



Review

Improvement of heavy metal removal from urban runoff using modified pervious concrete



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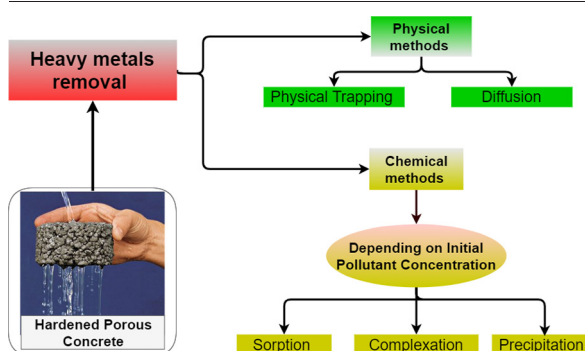
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HIGHLIGHTS

- Open-water storage and extra land acquisition are not required for porous concrete.
- High effluent pH, decalcification and leaching are major drawbacks of porous concrete.
- Adsorbent materials added to the porous concrete enhance its removal efficiencies.
- Reduced graphene oxide addition reduces the leachability of removed heavy metals.
- Addition of pozzolanic materials lower the effluent pH without lowering removal.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 August 2021

Received in revised form 22 December 2021

Accepted 2 January 2022

Available online 5 January 2022

Editor: Ashantha Goonetilleke

Keywords:

Stormwater
Heavy metals
Water pollution
Treatment
Concrete

ABSTRACT

Heavy metals are one of the major chemical pollutant groups in urban runoff. The application of porous concrete is a potential alternative to conventional runoff management systems with the ability to remove heavy metals. Hence, a thorough understanding of the heavy metal removal mechanisms and constraints of conventional porous concrete opens a path for the development of effective modifications. This review critically discusses the major contributors in ordinary porous concrete which supports heavy metal removal. The effects of initial concentration, contact time and competing ions on heavy metal removal using porous concrete are also discussed. Additionally, the effect of decalcification, atmospheric carbonation, acid influent on heavy metal removal is reviewed. The major drawback of porous concrete is the high pH (>8.5) of the effluent water, decalcification of the porous concrete and leaching of adsorbed pollutants. Overall, the addition of adsorbent materials to the porous concrete increases removal efficiencies (7% - 65% increase) without neutralizing the effluent pH. Meanwhile, the addition of Reduced Graphene Oxide is successful in reducing the leachability of the removed heavy metals. The addition of pozzolanic materials can lower the effluent pH while maintaining similar removal efficiencies to unmodified porous concrete. Therefore, developing a novel method of neutralizing the effluent pH must be prioritized in future studies. Additionally, the toxicity that can occur due to the abrasion of modified porous concrete requires study in future research. Further, advanced characterization methods should be used in future studies to understand the mechanisms of removal via the modified porous concrete materials.

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1. Introduction

Increased level of anthropogenic activities such as rapid clearing of vegetation for the construction of infrastructure has caused major alterations in the structure and function of the environment, turning many pervious landscapes into impervious surfaces (Shuster et al., 2005; Mullaney and Lucke, 2014; Chandrappa and Biligiri, 2016b; Gavric et al., 2019). Many pollutants accumulate on these impervious surfaces which include nutrients, heavy metals and hydrocarbons originating from traffic activities, construction activities, industrial, commercial, residential activities and atmospheric deposits during dry periods with no rainfall (Helmreich et al., 2010; Mullaney and Lucke, 2014; Wang et al., 2017a, 2017b). With precipitation, these pollutants get washed off, mix with the runoff and are conveyed to waterways causing severe pollution to urban water sources (Mangani et al., 2005; Wang et al., 2017a, 2017b). As a result, urban runoff is identified as a major source of non-point pollutants that will eventually lead to the deterioration of the water quality of the receiving bodies of water (Reddy et al., 2014; Chandrappa and Biligiri, 2016b; Zuraini et al., 2018; Sidhu et al., 2020).

Non-point source pollution is identified as the primary cause of water quality degradation worldwide (Tasdighi, 2017). Consequently, a large fraction of the world's population does not have access to safe drinking water. Thus, consumption of polluted water is a leading cause of deaths worldwide, equating to approximately 14,000 deaths per day (Kulasooriya, 2014). Furthermore, the toxicity of pollutants carried by urban runoff significantly affects aquatic life (Sandahl et al., 2007; Nason et al., 2011). Therefore, the recent focus on treating urban stormwater to meet water quality objectives for reuse and/or safe discharge to open water environment waters has increased (Mullaney and Lucke, 2014). This had led adaptation of policies to address sustainable stormwater management in many nations.

Conventionally, most of the urban planners and developers have adopted detention and retention basins such as swales, bio-retention basins, settlement ponds and wetlands to improve the stormwater quality (Mullaney and Lucke, 2014; Chandrappa and Biligiri, 2016b). However, water from such basins requires engineered treatment before discharging into natural water bodies, making the stormwater management process uneconomical (Chandrappa and Biligiri, 2016a). A

comprehensive summary of the disadvantages of these conventional stormwater treatment systems is illustrated in Fig. 1. Most treatment options have open water storage which leads to drowning hazards and breeding of pests. When regular flow is absent (i.e., no rain periods) for ponds, anaerobic conditions can occur in the stagnated water leading to malodour (Noor, 2014; Vincent and Kirkwood, 2014). Further, ground water recharge is limited to areas where detention and retention basins are constructed thereby creating an uneven ground water recharge. Additionally, these treatment devices require significant land uptake which is inconvenient within highly urbanized areas (Geiger and Fach, 2005). Thus, treatment systems with little to no water storage, ground water recharge and the absence of a requirement for additional land uptake are beneficial in highly urbanized environments.

Porous concrete in urban runoff management is used as an alternative to conventional stormwater management methods. The absence of open water storage and the absence of the need for extra land acquisition are the major benefits of a porous concrete system. The utilization of porous concrete allows runoff attenuation and can reduce pollutant concentrations while infiltrating the captured water (Luck et al., 2009; Soto-Perez and Hwang, 2016). The pollutants in stormwater are removed by chemical and physical reactions between the porous concrete and the micro-organisms in the pores of the porous concrete (Kim et al., 2017; Chen et al., 2020). The literature contains many independent attempts made to improve the pollutant removal efficiencies of porous concrete (Holmes et al., 2017a; Holmes et al., 2018; Yousefi and Matavos-Aramyan, 2018; Liu et al., 2019; Muthu et al., 2019; Ortega-Villar et al., 2019; Shabalala and Ekolu, 2019; Azad et al., 2020; Cheng et al., 2020).

This is the first review where individual research studies are discussed critically to understand the mechanisms involved in pollutant removal via porous concrete. Since a wide variety of pollutants are found in the urban environment, the review is focused on the removal of strategic pollutants found in stormwater. Therefore, the objectives of this review article are to (i) identify the strategic stormwater pollutants in an urban runoff (ii) evaluate the ability of porous concrete in the removal of the selected strategic pollutants. A critical discussion of pollutant removal capability of individual components of the porous concrete

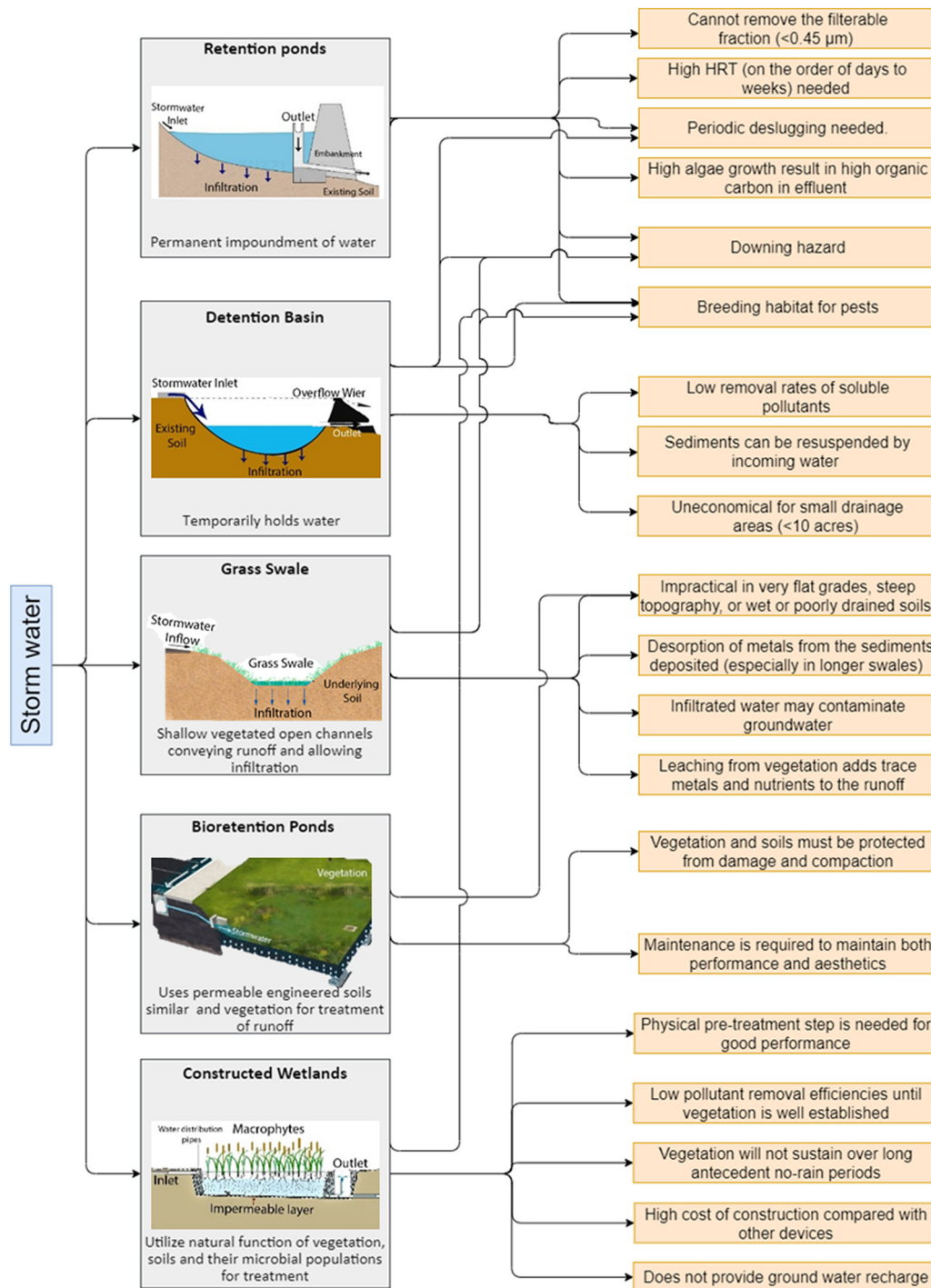


Fig. 1. Disadvantages of conventional urban runoff treating devices (United States Environmental Protection Agency (US EPA), 1999; Drake and Guo, 2008; Massachusetts Department of Environmental Protection (MaasDEP), 2008; Gaborit et al., 2013; Tennessee Stormwater Manual (TSW), 2014; Leber, 2015; Wiest et al., 2018; Gavric et al., 2019; Clary et al., 2020; Jain et al., 2020; Loh and Mah, 2020; Ekka et al., 2021; Kalev et al., 2021; Nayeb Yazdi et al., 2021; Sharma et al., 2021).

matrix is followed by identification of the dominant removal mechanisms, the time taken for removal of pollutants, the long-term performance, and the dependence of removal efficiency on competing ions. This enables the identification of the constraints of porous concrete in the treatment of stormwater; (iii) evaluation of the effectiveness of the currently reported modifications of porous concrete. Thereby enabling the identifications of waypoints for developing further modifications to the function of porous concrete. Concluding the review, this paper highlights priority areas for the modifications required for the enhancement of stormwater treatability utilizing porous concrete.

2. Common stormwater pollutants

The most common pollutants found in an urban environment are nutrients, sediments and heavy metals (Helmreich et al., 2010; Mullaney and Lucke, 2014). Primary sources of heavy metals include tyre wear, motor oils, grease, fuel, metal plantings, asphalt paving, fertilizers and exposure of buildings to rain (Helmreich et al., 2010; Mullaney and Lucke, 2014; Clary et al., 2020; Qureshi et al., 2021). Sediments mainly occur due to construction activities, maintenance activities, wear of pavements, vehicles, and erosion (Mullaney and Lucke, 2014). Nutrients such as nitrogen and

phosphorous prevail primarily due to the use of fertilizer and the decaying of organic matter (Mullaney and Lucke, 2014). However, the types of pollutants and their concentrations depend on land use, population density, geology, topography, stormwater duration and intensity within the catchment (Nason et al., 2011; Mullaney and Lucke, 2014). Hence, a significant variation is observed among the reported concentrations of pollutants in urban runoff.

Considering the toxicity, non-degradability and bioaccumulation heavy metals pollution are considered one of the most critical pollutants found in stormwater runoff (Geiger and Fach, 2005; Akpor, 2014; Ma et al., 2016; Saleh et al., 2017; Sidhu et al., 2020). "Heavy metals" is a general collective term, which applies to the group of metals and metalloids with an atomic density greater than 4000 kg/m³, or 5 times more than that of water (Duruibe et al., 2007). Even though some heavy metals act as essential micronutrients for living organisms, they can cause severe poisoning (Duruibe et al., 2007; Saleh, 2015; Alhashimi and Aktas, 2017). Further, in animals and plants exposed to heavy metal contaminated water and soils, the metals accumulate in their tissues (Duruibe et al., 2007; Tchounwou et al., 2012). When heavy metals are ingested, they are acidified in the acid medium of the stomach and oxidized into their oxidative states. In an ionic solution, the most stable oxidation state of a heavy metal (e.g., Pb⁺² for Pb) is the most toxic form of the respective heavy metal. These ions react with the body's biomolecules such as proteins and enzymes to form highly stable bio-toxic compounds which are difficult to dissociate (Duruibe et al., 2007; Hashim et al., 2011; Engwa et al., 2018). Heavy metals like Iron, Copper and Chromium in oxidations states Fe³⁺, Cu²⁺ and Cr⁴⁺ have the potential to generate free radicals (OH radical) after a reduction reaction followed by a re-oxidation reaction with H₂O₂ (Engwa et al., 2018). The reaction with H₂O₂ is commonly referred to as Fenton Reaction where free OH radicals are produced. These free radicals lead to oxidative stress and cause other cellular damage as well (Engwa et al., 2018). Additionally, Heavy metals like Arsenic, Lead, Mercury and Nickel have carcinogenic effects. Carcinogenic effects are caused when signalling proteins or regulatory proteins that take part in apoptosis, cell cycle directive, DNA repair, DNA methylation, cell growth and differentiation are targeted by the heavy metals (Tchounwou et al., 2012; Engwa et al., 2018). Additionally, heavy metals can cause serious illnesses such as nervous system damage and kidney failures. Furthermore, these pollutants can be

deadly at high concentrations (Abdullah et al., 2019; Al-Saydeh et al., 2017; Gunathilaka et al., 2015).

A high concentration of heavy metals in urban stormwater is identified as a common issue worldwide and can exceed the threshold values recommended in guidelines for recreational and portable uses (Ma et al., 2016; Clary et al., 2020). The direct risk imposed on humans by single heavy metals in urban runoff is generally not significant due to low concentrations. However, multiple heavy metals in urban runoff can create a toxic effect on human health (Ma et al., 2016). Cu, Pb, Zn, Cr, Cd, Fe, Mn, Al, Hg and Ni have been detected in the urban runoff by past studies (Kayhanian et al., 2008; Helmreich et al., 2010; Mullaney and Lucke, 2014; Reddy et al., 2014; Huber et al., 2016; Ma et al., 2016; Neto et al., 2016; Sounthararajah et al., 2017; Wang et al., 2017a, 2017b; Sakson et al., 2018; Kayhanian et al., 2019; Chen et al., 2020; Sidhu et al., 2020). The heavy metals Cu, Pb and Zn are found in all reported cases making them the most common heavy metals found in urban runoff. Further, Kayhanian et al. (2008) noted that Cu and Zn are the primary causes of toxicity of urban runoff. Additionally, Sakson et al. (2018), as well as Ma et al. (2016), found that the toxicity of Pb present in urban runoff is more toxic than Cu and Zn. Through the summary of sources presented in Fig. 2, it can be observed that sources of Cu, Pb and Zn are mostly traffic-related. A similar result was observed by Shajib et al. (2019) who noted that Cu, Pb and Zn principally originate from vehicular activities. The quality of stormwater degrades due to the strong mobility and toxicity of Cu, Pb and Zn (Nabizadeh et al., 2005; Helmreich et al., 2010; Mullaney and Lucke, 2014; Ma et al., 2016; Chen et al., 2020). Thus, in this study, the behaviour of porous concrete in the removal of Cu, Pb and Zn is discussed in depth. The removability of the other ions present in urban runoff is also reviewed.

The concentration of heavy metals present in stormwater varies widely due to many factors such as weather, traffic characteristics, land use patterns, antecedent dry periods and climate. Hence, a wide range of Cu (1.42 × 10⁻⁶–3.07 × 10⁻¹ mM), Pb (4.83 × 10⁻⁸–8.25 × 10⁻³ mM), and Zn (9.17 × 10⁻⁷–4.79 × 10⁻¹ mM) have been reported in the literature (Kayhanian et al., 2003; Water Research Foundation (WRF) et al., 2015; Sakson et al., 2018). Thus, in designing a treatment scheme, site-specific data acquisition is very important. Fig. 3 contains the speciation of Zn and Pb, modelled with Visual MINTEQ considering a fixed ionic

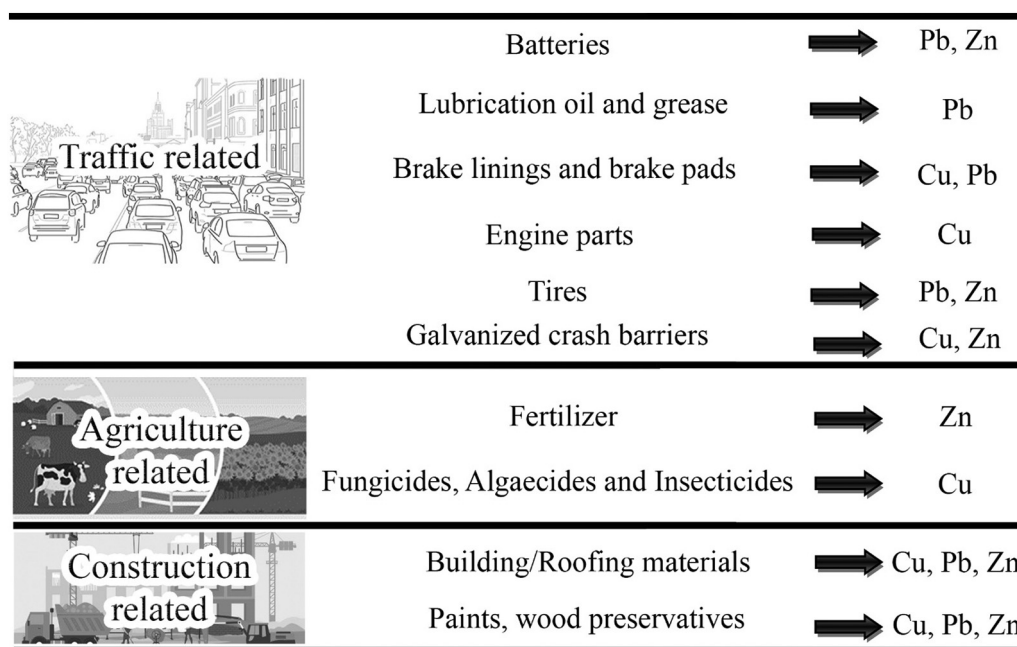


Fig. 2. Major sources of Cu, Pb and Zn in the urban environment. (Gobel et al., 2007; Helmreich et al., 2010; Nason et al., 2011; Gong et al., 2012; Ahmad, 2018; Clary et al., 2020).

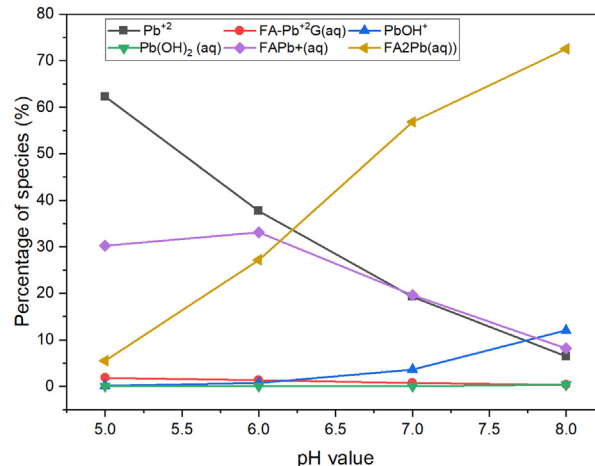
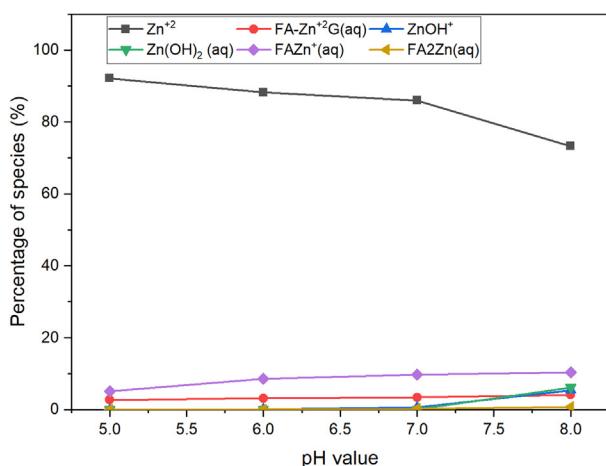


Fig. 3. Speciation of Zn and Pb in typical stormwater conditions. FAPb + /FAZn + is the monodentate binding of Pb/Zn and fulvic acid and FA2Pb + /FA2Zn + is the bidentate binding of Pb/Zn and fulvic acid. (Ionic strength = 10 mM, dissolved organic matter content = 5 mg/L, Concentration of Pb and Zn are 2.41×10^{-4} mM, 7.65×10^{-2} mM respectively).

strength of 10 mM and a dissolved organic matter content of 5 mg/L, which is typically found in stormwater. Application of Visual MINTEQ simulations to heavy metal speciation on typical stormwater conditions identifies the presence of dissolved forms of heavy metals. In the model, the dissolved organic matter is assumed to be contributed solely by Fulvic Acid (FA). Heavy metals forms complexes with the dissolved organic matter in the stormwater. This complexation of heavy metals with organic matter contributes to their reduced bio availability (Smith et al., 2015). However, the proportion of complexed heavy metals reduces considerably when the pH of the solution is reduced.

In addition to being bound to organic matter, heavy metals in stormwater consist of both dissolved and particulate phases. Kayhanian et al. (2003) and Water Research Foundation (WRF) et al., (2015) observed 49% and 58% medians for dissolved Cu concentrations, respectively. The use of de-icer on roadways causes the ionic strength of the water to increase. The increase in ionic strength increases the dissolution of heavy metals which increases the dissolved heavy metals content in stormwater (Behbahani et al., 2021). This is due to the weakly bound metals in the particulates being desorbed and replaced by major cations such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} in high salinity water. Nason et al. (2011) state that the dissolved fraction of Cu can approach 100% during snowmelt. Further, the fraction of metal elements (mainly Zn and Cu) in the dissolved phase is significantly higher during rainfall events when the rainfall pH is low (pH 3.8) (Ong et al., 2016). Significant desorption of Zn from the particulates in urban runoff was observed, especially at pH 4, compared to other metals (Harada and Komuro, 2010; Clary et al., 2020). The leaching of the bound heavy metals at an acidic pH can account for such observations (Smith et al., 2015). Thus, if the acidity of the runoff increases due to external factors such as acid rain, the dissolved fraction of heavy metals could be increased.

The dissolved fraction of the heavy metal is a significant concern to aquatic creatures. Accumulated heavy metals in aquatic creatures could ultimately enter humans via the food chain (Clary et al., 2020). Therefore, various regulations on the maximum concentration of heavy metals allowed in the water supporting aquatic life are highlighted. The permissible limits stressed by the USEPA for acute exposure to Cu, Pb and Zn in freshwater supporting aquatic life are 2.05×10^{-4} mM, 3.14×10^{-4} mM and 1.83×10^{-3} mM respectively (United States Environmental Protection Agency (US EPA), 2014). In chronic exposure, the maximum permissible Pb concentration is reduced to 1.21×10^{-5} mM (United States Environmental Protection Agency (US EPA), 2014). As the permissible limits lie well below the highest concentration of Cu, Pb and Zn present in stormwater, the need for treatment is clear. If they were directly discharged into the aquatic environment or infiltrated into the groundwater table, they

pose a severe threat to the ecological environment and human health (Chen et al., 2020).

3. The ability of porous concrete to treat heavy metals (copper, lead and zinc)

Porous concrete is a Best Management Practice (BMP) used for the management of stormwater. The distinct feature of porous concrete is the limitation of fine aggregate content in the mix design (Holmes et al., 2017a; Vadas et al., 2017). Thus, permeable concrete hardens into a highly porous material with a high degree of interconnected and tortuous voids (>10% voids by volume) (Chandruppa and Biligiri, 2016a; Holmes et al., 2017a; Vadas et al., 2017). Furthermore, the void formation is supported using narrowly graded coarse aggregates which hinders the dense packing of the mix (Eisenberg et al., 2015). Porous concrete can be produced using a wide variety of aggregate sizes and shapes, while 4.75 to 9.5 mm coarse aggregate can be employed to produce the desired surface texture, with 5.75 mm the most utilized size (Eisenberg et al., 2015). Typically, the volume of aggregates in porous concrete is about 50–65% of total volume compared to 60–75% in conventional concrete (Chandruppa and Biligiri, 2016b). The focus of the design of porous concrete is to create a mix that maintains permeability and strength with sufficient paste viscosity to allow the mixture to be workable without paste drain. Therefore, to achieve the correct paste viscosity, a lower water-to-cement ratio (0.27 to 0.40) than conventional concrete is used (Chandruppa and Biligiri, 2016b; Eisenberg et al., 2015).

The permeability of porous concrete is identified as a major concern when used in water management (Zhong and Wille, 2016). The permeability depends upon the aggregate size, level of compaction, gradation and cement content. In newly installed porous concrete permeability is between 500 and 7600 cm/h, which is equivalent to 0.1–2 cm/s (Chandruppa and Biligiri, 2016b; Eisenberg et al., 2015). The presence of interconnected pores is the main driver of the higher permeability observed in porous concrete. This interconnected pore skeleton, which aids in water transportation, is also referred to as effective porosity (Chandruppa and Biligiri, 2016b). Generally, the porosity of a typical porous concrete varies in the range of 15–25% with a minimum of 15% as prescribed by the National Ready Mix Concrete Association (NRMCA) (Chandruppa and Biligiri, 2016b; Eisenberg et al., 2015). However, the presence of pores inside the mix negatively affects the strength of the concrete. Typically, the compressive strengths of conventional porous concrete with porosities between 15% and 30% range from 7 to 25 MPa (Zhong and Wille, 2016). Thus, the use of porous concrete is limited to applications requiring lower strength requirements.

Many studies have identified the potential of porous concrete in the removal of heavy metals (Muthu et al., 2018; Muthu et al., 2019; Shabalala and Ekolu, 2019; Azad et al., 2020). The mechanisms of removing metals within the porous concrete are complex due to the presence of many factors such as size, distribution and tortuosity of voids (Holmes et al., 2017a). Understanding the major mechanisms in which metals are removed is essential when exploring methods of modifying porous concrete. The mechanisms through which the heavy metals are removed by porous concrete can be broadly categorized into physical (water trapping and diffusion) and chemical processes (sorption, complexation and precipitation) (Haselbach et al., 2014; Holmes et al., 2017a; Muthu et al., 2018). Additionally, Chandrappa and Biligiri (2016b) noted that biological purification could occur via microbes residing in the pores of pervious concrete. The individual contribution of constituents and the variability of pollutant removal efficiency due to characteristics of the porous concrete and the characteristics of the pollutants are discussed in the following section.

3.1. Pollutant removal capability of cement paste and aggregates

Both fundamental components of permeable concrete, cement paste and aggregate, have the individual capacity to remove contaminants from the solution (Holmes et al., 2017a, 2017b). Chen et al. (2020) noted that the water purification capacity of the porous concrete is significantly influenced by its paste adsorption capacity. The highly alkaline conditions (pH > 12) formed due to cement hydration causes metals to precipitate or heavy metal ions to sorb with cement hydration products like calcium-silica-hydrate (C-S-H) gel (Johnson et al., 2000; Chen et al., 2009). Several researchers have shown evidence of the above phenomena where physical fixation and sorption were identified as the main mechanisms of removal (Johnson et al., 2000; Fan et al., 2018). The ionic strength of the solution also plays an important role in the adsorption of pollutants where it may affect the adsorbents surface potential or act as competing ions (Ma et al., 2021). In hydrated cement paste, ionic strength of approximately 0.23–0.17 mol/L was observed by Cherif et al. (2021) due to the presence of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and OH^- ions. Different ions behave in different ways. For example, Ma et al. (2021) observed that Pb adsorption by thermally modified waste concrete decreased more than 45% when the initial ionic strength of the solution was increased from 0.05 mol/L to 2 mol/L using $\text{Ca}(\text{NO}_3)_2$. However, in the same study when ionic strength was increased by the addition of NaNO_3 Pb removal increased by approximately 10%. However, no studies focused on the effect of ionic strength on the removal of heavy metals utilizing porous concrete were found in the available literature.

Cement hydration predominantly produces calcium-silicate hydrate (C-S-H) and calcium hydroxide (CH), also known as portlandite. The C-S-H is observed to have significant cation exchange capacity (Fan et al., 2018). The heavy metal ions have a high affinity to the C-S-H compared with alkali metal ions such as Ca^{2+} , Al^{3+} , and Si^{4+} in the solidified cement matrix.

Therefore, cation exchange occurs between C-S-H and heavy metal ions easily when compared to other available cations (Fan et al., 2018). The Ca^{2+} ions in the cement matrix migrate to participate in the co-precipitation of metal species on the surface of the concrete particles (Johnson et al., 2000). By observing the elemental maps of the concrete surface after adsorption, Johnson et al. (2000) noted that isomorphous substitution of Ca^{2+} (ionic radii = 1.0 Å) by Pb^{2+} (ionic radii = 1.17 Å) can occur. This phenomenon is graphically illustrated in Fig. 4. As Johnson et al. (2000) used synthetic influent (by dissolving $\text{Pb}(\text{NO}_3)_2$ only) with an initial pH of 3.0, free Pb^{2+} ions will be present in the influent thus enabling isomorphous substitution to occur. Furthermore, Holmes et al. (2018) and Harada and Komuro (2010) observed that most surface Ca was displaced by Zn. Ettringite, also known as calcium sulfoaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$) is another mineral found in Portland cement paste. The surface of Ettringite is electronegative and therefore can attract metal ions onto the surface (Wang et al., 2019). Harada and Komuro (2010) identified that ettringite can remove Pb as well as Zn. Monosulfate aluminate hydrate is another compound found in hydrated cement paste which has a composition similar to ettringite and a fibrous morphology (Hampson and Bailey, 1983). Hence, monosulfate aluminate hydrate can also have the potential to remove heavy metals similar to ettringite but, no studies have been found in the available literature to substantiate this hypothesis. However, as the composition of hydrated cement principally contains C-S-H gel, calcium hydroxide, and ettringite the contribution to heavy metal removal from minor phases like monosulfate aluminate hydrate, ferric aluminium hydroxides and garnets are expected to be less.

Cement binder in porous concrete provides Ca and alkalinity as leaching products and has a high surface area (Sansalone et al., 2008; Haselbach et al., 2014). Therefore, as water infiltrates through the porous concrete structure, complexation and precipitation of dissolved metals in the solution can occur (Haselbach et al., 2014; Holmes et al., 2017b). The effect of cement content on the removal of Cu and Ni using porous concrete was studied by Yousefi and Matavos-Aramyan (2018) applying the factorial design method. The cement content was found to negatively affect the removal efficiency of Cu and Ni. However, only 8 levels of tests were conducted to evaluate the effect of the 7 factors in the study of Yousefi and Matavos-Aramyan (2018). This reduction of levels hinders the ability to distinguish the effect of individual factors and the combined effect of factors. Therefore, this lowering of the removal efficiency cannot be correlated only to the change of the cement content. However, a similar trend can be observed for Cu removal, as shown in Fig. 5, which summarises the removal efficiencies observed by past studies using different types of Portland cement porous concrete. Nevertheless, for Pb and Zn, such a trend cannot be observed because of differences in other contributing factors such as initial pH, initial concentration of pollutants and temperature. The use of additional cement mortar content has shown a higher Pb elimination rate of

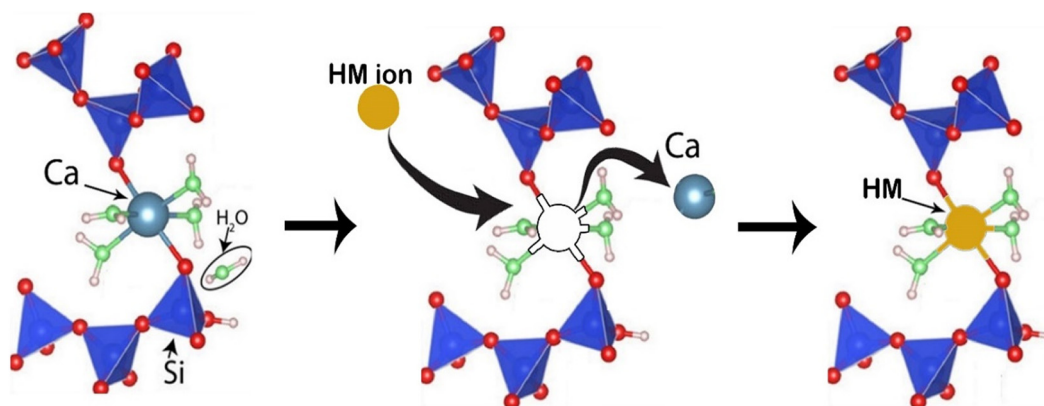


Fig. 4. Interaction of Heavy Metal (HM) ions with C-S-H gel, The isomorphous substitution of Ca^{2+} by HM ion (Johnson et al., 2000).

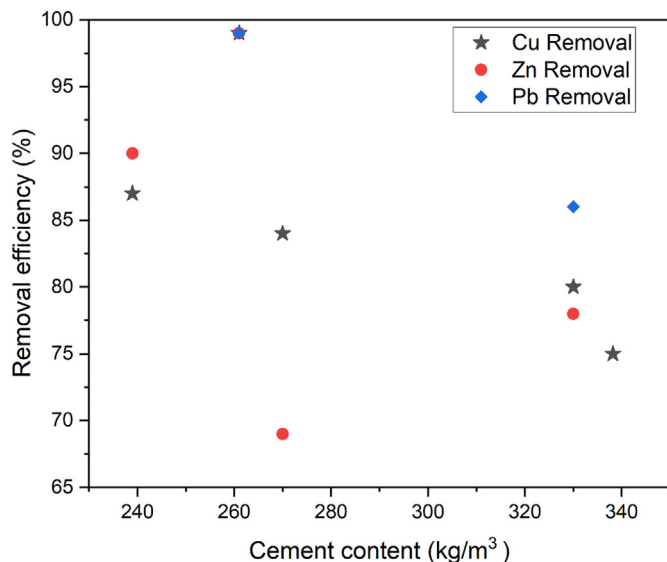


Fig. 5. Removal of heavy metals with different cement contents. Cement types used are Type II, Ordinary Portland Cement, Type I/II, CEM I, Type V and Aggregate types are ASHTO No. 8, No. 8 Basalt Aggregates, Limestone, Granite and Crushed gravel. (Calkins et al., 2010; Haselbach et al., 2014; Holmes et al., 2017; Shabalala and Ekolu, 2019; Azad et al., 2020).

73.1% (Ortega-Villar et al., 2019). This is slightly above the removal rate observed by Holmes et al. (2017a, 2017b) which was 62% without any modifications to the cast porous concrete. However, the differences in the design void content and the variation of aggregate/cement ratios could have impacted the variation in the results. Therefore, there is a need to compare the effect of cement content in heavy metal removal using porous concrete via further studies, especially for the removal of Zn and Pb.

3.2. Pollutant removal capability of cement paste and aggregates

Aggregates containing high quantities of lime provide high removal capacities when used on their own as an adsorbent (Geiger and Fach, 2005). It was stated that the heavy metals had primarily precipitated due to the increase of pH. Limestone aggregate (CaO and CaCO₃ content of approximately 51.88% and 92.60%, respectively) showed removal efficiencies over 99% for Pb and over 70% for Zn removal compared to gravel (CaO and CaCO₃ content of approximately 0.75% and 56.39%, respectively) achieving approximately 90% and 35% of Pb and Zn removal, respectively (Holmes et al., 2017b). It was also found that the heavy metal could penetrate a limestone aggregate. The diffusion of Pb and Zn into the limestone aggregate core was observed, with the Pb being the primary diffuse layer, followed by Zn. This could be the reason for lower Zn removal efficiencies observed when compared with Pb removal efficiencies.

In porous concrete, Holmes et al. (2017a, 2017b) showed that the type of aggregate (inert glass beads, limestone or pea gravel) only had a slight effect (4–5% change) on the removal capacities of concrete. As the cement paste alone can create high pH values (>12) (Johnson et al., 2000; Chen et al., 2009), the ability of the aggregate to further increase pH is not significant in the porous concrete despite having removal capacity itself when used independently as an adsorbent. In addition, the cement paste creates a coating over the aggregate hindering direct contact with the solution. The size of the aggregates can also result in changes in the removal efficiency. As the specific surface area increases, the removal efficiencies increase, especially with fine aggregate (<75 μm in size). However, the metals adsorbed on fine particles could be readily remobilized by pH changes in the influent water (Holmes et al., 2017b). Also, the mixing of concrete could result in these fines being incorporated into the concrete matrix, resulting in the loss of functionality (Holmes et al., 2017b).

Aggregates capable of creating thick Interfacial Transition Zones (ITZ) have shown a higher removal rate than their counterparts (Holmes et al., 2017b). At the ITZ, the porosity is greater than the bulk cement pastes due to the precipitation and deposition of larger-sized portlandite crystals and the presence of relatively large pores (Nili and Ehsani, 2015). Thus, it creates an area with a high surface area, high calcium content and high capillary absorption, which favours higher removal rates. This phenomenon is more pronounced when the initial concentration of the metals is low (0.01 mM) (Holmes et al., 2017b). Limestone aggregate is capable of bonding well with the cement and reduces the thickness of the ITZ (Holmes et al., 2017b). Hence, lower removal efficiencies (58–64%) of porous concrete with limestone aggregates than that of gravels (98%) in Cd and Zn removal were observed at low (0.01 mM) initial metal concentrations by Holmes et al. (2017b). Due to the high porosity and weakness of ITZ compared to the bulk matrix, it governs the mechanical properties and durability of the concrete (Nili and Ehsani, 2015; He et al., 2019). Therefore, using porous concrete with a larger ITZ is more suitable when the strength of the porous concrete is of minor concern.

3.3. Effect of initial pollutant concentration on pollutant removal

A difference in concentration of the pollutant in the solution is known to affect removal ability. However, porous concrete filters are capable of fixing Pb, Cu and Zn regardless of the initial ionic concentration (Muthu et al., 2019). Moreover, there is a change in the dominant mechanism of removal depending on the initial concentration of the pollutant. Holmes et al. (2017b) found that precipitates formed in freely dispersed flocs at higher initial concentrations (1.0 mM) of heavy metals are not to be seen at lower concentrations (~0.01 mM). This phenomenon was also observed in the study of Holmes et al. (2017a) where precipitation had resulted in poorly formed crystal mineralogy at higher initial concentrations (~1.0 mM). The interstitial water within the porous concrete provides a significant source of alkalinity and self-buffering capacity causing precipitation in the pore space (Holmes et al., 2017b). As the pH of the influent is raised by alkali sources like Na₂O and K₂O, the solubility of the heavy metals decreases and precipitates are formed. Interestingly, Holmes et al. (2017a) observed that the accumulated precipitates formed in the dead-end pore space formed a diffuse front into the surrounding cement paste. However, the renewal of pollutant removal capacity due to the diffusion of surface accumulated heavy metals is not reported in the literature. At lower initial heavy metal concentrations (~0.01 mM) the fundamental removal mechanism was found to be adsorption where porous concrete made with limestone aggregates was used, Holmes et al. (2017b).

For example, if the pH of freshwater is highly alkaline (pH > 9.6), it will result in damage to outer surfaces such as eyes and gills and even cause the death of the fish. Conversely, an increment of sorption sites is beneficial at lower concentrations of heavy metals (typically found in stormwater). Additionally, if porous concrete is used in places with high abrasive loads, the additives used can enter the environment due to the lower abrasion resistance of porous concrete (Xie et al., 2019). Hence, in the design of modified porous concrete, the possibility of additional environmental pollution due to the release of harmful substances to the environment needs to be considered.

3.4. Effect of contact time on removal efficiency

The contact time is a measure of how long the water is in contact with the surface of porous concrete. In the treatment of stormwater runoff achieving high removal efficiencies in a shorter time is desirable since it reduces the need for the detention of runoff. The efficiency of pollutant removal by porous concrete is affected by the contact time and surface area of the paste in the porous concrete matrix (Chen et al., 2020). The surface area and contact time depend on the volumetric structural parameters of the bulk porosity of the aggregate and the paste to the aggregate ratio in the porous concrete matrix (Chen et al., 2020). Fig. 6 shows a collection of removal efficiencies observed at different equilibrium times in the

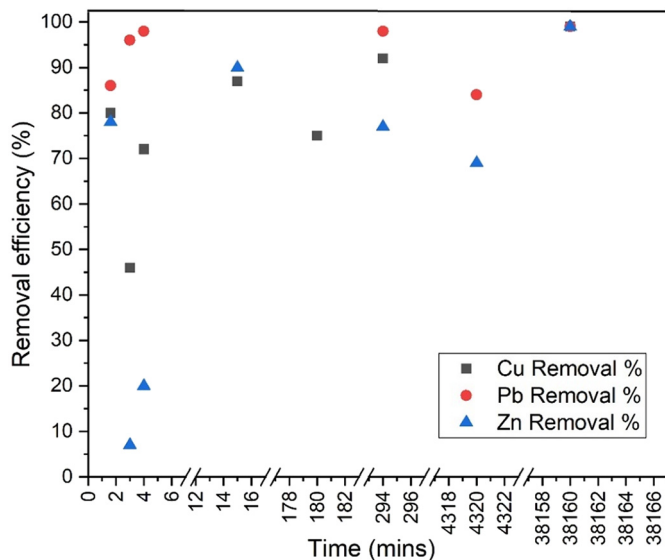


Fig. 6. Variation of removal efficiencies of Cu, Pb and Zn with contact time for porous concrete made with different Portland cement types. Cement types used are Type II, Ordinary Portland Cement, Type I/II, 53 Grade Portland cement, CEM I, Type V and Aggregate types are ASHTO No. 8, No. 8 Basalt Aggregates, Limestone, Granite and Crushed gravel (Calkins et al., 2010; Haselbach et al., 2014; Holmes et al., 2017a; Muthu et al., 2019; Shabalala and Ekolu, 2019; Azad et al., 2020).

literature. It is clear from Fig. 6 that, despite the changes in other operating factors throughout the studies, the maximum removal efficiency is reached in less than 18 min. This trend can be observed for all three heavy metals. All three heavy metals show removal efficiencies of over 75% over the total time range from 1 min to 26 days (38,160 min). Although Pb removal value over 85% is observed irrespective of the contact time, Cu and Zn removal vary without a clear trend. The lowering of the removal efficiencies observed after 18 min can be due to atmospheric carbonation changing the pH of the water, the wash of heavy metal precipitates, changes in the characteristics of influent water qualities including ionic strength, initial pH and the presence of other cations and anions. Considering a typical porous concrete pavement that has a thickness of 200 mm and a typical permeability of 2 mm/s, the contact time for water passing is less than 2 min (lowest typical permeability 1.67 min). From the reported studies, only Azad et al. (2020) has reported removal efficiencies of 80%, 86% and 78% for Cu, Pb and Zn removal for a contact time of 1.6 min. Hence, the possibility of achieving desirable removal of the heavy metal pollutants within a short period of contact time (ideally less than 2 min) needs to be evaluated. Also, the possibility of using porous concrete with lower permeability values, capable of providing higher contact times (>2 min), needs to be evaluated. If such an approach is adopted, the design must consider ways of providing resistance to clogging of the porous concrete.

3.5. Long term performance

The ability of porous concrete to retain its heavy metal removal functionality over the long term depends upon the total adsorption capacity and the ability of porous concrete to renew complexation sites. Generally, the maximum adsorption capacity is used to predict the useful life of the porous concrete in heavy metal removal (Harada and Komuro, 2010). Harada and Komuro (2010) estimated expected service life of 41 years for a porous concrete cylinder of 19.6 m³ for the removal of Zn. However, the influent pollutant concentration was assumed to be 4.59×10^{-4} mM. As Zn concentrations of much higher order are observed in the literature (Kayhanian et al., 2008; Huber et al., 2016; Sakson et al., 2018), the removal capacity will be affected due to other ions in the runoff. Therefore, this estimate may not be valid for locations with high Zn contents and the

presence of other heavy metals. The partial renewal of complexation sites could occur from the diffusion of metal complexes formed in the interior of the concrete matrix into internal pores before subsequent storm events (Haselbach et al., 2014). This was not visible in the results obtained by Haselbach et al. (2014) where the removal efficiency varied without a clear trend between the simulated events. However, a decrease in average removal efficiencies was observed for Cu (87% to 81%) and Zn (90% to 85%) when accelerated loadings of Cu and Zn were experienced by the porous concrete specimens (Haselbach et al., 2014). Over the long term (266 days of testing), no significant lowering of removal efficiency was observed by Holmes et al. (2018), which is contrary to the observation of Vadas et al. (2017), where accelerated loading resulted in a reduction of removal efficiencies in porous concrete specimens subjected to synthetic stormwater. Vadas et al. (2017) simulated 1 year of pollutant load by accelerated loading of pollutants (spiked concentrations of pollutants passed in a short time) whereas Holmes et al. (2018) maintained the same pollutant concentration for the entire period. Holmes et al. (2018) observed the rapid formation of precipitates that self-nucleate and form networks of sorption sites, which may not happen when accelerated loading of porous concrete occurs. Further, accelerated loading can result in excessive precipitation of pollutants leading to the blocking of available active sites. Additionally, the synthetic stormwater constituents vary in both studies, Vadas et al. (2017) included Cu, NO₃⁻, NH₄⁺, PO₄²⁻ and CaCl₂ in addition to constituents employed in Holmes et al. (2018). The presence of additional ions can introduce a competing ion effect which may result in the lowering of the removal capacity of the heavy metals, resulting in conflicting observations. Hence, there is a need to study whether the porous concrete can renew sorption capacity due to the diffusion of adsorbed pollutants into the cement matrix.

3.6. Effect of competing ions and water head on pollutant removal

The sorption mechanism is affected by the prevalence of other ions in the solution. This is due to the competing effect of the ions available in the solution to attach to the surface of an adsorbent. As Cu, Pb and Zn removal occur due to surface complexation and solid formation with hydroxides (OH⁻) and carbonates which are bound to calcium in the concrete (Haselbach et al., 2014), these ions could compete, affecting the removal efficiency when they are present together. The stability constants for the formation of solid hydroxides and carbonates of Cu are 19.3 and 9.6, respectively and for Zn are 16 and 10. Further, Stumm and Morgan (1995) reported that strong complex formation between the metal ions and surface hydrous oxides follows the order Zn > Cu > Pb. Therefore, higher Zn removal is expected compared to Cu removal when the ions are coexistent in the infiltrated water stream. This was observed by Muthu et al. (2019) where Zn fixated to a greater degree in the presence of other two metals. Hence, Zn removal is least affected by the presence of Cu and Pb. However, the lower removal efficiencies of Zn observed in Fig. 6 especially in contact times less than 5 min hinders this advantage. Therefore, in designing porous concrete treatment systems focus should be given to improving Zn removal despite its removal being least affected by the presence of other heavy metals. In addition, there is a high composition of organics and nutrients in urban runoff. Also, a fraction of heavy metals present in stormwater is bound to the organic molecules. Therefore, the effect of organics and nutrients on heavy metal removal considering their competitiveness with heavy metal removal needs to be evaluated. Further, the ability of porous concrete in fixating the heavy metals bound to the organic matter has to be evaluated.

The water head is the height of the influent water column that is present above the porous concrete. Increasing levels of water head result in increased pressure leading to reduced contact times for the water passing through concrete. The degree of Cd, Zn, and Pb removal increased with decreasing water head regardless of the heavy metals present, either as individual ions or mixed in simulated wastewaters (Muthu et al., 2019). Cd and Zn removal in porous concrete increased up to 3 and 13 times (individually) and 3 and 2 times (when in combination with other pollutants) when

the water head was reduced from 30 cm (3 min contact time) to a trickling water head (294 min contact time) (Muthu et al., 2019). When there was no water head the removal of Zn increased but the variation in the removal in Cu was marginal while Pb removal showed no change. This finding suggests that Zn removal in PC was more dependent on the effective pollutant contact time relative to Cu and Pb (Muthu et al., 2019). However, in Fig. 6 no exact trend of increase in the Zn removal is seen except for the data from Muthu et al. (2019).

3.7. Ability of porous concrete to treat other heavy metals

Porous concrete has been used for the successful removal of Cd, Ni, Co, Fe and Mn (Ortega-Villar et al., 2019; Shabalala and Ekolu, 2019; Azad et al., 2020). Ortega-Villar et al. (2019) observed removal rates of Fe (83%) close to twice the removal rate of Mn (48%). The removal rate of Fe (83%) is comparable with the Pb removal rate (73%) in the same study. The high removal of Fe and Pb compared to Mn is linked with the higher tendency of Fe and Pb to absorb into solids (Ortega-Villar et al., 2019). Holmes et al. (2017a, 2017b) observed similar removal of Cd compared with Zn at varying initial concentrations when the ions were present simultaneously in the influent. A similar observation for Cd removal (76%) was made by Azad et al. (2020) which is close to Zn (77.5%) removal rate. This similarity of Cd and Zn removal was also observed with varying contact times by Muthu et al. (2019). Thus, porous concrete has a similar removal potential for Cd compared with Zn even when both the metals co-exist. In acid mine drainage, Shabalala and Ekolu (2019) noted that the mechanism of removal of Ni by porous concrete is similar to the removal mechanisms of Cu, Pb and Zn which is via hydroxide precipitation. Conversely, the same study reports that removal of Co is due to its co-precipitation or adsorption onto iron and aluminium hydrosulphates or hydroxides.

3.8. Constrains of unmodified porous concrete

3.8.1. Decalcification

Decalcification is a degradation process in cementitious materials occurring primarily due to the leaching of calcium and hydroxide ions from the cementitious matrix (Segura et al., 2012). The decalcification of the cement paste deteriorates the concrete decreasing mechanical strength and durability (Mainguy and Coussy, 2000; Heukamp et al., 2001; Thomas et al., 2004; Segura et al., 2012). When exposed to freshwater, concrete takes a longer time for decalcification than when exposed to aggressive agents (Heukamp et al., 2001; Thomas et al., 2004), as when exposed to aggressive agents the decalcification rate is increased (Mainguy and Coussy, 2000). Therefore, in porous concrete, long-term performance and service life depend strongly on the characteristics of the influent water samples. For instance, the protons from acidic wastewater diffusing into porous concrete filters can rapidly decalcify the porous concrete hydrates (portlandite, C-S-H, ettringite) and un-hydrated cement. Consequently, the porous concrete matrix and immobilized heavy metals may leach out and make porous concrete non-functional (Muthu et al., 2019). Furthermore, in the long run, a significant loss of strength (easily excavatable by hand) due to loss of cement paste in the uppermost layer of porous concrete was observed by Holmes et al. (2018). The proposed reason is the displacement or diffusion of Ca by heavy metals (Holmes et al., 2018). This degrades the structural integrity of the porous concrete. Additionally, the leaching of Ca^{2+} from the cement paste is said to increase the porosity of the cement paste, thus promoting further degradation of the concrete (Yin et al., 2018). Holmes et al. (2017a, 2017b) observed increased removal due to high porosity and high capillary absorption. Hence, there can be a positive effect of the increased porosity due to decalcification on the removal of heavy metals. However, there is no evidence found in the reported literature about benefits to heavy metal removal ability due to the increase of porosity in the cement paste due to decalcification.

To date, there are no published studies focused on modifying porous concrete to reduce decalcification due to heavy metal sorption. The

possibility of using self-healing methods such as biomineralization bacteria addition and autogenous healing should be evaluated in future research to potentially prevent the further degradation of the cement paste. The addition of adsorbent materials to the concrete matrix capable of adsorbing the heavy metals could also help overcome decalcification. This phenomenon can be successful if the pollutants have a stronger affinity towards the added adsorbent material than the cement paste. However, more research is required to explore this hypothesis and study any adverse effects that may occur due to the addition of such adsorbent materials (e.g., the effect on the permeability of the porous concrete, effect on long term stability).

3.8.2. Atmospheric carbonation

Atmospheric carbonation can degrade cement-based solidified wastes and increase the release of heavy metals to the environment with time (Chen et al., 2009; Muthu et al., 2019). In carbonation, hydration products (portlandite and C-S-H) react to form calcite (Garrabrants et al., 2004; Van Gerven et al., 2007). Furthermore, un-hydrated grains can also react with carbonic acid and be dissolved in water (Fernandez Bertos et al., 2004; Yin et al., 2018). The consumption of calcium hydroxide (CH) by carbonic acid decreases the pH of the cement paste. Furthermore, it causes an increase in porosity, which has a positive effect on the further degradation of concrete (Yin et al., 2018). This reaction leads to the lowering of pH in the pore water of the concrete from around a pH of 13 to a pH of 8 (Van Gerven et al., 2007). This can change the solubility of heavy metals in the matrix. This was observed by Mollah et al. (1993) where the peak intensities of hydroxyl bands were reduced in a CO_2 cured solidification/stabilization system. The peaks of the metal hydroxide and calcium hydroxide observed using Fourier Transform Infrared Spectroscopy reduced when the solidification/stabilization system was exposed to carbonation. Moreover, the heavy metal hydroxides were converted to carbonates increasing their solubility in water and hence permeating from the cement matrix when exposed to carbonation (Van Gerven et al., 2007). Additionally, the hydrated and un-hydrated products tend to react with carbonic acid to form calcium bicarbonate. As the solubility of calcium bicarbonate in water is high, this will dissolve under the flow of water and enter the effluent water.

3.8.3. Leaching due to acids

The effect of acidic inflow into porous concrete could dissolve the heavy metals attached to the concrete matrix, especially precipitated hydroxides (Fan et al., 2018). Muthu et al. (2019) reported that the leaching of Zn, Cu and Pb were observed to be 16%, 12% and 10% when 1 M HNO_3 solution (pH = 0) was passed through porous concrete samples used for heavy metal removal. However, Harada and Yanbe (2018) stated that at a pH value of 2.0, no release of heavy metals occurred. The same study observed that heavy metal recovery or leaching occurred at levels of 8–22% for Pb and 42–74% for Zn at a pH value of 0.5. Additionally, when the pH value decreased to zero, recovery increased to 30–60% for Pb and 75–125% for Zn. Therefore, the leaching of heavy metals previously bound to the porous concrete increases when the pH of the influent is reduced beyond pH of 2. As the typical pH value of stormwater is 6.5–8.5 there is no foreseeable threat of desorption of adsorbed heavy metals from the porous concrete. In addition, a typical acid rain where pH is around 4–5 also does not pose a threat of desorption. However, there is no evidence of the resistance to desorption in the long-term usage of porous concrete. Hence, there is a need to conduct studies focused on the desorptive potential of porous concrete used for long-term applications in the future.

3.8.4. The effluents' pH and long-term stability

Hydration of cement in porous concrete generates $\text{Ca}(\text{OH})_2$ and porous concrete will also contain CaCO_3 and MgCO_3 . Thus, porous concrete can increase the alkalinity and the pH of the water passing through (Kuang and Sansalone, 2011). This is beneficial in the treatment of low pH water streams like acid mine drainage, as the effluent pH could be increased after treatment. The effluent pH was observed to decrease with the storm duration by Kuang and Sansalone (2011). In the same study, after a dry

period of 3 days between runoff feeds, runoff passing through the porous concrete showed a slight lowering (less than 2%) of effluent pH during the first 3 subsequent simulated runoff events. After the first 3 subsequent events, there was no change in effluent pH among subsequent runoff events (third to the seventh event). Further, in the same study comparing the effluent pH at the start of a single event and the end after 6 h, an approximate 7% reduction in effluent pH was observed. Muthu et al. (2018) observed calcium ions present in the effluent despite the influent having no calcium ions. Therefore, the leaching of portlandite could account for the lowering of pH observed between subsequent events and during these events. Fig. 7 depicts the changes in the effluent pH with varying influent pH values. In most cases, the effluent pH value is raised to a value above a pH of 8.5. The pH of the effluent water needs to be reduced to a safe level (<8.5) before discharge into natural water bodies. The effectiveness of either by using a separate treatment system like aluminium sulphate barriers or by modifying porous concrete mix design itself utilizing additions such as pozzolanic materials needs to be evaluated for reduction of the effluent pH.

Another major drawback of cement-based stabilization methods is that it suffers from poor long-term stability (Fan et al., 2018). Cement-based solidified and stabilised wastes are observed to be vulnerable to physical and chemical degradation processes (Chen et al., 2009). The chemical processes such as further hydration, carbonation, ettringite or thaumasite formation, will result in a change of porosity, volume, and solidified waste performance. In addition, atmospheric carbonation can degrade cement-based solidified wastes and increase the release of heavy metals to the environment with time (Chen et al., 2009). There is limited published literature on the long-term stability of heavy metals removed by porous concrete at present. Understanding the long-term stability should be prioritized in future research to benefit from the full potential of porous concrete in heavy metal removal.

3.8.5. Clogging of porous concrete

Clogging of porous concrete happens due to the blocking of pores by the suspended solids in the influent water (Deo et al., 2010; Kayhanian et al., 2019). Thus, during its lifetime, the permeability of the porous concrete decreases. Deo et al. (2010) observed significant permeability reductions when finer sand (particle size range: 0.84 mm – 0.10 mm) is used than coarse sand (particle size range: 1.8 mm – 0.84 mm). The same study reports that in porous concrete with similar porosity, the clogging susceptibility of specimens with very large (5–6 mm) or very small (1–2 mm) pore sizes was low. Additionally, Kia et al. (2018) noted that clogging of porous concrete with low porosity is more rapid compared to samples with high

porosity. Kayhanian et al. (2019) found that the reduction of porosity via clogging in porous pavements is related to particle accumulation in the upper surface and that the trapped particles can be removed by vacuuming. On the other hand, reduced permeability due to clogging will help increase the contact time available for the water passing through the porous concrete. Thus, it can increase the removal of heavy metals. However, Brugin et al. (2017) state that the progressive clogging of porous concrete can result in a loss of permeability of up to 98%. Such a high loss of permeability will result in loss of productivity of the porous concrete and will need to be replaced. As the reduction of permeability due to clogging is progressive, knowledge on the variation of heavy metal removal with permeability reduction rate is required. Further, Mullaney and Lucke (2014) state that vacuum sweeping is ineffective in cleaning completely clogged porous pavements where pressure washing is very effective. Heavy metal removal precipitates and the precipitates are trapped in the pore spaces in the porous concrete (Holmes et al., 2017b). Through pressure washing, there is a possibility of mobilizing these precipitated heavy metals from porous concrete. However, there are no studies in reported literature that focus on the consequences of using pressure washing on the mobility of heavy metals.

4. Application of modified porous concrete pavement

Various modifications have been applied to porous concrete to enhance its performance. Table 1 summarises the summary of the modifications to porous concrete outlining the focus of the reported literature. An in-depth discussion of these modifications is undertaken in the following subsections.

4.1. Addition of fly ash and pumice pozzolan

Pozzolans are siliceous or siliceous and aluminous materials that have little or no cementitious properties on their own. Pozzolanic materials react with calcium hydroxide and water in the hydrated cement and contribute to increasing the mechanical performance of the concrete (Holmes et al., 2018; Tran et al., 2019). With a decrease in the quantity of $\text{Ca}(\text{OH})_2$, the effluent pH could be expected to be lowered. Holmes et al. (2017a), Holmes et al. (2018) and Shabalala and Ekelu (2019) observed a final pH of 11.5, 12.1 and 11.5 for unmodified porous concrete and 11.4, 11.8 and 10.60 for fly ash modified porous concrete, respectively. The first two studies used Class C fly ash as a 25% cement replacement while the last study used Class F fly ash as 30% cement replacement. The reduction in pH is due to the pozzolanic reaction of fly ash. However, Holmes et al. (2017a) observed that the solution pH was raised from an initial value of 7.5 to 11.9 and 12.5 by the high sulphur and high carbon in the fly ash addition to the porous concrete (24% cement replacement with fly ash) samples, compared to 11.5 in the unmodified sample. The pozzolanic activity of the latter two fly ash types are lower than the Class C and Class F fly ash which is a possible reason for the difference in final pH values. Furthermore, Cheng et al. (2020) observed a reduction of pH from 12.3 to 10.1 when 10% silica fume was added as a cement replacement (mass-based). Also, the same study shows that the pH reduced to 9.4 when both silica fume (10%) and fly ash (20%) was added in combination as cement replacement.

Consequently, a decrease in the heavy metal removal could be expected with the addition of pozzolanic materials to the porous concrete mix due to a reduction in pH. Yousefi and Matavos-Aramyan (2018) observed that the addition of pumice pozzolan negatively affected Cu removal. However, the same study found that the addition of pumice aggregate increased the removal efficiency of Cu. In a more recent study by Azad et al. (2020), 10% pumice pozzolan was added as a replacement for cement. Increments of approximately 19%, 13.5% and 9% were observed in the removal efficiencies of Zn, Cu and Pb, respectively. However, beyond 10% replacement of cement (i.e., 20%, 30% and 40%) the removal efficiency increased only marginally (<4%). The chemical compositions of the 2 pumice pozzolans were almost identical except for the SiO_2 content, where Azad et al. (2020) used pumice pozzolan with 10% lower SiO_2 content than Yousefi and Matavos-

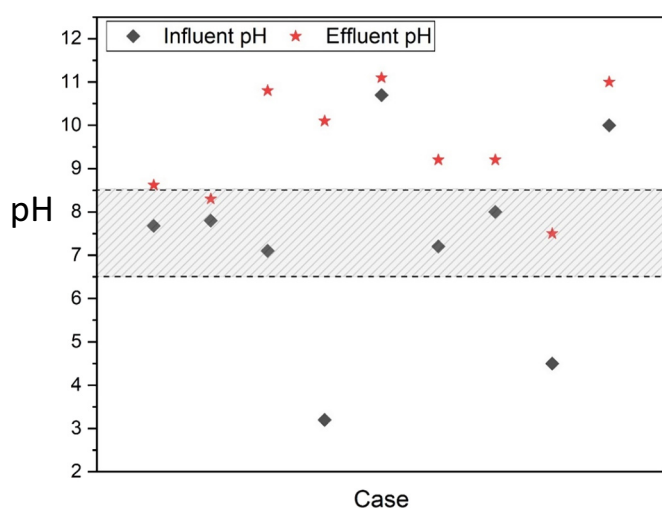


Fig. 7. The changes to the effluent pH with varying influent pH values (Kuang and Sansalone, 2011; Muthu et al., 2018; Kayhanian et al., 2019; Muthu et al., 2019; Razzaghamanesh and Borst, 2019).

Table 1
Summary of modifications done to porous concrete used in heavy metal removal.

Category of addition	Material used (type of modification)	Tests carried out	Reference
Supplementary cementations materials	Class C fly ash (cement replacement)	Removal of Cd, Pb and Zn from synthetic influent using column testing Effect on effluent pH SEM-EDX imaging after removal	Holmes et al. (2018)
	Class F fly ash (cement replacement)	Removal of Ca, Mg, Na, Mn, Fe, Al, Co, Pb, Zn and SO_4^{2-} from acid mine drainage using batch testing Effect on effluent pH	Shabalala and Ekolu (2019)
	High sulphur and High carbon fly ash (cement replacement)	Removal of Cd, Pb and Zn from synthetic influent using batch testing Effect on effluent pH Effect on effluent electrical conductivity Leachability of Cd, Pb and Zn from porous concrete SEM-EDX imaging after removal of heavy metals	Holmes et al. (2017a)
	Zeolite (Clinoptilolite) and Pumice pozzolan	Removal of Cu and Ni from synthetic influent using column testing Effect on effluent pH Effect on compressive strength and permeability	Yousefi and Matavos-Aramyan, 2018
	Zeolite and Pumice pozzolan	Removal of Cu, Pb, Zn, Cd, Chemical Oxygen Demand, Total Suspended Solids and Turbidity from synthetic influent. Effect on compressive strength, void ratio and permeability	Azad et al. (2020)
Superplasticizers	Poly-carboxylic based superplasticizer (water reducer)	Removal of Cu and Ni from synthetic influent using column testing Effect on compressive strength and permeability	Yousefi and Matavos-Aramyan (2018)
Nanoparticles	Fe_2O_3 nanoparticles (surface coating)	Removal of Pb, Fe, Mn, PO_4^{3-} , NO_3^- and Chemical Oxygen Demand, from synthetic influent using column testing. Effect on compressive strength, void ratio and permeability	Ortega-Villar et al. (2019)
Others	Iron oxide (surface coating)	Removal of with Cu and Ni from synthetic influent using column testing Effect on effluent pH Effect on compressive strength and permeability	Yousefi and Matavos-Aramyan (2018)
	Reduced graphene oxide (additive)	Removal of Cu, Pb and Cd from synthetic influent using column testing Effect on effluent pH Effect on leachability of removed heavy metals	Muthu et al., 2019

Aramyan (2018). However, the particle sizes of the two pozzolans were not disclosed in both studies. It could be observed that although replacement of cement by 10% pumice increases the removal efficiency significantly, further addition does not yield such results. The reason for this could be the finite number of pollutant ions available in the solution making the effective concentration low. Further, the addition of pumice greater than 10% resulted in the loss of compressive strength of the porous concrete mixes. However, no observations were made on the effect of effluent pH of the treated water in this study. More experimental studies are required to quantify the capacity of the modified porous concrete as well as the long-term performance of the modified porous concrete.

The addition of high carbon fly ash and high sulphur fly ash as an admixture was tested by Holmes et al. (2017a). They reported that these combinations were less effective in metal removal at higher metal concentrations but improved removal at lower metal concentrations. Comparing the effluent pH values of porous concrete made with class C fly ash (11.4) and high sulphur fly ash (11.9), no evidence of the formation of acidic substances was observed in the Holmes et al. (2017a) study. The excessive sulphur content present in fly ash employed reduced durability and heaving due to extensive ettringite formation (Holmes et al., 2017a). Furthermore, carbon levels exceeding 6% in fly ash deleteriously impacted the durability. This is due to the increase in air entrainment, thereby increasing susceptibility to freeze-thaw failure. (Holmes et al., 2017a). Liu et al. (2019) used 3-thiocyanatopropyltriethoxysilane (TCPS) modified class F fly ash beads (T-fly ash) to modify porous concrete to assess Cd removal. The TCSP formed a metal chelate with Cd after removal. The T-fly ash resulted in a greater than 97% increase in Cd removal capacity compared to unmodified class F fly ash. In this modification, fly ash reacts in the concrete mixture, and thus, the fly ash beads are fixed in the concrete. Liu et al. (2019) observed a complete removal of Cd when the initial concentration is below 8.90×10^{-1} mM. With increased Cd concentration, free Cd was detected in the solution, owing to the finite adsorption capacity of the modified porous concrete. However, benchmarking the effectiveness of the performance with unmodified porous concrete was not reported in this study. Thus, evaluating the effectiveness of the T-fly ash or fly ash incorporation to unmodified porous concrete cannot be determined.

4.2. Addition of zeolites

Natural zeolites composed of hydrated crystalline aluminosilicates are used in wastewater treatment as an adsorbent material and the construction industry as a pozzolanic additive (Wang and Peng, 2010; Tran et al., 2019). Zeolites are good adsorbents of heavy metals due to their large cation exchange capacity (Ok et al., 2007; Yousefi and Matavos-Aramyan, 2018; Azad et al., 2020). Furthermore, zeolites can enhance the concrete mechanical properties and act as a pozzolanic material by creating denser cement paste (Tran et al., 2019). Additionally, zeolites possess a high capacity for absorbing and desorbing water due to the presence of pores at the micro-macro level and therefore used as internal curing agents in concrete (Tran et al., 2019). The addition of 10% (w/w of cement) natural zeolite (Clinoptilolite) increased the Cu removal capacity (43% increase) of the porous concrete (Yousefi and Matavos-Aramyan, 2018). Azad et al. (2020) also studied the effect of zeolite addition on porous concrete as a cement replacement in the range of 10–40%. The removal efficiency increased by 20%, 15% and 13% with respect to a 10% addition of the zeolite for Zn, Cu and Pb. However, further addition (>10%) yields only a marginal increase in efficiency (<2%) for the removal of all 3 heavy metals. Additionally, zeolites are also beneficial in decreasing the leaching degree of fixated heavy metals by strengthening the hydrated porous concrete microstructure (Muthu et al., 2019).

Despite the benefits of zeolite addition, they consume a high quantity of superplasticiser to compensate for the loss in workability due to their microporous structure (Tran et al., 2019). Further, a compressive strength reduction is observed owing to the high amount of mixing water required by the porous structure and the high surface area of natural zeolites (Tran et al., 2019). This can result in a loss of strength in the porous concrete which decreases the suitability of this modification.

4.3. Iron oxide and reduced graphene oxide addition

Increasing active sites in the porous concrete can help increase the pollutant removal capacity of the porous concrete. These materials include iron oxides, graphene oxides and reduced graphene oxides. Iron oxides are widely used as surface coating adsorbents. Iron oxides have a high

surface area, high levels of surface defects and a high density of reactive surface sites (Acheampong et al., 2013; Ahmedzeki, 2013; Sizirici and Yildiz, 2016). Iron oxide coated bricks and gravel, as well as cement, are used successfully for Cu, Pb and Zn removal (Sizirici and Yildiz, 2016). The effect of the addition of iron oxide to porous concrete was evaluated by Yousefi and Matavos-Aramyan (2018) where iron oxide (98% purity) was mixed with other ingredients rather than being used as a surface coating. The addition of 10% (w/w of cement) of iron oxide (98% purity) increased the Cu removal capacity (65% increase) of porous concrete (Yousefi and Matavos-Aramyan, 2018). Furthermore, when zeolite (10% w/w) and iron oxide (10% w/w) and polycarboxylate superplasticizer (20% w/w) were simultaneously added, a synergy effect (114% increase) was observed by Yousefi and Matavos-Aramyan (2018). However, the optimum increase of 155% was observed when zeolite (5% w/w) and iron oxide (5% w/w) and polycarboxylate superplasticizer (10% w/w) was utilized. This could be due to factors such as lowering of pH due to high pozzolanic reactivity, densification of the porous concrete due to the additives and pozzolanic reactivity. The measurement of parameters such as compressive strength and degree of hydration could be used to determine the underlying rationale in future research.

Graphene oxides and reduced graphene oxides have a very high specific surface area, a characteristic of good adsorbent material. The addition of Reduced Graphene Oxide (RGO) (0.06% wt.) increased the pollutant removal capacity of porous concrete where Zn, Cu and Pb removals increased by 31%, 15% and 26%, respectively (Muthu et al., 2019). This highlights that the RGO added increased active sites for metal adsorption. A combination of electrostatic attraction, chemisorption and hydroxide precipitation were identified as the mechanisms of removal (Muthu et al., 2019). However, the exact phenomena responsible for the increment in the removals were not studied. In addition to the improvement to the removal efficiency of Cu, Pb and Zn, the addition of RGO lowered the leaching of heavy metals due to an acidic influent (Muthu et al., 2019). This phenomenon was highlighted for Zn removal where leached Zn concentrations were reduced by approximately 50% after 8 h in leaching tests with HNO₃. The formation of hydroxides was reduced whereas Zn had probably bonded to the surface of the RGO. This gives a favourable indication that additives could help to resist the leaching of the sorbed ions in the concrete mix. Porous concrete is more prone to abrasion when compared with impervious concrete (Xie et al., 2019). However, due to abrasion, the RGO could be released into the environment from the porous concrete. Furthermore, RGO has certain toxicity and can lead to health issues like chromosomal aberrations, DNA fragmentations and cytotoxicity (Ou et al., 2016). Hence, the degree of release of RGO's must be evaluated to determine any indirect adverse impacts. Advanced characterization techniques should be employed to clearly understand the mechanism behind resistance to leaching. Thus, enabling more effective methods of modifying porous concrete as well as predictive modelling of the modifications.

4.4. Superplasticizer addition

Superplasticizers are used in construction to lower the water demand of the concrete while maintaining sufficient workability. Superplasticizers are polymers and allow a reduction in water content by 30% or more (Pourchet et al., 2006). Major types of superplasticizers are sulfonated naphthalene formaldehyde, sulfonated melamine formaldehyde; modified lignosulfonates and poly-carboxylic acids. The different types of superplasticizers have different mechanisms by which they increase the fluidity of the concrete. The sulfonated naphthalenes create electrostatic repulsion between cement particles whereas poly-carboxylic disperse cement due to a steric hindrance effect (Pourchet et al., 2006). Hence, the effect of each type of superplasticizer type on the heavy metal removal efficiency varies. However, limited published literature is available which assesses the effect of the addition of superplasticizers on the removal of heavy metals. Poly-carboxylic based superplasticizers are the latest generation and the main superplasticizer in use today (Martirena et al., 2014). Yousefi and Matavos-Aramyan (2018) noted that superplasticizers based on polycarboxylate do not affect heavy metal adsorption. The effect of other

types of superplasticizers on the heavy metal removal efficiency of porous concrete requires evaluation in future studies.

4.5. Addition of nanoparticles

Nanoparticles are gaining significance in new applications due to their modifiable chemical, physical, and mechanical properties compared to their bulkier counterparts (Janus et al., 2020; Saleh, 2020). Nanoparticles can remove heavy metals to a significant level due to their high surface area and reactive centres (Saleh, 2021). Furthermore, nanoparticles can improve the mechanical properties of cement-based products, and can act as heterogeneous nuclei for cement pastes. This further accelerates cement hydration due to their high reactivity while they also act as nano reinforcement, as pozzolanic materials, and as nano-filler densifying the microstructure, resulting in a reduced porosity (Khoshakhlagh et al., 2012; Kawashima et al., 2013; Singh et al., 2013). In addition to the improvements in the mechanical properties, materials such as nano-TiO₂ are found to have the ability to decompose environmental pollutants via photocatalytic degradation (Singh et al., 2013). The addition of photocatalytic layers to permeable pavements is an emerging technique proposed to decrease air and water pollution in urban areas (Ortega-Villar et al., 2019). These catalysts can produce active oxygen species such as hydroxyl radicals (OH) or superoxide ions (O₂⁻). Thereby, oxidizing organic and inorganic compounds. As the photocatalytic functionality is only realized in the effective surface area receiving light, mixing photocatalytic materials homogeneously throughout the porous concrete lowers the photocatalytic efficiency (Janus et al., 2020). Ortega-Villar et al. (2019) studied the effect of the addition of Fe₂O₃ nanoparticles on Pb removal. A mortar mixture with Fe₂O₃ nanoparticles was applied using a dry brush to cast porous concrete specimens. The unaltered presence of Fe₂O₃ on the porous concrete samples was observed. Ortega-Villar et al. (2019) observed that the addition of nanoparticles marginally increased Pb removal by approximately 7% and 8%, corresponding to 3% and 5% nanoparticle addition, respectively. Pb removal by Fe₂O₃ nanoparticles was observed to be dominated by hydroxide precipitation when the pH is above 6 (Ahmadi et al., 2014). However, in the study of Ortega-Villar et al. (2019), the pH of the solution is not stated. As such, the removal mechanism following nano-particle addition was not identified in their study. Therefore, future studies need to aim at identifying the mechanism of removal following nano-particle modification. As homogenous embedding of photocatalytic materials in the concrete improves mechanical properties, future studies should focus on optimizing the mixing of photocatalytic materials to maximize the beneficial effect on both mechanical and pollutant removal abilities of the composites. Additionally, the lack of competitiveness of most photocatalytic cementitious materials limits their usage (Janus et al., 2020). Therefore, there is a need to identify new photocatalytic materials as well as new incorporation strategies for the casting of functional binders. Further, Hassan et al. (2010) observed that photocatalytic materials (TiO₂) applied (as a surface layer) on non-porous concrete were released when the test sample was subjected to wear from abrasion. As porous concrete is more prone to wear, the release of such materials will be more than in non-porous concrete. No studies have evaluated this phenomenon to date thus additional investigation is required in future research.

5. Conclusions

Porous concrete enables the management of urban runoff without the need for extra land acquisition and the absence of open water storage. Hence, it is an attractive method for the treatment of urban runoff. The key findings on the ability of porous concrete in the treatment of heavy metals are as follows:

- Heavy metal fixation in porous concrete is broadly split into physical and chemical processes with the dominating process depending upon the influent characteristics. Both the aggregates and the cement paste in the porous concrete matrix have individual heavy metal fixating capacities. However, the individual capacity of the aggregates is significant only if the Ca content of the aggregates is high (e.g., limestone aggregates).

- The dominant processes in the removal of heavy metals are precipitation due to the formation of heavy metal hydroxides and sorption via cation exchange. Initial heavy metal concentration dictates the most prominent method of heavy metal removal, where at high initial heavy metal concentrations precipitation dominates while at low initial heavy metal concentrations the sorption dominates.
- The removal of heavy metals via porous concrete reach their maximum removal efficiency (>75%) within 18 min. However, the current treatment methods employing porous concrete require the storage of runoff due to the high infiltration capacity of the porous concrete.
- Decalcification due to displacement of Ca ions in porous concrete causes degradation of porous concrete.
- Low pH values, less than pH of 2, are required to leach adsorbed heavy metals from the porous concrete. The effluent pH of water passed through porous concrete requires treatment to lower its pH value, as in most of the studies the effluent pH is above 8.5.

Research on the improvement of heavy metal removal using porous concrete is focused mainly on improving the removal efficiency of heavy metals. The highlights of previous studies concerned with improving the heavy metal removal through porous concrete are:

- The addition of pozzolanic materials like pumice, fly ash, silica fume and natural zeolites decrease the pH due to pozzolanic reaction. The overall efficiency of the removal of heavy metals is not reduced.
- The addition of RGO and iron oxide increases the removal of heavy metals, whereas RGO lowers the leaching of heavy metals due to acidic influent.
- The addition of Poly-carboxylic Acid superplasticizer to porous concrete does not affect the heavy metal removal ability of porous concrete.
- The addition of iron oxide and Fe₂O₃ nanoparticles have increased the removal of heavy metals.

CRedit authorship contribution statement

Pamodithya Wijewardana: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Nadeeshani Nanayakkara:** Conceptualization, Supervision, Writing – review & editing. **Chamila Gunasekara:** Conceptualization, Supervision, Writing – review & editing. **Anurudda Karunarathna:** Conceptualization, Supervision, Writing – review & editing. **David Law:** Conceptualization, Supervision, Writing – review & editing. **Biplob Kumar Pramanik:** Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Scholarship provided by the School of Engineering, RMIT University and the NORAD WaSo-Asia Grant to the first author is gratefully acknowledged. This research was supported by the Australian Research Council Industrial Transformation Research Hub IH200100010 (Industrial Transformation of Reclaimed Waste Resources to Engineered Materials and Solutions for a Circular Economy), and the University of Peradeniya Research Grant URG/2021/19/E, which are gratefully acknowledged.

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