METHODS OF QUANTIFYING THE PERFORMANCE OF NUTRIENT REMOVAL MEDIA

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INTRODUCTION

Non-Point source pollutants carried by stormwater runoff are acknowledged to be a significant source of contaminants in rivers and lakes. One contaminant, phosphorus, usually in the form of phosphate, can lead to excessive algae growth which can lead to lack of oxygen, which in turn impacts aquatic life. Algae blooms can also cause taste and odor problems if the water body is a drinking water source. Due to these problems, many regions are developing Total Maximum Daily Loads (TMDLs) for phosphorus, or are otherwise regulating the phosphorus content of stormwater discharges.

Attempts to solve this water quality problem have lead to the study and development of several media and soil-based media mixes capable of treating removing phosphorus from stormwater. The most common solutions are granular media through which polluted water can be filtered. These media use two mechanisms for phosphorus removal: filtration and adsorption.

Calculating the amount of phosphorus removed by filtration is not trivial but it is relatively straightforward to understand. It requires knowledge of how much phosphorus is particulate bound, what size particles it is bound too and what sediment (TSS) size particles are separated out by filtration by the media. This information can be difficult to obtain but once you have it removal is calculated by simply multiplying the particulate bound fraction by the particle removal percentage.

Adsorption is more complicated phenomenon and some of the information being tested and marketed is difficult to interpret. The two basic performance parameters are capacity and kinetics. Scientific data is readily available, for example Boujelben (2008), Wang (2009), Arias (2006), Bellier (2006), and the data have been fit to models. Equilibrium data is often fit to a Freundlich isotherm and kinetic data can be fit to a first or second order chemical reaction rate equation. None of this is necessarily applicable to a stormwater engineer trying to size a system.

This paper discusses capacity and kinetics and puts them in the context of sizing stormwater treatment systems. More importantly it also discusses the concept of breakthrough, which is a function of capacity and kinetics combined, but which cannot be easily calculated form those parameters. However, breakthrough is the most useful number of all for stormwater sizing. Finally, the paper describes some relatively simple tests that can be performed to generate data relevant to system sizing.

DISCUSSION

Kinetic data

Kinetic data is used to describe the rate of reaction between the adsorbent and the absorbed species. In other words, kinetic data describes how fast a given media can adsorb phosphorus. Kinetics are relevant in flow situations because the kinetics have to be fast enough to allow for the required removal in the contact time that is available in the system.

In simple systems, rate constants can be determined and the process can be modeled. This allows for prediction of the rate of adsorption. Models have also been developed for flowing systems *[Sansalone]*, though not for complex flows such as those in a BMP. These flows will vary in terms of rate and nutrient concentration so any model would be very complex.

Even if the kinetics of a media can be determined the result is of limited practical use. The information would tell the user if the design contact time is adequate to achieve removal but it would not provide any information on how much contaminant can be absorbed. Thus it provides no insight into the lifetime of a given design.

Equilibrium data

Equilibrium data provides information about the total capacity of a media to remove a pollutant, usually reported in units of mg absorbate/g absorbent. It assumes that time is not a factor. In principle this information could be used to predict the lifetime of an adsorbent filter. This apparent usefulness has lead to the practice of reporting the capacity of adsorbent media.

In theory a system could be sized for adequate capacity using the equilibrium data and adequate contact time using the kinetic data. Whichever method gave the largest amount of media would be properly sized. In practice when considering the treatment of stormwater there are a number of problems with this approach.

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The first problem lies in the nature of equilibrium adsorption capacity data. First, it assumes an infinite contact time so it is always a best case scenario. In practice an exposure time of 1-5 days is used to generate adsorption capacity data. It is not a trivial exercise to try to predict capacity in a stormwater treatment device where exposure time in on the order of minutes based on data generated after five days exposure. Second, equilibrium capacity depends on the concentration of the adsorbate. This is why capacity is usually reported in scientific literature as an isotherm. An isotherm is a curve that shows how capacity increases as adsorbate concentration increases, keeping exposure time constant.

A system designer with an isotherm and could use the expected average influent concentration to estimate the filter maximum capacity. Then the filter could be sized to last the desired number of years, knowing the phosphorus loading per year and the capacity of the filter. The size of the filter could be increased by some safety factor to account for the non-equilibrium conditions. However, this process is very cumbersome and the appropriate safety factor is unknown.

In the interest of simplicity capacity data is often presented as a single number. Since the same media will have a much higher capacity if tested in 1 mg/L phosphorus solution instead of a 0.5 mg/L solution the data can also be misleading. If media A is tested with a high concentration solution and media B is tested with a low concentration solution, A will have a higher capacity value, even though it might have a lower value if the two media were tested at the same concentration. So, without the test conditions the two different numbers cannot be compared. If the test conditions are known but are different it is still difficult to compare the two numbers because there is no simple relationship between adsorbate concentration and capacity. What is really required is full isotherms for both media.

There is another problem with trying to size using kinetic and equilibrium data that overshadows the above issues. Adsorptive filters are subject to breakthrough, so neither kinetics nor equilibrium data are really an adequate predictor of lifetime. Even if very good data is available, it cannot be used for filter sizing.

Breakthrough Data

Breakthrough data combines a practical value of a media’s sorption capacity (at a less than infinite contact time, for example) with kinetic performance values that change to reflect the diminishing capacity of the filter media over time. In this way, breakthrough data provides a more realistic estimate of lifetime than equilibrium or kinetic data alone.

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As water containing a pollutant flows through a bed of adsorptive media, the pollutant concentration changes as both a function of depth in the media bed and time. The effluent concentration increases with time as more and more of the adsorptive capacity of the media is used up, until "breakthrough" occurs and the effluent concentration has reached some predetermined percentage of the influent concentration. At breakthrough the media will no longer be providing the required removal, even though the contact time has not changed and the media is not completely saturated.

Most theories used to describe this breakthrough behavior are based on an assumption that the adsorption process can be described as a first- or second-order reaction rate expression, and that the rate of this reaction is controlled by the remaining unused capacity of the media at a particular time. Using a model such as that proposed by Bohart and Adams (1920) or Thomas (1944), one can predict the performance of a large bed of media based on experiments conducted on a small-scale apparatus, assuming adequate information is known.

Breakthrough data available in the literature is generated by continuous testing. A test solution is continuously pumped through a media bed and samples are taken at regular intervals. Testing typically continues until the removal rate drops down to 10% or less. Media lifetime predicted by this type of data is more realistic than that predicted by kinetic or equilibrium data, but this data still suffers from one major flaw. Stormwater devices are not subjected to continuous flow.

Non-continuous testing

The intermittent nature of the flow that stormwater treatment Best Management Practices (BMPs) are exposed to adds one additional complication to the sizing of adsorbent filters for this application. It has been observed that some media will regenerate themselves during a rest period. In other words, removal is higher once flow re-starts after an interval of no flow than it was before flow stopped.

The exact reason for this is not known. It is hypothesized that during flow there is not enough time to access the microporosity found in most high surface area adsorbents so some of the surface area is effectively wasted. During a no flow period contaminants can migrate or diffuse into the micropores and this frees up some of the surface that is accessible during flow.

A system that is exposed to stops and starts will last longer than one that runs continuously so to get more accurate sizing it is necessary to include periodic intervals of no flow in the breakthrough test. The frequency and duration of the rest period appears to impact lifetime so these should be standardized. Running continuously would be simplest and would allow for comparison of media but continuous exposure of the adsorbent media to contaminated flow is not representative of the conditions in a typical stormwater BMP. So data generated in a continuous test would result in over sizing and thus unnecessary expense for users.

Other variables that need to be taken into account to avoid large discrepancy between small-scale experimental results and that of large installations include media gradation size (which strongly affects the surface area available for adsorption reactions to take place upon), influent concentration and surface loading rate (the flow rate of influent water per cross-sectional area of the filter media perpendicular to the direction of flow). Ultimately, all of these variables should be standardized so that stormwater engineers can be provide with useful performance data that will allow them to properly size devices and compare media.

EXPERIMENTAL

This section presents a method for testing for breakthrough using intermittent flow that has been adapted specifically for stormwater applications. The following equipment was used for the breakthrough testing:

- On/off programmable digital timer
- Peristaltic pump
- Column
- Influent and effluent tanks
- Tubing
- Hach DR890 Colorimeter

The feed pollutant solution was prepared in the feed reservoir tank. After preparing the solution, a sample was taken and analyzed for its final concentration. The phosphorus source used was potassium dihydrogen ortho-phosphate. The testing concentrations were 0.5mg/L and 0.2mg/L TDP (total dissolved P). The ionic strength of the solution was adjusted to 0.01 KCl and the pH was adjusted to 7.0.

The feed solution was then pumped by a peristaltic pump to a column that was filled with media. The diameter of the column was 4.1cm. Depending on the testing requirements, different bed depths of media can be selected and tested. In order to minimize errors due to wall effect and channeling, the test column should meet the criteria in Table 1.

Factor	Description	Requirement
L/D	Column length / Column diameter	> 4
D/d	Column diameter / Particle size of the media	> 10

Table 1: Basic requirements of the column sizing

For low hydraulic conductivity media, the feed solution was pumped down-flow through the column. For high hydraulic conductivity media, the feed solution was pumped up-flow.

To run the non-continuous testing automatically, the power of the peristaltic pump was controlled by an on/off programmable digital timer. The timer automatically turned the pump on for a certain period and then turned it off for another certain period. The pump runtime in one storm was calculated by the volume of the media (bed volume), surface loading rate (SLR) and desired bed volumes in one storm.

A manageable testing interval of 2 hours was chosen, based on a typical storm in the mid-Atlantic states. The pump was started on the hour and then stopped at 49 minutes past the hour to allow the media to rest for1 hour and 11 minutes. This two-hour interval was considered as one storm event, so there were 12 storm events in one day. Effluent was collected periodically and then analyzed for TDP by using a colorimeter.

A schematic of the breakthrough apparatus can be seen in Figure 1 and the results of a test run can be seen in Figure 2.

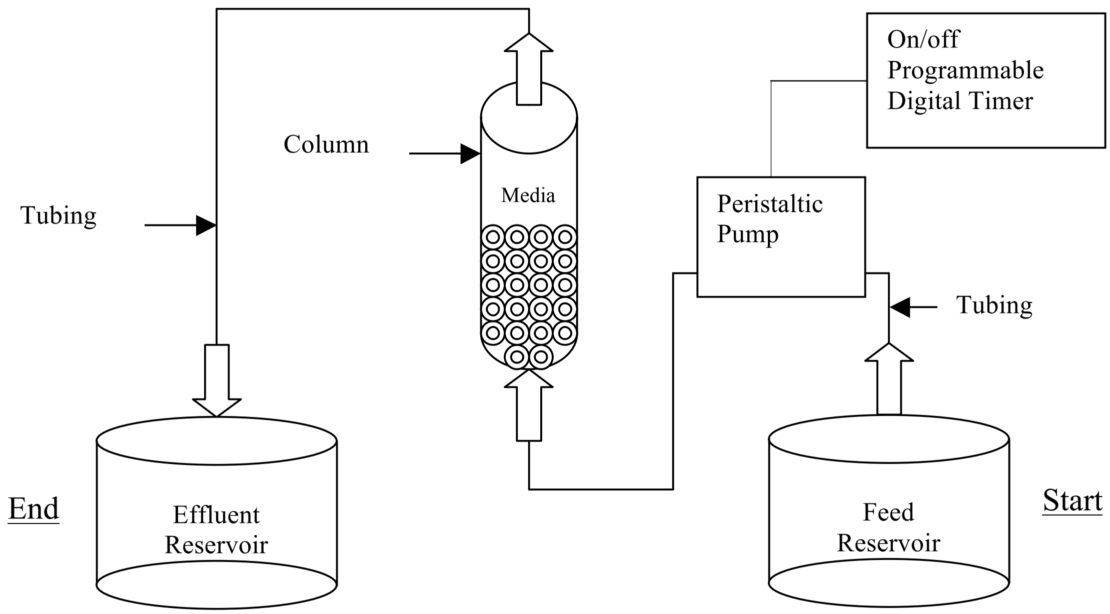

Figure 1: Schematic of Breakthrough Testing

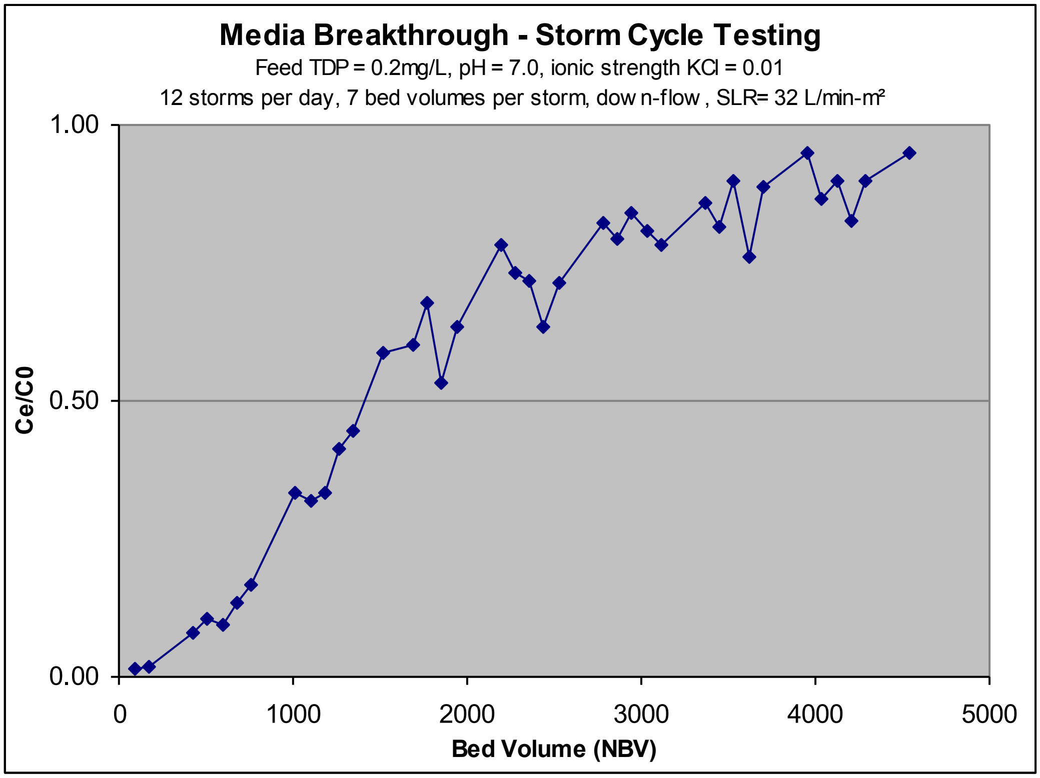

Figure 2 – Breakthrough Test Results

The peaks and troughs within the performance trend are a result of some samples being taken near the end of a storm cycle while other samples were taken at the beginning of a storm, just after a rest period. This kind of behavior could not be modeled but it is what a stormwater engineer could expect to see by randomly sampling the effluent from an adsorptive media filter. It is noteworthy that the media was still removing 50% of the influent phosphorus, under dynamic conditions, after 1500 bed volumes.

CONCLUSIONS

Phosphorus is a contaminant of concern for stormwater management specialists. A number of media are available that will remove particulate bound and dissolved phosphorus. The most common mechanism for removing dissolved phosphorus is adsorption. Adsorption is well understood as a chemical process and data on the fundamental parameters: reaction kinetics and equilibrium capacity, is available in the literature for many kinds of media.

Kinetic and equilibrium data are not sufficient to accurately size a stormwater treatment BMPs. A continuous breakthrough test provides a more realistic estimate of media volume required to properly size a filter system but the best estimate comes from a non-continuous breakthrough test. In this type of test the media is exposed to periods of flow and then rest, in a way that simulates real life exposure. This type of testing is somewhat complex as there are a number of factors to consider, including the frequency and duration of the rest period, but it is not overly difficult to generate and it should prove most useful to stormwater engineers trying to size systems.

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