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by

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Use of Granular Activated Carbon to Remove Trace Organics From the Effluent of a Class-B Refinery, A Case Study

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ABSTRACT

A recent study by Raphaelian and Harrison (1978) at SOHIO's Toledo refinery demonstrated that the activated sludge biological treatment system reduced concentrations of trace organic compounds in the wastewater by over 99%. Addition of a pilot-scale mixed media filter and granular activated carbon (GAC) filter produced additional removals ranging from 12 to 98% for those compounds that could be quantified.

The estimated cost of adding a full-scale GAC system to the SOHIO refinery is $6,800,000. The yearly operational cost for an 8.6 MGD flow is $1,720,000, including amortization, and the annual energy requirement is estimated at 12.775×10^6 kwh(e); this is equivalent to 2.2×10^4 bbl crude oil, or 0.0503% of average annual refinery throughput.

1 INTRODUCTION

The public awareness of this nation's environmental problems has led to the imposition of ever stricter controls regulating wastewater effluent quality for U.S. refineries. The regulations chosen must reflect the realities of what is technically achievable for a given effluent quality against what is practical based upon cost-benefit analysis. This paper is an outgrowth of two studies conducted by Argonne National Laboratory. The first study, conducted by Raphaelian and Harrison (Ref. 1), addressed trace organic removals by conventional biological treatment and add-on pilot-plant granular activated carbon (GAC) filtration at the SOHIO/Toledo refinery. The second study (Ref. 2) assessed the energy and dollar costs for full scale GAC and powdered activated charcoal added on to activated sludge treatment.

2 REFINERY DESCRIPTION AND SAMPLING PROCEDURE

SOHIO's Toledo refinery, a Class B refinery meeting the 1977 EPA standards for best practical control technology currently available, was selected for testing the efficacy of GAC for removal of refractory organics from the refinery effluent. The Toledo/SOHIO treatment system consisted of an API separator, dissolved air flotation (DAF), extended aeration activated sludge (AS), and final clarifier (FC). A pilot-plant mixed media filter (MMF) and regenerated GAC columns were added to the system for the study. Composite wastewater samples were collected every 4 hours for 4 days.

Effluents from the DAF, AS, FC, MMF, and GAC units were sampled. Sampling was conducted one month after a refinery turnaround period by which time the wastewater treatment system had reached steady state. No upsets or significant changes in wastewater flow were noted during the 4 days. The wastewater samples were extracted and separated into acidic, basic, and neutral fractions by the EPA's R.S. Kerr Laboratory, Ada, OK.

3 ANALYTICAL PROCEDURES

The fractions obtained from the R.S. Kerr Laboratory were analyzed by using a computer-controlled, capillary column gas chromatograph interfaced to a mass spectrometer (GC/MS). Organic compounds in the DAF samples were sufficiently concentrated so that several hundred compounds could be identified by comparison to standards or by mass fragmentograms. Organic chemical concentrations in the remaining samples were far lower. However, by using the DAF as a "standard", many compounds that were found in the DAF effluent were also identified in the FC and AC effluents

The mass spectrometer is usually not used as a quantitative instrument. By counting the total number of ions produced by a single compound, a good estimate may be made of the quantity of the compound present. Alternatively, the counting of a single ion,

usually the predominant ion, may be used to gauge the quantity present. The latter method was used to quantify compounds found in the AS, MMF, and AC effluents. The results are estimates and do not take into account the efficiency of extraction of the original wastewater samples. However, using current techniques, more accurate quantitation of such dilute solutions is not possible.

4 REMOVALS OF ORGANIC COMPOUNDS FROM REFINERY WASTEWATER

The study of Raphaelian and Harrison (Ref. 1), from which most of the following data were obtained, has shown that the activated sludge unit significantly reduces the organic loading in the wastewater (Cf Tables 1 and 2). Typical organic removals exceed 99%. Although the removal figures are carried out to 4 places to show relative removals among different compounds, there is sufficient uncertainty in the analytical methods so that these numbers should be regarded only as good approximations of the actual organic removals in the treatment system. The traditional performance parameters for refinery wastewater systems are given in Table 3.

Additional removals of organic compounds achieved by the activated carbon columns are also significant. Removals achieved by the activated sludge unit were so great that it was not possible to calculate reliable average percent removals for activated carbon for some classes of compounds (e.g. phenols, pyridines, quinolines). The approximate daily output of organic compounds from the AS unit, based upon the mass spectral data, is 1500 g in the 8.6 million gallons of wastewater. Carbon columns would reduce this, on a total flow basis, to ≈150 grams per day. These values do not take into account the extraction efficiency in the analytical procedure. Tests by the API and EPA (Ref. 3) indicate that failure to correct for extraction efficiencies could produce results which underestimate the actual amounts present by 33 to 50%.

5 GAC COST ESTIMATES, SOHIO/TOLEDO AND INDUSTRYWIDE

Cost estimates were prepared for the addition of a GAC unit to the existing treatment system at the SOHIO/Toledo refinery and for industrywide adoption of GAC (Ref. 2). Several assumptions were made in preparing these estimates: 1) removals of specific organic compounds calculated for the SOHIO refinery correlate directly to the traditional industry performance standards, COD and TOC: 2) in order to achieve reductions in organic loading similar to those observed in the SOHIO test, it is necessary to reduce COD and TOC by the same percentages as was attained by the SOHIO pilot-plant GAC unit, 66% and 54% respectively; and 3) the effluents from the biological units in all refinery classes are equally amenable to GAC treatment. None of these assumptions is confirmable without additional studies.

Table 1. Concentration of Alkylated Benzenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3μL Injection)

Compound	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	g/Day[c] in AS Effluent	Percent Removal by Activated Carbon	g/day[c] in GAC Effluent
Toluene	101	38	99.87	4.26	84.1	0.68
Ethyl benzene	35	13	99.95	0.57	66.7	0.19
p and m-Zylenes	187	70	99.97	1.8	76.6	0.42
o-Xylene	101	38	99.97	0.99	77.3	0.22
i-Propyl benzene	5	2	ND	--	ND	--
n-Propyl benzene	13	5	99.94	0.25	T	--
m-Ethyl toluene	93	35	99.98	0.60	71.2	0.17
o-Ethyl toluene	32	12	99.98	0.21	T	--
1,3,5-Trimethyl benzene	43	16	99.97	0.42	ND	--
1,2,4-Trimethyl benzene	176	66	99.98	1.1	44.9	0.63
1,2,3-Trimethyl benzene	96	36	99.98	0.62	60.0	0.25
n-Butyl benzene	8	3	T	--	ND	--
m-n-Propyl toluene	19	7	99.97	0.19	ND	--
o-n-Propyl toluene	13	5	99.96	0.17	ND	--
m-Diethyl benzene	13	5	T	--	ND	--
1,c-Dimethyl-5-ethyl benzene	29	11	99.98	0.19	ND	--
1,3-Dimethyl-4-ethyl benzene	37	14	99.98	0.24	ND	--
1,2-Dimethyl-4-ethyl benzene	43	16	99.99	0.14	ND	--

Table 1. Concentration of Alkylated Benzenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3μL Injection)(Contd.)

Compound	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	g/Day[c] in AS Effluent	Percent Removal by Activated Carbon	g/day[c] in GAC Effluent
1,3-Dimethyl-2-ethyl benzene	16	6	ND	--	ND	--
1,2-Dimethyl-3-ethyl benzene	13	5	T	--	ND	--
1,2,4,5-Tetramethyl benzene	27	10	99.98	0.18	ND	--
1,2,3,5-Tetramethyl benzene	48	18	99.98	0.31	T	--
1,2,3,4-Tetramethyl benzene	64	24	99.99	0.21	51.4	0.10

[a]Neutral DAF fraction diluted 100 times.

[b]Neutral fraction of final clarifier effluent.

[c]Calculated value based on 8.6 mgd flow and % removals listed.

T Trace

ND Not detectable

Source: Ref. 1, with the exception of columns 5 and 7 which are from Ref. 2.

Table 2. Comparison of Percent Removal by Activated-Sludge and Activated-Carbon Units for Various Classes of Organic Compounds

	Percent Removal Range by Activated-Sludge Unit	Average Percent Removal by Activated-Sludge Unit	Percent Removal Range by Activated-Carbon Unit	Average Percent Removal by Activated-Carbon Unit
Alkanes	99.33-99.98	99.65 (25)	58.8-97.9	83.5 (18)
n-Alkanes	99.33-99.98	99.58 (19)	70.2-97.9	85.9 (15)
Branched Alkanes	99.73-99.96	99.88 (6)	58.8-78.7	71.9 (3)
Cycloalkanes	99.76-99.98	99.81 (10)	NM	NM
Alkylated Benzenes	99.94-99.99	99.97 (18)	44.9-77.3	66.5 (8)
Toluene	99.87	99.87 (1)	84.1	84.1 (1)
C_2-Benzenes	99.95-99.97	99.96 (3)	66.7-77.3	73.5 (3)
C_3-Benzenes	99.94-99.98	99.97 (6)	44.9-71.2	73.5 (3)
C_4-Benzenes	99.96-99.99	99.98 (8)	51.4	51.4 (1)
Alkylated Indans, Tetralins	99.93-99.99	99.98 (10)	50.0	50.0 (1)
Alkylated Naphthalenes	99.69-99.99	99.93 (20)	12.0-69.8	49.4 (13)
Naphthalene	99.99	99.99 (1)	37.7	37.7 (1)
Methyl Naphthalenes	99.99-99.99	99.99 (2)	33.3-44.9	39.1 (2)
C_2-Naphthalenes	99.94-99.98	99.98 (6)	12.0-55.8	34.1 (5)
C_3-Naphthalenes	99.69-99.97	99.89 (11)	45.2-69.8	71.1 (5)
Alkylated Benzothiophenes & Dibenzothiophenes	99.81-99.93	99.88 (8)	71.4-82.9	77.1 (2)
Alkylated PNAs	99.65-99.9	99.86 (10)	52.8-76.1	64.5 (2)

NM Not measurable, ( ) Number of compounds Source: Ref. 1, Table 3.8

Table 3. ANL Carbon Study Removal of Traditional Pollutants

Pollutant	AS Bio Plant Effluent	MMF Pilot Filter Effluent	GAC Pilot Carbon Column Effluent
COD			
mean concentration, mg/l	48	44	<15
maximum concentration, mg/l	51	51	<15
minimum concentration, mg/l	44	38	<15
mean percent removal	-	8	>66
TOC			
mean concentration, mg/l	24	22	<10
maximum concentration, mg/l	29	26	12
minimum concentration, mg/l	17	18	<5
mean percent removal	-	8	>54
Phenols			
mean concentration, ppb	22	20	<10
maximum concentration, ppb	40	20	<10
minimum concentration, ppb	10	10	<10
mean percent removal	-	9	>50

Source: Ref. 2, Table 3.9.

It is estimated that to equip the SOHIO/Toledo refinery with an add-on polishing system consisting of dual media filters, granular carbon absorption system, and a carbon regeneration system, a capital outlay of $6,800,000 and an annual operating cost of $826,000 (1978 dollars) would be required. The annual cost, assuming a 15 year amortization of the capital cost, would be $1,720,000 (Ref. 2). These estimates were based upon a study of the historical data for GAC costs. Table 4 lists the design criteria for this system.

A similar procedure was used to estimate the total annual cost for equipping all U.S. refineries with GAC polishing. Approximate daily flows for each of the 309 U.S. refineries surveyed by the U.S. EPA (Ref. 3) and cost factors based upon refinery size were used to extrapolate the cost for GAC at SOHIO's Toledo refinery to all U.S. refineries. GAC treatment for refineries having a daily flow below 0.5 MGD does not include carbon regeneration. The industry-wide estimates for GAC addition are: capital costs - 417×10^6, operating and maintenance - 68.7×10^6/yr, annual cost assuming 15-year amortization - 217×10^6/yr.

Table 4. GAC System Design Basis for the Class B Refinery[1]

Biological Treatment Effluent	
Average Flow	6,000 gpm
Average COD loading	3,443 lb/day
Average TOC loading	1,721 lb/day
Average TSS loading	>717 lb/day
Dual Media Filters	
Type	Dual Media Gravity Filters
Filtration Rate	3.0 gpm/ft^2
Backwash Rate	20 gpm/ft^2
Filter Run Time	12 hr minimum
Backwash Duration	15 minimum
Terminal Headloss	3.5 ft
Solids Capture	0.07 lb TSS/ft^2/ft Headloss
Filter Area	2,000 ft^2 Surface Area
No. of Units	5 @ 400 ft^2 each cell (20ft × 20ft)
Backwash Pumps	3 - 4,000 gpm (1 spare)
Backwash Surge Tank	360,000 gal.
Granular Activated Carbon Columns	
Carbon Capacity	0.25 lb COD/lb Carbon
Hydraulic Loading	4 gpm/ft^2
Contact Time	30 minutes (Empty Bed)
Carbon Make-Up Rate	10 percent of inventory
Regeneration Fuel	6,000 BTU/lb Carbon
Regeneration Steam	1 lb steam/lb Carbon
Furnace Size	16,000 lbs/day
Adsorbers	5 @ 20 ft diameter, 16 ft bed depth
Carbon Make-Up	1,400 lbs/day
Average COD Removal	66 percent
Average TOC Removal	54 percent

[1]Source, Ref. 2, Table 5.2.

Each additional treatment system may also be considered as an energy penalty. The energy consumed by the addition of a GAC unit to the SOHIO/Toledo refinery is estimated to be 0.0503% of the annual throughput of the refinery, a crude oil equivalent of 2.203×10^4 bbl/yr. Extension of GAC treatment to all U.S. refineries would require an estimated energy penalty of 0.0441% of the annual refinery throughput or the equivalent of 2.354×10^6 bbl of crude oil. Both estimates assume regeneration of carbon for refinery wastewater flows exceeding 0.5 MGD.

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