Activated sludge combined with powdered activated carbon (PACT process) for the petroleum industry wastewater treatment: A review

Shahryar Jafarinejad
Chemical Engineering Division, College of Environment, UoE, Karaj, Iran
*Corresponding author's E. mail: jafarinejad83@gmail.com

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ABSTRACT

Treatment of petroleum industry wastewater by a conventional process such as activated sludge may be hindered by the presence of recalcitrant organic compounds; therefore, tertiary treatments for wastewater polishing are required. Powdered activated carbon (PAC) adding to the activated sludge process can lead to a higher quality of treated wastewater, a more stable system and the production of reusable water. In this study, history, principles, mechanisms, and advantages of powdered activated carbon treatment (PACT) process, selection of carbon, typical configuration of a refinery wastewater treatment plant (WWTP) consisting of the PACT process, and application and/or performance of the PACT technology for the petroleum industry wastewater treatment have been reviewed. Several laboratories, pilot and full scale studies have demonstrated that PACT technology can be useful for the petroleum industry wastewater treatment. PACT process can generally be applied for the petroleum industry wastewater in those cases where stringent standards require to be met for certain contaminants.

INTRODUCTION

Petroleum industry includes activities or sectors such as exploration, development and production; hydrocarbon processing (refineries and petrochemical plants); storage, transportation, and distribution; and retail or marketing (Jafarinejad, 2016a,b; 2017a).

Large amounts of wastewaters are generated in the petroleum industry (Jafarinejad, 2017a,b) which contain a diverse range of contaminants such as oil, phenols, sulfides, dissolved solids, suspended solids, toxic metals and biological oxygen demand (BOD)-bearing materials, etc (Beychock, 1967; Santos et al., 2016). Management and treatment of these complex wastewaters are a great problem (Tyagi et al., 1993). Due to the compliance with the regulations set by regulatory agencies, the related harm prevention on the surrounding environment, and water reuse issues, the petroleum industry wastewaters need treatment with appropriate treatment technologies (Ghorbanian et al., 2014).
Process wastewater pretreatment, primary treatment, secondary treatment, and tertiary treatment or polishing are general classifications of petroleum industry wastewater treatment (U.S. EPA, 1995; Benyahia et al., 2006; IPIECA, 2010; European Commission and Joint Research Center, 2013; Goldblatt et al., 2014; Jafarinejad, 2017a,b). In secondary treatment, dissolved oil and other organic pollutants may be consumed biologically by microorganisms (U.S. EPA, 1995; Jafarinejad, 2016c; 2017a,b). In real, organic matter can be oxidized into simple products (CO₂, H₂O, and CH₄) under aerobic, anaerobic or semi aerobic conditions by microorganisms (naturally occurring, commercial, specific groups, and acclimatized sewage sludge). A C:N:P ratio (100:5:1) may be appropriate for growth of microorganisms (Ishak et al., 2012; Jafarinejad, 2017a,b). Biological treatment processes can be classified into two categories:

- Suspended growth processes such as activated sludge process (ASP), powdered activated carbon treatment (PACT) process, sequencing batch reactors (SBRs), continuous stirred tank bioreactor (CSTB), membrane bioreactors (MBRs), and aerated lagoons; and
- Attached growth processes such as trickling filters (TFs), fluidized bed bioreactor (FBB), and rotating biological contactor (RBC) (EPA, 1997; IPIECA, 2010; Ishak et al., 2012; Jafarinejad, 2017a,b).

Treatment of petroleum industry wastewater by a conventional process such as activated sludge may be hindered by the presence of recalcitrant organic compounds; therefore, tertiary treatments for wastewater polishing are required. Powdered activated carbon (PAC) adding to the activated sludge process can lead to a higher quality of

Fig. 1: Schematic of a typical powdered activated carbon treatment (PACT) process (modified from Meidl, 1992; 1997; IPIECA, 2010; Jafarinejad, 2017a).
treated wastewater, a more stable system and the production of reusable water (Campos et al., 2014). In this study, history, principles, mechanisms, and advantages of powdered activated carbon treatment (PACT) process, selection of carbon, typical configuration of a refinery wastewater treatment plant (WWTP) consisting of the PACT process, and application of the PACT technology for the petroleum industry wastewater treatment have been reviewed.

History of the PACT process

PACT system has been developed (U.S. Patent 3,904,518) by DuPont in the early ’70s (Sublette et al., 1982; Campos et al., 2014). Robertaccio et al. (1972) and Robertaccio (1973) have reported on pilot scale treatment of wastewater from DuPont’s Chambers Works plant in Deepwater, New Jersey (Sublette et al., 1982) and in real, the first installation was in New Jersey. Synergistic treatment improvements and lower costs in comparison with the sequential treatment processes have been seen (Heath, 1986; Foy and Close, 2007). In the 1980s, DuPont sold the patent to Zimpro. DuPont and Zimpro have designed most of the PACT systems in the world (Foy and Close, 2007). In real, according to Meidl (1992), DuPont, General Electric, Giba-Geigy, Koch refining, Unocal, Exxon, Tenneco, Alcoa, BP oil, Bostik, Nalco, Tosco and others are some major users of the PACT technology (Meidl, 1992).

Some researches was carried out and published on the theory of PACT technology in the 1970s. This process was a proprietary technology, therefore, there is limited published information on the application of this process (Foy and Close, 2007).

Principles of the PACT process

Activated carbon (both PAC and granular activated carbon (GAC)) has been utilized for a long time in water and wastewater treatment due to its large surface area for adsorption (Tri, 2002; Jafarinejad, 2015; 2017a). PAC has a

Fig. 2: Effect of sludge age on effluent soluble total organic carbon (TOC) in activated sludge and PACT systems (Meidl, 1997).
diameter of less than 200 mesh (Tri, 2002). Activated sludge treatment with PAC or PACT process is similar to the conventional activated sludge process, but in this process, PAC is added directly into the aeration tank or mixed with the influent of this tank. The removal of contaminants is achieved and enhanced by a combination of biodegradation and adsorption (Tri, 2002; IPIECA, 2010; Jafarinejad, 2017a). A schematic of a typical PACT process is shown in Fig. 1. Most of the PAC is recycled with the activated sludge, but the system needs a continuous makeup of fresh carbon (IPIECA, 2010; Jafarinejad, 2017a).

According to Tri (2002) and Jafarinejad (2017a), the PACT process could generally remove organic compounds more efficiently than what would be expected from either biodegradation or adsorption alone. The dosage of PAC and the mixed-liquor-PAC-suspended-solids concentration are related to the sludge age as follows:

\[ X_p = \frac{X_i \theta_c}{\theta} \]  

(1)

Where, \( X_p \) is equilibrium PAC mixed-liquor-suspended-solids (MLSS) content (mg/L), \( X_i \) denotes PAC dosage (mg/L), \( \theta_c \) is solid retention time (SRT) (d), and \( \theta \) denotes hydraulic retention time (HRT) (d). The organic removal per unit of carbon is enhanced with higher sludge ages which it improves the process efficiency (Tri, 2002; Jafarinejad, 2017a). In real, the surface area in the treatment zone is enhanced with increasing the SRT which is provided by the carbon; thus, the amount of bacteria therein will also be increased. Effect of sludge age on effluent soluble total organic carbon (TOC) in activated sludge and PACT systems is shown in Fig. 2. According to Fig. 2, in activated sludge process, there is no considerable decreasing in effluent soluble TOC by increasing sludge age; however, at a constant carbon dose, PACT system is able to remarkably reduce soluble TOC solely by increasing sludge age (Meidl, 1997).

Because the addition of carbon does not entail any main preparation, space, or capital investment and this modification could be readily incorporated into most existing plants; therefore, it can be very feasible solution in wastewater treatment (Stadnik and Flynn, 1977; Nayar and Sylvester, 1979). PACT technology has been widely applied in organic chemicals, petrochemicals, refineries, textile/dyes, pulp and paper, pharmaceutical industries, industrial and municipal water re-use, leachates, contaminated groundwater treatment, etc (Meidl, 1997; Foy and Close, 2007).

Mechanisms of the pact process

In the PACT process, the removal of pollutants is attained and enhanced by a combination of biodegradation and adsorption (Tri, 2002; IPIECA, 2010; Jafarinejad, 2017a). In real, according to Sublette et al. (1982), there is an apparent synergistic effect which is originated from the stimulation of biological activity through removal of inhibitory substances or concentration of nutrients and the bioregeneration of the adsorptive capacity of activated carbon (Sublette et al., 1982).

Advantages of the pact process
Improved removal of BOD; improved removal of chemical oxygen demand (COD) and refractory organics; improved stability to shock loads and toxic upsets; less tendency to foam in aerator (Sublette et al., 1982); the operational flexibility enhancement of the treatment system (Meidl, 1992); lower effluent toxicity (Meidl, 1997; Sublette et al., 1982); metals control without a separate precipitation step; volatile organic compound (VOC)/odor control and minimization; color removal (Meidl, 1992; 1997); improved sludge settling and dewatering (Sublette et al., 1982) or less wet solids for disposal and simplified residual management (Meidl, 1997) are some advantages of PACT process over conventional activated sludge.

**Selection of carbon**

The treatment efficiency and the operation cost can be affected by the carbon selection. The common sources of activated carbon are wood, lignite coal, bituminous coal, and coconut shells which have different characteristics. Iodine numbers usually show the sorption capacity of carbon for

<p>| Table 1: The performance of PACT/WAR system for a refinery wastewater (Meidl, 1997) |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Actual influent</th>
<th>PACT effluent</th>
<th>Discharge standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD (mg/L)</td>
<td>718</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1494</td>
<td>78</td>
<td>250</td>
</tr>
<tr>
<td>Phenolics (mg/L)</td>
<td>70</td>
<td>Nil</td>
<td>1</td>
</tr>
<tr>
<td>Sulfide (mg/L)</td>
<td>142</td>
<td>Nil</td>
<td>0.5</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>2</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>75</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>6.6</td>
<td>6-8.5</td>
</tr>
</tbody>
</table>

<p>| Table 2: The performance of PACT system for refinery wastewater (Meidl, 1992) |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>PACT influent</th>
<th>PACT effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>616</td>
<td>129</td>
</tr>
<tr>
<td>BODS (mg/L)</td>
<td>149</td>
<td>&lt;6</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>31</td>
<td>7</td>
</tr>
<tr>
<td>NH$_3$-N (mg/L)</td>
<td>16.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cyanide (mg/L)</td>
<td>4.78</td>
<td>0.154</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>9.55</td>
<td>0.053</td>
</tr>
<tr>
<td>Color (APHA units)</td>
<td>109</td>
<td>38</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>14.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Toxicity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainbow trout (LC$_{50}$-96 hours)</td>
<td>&gt;100</td>
<td></td>
</tr>
<tr>
<td>Sea urchin (NOEC), %</td>
<td>&gt;90</td>
<td></td>
</tr>
<tr>
<td>Sea urchin (LOEC), %</td>
<td>&gt;90</td>
<td></td>
</tr>
<tr>
<td>Water flea (NOEC), %</td>
<td>&gt;90</td>
<td></td>
</tr>
<tr>
<td>Water flea (LOEC), %</td>
<td>&gt;100</td>
<td></td>
</tr>
</tbody>
</table>

LC$_{50}$: Concentration of sample in water which achieves 50% fish mortality in 96 hours.
NOEC: No Observable Effect Concentration
LOEC: Lowest Observable Effect Concentration

<p>| Table 3: The performance of PACT system for a petrochemical wastewater (Meidl, 1997) |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (gallon/day)</td>
<td>90000</td>
<td></td>
</tr>
<tr>
<td>SBOD (mg/L)</td>
<td>1600</td>
<td>&lt;30</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>3600</td>
<td>135</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>Total suspended solids (mg/L)</td>
<td>650</td>
<td>60</td>
</tr>
</tbody>
</table>
aromatic compounds (short chain) and molasses number for coloring compounds (long chain). Iodine numbers for lignite, virgin bituminous, and bituminous are 550, 800, and 700, respectively, whereas, molasses numbers for lignite, virgin bituminous, and bituminous are 425, 225, and 325, respectively. The relative cost for virgin bituminous>lignite>bituminous. In real, the optimum carbon is wastewater specific (Foy and Close, 2007).

Activated carbon is generally applied in powdered or granular form. According to Grieves et al. (1980), Wong et al. (1992), and Foy and Close (2007), PAC is more common for petroleum industry wastewater treatment due to its economical and treatment capability.

Application of the pact process for the petroleum industry wastewater treatment

Several laboratory, pilot and full scale studies have demonstrated that PACT technology can be useful for the petroleum industry wastewater treatment (Rizzo, 1976, 1979; Crane, 1978, 1979; Nayar and Sylvester, 1979; Grieves et al., 1978a,b, 1979, 1980; Meidl, 1997; Guarino et al., 1988; Yaghmaei et al., 2005; Foy and Close, 2007; Campos et al., 2014). PACT process is generally applied for the petroleum industry wastewater in those cases where stringent standards require to be met for certain contaminants (IPIECA, 2010; Jafarinejad, 2017a). At this time, the largest applications of the PACT technology can be found in the petroleum refineries and petrochemical plants (Meidl, 1997).

Nayar and Sylvester (1979) showed that in a biological reactor containing a pure culture of E. coli subjected to a variety of feed upsets involving phenol, the powdered activated carbon addition could greatly control upsets in biological process and permit operation with an input phenol concentration above 1000 mg/L (Nayar and Sylvester, 1979).

Tri (2002) investigated the biodegradation of the oily wastewater by activated sludge process and biological activated carbon (BAC) process operated in sequencing batch reactor (SBR) mode by adding PAC into the reactor at different doses of 100 – 500 mg/L. The removal efficiency of activated sludge process reported to be 80% for COD and 90% for oil and grease at HRT of 13h and a tendency of effluent quality improvement of the BAC process was observed at PAC dose of 500 mg/L and HRT of 3h compared to the activated sludge process (Tri, 2002). Yaghmaei et al. (2005) compared PACT and bioaugmentation of activated sludge treatment (BAST) processes for the treatment of furfural-containing wastewater (Pars oil refinery wastewater with furfural concentrations of 100-2000 ppm). A little higher COD removal efficiency in PACT process and the same furfural removal in both processes were reported, however, at low HRT, BAST process demonstrated better results in both furfural and COD removal than PACT process. Settability of effluent sludge in BAST process was better than in PACT process and due to the rapid growth of microbial biomass in BAST process, the MLSS concentration in this process was higher than in PACT process and thus, BAST process has a lower need to return sludge than PACT process. They concluded that because of both high performance and optimum conditions with economical operation, BAST process may be an attractive alternative to existing PACT process for the treatment of furfural-containing wastewater, especially in developing countries (Yaghmaei et al., 2005).

Campos et al. (2014) compared the efficiency of PACT process with activated sludge in the treatment of oil refinery wastewater and reported that by applying Norit (SAE Super 94009-7) PAC under HRT of 24 h, SRT of 30 d, carbon replacement of 150 mgPAC/L_{effluent} and 4.5 gPAC/L_{reactor}, the removal efficiencies were 98% for COD and 99% for phenol, and there was an overall reduction in Ceriodaphnia dubia chronic toxicity. In addition, the PACT process was more stable in comparison with the activated sludge (Campos et al., 2014).

According to Meidl (1997), the simplified process flow diagram (PFD) of a refinery WWTP consisting of PACT process is shown in Fig. 3 which includes equalization, free oil and emulsified oil separation systems, PACT aeration basin, clarifier, treated effluent guard pond, gravity thickener, wet air regeneration (WAR) system, centrifuge dewatering, etc. The performance of this plant for a refinery wastewater is given in Table 1 which all discharge standards are met (Meidl, 1997). In the other work, the performance of PACT system for a refinery wastewater was given which is shown in Table 2. This table illustrates that for example, COD, BOD, oil and grease removals in this system are 79.05%, >95.07%, and 95.27%, respectively (Meidl, 1992).

Also, a six-month pilot test of the PACT system and activated sludge conducted at a petrochemical for a complex, high-strength organic wastewater from the production of organic acids, solvents and aromatics demonstrated that effluent COD and BOD for PACT system were 100 and 14 mg/L, respectively, whereas, these parameters for activated sludge were 285 and 32 mg/L, respectively. The performance of the full-scale PACT system for this wastewater is given in Table 3. According to Meidl (1997), the PACT system is about 10% less in capital costs than the activated sludge. Also, anticipated cost per cubic meter treated is $0.98 for the PACT system, versus $1.05 for the activated sludge. In addition, the amount of dewatered sludge for the PACT system is less than the activated sludge (Meidl, 1997).

According to Foy and Close (2007), in 2005, Burns & McDonnell added PAC to the activated sludge process (in real, modified and installed a PACT system) at a petrochemical facility to decrease whole effluent toxicity (WET). After addition of PAC to the ASP, COD removal, ammonia removal, and toxicity (survival) were 90%, 100%, and 100%, respectively. It is necessary to note that the addition of PAC to an existing WWTP may need mechanical changes beyond the PAC feed system to avoid material erosion, settling, motor overloads, and line plugging (Foy and Close, 2007).

In 2011, China Petroleum & Chemical Corporation (Sinopec Corp.) selected Siemens Water Technologies to provide a system to treat wastewater at Anqing refinery, in
Anhui Province, China. The complete wastewater treatment solution consisted of a PACT system, a Zimpro WAR hydrothermal unit, and a hydro-clear sand filtration system to treat salty and oily wastewater from refining and petrochemical production activities from existing and upgraded units (Abdelwahab et al., 2009; Chen, 2004; Dimoglo et al., 2004; Diya’uddeen et al., 2011; Ji et al., 2002; Khaing et al., 2010; Qin et al., 2007; Rubio et al., 2002; Rocha et al., 2012; Shokrollahzadeh et al., 2008; Siemens, 2011; Zhong et al., 2003).

CONCLUSIONS

In the PACT process, the removal of pollutants is attained and enhanced by a combination of biodegradation and adsorption. Improved removal of BOD, COD and refractory organics; improved stability to shock loads and toxic upsets; less tendency to foam in aerator; the operational flexibility enhancement of the treatment system; lower effluent toxicity; metals control without a separate precipitation step; VOC/odor control and minimization; color removal; improved sludge settling and dewatering or less wet solids for disposal and simplified residual management are some advantages of PACT process over conventional activated sludge. The PACT system may be about 10% less in capital costs than the activated sludge. By applying PACT technology for the petroleum industry wastewater treatment, all discharge standards can usually be met. Comparison of the performance of the PACT system for refinery wastewater with liquid effluents levels form the petroleum industry is shown in Table 4. PACT process is generally applied for the petroleum industry wastewater in those cases where stringent standards require to be met for certain contaminants. At this time, the largest applications of the PACT technology can be found in the petroleum refineries and petrochemical plants. The addition of PAC to an existing WWTP may need mechanical changes beyond the PAC feed system to avoid material erosion, settling, motor overloads, and line plugging.

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