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Research paper

Halloysite nanotubes as a fine grained material for heavy metal ions removal in tropical biofiltration systems

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ABSTRACT

Biofiltration systems are landscape depressions or shallow basins used to slow and treat on-site stormwater runoff and are considered as one of the important components of a sustainable drainage system. Biofilters generally consist of two components: a filtration media which is sand-dominant and a top vegetated soil layer. The efficiency of a biofiltration system is normally assessed by two key parameters namely hydraulic conductivity and percentage removal of pollutants. In tropical areas like Malaysia where rainfall intensity is normally high, hydraulic conductivity of the biofiltration systems needs to be high enough to prevent ponding and possible flooding of the system. To date, several studies have been done on development and maintenance of such systems; however, few have studied such systems under tropical climates with heavy and intense rainfall which needs high hydraulic conductivity. The present study aims to identify proper soil filter media that not only can remove heavy metal ions efficiently but also has reasonably high hydraulic conductivity. For this, a soil column experimental set up was developed and the effectiveness of adding different fine grained materials such as fly ash, halloysite nanotubes (Hals) from two different origins (Imerys from NZ and HalloPure from I-Minerals, Idaho), and zeolite in sand-based soil media was assessed. To assure the validity of the results for each proposed filter media three replicates were prepared. The performance in removing heavy metal ions Fe(III), Mn(II), Cu(II), Zn(II), Ni(II), and Pb(II) was then evaluated for each soil composition using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) test. Synthesized stormwater was used to provide consistency of pollutant concentration in experiments. The watering dosage was calculated based on hydrological data of a Malaysian catchment. Infiltration rate of each soil composition was also measured for further comparison. Results showed that increasing the percentage of fine materials can improve the heavy metal ions removal; however, the drawback would be significant decrease in infiltration rate. In general, Hals were found to fulfill the requirements for both high percentage removal and high infiltration rate compared to zeolite and fly ash. Moreover, the effect of aspect ratio, surface area, particle size and chemical composition of each fine material on its efficiency in heavy metal ions removal and infiltration rate were compared.

1. Introduction

Stormwater has been a major concern in urbanized areas as it contributes in ground/surface water pollution and it also causes ponding and flooding. Stormwater contamination is mainly due to sediments, heavy metals, nutrients, oil and grease, and pathogens. The source of heavy metals are automobiles fluid leaks, tires, paints and atmospheric deposition (Davis et al., 2003) while excess nutrients such as nitrogen and phosphorus come from fertilizers, wastes, vegetation remainder, and concentrated sewage from septic tanks or sewer overflow (Hunt et al., 2006). To date, several solutions have been proposed and practiced to manage both quality and quantity of stormwater from which wetlands, green roofs, and biofiltration systems are quite well-established (Blecken et al., 2009).

Biofiltration systems are landscaped depressions or shallow basins that can slow down and treat stormwater on-site. Biofiltration system is considered as a low-energy treatment technology with the potential to provide both water quality and quantity control (Hatt et al., 2009). Biofiltration systems consist of a layered soil media with different range of particle sizes which accommodates vegetation on its top surface. In general, soil contributes in removing sediments and heavy metal ions while plants contribute in removing nutrients. To date, several studies

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have been conducted both in lab and field scales to assess the functionality and performance of such system for different soil media, plant species, and climates (Davis et al., 2003; Hsieh and Davis, 2005; Dietz and Clausen, 2005; Hatt et al., 2008). It has been found that biofiltration systems are able to successfully remove several types of pollutants and bring their concentration down to the acceptable levels for release to nature. In tropical regions, however, very limited studies have been reported in literature. The high intensity and frequency of rainfall in tropical climate in one hand and high urbanization rate in many of tropical countries on the other hand, may change the design criteria for biofiltration systems. In general, the soil media in a tropical biofilter needs a higher infiltration rate to cope with higher rainfall intensity. However, this higher infiltration rate should not compromise the pollutant removal efficiency.

To date, several soil compositions have been studied to achieve appropriate soil media for biofiltration system. Fly ash is one of the promising adsorbents due to its low-cost and excellent removal capabilities for certain metals ions. Fly ash is the byproduct produced from burning pulverized bituminous, hard coals in power station furnaces (Sear, 2001). The furnace typically operates at temperature higher than 1400 °C to generate steam for electricity production. The fusion of mineral impurities and exhaust gas during the combustion process can result in the production of fly ash. Fly ash commonly consists of 38–52% silicon dioxide (SiO_2), 20–40% aluminum oxide (Al_2O_3), 6–16% iron oxide (Fe_2O_3), and 1.8–10% of calcium oxide (CaO). Due to its particle size, fly ash is usually utilized in concrete and cement mixture, although > 40% of its production results in disposal to landfill (Sear, 2001). Fly ash is considered as fine aggregate material in soil classification and it has been used in several water filtration applications. Babel and Kurniawan (2003) studied the adsorption capacity of fly ash for Cu^{2+} and Cr^{6+} ions. Authors reported the adsorption capacity of 1.39 mg Cu^{2+}/g at pH 8.0 and 2.92 mg of Cr^{6+}/g at pH 2.0. Yeheyis et al. (2008) studied the environmental applications of both fresh and landfilled coal fly ash. The results showed that both the fresh and landfilled fly ash can absorb the heavy metal ions well. The study also concluded that both types of fly ash are environmentally safe and can be used for different applications. In another research, Gupta et al. (2009) studied possible materials that can be used as low-cost adsorbents for treating different water pollutants. The authors used fly ash for absorption of Cu(II) and it was conformed to the Langmuir absorption. The study stated that fly ash is highly available despite mentioning the cost of using it. Hegazi (2013) studied the effect of fly ash dose on removal percentage of metals. The author showed that by increasing the fly ash concentration from 20 to 60 g/L, the percentage removal increased from 46% to 87%, 22% to 76%, 37% to 99%, and 95% to 96% for Fe(III), Pb(II), Cu(II), and Ni(II) ions, respectively. The author also highlighted the possibility of metal leachate as fly ash contains metals. However, it was not a concern in that study due to the fact that the concentration of the heavy metals ions were < 1% of total content thus leaching was unlikely to occur. Haynes (2014) investigated the use of several industrial waste products in the removal of stormwater pollutants including heavy metals. The study showed that fly ash has a strong capacity to absorb heavy metal ions; however, it has a very low hydraulic conductivity due to its small particle size. Clogging can thus occur as the consequence of using fly ash alone. To overcome this issue, the study recommended that fly ash can be either added to coarse sand or it could be pelletized. In another study, Grace et al. (2016) studied the potential use of waste products from a variety of sectors in water treatment process. It was found that fly ash can uptake heavy metal ions from water but it has the disadvantage of being able to leach metals as well. However, this disadvantage can be mitigated through the introduction of certain precautionary measures such as leaching behaviour test, forced extraction, immobilisation of elements, and destruction of persistent pollutants.

The other fine material used in biofiltration is zeolite and it has been found that natural zeolite cannot remove heavy metal ions well compared with synthesized zeolite due to the high level of impurities in it (Pitcher et al., 2004). Zeolite is a microporous aluminosilicate mineral usually found in volcanic rocks. Zeolite contains a wide variety of cations such as Na(I), K(I), Ca(II), and Mg(II). Zeolite naturally contains some metals such as Ti, Sn, and Zn. Cortés-Martínez et al. (2009) studied the removal of cadmium (Cd) by Zeolitic rocks and the results showed that the zeolitic rocks can remove the heavy metal ions effectively. Wu and Zhou (2009) studied the removal of heavy metal ions from stormwater using a commercial porous iron sorbent and its mixture with zeolite and crystal gravel. It was found that absorption process of heavy metal ions can be influenced by the pH of the sample, surface complexion of the sorbent and electrostatic attraction. The sorbents also showed high affinity for certain heavy metal ions but were less effective at removing others. It was thus concluded that there is a potential for the use of P4 (mixture of Ferrosorp Plus and zeolite) as a sorbent in stormwater treatment. Reddy et al. (2014b) investigated the potential of several filter materials to absorb heavy metal ions from urban stormwater, one of which was zeolite. The results of the experiment showed that zeolite can absorb between 90 and 100% of heavy metal ions. Most of the heavy metal ions were removed through absorption by the negatively charged surface of the filter material. Haynes (2014) also studied the use of zeolites in removing pollutants from stormwater, especially heavy metal ions. It was found that both natural and synthesized zeolites were effective at absorbing heavy metal ions from an aqueous solution. The author also recommended that zeolite can also be used in constructed wetlands and in add-on filters at the wetland outflow. Since synthesized zeolite requires considerable time and energy, authors suggested that the product's cost for practical application could be a concern.

Reddy et al. (2014a) studied the performance of biochar as an absorbent in stormwater treatment by biofiltration systems. It was found that biochar performance in heavy metals ions removal is not satisfactory due to its chemical properties and behavior. In this study, the removal percentages of 18, 19, 65, 75, 17, and 24% were achieved for Cd(II), Cr(VI), Cu(II), Pb(II), Ni(II), and Zn(II), respectively. Lim et al. (2015) compared few materials including coconut coir, compost, commercial mix, sludge, and potting soil (loamy sand) for heavy metals ions (Cu(II), Zn(II), Cd(II), Pb(II)) removal. Two different stormwater concentration dosing were used to observe the behavior of the materials in higher pollutants loading. It was found that the removal percentages in higher pollutants concentration are generally better than the one for low concentrations. Overall, all materials could remove > 90% of the heavy metals ions in high-concentration loading except for coconut coir which only removed 74% of Cu(II) and 82% of Pb(II). Authors concluded that potting soil and commercial mix are the best choice for biofiltration media in both low and high pollutants loading. However, sludge and compost were only recommended for high-concentration loading.

Using nano-materials such as carbon nanotubes and nanoclays (e.g. layered silicates such as montmorrilonite or MMT and Kaolin) for water purification have been reported by some researchers (Patel et al., 2006; Yuan and Wu, 2007). Hal is a member of the kaolin group of clay minerals and typically found in microtubular crystals (Pasbakhsh et al., 2016). Halloysite is an abundant and novel nano-material which can be used in water filtration application (Zhao et al., 2013; Makaremi et al., 2015) due to its unique hollow tubular morphology, its unique chemical structure (SiO_2 at the surface while Al_2O_3 is in the lumen and edges) and high surface area (20–70 m^2/g). Hal has already attracted the attention for decontamination of industrial effluents (Pasbakhsh and Churchman, 2015). Yuan et al. (2015) highlighted the considerable potentials of Hal as a new adsorbent for different applications. Authors elaborated the unique properties of Hal such as their high specific surface area compared with Kaolin group. It was concluded that despite the tubular shape of Hal that promotes adsorption capacity, their interlayer is hardly accessible for ions and molecules. Therefore, it is recommended that the modifications could be needed to improve the