

Heavy metal removal from motorway stormwater using zeolites

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Abstract

The possibility of using zeolites to reduce the levels of heavy metals present in motorway stormwater has been investigated. Currently, the primary pollutant removal mechanism used in treating stormwater is retaining the large volume of stormwater in detention ponds to allow time for the contaminants (mainly those associated with particulate matter) to separate out. There is also a need to reduce the levels of heavy metals in the dissolved phase, possibly by introducing some kind of ion exchange material into the treatment facility. Batch experiments have been conducted on two zeolites (synthetic MAP and natural mordenite) to test their ability to remove dissolved heavy metals from simulated and spiked motorway stormwater. Synthetic zeolite MAP showed almost complete removal (>91%) of the studied heavy metals (Zn, Cu, Pb, Cd) from both solutions. However, the use of such synthetic zeolites could have serious environmental implications as it was found to increase sodium levels to 295 mg/l, remove calcium and increase the pH of the spiked motorway stormwater to 8.5. Mordenite was less effective at reducing the levels of heavy metals (42–89% in synthetic solution, 6–44% in motorway stormwater) and exhibited a preference for Pb>Cu>Zn ~ Cd. It is proposed that the uptake of heavy metals is partially inhibited by the other dissolved contaminants present in motorway stormwater.

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1. Introduction

Stormwater runoff from motorways contains contaminants from the road surface including heavy metals (V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb), arising from the wear-and-tear of vehicle parts and additives in oil and petrol (Ward, 1990; Sansalone and Buchberger, 1997; Davis et al., 2001). Methods for treating motorway stormwater usually involve retain-

ing the large volume of water in a detention pond to allow the pollutants to separate out before controlled release into a local watercourse. This helps to reduce the heavy metal load associated with particulate matter (Yousef et al., 1990; Pontier et al., 2001) but is less effective for metals in the dissolved phase of the stormwater. The removal of soluble heavy metals can be aided by clay lining in detention ponds (Hares and Ward, 1999) and certain types of reeds in wetland systems (Ellis et al., 1994; Mungur et al., 1995; Shutes et al., 1999).

There are several problems associated with the removal of heavy metals from motorway stormwater

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drainage facilities. For example, a lack of maintenance in detention ponds leads to a build up of contaminated sediment which can be re-suspended in a storm event (Stanley, 1996). Heavy metals can also be leached from the sediment with changing environmental conditions such as pH (Yousef et al., 1988). Dissolved de-icing salt in the stormwater is believed to have a detrimental effect on the development of some reeds in wetland systems (Hootsmans and Wiegman, 1998) and for some metals, especially cadmium, soluble chloride complexes can form increasing the environmental mobility and bioavailability (Bingham et al., 1984; Warren and Zimmerman, 1994).

An ion exchange material could provide additional stormwater treatment by replacing any toxic heavy metal cations in the runoff with cations such as sodium, calcium or magnesium. This technology could then reduce the heavy metal levels in motorway stormwater through retention within the ion exchange material, which could be re-generated for further use. Such methods would ideally be unaffected by the seasonally high salt content of motorway stormwater, due to the application of de-icing agents during winter.

Zeolites are a suitable choice as they have a large cation exchange capacity and an affinity for heavy metals (Kesraoui-Ouki et al., 1994; Curkovic et al., 1997). They have a three-dimensional framework consisting of silica and alumina tetrahedral units linked by shared oxygen atoms. The isomorphous replacement of Si^{4+} by Al^{3+} results in a net negative charge which is compensated by alkali and alkaline-earth metal cations within the framework (Dyer, 1988).

Zeolites are natural materials mined in various deposits throughout the world and can also be produced synthetically to tailor the properties for specific applications. Natural zeolites, in particular clinoptilolite, have been studied extensively for the removal of heavy metals from wastewater due to their wide availability and low cost (Pansini, 1996; Colella, 1999). Studies on synthetic zeolites tend to focus on determining thermodynamic parameters (Harjula et al., 1992; Biškup and Suboti, 1998) and they have generally not been considered for environmental applications. This study compares the ability of a synthetic zeolite (MAP) and a natural zeolite (mordenite) at reducing the levels of heavy metals in simulated and spiked motorway stormwater.

2. Experimental

2.1. Materials

The properties of the zeolites tested are detailed in Table 1. In order to ensure the method is economical, the zeolites were used and stored as provided, that is with no pre-treatment.

2.2. Metal solutions

Mixed metal solutions were prepared using doubly de-ionised water (18 mΩ) and filtered (Whatman no.1, 11 μm) motorway stormwater collected from a detention pond at Oxted (Surrey, UK) which receives runoff from the London Orbital M25 motorway (Hares and Ward, 1999). This allows comparison between an 'ideal' heavy metal solution and 'real' motorway stormwater containing heavy metals with other contaminants, e.g. dissolved organic compounds, sodium chloride and water hardness. It was necessary to spike the motorway stormwater as the metals present were very low due to the wet weather at time of collection (March 2002). Heavy metal concentrations used were 25, 50, 250 and 500 μg/l of Cd, Pb, Cu and Zn, respectively (standards in nitric acid, Aristar, BDH, Poole, UK). This was designed to mimic a high pollutant load and to be concentrated enough to allow the effect of the zeolites to be measured. No pH adjustment was carried out in order to preserve the metal concentration and speciation.

2.3. Batch experiments

Batch experiments were used as a quick and simple method to test if zeolites would be suitable for this application as the synthetic zeolite MAP had previously been found to be unsuitable for column

Table 1
Characterisation of zeolites used

	Type	Origin	Size	Si/Al ratio	Form
MAP	synthetic P	INEOS Silicas, UK	1–10 μm	1	Na
Mordenite	natural	Resource Refineries, New Zealand	<2 mm	6	Na, Ca, K, Mg

tests due to its fine consistency (Pinheiro, 1998). The procedure involved mixing 0.50 ± 0.02 g zeolite with 50 ml of solution and shaking for 10 min using a platform mechanical shaker (IKA LABORTECHNIK, HS250 basic) at 4 Hz (240 rpm). A short shaking time was chosen to reflect the duration the stormwater would be in contact with the zeolite in situ in a treatment facility. Polypropylene containers were used and all samples were run in duplicate. The aqueous phase was separated by centrifuging the mixture for 3 min at 50 Hz (3000 rpm), then transferred by pipette into a Sterilin™ (trace metal free container) and stored in a fridge (<4 °C) prior to analysis. pHs of solutions before and after contact with the zeolites were recorded on a calibrated pH meter (WPA CD70).

2.4. Analytical procedures

All solutions were analysed by inductively coupled plasma mass spectrometry-ICP-MS (Finnigan MAT SOLA, Bremen, Germany) for $^{65}\text{Cu}^+$, $^{66}\text{Zn}^+$, $^{112}\text{Cd}^+$ and $^{208}\text{Pb}^+$ using a high solid nebuliser (V-groove) and on-line internal standardisation (100 µg/l of $^{74}\text{Ge}^+$, $^{115}\text{In}^+$ and $^{209}\text{Bi}^+$). Quality control checks were undertaken with the certified reference material TMDA 54.3 (National Water Research Institute, Environment Canada). Flame AAS (Perkin Elmer 5000) was used to analyse the solutions for Na, Ca and Mg to observe which cations were being exchanged between the zeolite and the solution.

3. Results

3.1. Heavy metal removal

The performance of the zeolite in reducing the heavy metal levels in both synthetic solutions and

Table 2
Heavy metal removal (%) by each zeolite for both solutions

Zeolite	Solution	Pb	Cu	Zn	Cd
MAP	Synthetic solution	100 ^a	98.4	96.8	100 ^a
	Motorway stormwater	100 ^a	91.6	96.5	100 ^a
Mordenite	Synthetic solution	89.2	53.4	41.8	45.0
	Motorway stormwater	44.2	32.4	10.1	6.0

^a Levels of metal reduced below detection.

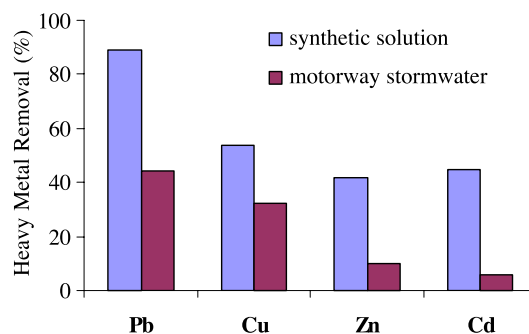


Fig. 1. Comparison of the % metal removed from synthetic solution and motorway stormwater by mordenite.

motorway stormwater was assessed by calculating the percentage of metal removed after the 10-min mixing period. The following equation was used for each metal tested:

$$\% \text{ Metal Removal} = [(C_i - C_x)/C_i] \times 100$$

where C_i is the initial metal concentration and C_x is the metal concentration after contact with the zeolite.

The synthetic zeolite MAP was found to be very effective in removing almost all of the metals from both solutions. Comparing the removal efficiencies (%) for the different zeolites in Table 2 shows that the synthetic zeolite performs considerably better than the natural one. A selectivity series can be determined for mordenite: $\text{Pb} > \text{Cu} > \text{Zn} \sim \text{Cd}$ which is as found for mordenite by Yuan et al. (1999). The uptake of heavy metals from motorway stormwater by mordenite is reduced although the selectivity remains the same (see Fig. 1).

3.2. Solution pH

The pH of the solution after contact with synthetic zeolite MAP increased to 8.5–9.0 regardless of the initial pH (3.2 for the synthetic solution, 7.1 for the

Table 3
Elemental levels released from zeolites into synthetic heavy metal solution (mg/l)

	Na	Mg	Ca
MAP	34 ± 7	nd	nd
Mordenite	7 ± 1	0.1 ± 0.01	0.1 ± 0.03

Mean \pm standard deviation ($n=2$); nd = not detected.

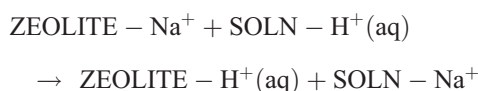
Table 4

Elemental levels released from zeolites into spiked motorway stormwater (mg/l)

	Na	Mg	Ca
Initial	82 ± 2	5.1 ± 0.02	134 ± 0.4
MAP	295 ± 6 (+213)	0.5 ± 0.02 (−4.6)	nd (−134)
Mordenite	120 ± 31 (+38)	6.8 ± 0.08 (+1.7)	128 ± 0.2 (−6)

Mean ± standard deviation ($n=2$); (values in brackets represent the increase/decrease in concentration after contact with the zeolite); nd=not detected.

stormwater). This is typical of synthetic zeolites and is due to hydronium ion exchange reducing the concentration of protons in solution:



Mordenite had a less dramatic effect on the solution pH (slight increase to 3.6 in synthetic solution, and a decrease to 5.3 in motorway stormwater).

3.3. Exchangeable ions

Sodium is released into solution by both zeolites, indicating an ion exchange process has occurred (see Table 3). Mordenite also exchanges calcium and magnesium but to a lesser extent. The higher levels of sodium released from synthetic zeolite MAP can be assigned to the higher metal removal and the hydronium ion exchange. The motorway stormwater initially contained sodium, calcium and magnesium due to de-icing salts and natural water hardness (see Table 4). On contact with the zeolite, the calcium levels are lowered (completely in the case of MAP) and the concentration of sodium increases as a result of this ion exchange process. Magnesium appears to be taken up by MAP but is released from mordenite.

4. Discussion

4.1. Zeolite metal up-take

As expected from its higher aluminium content (hence higher ion exchange capacity), the synthetic zeolite MAP removes higher amounts of heavy metals

from solution. Other explanations is that the sample was pure zeolite (mordenite contains other mineral impurities) and is in the readily exchangeable, homo-ionic sodium form (White et al., 1995). In addition, MAP has a small particle size and a larger internal surface area for heavy metal cations to access (Maliou et al., 1994).

There appears to be dissolved contaminants in motorway stormwater which interfere in the exchange of heavy metal ions by mordenite. This could be due to a change in the metal species or competition from other cations. The motorway stormwater solution had a higher pH (7.1) compared to the synthetic metal solution (3.2) and this could partly explain the lower uptake. Solution pH affects metal speciation. Mier et al. (2001) studied the removal of lead and cadmium by clinoptilolite in solutions at various pH values and found better removal at acidic pH's where the metal species were dominantly cationic. Other considerations are the organic content of the motorway stormwater which could complex with the metals making them less likely to be removed from solution by the zeolite (Mier et al., 2001) and competition from Ca^{2+} (Zamzow et al., 1990).

4.2. Removal mechanism

The release of sodium from the zeolite into solution is indicative of an ion exchange removal process but at the resultant alkaline pH after contact with synthetic zeolite MAP, heavy metals tend to be fairly insoluble (Pourbaix, 1966). This is a potential problem, if the heavy metals have simply precipitated on the surface and are not contained within the zeolite. As such, in this state they could be re-dissolved into solution if the pH becomes acidic. The removal mechanism for mordenite is likely to be ion exchange, although the impurities present in natural zeolites (e.g. calcite) have been found to adsorb some metals (Curkovic et al., 1997).

4.3. Suitability for application

The synthetic zeolite MAP showed very good heavy metal removal from both solutions and did not appear to be affected by the calcium present in the motorway stormwater. However, there are potential environmental implications in using such ion

exchange materials in a motorway stormwater detention pond. The large amount of sodium released would add to the already high levels found during winter periods, exceeding the environmental quality standard for freshwater of 170 mg/l. Calcium removal may lead to fewer exchange sites available for heavy metals, reducing the useful lifetime of the zeolite. Another concern is that the presence of water hardness is a factor in reducing metal toxicity (Yousef et al., 1988). Heavy metal speciation and mobility is also influenced by solution pH but at the alkaline levels resulting from contact with synthetic zeolite MAP heavy metals are likely to become insoluble and less mobile. The pH increase may not be so significant on scale-up to a treatment facility.

The most suitable way of applying the zeolites to a stormwater detention pond would be to contain the zeolite material in some type of filter bag to enable periodic regeneration of the heavy metal contained zeolite and to prevent releasing the zeolite to the environment. Considering these practicalities, a granular zeolite such as mordenite may be more suitable as it has a larger particle size. A potential disadvantage of using any type of zeolite is that the occasional high concentration of sodium present in motorway stormwater may re-exchange the heavy metals within the zeolite.

5. Conclusions

Zeolites are able to substantially lower the levels of heavy metals in motorway stormwater. The natural zeolite mordenite was not as effective and the uptake of heavy metals appeared to be inhibited by other dissolved components in motorway stormwater. The synthetic zeolite MAP was very good at removing the studied heavy metals but the effect of high levels of released sodium, removed calcium and an increase in solution pH need to be considered further.

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