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Fate and transport with material response characterization of green sorption media for copper removal via adsorption process

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HIGHLIGHTS

- The coconut coir has the highest affinity for copper leading to a better removal at the neutral pH condition.
- Acid rain impact could reduce the adsorption/absorption capacity of green sorption media.
- There is a high correlation between the porosity of the micro pore structure and the adsorptive capacity of copper removal.

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ABSTRACT

Green adsorption media with the inclusion of renewable and recycled materials can be applied as a stormwater best management practice for copper removal. A green adsorption media mixture composed of recycled tire chunk, expanded clay aggregate, and coconut coir was physicochemically evaluated for its potential use in an upflow media filter. A suite of tests were conducted on the media mixture and the individual media components including studies of particle size distribution, isotherms, column adsorption and reaction kinetics. Isotherm test results revealed that the coconut coir had the highest affinity for copper (q_{max} = 71.1 mg g^{-1}), and that adsorption was maximized at a pH of 7.0. The coconut coir also performed the best under dynamic conditions, having an equilibrium uptake of 1.63 mg g^{-1}. FE-SEM imaging found a strong correlation between the porosity of the micro pore structure and the adsorptive capacity. The use of the green adsorption media mixture in isolation or the coconut coir with an expanded clay filtration chamber could be an effective and reliable stormwater best management practice for copper removal.

1. Introduction

Impairment due to excessive copper levels is a threat facing a large number of water bodies in the United States. According to the United States Environmental Protection Agency, 844 water bodies nationwide are listed on its impaired water list whose cause of impairment is copper (USEPA, 2014). Copper is a pollutant of concern in stormwater runoff due to its toxic effects on aquatic ecosystems, its non-biodegradable nature, and its ability to accumulate in sediments and tissues of living organisms. It is acutely toxic to a number of invertebrates and fish, particularly when the alkalinity or pH of the water body is low, as bound copper separates and becomes a toxic free ion. A number of studies have discovered high levels of copper in stormwater runoff from both urban (Dean et al., 2005; Hilliges et al., 2013; Kayhanian et al., 2003; Nason et al., 2012) and agricultural (Dietrich and Gallagher, 2002; Graves et al., 2004) settings. Contributing sources of copper in urban stormwater runoff include wood siding treated with CCA (copper, chromium, and arsenic), copper gutters, pipes, roofing, break wear, and vehicle exhaust. In surface water bodies that suffer from severe algal growth, copper sulfate ($CuSO_4$) is a commonly applied copper-based algaecide. Due to the high dosage, ranging from 0.3 mg L^{-1} to 2.0 mg L^{-1} (Nor, 1987), copper sulfate application for algae control is a major source of direct copper loading to stormwater wet detention ponds. However, application of $CuSO_4$ can be lethal to a range of non-target organisms. The necessary dose required to kill algae was found to be 10 to 100 times the amount that is lethal to

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zooplankton, a natural consumer of algae (Cooke and Kennedy, 2001). Bacteria living in nitrogen-removing biofilms are especially susceptible, as exposure to copper has been shown to change the structure, metabolism, and physiology of biofilms (Barranguet et al., 2002). Destruction of these communities can decrease a stormwater detention pond's nitrogen-removal efficiency through the elimination of nitrifying and denitrifying bacteria.

Removal of metal ions using adsorption media is accomplished by a variety of mechanisms, including physical adsorption, ion exchange, complexation, and surface micro-precipitation (Pehlivan et al., 2006). Employing a copper-removing adsorption media in a fixed-bed filter is a stormwater best management practice (BMP) that can be used to reduce copper levels in the water column and sediments of stormwater detention ponds. The use of adsorptive media for copper removal in industrial and municipal waste streams has been found to be effective and has resulted in a great volume of publications. Previous studies have shown copper adsorption occurs through electrostatic attraction and ion exchange in clay-type materials (Musso et al., 2014), through a combination of ion exchange with hydroxyl and carboxylic functional groups and electrostatic attraction in coconut coir (Acheampong et al., 2011), and primarily through ion exchange for tire rubber (Calisir et al., 2009). More specifically, many researchers have conducted studies on “green” sorption media, defined here as being comprised of renewable, recycled, or locally-sourced materials. Among the materials analyzed are cedar sawdust (Djeribi and Hamdaoui, 2008) sugar beet pulp (Huguenot et al., 2010; Pehlivan et al., 2006), fly ash, corncob and corncob char (Huguenot et al., 2010), tea processing waste (Amarasinghe and Williams, 2007), green algae (Deng et al., 2006), brown seaweed (Antunes et al., 2003), sour orange residue (Khormaei et al., 2007) lentil shell, wheat shell, and rice shell (Aydin et al., 2008), clays (Musso et al., 2014), tire rubber (Calisir et al., 2009), and coconut materials (Acheampong et al., 2011). Equilibrium adsorption isotherms were found to follow the Langmuir and Freundlich models for many of the media, as demonstrated by Calisir et al. (2009), Huguenot et al. (2010), and Pehlivan et al. (2006), among others. Acheampong et al. (2011) and Musso et al. (2014) utilized X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) to characterize the adsorption patterns and mechanisms in coconut materials and tire rubber.

This study aims to build on the body of work surrounding green adsorption media for copper removal by analyzing three low-cost, minimally processed adsorbents (expanded clay aggregate, recycled tire chunk, and coconut coir) and a (1:1:1 by volume) mixture of the three. The objectives of this study are to deepen our understanding of physical and chemical properties of the proposed green adsorption media mixture related to copper fate and transport based on a wealth of laboratory tests including studies of isotherm, reaction kinetics, column breakthrough and particle size distribution. The material response to copper adsorption was characterized through the use of XRD (X-ray diffraction) and FE-SEM (field-emission scanning electron microscopy) with an energy dispersion spectroscopy (EDS). In addition, this study also aims to answer three main science questions. First, what are the copper adsorption capacities of the adsorption media mixture and individual media components? Second, how do the adsorptive characteristics of the media affect the shape of the breakthrough curve and the life expectancy of the media? Third, how can the material response verify the efficacy of the recipe? In the following sections, we have demonstrated the physical characteristics of the green adsorption media, evaluated the adsorptive removal characteristics of the green adsorption media, and investigated the material response under different conditions.

2. Methods and materials

2.1. Physical characteristics

The green adsorption media mixture used in this study consisted of coconut coir, 3/8″ expanded clay, and 3/8″ tire chunk in a 1:1:1 ratio (by volume) mixture. The expanded clay aggregate was obtained from a CEMEX construction materials plant, located near Orlando, FL. The coconut coir was manufactured by Sunleaves™ as a growing medium for hydroponic gardening. The tire chunk was obtained from Global Tire Recycling in Wildwood, Florida. No preprocessing of the media was done before physical or chemical analysis commenced. The media mixture and individual components were analyzed using ASTM standards to determine their physical characteristics, including dry density (ASTM C29), void ratio (ASTM C29 M-09), and porosity. In addition, the particle size distribution (ASTM C136-01) was obtained for the media mixture. A full definition of the mass/volume relationships provided by these parameters provides information for determining the hydraulic residence time/system flow rate relationship in the lab and field settings.

2.2. Adsorption equilibrium (isotherm) study

Conducting an equilibrium study of the adsorption media mixture allows characterization of the sorption mechanisms and comparison of the adsorption capacities and affinities of the different types of media mixture for copper in solution. The Langmuir and Freundlich isotherm equations were employed to provide a basis of comparison. Nonlinear forms of the equations were employed and were fitted to the data using least-squares regression. To discern the effect of pH on copper adsorption to the media, equilibrium tests at a 60 min contact time were conducted at a pH of 3.85, a pH of 5.6, which represents typical conditions during acid rain, and a pH of 7.0, which represents typical conditions for normal stormwater runoff. The experimental setup included the use of 300 mL distilled water spiked with Fisher Scientific 1000 ppm copper standard (copper nitrate), which was added to each of three 500 mL flasks containing media. The flasks were then mixed thoroughly on a New Brunswick Scientific *Excella E2* shaking platform at 200 rpm and were covered with parafilm to avoid external disturbances. After mixing, the solution was extracted from the flasks, filtered through a 0.45 μm filter, and analyzed for total copper in triplicate using the United States Environmental Protection Agency (USEPA) Bicinchoninate method no. 8506 and a HACH DR 2800 spectrophotometer. The detection limit is 0.04–5.00 mg L^{-1} with a precision of 0.01 mg L^{-1}. For all media types, a constant mass of media was used with varying adsorbate concentrations of 0.2, 0.6, 1.0, 2.0, and 3.0 mg L^{-1}. In all equilibrium tests, the temperature was kept at 23 °C ± 1.0 °C and the pH was adjusted using HCl or NaOH solution.

2.3. Reaction kinetics

The kinetics of the adsorption reaction were observed experimentally and fit to the Lagergren kinetic equations for adsorption. The data was fit to both first and second-order kinetic equations by minimizing the root mean square error (RMSE) between the kinetic adsorption data and models. The Lagergren pseudo-first and pseudo-second order kinetic equations are given as:

$$q = q_0\left(1 - e^{-k_{P1}t}\right) \quad (1)$$