The Effect of Manganese Oxides and Ferric Hydroxides on the Treatment of Greywater in Unsaturated Constructed Wetlands

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Onsite reuse of greywater for various purposes is increasingly common but requires treatment to meet legal and safety standards for both users and the environment. Constructed wetlands (CWs) are effective for greywater treatment, providing both efficient contaminant removal and ecosystem services. While greywater usually has low concentrations of bulk organic contaminants, it may contain high levels of organic micropollutants, which pose risks when reused for irrigation. CWs can remove some biodegradable or non-mobile micropollutants, though many are poorly removed. Enhancing removal efficiency is possible using reactive filtration bed additives like iron hydroxides and manganese oxides. The study aimed to determine the impact of these amendments on organic micropollutants removal and the abundance of functional genes. A vertical-flow CW with an intermittent feeding regime and unsaturated bed was used, promoting aerobic processes. The system was fed with artificial greywater containing 26 organic micropollutants at concentration 10 or 50 µg/L. Ferric hydroxides improved organic micropollutants removal by 28%, and manganese oxides by 7%, compared with the efficiency in treatment filled with sand. Vegetation did not affect organic micropollutant removal in control sand-filled CWs but increased it by 7% in manganese oxide columns. In the systems with iron hydroxides, vegetation reduced organic micropollutant removal by 9%. The removal processes mediated by the (hydr)oxides could be assumed to be oxidation and also sorption. The highest overall removal of organic micropollutants, 84%, was achieved in the planted systems with ferric hydroxide. However, some compounds, such as artificial sweeteners, fluconazole, and hydrochlorothiazide, remained resistant to both biotic and abiotic degradation and require further attention. This study found that media type significantly affected the absolute abundance of 15 genes ($p<0.05$). Ferric hydroxide supported higher prokaryotic and fungal community growth than sand and manganese oxide ($p<0.05$), showing the highest abundance of bacterial 16S rRNA, archaeal 16S rRNA, and fungal ITS genes. Manganese oxide had the lowest prokaryotic and fungal community abundance among all media tested. The abundance of the gene involved in the Fe-oxidizing process (encoding MtoA c-type cytochrome) was only detected in the presence of ferric hydroxide, while the proportion of genes associated with the Mn-oxidizing process (*mnxG* and *mcoA*, belonging to multicopper oxidases group) was the highest in the manganese oxide-filled CWs. The proportion of key genes related to the indirect electron transport chain for both Fe and Mn-reducing processes (*mtrA*, *mtrB*, *cymA*) tended to be lower in the presence of ferric hydroxide($p<0.05$) compared to manganese oxides and sand ($p<0.05$). In the CWs filled with ferric hydroxide or manganese oxides, *mnxG* genes dominated over *mcoA* and mtrA, mtrB, and cymA genes.