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Stable copper-zeolite filter media for bacteria removal in stormwater

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HIGHLIGHTS

- Six new filter media were developed by calcination or $Cu(OH)_2$ coating on Cu^{2+}-treated zeolite (ZCu).
- All new media showed more than 97% reduction in copper leaching compared to ZCu.
- $Cu(OH)_2$-coated ZCu showed better and more stable bacteria removal than ZCu.
- New media maintained bacterial inactivation efficiency during drying event.
- Applying new media in sand filter was successful in terms of bacterial removal and inactivation.

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ABSTRACT

Cu^{2+}-exchanged zeolite (ZCu) as antibacterial media shows great potential for bacteria removal from stormwater, but its stability in high salinity water needs attention. In this study, stable antibacterial media were developed by modifying ZCu through calcination and in situ $Cu(OH)_2$ coating. Their stability and *Escherichia coli* removal efficiency along with impact of salinity were examined in gravity-fed columns. While copper leaching from ZCu was 20 mg/L in test water of salinity 250 μS/cm, it was reduced by over 97% through $Cu(OH)_2$ coating and/or calcination. ZCu coated with $Cu(OH)_2$ followed by heat treatment at 180 °C (ZCuCuO180) exhibited more consistent *E. coli* removal (1.7–2.7 log) than ZCu (1.2–3.3 log) in test water of varied salinity but constant contact time 22 min. ZCu calcined at 400 °C (ZCu400) effectively inactivated removed bacteria during 24 h drying period. In the presence of native microbial communities, new sand filters, particularly those having ZCu400 at the top to inactivate bacteria during drying periods and ZCuCuO180 midway to capture and inactivate microbes during wet events, provided the best bacterial removal (1.7 log, contact time 9 min). Copper leaching from this design was 9 μg/L, well below long-term irrigation standard of 200 μg/L.

1. Introduction

Stormwater, via harvesting, is gaining prominence as an alternative water source to ensure reliable water supplies for cities and towns [1]. Stormwater filters and biofilters are becoming popular for stormwater harvesting [2]. They are gravity-fed filter beds, vegetated or non-vegetated, removing microbes mainly by means of sedimentation, straining, adsorption and die-off. However, distinct characteristics of stormwater pose challenges for filter performance, since stormwater biofilters are often located within urban environments, thus exposed to highly variable hydraulic and pollutant loadings, intermittent wetting and drying conditions, and high seasonal variations [3,4]. Limited field and laboratory investigations have shown that their performances are highly variable (ranging from good removal to net leaching), and effluent water quality can hardly meet requirements even for the lowest level of stormwater reuse, i.e. non-restricted irrigation [5–8].

Inadequate microbial removal capacity of sand media used in stormwater filters and biofilters plays a key role in these observations, while survival/growth and remobilisation of microbes from the media contribute to net leaching. Filter performance is further worsened by the highly variable and intermittent nature of stormwater runoff, with the latter exposing filters to varying duration of dry periods [8,9]. Antibacterial media exert bactericidal

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effects through contact with bacterial solution or slow release of antibacterial agents [10–12]. A few studies examined the bactericidal effects of immobilising heavy metals (e.g. Ag, Cu, and Zn) on a range of media (such as activated carbon, zeolite etc.) for wastewater treatment [10–13] where operational conditions of filter media including inflow concentrations, temperature, salinity, and hydraulic loading are relatively stable.

Effectiveness of these antibacterial media was further justified for stormwater treatment. 15 types of Cu, Zn, Fe, Ti, and quaternary ammonium salts modified media were developed and examined for 5 months subjected to inflow concentrations (about 1–48,000 MPN *Escherichia coli*/100 mL), temperature (11 to 21 °C), hydraulic loading (14–100 mm rain events), and drying periods of varying length (1–4 weeks) [14]. It was found that Cu^{2+}-exchanged zeolite (ZCu) was effective to reduce bacterial level by 2 log consistently. However, high copper concentrations in the outflow (30–40 mg/L) were observed. Excessive leaching of Cu^{2+} is mainly due to ion-exchange with other cations in solution. This level of copper concentration is much higher than the stormwater harvesting guidelines (i.e. 2 mg/L in drinking water, and 0.2 mg/L in water for irrigation) [6,15], posing significant health issues in humans and toxicity to plants.

The aim of this study is to develop stable Cu-zeolite media for effective bacterial removal from stormwater by sand filters, specifically with three main objectives:

- to prepare stable yet effective Cu-zeolite media by calcination of ZCu or in situ $Cu(OH)_2$ coating on ZCu;
- to investigate the impact of salinity on the stability and *E. coli* removal performance of the antibacterial media; and
- to design and investigate new sand filters with the stable Cu-zeolite media for improved bacterial retention and inactivation.

2. Materials and methods

2.1. Materials

Natural zeolite (Escott Zeolite from Zeolite Australia, basic physicochemical properties listed in [16]), was used as base media comprising three size fractions: non-graded 0.1–0.6 mm (Z0), graded 0.3–0.6 mm ($Z0_{0.3}$) and 0.1–0.3 mm ($Z0_{0.1}$). They were washed thrice with 10 volumes of tap water, dried at 105 °C overnight then stored in a dry container for use. Washed sand, washed coarse sand, gravel of size 0.075–0.6 mm, 1.0–2.0 mm and 2.0–3.4 mm respectively were used, Daisy Garden Supplies, Melbourne. The former two were used directly, while gravel was washed 5 times with 10 volumes of tap water and dried in air. The chemicals included NaCl, $CuCl_2$, NaOH and ethylenediaminetetraacetic acid disodium salt (EDTA) (all from Merck Chemicals).

2.2. Preparation and characterisation of stable antibacterial media

2.2.1. Modification of zeolite by copper chloride

Zeolite of three size fractions (Z0, $Z0_{0.3}$, $Z0_{0.1}$) was treated by $CuCl_2$ following the method described in [14] with a slight change in NaCl treatment time: 48 h was used in this study. The so prepared Cu^{2+}-exchanged zeolite was denoted as ZCu, $ZCu_{0.3}$, and $ZCu_{0.1}$ respectively.

2.2.2. Heat treatment of copper-treated zeolite

Heat treatment has been reported to reduce the elution of metal ions into contacting liquid [17]. To test possible improvements to Cu^{2+}-exchanged zeolite, as well as the impact of different temperatures on the phenomena, $ZCu_{0.3}$ was heated using LAB Muffle Furnace CEMLL at a rate of 5 °C/min to a set temperature, which was then maintained for 2 h before cooling naturally to room temperature. The following set temperatures were trialled: 400 °C, 600 °C, and 800 °C, and the produced media were denoted as $ZCu400_{0.3}$, $ZCu600_{0.3}$ and $ZCu800_{0.3}$, respectively. ZCu and $ZCu_{0.1}$ were treated in a similar way at temperatures 400 °C and 800 °C respectively producing ZCu400 and $ZCu800_{0.1}$.

2.2.3. Modification of copper-treated zeolite by CuO

An attempt was made to further reduce metal elution using CuO coating. $ZCu_{0.3}$ was gently stirred in 1 wt% $CuCl_2$ for 10 min; then the pH of the slurry was slowly adjusted to 7 using 2 M NaOH. The mixture was stirred for another 2 h and left still overnight. The media was separated from the mixture and washed once, before being dried at 65 °C overnight. The dry media was then heat-treated at 400 °C following a procedure similar to preparing $ZCu400_{0.3}$. After cooling, the media was washed five times with DI water then dried at 105 °C overnight. The produced media was denoted as $ZCuCuO400_{0.3}$. ZCu and $ZCu_{0.3}$ were treated similarly but at 180 °C producing ZCuCuO180 and $ZCuCuO180_{0.3}$ respectively.

In total, nine types of antibacterial media were prepared including:

- Graded 0.1–0.3 mm: $ZCu800_{0.1}$;
- Graded 0.3–0.6 mm: $ZCu_{0.3}$, $ZCu800_{0.3}$, $ZCu600_{0.3}$, $ZCu400_{0.3}$, $ZCuCuO400_{0.3}$, $ZCuCuO180_{0.3}$;
- Non-graded 0.1–0.6 mm: ZCuCuO180, ZCu400.

The seven types of graded media consisting of two size fractions were tested in columns to investigate their stability and bacterial removal efficiency in test water of varied salinity (Section 2.3 and Table 1), and untreated zeolite ($Z0_{0.1}$, $Z0_{0.3}$) were used as controls. The two non-graded antibacterial media were combined with washed sand in a variety of arrangements to investigate the promising layout for bacterial removal (Section 2.4 and Table 1). The copper content of antibacterial media was measured using inductively coupled plasma mass spectrometry (ICP-MS) in a NATA-accredited laboratory.

2.3. Performance evaluation of antibacterial media at various salinity-pure media assessment

The stability and bacterial removal efficiency of seven types of antibacterial media and two untreated controls ($Z0_{0.3}$ and $Z0_{0.1}$) were tested in columns (three replicates for each media). Table 1 summarises the experimental setting and operational conditions. The filter media were packed into columns (18 mm in diameter, 340 mm in length, with a fine screen mesh placed at the bottom, and sand-blasted interior walls to prevent edge effects) in accordance with the aforementioned method [14]. In brief, moist filter media was added incrementally through the top of each column, which was partially filled with DI water. After addition of filter media, the latter was thoroughly packed by dropping a stainless steel rod (ID 7 mm, weight 110 g) from 10 mm height above the top media surface to remove any trapped air bubbles.

The columns were flushed using nine pulses of 70 mL DI water to allow media to settle and remove fine granules produced during the packing. Each pulse was applied after the columns were completely drained. Thereafter, outlets of columns were restricted to maintain superficial velocity of 236 mm/h, translating to contact time between water and media of 22 min. To condition the media, the filter columns were dosed with 29 pulses of 70 mL DI water spiked by NaCl to achieve salinity 250 μS/cm. The water was applied in pulses to mimic the intermittent nature of stormwater