

HEAVY METAL REMOVAL FROM STORMWATER RUNOFF BY SORPTION

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ABSTRACT

In this study, several sorbents (i.e. alumina, activated bauxsol coated sand (ABCS), bark, bauxsol coated sand (BCS), fly ash (FA), granulated activated carbon (GAC), iron oxide coated sand (IOCS), natural zeolite (NZ), sand, and spinel) are investigated with the long-term goal of developing a feasible technology for heavy metal removal during secondary treatment of stormwater. The sorbents are tested in batch tests for their As, Cd, Cr, Cu, Ni and Zn removal efficiency from synthetic stormwater samples, where all of these metals co-existed at a starting pH of 6.5. It is found that each sorbent has different affinity to the heavy metals, with heavy metal cations (i.e. Cd, Cu, Ni and Zn) removed more effectively than heavy metal anions (i.e. As and Cr) by all sorbents except IOCS, which has a high affinity towards As. The results further indicated that alumina and BCS outperform the other sorbents, possibly due to high surface area of alumina and the favourable sorption sites of BCS; whereas NZ, sand and bark were the least efficient. On the other hand, although FA effectively retained Cd, Ni and Zn, the leaching of As, Cr, and Cu is a concern.

KEYWORDS

Heavy metal; Sorption; Filtration; Stormwater runoff; Multiple sorbents

1 INTRODUCTION

Urban stormwater runoff, especially road runoff, is rich with heavy metals that, unlike other organic pollutants, are not degradable in the environment. Moreover, due to accumulation they can cause both short and long term toxicity. Urban runoff is also a significant source of heavy metals observed in sediments [1]. Thus, special interest should be directed to heavy metal removal to reduce their concentrations to acceptable levels to protect the quality of receiving waters [2]. When treating urban stormwater a common approach is to detain the water in wetlands or basins, followed by treatment through sand filtration [3]. Nevertheless, settling based stormwater treatment facilities and sole sand filtration fail to specifically target the colloidal and dissolved metal species. Hence, there is a need for secondary treatment of stormwater.

Filtration of the stormwater, where heavy metals including dissolved fractions are primarily removed via sorption, is one of the most promising technologies. Furthermore, several low cost sorbents are already available or can be developed as filtration media, and the method can readily be combined with other methods [1]. Here, 10 sorbents have been selected to be

tested in batch experiments for heavy metal removal. These sorbents are: activated bauxsol coated sand (ABCS), alumina, bauxsol coated sand (BCS), bark, fly ash (FA), granulated activated carbon (GAC), iron oxide coated sand (IOCS), natural zeolite (NZ), sand, and spinel ($MgAl_2O_4$). These sorbents are used for the simultaneous removal of As, Cd, Cr, Cu, Ni and Zn, as dissolved fractions of these metals reportedly pose environmental concerns [4]. Consequently, the primary purpose of this study was to compare these 10 sorbents in terms of their heavy metal removal efficiency and then select the most promising ones for further investigation before running more costly and time consuming column and field tests.

2 MATERIALS AND METHODS

As discussed previously, 10 different sorbents presented in Table 1 are used in batch tests to study their heavy metal removal pattern. All sorbents are sieved (or crushed if required) to the desired particle size of 0.6-1 mm and dried at 40 °C for 3 hours without additional treatment before being used in batch experiments, except for sand which is first acid washed for 24 hours. Adsorption experiments were carried out using synthetic stormwater samples in 50 mL

Table 1. Overview of the sorbents used in the study.

Sorbent	Supplier	pH _{pzc} ¹	Par. size, mm	Surface area ²	Literature
GAC	Kemira, Denmark	6.1	0.6-1.0	784.5	[5]
ABCS	Vireotec, Australia	~8.3 ³	0-0.5	42.2	[6]
NZ	Euremica, UK	5.6	0-1.0	24.2	[7]
Bark	Zugol, Sweden	-	0.6-1.0	0.32	[8]
Alumina	Haldor Topsøe, DK	9.1 ⁴	0.6-1.0	238.9	[9]
BCS	Vireotec, Australia	~8.3 ³	0-0.5	4.6	[6]
Fly ash	MSWI, Denmark	6.2	0-0.5	2.5	[10]
Spinel	Haldor Topsøe, DK	-	0.6-1.0	11.8	-
Sand	Dansand, DK	0.7	0.6-1.0	0.1	[11]
IOCS	Prepared in the lab	~9	0.6-1.0	1.5	[12]

¹Point of zero charge, ²BET-N₂ single point analysis (m²/g), ³pH_{pzc} of red mud from [13], ⁴from [14].

Table 2. Initial concentrations (C_0) of the heavy metals used in the experiments.

	Heavy metals and initial concentrations (µg/L)					
	As	Cd	Cr	Cu	Ni	Zn
DDV ¹	4	5	7	12	160	110
Batch 1	0.9	0.1	0.4	2.6	0.6	22.5
Batch 2	2.6	3.0	3.5	7.6	12.3	67.6
Batch 3	14	10.4	18	36.1	58.9	340
Batch 4	23	23.1	34.2	20.4	89.9	543
Batch 5	52	221	376	588	178	1350
Batch 6	128	160	212	246	545	3400
Batch 7	396	735	784	1250	2220	13700
Batch 8	1000	2670	2830	1820	8640	52300

¹Danish discharge values [15].

conical PE flasks at room temperature (22 ± 1 °C). The required concentrations of As, Cd, Cr, Cu, Ni and Zn samples were obtained by step-by-step diluting their commercial stock solutions at 1000 mg/L to the desired concentrations (see Table 2). The ionic strength of the water samples was controlled using 0.01 M NaCl, and all samples had 3 mM NaHCO₃ to minimize the pH changes during the experiments. All the samples were sent to a commercial laboratory (Analytica, Sweden) for quantifications of heavy metal concentrations. Solution pH values were measured potentiometrically.

3 RESULTS AND DISCUSSIONS

The results of simultaneous removal of As, Cd, Cr, Cu, Ni and Zn using alumina, ABCS, bark, BCS, FA, GAC, IOCS, NZ, sand and spinel are presented in Figures 1-6, where effluent heavy metal concentrations (C_e , µg/L) are depicted on the x-axis vs. the solid phase metal concentrations (q_e , µg/g) on the y-axis. Sorbed amount of heavy metal is determined for each sorbent by simply the equation [1].

$$q_e \approx (C_0 - C_e) / X, \quad (1)$$

where C_0 and C_e are the corresponding heavy metal concentration in µg/L before and after the treatment, respectively, and X is the amount of sorbent used in g/L.

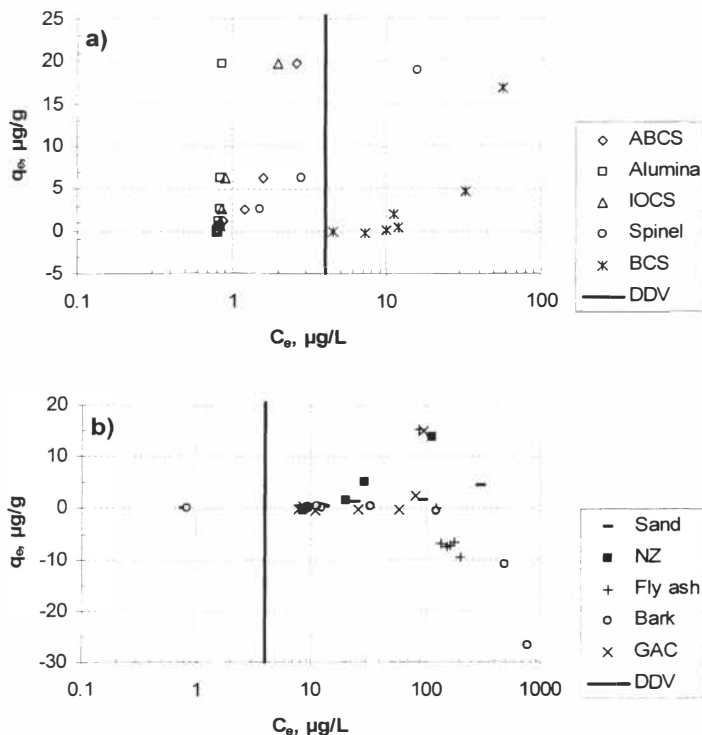


Figure 1. As removal from water using several sorbents: a) sorbents with high As removal efficiency, b) sorbents with moderate or low As removal efficiency.

The amount of heavy metal sorbed increases with increasing initial heavy metal concentration in nearly all of the batches as expected, possibly due to the enhanced mass transfer [16]. However, it can be seen from Figures 1-6 that, while some of the sorbents (i.e. alumina, BCS, GAC) removed the heavy metals very effectively; surface saturation or a monolayer of a sorbate is not observed in many cases at the experimental conditions used. This is primarily due to the fact that the initial heavy metal concentration ranges in relation to the sorbent dosages were not sufficiently high, again, in an attempt to resemble real life stormwater conditions.

3.1 Simultaneous removal of the heavy metals using several sorbents

3.1.1 Alumina

At the experimental conditions used alumina removed As, Cd, and Ni below the Danish discharge values [15] (see Table 2) as can be seen from Figures 1, 2 and 5. The removal efficiency is respectively largely independent of the initial heavy metal concentration. The alumina surface is expected to be positively charged at the experimental pH (note that the pH_{pzc} of alumina is about 9, but decreases when forming hydroxides), which enhances As and Cr removal. Surprisingly, alumina performed equally well for the Cd, Cu, Ni and Zn.

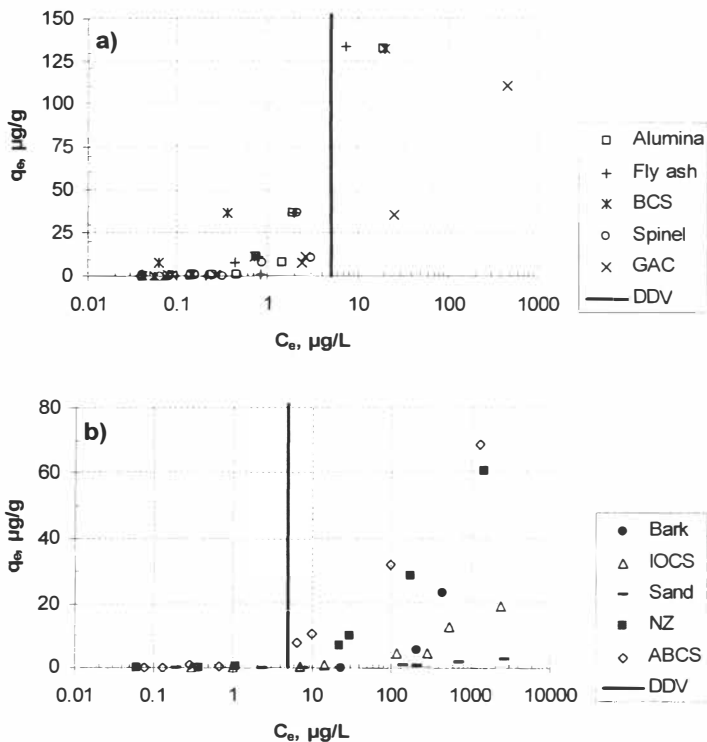


Figure 2. Cd removal from water using several sorbents: a) sorbents with high Cd removal efficiency, b) sorbents with moderate to low Cd removal efficiency.

3.1.2 Activated bauxsol coated sand (ABCS) and bauxsol coated sand (BCS)

The heavy metal removal efficiencies of BCS and ABCS towards the heavy metals are given in Figures 1-6. It is evident that, ABCS efficiently retains As and Cu in the presence of the other heavy metals to values below the Danish discharge standards, but the sorbent fails to remove Cr, Cd, Ni and Zn as efficiently as As and Cu. This is probably due to the fact that during the activation of seawater neutralized red mud (bauxsol) (the raw material of BCS and ABCS), while the reactive surface charge increased and the equilibrium pH decreased, several minerals in the Bauxsol that carry a negative surface charge at near neutral pH values are also destroyed. This postulation is supported by the observation that BCS performs significantly better than ABCS for removing the cations like Cd, Ni and Zn.

3.1.3 Bark

Bark is tested in several studies for heavy metal removal as a cost-effective alternative to AC [17]. In this study bark suffered from low efficiency for all heavy metals, especially for As

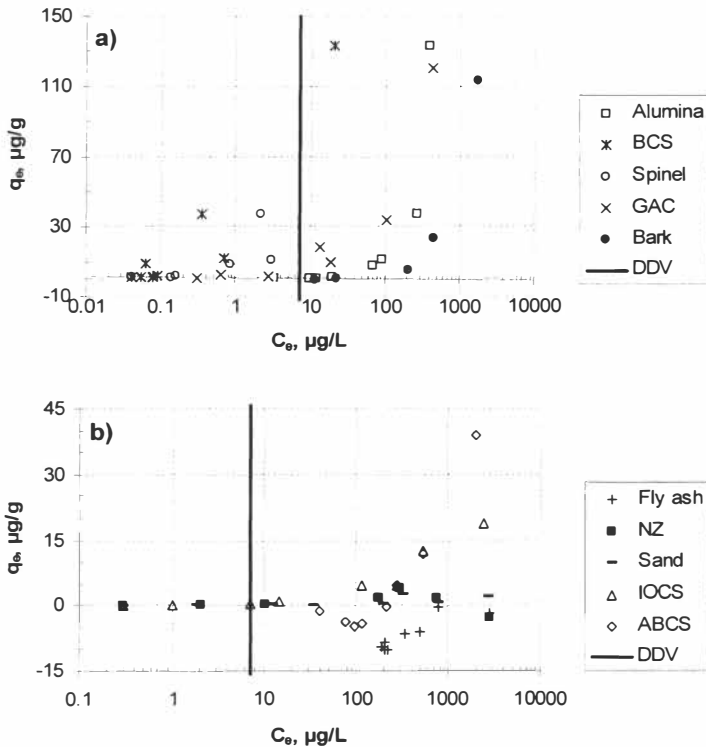


Figure 4. Cr removal from water using several sorbents: a) sorbents with high Cr removal efficiency, b) sorbents with moderate to low Cr removal efficiency.

mainly due to leaching. It is noted that, leaching is also observed for Cr at low initial Cr concentrations. Furthermore, water discoloration is observed most likely due to the release of phenols, and although a chemical pre-treatment has been previously recommended to overcome the problem [18], in the current study bark is used without any pre-treatment to keep the sorbent cost low.

3.1.4 Fly ash (FA)

FA is reported to be an efficient scavenger for heavy metals [19]. FA contains carbon, silica, alumina and iron oxides [18], and these oxides are possibly responsible for the heavy metal removal. Similarly, here it is evident from Figures 1- 6 that FA is effective towards the heavy metals. This is, at least partly, due to the fact the FA surface is negatively charged (as the pH_{zpc} of fly ash is 6.2 [10], which in turn favours the heavy metals cation removal, while suppressing As and Cr removal. Indeed, FA has the least affinity to Cr and As, and this poor performance is not only due to the lower affinity towards these anions at the high pH, but also because of significant leaching of these metals from fly ash (see Figures 1, 3), which is significant at the lower initial heavy metal concentrations. It is noted that previously

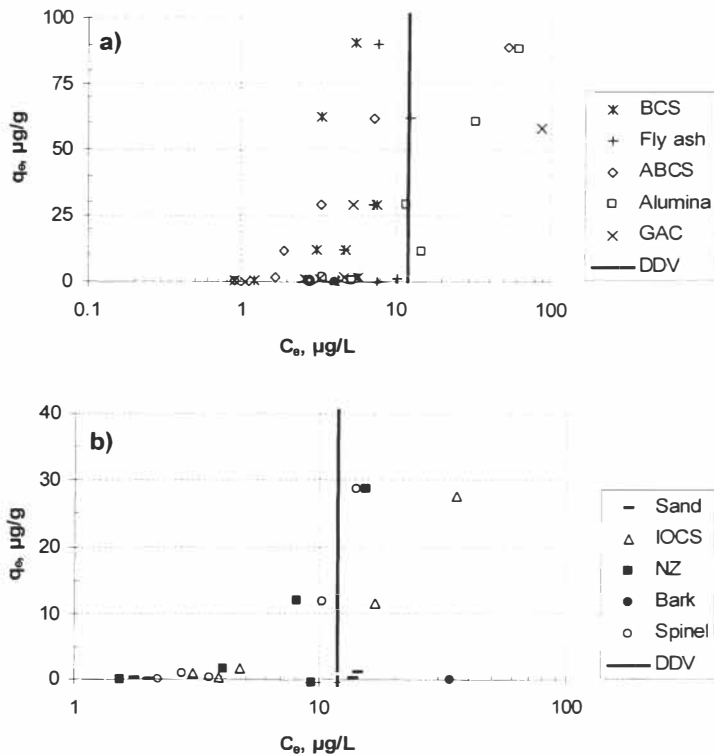


Figure 4. Cu removal from water using several sorbents: a) sorbents with high Cr removal efficiency, b) sorbents with moderate to low Cr removal efficiency.

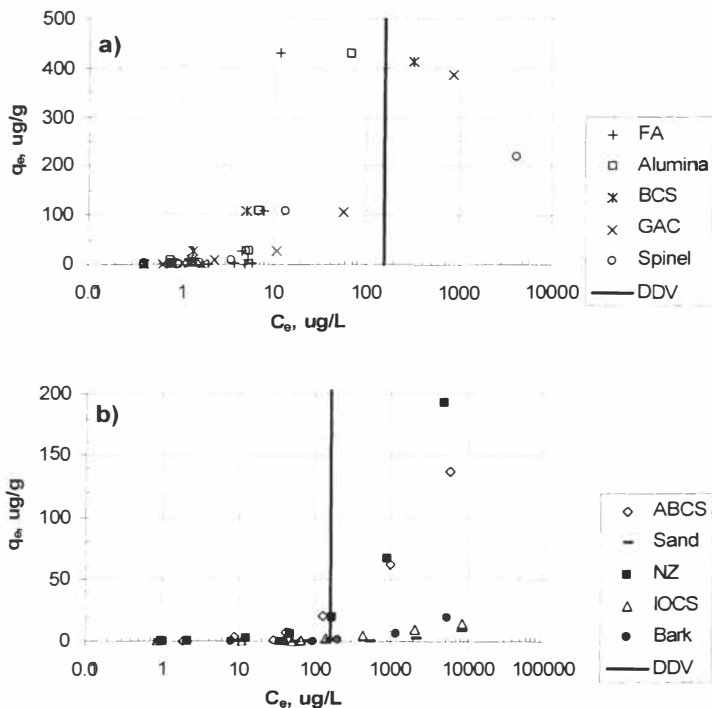


Figure 5. Ni removal from water using several sorbents: a) sorbents with high Ni removal efficiency, b) sorbents with moderate to low Ni removal efficiency.

FA is reported to have very high affinity towards Cr(VI) at acidic pHs [19]. This may be due to the possibility that the leaching of Cr is not significant at very acidic pHs. There are methods to prevent the leaching, but it was beyond the scope of the study to further examine the sorbent.

3.1.5 Granulated activated carbon (GAC)

Activated carbon (AC) and granulated activated carbon (GAC) are often used for organic matter removal, but heavy metal removal using GAC is also advocated [20]. The heavy metal removal using GAC is primarily attributed to its high porosity and high surface area; with the heavy metal ions attaching to the surface binding sites and channels. Here, it is interesting to note that GAC is the most effective sorbent for Cr removal compared with the other sorbents tested, but it has the least affinity to As compared to that of the other heavy metals. The discrepancy may simply be due to the fact that when As and Cr anions compete for the same limited sorption sites, the surface favours Cr anions (note that the opposite is reported for BCS). In addition, it is also clear that Cr and As removal is not due to simple electrostatic attraction. Here, diffusion into pores inside the GAC probably has more effect on the overall heavy metal removal than the negatively charged outer surface.

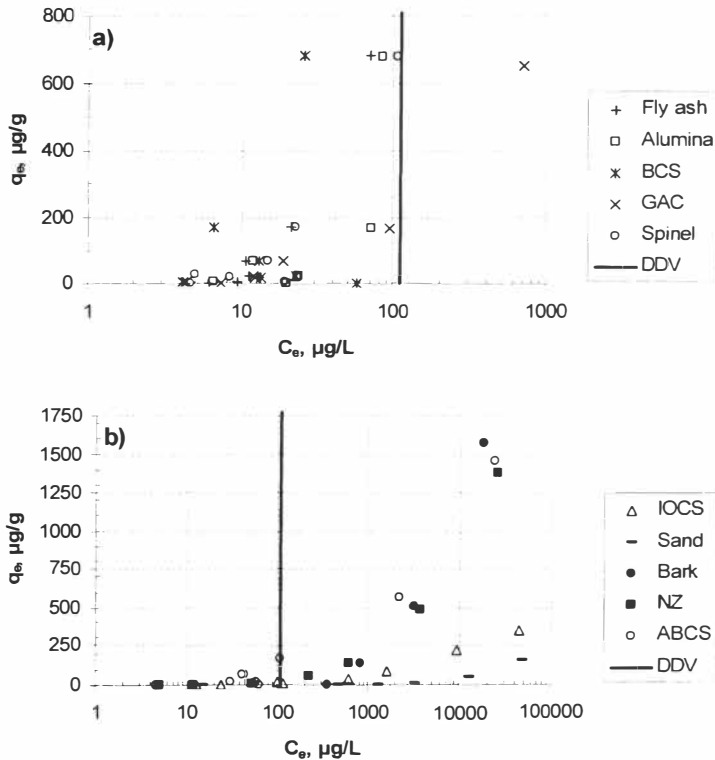


Figure 6. Zn removal from water using several sorbents: a) sorbents with high Zn removal efficiency and b) sorbents with moderate to low Zn removal efficiency.

3.1.6 Iron oxide coated sand (IOCS)

According to the overall heavy metal removal results, IOCS has poor heavy metal removal efficiency compared to that of the other sorbents, except for sand, bark and NZ. Interestingly, here IOCS is the sorbent with the highest affinity to As, and according to the results As is treated to below the Danish guideline values, independent of the initial concentrations (see Figure 1). This is due to the fact that the pH_{pzc} of IOCS is between 8 and 9 [12] and the surface is positively charged at the experimental pH range, which in turn attracts the negatively charged anions like As and Cr. On the other hand, it is found to be the least efficient sorbent for Zn, Ni, and Cd after sand. This is rather surprising, as IOCS has been previously reported to be capable of effectively removing Cu, Cd, Ni and Pb [21]. It is suggested that the observed low heavy metal sorption onto IOCS may be due to the difference on the experimental conditions. Here, electrostatic attraction is postulated to be main removal mechanism for As and Cr. On the other hand, the main removal mechanisms for Cu removal using IOCS is previously postulated as pore diffusion [22], and the same mechanism may be valid here.

3.1.7 Natural zeolites (NZ)

It is observed that NZ has moderate to low affinity towards all heavy metals studied here, and a minor As leaching (at low initial As concentrations) and a moderate Cr leaching (at the highest initial Cr concentration) is observed. According to the supplier information the NZ already had 5mg/kg As and 18 mg/kg Cr. On the other hand, it is also possible that already adsorbed As and Cr (during the treatment) may have been desorbed from NZ when the surface has higher selectivity for any other heavy metal ions that co-exists in the solution along with As and Cr. This is supported by the observation that the affinity of zeolites towards the heavy metals in a decreasing order is Cu, Cd, Zn, Ni, As, and Cr, suggesting the adsorption of heavy metal cations over that of the anions.

3.1.8 Sand

Here, it is found that sand has a minor heavy metal removal efficiency compared to the other sorbents. This is attributed to the very low surface area of sand. Similarly, another study reports minor sorption of heavy metal ions on sand (Ni > Cu > Cd > Cr > Zn) in the absence of As, and at the presence of several other ions [23]. The pertinent data indicates that the magnitude of the heavy metal removal using sorbents prepared from coating a sorbent to sand (IOCS, BCS and ABCS) is significantly greater than that of sand.

3.1.9 Spinel

Spinel has moderate to high heavy metal removal efficiency as can be seen from Figures 1-6. To the authors' knowledge there are no studies reporting the usage of spinel for heavy metal removal, though the results suggest that spinel has higher affinity towards heavy metals compared to NZ, bark, IOCS and sand. The surface area of spinel is not high, but it is highly porous according to the supplier information. Thus, this high porosity may be the main driving force behind the sorption by increasing the internal surface area.

4 CONCLUSIONS

In this study 10 sorbents are tested in batch tests with a long term goal of developing a filter for secondary treatment of stormwater. All sorbents removed the heavy metals (i.e. As, Cd, Cr, Cu, Ni and Zn) but the magnitude of the removal varies to a great extent. For example, while sand fails to remove all heavy metals to acceptable guideline levels, alumina, BCS and GAC can efficiently remove the heavy metals down to guideline values, with some dependence on the initial heavy metal concentration. The sorbents, with the exception of IOCS and sand, have higher affinity to Cd, Cu, Ni and Zn compared to that of As and Cr.

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