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

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HIGHLIGHTS

- Multiple cycles of adsorption and desorption confirm that hydrochloric acid has good potential for copper desorption.
- A rapid desorption reaction can be delineated with the Lagergren pseudo-second order model.
- Surface sorption of CuO species is significant in the media mixture and coconut coir.

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ABSTRACT

Multiple adsorption and desorption cycles are required to achieve the reliable operation of copper removal and recovery. A green sorption media mixture composed of recycled tire chunk, expanded clay aggregate, and coconut coir was evaluated in this study for its desorptive characteristics as a companion study of the corresponding adsorption process in an earlier publication. We conducted a screening of potential desorbing agents, batch desorption equilibrium and kinetic studies, and batch tests through 3 adsorption/desorption cycles. The desorbing agent screening revealed that hydrochloric acid has good potential for copper desorption. Equilibrium data fit the Freundlich isotherm, whereas kinetic data had high correlation with the Lagergren pseudo second-order model and revealed a rapid desorption reaction. Batch equilibrium data over 3 adsorption/desorption cycles showed that the coconut coir and media mixture were the most resilient, demonstrating they could be used through 3 or more adsorption/desorption cycles. FE-SEM imaging, XRD, and EDS analyses supported the batch adsorption and desorption results showing significant surface sorption of CuO species in the media mixture and coconut coir, followed by partial desorption using 0.1 M HCl as a desorbing agent.

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1. Introduction

Non-point sources of copper loading have impaired a large number of water bodies in the United States by causing copper concentrations in the water column to exceed ambient water quality threshold (US EPA, 2014). Non-point sources include runoff from highways (Davis et al., 2001; Nason and Bloomquist, 2012; Kayhanian et al., 2003; Dean et al., 2005; Hilliges et al., 2013; US EPA, 2014) and agricultural lands (Kayhanian et al., 2003; Graves et al., 2004; Dean et al., 2005; Pitt et al., 2008; Hoang et al., 2009; Nason et al., 2012; Hilliges et al., 2013), and use of copper sulfate ($CuSO_4$) as an algaecide in both natural and manmade water bodies

(Chang et al., 2014). The use of green adsorptive filter media, or green adsorption media, to remove copper in stormwater runoff may be regarded as a best management practice (BMP). The term "green" is used here to define media composed of recycled and/or renewable materials; however, once the filter media has reached its adsorptive capacity, it must be replaced and the spent media may need to be disposed as a hazardous waste if copper recovery is not lucrative. To conduct copper recovery, desorption of adsorbed copper has to be achieved through the use of various desorbing agents, primarily acids (Vilar et al., 2007; Singh et al., 2008; Njikam and Schiewer, 2012; Li et al., 2015) and complexing agents (Singh et al., 2008; Njikam and Schiewer, 2012), whose effectiveness may vary between media types, depending on the sorption mechanism involved. Regeneration of the media's sorption sites is important in establishing the media as a cost-effective and sustainable solution for copper removal in stormwater runoff (Tassist

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et al., 2009). The desorbed copper in solution may be removed from the waste stream and recovered using a number of technologies such as reverse osmosis and nanofiltration (Al-Zoubi et al., 2010; Mullett et al., 2014), chemical synthesis (Zhang and Zhang, 2014), precipitation (Xie et al., 2005; Tassist et al., 2009; Chen et al., 2014), and electrolysis (Tassist et al., 2009).

Studies of heavy metal desorption from both green adsorption media and inorganic adsorption media have similar mechanisms (Vilar et al., 2007). Adsorption isotherm equations have been successfully applied to describe equilibrium desorption data, including Langmuir and Freundlich isotherms (Cox et al., 1997; Li et al., 2015), whereas some mechanistic models of desorption equilibrium have been developed (Cox et al., 1997; Vilar et al., 2007; Febrianto et al., 2009; Li et al., 2015). Desorption kinetics have been shown to follow Lagergren pseudo first- and second-order kinetics (Singh et al., 2008; Febrianto et al., 2009; Njikam and Schiewer, 2012) by assuming that the rate of desorption is proportional to the number of metal-filled sites. Adsorption and desorption hysteresis is another phenomenon that has been studied experimentally for sorption media exposed to multiple adsorption/desorption cycles (Cox et al., 1997; Singh et al., 2008; Piwowarczyk and Holden, 2011; Li et al., 2015).

This study aims to evaluate the desorption characteristics of a green sorption media mixture composed of recycled tire rubber, expanded clay aggregate, and coconut coir and answer two science questions. First, what is the potential for copper removal and recovery using strong acids as a desorbing agent? Second, how does the adsorptive capacity of the sorption media vary through multiple adsorption/desorption cycles?

2. Methods and materials

2.1. Adsorption tests

Batch adsorption tests were carried out to produce copper-loaded media with which to conduct the desorption tests. The tests were conducted using 300 mL distilled water spiked with Fisher Scientific 1000 ppm copper standard (copper nitrate). Varying copper solution concentrations of 0.2, 0.6, 1.0, 2.0, and 3.0 $mg \cdot L^{-1}$ were added to 500 mL flasks containing 50 g of expanded clay and tire chunk, 30 g of media mixture, and 10 g of coconut coir. The flasks were then mixed thoroughly for 30 and 60 min on a New Brunswick Scientific *Excella E2* shaking platform at 200 rpm and 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 in triplicate using the United States Environmental Protection Agency (USEPA) Bicinchoninate Method no. 8506 and a HACH DR 2800 spectrophotometer. In all tests, the temperature was kept at 23 °C ± 3.0 °C, and the pH was adjusted to 3.75 ± 0.1 using $HCl_{(aq)}$.

2.2. Screening of desorbing agents

Desorption tests with 4 different desorbing agents were carried out on the copper-loaded media in contact with adsorbate solution for 60 min at a pH of 3.85. The selected desorbing agents were DI water, 0.1 M HCl, 0.1 M HNO_3, and 0.1 M H_2SO_4. For each desorbing agent, duplicates of 5 g media mixture, tire chunk, and expanded clay, and 1 g of the coconut coir were exposed to 30 mL of desorbing solution for 180 min on a shaking platform at 200 rpm. All media were oven-dried at 75 °C for a minimum of 36 h prior to the test. After mixing, the solution was extracted from the flasks, adjusted to a pH between 4 and 6 using 5.0 N KaOH, filtered through a 0.45 μm filter, and analyzed individually using the USEPA Bicinchoninate Method no. 8506.

Relative desorption strength among the 4 desorbing agents was evaluated using the desorption efficiency as the common indicator, defined below:

$$Desorption\ Efficiency = \frac{C_e V}{q_{0D} m} \times 100\% \tag{1}$$

where q_{0D} is the solid-phase copper concentration ($mg \cdot g^{-1}$) before desorption, m is the mass of media (g), C_e ($mg \cdot L^{-1}$) is the liquid-phase copper concentration in the desorbing solution, and V (L) is the volume of desorbing solution.

Batch desorption tests were conducted on media in contact with adsorbate solution for 30 min with 300 mL 0.1 M HCl as the desorbing agent. The desorbing agent was added to 500 mL flasks containing 50 g of expanded clay and tire chunk, 30 g of media mixture, and 10 g of coconut coir. The flasks were then mixed thoroughly for 30 min on a shaking platform at 200 rpm.

2.3. Desorption equilibria

Batch desorption tests were carried out on the media to establish the equilibrium desorption isotherms for the media mixture and individual media. Data from the batch desorption tests were fit to both the Freundlich and Langmuir equations for desorption isotherms:

$$q = K_{f,D} C_{e,D}^{1/n} \tag{2}$$

$$q = q_{max,D} \frac{K_{L,D} C_{e,D}}{1 + K_{L,D} C_{e,D}} \tag{3}$$

where q is the solid-phase copper concentration ($mg \cdot g^{-1}$), $C_{e,D}$, ($mg \cdot L^{-1}$) is the copper concentration in the desorbing solution, $K_{f,D}$ ($mg \cdot g^{-1}$) is the Freundlich desorption coefficient, n (dimensionless) is the nonlinearity factor, $K_{L,D}$ ($mg \cdot L^{-1}$) is the Langmuir desorption coefficient, and $q_{max,D}$ ($mg \cdot g^{-1}$) for the desorption isotherm an indicator of the desorption capacity of the sorbent–desorbate system. The Freundlich and Langmuir isotherm parameters for adsorption and desorption were optimized by minimizing root mean squared error (RMSE) between the experimental data and the predicted isotherm equation.

2.4. Desorption kinetics

The kinetics of the desorption reaction were observed experimentally and fit to both the classical rate-law kinetic equations and the Lagergren kinetic equations for sorption. The rate law kinetic equations were adapted for desorption reactions by assuming that the adsorbed copper concentration, $q(t)$ is related to the initial adsorbed copper concentration, q_0, by a reaction rate coefficient, k. The data was fit to both first- and second-order kinetic equations by minimizing the sum of the squared error between the kinetic desorption data and the model. For first-order kinetics, the kinetic equation takes the form:

$$q = q_0 e^{-k_{1D} t} \tag{4}$$

where k_{1D} (min^{-1}) is the reaction rate constant and t is the reaction time. For second-order kinetics, the kinetic equation takes the form:

$$\frac{1}{q} = \frac{1}{q_0} + k_{2D} t \tag{5}$$