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Removal of *E. coli* from urban stormwater using antimicrobial-modified filter media

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HIGHLIGHTS

- 15 antibacterial filter media were prepared for enhanced bacterial removal from urban stormwater.
- Their performances were evaluated over 24 weeks under typical stormwater operational conditions.
- Filter media modified with copper compounds exhibited robust antibacterial efficiency.
- Filter media modified with Cu^{2+} and $Cu(OH)_2$ showed effective bacteria removal during wet events.
- Filter media modified with $Cu(OH)_2$ showed very good stability in stormwater.

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ABSTRACT

Stormwater filters featuring traditional sand filter media cannot reliably treat indicator bacteria for stormwater harvesting. In this work, copper-modified zeolite and granular activated carbon (GAC) were prepared through Cu^{2+} impregnation and *in situ* $Cu(OH)_2$ precipitation. Their antibacterial properties and stability in natural stormwater were studied in gravity-fed columns for 24 weeks, under typical stormwater operational conditions. 11 types of other filter media, prepared using zinc, iron, titanium and quaternary ammonium salts as antibacterial agents, were tested in parallel by way of comparison. Cu^{2+}-immobilised zeolite and $Cu(OH)_2$-coated GAC yielded an estimated 2-log reduction of *E. coli* within 40 min with the presence of other native microbial communities in natural stormwater. Even at high flow velocity (effective contact time of 4.5 min), both media demonstrated 0.8 log removal. Both media and Cu^{2+}-treated GAC showed effective inactivation of the removed *E. coli* during dry periods. Copper leaching from $Cu(OH)_2$-coated GAC was found to be below the NHMRC specified drinking water standard, while that from Cu^{2+}-immobilised zeolite varied with the salinity in stormwater. These findings could provide useful information for further development of passive stormwater harvesting systems.

1. Introduction

Stormwater filters and biofilters are gravity-fed filter beds, vegetated or non-vegetated, placed within urban landscapes that are never back-washed [1]. They remove nutrients and metals effectively by means of biological uptake, straining and adsorption [1–3]. However, field and laboratory investigations have shown that their effluent seldom meets bacterial indicator targets for outdoor irrigation [4–7]. This is partially due to the inadequate microbial removal capacity of sand media used in these filters, as well as survival and detachment of microbes under intermittent stormwater inflows [8]. Therefore, stormwater filters and biofilters require novel media in order to ensure effective pathogen removal [9].

As inorganic antimicrobials, zeolites and activated carbon containing Ag, Cu or Zn have proliferated for food preservation, self-disinfection fabrics, etc. [10,11]. Ag-activated carbon has been

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tested for water treatment and demonstrated very good bacterial removal efficiency [12,13]. An investigation of Cu^{2+}-treated zeolite for water treatment, subjected to controlled conditions and 6 h hydraulic residence time, showed around 1–3 log removal for a wide range of microbes [14,15]. However, longevity in efficiency and stability – yet to be addressed – is essential for field application.

Compared with the metal ion treatment of filter media, metal hydr(oxide) coating exhibits better stability in water due to its low solubility constant. In addition, metal hydr(oxide) coating shows effective bacteria removal through electrostatic attraction [12,16,17]. More importantly, the slow release of metal ions from the coating layer in solution at an effective level may exert an antimicrobial effect from the media. Kennedy et al. [18], for example, examined the bactericidal effects of CuO/Cu_2O-coated carbon and showed 4 log removal of *E. coli*. However, the coating processes required expensive organometallic precursor and toxic organic solvent, prohibiting large scale field applications. In addition, $Cu(OH)_2$, an effective component in Bordeaux mixture as a pesticide and fungicide, has not been investigated as antimicrobial coating for any water treatment media. Consequently, CuO coating through $Cu(OH)_2$ precipitation has not been investigated for antimicrobial use.

The above findings cannot be used directly for advancements of stormwater filters and biofilters, as urban runoff is a unique water source. For example, stormwater biofilters are located within an urban environment (often being an amenity feature), thus are exposed to highly variable hydraulic and pollutant loadings, intermittent wetting and drying conditions, and highly seasonal variations [19]. The distinct characteristics of stormwater will pose questions for the aforementioned modified materials: for example, will variability, and sometimes high salinity, of stormwater lead to excessive heavy metal leaching from antimicrobial media?

This study therefore aims to develop and evaluate antibacterial media for urban stormwater treatment. Specifically, this work's objectives are to:

- Develop simple yet scalable processes to modify GAC and zeolite with $Cu(OH)_2$, CuO, and Cu^{2+} producing 4 types of copper modified media;
- Evaluate their stability and bacteria removal performance, inactivation efficiency over semi-long term experimental duration, under typical stormwater operational conditions including relatively high filtration rates, intermittent operation patterns, and variable salinity in stormwater;
- Investigate the main bacterial removal mechanisms subjected to stormwater conditions;
- Prepare 11 other antibacterial media using zinc, iron, titanium, and quaternary ammonium salts (consulted in literature for other types of water treatment), evaluating their stability and bacteria removal efficiency for stormwater operational conditions (in comparison with copper treated media).

2. Experiments

2.1. Modification of zeolite and granular activated carbon with antibacterial agents

The chemicals (CAS number in parentheses) and their sources, featured in this study, comprise zinc sulfate heptahydrate (7446-20-0), copper(II) chloride (7447-39-4), iron(III) chloride (7705-08-0), hexadecyltrimethylammonium chloride (QAC) (11202-7), sodium hydroxide (1310-73-2) and ethylenediaminetetraacetic acid disodium salt (EDTA) (6381-92-6), Merck Chemicals, Australia; dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (Si-QAC) (27668-52-6), Sigma–Aldrich; TiO_2 sol–gel [20]. Natural zeolite (particle size 0.3–0.6 mm), Zeolite Australia; and granular activated carbon (GAC) (particle size 0.3–0.6 mm), Activated Carbon Technologies Pty Ltd, constituted base media. The basic physicochemical properties of natural zeolite and GAC were listed in [21,22].

Modification of zeolite by Cu^{2+}, Fe^{3+}, Zn^{2+}: Zeolite was mixed with 2 M NaCl for 72 h to produce Na-zeolite. NaCl solution was replaced every 24 h. After being washed with deionised (DI) water, Na-zeolite was mixed with 0.015 M $CuCl_2$ solution (metal content 5% by weight of zeolite) for 48 h. The $CuCl_2$ solution was replaced every 24 h. This sample was then washed and dried at 105 °C overnight to produce Cu^{2+} modified zeolite, denoted as Cu-Z. Following a similar procedure, Fe-Z and Zn-Z were prepared. Zn/Cu/Fe-Z was concocted by impregnating Na-zeolite in 0.015 M solutions of $ZnSO_4$, $CuCl_2$ and $FeCl_3$ for 24 h each sequentially. All mixing was under agitation from a rotary platform at 150 rpm.

Modification of zeolite by CuO: 3 g $CuCl_2$ was added into aqueous slurry of zeolite (80 g zeolite in 300 mL DI water). The mixture was rotated gently for 1 h, after which the pH of the slurry was adjusted to 8 with 2 M NaOH. After mixing for 1 h, the particles were separated, washed with DI water and dried at 60 °C overnight. The dry media was then heat-treated at a rate of 5 °C/min to 400 °C and maintained at that temperature for 1 h before cooling by means of a temperature controlled programmer. After cooling, the CuO impregnated particles were washed five times with water. The washed sample was dried at 105 °C to attain the final product CuO-Z.

Modification of GAC by Cu^{2+}: 10 g GAC was mixed with 500 mL of 0.015 M $CuCl_2$. The slurry was gently rotated for 24 h. Particles were then separated, washed and dried at 105 °C for use (Cu-G).

Modification of GAC by $Cu(OH)_2$: The preparation procedure was similar to that of CuO-Z, excepting a lower heat treatment temperature of 180 °C for preparing $Cu(OH)_2$-G.

Modification by other antibacterial media: $Zn(OH)_2$, $Fe(OH)_3$, TiO_2, QAC, and Si-QAC modified media were prepared following the aforementioned methods [12,23–26]. Prepared media were denoted as $Zn(OH)_2$-Z, $Zn(OH)_2$-G, $Fe(OH)_3$-Z, TiO_2-Z, TiO_2-G, QAC-Z, SiQAC-Z and SiQAC-G.

Table 1
Combinations of base media with antibacterial agents.

Antibacterial agent	Modified filter media	
	Zeolite-based media	GAC-based media
Nil	Z0	G0
Metal ions	Cu-Z, Zn-Z, Fe-Z, Zn/Cu/Fe-Z[b]	Cu-G[b]
Metal hydroxide	$Fe(OH)_3$-Z[b], $Zn(OH)_2$-Z[b]	$Zn(OH)_2$-G, $Cu(OH)_2$-G[b]
Metal oxide	CuO-Z[b], TiO_2-Z[b]	TiO_2-G[b]
Quats[a]	SiQAC-Z[b], QAC-Z	SiQAC-G[b]

[a] Quats – Quaternary ammonium salts.
[b] Media have never been tested for water treatment, while all the listed media have never been tested for stormwater applications.