Removing Trace Metals From Stormwater at an Industrial Hard Chrome Plating Facility

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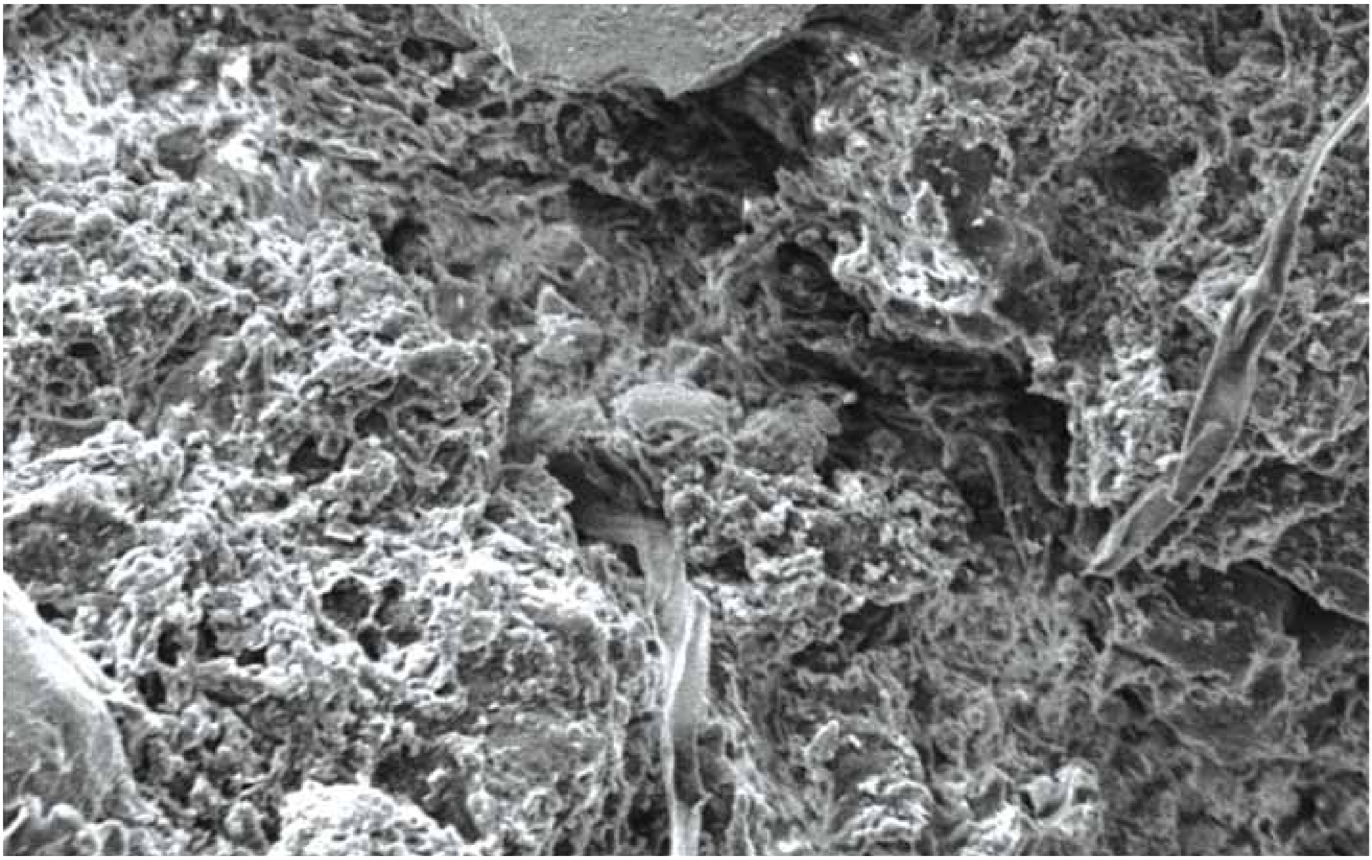

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Figure 2. Sorption media surface magnified 1,500 times

Industrial stormwater can contain trace metals above regulatory limits. Although standard water treatment processes are available to treat this water, they are generally expensive and require more maintenance than small companies can afford. Lower-cost, lower-maintenance alternatives are needed.

Peat is a natural material and has long been known for its ability to remove metals from water. At least five different mechanisms on the peat surface are involved in metal removal (Brown et al. 2000). Various studies have evaluated the ability of peat to remove metals, and copper concentrations up to 8.9% have been reported in samples used to treat wastewater (Lapakko and Eger 1988, Premi 1970).

Peat, although relatively inexpensive, tends to be non-uniform and somewhat difficult to handle. Although loose, fibrous peat can have hydraulic conductivities on the order of 10^{-1} centimeters per second, more decomposed and compacted peat can have conductivities of 10^{-3} to 10^{-4} centimeters per second. These lower conductivities reduce the overall flow rate and increase the potential for channelization.

American Peat Technology (APT) has developed a granulation and low-temperature hardening process to convert loose natural reed sedge peat into an engineered sorption media called APTsorb (Figures 1 and 2). The granules maintain their structure when wet and can be sized to any specification, which makes them readily adaptable to a variety of treatment systems. The standard media is 0.6 to 2 millimeters and has an estimated hydraulic conductivity around 1 centimeters per second. Metal removal capacities measured in laboratory equilibrium tests have ranged from 1 to 15% dry weight metal.

Background

Diamond Chrome Plating Inc. in Howell, MI, is owned by Superior Technology and was established in 1954. Diamond Chrome is primarily an industrial hard chrome facility that plates components for aircraft, military, and industrial customers.

The company's total site comprises about 1½ acres. Stormwater is generated from rooftops, storage areas, and parking lots. Prior to

2006, the company had a general stormwater permit, but due to elevated metals in the stormwater, the Michigan Department of Environmental Quality (MDEQ) determined that a general permit was not appropriate. In 2007, the state of Michigan issued a permit that required stormwater to be monitored, controlled, and treated if necessary. During the monitoring phase, elevated levels of total chromium, hexavalent chromium, cadmium, and zinc were measured. The original permit set limits for hexavalent chromium and cadmium; a new permit issued in November 2014 contained limits for total and hexavalent chromium.

Previous experimental work had shown that the peat-based sorption media removed trace metals in the laboratory and small-scale field tests and had a high affinity for trace metals (Eger et al. 2008). However, hexavalent chromium is generally present as an anion (CrO_{4}^{-}) and is not readily adsorbed. When ferrous sulfate is added, the hexavalent form is converted to the trivalent form (Cr^{+3}), which is typically present as a cation. Staff at Diamond Chrome Plating conducted additional tests onsite and decided to use the peat media for full-scale treatment of their stormwater.

System Design. The treatment system includes two holding tanks and seven parallel treatment tanks. Stormwater is initially collected in a 4,000-gallon interceptor tank. As water accumulates, it is pumped to the treatment tanks at about 150 to 200 gallons per minute. In the original design, a small metering pump injected a ferrous sulfate solution to reduce chromium +6 to chromium +3 as the water was pumped to the media. The addition location was changed several times but has now been returned to its original location before the media. The water enters a header, which distributes flow equally between the seven treatment tanks. Each 1,000-gallon tank contains roughly 425 gallons of APTsorb. A total of 12,000 pounds of APTsorb was used in the system.

Figure 1. Peat granules

Stormwater enters the top of each tank, is filtered through a 600-micron bag, and then gravity-flows through the media. The treated water is collected in a gravel drainage layer containing perforated pipes. During periods of heavy flow, the stormwater is pumped to a 46,000-gallon storage tank, which drains back to the stormwater interceptor tank as input flow decreases.

Methods

Influent samples are collected from the 4,000-gallon interceptor tank about 30 minutes after it fills. Initially, influent samples were not collected on a regular basis, but beginning in November 2014, influent samples were collected at the same time as effluent samples. Outflow samples are four- to six-hour composite samples collected with a flow-activated Isco automatic sampler. Samples are placed into laboratory-provided preserved sample bottles. All samples were analyzed for total metals at Fibertec Environmental Laboratory in Holt, MI. Total chromium, cadmium, and zinc were analyzed with ICP/MS (EPA 200.8). Hexavalent chromium

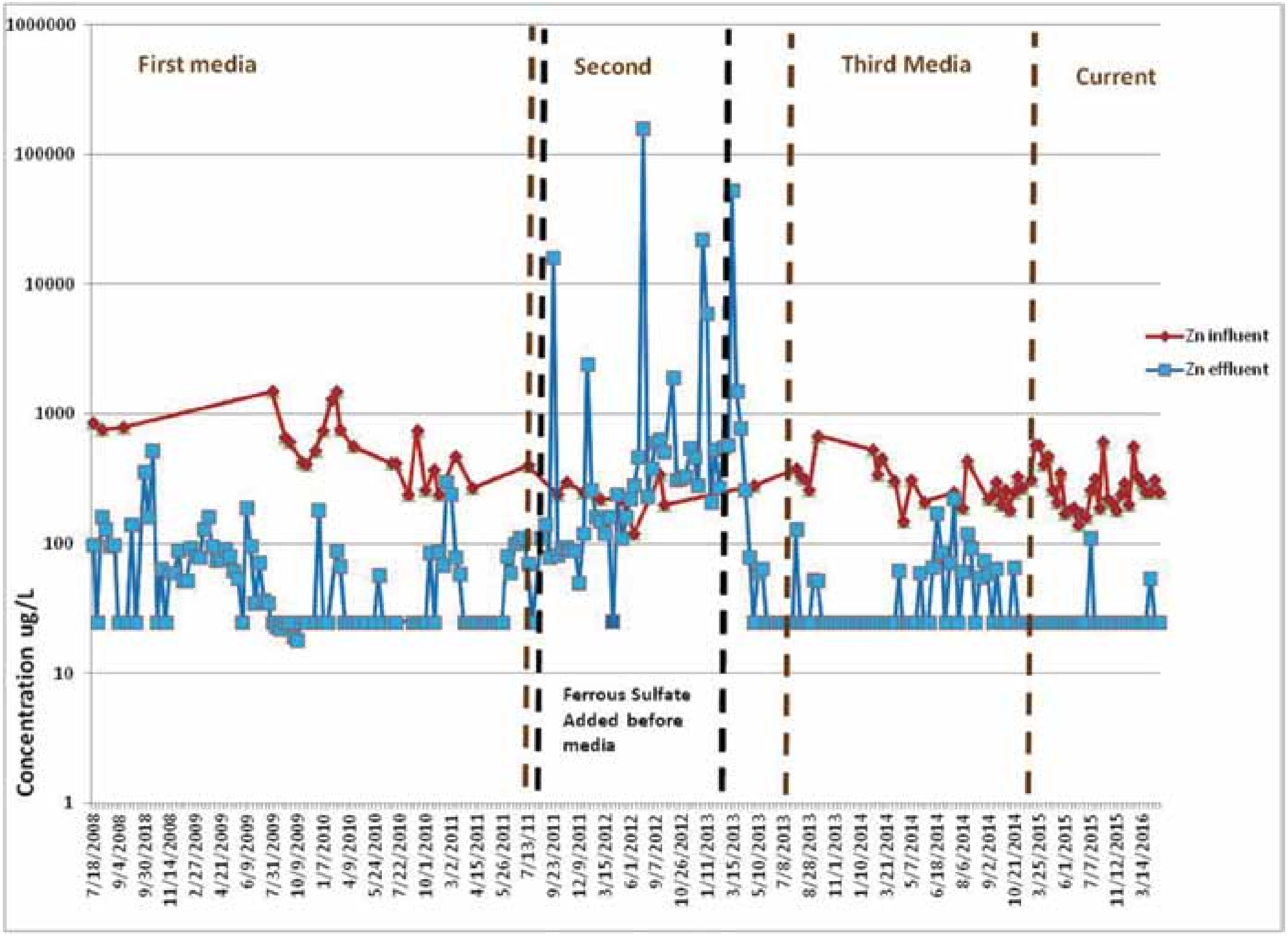

Figure 3. Zinc concentration vs. time, July 2008–May 2016

was analyzed with a colorimetric procedure (SM 3500-Cr B).

Results

Pre-treatment Sampling. Samples were collected initially to determine the concentration in the stormwater and to decide if treating only the first flush was an option. Composite samples of the first 4,000 gallons and four- to six-hour composites of the outflow were collected for a six-month period from January through June 2008. Metal concentrations in the initial flush were higher, but metals were elevated in all the stormwater runoff. Average concentrations of both cadmium (219 µg/L) and hexavalent chromium (385 µg/L) exceeded their respective limits of 55 and 32 µg/L (Table 1).

System Operation and Performance. Treatment started on July 7, 2008, and the concentrations of metals in the outflow decreased substantially. The first batch of media treated about 3.6 million gallons of stormwater before chromium concentrations started to increase and the media was replaced. Overall removal for chromium, cadmium, and zinc were all around 90% (Table 2).

The first batch of media had been loaded into the tanks using a bucket elevator. This equipment was not available at the time the media needed to be changed, so a screw auger was used to load the second batch of media. There was concern that the abrasion created by the auger would affect the media and create more fines, but it was the only option available at the time. In addition, since the original permit did not contain a permit limit for total chromium, ferrous sulfate addition was moved to after the media and the sampling frequency of the input was markedly reduced. After the ferrous sulfate was moved, zinc concentrations increased dramatically, exceeding the input by as much as an order of magnitude (Figure 3). The ferrous sulfate was an industrial byproduct and contained elevated levels of zinc and potentially low levels of cadmium. When the problem was

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identified, the ferrous sulfate was moved back to the original location before the media, and zinc concentrations dropped substantially. Several months later, the ferrous sulfate was replaced with a high-purity product, and no further problems have been observed.

Table 1. Stormwater Quality Before Treatment

	First Flush		Complete Event		Permit Limits, μg/L	
Parameter	Number of Samples	Average concentration, μg/L	Number of Samples	Average Concentration, μg/L	Original	Revised[a]
Total Chromium	26	575	14	526	No limit	130
Hexavalent Chromium	21	510	15	385	32	15
Cadmium	26	398	14	219	55	No limit, monitor only
Zinc	26	713	14	565	No limit, monitor only	No limit, monitor only

[a] In 2014, a new permit was issued that established a daily maximum limit of 15 μg/L for hexavalent chromium and a monthly average of 130 μg/L for total chromium. There were no limits for cadmium or zinc.

Due to the limited amount of input data and the change in operation, it was difficult to estimate treatment efficiency. Limited data, taken after the ferrous sulfate was returned to the front of the media, showed about 85% removal of both cadmium and zinc (Table 3). However, the additional fines generated by auguring the media and the accumulation of fine solids in the bed prematurely reduced the permeability of the media, and the bed began to plug. The media was replaced after about 1.9 million gallons of water had been treated.

The third batch of media was loaded into the tanks with a conveyor belt, and the ferrous sulfate was moved to the interceptor tank to provide a longer contact time with the stormwater. Although this was very effective in eliminating hexavalent chromium in the influent, a representative sample of the untreated input could not be collected, and MDEQ requested that the ferrous sulfate be moved back to the original location before the media. Influent samples were collected only periodically until the new permit was issued in November 2014, after which influent and effluent samples were collected for each event. Although removal of cadmium and zinc were similar to previous values (81–85%), chromium removal decreased, and the media was replaced after about 1.5 million gallons had been treated (Table 2).

For the current batch of media, Diamond Chrome developed a new method to load and unload using a hydraulic inductor system. This successfully placed and removed the media quickly and without damaging the media. Since the new system was installed, performance has improved and removal efficiency is similar to the original values. Because of improvements in best management practices and general housekeeping, influent concentrations of total chromium have been reduced to about 50% of the initial values (Table 2).

Mass Removal. For the initial batch of media, there were sufficient data to estimate the total mass removed by the media. Mass removal was estimated by the following equation: (Average influent concentration – Average effluent concentration) x total volume treated.

The metal concentration of the media was estimated by dividing the total metal mass removed by the total amount of APTsorb in the system. Mass removal ranged from 2,780 grams for cadmium to 6,609 grams for total chromium. The calculated metal concentration on the media for

Table 2. Stormwater Treatment Performance, July 3, 2008–May 2, 2016

	Influent				Effluent				% Removal			
Media Batch	Cr	Cd	Zn	Sample Number	Cr	Cd	Zn	Sample Number	Cr	Cd	Zn	Volume Treated, Millions of Gallons
1	488	146	646	22-23	40	13	71	58-88	92	91	89	3.6
2[a]	860	27	241	5-9	65	14	4,730	14-58	92	49	-1,860	
2[b]	860[c]	27[c]	241[c]	6-10[c]	85	2.9	33	9	90	89	86	1.9
3	150	26	304	25-26	82	5	45	56-57	45	81	85	1.5
Current	201	43	295	30	41	3	29	30	80	94	90	0.7

[a] Ferrous sulfate addition moved to after media

[b] Ferrous sulfate addition moved back to before media

[c] Average values for entire treatment cycle

Table 3. Mass Removal

Parameter	Influent, μg/L	Effluent, μg/L	Mass, gm	Estimated Loading Capacity, mg/kg	Metal Concentration on Media
Total Chromium	526	40	6,609	1,346	1,200
Cadmium	219	15	2,780	>566	300
Zinc	565	83	6,568	>1,338	Not analyzed

total chromium was 1,346 milligram per kilogram. Because chromium removal was decreasing, it appeared that the media had become saturated, so this concentration is an estimate of the total removal capacity.

Because cadmium and zinc were still being removed when the media was changed, the calculated media concentrations do not reflect total removal capacities, since they would be greater than the estimated values of 566 milligrams per kilogram for cadmium and 1,338 for zinc (Table 3).

Before the media was replaced, media samples were removed from one of the tanks and the media was washed and digested with nitric acid. Measured values were in the general range of the concentrations estimated by metal removal calculations (Table 3).

Table 4. Results From TCLP Test

EPA Hazardous Waste Code	Contaminant	Regulated Level, mg/L	TCLP Results, mg/L	% Adsorbed Metal Released
D004	Arsenic (As)	5	ND	
D005	Barium (Ba)	100	1	
D018	Benzene	0.5	0.26	
D006	Cadmium (Cd)	1	0.1	0.4
D007	Chromium (Cr)	5	ND	<0.01
D008	Lead (Pb)	5	ND	
D009	Mercury (Hg)	0.2	ND	
D010	Selenium (Se)	1	ND	
D011	Silver (Ag)	5	ND	
Not listed	Zinc	Not TCLP regulated	2.8	4.6

Mass removal was not estimated for the second and third batch of media because only limited influent data were available, and the significant changes in operating conditions made it almost impossible to compare results.

TCLP Test. Because chromium and cadmium are both Resource Conservation and Recovery Act (RCRA)-listed metals, any media containing these metals must be tested to ensure that it is non-hazardous. For the first batch of media, essentially no chromium (<0.01 mg/L) and only small amounts of cadmium (0.1 mg/L) were leached from the media, and the spent material easily qualified as non-hazardous. On a mass basis, about 5% of the zinc and less than 0.5% of the cadmium were removed in the Toxicity Characteristic Leaching Procedure (TCLP) extraction (Table 4). The second and third batches of media also passed TCLP requirements.

Discussion. A variety of treatment methods are available to remove metals from stormwater. Many are expensive and have high operation and maintenance costs. Ion exchange, using commercial resins, is a lower-maintenance alternative, and a wide variety of commercial resins are available for specific applications. However, commercial resins are expensive and need to be either regenerated onsite or sent back to the supplier. Onsite regeneration is often problematic, particularly for small companies, and generates solutions that require disposal and possibly additional treatment. Commercial resins can physically plug when exposed to even low levels of suspended solids, and the tanks and media cannot be effectively backwashed (Eger et al. 2016).

In contrast, peat sorption media overcomes some of the shortcomings of commercial ion exchange resins. Due to the nature of the sorption bonds, it does not lend itself to regeneration, but the low cost of the media preserves its cost effectiveness. It also removes suspended metals and can be easily backwashed onsite. In a mine drainage pilot study, the media removed around 75% of the suspended copper and was easily backwashed (Eger et al. 2016). At that site, overall copper removal with a single tank of peat media was comparable to a much more complex and labor-intensive commercial resin system.

The initial batch of media at Diamond Chrome operated successfully for three years with no flow problems and essentially no maintenance. Changes in media handling and operation reduced the performance of subsequent media. Although the problems with the second batch of media could be identified, it is much harder to understand the performance of the third batch of media. When the third batch of media was replaced after only 1.5 million gallons, chromium was still being removed, but the removal efficiency varied substantially. For the four months prior to media replacement, removal generally ranged from 28 to 53%, and total chromium periodically exceeded the permit limit. It is unclear why removal decreased prematurely, as Diamond Chrome staff could not recall any operational

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changes that might have affected performance. Chromium chemistry is complex, and the exact form is a function of a multitude of factors. With stormwater, there is always the possibility of organic contamination. Excess organics in the influent stormwater could complex some of the chromium and reduce treatment efficiency.

After operating conditions became standardized and a non-damaging method was developed to load and unload the media, performance has returned to near initial levels, and for the past year and a quarter, there has been no operational problems or maintenance required. As the result of improvements in best management and housekeeping, influent chromium concentrations are about 50% lower than when treatment began (Table 3).

Diamond Chrome designed and built the treatment system at a total cost of around $85,000. The peat media for this system costs about $15,000, so treatment costs have ranged from $5,000 to $7,500 per year. Initially, when the media needed to be replaced, it was easily removed from the treatment tanks with a vacuum truck and taken to a sanitary landfill. Because the material was wet, the disposal cost was about $900 per ton for a total cost of $5,500. Now with the new inductor system, the material is pumped directly into a roll-off container lined with a filter fabric. The media drains quickly and disposal costs have dropped to around $100 per ton for a total cost of only $800.

Conclusions

APTsorb has effectively treated stormwater from Diamond Chrome Plating for more than seven years. The initial media had no operating problems or maintenance issues. Changes in procedures and operation affected performance and lifetime, but given the low cost of the media, there was little effect on the overall annual cost. Now that the operation of the system has been stabilized and returned to the initial conditions, performance is similar to original levels, with removal efficiencies ranging from 80–94%. All media has passed TCLP tests and has been disposed of in a sanitary landfill.

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