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An Investigation into the Release of Chemical Oxygen Demand in Organic Filter Media

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유기성 여재로부터 화학적 산소요구량 물질의 방출에 관한 연구

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요 약

강우시에 주기적으로 포화상태에 이르는 강우 유출수 처리시스템에 의한 질소저감 능력을 향상시키기 위하여 유기성 여재가 널리 적용되고 있다. 그러나 이와 같은 물질은 추가적인 유기탄소원이 되기도 하지만 처리수의 COD를 증가시키는 원인이 되기도 한다. 본 연구에서는 여러 가지 형태의 유기성 여재의 회분식 용출시험을 통하여 COD 방출량을 정량화하고자 하였다. 연구결과에 따르면 초기 pH가 7.5-7.7인 수돗물 수준에서 쉽게 유기물질이 용출되는 것으로 나타났다. COD 방출이 가장 큰 여재는 노지 벌초물(yard clipping)과 우드칩이었으며 다음으로 퇴비와 목피 순서로 나타났다. 또한 여재의 크기가 작으면 작을수록 비표면적의 증가로 인하여 방출량이 증가하였다. 연구결과로부터 도출된 경험적인 공식에 따르면 유기성 여재로부터 COD 방출은 여재형태에 따라 3-5개월에서 길게는 26개월이 지속되는 것으로 예측되었다. 이와 같은 연구결과는 강우유출수 처리시설에서 유기성 여재의 안전한 적용을 위한 잠재적인 COD 물질의 방출량을 계산하는데 기여할 것으로 사료된다.

핵심용어 : 강우유출수, COD, 유기성 여재, 방출, 용출

Abstract

To improve the nitrogen reduction capability of stormwater treatment systems subjected to intermittent saturation, organic materials are often added as filter media. However, these materials can be an additional source of organic carbon and increase the chemical oxygen demand (COD) in the outflow. In this study, different types of organic filter media were subjected to a batch leaching test to observe and quantify the release of COD. Results reveal that the initial pH of the tap water used for soaking which is 7.5-7.7 is conducive to the release of organics from the media to the leachate. The highest amount of COD released was observed in yard clippings and woodchip followed by compost and bark mulch. The leaching of organics also increased as the size of the media decreases due to higher surface area per volume. In addition, empirical regression analysis predicted that COD from these organic media will be exhausted from the material in 3-5 months to up to 26 months depending on the type of media. The results of this study can serve as a guide in estimating the potential release of COD in organic media in order to ensure their safe application in stormwater treatment facilities.

Key words : COD, filter media, leaching, organic, stormwater

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1. INTRODUCTION

Sustainable stormwater treatment systems typically employ a filter media bed composed of inorganic and organic materials. Organic media is added to the filter bed to serve several purposes. For instance, when woodchips become saturated for a period of time, they release organic carbon that is needed for denitrification, a crucial process under anaerobic conditions to lowering nitrate (NO_3-N) levels and the total removal of nitrogen from stormwater (Kim et al., 2003; Hsieh and Davis, 2005). Chen (2015) conducted experiments on pilot-scale wetlands employing different types of media and observed that the one containing woodchips has the lowest chemical oxygen demand (COD) removal but the highest NO_3-N removal. The findings are in agreement with the study by Saeed and Sun (2011) using laboratory-scale hybrid wetlands. The results showed that eucalyptus wood mulch provided a carbon source for the removal of NO_3-N via denitrification and that the effluent NO_3-N concentration increased with the decrease of effluent COD concentration. Ammonia (NH_4-N) removal, which can sometimes be a limiting factor for eliminating nitrogen, was also observed to increase in the wood mulch wetlands due to its higher oxygen transfer capacity providing sufficient dissolved oxygen (DO) for nitrification. Therefore, simultaneous nitrification and denitrification can be observed within a media containing organic materials. Wood mulch is also utilized in the surface layer of some best management practices (BMPs) and constructed wetlands to facilitate initial filtration of pollutants, retain moisture for plant growth, and provide a source of organic matter as well as habitat for organisms that are critical to biological processes.

Several works demonstrated that amending topsoil with organic materials such as compost can alter soil properties and help increase infiltration rates, retain moisture, and decrease peak flows (Pitt et al., 1999; Hunt et al., 2008; Gülbaz and Kazezzyilmaz-Alhan, 2016). However, the amount of compost should be controlled due to its tendency to leach certain amounts of nutrients. Pitt et al. (1999) mentioned higher concentrations of these pollutants in the runoff from sites with amended soils as compared to regular top soils. The saturated condition during rainfall, especially in extended periods of time, encourages leaching of soluble nutrients such as NH_4^+ and NO_3-N from compost-amended bioretention mixes (Hurley et al., 2017). However, the saturated condition is favorable because it provides anaerobic conditions conducive for denitrification that leads to lower levels of NO_3-N (Kim et al., 2003; Hsieh and Davis, 2005). Therefore, one such solution for this to optimize the amount and positioning of the organic material in the media profile in such a way that is conducive for effective nutrient removal and overall bioretention performance.

The leaching of organic matter from woody materials have been mentioned in previously published studies. Robertson (2010) reported that the amount of organics released from softwood and hardwood is different and that leaching increased with increasing stormwater retention time. However, Niu et al. (2013) found that as COD release increases, consumption rates also increased when they estimated the net release of COD from woodchips. In addition, the characteristics of the biodegradable organics in the stormwater can also affect the COD concentration in the outflow. Aside from retention time and characteristics of the inflow, the type of wood as well as grain size has also been reported to affect the release of organics. Mclaughlan and Al-Mashaqbeh (2008) performed sequential batch leaching tests to investigate the mass of dissolved organic carbon (DOC) released from pine, hardwood, and compost organics or yard wastes at different media size ranges.

In terms of selecting the proper material for carbon source, age seems to be an essential factor. Robertson (2010) conducted experiments comparing the NO_3-N removal rate of fresh woodchips versus aged woodchips. It was observed that the denitrification capacity of fresh woodchips was lowered to 50-79% after 2 years and 40-59% after 7 years. Although the decrease was significant during the initial stage, the slight difference between the 2nd and 7th year values indicates that woodchips can deliver stable NO_3-N removal rates over a period of time after the initial usage of the leached organics.

The use of organic materials has always been recommended in design guidelines. However, the release of carbon can be a burden if it is not controlled and can cause high concentrations of COD in the outflow. Therefore, quantifying the leaching phenomenon is necessary to be able to predict potential COD release and control the amount of organics in the filter media bed. Comparison between different materials is also necessary in order to provide guidance for filter media selection and ensure their safe application. In this study, different types of organic filter media were subjected to a batch leaching test to observe and quantify the leaching of COD for use in stormwater treatment facilities.

2. MATERIALS AND METHODS

2.1 Batch leaching test

The release of COD from different types of organic media was measured by conducting a batch leaching test. Four types of organic media namely woodchip, yard clippings (leaves and stems), compost, and bark mulch were tested as shown in Fig. 1. In addition, woodchip was further grouped into 3 different

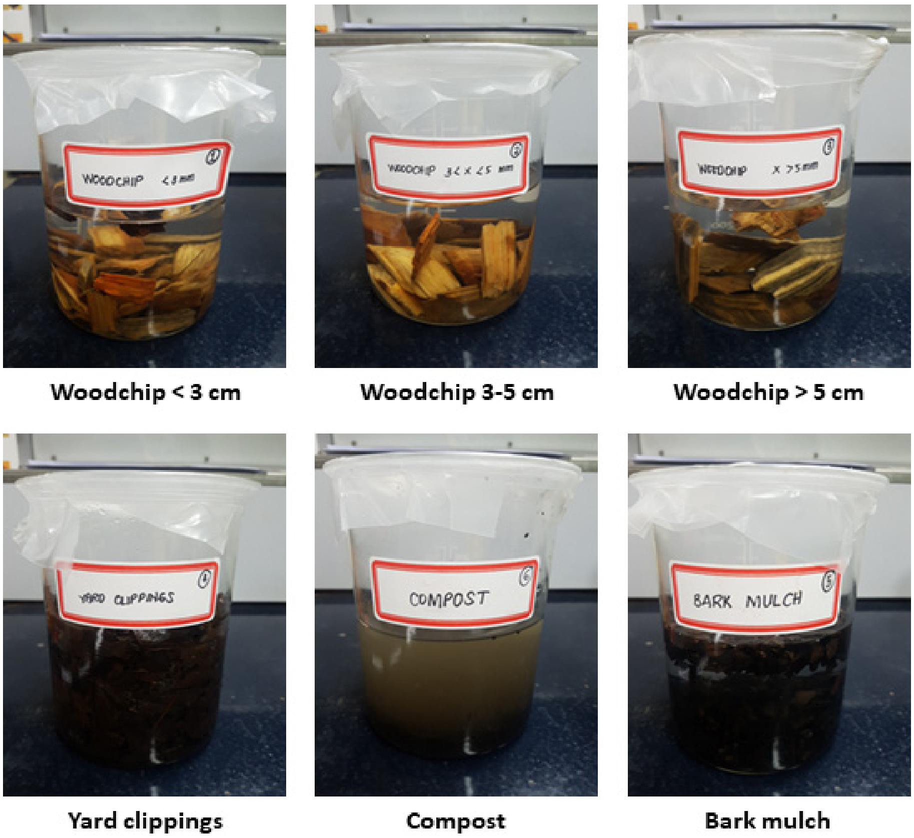

Fig. 1. Batch leaching test for different types of organic media

sizes, <3 cm, 3-5 cm, and >5 cm, to observe the effect of woodchip size in the release of organic matter.

In this test, samples of the media were prepared by light washing to remove foreign materials and dirt. Then, they were air-dried for 24 hours. The leaching test was conducted by soaking 50 g of each sample in 500 mL of water representing a 1:10 solid to liquid ratio. Although the standard method for leaching test involves shaking the solid-liquid mix for a specific period, no disturbance was made in this test to simulate the condition of the media in the treatment system. After 24 hours, the liquid or leachate is separated from the media and collected for sampling. Then it was replaced with a new batch of 500 mL of water. This step was repeated so that the pH, electronic conductivity (EC), and COD from each batch of leachate water can be measured.

2.2 Water quality measurements and analysis

A portable pH meter, Istek P15, was used to measure the pH while EC was measured by a conductivity meter, YSI 30. Both meters have probes that can be submerged in the sample to be able to get the necessary readings. Meanwhile, COD was measured to represent the organics release. It was done by following the Standard Methods for the Examination of Water and Wastewater (APHA et al., 1998) using potassium dichromate method. The organic matter in the samples were oxidized by potassium dichromate in a sulfuric acid solution with a silver compound added as a catalyst. After oxidation, the remaining dichromate was measured by titration using a ferrous ammonium sulfate solution as the titrant and ferroin (1,10-penanthroline ferrous sulfate) as the indicator.

Empirical regression analysis was also conducted in order to come up with simple models predicting the long-term release of COD. The linear models were developed in Microsoft Excel using the scatter plot function to create the graph showing the relationship between the saturation time and corresponding COD concentrations in the leachate. The best fit regression line was selected in terms of the coefficient of determination (R^2).

3. Results and Discussion

3.1 Trends in pH and EC

The pH and EC during the batch leaching period was found to change in time as seen in Fig. 2(a). According to McLaughlan and Al-Mashaqbeh (2009), the pH of a leaching test is considered the most significant factor affecting the amounts of leached elements from a solid organic media. Considering an initial tap water pH of 7.5-7.7, the highest decrease of

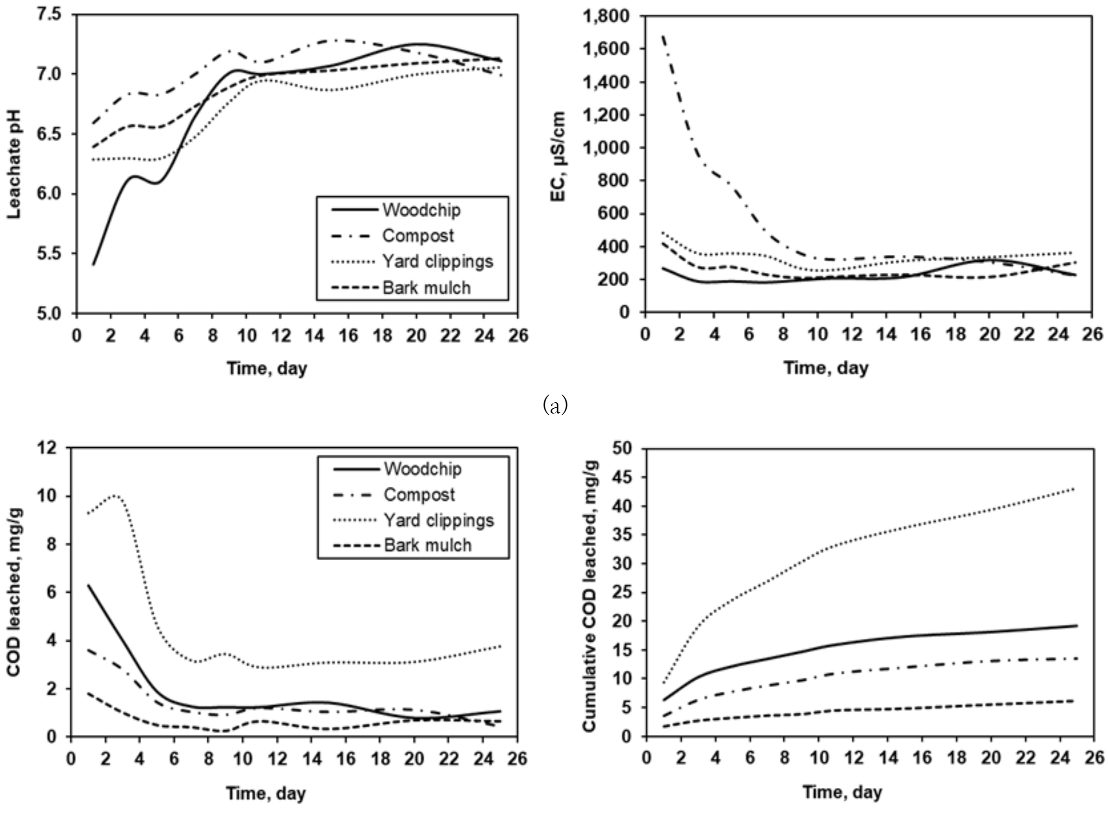

Fig. 2. Trends in (a) leachate pH and EC and (b) leaching of COD from different types of organic media over time

pH after the first 24 hours was in woodchip with 5.4, followed by yard clippings at 6.3, bark mulch at 6.4, and compost at 6.6. These values gradually increased up to 10 days reaching 7.2 for compost, 6.9 for bark mulch, 6.8 for yard clippings, and 7.0 for woodchip. It has been previously reported that organic carbon concentrations increase with leachate pH until a certain plateau occurs although it was considered as a general property of soils, sediments, and waste materials (Comans et al., 2001). Cokgor et al. (2009) who studied the influence of pH and temperature on the generation of soluble fermentation products from primary sludge reported that pH up to 7.5 resulted to 26% higher soluble COD generation as compared to a pH range of 6.5–7.0. Thus, replacing the tap water every 24 hours after sampling encouraged the release of COD especially during the initial period. Meanwhile, the lowest decrease in pH observed in the leachate from compost can be a result of its buffering capacity (Wong et al., 1998).

EC from all the media were observed to be relatively higher in the leachate from the first 24 hrs but decreased and became more stable during the following days. The trends were similar for yard clippings (481–361 $\mu S\cdot cm^{-1}$), woodchip (268–227 $\mu S\cdot cm^{-1}$), and bark mulch (416–302 $\mu S\cdot cm^{-1}$). However, an exponential decline was observed from the leachate of compost which ranged from 1,674 to 223 $\mu S\cdot cm^{-1}$.

3.2 Effect of media type and size on COD leaching

The release of COD from different organic media subjected to batch leaching test is shown in Fig. 2(b). The highest COD per mass of the media was observed during the first 5 days (120 hrs) of saturation. This was followed by relatively lower values until the 8th to 10th days which became more stable to up to 20 more days. This trend was in agreement with the variation of pH that was observed in the previous section. It can also be explained in terms of various fractions of DOC, some of which can be readily mobilised while other fractions can be released in later time periods (Munch et al., 2005; Wehrer and Totsche, 2005). However, it is important to note that leaching of organics from the materials should take time. Thus, the high COD concentration during the first 5 days can be attributed to sawdust (small wood shavings) that may have been detached from the organic materials during the initial period.

The media that released the highest COD was yard clippings from 9.3 to 3.8 mg/g, followed by woodchip from 6.3 to 1.1 mg/g, compost from 3.6 to 0.4 mg/g, and bark mulch from 1.8 to 0.6 mg/g. Similar to the results of a previous study by McLaughlan and Al-Mashaqbeh (2008), the release rates started high but rapidly declined during an initial period followed by slower rates during the remaining period. However, as opposed to their findings, the leachate from the compost in this study has lower COD than woodchip. This may be attributed to the different composition of the compost used in this study. Moreover, yard clippings released the highest amount of COD per gram of sample since it has the lightest weight. This means greater amount or volume of stems and leaves per gram resulting to higher release of COD as compared to the other types of media.

The comparison between woodchip of different sizes is presented in Fig. 3. The COD concentrations were higher in the smallest sized woodchip and decreases as the woodchip size increases. Smaller-sized media provides a higher total surface area per volume ratio as compared to larger-sized media. Thus, the higher surface area in the smallest woodchip provided a higher rate and amount of organics that can be released. The release rates are considerably similar among the woodchip sizes as seen by the consistent gaps between the plot lines.

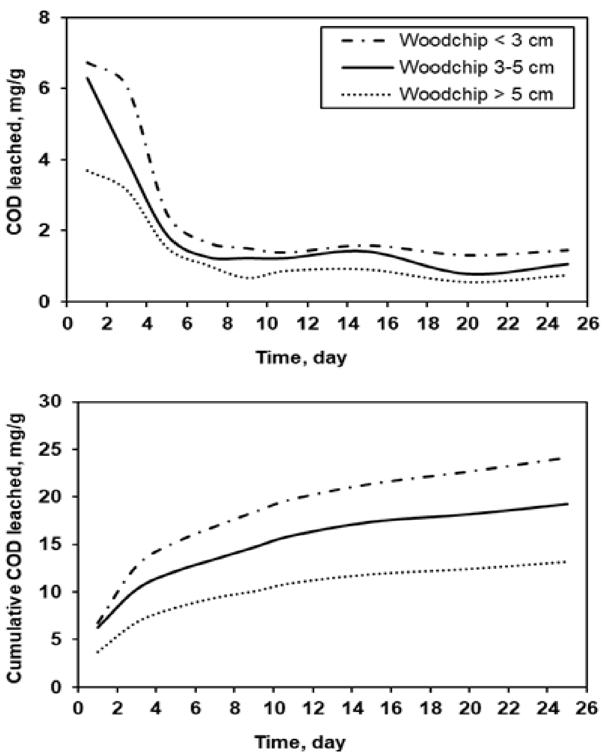

Fig. 3. Effect of woodchip size on the release of COD

Fig. 4 shows the cumulative fraction of leached COD over time. Considering only the saturated conditions and excluding the dry period in between rainfall events, it seems that it would take only 2 days for woodchip and 4 days for the other media types to release half of their COD content. This is assumming that the remaining COD after the leaching period conducted in this study is neglible as compared to the rest of the leached amount. However, as mentioned previously, this is highly likely due to the sawdust particles that may have been detached from the media during the first few days of saturation. In addition, 90% of the total COD from woodchip and compost were released after two weeks. However, the data from compost can vary significantly or possibly be much higher if a compost of different composition is used. On the other hand, yard clippings and bark mulch released 90% of COD after three weeks. These seemingly high percentage of release of organics from filter media in a short period of time is most likely due to the relatively short experimental period in this study. Leaching of organics typically takes longer than 25 days and a longer experiment might produce more accurate results.

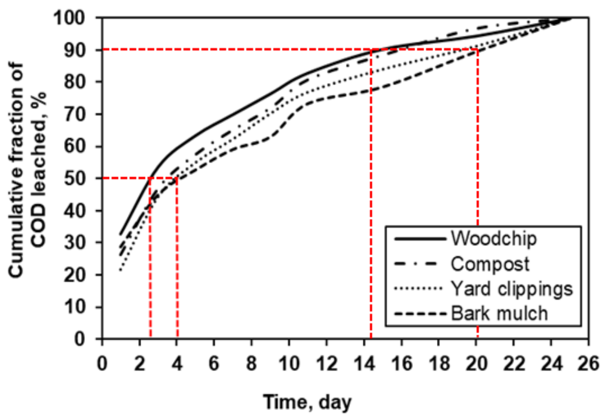

Fig. 4. Cumulative fraction of COD released from different types of media

3.3 Empirical regression analysis

The relationship between the release of COD from different media and the hydraulic retention time represented by the saturation time during the leaching test is shown in Fig. 5. The regression lines shown can be represented by Eq. 1. In the equation, *C* is the amount of organic matter released as COD in mg/L, *k* is the release rate in mg/L-day, *t* is the hydraulic retention time (HRT) in day, and *b* is the release rate constant.

The equation for each media is summarized in Table 1 along with the corresponding R^2 values and the retention times required to lower the leaching to 50% ($t_{50\%}$) and 5% ($t_{5\%}$). As shown in the table, COD leaching decreased by 50% from all the media after 2 to 4 days and this can be attributed by the washout of sawdust particles from the media. It would take 3-5 months to reduce leaching from woodchip and compost to 5%. In contrast, it would require up to 26 months to deplete the organic materials from other media with high organic content and lower release rates.

$$C = k * t^{-b} \quad \text{(Eq. 1)}$$

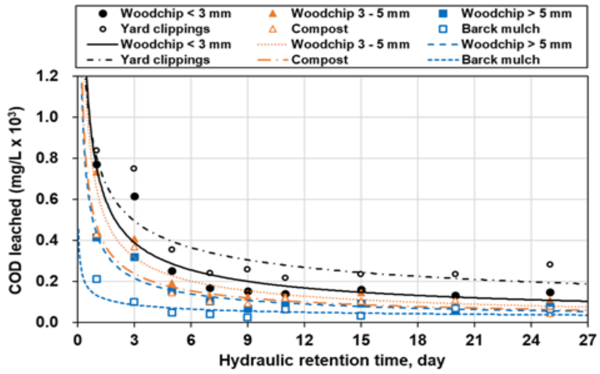

Fig. 5. Power function lines representing the relationship between COD released from organic media and hydraulic retention time

Table 1. Regression models for COD leaching from different oranic media

Media	Equation	R^2	$t_{50\%}$ (days)	$t_{5\%}$ (months)
Woodchip 〈 3mm	$y = 759.56t^{-0.608}$	0.839	3	4.5
Woodchip 3-5 mm	$y = 653.52t^{-0.658}$	0.882	2	2.7
Woodchip 〉 5 mm	$y = 435.33t^{-0.639}$	0.858	3	3.9
Yard clippings	$y = 806.48t^{-0.443}$	0.744	4	26.4
Compost	$y = 475.15t^{-0.631}$	0.817	3	4.5
Bark mulch	$y = 132.84t^{-0.402}$	0.395	2	18.0

4. Conclusions

Organic media used in stormwater runoff treatment systems tend to release COD in the stormwater than can end up in the outflow. Thus, in this study, a comparison of different types of organic media was presented. The highest amounts of COD were observed to be released during the first 120 hrs or 5 days of continued saturation. Yard clippings released the highest amount of up to 9.3 mg/g of media due to its relatively lighter weight followed by woodchip with 6.7 mg/g during this initial period. From comparing different sizes of woodchip, results revealed that the release of organics tend to increase as the size decreases due to higher surface area per volume of the media. Moreover, the release of organic matter according to hydraulic retention time showed a power function. Based on the developed regression models, the release of COD can be reduced by 50% after 2-4 days depending on the amount of sawdust that is initially attached to the media. From then on, the remaining COD is slowly released for up to 3-5 months from woodchip and compost. On the other hand, it would take up to 18 months for bark mulch and 26 months for yard clippings due to their relatively lower release rates. Based on these findings, the ideal organic material for use in stormwater treatment systems is woodchip for granular media and compost for the fine media. The release of COD from woodchip is also not very high as compared to yard clippings and it can provide a carbon source for denitrification for a considerable period of time. It is also a cheap and easily available material in Korea and is not as light in density as bark mulch and yard clippings so there is no risk of floating or washing off during high flows. On the other hand, compost in soil media makes it more conducive for certain microbial processes that are needed in the removal of pollutants such as nitrogen. The results were obtained from an experiment using tap water with initial pH values of 7.5-7.7 which was found to be conducive for the solubility of COD. The pH of stormwater runoff may differ and may affect the results. However, the findings in this study provides a preliminary understanding into the release of organic matter from filter media which can be used in stormwater treatment systems. This can also serve as a guide to filter media selection for systems employing organic media in the future.

Acknowledgement

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