Effect of As, Cr, Cd, Ni and Zn on Cu removal using alumina and granulated activated carbon

Effets des paramètres As, Cr, Cd, Ni et Zn sur la remobilisation du cuivre utilisant l'alumine et le carbone activé

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RESUMÉ

Le but global était d'identifier les sorbants les plus appropriés pour être utilisés dans des filtres de traitement des eaux de ruissellement, lesquelles sont riches en métaux lourds. Cet article présente des résultats sélectionnés se concentrant sur l'effet compétitif des métaux lourds présents sur la sorption du Cu sur 2 sorbants (alumina et carbone actif granulé; GAC). Ensuite, les expérimentations ont été conduites utilisant un seul métal (Cu) et cinq systèmes binaires de métaux (Cu+As, Cu+Cd, Cu+Cr, Cu+Ni et Cu+Zn). Dans les 6 systèmes, plus de 99% du Cu a été enlevé par alumina et dans le même temps, 98% du GAC était supprimé. Ces résultats indiquent que l'absorption du CU par l'alumine et GAC n'est, sous condition expérimentale, pas affectée par la présence d'AS, Cd, Cr, Ni et Zn.

ABSTRACT

The overall aim was to identify the most proper sorbent to be used in filters for treatment of road runoff, which is rich in heavy metals. This paper presents some selected results focusing on the competitive effect of co-existing heavy metals to the sorption of Cu on two sorbents (alumina and granulated activated carbon; GAC). Herein, batch experiments were carried out using one single metal system (Cu) and five binary metal systems (Cu+As, Cu+Cd, Cu+Cr, Cu+Ni and Cu+Zn). In all six systems, more than 99% of Cu was removed by alumina, while GAC removed >98%. These results indicate that the sorption of Cu by alumina and GAC is, under the experimental conditions, not affected by the presence of As, Cd, Cr, Ni and Zn.

KEYWORDS

Heavy metals, processes, road runoff, sorption, sorbents.

1 INTRODUCTION

Stormwater constitutes an important part of the global water cycle, and is expected to receive increased attention in the future due to effects from climate change and the high pollutant load. A wide variety of contaminants, such as heavy metals (i.e. As, Cd, Cu, Cr, Ni and Zn) are present in stormwater in quantities that may adversely affect the water quality of receiving waters (Makepeace, 1995). Furthermore, in many cases will the guideline values for what should be discharged into surface waters, according to the Danish Environmental Protection Agency, be exceeded (Danish EPA, 1996).

Treating stormwater which contains heavy metals even at relatively low concentration is important for maintaining a good environmental quality. Best management practices (BMPs) including settling based options (i.e., detention ponds, wetlands) are traditionally applied for stormwater treatment. However, colloidal and truly dissolved metals will not be removed by settling and are consequently directly discharged into surface water bodies or infiltrated into groundwater. Therefore, these approaches will probably not be sufficient in many cases under the upcoming EU Water Framework Directive (European Commission, 2000). Sorption is considered as an efficient treatment method to treat colloidal and dissolved metals in many water and wastewater treatment schemes. A number of sorbents including zeolites, mulch, activated carbon, iron-coated sand, peat, aluminium/iron/manganese oxides have been studied to remove metals from water solution (Färm, 2002; Jang et al., 2005; Naidu et al., 1998; Pitcher et al., 2004; Ricordel et al., 2001). However, most of these studies focused on the single metal removal although the metals such as As, Cd, Cr, Cu, Ni, Zn, co-exist in stormwater and will affect each other in sorption processes. Relatively few studies have been conducted on the simultaneous sorption of several metals (Goel et al., 2005, Genç-Furhman et al,. 2006).

The aim of this study was to investigate how the presence of As, Cd, Cr, Ni and Zn will influence the sorption behaviour of Cu on two promising sorbents; alumina and granulated activated carbon (GAC). Herein, one single metal system (only Cu) and five binary metal systems (Cu+As, Cu+Cd, Cu+Cr, Cu+Ni and Cu+Zn) were designed and the sorption data of Cu in single and binary systems were compared.

2 MATERIALS AND METHODS

2.1 Sorbents

The GAC was supplied by Kemira, Denmark and alumina was supplied by Haldor Topsøe A/S, Denmark. Both alumina and GAC were grinded and sieved to be 0.6-1 mm particle size. The surface characteristics of both sorbents are summarized in Table 1.

Sorbent	pH_{pzc}[a]	Surface Area (m^2/g)
Alumina	9.1[b]	238.9 [d]
GAC	6.15[c]	784.5 [d]

[a] point of zero charge, [b] from Stumm and Morgan, 1996;
[c] from Cheremisinoff & Ellerbusch, 1978; [d] from Genç-Fuhrman et al., 2006

Table 1 Characteristics of alumina and GAC

2.2 Heavy metal concentrations and quantifications

It was aimed to use realistic concentration ranges, where the concentration of heavy metals should be similar to that found in stormwater. The metal chosen for the investigation in single component studies was Cu, whose concentration is designed in accordance to the Cu concentration in stormwater. In binary systems, Cu+As, Cu+Cd, Cu+Cr, Cu+Ni and Cu+Zn were selected, with a 1:1 ratio of mole concentration of metals for comparative purposes. Table 2 presents the design concentration of metals in the 14 batches.

The experimental As, Cd, Cr, Cu, Ni and Zn samples were obtained by step-by-step diluting their commercial stock solution at 1000 mg/L to the desired concentrations. The reagents for pH adjustment was 1 M HCl and 1 M NaOH, which were prepared from concentrated HCl and weighed amount of NaOH by dilution with distilled water.

The metal concentrations in the samples were determined using atomic absorption sepctrophotomer (Perkin-Elmer Model 200, 600 and 5000.

Batch	Cu(µmol/L)	Cu (µg/L)	As(µg/L)	Cd(µg/L)	Cr(µg/L)	Ni(µg/L)	Zn(µg/L)
1	0.6	36.1	42.6	63.9	29.5	33.4	37.1
2	3.9	246	290	435	201	227	253
3	9.3	588	693	1,040	481	543	605
4	19.7	1,250	1,474	2,211	1,023	1,155	1,286
5	28.6	1,820	2,146	3,219	1,489	1,681	1,873
6	62.9	4,000	4,716	7,076	3,273	3,696	4,115
7	125.9	8,000	9,432	14,152	6,546	7,391	8,231
8	251.8	16,000	18,864	28,303	13,092	14,782	16,462
9	393.4	25,000	29,475	44,224	20,456	23,097	25,722
10	503.6	32,000	37,728	56,607	26,184	29,565	32,924
11	708.1	45,000	53,056	79,603	36,821	41,575	46,299
12	1,007.1	64,000	75,457	113,213	52,367	59,129	65,847
13	1,573.7	100,000	117,901	176,895	81,824	92,390	102,886
14	2,360.5	150,000	176,852	265,343	122,736	138,585	154,329

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

2.3 Batch experiment

Sorption experiments were carried out using synthetic stormwater samples (containing 10 mM NaCl, 3 mM $NaHCO_3$ and pH controlled to be 6.5 ± 0.2) in 50 mL conical PE flasks at room temperature (22 ± 1°C). The reason for preparing the synthetic samples was to better define and control the water composition to establish a better understanding of the processes. A shaking time of 48 hours was used to give enough time to reach equilibrium. Each test tube was filled with 50 ml samples of varying concentrations and adjusted to the pH 6.5 by using 1 M HCl or 1 M NaOH. 1 g alumina or 1 g GAC was added into each test tube and shaken at 60 rpm for 48 hours. Afterwards, the samples were separated by centrifugation at 2000 rpm for 20 minutes. The supernatants were transferred and acidified to be pH 1.5 for storage and future measurements. To account for metal sorption onto the sample cups and metal leaching from sorbents, two sets of control batches were included. No significant metal sorption onto the beaker walls was observed. Some leaching of As was observed when using GAC, in according to the results from Genç-Fuhrman et al., (2006).

2.4 Calculation of the speciation and saturation indices

The calculations of speciation of dissolved metal species and possible precipitation of metal salts/minerals for As, Cd, Cr, Cu, Ni and Zn were performed by PHREEQC Interactive 2.12.4 (Parkhurst & Appelo, 1999) with the database of Lawrence Livermore National Laboratory database (llnl.dat; Parkhurst et al., 2004).

The calculations were performed for the specific experimental conditions (0.01M NaCl, 3 mM $NaHCO_3$) and the measure equilibrium pHs-values. Fully oxidized conditions wee assumed (dissolved oxygen 5 mg/L; pe 9).

2.5 Analysis of sorption data

The metal concentration retained in the sorbent phase was evaluated by using

$$Q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of metals in solution, Q_e is the metal concentrations on sorbent, V is the volume and W is the weight of the sorbent. All equilibrium data after sorption were evaluated by the Freundlich model, while the removal efficiency of heavy metals was evaluated by calculating the %-removal.

3 RESULTS

3.1 Sorption isotherms of the metals in single and binary systems

The pH-values measured after the 48 hours of shaking were found to be in the range 6.5~8.3 and 7.5~9.5 for the alumina and GAC samples, respectively (Table 4).

The sorption results for the single Cu-system and five binary systems (Cu+As, Cu+Cd, Cu+Cr, Cu+Ni, Cu+Zn) using alumina and GAC are presented in Fig. 1 using a double logarithmic scale. In these figures, the equilibrium metal concentrations (C_e) are depicted on the x-axis vs. the solid phase metal concentrations (Q_e) on the y-axis. As expected, the amount of metal removed increased with increasing initial metal concentration in all of the samples. The Freundlich parameters along with correlation coefficients for all sorption results were calculated and present in Table 4. The correlation coefficients showed that the Freundlich model can fit all experimental data, indicating that the surfaces of alumina and GAC are heterogeneous.

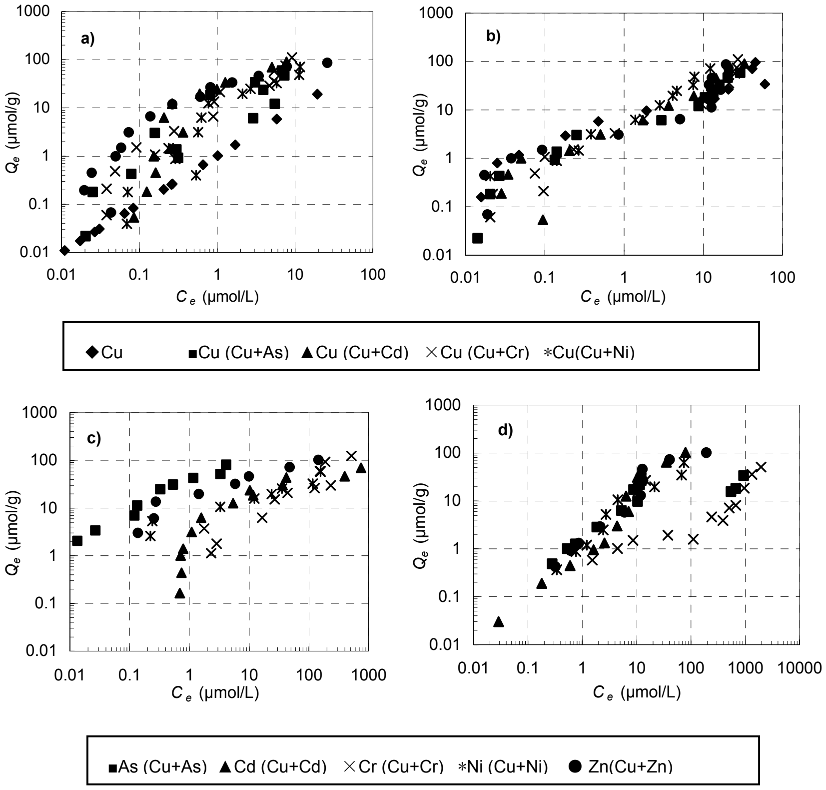

Fig. 1 Cu removed from water by a) alumina, b) GAC, and As, Cd, Cr, Ni and Zn in binary system removed from water by c) alumina, d) GAC; using sorbent dosage of 20 g/L, ionic strength (*I*) =0.01M NaCl, start pH= 6.5±0.2

		Systems																	
		Cu			Cu+As			Cu+Cd			Cu+Cr			Cu+Ni			Cu+Zn		
Sorbents	Metals	K_f[a]	*1/n*	R^2	K_f	*1/n*	R^2	K_f	*1/n*	R^2	K_f	*1/n*	R^2	K_f	*1/n*	R^2	K_f	*1/n*	R^2
Alumina	Cu	22.4	1.03	0.85	8.6	1.06	0.87	4.2	0.90	0.77	18.1	1.10	0.94	5.6	0.99	0.90	8.2	0.91	0.82
	Others[b]	/	/	/	0.2	0.63	0.96	0.002	0.42	0.86	0.03	0.74	0.90	0.001	0.38	0.95	0.007	0.45	0.91
GAC	Cu	0.05	0.67	0.90	0.1	0.79	0.92	0.5	0.85	0.89	0.6	0.87	0.96	0.9	0.86	0.98	0.08	0.71	0.89
	Others	/	/	/	0.7	0.93	0.97	6.5	1.13	0.95	0.09	1.22	0.94	0.4	0.92	0.94	1.1	0.93	0.95

[a] all constants were calculated based on the unit of mol/L; [b] others refer to the co-existing metals in binary system except Cu.

Table 3 Freundlich isotherm constants of all studied metals (with a significant correlation requirement R^2 > 0.467 for a 1% confidence using 13 data points (Montgomery & Runger, 1999))

3.2 Heavy metal speciation and saturation indices

The speciation calculation indicated that both As and Cr are present as anionic species. Accordingly, the dominating As specie is $HAsO_4^{2-}$ and $H_2AsO_4^-$ in the pH range of 6.5-9.5, and Cr is mainly present as CrO_4^{2-} and $HCrO_4^-$ at pH values above 6.5. It should be noticed that all Cr is dominated by Cr(VI). The other metals show a more complicated pattern. For example, the most important Cd species are $CdCl^+$ and Cd^{2+} below pH 9 and where the non-charged Cd(OH)Cl is dominating above pH 9. Cu is mainly dominated by non-charged $CuCO_3$ and positive-charged $CuOH^+$ in the pH range of 7.5-9.5, while Cu^{2+} is the main species at a pH value below 7.5 and the negative-charged $CuCO_3(OH)_2^{2-}$ is dominating at pH value over 9.8. The dominating Ni-specie is Ni^{2+} until about pH 9.5 and above this pH hydroxide species $Ni_4(OH)_4^{4+}$ and $Ni(OH)_2$ are also of importance. Zn is mainly present as Zn^{2+} below pH 8.5, while the dominant species are non-charged $Zn(OH)_2$ at pH over 8.5.

The details from the calculation of saturation indices are presented in Table 4. The major part of the alumina batches was undersaturated with respect to Cu-salts/minerals except for the Cu+As samples, Cu+Cr samples and Cu+Zn samples in batch 7-14, batch 11-14 and batch 14, respectively. It can be explained by tha fact that these batches had higher equilibrium pH-values (Table 3). In Cu+Cd system, the precipitation of $CdCO_3$ is taking place for all batches.

On the other hand, most samples with sorbent GAC are oversaturated with respect to Cu, Cd, Ni, Zn minerals/salt, because the equilibrium pHs in samples with sorbent GAC are higher than those with sorbent alumina.

	Systems	pH range[a]	Batch Number													
			1	2	3	4	5	6	7	8	9	10	11	12	13	14
Alumina	Cu	7.17-8.03													Cu	Cu
	Cu+As	7.61-8.19							Cu[b]	Cu	Cu	Cu	Cu	Cu	Cu	
	Cu+Cd	6.88-8.12	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
	Cu+Cr	7.43-8.30											Cu	Cu	Cu	Cu
	Cu+Ni	6.71-8.26														
	Cu+Zn	6.45-8.04														Cu
GAC	Cu	8.60-9.09						Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
	Cu+As	9.02-9.60			Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu, As	Cu, As	Cu, As	
	Cu+Cd	8.01-9.49		Cd	Cd	Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd	Cu, Cd
	Cu+Cr	8.69-9.42			Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
	Cu+Ni	8.45-9.43			Cu	Cu	Cu	Cu, Ni	Cu, Ni	Cu, Ni	Cu, Ni	Cu, Ni	Cu, Ni	Cu, Ni	Cu, Ni	
	Cu+Zn	7.56-9.39				Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn	Cu, Zn

[a] the pH range from batch 1 to batch 14 in the system

Table 4 Oversaturated metal minerals/salts (*SI* > 0), estimated by PHREEQC modeling (*I* = 0.01 M NaCl, buffer = 0.003 M $NaHCO_3$)

3.3 Comparing the removal efficiency of metals

Fig. 2a presents the removal efficiency (Re) of Cu in the different systems, while the corresponding data for the other metals are presented in Fig. 2b.

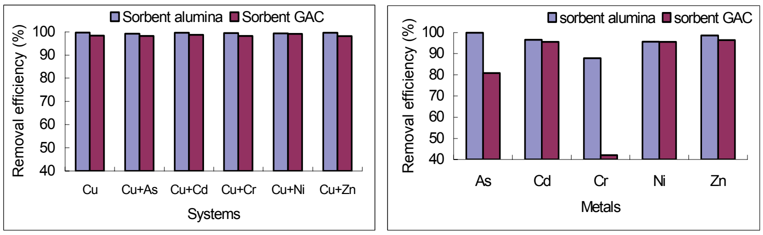

Fig. 2. Average removal efficiencies of (a) Cu in all systems and (b) the other metals in binary systems

It was found that alumina and GAC removed more >99% and >98% of Cu, respectively in all systems suggesting that the removal of Cu by alumina and GAC is independent of the presence of As, Cd, Cr, Ni or Zn, at least under the applied experimental conditions. This can be due to a greater selectivity for Cu for alumina and GAC, compared to the other metals. Another study with focus on the sorption of Cu and Cd to several different sorbents drew the same conclusion (Ulmanu et al., 2003). However, it can not be excluded that an important removal mechanisms for Cu is precipitation, at least in the GAC-systems, as well as in some alumina systems (Table 3). This is a removal process that is independent on the presence of other metals. Seco et al (1997) studied the sorption of a single Cu system and binary Cu-Ni, Cu-Cd and Cu-Zn systems on activated carbon, and found the sorption of Cu is scarcely affected by the competition of co-existing Cd, Ni, and Zn. Another study found that Cu posed higher sorption on carbon than Zn (Kononova et al., 2001). Fig. 2b illustrates that alumina is more efficient to remove As, Cd, Cr, Ni and Zn than GAC. Alumina is expected to be positively charged at the experimental conditions (Table 1 and 3), while GAC can be expected to have an average negative surface charge. The negatively charged surface of GAC can explain the relatively low removal of As and Cr since they are dominated by anionic species. In addition, most samples with GAC are oversaturated to produce precipitation of Cd, Cu, Ni and Zn minerals/salts, which will promote the removal. The better performance of can be explained by other removal mechanisms such as surface complexation ((hydr)oxide-complexes) and pore diffusion. As given in Fig. 2, the removal efficiency of other metals can be ranked from the largest to the smallest as:

As(99.9%) > Zn(98.6%) > Cd(96.6%) = Ni(95.7%) > Cr(87.9%) by alumina

Zn(96.4%) = Cd(95.6%) = Ni(95.6%) > As(80.8%) > Cr(42.1%) by GAC

4 CONCLUSIONS

This study showed, using batch experiments, that alumina and GAC can efficiently remove Cu with average removal efficiencies >99% and >98%, respectively at the initial Cu-concentration ranging from 36 µg/L to 150 mg/L. It is also showed that this sorption efficiency is independent of the presence of As, Cd, Cr, Ni and Zn.

Based on experimental conditions, PHREEQC is used to simulate the species of studied metals and the saturation indices with respect to possible oversaturation of metal minerals/salt. The simulation results indicate that the dominating species of Cd, Cu, Ni and Zn are cationic ions and non-charge, while As and Cr are dominated by anionic ions. For the batches with GAC, oversaturation with respect to Cd, Cu, Ni and Zn minerals/salt occur from batch 2, 3, 6 and 4, respectively. For the samples with alumina, Cd is oversaturated with respect to $CdCO_3$ for all batches, and the precipitation of Cu minerals/salt appeared from batch 7 in Cu+As system, from batch

11 in Cu+Cr system and in batch 13 & 14 in the single system. Cr is always below saturation in this experiment.

In the binary systems, the other metals were sorbed by alumina and GAC during the sorption process of Cu, and ranked in the following order: As>Zn>Cd =Ni>Cr on alumina, and Zn=Cd=Ni>As>Cr on GAC.

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