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Hydrous iron oxide for removal of inorganic contaminants in simulated stormwater: A batch sorption kinetics study

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Abstract−Urban stormwater runoff, which consists of inorganic and organic contaminants, is a major source of pollutants to receiving waters and therefore they need to be removed. Simultaneous removal of contaminants, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} (heavy metal cations), and SeO_4^{2-} (oxyanion) from a simulated stormwater by a hydrous ferric oxide (HFO) was studied in batch and column sorption experiments. In the batch experiment the rate of sorption of the ions was rapid at the beginning and reached equilibrium in approximately 300 min. The amounts of ions sorbed were proportionate to the respective initial concentration of the ions added to the HFO. Cluster analysis showed that all heavy metals had similar sorption behavior, whereas Se had a distinctly different sorption process. Of the three different kinetic models tested the pseudo-first order kinetic model fitted the data the best. The column experimental results beyond 180 min were consistent with those of the batch experiment that the removal efficiencies of the ions were in proportion to the ion concentration in the feed. Below 180 min, Cu appeared to be preferentially removed than Zn.

Key words: Sorption Kinetics, Hydrous Ferric Oxide HFO, Stormwater, Inorganic Contaminants, Heavy Metals

INTRODUCTION

Urban stormwater runoff is comprised of numerous micro-pollutants such as heavy metals, hydrocarbons, pharmaceutical care products and pesticides, derived from a variety of sources including building materials, vehicular movement, and human activities. Among the contaminants, the inorganic ones, Cd, Cu, Ni and Zn (heavy metals) and Se (non-metal) are commonly found to be in high concentrations to cause toxicity to living organisms and therefore they are of concern. Inorganic contaminants, unlike organic contaminants, are not biodegradable and therefore can accumulate in the environment for a long time. At elevated concentrations, they can cause both short-term (acute toxicity) and long-term (e.g., carcinogenic damages) damage to aquatic organisms and through the food chain to animals and humans. For example, in freshwater animals, chronic exposure to Cd, and Cu and their secondary metabolites may cause immuno-suppression, vertebral deformities and neurological disorder in both the peripheral and central nervous system [1], while Cd is known to enhance lipid peroxidation by increasing the production of free radicals in the lungs, which leads to tissue damage and cellular death [2,3]. Excessive concentration of Ni reduces skeletal calcification and diffusion capacity of gills, and affects protein metabolism [4], while selenium can cause selenosis leading to gastrointestinal disorder and neurological damage in humans [5]. Due to their toxicity, the discharge of these contaminants to natural water bodies may cause physical, chemical, as well as biological impacts on the environment both in the short-term and in the long-term and therefore they should be removed.

There is a dual objective in stormwater management: a) to reduce peak discharges and flooding, and b) to improve the quality of stormwater runoff. While historically the focus has been on the former, in recent times there are increasing numbers of treatment measures to improve the quality of stormwater runoff. These systems include sediment traps, gross pollutant traps, permeable pavements, grass swales, bio-retentions and constructed wetlands. In general, these systems are not effective in the removal of inorganic contaminants such as heavy metals, dissolved nutrients (mainly nitrogen), dissolved organic matter and pathogens. Apart from this, a key drawback of the current range of stormwater management treatment systems is that they are less reliable and requires continuous ongoing maintenance to ensure the performance rates.

Different types of treatment processes have been developed to remove inorganic contaminants from stormwater runoff, including physical and chemical treatments, such as conventional filtration, ion exchange, and membrane filtration system [6-8]. Among them, sorption processes have been recognized as efficient and economic methods of removing these inorganic contaminants from stormwater.

Both locally and commercially available materials are used as sorbents in removing contaminants present in stormwater. Such sorbents include sand and sorbents prepared by coating sands, sorbents obtained from waste materials, and natural materials such as oxides and hydroxides [9-12]. During the last few years, hydrous ferric oxide (HFO) has been used commercially as a porous iron oxide sorbent to remove inorganic contaminants such as Ni, Zn, Cu, Se and Pb [13,14]. Studies on sorption of inorganic ions on HFO have demonstrated that sorption occurs in two steps: i) a rapid surface exchange or sorption, followed by ii) a very slow uptake that may continue for days to years [15,16]. The rapid sorption of inorganic ions on sorbents including HFO proceeds by the formation of inner (specific sorption) or outer surface (non-specific sorption) complex formation on the sorbents [17]. The slow uptake has been

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characterized as i) substitution for a matrix ion (lattice penetration), ii) entrainment of ion into the solid phase through the aging process (i.e., recrystallization), and iii) diffusion into pores [7,18,19].

Earlier studies were limited to removal of individual ions or a combination of few ions [20]. Only few studies have been reported on the use of HFO to remove a mixture of ions from stormwater runoff [21,22]. The presence of one ion may enhance or reduce the sorption of another [23,24]. The reduction of sorption of one ion by another is commonly explained as due to competition of the ions for sorption sites when these sites are limited in comparison to the quantity of ions in solution [25], and enhancement of sorption is probably due to sorption of one ion providing more charges for sorption of another ion of opposite charge (e.g., anion sorption increasing cation sorption [26]. It is therefore important to understand and quantify the heavy metal cations and oxyanions removal properties of sorbents when these ions co-exist. Predicting the rate at which these contaminants are removed in a given solid/solution system such as the HFO/stormwater system is one of the crucial factors for the effective sorption system design [27,28].

This study focused on the simultaneous sorption of a number of inorganic contaminants of concern (Cd, Cu, Ni, Zn and Se) on HFO from an urban stormwater runoff sample spiked with these contaminants. Batch and column kinetic sorption experiments were performed to evaluate the sorption rate and capacity of HFO for these contaminants. The sorption data is explained with the help of cluster analysis and different kinetic models.

MATERIALS AND METHODS

1. Batch Sorption Kinetics

The batch kinetic experiments were carried out for a mixture of four heavy metals (Cd, Cu, Ni, Zn) and an (Se) in 150 mL screw cap top borosil glass bottles at 25±2 °C. Before the test was conducted, all batch reactors and sample collecting tubes were soaked overnight in 10% (v/v) HNO_3 solution, triple rinsed with deionized water and dried in an oven at 105 °C to remove metal impurities in the glassware. Each bottle contained 1.5 g HFO of 175-300 μm in size, purchased from Sigma Aldrich (USA) to obtain 10 g/L sorbent dosage in 150 mL solution. X-ray diffraction analysis indicated that the HFO was amorphous with the presence of some nanosize iron oxide particles.

Stormwater was collected from a canal in a residential area south of Sydney, Australia. This stormwater had a low concentration of heavy metals and it was spiked with Cu, Cd, Ni, Se and Zn to produce the same concentrations as commonly occurs in stormwater [29]. The final ionic concentrations were: Cu 1,250 μg/L; Cd 125 μg/L; Ni 120 μg/L, Se 120 μg/L, and Zn 5,500 μg/L. The metals and Se of predetermined concentrations were premixed in a vessel by using their corresponding metal chlorides and SeO_2. The desired concentrations of these elements for the batch sorption study were obtained by diluting the stock solution. The pH of the mixed solution was 5.6 but adjusted to 6.8±0.2 by adding dilute NaOH solution. Premixed metal solution was used in the experiments in order to avoid the possibility of preferential sorption of any heavy metal type or Se that may have occurred if added separately. A blank solution containing, an equal amount of HFO as the test sample was mixed with 150 mL of milliQ water and shaken along with sample bottles. All samples were kept in a shaker at 25±2 °C, rotated at 100 rpm and 1 mL sub-samples were withdrawn from the original sample at time intervals of 0 (taken at the start of the experiment typically between 0 and 10 min), 30, 60, 120, 240, 480, 960 and 1,920 min. Each sub-sample was diluted to 10 mL and filtered through a 0.45 μm filter. The filtrates were finally analyzed using ICP/MS (Perkin Elmer). Fig. 1 shows the schematic of the batch experiment.

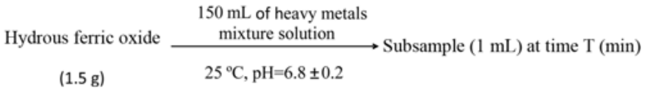


Fig. 1. Schematic of batch experiment.

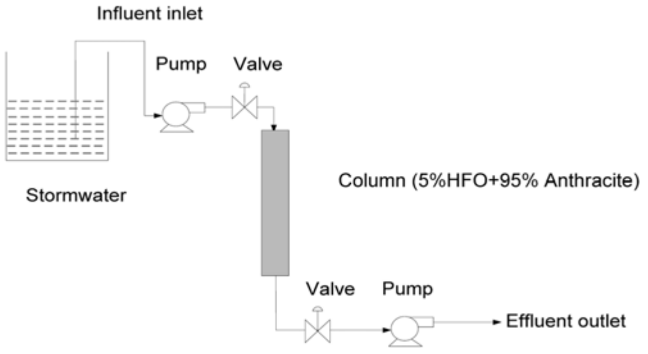


Fig. 2. Column setup.

2. Column Sorption Kinetics

Stormwater having low concentrations of contaminants was collected from stormwater channels and was spiked with Cu, Cd, Ni, Se and Zn to produce the same concentrations of the contaminants as in the batch study. A Perspex column with an internal diameter of 3.2 cm and a height of 30 cm was filled with a media containing a mixture of 5% HFO and 95% anthracite (Fig. 2). This ratio was selected because of the need to minimize the amount of HFO out of economical considerations and yet produce a good result. The media was well mixed before packing in the column. Anthracite was chosen as filling materials due to its inert property towards heavy metals and Se. The column had ports for influent feeding, and effluent collection.

The experiment was conducted by passing the simulated stormwater influent through the column at a rate of 1 m/h using a peristaltic pump (Masterflex) continuously for 8 h. The effluents were collected at intervals of 10 min, 30 min and afterwards every 1 h. The collected samples were filtered through 0.45 μm filter disks and analyzed for the contaminant ions using ICP/MS (Perkin Elmer).

RESULTS AND DISCUSSION

1. Batch Sorption Kinetics

The solid phase sorbate concentration, qe (μg/g) was evaluated by analyzing the corresponding sorbate concentrations before and after sorption using the following equation:

$$\mathrm{qe}=\frac{\mathrm{Co}-\mathrm{Ce}}{\mathrm{X}} \tag{1}$$

where Co and Ce are the initial and equilibrium sorbate concentra-

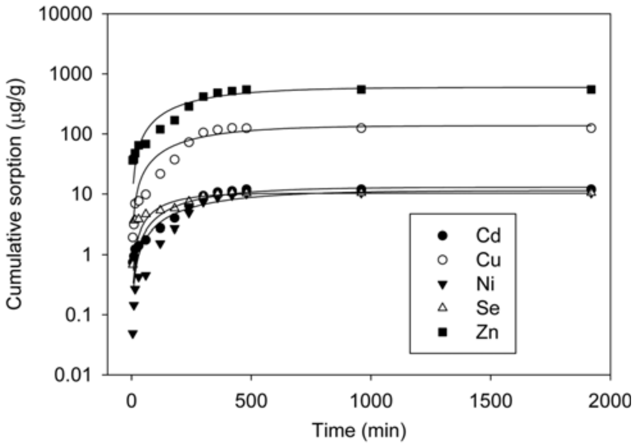


Fig. 3. Cumulative sorption of Cd, Cu, Ni, Se and Zn on HFO.

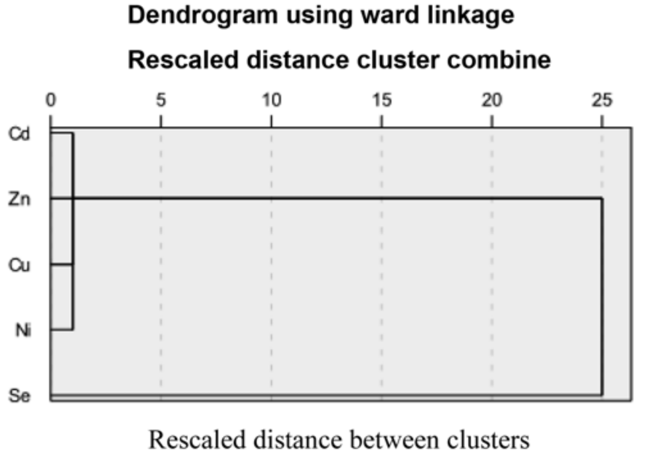


Fig. 4. Similarities and dissimilarities in sorption process between the contaminant ions.

tions in solution (μg/L), and X is the sorbent dosage (g/L).

The data on the cumulative sorption of the different inorganic ions onto HFO with time was fitted with a simple nonlinear regression equation, the exponential rise to maximum [$f=a_*(1-\exp(-b_*x))$], using Sigma-Plot (where a and b are constants), x represents time (min) and f represents the cumulative sorption (Fig. 3). A rapid sorption of the ions occurred at the beginning followed by saturation after approximately 300 min. The amounts of ions sorption were in the order Zn>Cu>Cd, Ni, Se, which followed the order of decreasing concentration of ions in the stormwater sample used in this study. This sorption trend, which closely follows the ionic concentrations in the feed, indicates that there was no marked competition between the ions for sorption. The absence of significant competition may be because the amounts of ions sorbed were low (<500 μg/g) in comparison to the available sites for sorption in HFO. The sorption densities are much lower than the sorption capacity of 40,000 μg/g for Cu and Ni sorption at pH 6.8 on a crystalline Fe oxide reported by Sen et al. [30]. More than 90% of each of the ions in solution was sorbed probably because of surface precipitation at the close to neutral pH used in the study.

1-1. Cluster Analysis

To differentiate the sorption processes among the contaminant ions, a multivariate analysis (cluster analysis using Ward's method [31,32] with a measure of the square of Euclidean distance with Z score normalisation) was conducted on the data.

Cluster analysis, also called data segmentation, is the grouping of a set of observations into subsets (called *clusters*) so that observations in the same cluster (subsets) are similar in some behavior and closely related to one another than observations assigned to different clusters. Hierarchical algorithm was used to establish clusters. Hierarchical clustering creates a hierarchy of clusters which may be represented in a tree structure called a dendrogram. The root of the tree consists of a single cluster containing all observations, and the leaves correspond to individual observations. Algorithm used for hierarchical clustering was *agglomerative*, in which one starts at the leaves and successively merges clusters together [33].

Ward's linkage is a method for hierarchical cluster analysis [34, 35]. Ward's function specifying the distance between two clusters is computed as the increase in the "error sum of squares" (ESS) after fusing two clusters into a single cluster in successive clustering steps so as to minimize the increase in ESS at each step. The distance between two points was measured by the Euclidean distance (ordinary distance between two points and is given by a Pythagorean formula ($p^2+b^2=h^2$, where p and b are length of two sides of a triangle and h is the hypotenuse). Fig. 4 shows the dendrogram obtained for the current sorption data. The X-axis in the dendrogram represents rescaled distance between the clusters.

The dendrogram obtained produced two clusters for broad distinction between the contaminant ions. The first cluster had Cd, Cu, Ni and Zn. The second cluster had Se. All these ions are known to be sorbed on metal oxides initially at the surfaces followed by possibly slow intra-particle diffusion in the interior of the particles (16, 30). As Se is sorbed as an oxy-anion (SeO_4^{2-}), it might have had a different kinetics of sorption than the heavy metal cations, Cd, Cu, Ni and Zn and hence present in a different cluster in the dendrogram. The heavy metal cations have similar sorption mechanisms and therefore grouped themselves into the same cluster. Despite the surface diffusivity of the heavy metal cations in HFO known to be different (10^{-11} to 10^{-15} cm^2/sec, [16]), these cations grouped themselves in a single cluster. Perhaps within the 15 hours of the sorption trial in the current study the diffusivity of these ions was very low and might not have been very different between the ions.

In terms of the electronic structure of the elements, Cd, Cu, Ni, and Zn belonged to the d-block elements in the periodic table and have similar electronic behavior, whereas Se belongs to the 4p block. The different electronic configuration of these elements might have also affected sorption behavior and separated Se from the rest of the ions in the cluster analysis.

1-2. Kinetic Models

A number of predictive kinetic equations have been used in the literature to quantify the sorption of elements and its associated rate constants. In the current study, three equations were evaluated for their ability to model the rate of sorption of contaminant ions onto HFO: the pseudo-first order, pseudo-second order and Elovich equations. The pseudo-first and pseudo-second order equations are similar to the first- and second-order equations except that they are based on sorption capacity (solid/liquid phases), whereas the latter equations are based on solution concentrations (liquid-phase systems).

Table 1. Physio-chemical characteristics of stormwater collected for this study

Parameters	Unit	Range	Average value
pH	-	6.68-7.28	7.0
TOC	mg/L	3.48-9.52	5.7
COD	mg/L	30-65	40.0
Turbidity	NTU	2.5-40	25.4
Total suspended solids	mg/L	0.5-28	7.9
Conductivity (EC)	dS/m	0.13-0.97	0.74
True colour	PtCo	28-270	85.6
Bicarbonate	mg/L $CaCO_3$ equivalent	30-95	72.5
Total dissolved salts	mg/L	90-660	503.3
Water hardness	mg/L $CaCO_3$ equivalent	22-135	95.7
Dissolved salts			
Potassium	mg/L	0.5-7.9	6.3
Sodium	mg/L	6.4-126.0	88.1
Calcium	mg/L	7.2-32.2	25.3
Magnesium	mg/L	1.0-13.3	9.9
Chloride	Mg/L	17-176.4	129.4
Sulphate	mg/L SO_4^{2-}	3.6-86.2	51.2
Metals			
Cadmium	mg/L	0.001-0.002	0.001
Copper	mg/L	0.029-0.049	0.020
Iron	mg/L	0.53-2.55	0.65
Nickel	mg/L	0.002-0.10	0.038
Lead	mg/L	0.019-0.022	0.020
Selenium	mg/L	0.001-0.004	0.002
Zinc	mg/L	0.026-0.123	0.041

The raw stormwater was spiked to increase the concentrations of Cu, Cd, Ni, Se and Zn, see section 2.1 and 2.2

The reaction rates in pseudo-first and pseudo-second order models depend on the effective concentration of the sorption sites available on the adsorbent surface.

The pseudo-first order equation is expressed as:

$$\frac{dq_t}{dt} = k_{p1}[q_e - q_t] \tag{2}$$

where k_{p1} (1/min) is the pseudo-first order rate constant, q_t (μg/g) is the accumulation of sorbate ion at time t (min), q_e (μg/g) is the maximum ion sorption at equilibrium.

The pseudo-second order equation is expressed as:

$$\frac{dq_t}{dt} = k_{p2}[q_e - q_t]^2 \tag{3}$$

where k_{p2} (g/μg/min) is the second-order rate constant, q_t (μg/g) is the accumulation of metal at time t (min), q_e (μg/g) is the maximum metal sorbed at equilibrium.

The simple Elovich equation can be expressed as;

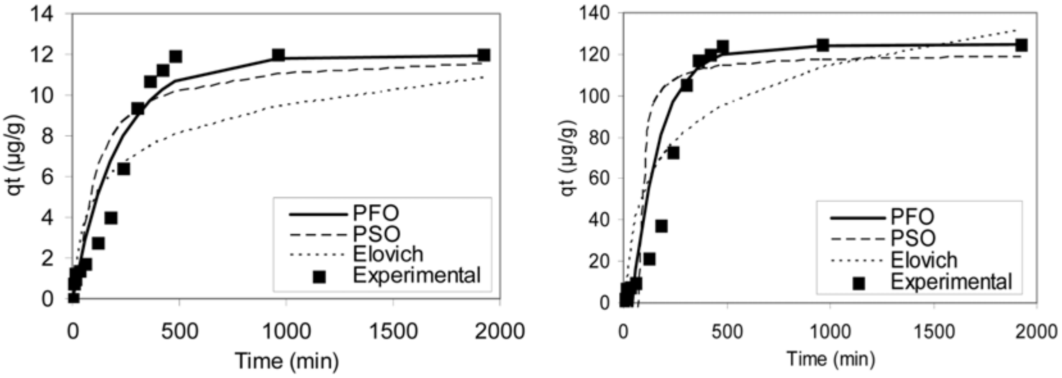
$$q_t = \alpha \ln(a\alpha) + \alpha \ln t \tag{4}$$

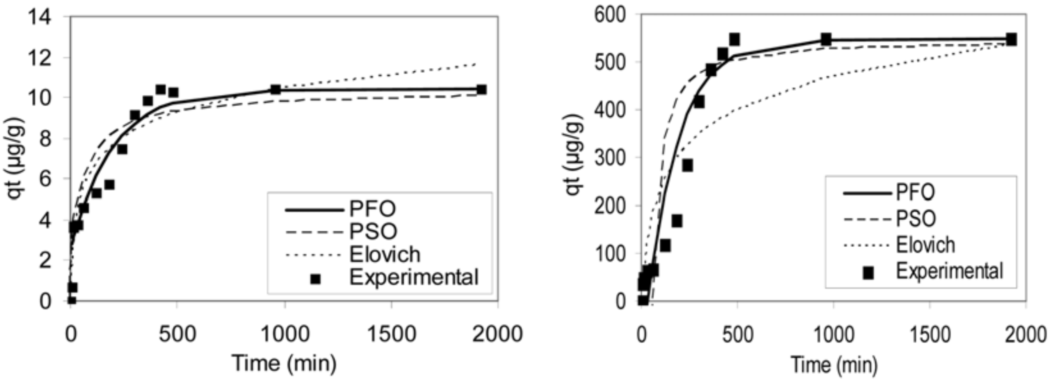
where α is the initial sorption rate μg/g/min and a (g/μg) is the desorption constant. This equation describes the kinetics where the rate of sorption decreases exponentially with an increase in the amount of sorption.

The above three kinetic models were tested to determine the model that fit best to the cumulative sorption data for each contaminant ion. Table 2 summarizes the model constants and coefficient of deter-

Table 2. Coefficient of determination (R^2) and rate constants (k_{p1}, k_{p2} and a) obtained from the kinetics model fits to the sorption data

Contaminant	Pseudo-first order kinetics (PFO)		Pseudo-second order kinetics (PSO)		Elovich kinetics	
	k_{p1} 1/min	R^2	k_{p2} (g/μg/min)	R^2	*a* (μg/g/min)	R^2
Cd	0.0067	0.82	0.00010	0.66	2.00	0.70
Cu	0.0076	0.89	0.00039	0.69	26.26	0.72
Ni	0.0063	0.88	0.00017	0.70	1.76	0.80
Zn	0.0060	0.88	0.00005	0.67	101.82	0.72
Se	0.0062	0.87	0.00333	0.66	1.76	0.80


(a) Cd (b) Cu


(c) Ni (d) Zn

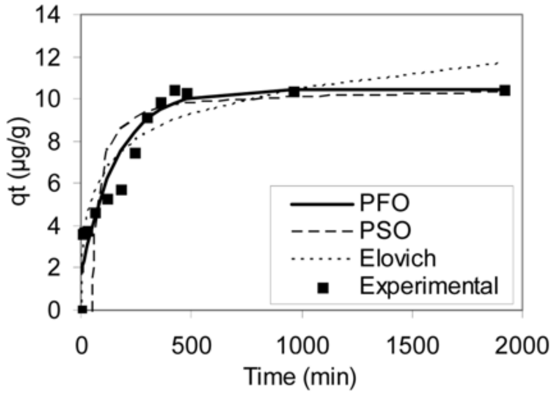

(e) Se

Fig. 5. Kinetic plots for the contaminants (a) Cd, (b) Cu, (c) Ni, (d) Zn, (e) Se sorption on HFO and model (pseudo-first order (PFO); pseudo-second order (PSO); Elovich) fits to the data.

minations (R^2) for the data fits. This table and Fig. 5 show that the pseudo-first order kinetic model fitted the data the best (R^2=0.82-0.89 compared to R^2=0.66-0.80 for the other two models). The results are in agreement with those of Farley et al. [36] on heavy metal sorption on metal oxides where it was reported that at low concentrations of metal ions the kinetics of sorption followed first-order kinetic model. Ho and McKay [37] reviewed over 250 sorption studies in literature, including sorption of heavy metals and oxyanions on different materials, and found that in the majority of the studies the kinetics of sorption fitted the first-order kinetic model. However, other kinetic models were not tested in most of these studies. The values for the constants (k_{p1}, k_{p2}, α) derived from the models (Table 2) relate to the experimental conditions used in the study such as sorbate concentration, solution pH, temperature and agitation rate and expected to change with change in these conditions [27].

At longer sorption times, the Elovich equation ignores the simultaneously occurring desorption process [27]. Therefore, the applicability of the Elovich equation is restricted to the initial times of sorption processes when the system is relatively far from equilibrium. Accordingly, at times close to equilibrium the fit of the data to Elovich equation became poor, as can be seen for Ni and Se at and above 1920 min (Fig. 5).

At shorter sorption times, the ions are removed mostly by the surface sorption and at longer sorption times (beyond 1-10 days) by intra-particle diffusion [38]. Within the 15 hr of the sorption period used in the current study, it is unlikely that significant amounts of

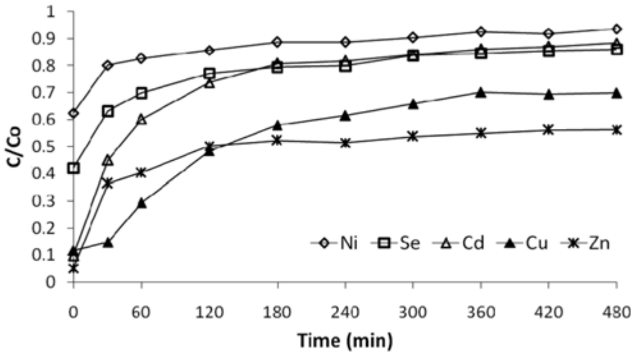


Fig. 6. Breakthrough curves for contaminants removal by HFO.

the ions diffused into HFO, and therefore diffusion models were not considered.

2. Column Sorption Kinetics

The breakthrough curves show that C/C_0 beyond 180 min followed the order Ni, Cd, Se>Cu>Zn, which is the reverse order of the concentration of these ions in the feed. This shows that the higher the concentration in the feed, the higher the removal of these ions by the HFO column. Therefore, at times greater than 180 min there is no marked competition between these ions. The C/C_0 pattern was different at times<180 min for Cu and Zn. At these times the proportion of Cu removed was higher than Zn even though the Cu concentration in the feed was approximately five times less than Zn. This may be because of the presence of some nano size iron oxide particles in HFO (see Materials and Method section) which have high affinity for Cu than Zn [39]. At longer times the sorption capacity of these nano size iron oxides might have exhausted, leaving the bulk of the HFO, which has a lower sorption affinity than the nano size particles to sorb the ions.

3. Field Application of the Study

Stormwater consists of a wide range of anthropogenic contaminants, some of which are not effectively removed by current stormwater treatment measures. These contaminants include inorganic contaminants such as heavy metals, oxyanions and dissolved nutrients (mainly nitrogen), organics and pathogens. A typical stormwater treatment system usually consists of a treatment train or a series of treatment measures. Each treatment measure within the treatment train removes particular contaminants. This study shows that columns of HFO can effectively remove heavy metals and oxyanions. A filter media containing HFO can be used within a treatment train to remove these inorganic contaminants. This filter media can be applied within a treatment train where other treatment systems are used to remove other contaminants of interest such as nutrients and organics to produce high quality effluent.

CONCLUSIONS

This study examined the simultaneous sorption of some common stormwater inorganic contaminants (Cd, Cu, Ni, Se and Zn) on HFO. The results suggested that these contaminants' sorption was rapid at the beginning followed by a slow process. Both the batch and column experiments showed that the amounts of ions removed by HFO were proportionate to amounts added to HFO. This suggested that there was no marked competition between the contaminants for sorption on HFO, probably because the amounts of sorbates in solution were much lower than the sorption sites available on the sorbent. Cluster analysis suggested that the heavy metals, Cd, Cu, Ni and Zn had similar kinetic processes, whereas Se, which was present as an oxyanion (SeO_4^{2-}), appeared to have had a different process. Three kinetics models (pseudo-first order, pseudo-second order, and Elovich) were tested to explain the data. The pseudo-first order kinetic model fitted the data the best.

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