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Use of Sorption Isotherms to Improve the Efficacy of the Storm-water Filters

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Use of Sorption Isotherms to Improve the Efficacy of the Storm-water Filters

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Abstract

Sorption has been widely used as an inexpensive and environmental friendly water treatment technology. A large variety of adsorbents with different adsorption mechanisms have drawn interests, and combinations of adsorbents will enhance sorption of mixed solutions. However, current sorption research tends to focus on single material. The objective of this study was to develop sorption isotherms for ZPG®, (Zeolite, Perlite, Granular Activated Carbon), used in a stormwater filter cartridge. Contaminants of concern include Cu^{2+} and quaternary ammonia compounds (QAC). Adsorption isotherms were established for Cu^{2+} and QAC, and the best fit for the isotherm data was a Langmuir isotherm for Cu^{2+} and Freundlich isotherm for QAC. The Empirical Constant for Cu^{2+}, Qo, which represents the maximum adsorption capacity, was 4.61µg/L. The equilibrium constant K, which represents the distribution of the contaminants between water and ZPG particles, was 11µg/g for Cu^{2+} and 8µg/g for QAC. The adsorption isotherm, adsorption rate, and maximum adsorption capacity are used as the criteria, and the result can be used for performance evaluation with the safety limits for the aquatic organisms presented in the Mammoth Cave National Park.

Background and Criteria

Mammoth Cave National Park is home to the world's longest cave and one of the most diverse cave biological communities in the world. With approximately 400,000 annual visitors, stormwater filters are used in the parking lot areas to prevent anthropogenic contaminants from entering into cave and groundwater. This is done to protect the aquatic habitat of rare and endangered species. However, field data have shown that the performance of the stormwater filters fluctuates. Toxic contaminants with concentrations higher than chronic effects level are sometimes found at the filter effluent. Two major contaminants are considered in this study, copper (Cu^{2+}) and Quaternary Ammonium Compounds (QAC).

Copper is a common contaminant found in vehicles, tires, and especially from parking lot runoff. Field concentration of Copper(II) ion is found to be between 2.8 to 92.0 µg/L. Cave fish, and aquatic invertebrates such as isopods and amphipods are vulnerable to copper (Dobbs, et al, 1994; Rayburn et al., 2003). Copper toxicity to aquatic organisms is due to binding to gill membranes and causing damage, and it interferes with osmo-regulatory processes. Chronic limits of copper for aquatic organisms range from 2.5 to 104µg/L.

High concentration of Lysol® Disinfectant Cleaner is used in the park to reduce risk of transferring *Geomyces destructans* spores, which is the cause of White Nose Syndrome, a disease that has threatened North America's bat population. Quaternary Ammonium Compounds (QAC) are one of the major chemicals in Lysol® , and they are toxic to fishes and aquatic invertebrates (Tezel, 2009).

Figure 1: ZPG cartridges in filter system.

The objective of this project was to determine the adsorption isotherm, and adsorption rate of ZPG®. A second goal was to evaluate the effectiveness of the treatment media. The scope of the project included lab studies with some field validation.

Materials and Methodology

The filters used a zeolite-perlite-activated carbon granules (ZPG®) to sorb dissolved contaminants in the sotrm runoff. The ZPG used in the isotherm studies was provided by Mammoth Cave facilities management from the Stormwater Management StormFilter® used by the Park. Each constituent in the ZPG media has different properties, and a combination of media provide a more effective configuration than single media, and meet a wide range of treatment goals (Table 1).

The batch method was used to establish sorption isotherms. Batches were set up with 20g of ZPG® filter media and different concentrations. Composition of each media in volume was about 50% Zeolite, 40% Perlite, and 10% GAC. The bottles containing the ZPG and solution waters were put into a shaker at 25°C, and rotated at 125 rpm for known lengths of time. Initial concentrations of Cu2+ or QAC were measured. The amount remaining in solution were measured at various time periods. The copper concentration was measured using the Hach Porphyrin method (Hach, 2005). The QAC concentrations were analyzed using the Hach direct binary complex method and measured on a spectrophotometer (Hach, 2005).

Results and Discussion

Adsorption of Copper

Results of the copper studies are shown in Figures 2 through 4.

Table 1: Summary of ZPG constituents' properties.

Constituent	Properties
Zeolite	used in the water filter. Clinoptilolite (Na7.3Si29Al7O72•23.9H2O), a sodium rich zeolites. The enrichment of sodium and the small pore size provide the clinoptilolite high cation exchange capacity (CEC). Cations of heavy metals such as zinc, copper, and lead are removed from water by displacement of light metal cations, Na+, in the zeolite matrix.
Perlite	pretreated Expanded Perlite, EP, is used in the water filter. It is mainly composed of Silicon dioxide, SiO2, and Aluminum Oxide Al2O. EP has high porosity, low density, high surface area, and inert chemical property, which give EP excellent ability to trap sediments and adsorb oil and organic pollutants
Granular Activated Carbon	is one of the most widely used materials to remove organic contaminants from water through adsorption. It has an extensive internal surface area with high porosity and high carbon content which provides high adsorption capacity.

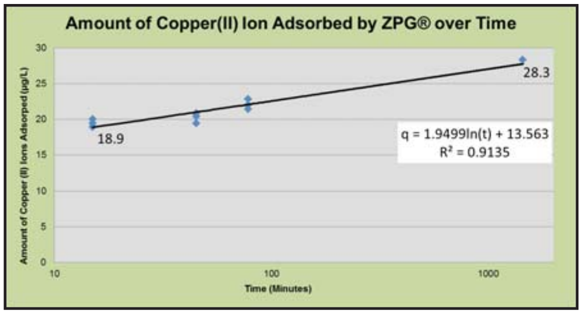

Figure 2: Initial concentration of 40µg/L of Copper(II) ion is used to determine the amount of Cu^{2+} adsorbed to ZPG®. The nature logarithm curve indicates that the adsorption rate decreases over time, dq/dt = 1.95/t.

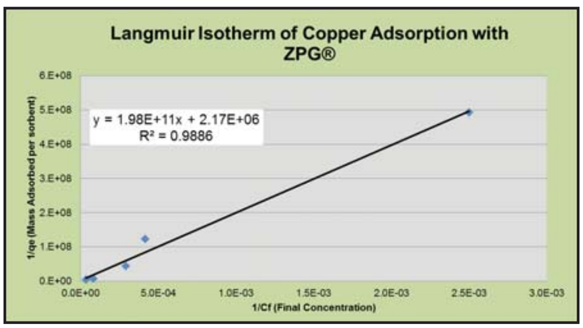

Figure 3: Langmuir isotherm is found to best describe the Cu^{2+} adsortion process onto ZPG®, Physisorption and chemisorption are both expected to contribute in the treatment process. Equilibrium oncentration of Cu^{2+} in solution, C_e, is 4.61µg/L. The adsorption capacity of ZPG®, K_d is 11µg/g. The relationship between the adsorbed Cu concentration and Cu concentration in solution can be described by the equation, q = 5.06 x 10^{-12} C / 1 + 1.10 x 10^{-5} C.

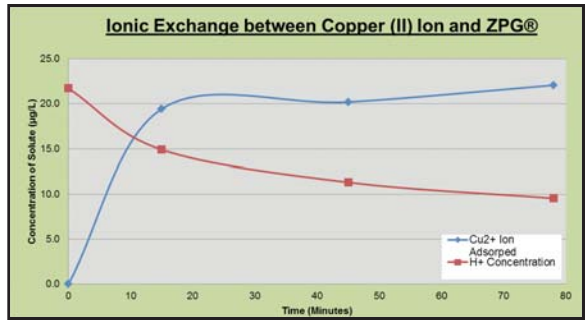

Figure 4: Langmuir isotherms indicate that chemisorption occurs, ionic exchange is expected between the dissolved Cu ion and sodium ion in zeolite. The exchange process can be determined by the change in pH value. An increase in pH value is found during the adsorption process. It agrees with the assumption that ionic exchange occurs. The increase in pH is due to the dissolution of sodium ion and the formation of NaOH, which is indicated by the decrease in H^+ concentration. The adsorption process seems to be a fast process in which the process slows down after a rapid increase in Cu^{2+} ion adsorbed in the first 15 minutes. Hydrogen concentration also slows down after about 45 minutes.

Adsorption of QAC

Results of the QAC sorption isotherm tests are shown in Figures 5 and 6.

Summary

The sorption of Cu^{2+} from water by ZPG® is best described by the Langmuir isotherm. The Freundlich Isotherm best describes the QAC sorption to ZPG®. The maximum sorption rate, which reduced the QAC concentration in half, was reached in about 15minutes; however, adsorption rate rapidly decreased afterward. The bottom line of these results indicates that when the contaminant concentration is high in the rain water, it will not be treated effectively in a short period of time, and may be released out the discharge effluent pipe.

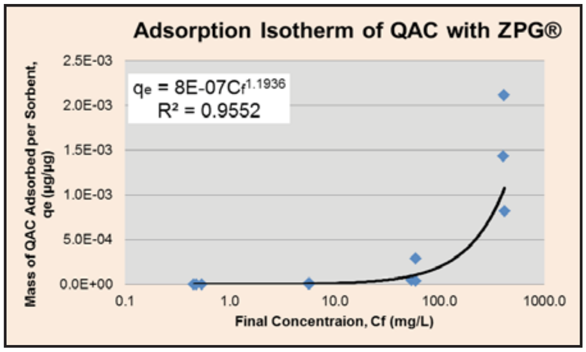

Figure 5: Freundlich isotherm is found to best describe the QAC adsorption process onto ZPG®. Chemisorption is negligible because QAC does not dissolve in water, and no ionic exchanged is expected. Physisorption is expected be the major contributing process in treatment. Granular Activated Carbon and Perlite are the major contributors in the adsorption process. The adsorption capacity of QAC onto ZPG®, Kd is 0.8µg/g. The relationship between the adsorbed QAC concentration and QAC concentration in solution can be described by the equation, $q_e = 8 \times 10^{-7} C_f^{1.1936}$.

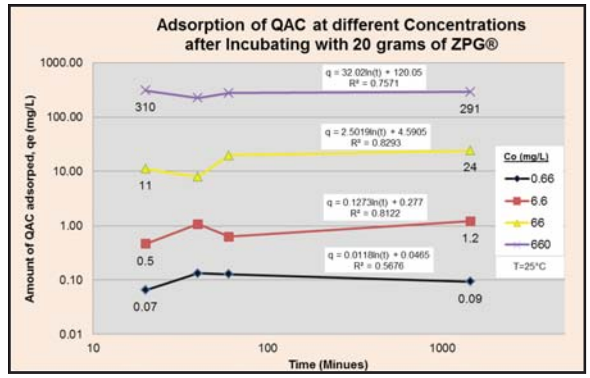

Figure 6: The amount of QAC adsorbed over time with different concentrations was compared. The process is best described by natural logarithm which means the rate of change of QAC adsorbed decreases over time. Also, the adsorption rate is higher with higher initial concentration. The difference in adsorption rate is due to the diffusion effect. The higher concentration of QAC has higher possibility to be adsorbed onto the filter media.

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