ACI-HERZOG Pretreatment Plant Effluent Surfactant Reduction

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Abstract *— ACI-HERZOG is the firm contracted to maintain and operate the Puerto Rico Tren Urbano system. As part of their duties, they are required to wash down train cars periodically. The water generated from the wash down process must be treated for pH and temperature, in accordance with federal and state pretreatment regulations. Recently, the Environmental Protection Agency released more strict regulations with regards to stormwater discharges. With the possibility of pretreatment standards also becoming more stringent, the firm may eventually be required to treat their process waters for surfactants. Thus, a proposal was put forth to install an activated carbon filtration system with a caustic soda regeneration system. To this end, company carwash effluent and surfactant data was compiled, and, through a series of volume conversions and surfactant calculations, it was determined that a skid mounted, double vessel 1 ton, 16 gallons per minute GAC system can achieve the project goal of reducing the surfactant levels in the carwash effluent by at least 50 % of its current average.*

Key Terms *— Activated carbon, effluent, regeneration, sodium dodecylbenzenesulfonate.*

INTRODUCTION

ACI-HERZOG is the private rail transit operator that operates and maintains the Puerto Rico Tren Urbano system. The firm's headquarters, where the project took place, is the Operations and Administration building of the Integrated Transport Authority in Guaynabo. The operator's responsibilities include providing maintenance and repair services for trains as well as for any facilities related to the rail transit system, as well as washing down train cars periodically.

Under the water treatment standards promulgated by the Puerto Rico Aqueduct and Sewer Authority (PRASA), ACI-HERZOG is required to pretreat the effluent that is produced from these washdowns. At present, PRASA only requires that ACI-HERZOG treats the water for pH, keeping it between 6.5 and 7, which is considered the neutral pH level. As such, the car wash's pretreatment plant consists only of an equalization tank to stabilize the flow, and a neutralization tank, to maintain neutral pH levels. This results in a pretreatment method that does not treat the primary contaminant of the effluent, that is, surfactants. This design was intentional, as PRASA has not set specific limits to the amount of surfactants that can be released through an effluent. Instead, the agency only requires industries to monitor surfactant levels, sometimes imposing specific limits on entities they determine to be releasing excessive amounts of surfactants.

However, the Environmental Protection Agency (EPA) has recently released a set of new, more stringent standards related to stormwater discharges. As there exists a possibility that pretreatment standards might also get more stringent in the near future, it was necessary to consider how surfactant treatment could be retrofitted into the pretreatment plant. This scenario presented an ideal opportunity for proposing modifications to increase the plant's functions and efficiency.

The objective of this project was to reduce the amount of surfactant in the plant's effluent by at least 50% of its current average. The methods and technologies selected were chosen based on their price, efficiency, ease of maintenance, and practical use data.

MATERIALS AND METHODS

Activated Carbon

Activated carbon is an amorphous structured, highly porous material, with substantial surface area. This makes it highly adsorbent, that is, prone to attracting particles of foreign substances to its surface, causing them to adhere to it. The carbon atoms inside the material are randomly crosses-linked into aromatic configurations and are stacked unevenly. This random configuration increases the number of voids and cracks inside the carbon, increasing its adsorption capabilities. Furthermore, pore size and volume can vary based on the raw materials used for the carbon (such as coconut husks, wood, bamboo, etc.), the activation process parameters, and the post processing parameters. For additional efficiency, the raw materials can undergo pre-processing.

The carbon can be obtained in granular form, or powder form. Extruded activated carbon, which is powdered carbon that has a binding agent, can also be obtained.

By saturating activated carbon with certain chemicals, it is possible to turn the carbon's surface into a chemical catalyst, resulting in chemisorption. Already saturated activated carbon can be bought from distributors that prepare them for very specific applications, or the user can saturate it themselves through their own saturation method. Although these catalytic reactions add to the carbon's adsorption capabilities, the most effective way to increase efficiency is to make the carbon's pores only a few times larger than the foreign material's particles [1].

Applying a chemical substance to spent activated carbon through the process of backwashing, that is, the process of pumping a chemical substance with water in backwards fashion through the filtering media, is a cost-effective solution which can be implemented through an acid/base injection system. One of the most used chemical agents for this purpose is sodium hydroxide (Naoh), also known as lye or caustic soda. It is a solid state, white ionic compound made of hydroxide anions and sodium cations. It is highly soluble in water and has a pH of 14, making it a strong base solution [2]-[3].

Sodium Dodecylbenzenesulfonate

Sodium Dodecylbenzenesulfonate is a light yellow/white sand like material, which is used in pesticides, cleaning products, or as a standalone detergent. It only has minor effects on human health, and it is not listed on any federal agency as being hazardous to the environment. Nevertheless, it is unlawful to dispose of the product in large quantities via a sewer system.

Blue Marvel, which is the high foam liquid car washer used by ACI-HERZOG, is composed mainly of this material [4]. No other materials are mixed with this surfactant, thus making it the only chemical substance which must be treated.

There are various filtering media which can be used to remove this compound, such as the macroporous polymer-based adsorbents, HP20 and HP2MGL, zeolite, alumina, and activated carbon. Out of all the media, activated carbon has the third highest absorption rate (29.4 mg/g) [5]. Despite this, it was chosen as the filtering media for the project, due to its adequate adsorption rate, easy to implement designs, easy-to-modify characteristics, relatively low risk factor to the environment, and easy-to-dispose of nature. It is also very easily acquirable, as most distributors sell it, and it can be modified if additional efficiency is needed. For spent carbon, Veolia ES Technical Solutions, whose services ACI-HERZOG has already solicited in the past for nonhazardous waste disposal, has been selected to handle the spent carbon. As caustic soda will be used on the carbon, any spent carbon awaiting disposal will be placed in the hazardous material section of ACI-HERZOG's Vehicle Maintenance Area, and ACI-HERZOG personnel will ensure that all procedures relating to the handling of hazardous wastes are applied, such as filling the hazardous waste manifest, informing the contractor of the dangers posed by the waste, securing the containers in spill pallets before moving them, and properly connecting the cargo area ramp to the disposal truck's cargo bay.

GAC Tank Specifications

Activated Carbon tanks are cylindrical shaped tanks of varying heights and widths, made of stainless steel. Water enters the tank from the inlet pipe at the top of the tank and makes its way across the activated carbon, where it is filtered. The outlet at the bottom of the tank acts as the exit point for the flow. Pumps are used to move the flow from top to bottom, but it is possible to install the pumps at the bottom of the tank to inject the flow from bottom to top instead. GAC tanks can be acquired in skid mount form, in which the tanks, pumps, pipes and regeneration system are already installed, usually on a concrete or metal base.

Static Mixer Specifications

A static mixer is a specially crafted pipe that has a helical shaped piece of metal inside of it, which extends from one end of the pipe to the other. The purpose of the helical piece is to blend liquids, usually a chemical component with water. The chemical to be blended is inserted via the chemical inlet, which is a small inlet that is perpendicular to the main pipe. For the purposes of carbon regeneration, these pipes are used to mix acid/bases with an effluent, and the resulting mixture is used to remove some of the captured foreign materials from the carbon, thus regenerating it [6].

CALCULATIONS

Surfactant and flow data tables

To comply with PRASA's wastewater standards, ACI-HERZOG is required to perform tests on their pretreatment effluent on a quarterly basis. As such, the data needed to calculate the average surfactant level existed well before the project's commencement. Table 1 was created from 3 years' worth of this data.

Table 1
Surfactant Readings

Date of Reading	*Surfactant level*
May 19, 2017	25.7 mg/l
September 19, 2017	0.550 mg/l
December 17, 2017	13.9 mg/l
February 28, 2018	3.07 mg/l
May 24, 2018	61.3 mg/l
August 22, 2018	62 mg/l
May 28, 2019	0.185 mg/l
August 14, 2019	20 mg/l
November 21, 2019	46.2 mg/l
March 4, 2020	0.163 mg/l
June 2, 2020	14 mg/l
November 4, 2020	17.6mg/l
March 2, 2021	93.2 mg/l

Due to a breach in one of the plant's tanks, which was not repaired until October 2020, water was percolating into the tank from the ground, as well as the other tank. Thus, the flow measurements from January to October 2020 were unusually high. As such, the data in Table 2 is from November 2020, until the most recent data of March 2021. The units are in Millions of Gallons per day (MGD).

Table 2
Flow Readings

Date of Reading	*Flow level*
November 2020	0.000831 MGD
December 2020	0.001147 MGD
January 2021	0.001368 MGD
February 2021	0.000678 MGD
March 2021	0.001042 MGD

Surfactant and flow calculations

Equation (1) was used to calculate the average surfactant level. The numerator is the sum of all the surfactant values.

$$\frac{332.168\ \text{mg/l}}{13} = 27.68\,\frac{\text{mg}}{\text{l}} \tag{1}$$

This average must be converted into pounds per days, to later calculate the amount of Granulated Activated Carbon needed. An average flow must now be calculated, based on ACI-HERZOG's monthly flow measurement logs, to obtain a realistic estimate of the flow to be treated.

Using (1) as the template, the following average was obtained:

$$\frac{0.005066\ \text{MGD}}{5} = 0.001013\ \text{MGD} \qquad (2)$$

This average was multiplied by the conversion factor of 8.34. When written in equations, most surfactant concentrations are referred to as Methylene Blue Active Substances (MBAS), which are anionic surfactants that can be detected through colorimetric methods [7]. As Sodium Dodecylbenzenesulfonate is categorized as an MBAS, the concentration will appear as MBAS concentration in mg/l.

$$\text{MBAS}\left(\frac{\text{lb}}{\text{day}}\right) = \text{MBAS}\ \left(\frac{\text{mg}}{\text{l}}\right) * \text{flow (MGD)} * 8.34$$
$$= 27.68\frac{mg}{l} * 0.00103\ \text{MGD} * 8.34$$
$$= 0.23\frac{\text{lb}}{day} \qquad (3)$$

Activated carbon calculations

The MBAS in lb/day is multiplied by the volume conversion factors 1 kg/2.21 lb, 1000 g/1 kg, 1000 mg/g, and 1 kg/1000 g, and the carbon adsorption rate, 1 g GAC/29.4 mg MBAS, to obtain 3.54 kg. of carbon. Multiplying this by 2.21 lb/kg, a factor of 7.74 lb of carbon per day is obtained.

Because the trains tend to be washed on a need-by-need basis instead of by scheduling, not all days in a month have a flow reading. According to the data, out of the total 144 days that span from November 2020 to March 2021, only 102 days have a flow reading. If a safety factor is established and it is assumed that the plant has flow 250 days/year, and this number of days is multiplied by the factor of 7.74 lb./day, the carbon-per-year demand for the project can be calculated. This value, which is 1,935 lb./year, can be rounded up to 2000 lb./year.

COST ESTIMATIONS

Activated Carbon Costs

Each manufacturer sets the price for GAC based on its particle size, additional chemical properties (if the carbon was modified with chemical compounds), shape, and overall intended purpose. Per kilogram, the greatest price range observed for GAC is from $1.00 to $5.00, or $0.45 to $2.26 per pound. Its most common price range is between $1.00 to $3.50, or 0.45 to $1.58 per pound [8]-[9]. If a “middle ground” total price is calculated, the per unit price of $1.58 per pound is the most appropriate choice. Multiplying this price by the 2000 lb. of carbon needed, a total carbon price of $3,160 was obtained.

Skid mounted GAC Tank Costs

Environmental consultants from the Environmental Resources Management firm were contacted to determine the price of a skid mounted activated carbon system. These consultants, in turn, provided a line of contact to an activated carbon system supplier that they have worked with on previous projects. The supplier stated that a skid mounted, double vessel 1 ton, 16 gallons per minute GAC system can costs around $10,000, and a caustic soda feed system to regenerate the GAC can costs around $3,000, including installation. The price of installation for the GAC system can be around $3,000. The cost of a static mixer used specifically for water/wastewater treatment is around $1300 [10].

CONCLUSION

In response to new, stricter storm water regulations being implemented by EPA, ACI-HERZOG must implement more advanced water treatment methods to improve water quality across the board. To achieve this end, the project was introduced with the express purpose of improving ACI HERZOG’s carwash effluent, by reducing surfactants by 50 % of its current average. The approach selected was activated carbon filtration, a tried-and-true method well known for being a highly cost-effective alternative for surfactant removal.

For surfactants like Blue Marvel, activated carbon has an adequate adsorption rate of 29.4

mg/g. This detail is crucial, as absorption/adsorption rates between filtering media and specific chemical substance are usually not available. The discovery of filtering media such as HP20 and HP2MGL is also important, as these are more expensive but also more effective alternatives to activated carbon. With this information, it is possible to not only increase the number of alternatives of a project, but to design a project with superb accuracy, based on a media's absorption/adsorption rate.

The findings presented here could lead to changes in how filter-based water treatment systems are designed. No longer will the designer need to determine what media to use based on estimates. Instead, they can select the most appropriate media for a project based on the media's exact absorption/adsorption rate with regards to a chemical substance.

More research tests must be conducted between different filtering media and products, to further increase the number of known absorption/adsorption rates. It is also necessary to conduct additional tests with various physically or chemically modified filtering media, to determine what modifications make the filtering media more effective against specific chemical substances.

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