ABSTRACT

Petroleum reserves, international politics and economic considerations are driving the domestic petrochemical industry toward heavy and sour crude slates. A consequence of the change is increased concerns related to the wastewater effluent toxicity. In 2005, a powdered activated carbon-activated sludge (PAC-AS) treatment process was installed at a petrochemical facility to reduce whole effluent toxicity (WET). This case study presents information related to technology theory, application and post-implementation effluent quality.

WET at petrochemical facilities has been attributed to emulsified hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), amines, phenols and inorganic materials. The case study presented focuses on toxicity attributed to PAHs associated with fine particles. Activated sludge treatment, secondary clarification and tertiary filtration were ineffective at removing the pollutants. As a result, chronic toxicity to fathead minnows (Pimephales promelas) was observed, and treatment modifications were implemented to meet WET regulatory requirements.

Application of PAC to remove organic material from wastewater is a relatively proven technology in the textile, pulp & paper, pharmaceutical, chemical, and petrochemical industries. PAC was selected because of its ability to reliability attenuate toxic organic material in an existing bio-treater. There is limited published information on application of the technology; therefore, benchmarking against other facilities and lessons learned by wastewater operators were heavily relied upon to design and implement the project.

The time from concept to operation was approximately seven months and effectively doubled the facility’s treatment capacity. The modified treatment plant has reliably met WET requirements for approximately two years. Information presented should benefit petrochemical owners, industrial wastewater operators, and consultants that are preparing facilities for crude slate changes and modifications to upstream petroleum processing units.

INTRODUCTION

Petroleum reserves, international politics and economic considerations are driving the domestic petrochemical industry toward heavy and sour crude slates. A consequence of the change is increased concerns related to the wastewater effluent toxicity. In 2005, modifications were successfully implemented at a petrochemical facility to reduce WET. This report presents information related to PAC-AS history, theory and application. A case study concludes this document demonstrating the application of the PAC-AS technology.
HISTORY

Application of PAC to remove organic material from wastewater is a relatively proven technology in the textile, pulp & paper, pharmaceutical, chemical, and petrochemical industries. DuPont pioneered the incorporation of PAC in activated sludge reactors for treatment of wastewater. The first installation was located in New Jersey and treated wastewater from the Chambers Works chemical facility. DuPont engineers observed synergistic treatment improvements and lower costs relative to sequential treatment processes (Heath, 1986).

In the 1980s, DuPont sold the technology patents to Zimpro. For the past 50 years, DuPont and Zimpro have designed nearly all of the PAC-AS treatment processes, which number greater than 100. The largest PAC-AS system reported in literature is 53 million gallons per day (MGD) (U.S. Navy, 2002). Significant research was conducted and published on the theory in the 1970s; however, there is limited published information on application of the technology because it was a proprietary technology. For the case study presented in this document, benchmarking against other facilities and lessons learned by PAC-AS operators were heavily relied upon to design and implement the project.

PAC-AS reactors are often portrayed as a panacea for industrial wastewater problems. In reality, there are no technologies capable of remedying all challenges; however, PAC-AS systems can address a multitude of concerns when applied correctly. Benefits attributed to the addition of PAC include improvements in chemical oxygen demand (COD) removal, ammonia removal, shock resistance, reduction of volatilization, effluent toxicity, color removal, lower foam generation, settling, and sludge dewatering (Bettens, 1979; Thibault, 1977; Ng, 1987). In addition, carbon has been associated with the removal of some inorganic compounds (Wong, 1989).

AS reactors effectively remove compounds by biodegradation, biosorption and, to a lesser degree, volatilization (Wong, 1992). The addition of PAC to an activated sludge reactor adds a fourth removal mechanism (sorption) for reduction of non-biodegradable organic pollutants (Eckenfelder, 1989). If the non-biodegradable compounds are toxic to nitrifiers, their sorption can result in improved ammonia removal. The addition of PAC to an AS reactor can also attenuate volatile compounds reducing air emissions (Weber, 1986; Meidl, 1999) and improve solids removal efficiencies. The improved liquid-solids separation is attributed to ballasted flocculation and reduced foam generation (Bettens, 1979) in secondary clarifiers. The addition of PAC to AS has historically been applied to improve the removal of compounds that resist biodegradation and/or are toxic.

THEORY

The removal of pollutants in the PAC-AS process is attributed to volatilization, biodegradation, biosorption and sorption. The removal efficiencies of each independent reaction do not add to the efficiency observed in PAC-AS units (Heath, 1986). The difference is attributed to synergies between the four removal processes. The synergistic mechanisms of bio-regeneration, fixed-film treatment, sorption of inhibitory compounds, and sorption-desorption are presented in the following paragraphs. The mechanisms are theories based upon empirical observations and dominate mechanisms will vary based upon unique wastewater characteristics.

Bio-Regeneration

The mechanism of bio-regeneration is based upon the theory that PAC will attenuate biodegradable, slowly degradable, and calcitrant organic compounds (Bettens, 1979; Specchia, 1984; Ng 1987). The attenuation increase the microorganism/pollutant contact time from the hydraulic retention time (HRT) to the solid retention time (SRT) (Meidl, 1999). Over time, microorganisms are able to metabolize the biodegradable and slowly degradable compounds opening receptor sites to additional pollutants. Eventually, the available sorption sites will be occupied by calcitrant compounds and the carbon will need to be wasted from the
reactor. This theory explains why PAC isotherms and biological kinetics cannot independently predict the performance of a PAC-AS reactor.

Fixed-Film Treatment
Fixed-film treatment has been used to explain the improved pollutant removal efficiency relative to AS systems. Fixed bed reactors can support higher concentration of biomass; therefore, the reactors generally accommodate higher organic and shock loads relative to dispersed growth systems. In PAC-AS reactors, carbon particles are predominantly associated with biological floc (Hamoda, 1984). The carbon provides a site for the concentration of microorganisms, extra-cellular enzymes, and non-polar contaminants which facilitates organic pollutant removal (Orshansky, 1997). In addition, the carbon provides a structure upon which nitrifying bacteria attach increasing nitrification (Bettens, 1979). One notable difference between traditional fixed-film treatment units and PAC-AS units is the wasting of the support media. Clay, coke, char, and zeolites (Thibault, 1977; Hamoda, 1984; Smith, 1999) have been substituted for PAC in experiments. The performance of these systems was better than dispersed growth systems; however, removal efficiencies improved with increasing sorption capacity indicating that fixed-film theory does not independently account for synergies of PAC-AS systems.

Sorption Of Inhibitory Compounds
Pollutants in industrial wastewater can exhibit both treatment and effluent toxicity. Treatment inhibition can affect both heterotrophs and autotrophs contributing to elevated effluent COD and ammonia concentrations. Improve removal observed with PAC addition has been attributed to sorption of toxic compounds. This mechanism is most clearly evidenced by improved ammonia removal despite PAC’s low affinity for ammonia (Grieves, 1980; Eckenfelder, 1989). Evidently, PAC can protect nitrifiers from sorbable inhibitory compounds (Ng, 1987). For this mechanism to be effective, toxic compounds need to have high energy of sorption relative to other constituents in the wastewater. The energy of adsorption seems to indicate which organic pollutants are removed by sorption and which are removed by simultaneous sorption and biodegradation (Orshansky, 1997).

Sorption-Desorption
The sorption-desorption mechanism can result in both improvements and deterioration in effluent quality. PAC has the potential to attenuate pollutants and provide a more uniform organic loading to microbial populations. During a spike of organic material, the chemical equilibrium is shifted and PAC begins sorbing residual organics. As microorganisms metabolize the organic material in solution, the equilibrium reverses and the PAC begins to release organics. If PAC had not been present, a portion of the organic material would have passed through the reactor untreated. PAC provides a more uniform plant operation by buffering influent organic loads; however, this mechanism has also been associated with plant upsets.

As the PAC accumulates pollutants, the potential exists to displace inhibitory compounds during shock loadings of more strongly adsorbed compounds (Ng, 1987). A rapid desorption can increase the concentration of selected pollutants even though the influent concentration may be undetected. The adverse effect of this mechanism has been manifested in quicker recovery periods for AS units relative to PAC-AS system in several studies (Thibault, 1977). It appears that maintaining a relatively low SRT in PAC-AS reactors can minimize the potential for this adverse reaction.

APPLICATION
The successful application of the PAC-AS technology requires the selection of a carbon and modifications to a traditional biological treatment train. Unit processes of particular interest are the primary and secondary oil removal processes, aeration basins, and clarifiers. Abrasion and settling must also be considered for mechanical equipment and piping. Provided in the following paragraphs are parameters to be considered when designing a PAC-AS process.
Carbon Selection

The carbon selection affects the wastewater treatment process efficiency and the operation cost. Wood, lignite coal, bituminous coal and coconut shells are common sources of activated carbon that have different pore sizes and characteristics. For example, bituminous and sub-bituminous coal activated carbon (smaller pore size) are generally better suited for short chain hydrocarbons (i.e. TPH-GRO) sorption while lignite based carbon (large pore size) is better suited for longer chain hydrocarbons (i.e. TPH-DRO). The optimum carbon is wastewater specific although some trends exist which have developed from experience and research. These trends are:

1. compounds that are hydrophobic adsorb to carbon better than hydrophilic compounds
2. lower molecular weight compounds do not adsorb as well as higher molecular weight compounds (Dobbs, 1980), and
3. macro-porous carbon removes higher molecular weight compounds more effectively, relative to micro-porous carbon, because the compounds can enter the pore structure of the carbon.

Extensive sorption data has been published to describe carbon with parameters such as phenol sorption, methylene blue sorption, iodine number, and molasses number. Each provides comparative analysis for carbon such as internal pore size and adsorptive behavior for classes of compounds. Iodine numbers, molasses numbers, and relative cost are listed in the following table for a selection of carbon types.

<table>
<thead>
<tr>
<th>Material</th>
<th>Iodine No.</th>
<th>Molasses No.</th>
<th>Relative Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>550</td>
<td>425</td>
<td>100</td>
</tr>
<tr>
<td>Virgin bituminous</td>
<td>800</td>
<td>225</td>
<td>120</td>
</tr>
<tr>
<td>Bituminous</td>
<td>700</td>
<td>325</td>
<td>85</td>
</tr>
</tbody>
</table>

Manufacturer-provided values can be used to narrow carbon alternatives for wastewater-specific bench scale testing. Iodine numbers generally indicate the sorption capacity of carbon for aromatic compounds (short chain) and molasses number for coloring compounds (long chain). According the preceding table, the highest sorption capacity per unit cost for short chain organics is bituminous carbon (700/85) whereas lignite has the highest value for long chain compounds (325/85). The example illustrates that macro-porosity carbons (lignite) can have higher sorption and lower cost relative to micro-porosity carbons (bituminous) even though their surface area is less.

Because the calculated ratios can be relatively close, testing is recommended to confirm sorption capacity and life cycle cost. Isotherm experiments are considered the best way to compare the effectiveness of various activated carbons. As carbon particles are ground finer sorption becomes more difficult to predict using published data; therefore, pilot testing is of even greater importance for PAC-AS systems. That being said, neither of the refinery PAC-AS systems used to bench mark the case study were using the amount of PAC predicted by the pre-design isotherm testing. In general, pilot studies are better than theoretical calculations; however, neither is a substitute for operational observations and adjustments.

Activated carbon can be used in granular or powder form; however, the powder form is more common for refinery wastewater given the economics and the treatment capacity. Grieves et al. (1980) showed comparable treatment between the two forms, but treatment cost favored PAC. Another study, by Wong et al. (1992), chose full scale operation of a powder system in the study in lieu of GAC citing that PAC was more cost affective. The synergistic effects of a PAC-AS system (presented in preceding paragraphs) typically make PAC a more economical choice relative to GAC beds.
Pac Equipment
Material handling of PAC is a challenge because of its tendency to bridge, flood, float, harden and dust. Failure to consider these properties increases maintenance efforts and can result in a hazard to facility operators. Silos are generally used to store dry PAC before it is:

1. fed from the silos
2. wetted, and then
3. transferred to the biological reactor. During any of these three stages, the potential exists for plugging of equipment.

To avoid compaction and flooding, the bin activator and PAC feeder rate need to be coordinated. In this paper’s case study, the air fluidizer run time was adjusted to match the rotary airlock feed rate. The rotary airlock was installed to protect the feed screw from the progression of flooding, compaction and screw shaft damage. Other feed configurations are offered; however, compaction and flooding have not been reported with the presented configuration during the first two years of operation.

Direct addition of bulk dry PAC to a PAC-AS system would result in a significant portion of the carbon floating. To avoid flotation, a wetting cone and eductor are used to create a slurry of 1% to 5% solids. The quantity and pressure of utility water to create the slurry can be significant and should be considered early in the design process. Keeping the PAC is suspension until it reaches the PAC-AS reactor can be challenging. If fluid velocities are not maintained between 5 and 7 feet per second, PAC will begin to settle (Hassibi, 2007). At velocities greater than this range, slurries abrade pipe and fittings. PAC that settles in pipelines has a tendency to harden and line flushing is ineffective at removing the deposits.

Explosion hazards exist for activated carbon and especially for PAC due to high surface area and ease of dust formation (Hyun et al., 1999). Hyun concluded that the explosion hazard increased as activated carbon surface area increased. To mitigate this hazard, grounding the silo and fill line is recommended to prevent static discharges between flowing PAC and both the fill line and the silo.

Aeration Basin
Carbon has a high affinity for free and emulsified hydrocarbons; therefore, primary and secondary oil removal technologies are important pre-treatment requisites for refinery PAC-AS systems. Free oil increases PAC usage, decreases floc density, and inhibits both heterotrophic and autotrophic microorganisms. Operating PAC-AS systems at relatively long solids retention times reduces operation cost by reducing carbon usage and has been found to enhance treatment efficiency (Grieves et al., 1977). Therefore, removal of free oil and solids is essential which otherwise accumulate in aeration basins blocking adsorption sites, preventing microbial growth on carbon, and reducing oxygen transfer efficiency. Typically, the oil influent concentrations to PAC-AS processes are limited to 25-50 mg/L.

Oxygen transfer and mixing should be considered when designing PAC-AS units. Generally, the higher settling velocities associated with PAC-AS mixed liquor suspended solids (MLSS) makes mixing the limiting parameter. Aeration rates of 30 to 40 scfm/1000 ft³ are used in circular basins to minimize the settling and accumulation of solids in the unit process. Aeration rates exceeding these values tend to shear the floc and increases the suspended solids in the effluent.

Clarification
The addition of PAC to an existing AS unit will affect the design and operation of secondary clarifiers. In PAC-AS systems, the MLSS in maintained at a higher concentration. As a result, clarifiers are generally solids limited. Solids loading rates of 30 pounds per square foot per day are commonly used to design the process.
existing clarifiers, the installation of Stamford Baffles may be necessary to prevent carbon carry over especially during start-up when PAC is not fully incorporated into the biological floc.

PAC improves settling by ballasting biological floc. The carbon increases settling velocities and solids concentration in the return activated sludge (0.5 to 1.5% by wt.). As a result, the clarifier mechanism must be designed to withstand the higher torques required to move sludge. For a PAC-AS process, the force may be three times that of a traditional activated sludge process (3 pounds per foot).

Full length skimmer boxes are recommended in refinery applications. Periodically, biological processes will receive free hydrocarbons resulting from a plant upset. When this occurs, the PAC dose can be increased to remove the residual hydrocarbons. If the loading is significant, the oil can float large quantities of PAC. The ability to remove the floating PAC in a timely manner is facilitated by the full length skimmers.

Hydraulics
The hydraulic design of a PAC-AS process must account for PAC’s abrasive nature and settling characteristics. As presented earlier, PAC hardening becomes a problem at line velocities below 5 feet per second. However at velocities exceeding 7 feet per second, erosion of pipes, fittings, and valves becomes a concern. The following are recommendations for the hydraulic design of a PAC-AS process:

• Minimize pump speeds
• Minimize pipeline lengths and fittings
• Use plug and knife gate valves
• Provide a flush system for lines that are periodically inactive

CASE STUDY
A PAC-AC treatment process was installed at a petroleum refinery in 2005 to address chronic toxicity to fathead minnows (*pimephales promelas*). The treatment train originally consisted of grit removal, dissolved air filtration (DAFs), surge equalization, biological treatment, clarification, filtration and disinfection. In 1998, the treatment process was modified to a two-stage biological reactor system to protect nitrifiers from shock loads, toxicity and inhibitory compounds. An integrated fixed film activated sludge (IFAS) system, designed by Kaldnes, was installed preceding the activated sludge processes. The unit process successfully reduced effluent ammonia concentrations, recovered faster from shock loadings, and reduced the organic loading on the existing AS system.

In the 2000s, the DAFs were abandoned, foaming was observed in the secondary clarifiers, and WET exceeded National Pollution Discharge Elimination System (NPDES) permit requirements. The abandonment of the DAFs shifted oil removal to the surge tanks where oil was removed and solids settled. In addition, the IFAS process created a substrate limited environment in the AS process resulting in foaming. The reduced efficiency in oil removal, accumulation of solids, and foaming were all suspected of contributing to WET.

A pilot study was conducted in 2004 and PAC addition was proven to be effective at reducing WET. In March 2005, Burns & McDonnell was retained to design and provide
construction support for modifications to the treatment plant. Modifications included doubling the capacity of the treatment plant, adding PAC feed systems, and upgrading existing infrastructure to accommodate the addition of PAC. In October 2005, the plant was commissioned. The following paragraphs describe the wastewater sources, influent characteristics, toxicity, treatment train modifications and performance of the modified treatment train.

Wastewater Source
The wastewater treatment plant is operated by a domestic oil company. The facility accepts wastewater from a petroleum refinery, natural gas liquids fractionating and processing plant, and chemical plant. When the wastewater treatment plant was originally built, all three facilities were owned by a single organization. Currently, the chemical plant is owned and operated by a third party and contracts for wastewater treatment.

Influent Characteristics
Significant variance in both the wastewater flow and pollutant concentrations was observed. The variability is attributed to receiving wastewater from three facilities, minimal control over the chemical plant discharge and normal variance attributed to industrial sources. To provide a relatively uniform feed, two surge tanks are installed preceding the treatment plant having a capacity of 260,000 barrels. The following table presents average pollutant characteristics observed following the surge tanks, IFAS process and AS process. The values for the AS effluent changed significantly with the addition of PAC as presented in the “Performance” section of this report.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>IFAS Effluent</th>
<th>AS Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>340 mg/L</td>
<td>180 mg/L</td>
<td>60 mg/L</td>
</tr>
<tr>
<td>Ammonia</td>
<td>10 mg/L</td>
<td>4.0 mg/L</td>
<td>0.8 mg/L</td>
</tr>
<tr>
<td>TSS</td>
<td>NA</td>
<td>110 mg/L</td>
<td>NA</td>
</tr>
<tr>
<td>Toxicity (mean survival)</td>
<td>NA</td>
<td>NA</td>
<td>32%</td>
</tr>
</tbody>
</table>

Treatment Train Modifications
Both physical and operational changes were made to the treatment process. The changes were made to expand the capacity of the treatment plant and reduce WET. A biological reactor, clarifier, two PAC feed silos and a water reuse system were added to the treatment plant. In addition, course bubble diffusers and high torque clarifier mechanisms were installed in both the existing and new trains. The following sketch shows components of the modified treatment plant.

The biological population in the AS reactor was primarily material sloughed from the IFAS system since growth rates in the substrate limited AS environment were low. To maintain a MLSS that could respond to changing influent characteristics, the SRT was maintained at approximately 25 days. The practice was

Engineering, Architecture, Construction, Environmental and Consulting Solutions
© 2007 Burns & McDonnell
articles@burnsmcd.com
based upon the theory that extended aeration (long SRT) improves the removal of residual organics in refinery wastewater. The long sludge age contributed to the foaming, accumulation of oil, and low settling velocities in the biological process. The use of PAC to attenuate organic loading allowed the facility operators to decrease the SRT remedying the solid separation concerns. In addition, the HRT was increased to allow greater PAC and microorganism contact time with residual pollutants. The table below presents operational changes made to the treatment plant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average flow</td>
<td>2,000 gpm</td>
<td>3,500 gpm</td>
</tr>
<tr>
<td>SRT</td>
<td>25 days</td>
<td>12 days</td>
</tr>
<tr>
<td>HRT</td>
<td>8.6 hours</td>
<td>10 hours</td>
</tr>
<tr>
<td>MLSS</td>
<td>1,800 mg/L</td>
<td>3,000 mg/L</td>
</tr>
</tbody>
</table>

**Effluent Toxicity**

WET at petrochemical facilities has been attributed to emulsified hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), phenols, amines, and inorganic materials. Screening wastewater to identify toxic compounds is difficult because of synergistic and antagonistic toxic effects. Therefore, bench and pilot studies are recommended to identify methods of removing toxicity. Laboratory testing was used to determine the following characteristics of the site specific toxicity (Brown & Caldwell, 2004).

- Toxicity could be removed using a 0.2 um filter
- The toxicity is associated with TPH-DRO organics (C16 to C28)
- TPH-DRO concentrations greater than 0.5 mg/L resulted in unacceptable WET

TPH-DRO organics are slowly degraded biologically and strongly sorbed by activated carbon. Therefore, the addition of PAC was considered to be a likely candidate for toxicity removal. Sorption and wasting of PAC to sludge processing is probably the primary removal mechanism. Bio-regeneration is probably a secondary removal mechanism since PAC extends the biological contact time by a factor of approximately twenty-eight. The feasibility of PAC addition to the AS process was confirmed with pilot testing in 2004.

**Performance**

Modifications to the treatment plant were designed in three months and construction was completed in four months. During the entire construction period, the treatment plant remained in operation. In October 2005, PAC was added to the AS process and the effluent toxicity immediately complied with NPDES permit requirements. In addition to toxicity, several other effluent parameters decreased significantly as presented in the following table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD removal</td>
<td>65%</td>
<td>90%</td>
</tr>
<tr>
<td>Ammonia removal</td>
<td>80%</td>
<td>100%</td>
</tr>
<tr>
<td>Toxicity (survival)</td>
<td>32%</td>
<td>100%</td>
</tr>
<tr>
<td>Filter backwash frequency</td>
<td>24 hours</td>
<td>36 hours</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The addition of PAC to AS units has the potential to improve pollutant removal efficiencies, avoid the cost of entirely new treatment processes, reduce WET and be implemented quickly. A refinery wastewater treatment plant was used to illustrate PAC’s ability to enhance the removal of

1. compounds that resist biodegradation
2. organics
3. ammonia, and
4. solids.

The mechanisms of removal probably included sorption-wasting and bioregeneration. Modifications to the facility were made quickly (seven months) and the improved performance was observed immediately. The following recommendations resulted in observations made during the implementation of a PAC-AS unit process:

- Bench and pilot studies are recommended to select treatment technologies because of synergistic and antagonistic toxic effects of chemicals in wastewater environments.
- The addition of PAC to activated sludge processes has been used from nearly 50 years. The use of PAC-AS to remove toxicity has been applied successfully in multiple industries.
- There is multiple removal mechanisms that create the synergy observed in PAC-AS system. Site specific mechanisms will depend upon the biodegradability, sorption energy, and toxicity of compounds found in the wastewater.
- The addition of PAC to an existing treatment plant may require mechanical changes beyond the PAC feed system. These changes may be required to avoid material erosion, settling, motor overloads, and line plugging.
REFERENCES


Smith, Scot; Princz, Peter; (1999) Improvement of the Biological Degradability of Wastewaters Using Activated Zeolites. NATO’s Science for Peace Program, SfP-972494.


**Keywords:** Wastewater, Powder Activated Carbon, PAC-AS, WET, Toxicity, PAH, Hydrocarbon, Refinery.