removal of selected micro-pollutants occurring in greywater

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5. Results

The study details the levels of substances, like carbon, nitrogen, heavy metals (copper, nickel, zinc) and pharmaceuticals (ibuprofen and benzotriazole) in effluent after using specific additives in infiltration trenches. The findings are organized into tables and graphs based on time intervals (22 hours and 72 hours) and saturation levels (30% and a decrease, from 70% to 30%).

5. 1. Efficacy in removal of total carbon (TC)

The concentration of TC in influent dose shown as SGW in had a mean value of 79.29 mg/L which was applied to in each experimental set up. Combinations of experimental set ups (Appendix No. 1; Appendix No. 3) represent comparison of TC removal in individual scenarios.

Samples collected after 72 hours of contact time with saturation of 70% which later decreased to 30% showed overall decrease in total carbon (TC) concentrations over the course of the experiment (Appendix No. 1., a.). Concentrations of TC were reduced below the influent concentration after only 2/3 of the experiment time. The decrease in saturation from 70% to 30% assessed in TC levels stabilization in this set up preventing TC increase. Woodchips was the first filter material to reach below 79.29 mg/L of influent TC dose and had lowest concentrations in the second half of the experiment with 41.16% of peak efficiency (Appendix No. 5., A.). However, when we analyze woodchips and other tested filter materials with respect to mean efficiencies in TC removal, all the tested filter materials failed to accomplish effectiveness in TC removal (Appendix No. 2.; Appendix No. 4.).

Appendix 1. Concentration of TC after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe

indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 2. TC removal efficiency after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Samples collected after 72 hours of contact time at 30% saturation general decrease in TC levels. However, TC concentrations were below the SGW dosage only by the end of the experiment at tested woodchips (max. 9.64%) and limestone (max. 10.06% efficiency) while the remaining tested filter materials failed in TC removal (Appendix No. 5., B.). TC removal with application of all tested filter materials at 30% saturation did not show any feasible success in the given time frame of 6 months (Appendix No. 2., b.).

Samples collected after 22 hours of contact time at 70 - 30 % saturation had a general decrease of TC levels across the experiment (Appendix No. 1., c.). Sudden increase of TC concentrations in case of default group appeared four weeks after the start of the experiment on 29/07/2021. The sudden increase may be related to technical errors at the collection of samples or at laboratory analyses. Saturation decrease (from

70% to 30%) in a highlighted timeframe capture stable decrease of the TC. However, TC concentrations increased after this event and were no longer stable maintaining similar TC levels in each tested filter materials. In the second half of the experiment woodchips show the lowest TC concentrations compared to other tested filter materials (max. 48.72% efficiency) (Appendix No. 5., C.). Removal efficiencies of tested filter materials did not show any immediate results nor did one reliable filter material (Appendix No. 4., c.).

Appendix 3. Concentration of TC after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 4. TC removal efficiency. after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



Samples collected after 22 hours of contact time at saturation 30 % presented scattered data on TC concentration in the effluent which were higher than the dose of TC (79.29 mg/L) in SGW influent. Tested filter materials did not prove to be effective at 30% saturation after 22 hours (Appendix 5)

Appendix 5. Concentration of TC in filtering materials (FMs) [%]. Numeric indications (30, 70) stand for saturations [%].

Section A: Saturation – 70-30%, contact time – 72 hours.
Section B: Saturation – 30%, contact time – 72 hours.
Section C: Saturation – 70-30%, contact time – 22 hours.
Section D: Saturation – 30%, contact time – 22 hours.

5. 2 Efficacy in removal of total organic carbon (TOC)

The concentration of TOC in influent shown in the charts representing concentration had a mean value of 66.4 mg/L. Combinations of experimental set ups (Appendix No. 6; Appendix No. 8) represent comparison of TOC removal in individual scenarios.

Samples collected after 72 hours of contact time with saturation of 70% which later decreased to 30% showed successful removal of TOC in effluent from the start to the end of the experiment (Appendix No. 6, a.). Saturation decrease did not show significant change in the decreasing trend. As overall removal of TOC occurred below the influent dose (66.4 mg/L) all the tested filter materials could achieve moderate removal of TOC in the effluent ranging from 53.67% (woodchips) to 66.12% (biochar 5%) in mean efficiency (Appendix No. 10, A; Appendix No. 7, a.).





Appendix 7. TOC removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Samples collected after 72 hours of contact time at 30% saturation showed general decrease below the TOC dose (66.4 mg/L) in TOC levels the same as it was shown at 70% saturation but with few changes in individual filter material efficiencies (Appendix No. 6, b.). TOC removal efficiency in tested filter materials including default resulted in moderate removal ranging from 50.74 % (default) to 63.29 % (biochar 5%) in mean efficiency (Appendix No. 10, B.). Biochar 5% had the highest removal efficiency among others (Appendix No. 7, b.)

Samples collected after 22 hours of contact time at 70% which later decreased to 30% saturation had general decrease of TOC (Appendix No. 8). In this experimental set up default exceeded TOC dose (66.4 mg/L) in influent on 29/07/2021. The same change was not observed in the rest of the tested filter materials, technical errors may have caused this shift as other experimental set ups did not show similar results (Appendix No. 8). Saturation decrease (70-30%) did not prove any significant changes. TOC removal efficiency ranged between 48.92 % (default) and 62.69% (biochar 5%) in mean efficacy similar to previous set up (Appendix No. 10, c.). Biochar 5% had the highest removal efficiency among all tested filter materials (Appendix No. 9, c.).

Appendix 8. Concentration of TOC after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 9. TOC removal efficiency. after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



Samples collected after 22 hours of contact time at saturation of 30 % had gradual decrease in TOC concentrations (Appendix No. 8, d.). Effluent TOC concentrations were below the influent dose. The removal efficiencies ranged between 47.46 % (default) and 62.69 % (biochar 5%) (Appendix No 10, D.). Biochar 5% had better results among other tested filter materials with more reliable performance in this set up (Appendix No 9, d.).

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Appendix 10. Efficiency of TOC removal from GW by individual types of filtering materials (FMs) [%].
Numeric indications (30, 70) stand for saturations [%].
Section A: Saturation – 70-30%, contact time – 72 hours.
Section B: Saturation – 30%, contact time – 72 hours.
Section C: Saturation – 70-30%, contact time – 22 hours.
Section D: Saturation – 30%, contact time – 22 hours.
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| | | TOC [| [%] | |
|---|-------|--------|-------|-------|
| | MEAN | MIN | MAX | SD |
| | 58.41 | 24.91 | 80.06 | 17.21 |
| | 53.67 | 15.91 | 76.77 | 20.90 |
| | 54.63 | 27.85 | 78.86 | 16.89 |
| А | 66.12 | 51.40 | 83.28 | 10.33 |
| | 50.74 | 26.92 | 73.30 | 14.73 |
| | 52.88 | 22.25 | 72.13 | 15.81 |
| | 59.09 | 29.57 | 80.71 | 15.63 |
| В | 63.29 | 47.67 | 74.54 | 9.16 |
| | 48.92 | -50.39 | 80.38 | 31.35 |
| | 52.54 | 15.72 | 80.06 | 20.30 |
| | 53.95 | 26.03 | 80.40 | 17.73 |
| С | 65.59 | 47.24 | 78.49 | 9.26 |
| | 47.46 | 21.31 | 75.85 | 16.45 |
| | 52.20 | 14.82 | 77.01 | 17.57 |
| | 60.11 | 32.47 | 80.37 | 13.46 |
| D | 62.69 | 47.28 | 75.96 | 8.64 |

5. 3. Efficacy in removal of inorganic carbon (IC)

Laboratory analyses of samples collected after 72 hours of contact time at 70% saturation had a general decreasing trend at all testing filter materials, but the results were insufficient due to failure in decreasing the IC concentrations below the influent dose of 13.19 mg/L (Appendix No. 11., a.). Saturation decrease caused IC levels increase in all tested filter materials due to 3 weeks of break. Woodchips resulted in the lowest IC concentrations among other filter materials but was insufficient to filter IC (Appendix No 12., a.)

Appendix 11. Concentration of IC after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 12. IC removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Samples collected after 72 hours of contact time at 30% saturation shown general decreasing character in IC levels. However, results were insufficient to achieve IC concentrations below influent dose (13.19 mg/L) (Appendix No. 11., b.). Biochar

5% had higher chances of IC decrease than other filtering materials but could not meet the expectations (Appendix No. 12., b.).

Samples collected after 22 hours of contact time at 70 - 30 % saturation results present a general decrease of IC levels (Appendix No. 13., c.). Shorter contact time allowed to decrease IC concentrations below the given IC baseline in SGW (13.19 mg/L). Saturation decrease caused scatter of data after 3 weeks of break. At 22 hours contact time at 70 - 30 % saturation woodchips were more effective among others but was not sufficient to achieve IC concentrations below the initial dose (Appendix No. 14., c.).

Appendix 13. Concentration of IC after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 14. IC removal efficiency. after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



IC concentration at minimal contact time and saturation has more scattered distribution of data compared to results after 72 hours of contact time (Appendix No. 13., d.). Removal of IC concentrations was not effective in all tested groups (Appendix No. 14., d.). Limestone had better chances in removal but could not meet the expectations.

5. 4. Efficacy in removal of total nitrogen (TN)

Laboratory analyses of samples collected after 72 hours of contact time at 70% saturation had general decreasing character. Removal of TN concentrations was remarkably efficient compared to TC and IC as it is shown by decreasing trends of each filtering material. Biochar 5% had removal efficiency of 77.48 %. The default structure appeared to remove TN concentrations effectively without any additives applied at 75.47 %. Limestone had 74.15 % removal efficiency and at last woodchips had 71.04 % (Appendix No. 19., a.).

Appendix 15. Concentration of TN after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 16. TN removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Samples collected after 72 hours of contact time at 30% saturation after laboratory analyses showed a general decrease in TN levels the same as it was shown

at 70% saturation (Appendix No. 15., b.). At 30% saturation data on efficiency of TN removal had scattered values compared to 70-30%. The most effective filter material was biochar 5% with 83.76 % efficacy. Woodchips (80.6 %) and limestone (80.99 %) had similar performance (Appendix 16., b. ; Appendix 19., b.).

Samples collected after 22 hours with 70-30% saturation show general decreasing character in TN concentrations across tested filter materials in this set up. Saturation changes from 70-30% may have lead to TN concentrations stabilization toward the end of the experiment (Appendix No. 17., c.). Removal efficacies ranged between 68.49 % (default) – 74.41 % (biochar 5%) (Appendix No. 19., c.).

Appendix 17. Concentration of TN after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 18. TN removal efficiency. after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



TN concentrations in the last experimental set up had few data fluctuations but showed a general decrease character in its trend over the course of the experiment. All the changes in TN concentrations in tested filter materials appeared below the given TN dose in influent SGW (Appendix No. 17., d.). Biochar 5% had been most effective in removal performing at 81.6 % Limestone had 79.04 % of efficiency. Woodchips were not too far at efficiency performing at 78.49 % removal. Default had 72.6% of removal efficiency. Application of additives show 5.89 - 9 % efficiency in TN concentrations removal (Appendix No. 19., d.).

Appendix 19. Efficiency of TN removal from GW by individual types of filtering materials (FMs) [%]. Numeric indications (30, 70) stand for saturations [%].

Section A: Saturation – 70-30%, contact time – 72 hours.

Section B: Saturation – 30%, contact time – 72 hours.

Section C: Saturation – 70-30%, contact time – 22 hours.

Section D: Saturation – 30%, contact time – 22 hours.

| | Filter material efficie | ency in eli | minati | ng of T | N [%] |
|---|-------------------------|-------------|--------|---------|-------|
| | Filtration material | MEAN | MIN | MAX | SD |
| | Def70 | 75.47 | 62.94 | 87.77 | 7.76 |
| | Wood70 | 71.04 | 38.89 | 90.29 | 13.98 |
| | Lime70 | 74.15 | 55.95 | 86.19 | 10.29 |
| А | Bio70 | 77.48 | 60.43 | 90.06 | 8.46 |
| | Def30 | 75.15 | 63.15 | 85.63 | 8.09 |
| | Wood30 | 80.60 | 69.58 | 91.28 | 7.09 |
| | Lime30 | 80.99 | 67.58 | 92.58 | 7.85 |
| В | Bio30 | 83.76 | 77.98 | 91.41 | 4.19 |
| | Def70 | 72.27 | 42.62 | 87.84 | 11.32 |
| | Wood70 | 68.49 | 29.96 | 86.49 | 15.78 |
| | Lime70 | 72.25 | 42.21 | 87.68 | 13.05 |
| С | Bio70 | 74.41 | 53.79 | 90.30 | 10.55 |
| | Def30 | 72.60 | 58.86 | 89.74 | 8.95 |
| | Wood30 | 78.49 | 65.89 | 92.20 | 7.74 |
| | Lime30 | 79.04 | 69.46 | 92.33 | 6.90 |
| D | Bio30 | 81.60 | 70.95 | 91.90 | 5.09 |

5. 5. Efficacy in removal of ammonia ion (NH₄⁺)

Samples collected after 72 hours with saturation of 70-30% showed no success in removal of ammonia ions from effluent as results were not below the dose in influent (0.06 mg/L) (Appendix No. 21., a.). NH₄⁺ increase have been detected from 1st to 6th week at all tested additives including default structure. The highest peak in increase was detected on 5th week in effluent from tested woodchips additive (Appendix No. 20., a.). A rapid drop in NH₄⁺ concentrations coincided with saturations decrease (70-30%). NH₄⁺ concentrations were stable and had decreasing character after this event. NH₄⁺ concentrations in detail at removal by individual tested additives including default. Lowest NH₄⁺ concentrations were identical at biochar 5% and default structure (0.53 mg/L). Limestone had 0.58 mg/L NH₄⁺ concentration. Woodchips had 0.74 mg/L NH₄⁺ concentration being the highest (Appendix No. 24., A.).

Appendix 20. Concentration of NH4+after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 21. NH4+removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Samples collected after 72 hours of contact time at 30% saturation showed no sufficient efficiency in ammonia ions removal (Appendix No. 21., b.). Limestone could lower NH_{4^+} concentration up to 0.06 mg/L equaling to initial dose of NH_{4^+} . Furthermore, limestone had minor success in retaining low NH_{4^+} concentrations by the end of the experiment. Biochar 5% could decrease it up to 0.08 mg/L. Woodchips performed at lower efficiency of 0.11 mg/L. The default structure had 0.17 mg/L NH_{4^+} concentration in effluent (Appendix No. 24., b.).

Samples collected after 22 hours of contact time at 70-30% saturation had the same pattern in fluctuations appeared as in samples after 72 hours of contact time and 70-30% saturation. The exponential increase of NH_4^+ concentrations dropped in the 6th week and this event coincided with saturation change with 3 weeks break (Appendix No. 22., c.). Nevertheless, results from this experimental set up state that tested filter materials did not prove to be effective (Appendix No. 23., c.).

Appendix 22. Concentration of NH4+after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).







Samples collected after 22 hours of contact time at 30% saturation showed that ammonium ions (NH₄⁺) concentrations had very odd fluctuations. Shorter contact time showed with lower saturation showed unpredictability of NH₄⁺ concentrations trend by scattering data in comparison to other experimental set up (Appendix No 22., d.). Limestone could retain NH₄⁺ concentrations equal to initial effluent dose (0.06 mg/L) (Appendix No. 24., d.). Tested filter materials did not prove to reliable against ammonia ion pollution (Appendix No. 23., d.)

Appendix 24. Concentrations of NH4+ in tested filtering materials (FMs) [%]. Numeric indications (30, 70) stand for saturations [%].

Section A: Saturation – 70-30%, contact time – 72 hours.

Section B: Saturation – 30%, contact time – 72 hours.

Section C: Saturation – 70-30%, contact time – 22 hours.

Section D: Saturation – 30%, contact time – 22 hours.

| | Concentrations of NH4+ | in tested l | FMs [n | ng/L] | |
|---|------------------------|-------------|--------|-------|------|
| | Filter materials: | MEAN | MIN | MAX | SD |
| | Def70 | 0.53 | 0.06 | 2.34 | 0.68 |
| | Wood70 | 0.74 | 0.02 | 3.22 | 0.98 |
| | Lime70 | 0.58 | 0.09 | 1.90 | 0.56 |
| А | Bio70 | 0.53 | 0.14 | 1.78 | 0.57 |
| | Def30 | 0.17 | 0.05 | 0.77 | 0.19 |
| | Wood30 | 0.11 | 0.04 | 0.34 | 0.08 |
| | Lime30 | 0.06 | 0.00 | 0.20 | 0.05 |
| В | Bio30 | 0.08 | 0.01 | 0.20 | 0.05 |
| | Def70 | 0.57 | 0.09 | 2.20 | 0.66 |
| | Wood70 | 0.82 | 0.03 | 3.35 | 1.15 |
| | Lime70 | 0.66 | 0.03 | 2.09 | 0.67 |
| C | Bio70 | 0.60 | 0.06 | 2.44 | 0.76 |

| | Def30 | 0.12 | 0.02 | 0.25 | 0.07 |
|---|--------|------|------|------|------|
| | Wood30 | 0.10 | 0.00 | 0.27 | 0.07 |
| | Lime30 | 0.06 | 0.02 | 0.13 | 0.03 |
| D | Bio30 | 0.11 | 0.02 | 0.25 | 0.07 |

5. 6. Efficacy in removal of boron (B)

Samples collected after 72 hours at 70-30% saturation showed data in B concentrations behavior in tested filter materials including default structure. The first 2.5 weeks of the experiment showed a rapid increase in B concentrations. General behavior of B concentrations had higher values than B dose in influent (0.97 mg/L). Similar values in concentrations of B in tested filter materials across the experiment suggest that selected filter materials support B presence in effluent but not indicate removal efficiency as B concentrations at the start of the experiment were lower than influent dose and increased as the experiment proceeded (Appendix No 25., a.). Starting from the 2nd week concentrations of B met influent baseline of 0.97 mg/L and dates coincide with 3 weeks break for saturation decrease. Mean values of B stabilization range from 0.94 - 0.96 mg/L for all groups. Minimal values range in between 0.27 (default structure) and 0.59 mg/L (woodchips) (Appendix 29., a.). Tested filtering materials were not suitable for B removal in this experimental set up (Appendix No. 26., a.).

Appendix 25. Concentration of Boron after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).







Samples tested after 72 hours at 30% saturation had similar results of B concentrations over the course of the experiment as in previous set up but with minor differences in trend. It must be noted that biochar 5% dropped B concentrations below the influent baseline slightly in the 7th week in comparison to other tested groups (Appendix No. 25., b.). The mean value of B removal in tested filter materials showed a range between 0.90 – 0.95 mg/L in all tested groups. Minimal values ranged in between 0.07 to 0.26 mg/L (Appendix No. 29., b.). Tested filter materials could not accomplish feasible removal of B from effluent (Appendix No. 26., b.).

Samples collected after 22 hours at 70-30% saturation showed alternative pattern of B concentrations behavior. From the 2nd to 3^{rd} quarter major data fluctuations occurred. Shorter contact time could impact in higher concentrations of B. The lowest B concentration was observed in biochar 5% below the influent dose (0.97mg/L). 3 weeks of break for saturation change (70-30%) coincided with B concentrations decrease to influent dose level. The final week of the experiment presented a decrease and stabilization of B concentrations in all tested groups. These events coincide with shorter contact time and temperature drop in late October (Appendix No 27., c.). Mean B concentrations in filtering materials including default structure have a range in-between 1.00 - 1.02 mg/L. Minimal values of B range from 0.71 mg/L (woodchips) to 0.88 mg/L (limestone) (Appendix No. 29., c.). Removal efficiency data stated stabilization of B concentrations in effluent across all tested filter materials but did not prove effective removal of B (appendix No. 28., c.).



Appendix 28. Boron removal efficiency after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



Samples collected after 22 hours at 30% saturation appeared to have a similar drop in B concentrations compared to experimental set ups which included saturation change with a 3-week break. Saturation change did not occur at groups with 30% saturation, but the 3-week break was universal across all set ups. Due to the fact of no infiltration with SGW similar patterns in B concentrations in this set up can be seen. Low concentrations of B at the start of experiment and at the end may have appeared due to higher chance of precipitation during rainy seasons (Appendix No 27., d.). B concentrations ranged in between 0.96 - 0.99 mg/L. Minimal values varied from 0.70 mg/L observed in woodchips to 0.78 mg/L observed both in limestone and default (Appendix No. 29., d.). This experimental set up supported the idea that the selected filtering materials could stabilize the B concentration near influent dose but did not lead into effective removal of B from effluent (Appendix No. 28., d.).

Appendix 29. Concentration of B in filtering materials (FMs) [%]. Numeric indications (30, 70) stand for saturations [%].

Section A: Saturation – 70-30%, contact time – 72 hours.

Section B: Saturation – 30%, contact time – 72 hours.

Section C: Saturation – 70-30%, contact time – 22 hours.

Section D: Saturation – 30%, contact time – 22 hours.

| | Filter material: | MEAN | MIN | MAX | SD |
|---|------------------|------|------|------|------|
| | Def70 | 0.95 | 0.26 | 1.18 | 0.28 |
| | Wood70 | 0.90 | 0.11 | 1.12 | 0.31 |
| | Lime70 | 0.95 | 0.07 | 1.19 | 0.31 |
| Α | Bio70 | 0.93 | 0.08 | 1.16 | 0.30 |
| | Def30 | 0.95 | 0.26 | 1.18 | 0.28 |
| | Wood30 | 0.90 | 0.11 | 1.12 | 0.31 |
| | Lime30 | 0.95 | 0.07 | 1.19 | 0.31 |
| В | Bio30 | 0.93 | 0.08 | 1.16 | 0.30 |
| | Def70 | 1.01 | 0.80 | 1.16 | 0.11 |
| | Wood70 | 1.01 | 0.71 | 1.27 | 0.15 |
| | Lime70 | 1.02 | 0.88 | 1.23 | 0.12 |
| С | Bio70 | 1.00 | 0.85 | 1.21 | 0.12 |
| | Def30 | 0.97 | 0.78 | 1.09 | 0.10 |
| | Wood30 | 0.96 | 0.70 | 1.10 | 0.12 |
| | Lime30 | 0.99 | 0.78 | 1.16 | 0.11 |
| D | Bio30 | 0.96 | 0.77 | 1.08 | 0.11 |

5. 7. Efficacy in removal of copper (Cu)

Samples collected after 72 hours at 70-30% saturation showed Cu concentrations drop from the start in all of the observed groups and had significantly steady progression throughout the course. Baseline Cu concentration was 0.21 mg/L (Appendix No. 30., a.). All tested groups stayed below the baseline at some points leading to complete removal of Cu. Removal efficiency of Cu in observed groups had a mean range from 99.02 % to 99.25 % of removal (Appendix No. 34., A.). The most effective additive in the group was limestone with more reliable performance over the course of the experiment (Appendix No. 31., a.). However, it must be noted that other filtering materials including default with no additives accomplished removal. As default structure had similar efficacy in Cu removal (99.13 %) it must be stated that no additives were needed for Cu treatment (Appendix No. 34., A.).

Appendix 30. Concentration of Cu after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 31. Cu removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



In the case where 30% saturation at the same contact time of 72 hours general pattern of the progression showed more fluctuations in-between weeks of observation compared to previous set up. Although, overall trend had shown increases in Cu concentrations in all the tested groups, values of Cu remained below the influent baseline of 0.21 mg/L (Appendix No. 30., b.). Default structure in this set up had better success compared to other filter materials (Appendix No. 31., b.). However, range of removal efficiency was still high in other tested filter materials (99.37 % - 98.11 %) (Appendix No. 34., B.). It must be stated that lower saturation did not bring significant changes to the observed results.

Samples collected after 22 hours at 70 - 30% saturation presented Cu concentrations trend in observed groups to be below the influent Cu dose as it was observed in previous set ups. 3 weeks break did not effect Cu concentrations in this

case (Appendix No. 32., c.). Limestone had the highest removal rate at 99.34 % with minimal scatter of data among other types of filter materials (Appendix No. 33., c.). However, other materials did not show to be less effective as the range of efficacy in Cu removal ranged in-between 99.25 % (default and biochar 5%) - 99.34 % (limestone) (Appendix No. 34., C.).

Appendix 32. Concentration of Cu after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 33. Cu removal efficiency after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



showed smooth trend over the course of the experiment where all the tested groups had similar progression. Cu concentrations from all the observed groups remained below the influent baseline of 0.21 mg/L. An increase in Cu concentrations occurred Cu concentrations at the lowest saturation (30%) and contact time (22h) in the 5th week with its peak in the following week with woodchips having the highest value. However, this increase did not go above the baseline. Dates of 3 weeks break of no irrigation coincide with this gradual increase in Cu concentrations in all tested

(Appendix No. 34., d.).

groups (Appendix No.32. Efficiency of Cu removal from GW by individual types of filtering materials (FMs) [%]. performance in removal at 99.33 % (Appendix 30, 50) estanding (30, 50) estanding (30, 50) estanding [%].

including default had removal efficacy ranging from 288530%; contact time -72 hours.

(limestone)

Section B: Saturation – 30%, contact time – 72 hours.

Section C: Saturation – 70-30%, contact time – 22 hours.

Section D: Saturation – 30%, contact time – 22 hours.

| | Filter material | efficiency Copper [% | in elimi 6] | inating o | of |
|---|-----------------|-------------------------|----------------|-----------|------|
| | Filter material | MEAN | MIN | MAX | SD |
| | Def70 | 99.13 | 98.02 | 99.58 | 0.45 |
| | Wood70 | 99.02 | 97.91 | 99.46 | 0.44 |
| | Lime70 | 99.16 | 98.13 | 99.59 | 0.42 |
| А | Bio70 | 99.25 | 98.98 | 99.61 | 0.24 |
| | Def30 | 98.95 | 98.42 | 99.48 | 0.33 |
| | Wood30 | 98.11 | 89.35 | 99.51 | 3.10 |
| | Lime30 | 98.92 | 98.03 | 99.53 | 0.52 |
| В | Bio30 | 99.37 | 99.01 | 99.70 | 0.22 |
| | Def70 | 99.25 | 98.86 | 99.68 | 0.26 |
| | Wood70 | 99.21 | 98.96 | 99.60 | 0.22 |
| | Lime70 | 99.34 | 98.89 | 99.67 | 0.21 |
| C | Bio70 | 99.25 | 99.02 | 99.64 | 0.17 |
| | Def30 | 98.85 | 98.39 | 99.51 | 0.37 |
| | Wood30 | 99.03 | 98.54 | 99.60 | 0.33 |
| | Lime30 | 99.10 | 98.74 | 99.54 | 0.27 |
| D | Bio30 | 99.33 | 99.08 | 99.65 | 0.18 |

5. 8. Efficacy in removal of nickel (Ni)

Concentrations of Ni after 72 hours at 70-30% saturation conveys significantly smooth character of progression in tested groups throughout the course. Ni concentrations remained way below the influent baseline of 0.19 mg/L (Appendix No. 35., a.). Limestone performed at mean 99.48 % of removal rate, showing the highest

efficiency (Appendix No. 36., a.). Mean range of Ni removal varied from 98.88 % (woodchips) – 99.07 % (default) of efficiency across the whole experiment resulting in no need for filtering materials for Ni removal in this experimental set up (Appendix No. 39., A.).

Appendix 35. Concentration of Ni after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 36. Ni removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Results from the 30% saturation after 72 hours showed sudden increase of Ni concentration in tested woodchips material. The sudden increase did not show natural pattern in change. This record might refer to incorrect data on the 4th week). Disregarding the fact that woodchip's abnormal record remaining testing groups had shown smooth overall decrease in Ni concentrations (Appendix No. 35., b.). Removal efficiency data showed very limited scattering in Ni removal observed in all tested groups compared to previous set up except woodchips outlier. The most efficient additive was biochar 5% (Appendix No. 36., b.). Remaining groups did not fail and performed at 98.23 % – 99.01 % removal range (Appendix No. 39., B.).

Ni concentrations at lower contact time (22 hours) at 70 - 30% saturation showed steady progression below the influent Ni dose of 0.19 mg/L. No visible fluctuations appeared during the whole course. Visual representation of the data in boxplots show relatively bigger scattering of data in tested default and woodchips compared to remaining groups (Appendix No. 38., c.). Biochar 5% was the most effective at 99.22 %. However, remaining groups were as efficient as biochar 5% by the removal ranging from 99.06 % (default) – 99.11 % (limestone) (Appendix No. 39., C).

Appendix 37. Concentration of Ni after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 38. Cu removal efficiency after application of filtering materials during the experiment. C. 70-30% saturation at 22 hours. D. 30% saturation at 22 hours.



Results from the 30% saturation and 22 hours contact time showed similar characteristics in progression pattern of all tested filter materials including default structure. No major fluctuations occurred during the experiment (Appendix No. 37., d.). Although, progression pattern did not show any significant changes, removal

efficiency in percentual view indicates fluctuations in comparison between tested groups (Appendix No. 38., d.). Biochar 5% had removal of 99.30 %. Limestone had 99.1 %, followed by woodchips with the removal of 99.03 %. The least effective from all the groups observed was default structure at 98.71 % (Appendix No. 39., D). It must be stated that all groups performed at highest possible rates.

Appendix 39. Efficiency of TN removal from GW by individual types of filtering materials (FMs) [%]. Numeric indications (30, 70) stand for saturations [%].

Section A: Saturation – 70-30%, contact time – 72 hours.

Section B: Saturation – 30%, contact time – 72 hours.

Section C: Saturation – 70-30%, contact time – 22 hours.

Section D: Saturation – 30%, contact time – 22 hours.

| | Filter material effi | iciency in o | elimina | ting of Ni | i[%] |
|---|----------------------|--------------|---------|------------|------|
| | Filter material | MEAN | MIN | MAX | SD |
| | Def70 | 99.07 | 97.68 | 100.00 | 0.65 |
| | Wood70 | 98.88 | 97.63 | 99.89 | 0.64 |
| | Lime70 | 99.48 | 99.22 | 100.00 | 0.27 |
| А | Bio70 | 98.93 | 97.96 | 100.00 | 0.64 |
| | Def30 | 98.89 | 97.70 | 100.00 | 0.68 |
| | Wood30 | 98.73 | 97.74 | 99.73 | 0.60 |
| | Lime30 | 98.56 | 97.19 | 99.40 | 0.60 |
| В | Bio30 | 98.49 | 96.90 | 99.58 | 0.88 |
| | Def70 | 99.06 | 98.09 | 99.91 | 0.55 |
| | Wood70 | 98.40 | 95.25 | 99.38 | 1.28 |
| | Lime70 | 99.11 | 98.02 | 99.93 | 0.53 |
| C | Bio70 | 99.22 | 97.62 | 100.00 | 0.71 |
| | Def30 | 98.71 | 97.74 | 99.95 | 0.61 |
| | Wood30 | 99.03 | 97.06 | 99.84 | 0.73 |
| | Lime30 | 99.10 | 97.26 | 99.24 | 0.56 |
| D | Bio30 | 99.30 | 97.86 | 99.81 | 0.69 |

5. 9. Efficacy in removal of zinc (Zn)

Concentrations of Zn in tested filter materials including default at 70 - 30% saturation and 72 hours of contact showed decreased levels of Zn below the influent

baseline of 0.22 mg/L throughout the experiment. First half of the experiment Zn concentrations remained close to 0 mg/L in all observed groups. From the 5th week increasing Zn concentrations continued to grow till the end of the experiment. Dates of mentioned growth coincide with 3 weeks of break with no irrigation (Appendix No. 40., a.). In the removal efficiency limestone was dominant among other groups which showed 99.16 % of removal (Appendix No. 41., a.). Remaining groups had mean removal of 98.49 – 98.99 % (Appendix No. 44., A).

Appendix 40. Concentration of Zn after application of filtering materials during the experiment. A. 70-30% saturation after 72 hours. B. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).



Appendix 41. Zn removal efficiency. after application of filtering materials during the experiment. A. 70-30% saturation at 72 hours. B. 30% saturation at 22 hours.



Zn concentrations in observed groups after 72 hours at 30% saturation present steady trend for the first half of the experiment. However, from after 3 weeks break fluctuations with increase took place in all tested groups. The highest peak was depicted in biochar 5% (0.05 mg/L). It must be noted that all the fluctuations occurred below the influent baseline of 0.19 mg/L (Appendix No. 40., b.). Biochar 5% did not

show consistency in Zn removal by its scattered behaviour in the boxplot (Appendix No. 41., b.). Woodchips had the highest removal at 99.01 %. Mean removal in remaining groups was in-between 98.23 (biochar 5%) -98.78 (default) % (Appendix No. 44., B).

Zn concentrations at 22 hours of contact time at 70 - 30 % saturation state general increasing character. However, increase in Zn concentrations in tested groups had been raising, levels of the selected micropollutant stayed below the given influent baseline of 0.22 mg/L. In closer overview, first three weeks show steady progression where Zn concentrations did not exceed 0.01 mg/L. From 3rd week to 6th week minor increase of Zn was detected at multiple tested groups. Sudden increase first occurred in biochar 5% with its peak on 4th week. Woodchips peak occurred on 5th week. Following week resulted in Zn decrease in woodchips, but the remaining groups had major increase in Zn. Weeks 7-8 show stability in Zn concentrations in all groups. Woodchips on 8th week had repeating increase in Zn, with an interval of one-week remaining groups had shown increase respectively. These fluctuations could be related to 3 weeks break as dates coincide (Appendix No. 42., c). According to the removal efficiency chart, default structure was dominant in removal with 98.57 % (Appendix No. 43., c.). Woodchips (98.39 %), limestone (98.07 %), and biochar 5% (97.96 %) had similar results (Appendix No. 44., C). It must be noted that woodchips among other tested groups had the widest scatter of extracted data throughout the experiment period (Appendix No. 43., c.).

Appendix 42. Concentration of Zn after application of filtering materials during the experiment. C. 70-30% saturation after 22 hours. D. 30% saturation after 22 hours. Red timeframe indication: 3 weeks break (12/08/2021-2/9/2021).







Zn concentrations after 22 hours and 30 % saturation in tested groups show somewhat similar pattern with few differences compared to previous results. First 5 weeks of the experiment had shown stable progression of Zn in all the observed groups. Results from 6th week had shown major increase of Zn in all the groups. Gradual decrease in Zn with fluctuations was observed across weeks 6-9. These changes in Zn increase also coincide with 3 weeks of no action. Higher increase of Zn occurred on week 10 with gradual drop by the end of the experiment. It must be noted that all the changes of Zn concentrations in observed groups occurred below the influent baseline of 0.22 mg/L (Appendix No. 42., d.). The least data scatter can be observed in default structure, whereas remaining groups had relatively higher scatter across the experiment period (Appendix No. 43., d.). Default, limestone, and woodchips performed at high efficiency of 98.07 % – 98.57 % (default) with default structure leading groups Biochar 5% was the least effective compared to other groups with the removal of 97.99 %. Removal efficiency in all tested groups show high rates if minimal efficiency rates are considered (Appendix No. 44., D.).

Appendix 44. Efficiency of Zn removal from GW by individual types of filtering materials (FMs) [%]. Numeric indications (30, 70) stand for saturations [%].

Section A: Saturation – 70-30%, contact time – 72 hours.

Section B: Saturation – 30%, contact time – 72 hours.

Section C: Saturation – 70-30%, contact time – 22 hours.

Section D: Saturation – 30%, contact time – 22 hours.

| | Filter material efficiency in eliminating of Zn [%] | | | | |
|---|---|-------|-------|--------|------|
| | Filter material | MEAN | MIN | MAX | SD |
| | Def70 | 98.99 | 96.62 | 100.00 | 1.16 |
| А | Wood70 | 98.68 | 95.21 | 100.00 | 1.77 |

| | _ | | | | |
|---|--------|-------|-------|--------|------|
| | Lime70 | 99.18 | 97.02 | 100.00 | 1.13 |
| | Bio70 | 98.35 | 96.36 | 100.00 | 1.40 |
| | Def30 | 98.78 | 96.64 | 99.95 | 1.06 |
| | Wood30 | 99.01 | 97.35 | 100.00 | 1.14 |
| | Lime30 | 98.51 | 95.59 | 100.00 | 1.64 |
| В | Bio30 | 98.23 | 95.02 | 100.00 | 1.96 |
| | Def70 | 98.44 | 93.79 | 100.00 | 2.16 |
| | Wood70 | 98.09 | 94.60 | 99.72 | 2.00 |
| | Lime70 | 98.66 | 95.59 | 100.00 | 1.68 |
| С | Bio70 | 97.96 | 93.83 | 100.00 | 2.30 |
| | Def30 | 98.57 | 94.48 | 100.00 | 1.86 |
| | Wood30 | 98.39 | 95.65 | 100.00 | 1.58 |
| | Lime30 | 98.07 | 93.37 | 100.00 | 2.43 |
| D | Bio30 | 97.99 | 95.07 | 100.00 | 1.96 |