



Preliminary Laboratory Investigations into Zinc and Copper Adsorption by Crushed Bivalve Shells

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Abstract Crushed shells from three bivalve mollusc species (mussel, oyster and scallop) in two particle size ranges (63–150 μm and 710–1180 μm) were tested for their ability to remove dissolved copper and zinc ions from synthetic stormwater in a column. For comparison, zeolite (1–2 mm), which is commonly used for heavy metal ion capture, was also assessed. All shell types of both particle sizes were effective in removing zinc from solution with 97–100% removal efficiency which was similar to the removal efficiency by zeolite (97.6%). The removal of copper was most efficiently achieved with oyster shell with a particle size range of 710–1180 μm (83.6%), which was similar to the removal efficiency by zeolite (83.4%). Brunauer-Emmett-Teller (BET) surface area measurements showed significant decreases in the surface area of the shells after exposure to synthetic stormwater due to adsorption of heavy metals, visually confirmed by observation of a fine layer of metal precipitate adsorbed to the shell particle surfaces using Scanning Electron Microscopy (SEM). Overall, the results indicate that crushed bivalve shells

have excellent potential for the removal of dissolved zinc and copper from stormwater and should be tested in more complex stormwater studies. This work has significant implications for stormwater infrastructure design using a local, cheap and readily accessible waste material.

Keywords Bivalve shells · Dissolved metal ions · Urban stormwater

1 Introduction

Urban stormwater is typically directed into natural waterways and eventually discharged into coastal waters or lakes (Reddy et al., 2014). There is increasing international concern about the environmental effects of chemical contaminants carried by urban stormwater into natural aquatic systems, especially persistent pollutants (Brown & Peake, 2006). The major contaminants in urban stormwater include particulate matter and dissolved chemicals, including heavy metals and hydrocarbons derived from vehicle emissions, wear on road surfaces and vehicle components (Brown & Peake, 2006; Moores et al., 2012). Dissolved zinc and copper are two heavy metals of particular concern for urban stormwater discharges, especially when associated with road run off (Ladislas et al., 2012; Moores et al., 2012). Data from monitoring of heavy metal concentrations in New Zealand show that copper and zinc are usually the heavy metals that are most elevated in coastal and estuarine

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sediments (https://statisticsnz.shinyapps.io/heavy_metals_load_coastal_sediment/). The concentrations of copper, zinc and lead in the stormwater itself are rarely measured in Auckland, but a recent study of the stormwater in three pipes in Ōkahu Bay after six significant rainfall events showed concentrations with considerable fluctuation, ranging from undetectable to $121 \mu\text{g L}^{-1}$, undetectable to $365 \mu\text{g L}^{-1}$ and undetectable to $15.6 \mu\text{g L}^{-1}$ for copper, zinc and lead, respectively (Stimson & Hikuroa, 2017). The conventional methods used for removing dissolved heavy metal ions from wastewater include chemical precipitation, ion exchange, electrolytic recovery, floatation, membrane filtration, coagulation and flocculation (Dean et al., 1972; Al-Anbari et al., 2008; Kus et al., 2012; Reddy et al., 2014; Sharma et al., 2021; Xi et al., 2022). However, these methods are expensive, time-consuming and labour intensive to operate, and they generally require large quantities of corrosive chemicals.

A promising alternative for removing dissolved heavy metals through adsorption from stormwater involves the re-purposed use of common waste products such as bivalve mollusc shells. Shells of molluscs are primarily comprised of calcium carbonate (> 90% by mass) with a small amount of organic matrix (0.01–5%) containing protein and chitin (Suzuki & Nagasawa, 2013). Adsorption on bivalve shells occurs through ion-exchange where Ca^{2+} is exchanged with incoming metal ions from the aqueous solution. Crushed waste bivalve shells (species not mentioned) from a market in Nanning, China, were shown to remove heavy metals from electroplating wastewater with 90–100% efficiency, and one of the mechanisms for the metal removal was ion-exchange (Liu et al., 2009). It was demonstrated that adsorption of Cu, Fe and Zn was more efficient at the electroplating wastewater pH of 3 compared to aqueous metal solutions at a pH of 5. It is important to note that these pHs are significantly lower than the typical pH of 6.2–7.3 of urban wastewater (O’Sullivan et al., 2012), as heavy metal ion solubility and therefore their readiness for adsorption are heavily dependent on pH (Liu et al., 2009; Millero et al., 2009).

Removal of Pb^{2+} , Cd^{2+} and Zn^{2+} from neutral aqueous solution has also been demonstrated with the aragonite shells of razor clams (*Siliqua patula*) and calcite shells of oysters (species not mentioned) (Du et al., 2011). In that study, Scanning Electron Microscopy (SEM) images showed secondary precipitation of metal carbonates on the shell surfaces, to

varying degrees depending on the metal, demonstrating further metal adsorption beyond 1:1 ion-exchange with Ca^{2+} . Du et al. (2011) tested three different size ranges of the crushed shells and demonstrated that the smallest sized shell particles were the most efficient for metal removal, because of their greater surface area. However, as the shell particle size decreases, the space between particles for the stormwater to flow through decreases, affecting the flow rates that can be processed by the system. Therefore, a compromise needs to be made to ensure sufficient flow rate for practical stormwater filtration occurs, whilst maximising the removal of heavy metal ions from solution.

Bivalve mollusc fisheries and aquaculture generate considerable quantities of waste shell material which is normally dumped and for which commercial uses are being sought. The estimated amount of annual waste from New Zealand’s mussel aquaculture industry was around 90,000 tonnes in 2021 (Canterbury, 2021). Current methods of shell waste reduction and disposal in New Zealand include stockpiling, burial in landfills and adding to forestry roads to substitute for stone chip (Barnaby, 2004). Worldwide production of live shellfish was around 15 million t in 2015 (Morris et al., 2019), and considering that shells typically account for 75% of organismal weight (Tokeshi et al., 2000), the quantity of shell waste worldwide is considerable. Furthermore, world aquaculture production is increasing rapidly as food demands grow and wild marine capture stalls (FAO, 2014).

The aim of this study was to assess the potential for the waste shells of common species of molluscs found in New Zealand for the removal of heavy metal ions (Cu^{2+} and Zn^{2+}) that are commonly found in local urban stormwater. There is a major challenge in treating actual stormwater containing suspended sediment and metals attached to fine colloidal materials. Furthermore, stormwater typically contains a wide range of metals, organics, soluble salts, bacteria and viruses, making it a highly complex system that is difficult to use in experimental studies. Hence, this study used a synthetic stormwater with relevant concentrations of dissolved copper and zinc in water, to assess the removal capabilities of crushed shell material for these two heavy metals. The concentrations used, 50 and $200 \mu\text{g L}^{-1}$ for copper and zinc, respectively, were within the range of concentrations detected in previous assessments of stormwater in Auckland, New Zealand (Moores et al., 2009; Stimson &

Hikuroa, 2017). The three readily available bivalve shells were green-lipped mussel (*Perna canaliculus*), Pacific oyster (*Crassostera gigas*) and New Zealand scallop (*Pecten novaezelandiae*).

2 Materials and Methods

2.1 Shell Material

Fresh shells of the three different bivalve species (mussel, oyster and scallop) were obtained from local shellfish processing factories, immediately after processing. All shell material was cleaned by scrubbing with a stiff brush with cold tap water and then air-dried for 4–5 days at room temperature with minimal sun exposure. Whole shells were used for the crushing. Preliminary studies (Thind, 2013) demonstrated that different methods of shell crushing including ring mill, roller and jaw crushing testing resulted in characteristic particle sizes each with different surface areas, packing densities and corresponding porosity. Ring mill crushing resulted in shell particles predominantly in the size ranges of 63–150 μm and 710–1180 μm for all shell species (mussel, oyster and scallop). Roller and jaw crushers were found to be generally ineffective at crushing shell material. The roller crusher resulted in majority of the shell particles to be in 2.36–9.00-mm range even when the rollers were adjusted to 1-mm separation. The jaw crusher also resulted in the same particle range as the roller crusher even at the smallest possible jaw gap of 1.5 cm. Therefore, shell particle size ranges of 63–150 μm and 710–1180 μm produced by ring mill crushing of shells and then separated into the distinct size class with the use of a sieve shaker set were used for the column experiments. The characteristic particle size ranges produced by ring mill crushing were used because in an applied situation these will be the particle ranges of shell material that would be available from the commercial crushing of the shell. These two shell particle size ranges were tested separately for each shell species. In addition to the shells from three species of bivalves, industrial zeolite (Blue Pacific Minerals Ltd, Grade code: Z1 – DBC, 1–2 mm particle size range) was also characterised in the same manner as this mineral is currently used in urban stormwater filters for the removal of dissolved heavy metals (Pitcher et al., 2004).

2.2 Column Setup

Sorption experiments were carried out using custom-made Pyrex/borosilicate glass columns of 2-mm thickness with dimensions 6.0 cm (diameter) and 57 cm (height). The volume of shell or zeolite particles used in the column was kept at 300 cm^3 and this amounted to a column of 10.6 cm in height. The column used two Teflon discs of 5.9-mm diameter with 1-mm diameter holes at 2-mm spacing. The first Teflon disc was inserted at the bottom of the column followed by a thin layer of glass wool to prevent small particles of shells from leaving the column with passing eluent. The column was then packed with the shell material and then was covered by the second Teflon disc to allow liquid added to the top of the column to disperse evenly across the packed shell material and to prevent particles from being displaced (Fig. 1).

2.3 Adsorption Experiments

Experiments were conducted using a synthetic rather than natural stormwater. Since the focus of these experiments was on the removal of zinc and copper, it was preferred not to use natural stormwater given its composition variability. Using a synthetic stormwater allowed for more consistency and repeatability of the column influent composition and is common practice for stormwater filter development (Bremner et al., 2020). A synthetic stormwater solution was prepared by using copper (II) nitrate trihydrate (CAS# 10031-43-3, Sigma-Aldrich) and zinc nitrate hexahydrate (CAS# 10196-18-6, Sigma-Aldrich) dissolved in deionised water. The resulting solution contained concentrations of Cu^{2+} and Zn^{2+} ions of 0.05 and 0.2 mg L^{-1} , respectively. The pH of the solution was set to 6.88 by adjusting with HNO_3 or NaOH (0.1 mol L^{-1}) prior to adsorption experiments. This pH is a mid-range pH for urban stormwater which can range from 3.5 to 9.5 (Genç-Fuhrman et al., 2016). These experiments were performed as per the following steps:

1. Prior to performing each experiment, all the glassware including the columns and beakers, as well as fittings and Teflon discs, was left in Decon 90 (5% solution) overnight. The glassware was then washed thoroughly with deionised water three times followed by acid cleaning with 2 M HNO_3 and then washing with deionised water.

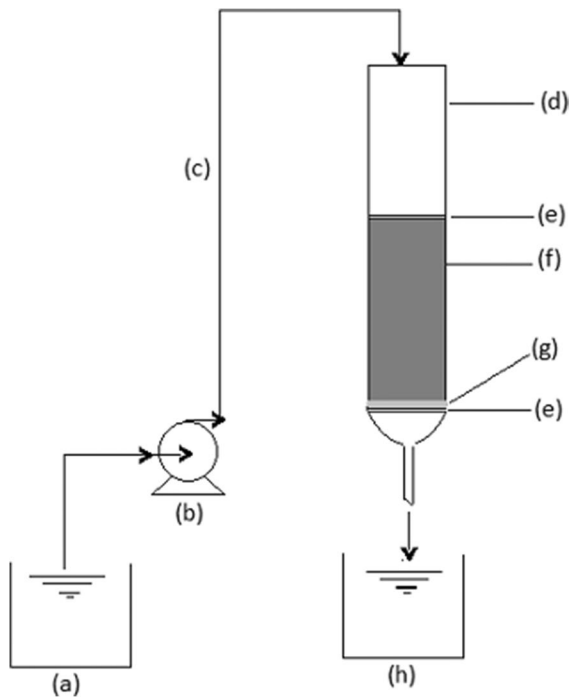


Fig. 1 Column set up for the adsorption experiments: (a) standard solution of synthetic stormwater ($0.2 \text{ mg L}^{-1} \text{ Zn}^{2+}$ and $0.05 \text{ mg L}^{-1} \text{ Cu}^{2+}$), (b) Masterflex peristaltic pump, (c) neoprene tube, (d) column, (e) Teflon disc, (f) packed shell particles, (g) glass wool, (h) beaker for eluent collection

2. The air-dried column was filled with the shell material or zeolite to a volume of 300 cm^3 .
3. The column was then washed with deionised water with pH adjusted to 6.88 to allow the column to settle. For particle size $63\text{--}150 \mu\text{m}$, the deionised water was passed through the column six times whilst for particle size $710\text{--}1180 \mu\text{m}$, the deionised water was passed through three times until consistent flow rate was reached indicating that the shell material had packed down.
4. An initial aliquot of 150 mL of synthetic stormwater was passed through the column to flush out any remaining deionised water to prevent the eluent samples from becoming diluted by residual deionised water in the column.
5. For columns containing shell material of the particle size $710\text{--}1180 \mu\text{m}$ or zeolite of $1\text{--}2 \text{ mm}$, 1 L of synthetic stormwater was delivered to the top of the column using a peristaltic pump at a flow rate of 2.9 mL s^{-1} which is a typical flow

rate for a bed filter for urban stormwater (Vigar et al., 2012). For the columns containing shell material of the range $63\text{--}150 \mu\text{m}$, this level of flow rate was not possible. Instead, 250 mL of synthetic stormwater was delivered to the top of the column using a slower flow rate of 5.0 mL min^{-1} . The eluent from columns containing shell of the particle size range of $710\text{--}1180 \mu\text{m}$ and zeolite ($1\text{--}2 \text{ mm}$) were collected in clean glass beakers in the following sequential ranges: $0\text{--}200 \text{ mL}$, $200\text{--}400 \text{ mL}$, $400\text{--}600 \text{ mL}$, $600\text{--}800 \text{ mL}$ and $800\text{--}1000 \text{ mL}$. For the columns containing shells of the particle size range $63\text{--}150 \mu\text{m}$, the eluent was collected in clean glass beakers in the sequential ranges $0\text{--}50 \text{ mL}$, $50\text{--}100 \text{ mL}$, $100\text{--}150 \text{ mL}$, $150\text{--}200 \text{ mL}$ and $200\text{--}250 \text{ mL}$.

6. Sub-samples of 20 mL were then taken from each sequential sample of eluent and stored at $4 \text{ }^\circ\text{C}$ in acid-cleaned borosilicate 20-mL vials to prevent metal ions (Zn^{2+} and Cu^{2+}) from being absorbed onto the glass walls.
7. Three replicates were run for each shell type and for each of the two shell particle size ranges, as well as for zeolite.
8. The 20-mL sub-samples of the eluent were analysed for copper and zinc content using ICP-AES using Varian ICP-OES software, version 4.0, run at 15.0 L min^{-1} using 1200 W power.

2.4 Surface Area and Pore Volume Analysis

The surface area of the shell particles following exposure to the solution in the column experiments was examined for each shell type in the shell particle size ranges of $63\text{--}150 \mu\text{m}$ and $710\text{--}1180 \mu\text{m}$. One sample from each of the three replicate shell columns after running synthetic stormwater solution was rinsed thoroughly with deionised water then thoroughly dried in an oven at $100 \text{ }^\circ\text{C}$ prior to analysis to remove any remaining moisture. The Brunauer-Emmett-Teller (BET) technique for determining surface area of particles is independent of sample mass; therefore, the sample mass used for these experiments varied between 2.0 and 3.0 g . Surface area analyses were performed using a Micromeritics TriStar 3000 instrument with version 4.00 software (made in USA). The BET theory with 97-point isotherm was used in determining surface area of the three types of shells and zeolite.

The pore properties of the samples of shell particles, including the BET surface area (SBET, $\text{m}^2 \text{g}^{-1}$) and pore size distribution, were obtained whilst its nitrogen adsorption-desorption isotherms were measured at -195.8°C . The Barrett-Joyner-Halenda (BJH) method was used for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling theory. This method measures the very fine scale porosity of solid materials at the mesopore (2–50 nm) and macropore (> 50 nm) scale.

2.5 Shell Surface Morphology Analysis

The morphology of the shell particles following exposure to the synthetic stormwater solution in the column experiments was examined for each shell type and the two shell particle size ranges of 63–150 μm and 710–1180 μm using environmental scanning electron microscopy (ESEM) (FEI Quanta 200F model). A small sample (1 mg) of shell particles was recovered from each column after running the heavy metal adsorption experiment. The sample was then rinsed in deionised water and then air-dried. The sub-sample was then sprinkled on to a SEM pin stub to which a double-sided conductive adhesive tape was attached. The sample was then sputter coated with platinum. The samples were examined at either 10 kV or 20 kV using either high vacuum ETD (Everhart Thornley) or low vacuum LFD (low field) detectors.

3 Results

3.1 Adsorption

3.1.1 Shell Particles of Size Range 63–150 μm

Columns of mussel, oyster and scallop shell at a size of 63–150 μm showed an adsorption of both Cu^{2+} and Zn^{2+} from synthetic stormwater. The extent of adsorption varied as the solution passed through the column with copper adsorption gradually increasing and zinc adsorption fluctuating (Fig. 2). Zinc ions were highly adsorbed in comparison to copper ions. For all shell types in the 63–150 μm size range, the eluent concentration of Cu^{2+} ions was greater than Zn^{2+} ions (Fig. 2).

The mean concentrations of Cu^{2+} and Zn^{2+} ions detected in the eluent as the stormwater flowed

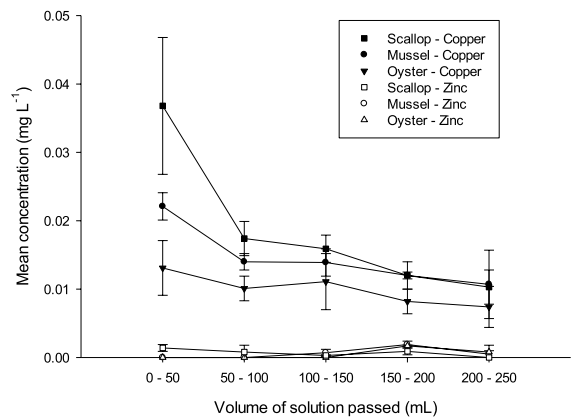


Fig. 2 Mean (\pm S. E.) copper (black) and zinc (white) concentrations detected in eluent after passing increasing volumes of synthetic stormwater through a column of scallop (squares), mussel (circles) or oyster (triangles) shell particles with a 63–150- μm size range. The initial concentrations of copper and zinc in the synthetic stormwater were 0.05 mg L^{-1} and 0.2 mg L^{-1} , respectively

through the mussel shell column with a 63–150- μm particle size range were $0.015 \pm 0.002 \text{ mg L}^{-1}$ and $0.0007 \pm 0.0003 \text{ mg L}^{-1}$, respectively. Therefore, the mussel shell provided 70.9% and 98.8% adsorption of copper and zinc ions, respectively (Table 1).

The mean concentrations of Cu^{2+} and Zn^{2+} ions detected in the eluent as the stormwater flowed through the oyster shell column with a 63–150- μm particle size range were $0.010 \pm 0.001 \text{ mg L}^{-1}$ and $0.0005 \pm 0.0003 \text{ mg L}^{-1}$, respectively. Therefore, the oyster shell provided 80.0% and 99.0% adsorption of copper and zinc ions, respectively (Table 1).

The mean concentrations of Cu^{2+} and Zn^{2+} ions detected in the eluent as the stormwater flowed through the scallop shell column with a 63–150- μm particle size range were $0.018 \pm 0.005 \text{ mg L}^{-1}$ and $0.0007 \pm 0.0002 \text{ mg L}^{-1}$, respectively. Therefore, the scallop shell provided 63.0% and 98.6% adsorption of copper and zinc ions, respectively (Table 1).

3.1.2 Shell Particles of Size Range 710–1180 μm

Columns of mussel, oyster and scallop shell at a size of 710–1180 μm showed an effective adsorption of both Cu^{2+} and Zn^{2+} from synthetic stormwater. The extent of adsorption varied as the solution

Table 1 Mean eluent concentrations (\pm S.E.) and adsorption efficiencies for copper and zinc ions after flowing stormwater through columns of mussel, oyster or scallop shells, with a size

Shell type	Mussel		Oyster		Scallop	
	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺
Mean concentration (mg L ⁻¹)	0.015 (2)	0.0007 (3)	0.010 (1)	0.0005 (3)	0.018 (5)	0.0007 (2)
Adsorption efficiency	70.9%	98.8%	80.0%	99.0%	63.0%	98.6%

range of 63–150 μm . The initial concentrations of copper and zinc in the synthetic stormwater were 0.05 mg L⁻¹ and 0.2 mg L⁻¹, respectively

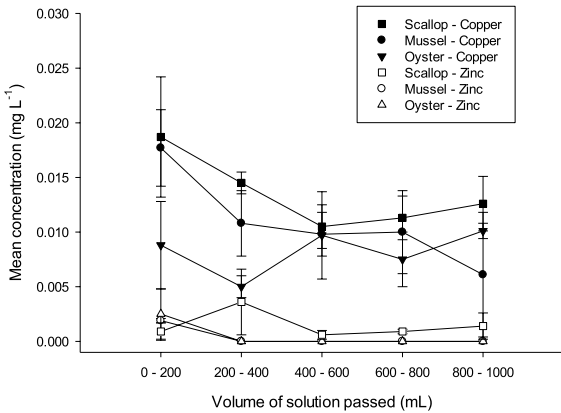


Fig. 3 Mean (\pm S. E.) copper (black) and zinc (white) concentrations detected in eluent after passing increasing volumes of synthetic stormwater through a column of scallop (squares), mussel (circles) or oyster (triangles) shell particles with a 710–1180- μm size range. The initial concentrations of copper and zinc in the synthetic stormwater were 0.05 mg L⁻¹ and 0.2 mg L⁻¹, respectively

passed through the column with copper adsorption gradually increasing and zinc adsorption fluctuating (Fig. 3). Zinc ions were highly adsorbed in comparison to copper ions. For all shell types in the 710–1180- μm size range, the eluent concentration of Cu²⁺ ions was greater than Zn²⁺ ions (Fig. 3).

The mean concentrations of Cu²⁺ and Zn²⁺ ions detected in the eluent as the synthetic stormwater

flowed through the mussel shell column with 710–1180- μm particle size range were 0.011 \pm 0.002 mg L⁻¹ and 0.0004 \pm 0.0004 (detection limit) mg L⁻¹, respectively. Therefore, the mussel shell provided 78.2% and 99.2% adsorption of copper and zinc ions, respectively (Table 2).

The mean concentrations of Cu²⁺ and Zn²⁺ ions detected in the eluent as the synthetic stormwater flowed through the oyster shell column with 710–1180- μm particle size range were 0.008 \pm 0.001 mg L⁻¹ and 0.0005 \pm 0.0005 (detection limit) mg L⁻¹, respectively. Therefore, the oyster shell provided 83.6% and 99.0% adsorption of copper and zinc ions, respectively (Table 2).

The mean concentrations of Cu²⁺ and Zn²⁺ ions detected in the eluent as the synthetic stormwater flowed through the scallop shell column with a 710–1180- μm particle size range were 0.014 \pm 0.001 mg L⁻¹ and 0.0015 \pm 0.0005 mg L⁻¹, respectively. Therefore, the scallop shell provided 73.0% and 97.0% adsorption of copper and zinc ions, respectively (Table 2).

3.1.3 Adsorption by Zeolite (1–2 mm)

Columns of zeolite of particle size range 1–2 mm showed effective adsorption of copper and zinc ions from synthetic stormwater. The extent of adsorption of the metal ions varied as the solution passed

Table 2 Mean eluent concentrations (\pm S.E.) and adsorption efficiencies for copper and zinc ions after flowing synthetic stormwater through columns of mussel, oyster or scallop

Shell type	Mussel		Oyster		Scallop	
	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺
Mean concentration (mg L ⁻¹)	0.011 (2)	0.0004 (4)	0.008 (1)	0.0005 (5)	0.014 (1)	0.0015 (5)
Adsorption efficiency	78.2%	99.2%	83.6%	99.0%	73.0%	97.0%

shells, with a size range of 710–1180 μm . The initial concentrations of copper and zinc in the synthetic stormwater were 0.05 mg L⁻¹ and 0.2 mg L⁻¹, respectively

through the column, with a gradual increase in copper adsorption whilst there was some fluctuation in zinc ion adsorption (Fig. 4).

The mean concentrations of Cu^{2+} and Zn^{2+} ions detected in the eluent as the synthetic stormwater flowed through the zeolite column with a 1–2-mm particle size range were $0.0083 \pm 0.0012 \text{ mg L}^{-1}$ and $0.0048 \pm 0.0007 \text{ mg L}^{-1}$, respectively. Therefore, the zeolite provided 83.4% and 97.6% adsorption of copper and zinc ions, respectively.

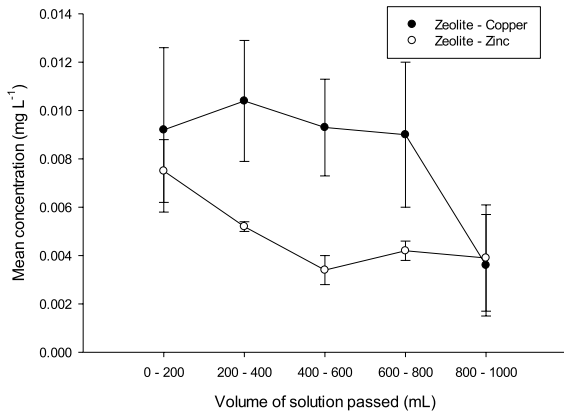


Fig. 4 Mean (\pm S. E.) copper (black) and zinc (white) concentrations detected in eluent after passing increasing volumes of synthetic stormwater through a column of zeolite particles with a 1–2-mm size range. The initial concentrations of copper and zinc in the synthetic stormwater were 0.05 mg L^{-1} and 0.2 mg L^{-1} , respectively

3.2 Surface Area and Pore Volume

For some of the shell particles, there was a decrease in surface area after adsorption of heavy metal ions in the columns (Table 3). Particles of oyster shell of 710–1180 μm had the highest decrease (55.6%) in surface area, followed by mussel shell (17.0%) of particle size 63–150 μm and scallop shell of particle size 710–1180 μm (15.4%). All other shell particles of mussel, oyster and scallop shell tended to show a decrease in surface area, but the results were not significant (Table 3). There was a small but significant decrease in the surface area of zeolite (5.4%).

For some of the shell particles, there was a decrease in pore volume after adsorption of heavy metal ions in the columns (Table 4). Particles of oyster shell of 710–1180 μm had the highest decrease (64.8%) in pore volume, followed by scallop shell (32.8%) and mussel shell (14.5%) of the same shell particle size range. All other shell particles of mussel, oyster and scallop shell tended to show a decrease in pore volume but the results were not significant (Table 4). There was a small but significant decrease in pore volume of zeolite (6.2%).

3.3 Shell Surface Morphology

The ESEM images of the three shell types (63–150 μm) showed formation of a fine layer of secondary crystalline metal carbonate complexes on the surfaces of the shell particles (Fig. 5). This phenomenon was also observed on the larger particle size shells (710–1180 μm) and on the surfaces of the zeolite particles.

Table 3 Estimated surface area for shell particles from three species of bivalve in size ranges of 63–150 μm and 710–1180 μm , and for zeolite before and after exposure to synthetic stormwater (note: * indicates a significant p -value)

Shell/zeolite	BET surface area before adsorption ($\text{m}^2 \text{g}^{-1}$)		BET surface area after adsorption ($\text{m}^2 \text{g}^{-1}$)		Change in surface area (%)	t -test p value
	Mean	SE	Mean	SE		
Mussel (63–150 μm)	1.29	0.01	1.07	0.03	17.0	0.0021*
Oyster (63–150 μm)	4.61	0.02	3.94	0.02	14.6	0.4274
Scallop (63–150 μm)	2.23	0.03	1.95	0.09	12.5	0.0415*
Mussel (710–1180 μm)	0.19	0.02	0.17	0.01	14.0	0.2221
Oyster (710–1180 μm)	1.72	0.05	0.77	0.04	55.6	0.0001*
Scallop (710–1180 μm)	0.46	0.00	0.39	0.01	15.3	0.0060*
Zeolite (1–2 mm)	28.27	0.17	26.73	0.34	5.4	0.0151*

Table 4 Pore volume for shell particles from three species of bivalve in size ranges of 63–150 μm and 710–1180 μm , and for zeolite before and after exposure to synthetic stormwater

Shell/zeolite	BJH pore volume before adsorption ($\text{cm}^3 \text{g}^{-1}$)		BJH pore volume after adsorption ($\text{cm}^3 \text{g}^{-1}$)		Change in pore volume (%)	<i>t</i> -test <i>p</i> value
	Mean	SE	Mean	SE		
Mussel (63–150 μm)	0.0064	0.0001	0.0057	0.0002	10.8	0.0394*
Oyster (63–150 μm)	0.0190	0.0013	0.0163	0.0018	14.4	0.2815
Scallop (63–150 μm)	0.0085	0.0003	0.0080	0.0006	6.1	0.4551
Mussel (710–1180 μm)	0.0009	0.0000	0.0008	0.0000	14.5	0.0499*
Oyster (710–1180 μm)	0.0069	0.0000	0.0024	0.0001	64.8	0.0001*
Scallop (710–1180 μm)	0.0019	0.0000	0.0013	0.0001	32.8	0.0056*
Zeolite (1–2 mm)	0.0546	0.0011	0.0512	0.0012	6.2	0.0033*

4 Discussion

The results of this study confirm that waste shell material can provide similar levels of adsorption of heavy metals from synthetic stormwater to those achieved using zeolite, which is much more commonly used for this purpose. One novelty of this study is that it tested the effect of different crushing methods on shell material to test the effect of crushed shell particle size on the removal of copper and zinc from synthetic stormwater. Both ranges of shell particle size were effective in removing copper and zinc from solution and there was not a significant difference between the removal of these metals using different crushed shell particle size ranges.

Another novelty is that all three New Zealand shellfish species (mussels, oysters and scallops) were effective in removing zinc from solution with 97–100% removal efficiency, which was similar to the removal efficiency of zeolite (97.6%), and an improvement upon the removal efficiency when using whole uncrushed shells (Xu et al., 2021). The removal of copper was most efficiently achieved with crushed oyster shell with a particle size range of 710–1180 μm (83.6%), which was similar to the removal efficiency of zeolite (83.4%). In addition, the adsorption efficiency is not significantly affected by the species of bivalve used. The shells from all three species of bivalve tested in this study adsorbed copper and zinc in the stormwater to similar degrees of efficiency.

The higher adsorption efficiency of Zn^{2+} versus Cu^{2+} ions by shell particles is likely to be primarily due to the higher concentration of Zn^{2+} (0.2 mg L^{-1} , i.e. 4 times higher) in comparison to Cu^{2+} (0.05

mg L^{-1}) ions in the synthetic stormwater. The higher concentration of zinc, as is typically found in urban stormwater, means that Zn^{2+} ions are more likely to interact with the shell surfaces and bind with them. This means that this study with both zinc and copper ions in synthetic stormwater is subject to the competition between these ions for adsorption sites on the crushed shell material.

Previous studies have emphasised that the most prominent mechanism for heavy metal removal from stormwater by shell material is ion exchange with Ca^{2+} , followed by surface complexation and then dissolution-precipitation at the shell surface in high concentration (Prieto et al., 2003; Erdem et al., 2004; Bozbaş & Boz, 2016; Xu et al., 2021). Theoretically, in these experiments at a pH of 6.88, there will be a combination of copper species present; the most abundant will be free ionic Cu^{2+} (30%) followed by copper (II) hydroxide (20%) (Zirino & Yamamoto, 1972). In contrast, zinc undergoes less complexation than copper and the proportion of zinc in the free ionic Zn^{2+} state is higher (51%) (Zirino & Yamamoto, 1972). These factors may encourage Zn^{2+} adsorption in favour of Cu^{2+} . Adsorption of heavy metals on the surface of zeolite occurs via the same ion-exchange mechanism, except zeolite can have sodium, potassium or calcium exchange with a heavy metal ion (Erdem et al., 2004).

There was a decrease in the BET surface area and a decrease in pore volumes as measured by BJH after adsorption and the ESEM images showed a fine “fuzz” of crystal formation on the surface of the shell particles consistent with the adsorbed Zn^{2+} and Cu^{2+} ions filling the surface of the shells

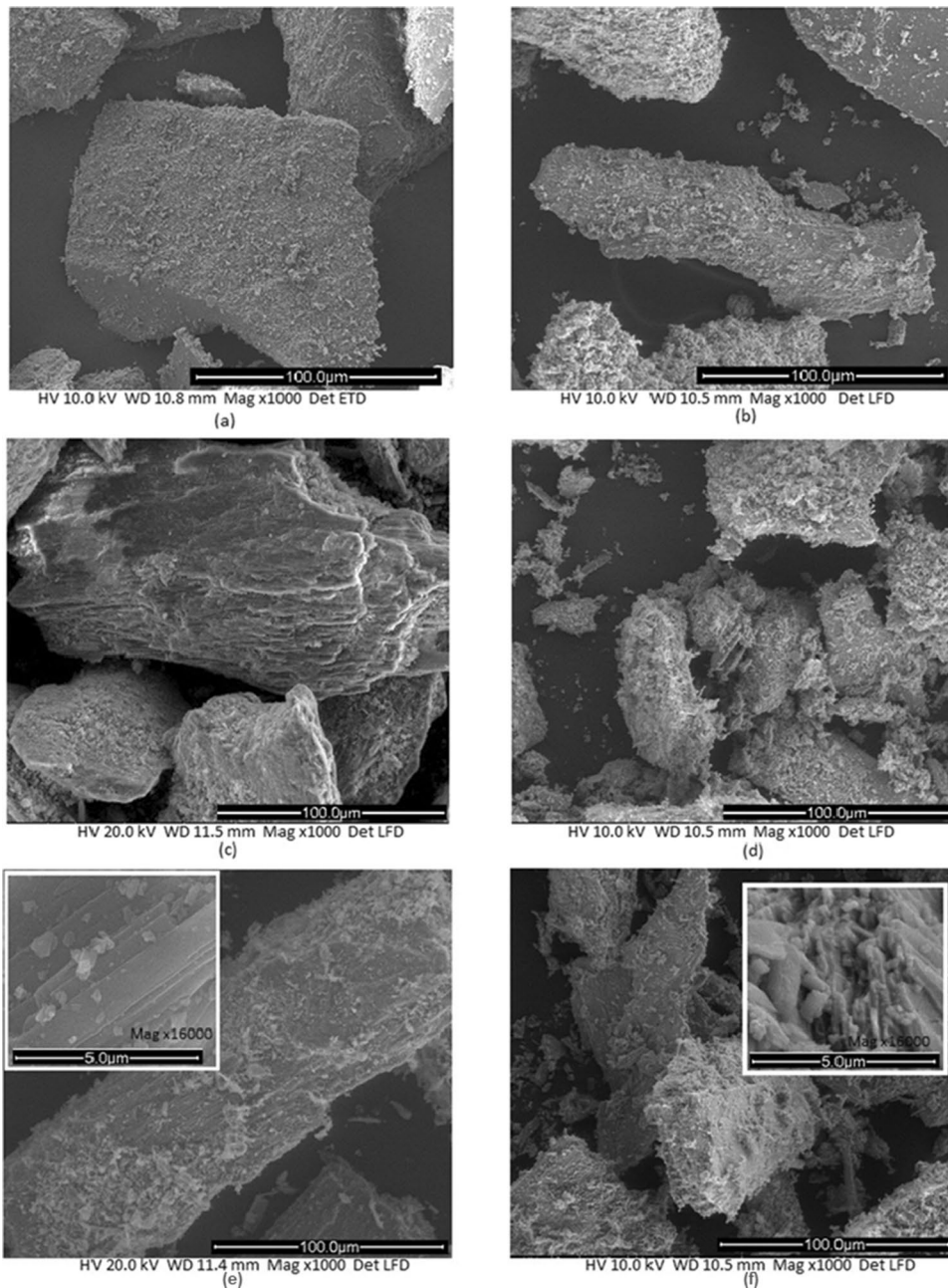


Fig. 5 SEM micrographs of shell particles in the size range of 63–150 μm for mussel, oyster and scallop, before and after adsorption of heavy metal ions. Mussel shell before (**a**) and

after adsorption (**b**) (1000 \times); **c**, **d** oyster shell before and after adsorption (1000 \times); **e**, **f** scallop shell before and after adsorption (1000 \times), respectively

by forming a fine crystalline layer. These fine flake-shaped crystallites on the surfaces of bivalve shell particles are most likely to be copper and zinc carbonate precipitates formed as a result of the metal ion adsorption (Kohler et al., 2007).

To build on these findings, future studies should test what volume of stormwater can be passed through the shell particles before the surfaces of the particles become saturated with heavy metals. In addition to this, the regeneration capacity of the shells should be

investigated. Future work could investigate adsorption trials with stormwater collected after a rain event. Actual stormwater runoff is extremely complex. At any given time, variable properties of stormwater include containing a suite of different metals at varying concentrations depending on location (Moore et al., 2009) and other contaminants including plastics such as rubber from car tyre wearing (Kennedy & Sutherland, 2008), pH (Genç-Fuhrman et al., 2016), sediment content (Blecken et al., 2012), hardness (Bailey et al., 1999) and dilution (Kayhanian et al., 2002). This variability and complexity mean that the treatment of urban stormwater is a significant challenge.

5 Conclusion

The results presented in this study indicate that waste bivalve shell of both particle size ranges (63–150 µm and 710–1180 µm) provided a similar efficiency for removing heavy metal ions from synthetic stormwater in a packed column situation to that of the commonly used zeolite (1–2 mm). In addition, changing the species of bivalve used for the waste shell material did not significantly affect the adsorption efficiency for heavy metal ions. Significant decreases in the BET surface area and BJH pore volume on the surface of shell particles occurred and secondary crystalline lattices of heavy metal carbonates formed on the surfaces of the shell particles following the adsorption of heavy metal ions from solution.

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Data Availability The authors declare that all data analysed during this study are included in the article.

Declarations

Conflict of Interest The authors declare no competing interests.

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