Complex organic media adsorption as a cost-effective stormwater treatment

R. D. Griffin[1] & H. Cantrell[2]
[1]*Ecology Auto Parts Inc., USA*
[2]*EcoShell Inc., USA*

Abstract

Ecology Auto Parts, an industrial recycling company, launched a three-year lab and field investigation program to determine whether complex organic media can be used to attain compliance with µg/L (part per billion) stormwater discharge standards. In addition to meeting concentration standards for oil and grease, pH, conductivity, turbidity and metals, key items included meeting the company objectives of: low cost, using gravity flow systems, eliminating hazardous chemicals, and using facility staff. Following extensive research and bench scale tests, the company settled on complex organic media (agricultural products) to provide the contaminant removals needed. The theory was that oil and grease and particulate matter could be removed by media filtration, with the metals on interest adsorbed on the media itself. A two-day field testing program using four tons of organic media were used in an existing collection and treatment basin. Stormwater from the facility was collected in a sump and sprayed onto the surface of a 0.75 meter deep bed. The results showed significant reductions in all parameters: 96% (Al), 85% (Cu), 95% (Fe), 97% (Pb) and 91% (Zn). 2015 results for additional installations indicate compliance with the new discharge standards. Oil and grease was non-detectable, suspended solids were reduced by 83%, hardness was reduced by 60% and turbidity by 75%. Conductivity was unchanged and pH was lowered by about one pH unit. Based on this field testing program, it is shown that complex organic media are the most cost-effective stormwater treatment methods for meeting industrial standards while meeting other cost-effective and low-hazard treatment goals.
Keywords: stormwater, adsorption, organic media, shells, trace and heavy metals, recycling, scrap.

www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/WS150261

1 Introduction and background

Increasing emphasis on better surface water quality has led to the adoption of stormwater discharge standards. In 2014, California adopted a general industrial stormwater permit which establishes stringent concentration standards for a variety of industries [1]. These standards are fixed according to their industrial Standard Industrial Classification (SIC) code. Trace metals are the main focus of the General Industrial Stormwater Permit. Table 1 details some of the regulated contaminants and their discharge concentrations (metals that are in the "sub-mg/L" (ppb) range are notable).

Table 1: Discharge standards.

Contaminant	Units	Concentration
pH	--	6.0–9.0
Suspended solids	mg/L	100
Oil and grease	mg/L	15
Aluminum (Al)	μg/L	750
Copper (Cu)	μg/L	33.2
Iron (Fe)	μg/L	1000
Lead (Pb)	μg/L	262
Zinc (Zn)	μg/L	260

The use of existing water treatment approaches dating back to the 19^{th} century – neutralization, chemical addition, coagulation, flocculation and filtration – have met with poor success in meeting 21^{st} century stormwater treatment goals. They also suffer from the use of hazardous chemicals and require high technology staff to operate the equipment. Accordingly, industrial dischargers, including scrap metal recycling facilities, have been forced to look for new approaches.

2 Scoping for potential solutions

Finding that commercial technologies would not meet the discharge standards in a cost-effective manner, Ecology Auto Parts began a research program to determine appropriate technologies in 2012. This program initially included interviews with emerging technology vendors and internet searches for alternative adsorption technologies.

These investigations led to new knowledge of ongoing intensive research world-wide for new approaches to water treatment. Included in these approaches were adsorption technologies involving agricultural products such as rice hulls, sugarcane bagasse, orange peels, black oak bark, exhausted coffee, waste nut shells and modified peat [2–4].

2.1 Initial evaluations

Following assessments of commercially available filtration equipment, Ecology Auto Parts launched a three-year program of its own investigating innovative passive treatment technologies for stormwater with particular attention to trace metals removal.

Sources of stormwater contaminants, including trace metals, are generally conceded to be from: general operations of facilities handling scrap metal, various oxidation products from reactive metals such as aluminum, and mechanical attrition of mobile equipment (such as zinc and copper from brakes and tires). While significant advances have been made in best management practices to eliminate these materials from stormwater they still occur in discharges. Consequently, Ecology Auto Parts' evaluations turned to effective treatment technologies.

The physical and chemical state of the metals in the discharge was evaluated next. This was based on the assumption that the most effective approach could only occur when the contaminant physical and chemical states were clearly understood.

In its initial attempts at determining the chemical state of total metals in its stormwater, Ecology Auto Parts found that the majority of the metals were in the dissolved, or ionic, state [5]. Consequently, mechanical filtration as a treatment approach – with pumps, pressure vessels, chemical addition plus a variety of filters – was deemed to be ineffective and the search turned elsewhere.

On this basis, Ecology Auto Parts' goals were re-defined. The selected treatment criteria would meet these goals:

- few moving parts;
- effective removals for trace metals;
- simple construction;
- low-cost;
- elimination of hazardous treatment chemical usage; and
- easy operation by facility staff rather than chemical technicians.

With these criteria, the company's attention turned to ion adsorption technology. Ion exchange resins were initially evaluated but, though effective, were found to be expensive, of a limited capacity, and easily blinded by the oil and grease and suspended particulate matter commonly found in stormwater discharges.

2.2 Pilot scale tests

Based on its research and on-site evaluations, Ecology Auto Parts moved to pilot scale tests using agricultural products with which it had some familiarity – residual shell media. EcoShell, a California based world-wide supplier of organic shell media, supplied their products for the pilot scale tests.

The initial tests were performed on a synthetic stormwater made from deionized water and a common soil sample. A 20 liter container was used to prepare a synthetic stormwater for treatment. The column dimensions were 5 cm diameter by 60 cm height; it was charged with 400 g of shell media. The media was a 20–30 mesh shell product with a specific gravity of 1.2. Tests consist of charging the packed column with a continuous flow of the synthetic stormwater. Samples were taken at various intervals to determine (over time) the removal efficiency for the metals and the capacity of the column.

Table 2 is a tabular presentation of the concentrations of the five elements of concern for the quantities of stormwater treated in the initial test. After 10 liters of treatment the results indicated that all five trace elements reached attainment with the California industrial stormwater permit standards!

Table 2: Initial pilot tests – metals.

Liters treated	***Al***	***Cu***	***Fe***	***Pb***	***Zn***
0	*1400*	*50*	*2600*	*48*	*360*
1	220	68	430	10	nd
5	170	26	430	13	84
10	210	27	510	14	100

As seen in Figure 1, the ability of the organic media to reduce these trace metals was dramatic and sustained throughout the 10 liter trial.

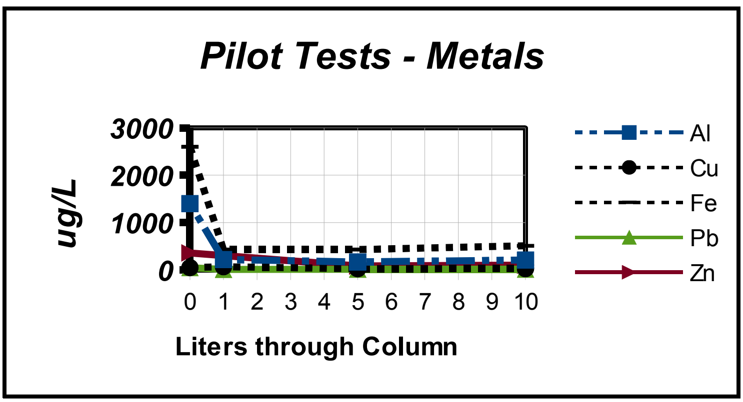

Figure 1: Outlet concentrations vs. volume treated.

To define the system capacity, further tests were performed to determine the efficiency after 50 bed volumes of water was passed through the column. Again, a synthetic stormwater sample was used with the same column, but at a reduced velocity through the bed.

Figure 2 shows the results of the second test using the same packed column. An expanded suite of parameters were tested before (dark bars) and after the adsorption media (light bars) in order to determine the effects on pH, conductivity, turbidity, hardness, color index, and COD, in addition to the trace metals of interest.

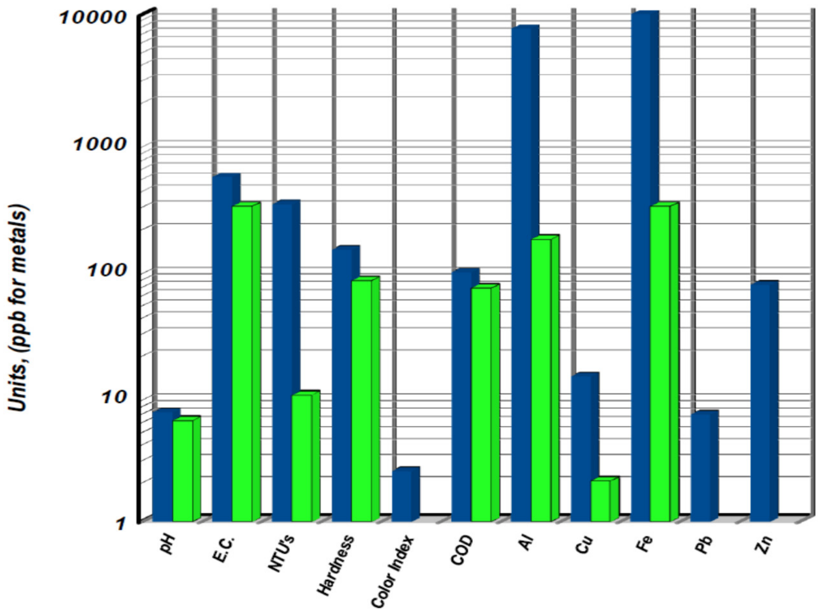

Figure 2: Extended sampling results – inlet vs. outlet.

The results for the water quality parameters far exceeded expectations. Significant improvements in turbidity, hardness, COD and color were found and all metals were in compliance with the California standards after 50 bed volumes of water were treated through the column.

These pilot tests demonstrated the efficacy of using organic media as the most cost effective treatment approach; attention then turned to full scale tests.

3 Full scale tests

3.1 Initial installation

A recycling yard in San Diego county was chosen for the initial full scale test because of smaller size (2 acres), the surface being covered with concrete (to avoid soil erosion problems), and existing treatment equipment was already installed. Due to the inherent simplicity of a packed bed system, the facility was prepared by bulk installing the media in the existing bin. Figure 3 is a picture of the system following the filling of the bed. Stormwater flows from the collection pump to an oil water separator; it then flows by gravity through the perforated headers onto the bed itself.

A readily available 12–20 mesh media from EcoShell was installed in the gravity flow bed. A 300 L/minute pump filled the oil–water separator tank; inlet flows entered the bed via perforated headers. The bed depth was approximately 0.75 meters with a free-board of 0.6 meters.

Figure 3: Inlet to bed – yard 22.

The initial testing came late in the stormwater season in 2014 when a three cm. rain event was forecast. A suite of on-site instrumentation (pH, conductivity, turbidity, and color) was ready as well as a supply of analytical laboratory sample bottles.

With the commencement of the rain event, samples were taken at the inlet headers and from the discharge points on the outlet of the bed at 30 minutes, 1 hour and after 6 hours. Samples for analytical analysis were sent to the laboratory for metals, suspended solids and oil and grease. The inlet and six hour outlet analyses are shown in Figure 4.

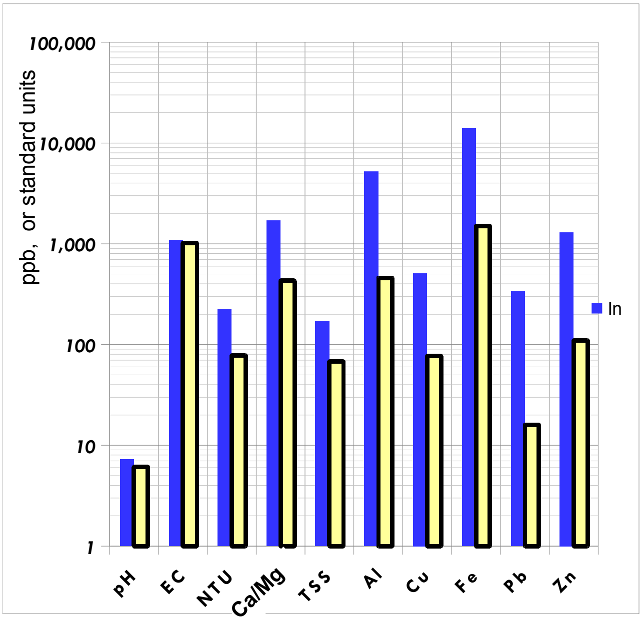

Figure 4: Inlet and outlet results after six hours of flow.

3.2 Follow up tests

Following the successful results at yard #22, an additional installation was chosen for the retrofit organic media; yard #5 in western Los Angeles County.

Samples from stormwater sampling at Yard #5 followed in early 2015 [6]. The results for several of the trace metals are seen in Figure 5 below. These results are for metals only and indicate that this organic adsorption media is highly effective for metals control in stormwater.

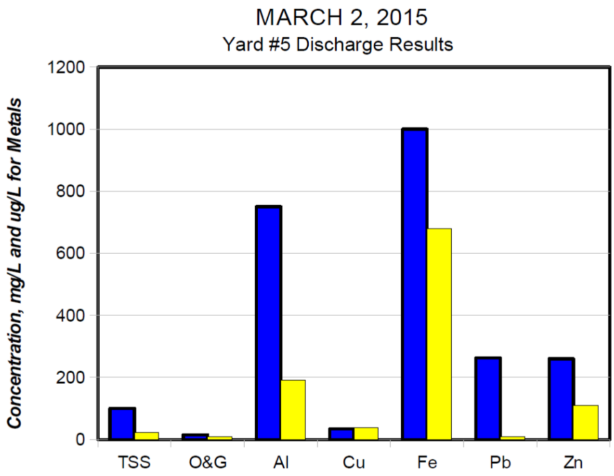

Figure 5: Yard 5 results: outlet vs. California 2015 standards.

These results indicate better than compliance for every standard except copper, which was only 5 ppb above the standard.

4 Results and discussion

Both the pilot scale tests and the full scale installations of the organic adsorption media indicate that complex organic media (shells) are an effective stormwater treatment technology.

Ecology Auto Parts is currently evaluating some of the key parameters identified in this project for the rest of the company's facilities. One issue that has been identified as that the organic media does have an initial colored discharge most likely due to organic materials in the shell material. This is remedied by an initial pre-wash of the media prior to placement.

Also, it is believed that the linear velocity through the media may have been too high for proper compliant absorption of the metals. This is being addressed by looking at potential flow controls at the discharge of the adsorption bid and the mesh size of the material. It is believed that by decreasing particle size to a 20–30 mesh, and by decreasing the face velocity through the bed by approximately 30% will be sufficient to maintain compliance with the discharge standards.

It was found that in addition to dramatic reductions in suspended solids and turbidity, more obvious contaminants such as oil and grease are easily absorbed due to the high surface area of the organic media. An inspection of the media beds following storm events indicated a thin layer of oily media resting on the surface of the bed. This was easily removed with shovels and additional material is quickly spread on top. This allows for ease of maintenance and maintains the system effectiveness.

Conductivity was essentially unchanged; pH dropped approximately one pH unit. Surprisingly, the hardness dropped by 80% and the trace/heavy metals showed reductions ranging from 97% (Pb) to 85% (Cu); fine particulate and sediments were reduced by 69 %.

4.1 Potential adsorption mechanisms

The mechanisms most likely responsible to the ion adsorption capacity of organic media are believed to be a function of the complex structures in the organic media itself.

Organic media, including agricultural waste materials, are exceedingly complex. These media are composed of basic cellulose but also include complex chemical groups such as lignins, tannins, humic and fulvic acid structures. A schematic of the structure of one of those substances – tannin – is seen in Figure 6 below. An evaluation of these structures indicate that there is a high degree of electron negativity by the poly-phenolic structures of lignins, tannins, humic and fulvic acid compounds. These structures, in conjunction with the basic cellulose of plants, lend themselves to cation adsorption of the metals in stormwater. The electron negativity of the exposed oxygen atoms is loosely attracted to the positive charged metal ions, thus adsorbing them.

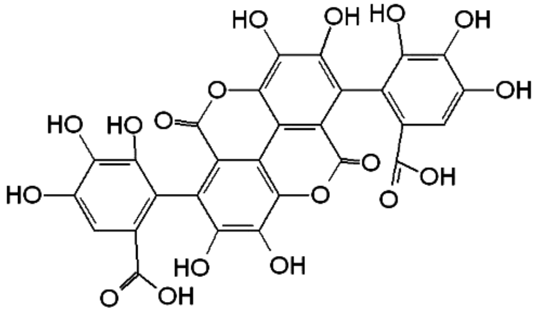

Figure 6: Approximate structure of tannin.

During transit through the bed some of these coloring compounds are lost, thus lowering the pH to the 6.3 to 6.7 range in the discharged water.

Oil and grease with particulate matter is collected by purely physical process on the surface interstices of the media matrix. The media bed acts like a chromatographic column in that that contaminants are collected in layers in the bed. When breakthrough occurs, the bed is exhausted and must be replaced.

5 Conclusions

Based on the results of these pilot and field studies, it appears that complex organic media (shell products) may be used to successfully meet the 2015 stormwater treatment standards established by the state of California. In addition, use of this technology meets the multiple goals of:

- few moving parts;
- high removal efficiencies for trace metals;
- simple construction;
- low-cost;
- elimination of hazardous treatment chemical usage; and
- easy operation by facility staff rather than chemical technicians.

Further investigations are ongoing to establish the final operating details using the complex organic media for effective stormwater treatment systems.

References

[1] California General Permit for Storm Water Discharges Associated with Industrial Activities, Order NPDES No. CAS000001, April 1, 2014.
[2] Kahn, N., Ibrahim, S., and Subramanian, P., Elimination of trace Metals from Wastewater Using Agricultural Wastes as Adsorbents, *Malaysian Journal of Science,* **23**, pp. 43-51, 2004.
[3] Kumar, U., Agricultural products and byproducts as a low cost adsorbent for trace metal removal from water and wastewater: A review, *Scientific Research and Essay,* **1**(2), pp. 33-37, 2006.
[4] Osman, H., Badwy, R., and Ahmad, H., Usage of Some Agricultural By-products in the Removal of Some trace Metals from Industrial Wastewater, *Journal of Phytology*, 2010, **2**(3), pp. 51-62.
[5] Griffin, R., Fallacy of the First Flush Discharge, and Field Tests Assessing Filtration as NAL-Compliant Treatment in a Scrap Yard, StormCon 2015, Paper # D62, Austin, Texas, 2015.
[6] Confidential Lab Reports, Ecology Auto Parts, Internal Communication, March 15, 2015.