Converting Activated Sludge Process to Two-stage PACT® Allows CNPC Produced Water Treatment Plant to Achieve Compliance with China's Tough New Discharge Standards

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Key Words

Chemical Oxygen Demand (COD), Freundlich Isotherm, Mixed Liquor Suspended Solids (MLSS), Powdered Activated Carbon (PAC), PACT® (Powdered Activated Carbon Treatment Technology), T2S PACT (True Two Stage Powdered Activated Carbon Treatment, Freundlich Isotherm

Introduction and Background

Oil and gas industry produced water, petrochemical, and refinery effluents are complex wastewaters, requiring multiple treatment steps, including oil removal, cooling, biological treatment, and in some cases advanced oxidation processes to allow surface water discharge in some parts of the world. In China, discharge requirements for the petrochemical industry are increasingly becoming more stringent, requiring maximum chemical oxygen demand (COD) concentration in the discharge to be limited to no greater than 50 mg/L. As a comparison, in the US, where discharge standards are measured as biochemical oxygen demand (BOD), the equivalent COD basis for discharge could be in the order of 200 to 300 mg/L.

CNPC Liaohe Shuguang Oilfield (Liaohe), located 560 km east-northeast of Beijing, China operates a fully saturated oilfield and as such produced water generated in the production of oil cannot be reinjected back into the reservoir after oil removal, and must be treated for surface water discharge. In 2015, the Design Institute for Liaohe (DI) designed and constructed a 10,000 m^3/d fully integrated produced water treatment system to meet the discharge standards for discharge to the Raoyang River. This integrated treatment system included two-stage oil removal, cooling, biological treatment in a four-train activated sludge system, and multimedia filtration.

A summary of key design and operating performance parameters for the original activated sludge treatment plant is presented in Table 1.

TABLE 1. Shuguang Wastewater Treatment Plant Influent Design and Effluent Limits

Parameter	Unit	Influent Design	Effluent Limit
COD	mg/L	≤700	≤50
BOD_5	mg/L	≥140	≤10
TSS	mg/L	≤20	≤20
Oil	mg/L	10	≤3
NH_3-N	mg/L	≤20	≤8
TOC	mg/L	-	≤20
TDS	mg/L	≤2500	--
Temperature	°C	25 to 35	--

The produced water generated by the Shuguang plant proved difficult to treat. The water chemistry contains large amounts of water-soluble organics (WSOs) many of which are measured as COD resistant to biological treatment and as such, the system could not reliably achieve the discharge standard of 50 mg/L COD. On most occasions, the effluent COD averaged nearly 200 mg/L.

The DI reached out to several technology suppliers for assistance in upgrading the recently commissioned wastewater treatment plant to achieve compliance with the discharge standards, under a proviso that the selected technology supplier would also have to offer a process performance guarantee, affirmed through a process performance test, and be responsible for additional upgrades if needed, to assure compliance with the stringent discharge standards. The DI selected PACT® technology supplied by Siemens Water Solutions as the preferred upgrade technology.

Solution Plan

Siemens' team of field services personnel from the US and China conducted powdered activated carbon contact studies using final effluent samples from the activated sludge treatment plant. The resulting adsorption data generally fits the Freundlich equation, an empirical expression commonly presented as:

$$\frac{X}{M} = K_f \, C_e{}^{n} \qquad (1)$$

where:

X = mass concentration of COD adsorbed, mg/L
M = mass concentration of the powdered activated carbon in the contactor, mg/L
K_f = Freundlich capacity factor
n = Freundlich intensity factor
C_e = concentration of the adsorbate (COD) at equilibrium, mg/L

Taking the natural log of both sides yields:

$$ln\frac{X}{M} = ln\ K_f + n \cdot \ln\ C_e \quad (2)$$

Plotting the values of $ln\frac{X}{M}$ vs. $\ln\ C_e$ yields the slope and intercept constants of n and K_f respectively. These coefficients are used to establish the requisite carbon dose needed to reduce the recalcitrant COD remaining in the secondary effluent to the discharge performance standard. This carbon dose can be applied to separate, post-secondary contact reactors or within the secondary biological reactor as occurs in a PACT system. The advantage of including the powdered activated carbon addition within the existing bioreactor system are several:

- Combined biological treatment and carbon adsorption polishing in a single treatment step minimizes the number of individual treatment units, treatment footprint, and consequently capital costs.
- When added to the biological reactors, powdered activated carbon removes difficult to degrade, recalcitrant, and inhibitory organics, allowing greater biological COD removal, optimizing carbon demand for remaining recalcitrant COD removal, and increasing nitrification efficiency.
- The presence of mixed liquor carbon suspended solids (MLCSS) can guard against process upsets from shock loadings and allow quicker recovery from spills and slug loadings.
- Activated carbon controls odor within an open-top bioreactor, such that many times waivers are granted where regional emission standards require covered bioreactors for petrochemical secondary process treatment units.
- No additional clarification capacity needed to accommodate the increased solids loading as the design solids flux increases to 4 to 5 times that of conventional activated sludge.

For the above reasons, the CNPC Liaohe Shuguang Oilfield customer elected to upgrade the recently completed activated sludge system to a PACT process.

Samples of the Liaohe de-oiled produced water and bio-treated effluent were shipped to Siemens Water Solutions headquarters in Wisconsin, USA, to validate the carbon adsorption screening work performed in the field and develop the upgrade plan. The headquarters of Siemens Water Solutions hosts a complete 1000 m2 pilot testing plant supported by more than 500 m2 of analytical testing laboratories, making it suitable for the analysis of industrial, municipal, and hazardous wastewaters, waters, and sludges. Validation work consisted of bench-scale PACT treatability testing using laboratory-scale bioreactors and laboratory analyses to screen powdered activated carbon types and dose, as well as process modelling to determine the optimum configuration of process trains needed to achieve the required treatment level at the lowest possible cost.

Carbon Contact Study Results

Figure 1 presents representative carbon contact results collected in the field that were used to evaluate suppliers of powdered activated carbon for use in the design upgrade. Carbon efficiency is measured as mg/L COD adsorbed per mg/L carbon concentration in the contact reactor, the value of X/M expressed as a percentage. As the equilibrium concentration of COD increases, so too does the mass of COD adsorbed onto the carbon, but at a much greater rate of increase. For instance, if the equilibrium COD concentration increases three-fold, from 50 mg/L, to 150 mg/L, the carbon adsorption efficiency increases from 9% to 54%, a 6-fold increase. This characteristic of Freundlich isotherms lends itself to the use of multi-stage contactors to maximize carbon adsorption efficiency when very low effluent COD concentration is desired, or carbon adsorption kinetics are poor, requiring large carbon dose for low concentration COD removal.

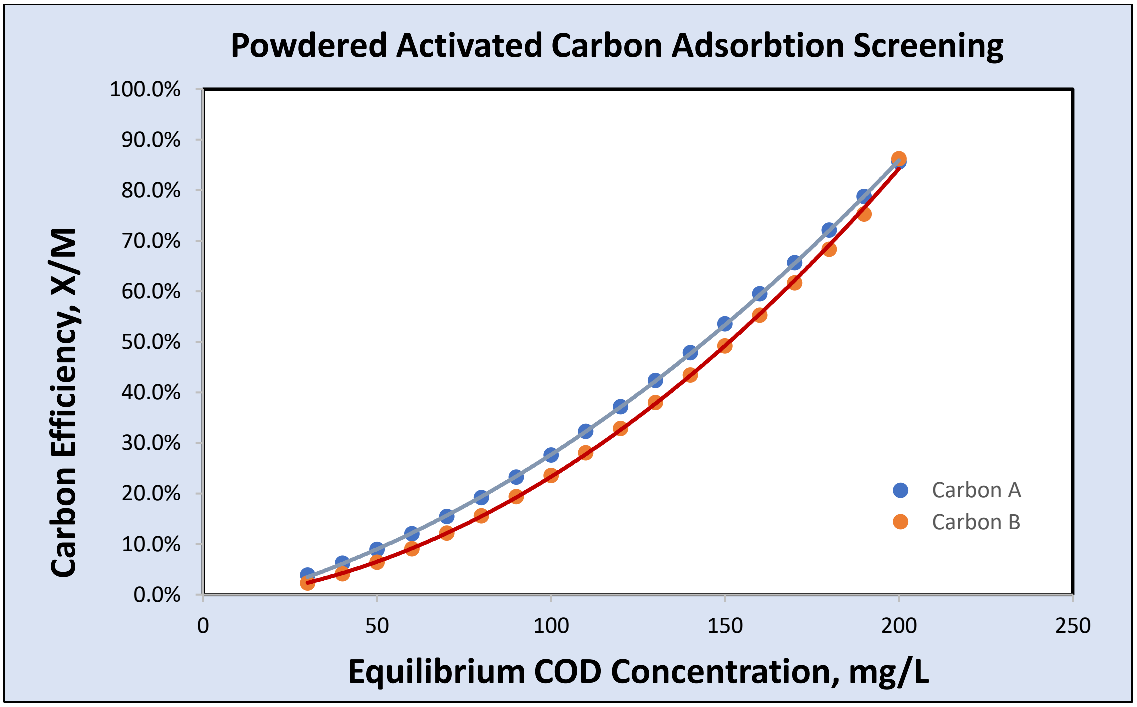

Figure 1. Carbon Isotherms from Select Powdered Activated Carbon Suppliers

Representative carbon isotherm results from the treatability study conducted in the US on Liaohe produced water samples are presented in Table 2. The resulting Freundlich constants, n and K_f, are derived in Figure 2.

Table 2. Carbon Contact Study Data

Carbon Dose (mg/l), M	COD (mg/l)	COD Adsorbed, X (mg/l)	Carbon Loading X/M	ln (COD)	ln (X/M)
0	123	na			
120	99	23.3	0.195	4.5998	-1.635
306	64	59.1	0.193	4.1529	-1.644
624	33	89.6	0.144	3.5010	-1.941
1235	22	101.3	0.082	3.0681	-2.501
2093	15	107.5	0.051	2.7233	-2.968

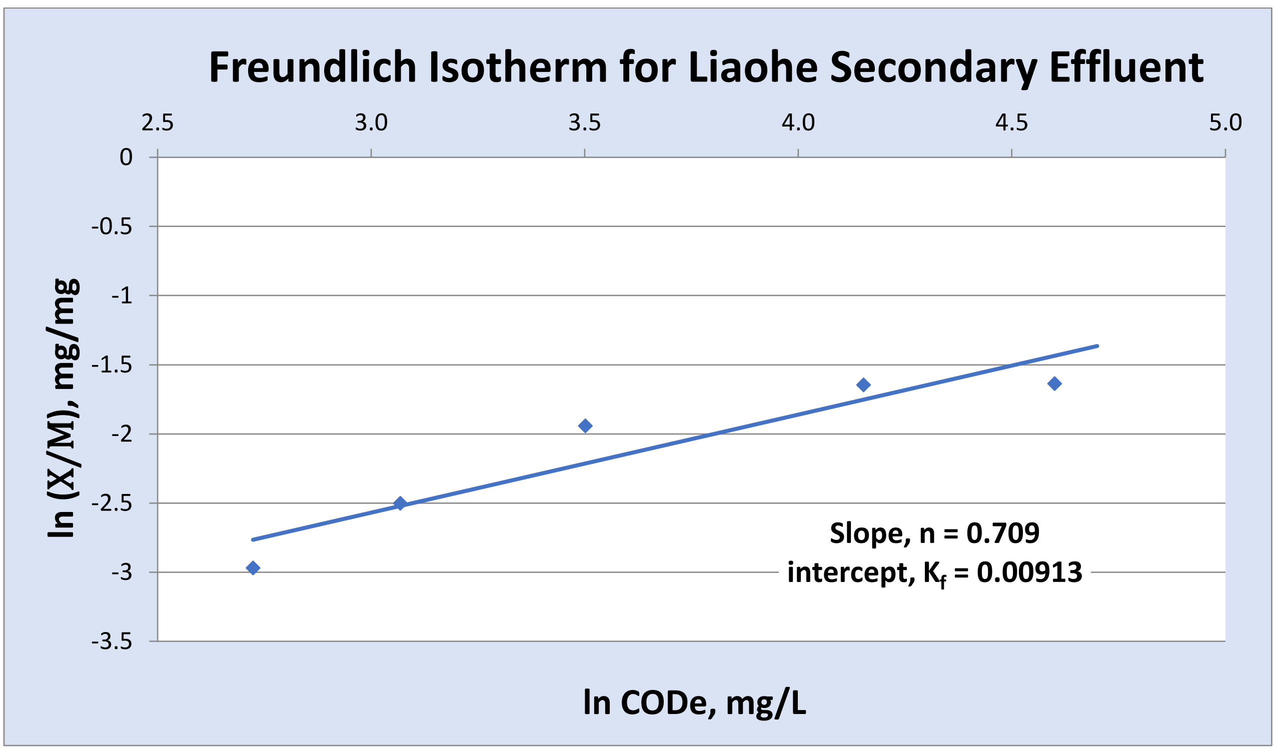

Figure 2. Freundlich Isotherm Constants, n and K_f

Single and Two-Stage Modeling Results

The newly commissioned biological wastewater treatment plant was designed for a hydraulic detention time (HRT) of just over 24 hours, providing 4, 2,720 m^3 bioreactor trains having a combined volume of 10,880 m^3. Given the yield rate for biogrowth, the resulting operating solids retention time (SRT) could be greater than 30 days. Thus, the existing aeration volume provided more than enough capacity to evaluate potential conversion to a two stage PACT process without having the need to construct additional carbon contact volume.

A single stage PACT reactor depicting recalcitrant COD removal by powdered activated carbon is presented in Figure 3 below.

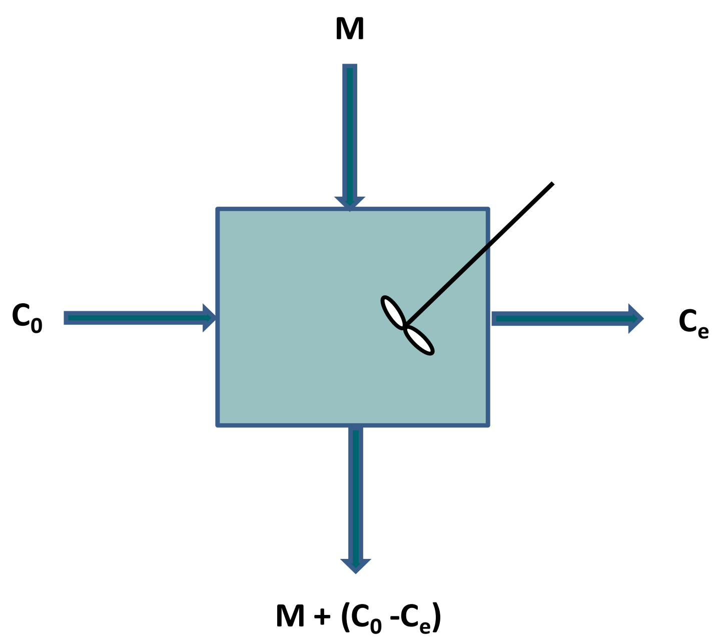

Figure 3. Single Stage PACT Reactor

Using Equation 1 above, the resulting Freundlich adsorption equation becomes:

$$\frac{C_0 - C_e}{M} = K_f \, C_e{}^{n} \qquad (3)$$

where:

C_0 = the inlet recalcitrant COD, mg/L

C_e = the filtered effluent COD following carbon contact, mg/L

M = the powdered activated carbon dose in the contactor

K_f and n are the experimentally derived Freundlich capacity and intensity factors, respectively.

The results of a two-stage countercurrent PACT system can be predicted from the single stage isotherm. Consider the two-stage countercurrent system shown in Figure 4 below.

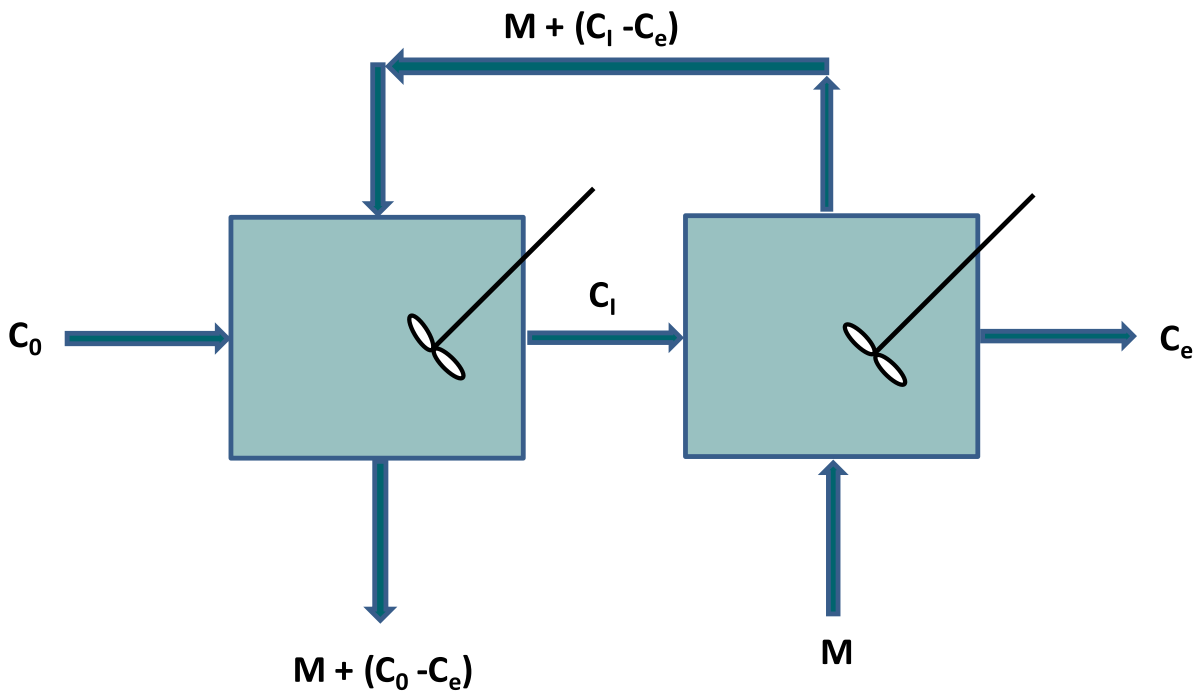

Figure 4. Two Stage PACT Reactor

The adsorption equation for the first stage contactor must consider the COD adsorbed onto the carbon from the second stage contactor and transported to the first stage contactor by sludge wasting:

$$\frac{C_0 - C_I + (C_I - C_e)}{M} = K_f \, C_I^{\,n} \qquad (4)$$

where:

C_I = the inter-stage filtered effluent COD, mg/L

C_e = the filtered effluent COD following the second stage, mg/L

The resulting adsorption equation for the first stage contactor is:

$$\frac{C_0 - C_e}{M} = K_f \, C_I^{\,n}$$

(5)

Similarly, the equation for the second contactor is:

$$\frac{C_I - C_e}{M} = K_f \, C_e{}^{n} \qquad (6)$$

Rearrangement of equations (5) and (6) yields:

$$M = \frac{C_0 - C_e}{K_f \, C_I{}^{n}} \qquad (5a)$$

$$M = \frac{C_I - C_e}{K_f \, C_e{}^{n}} \qquad (6a)$$

Equating (5a) and (6a) yields:

$$C_I^{n+1} + C_e^{n+1} - C_e^{n} \, C_0 - C_I^{n} \, C_e = 0 \qquad (7)$$

By substituting the known values of n, determined from the single stage isotherm, and C_0 and C_e into expression (7), the required inter-stage concentration C_I can be determined. Substitution of C_I into either (5a) or (6a) gives the required carbon dose.

Single and Two Stage PACT isotherms from samples of biotreated Liaohe wastewater are depicted in Figure 5. The two stage PACT systems offer significant advantage over the single stage PACT for this upgrade for the following reasons:

1. At the design effluent COD concentration of 50 mg/L, the required carbon dose rate in a single stage system would result in a total MLSS concentrations in excess of 12,000 mg/L, the maximum recommended MLSS concentration for PACT systems operating without on-site carbon regeneration systems.
2. At the design effluent COD concentration of 50 mg/L, the carbon dose rate for the two-stage system is almost half that of the single stage, as demonstrated by the carbon efficiency factor, X/M: 0.15 for the single stage and 0.27 for the two stage.
3. The actual flow rate at the time of the upgrade was only half the wastewater treatment plant's design flow capacity, 5,000 m3/day actual flow vs. 10,000 m3/day design capacity. This meant that until the produced water flow increased above 5,000 m3/day,

actual powdered activated carbon consumption could remain less than 3 mtpd. This could be easily managed by bulk carbon storage and sludge dewatering and disposal. At carbon consumption rates greater than 3 mtpd, on-site carbon regeneration using wet air oxidation technology is recommended.

4. At the recommended two stage PACT carbon dose and available first stage biotreatment volume, the resulting total MLSS (biomass + powdered activated carbon) concentration was well within the target range of PACT systems operating without carbon regeneration systems, 8,000 to 12,000 mg/L.

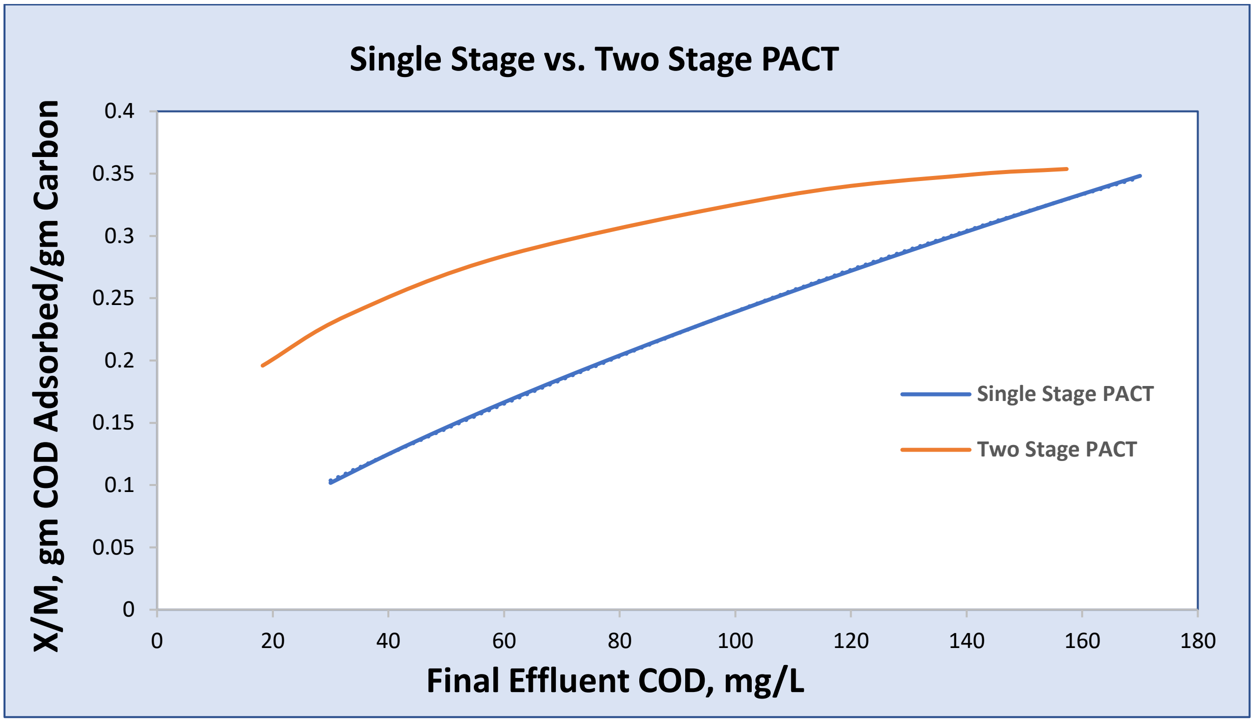

Figure 5. Single and Two Stage Design Adsorption Isotherm

Because of these advantages, Liaohe elected to upgrade the recently commissioned wastewater treatment plant to Siemens' T2S PACT®, a true two stage PACT system. The existing 4-train bioreactor design would allow for easy conversion a two stage PACT with minimal infrastructure changes.

Successful Commissioning of T2S PACT Upgrade

In 2017 the upgraded two-stage PACT system was commissioned and after achieving steady operating performance, Liaohe conducted the performance test under the guidance of local Siemens Water Solutions field engineers. A Process Flow Diagram schematic of the upgraded biological treatment plant now operating as T2S PACT is presented in Figure 6.

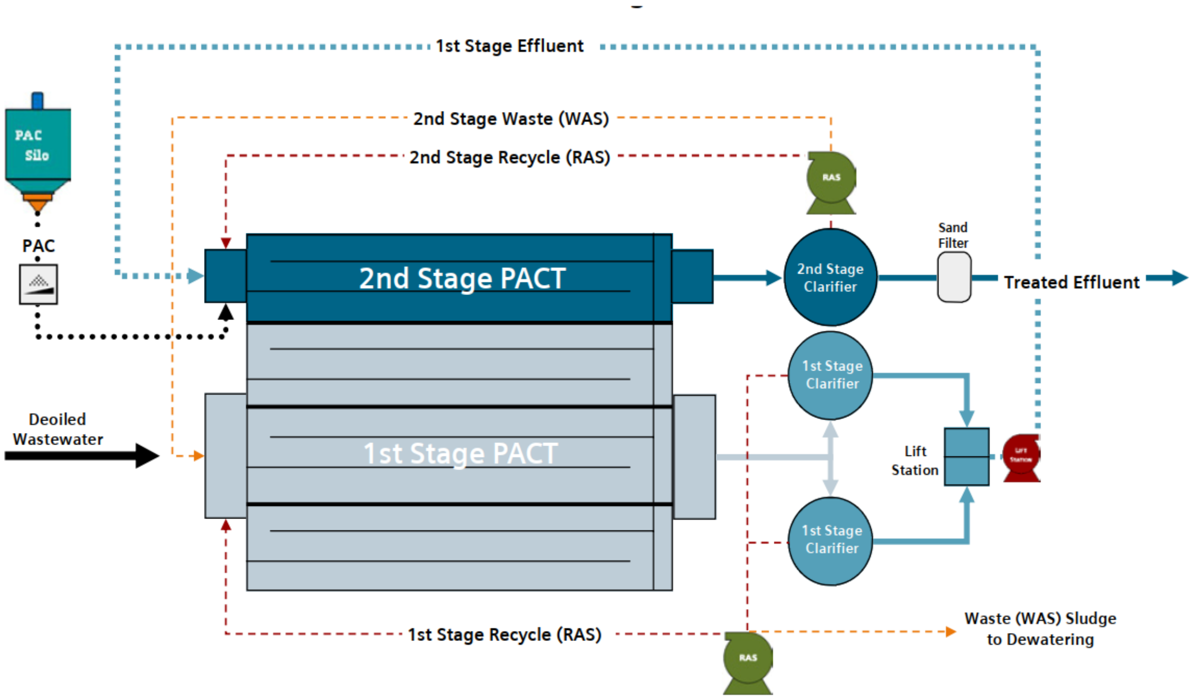

Figure 6. Process Flow Diagram – Liaohe T2S PACT

Three bioreactor trains, yielding a design HRT of 19.5 hours, and SRT of 20 days, provide first-stage PACT treatment. Following first-stage clarification, flow is routed to the remaining bioreactor train, where second-stage carbon contact occurs with the addition of virgin carbon. A new second-stage clarifier is installed for second-stage clarification. T2S PACT effluent is then routed to existing multi-media filtration units prior to discharge to the Raoyang River. Project process modifications included:

- Powdered activated carbon storage silo and delivery system
- New coarse bubble aeration
- Second stage clarifier
- Additional sludge dewatering press

An image of the upgraded Liaohe T2S PACT solution is presented in Figure 8.

Figure 8. T2S PACT in Operation at CNPC Liaohe Shuguang Oilfield Wastewater Treatment Facility

A chronological chart of feed and final effluent COD quality is presented in Figure 7. The feed COD is highly variable, with influent COD at times exceeding double the influent design COD concentration. Even so, except for the one extreme feed COD concentration event, the T2S PACT® system produced a final effluent COD fully compliant with the discharge standard, consistently producing effluent COD of 25 to 30 mg/L. The full-scale operating performance data confirms the validity of using carbon adsorption isotherms and PACT modeling to predict full-scale PACT operating performance.

Plans are now being developed to include Wet Air Regeneration (WAR) of the powdered activated carbon in anticipation of flows increasing to the design level of 10,000 m^3/day. At approximately 5% attrition rate, on-site regeneration of the carbon will reduce overall carbon consumption from 5 mtpd to 0.25 mtpd, a significant cost savings in carbon consumption cost and waste carbon disposal. An added benefit to this technology is the complete destruction of the waste biosolids, such that all that remains for disposal is non-hazardous ash from carbon oxidation, mineral oxides and the inert content of biosolids. The project is being planned for 2021 installation.

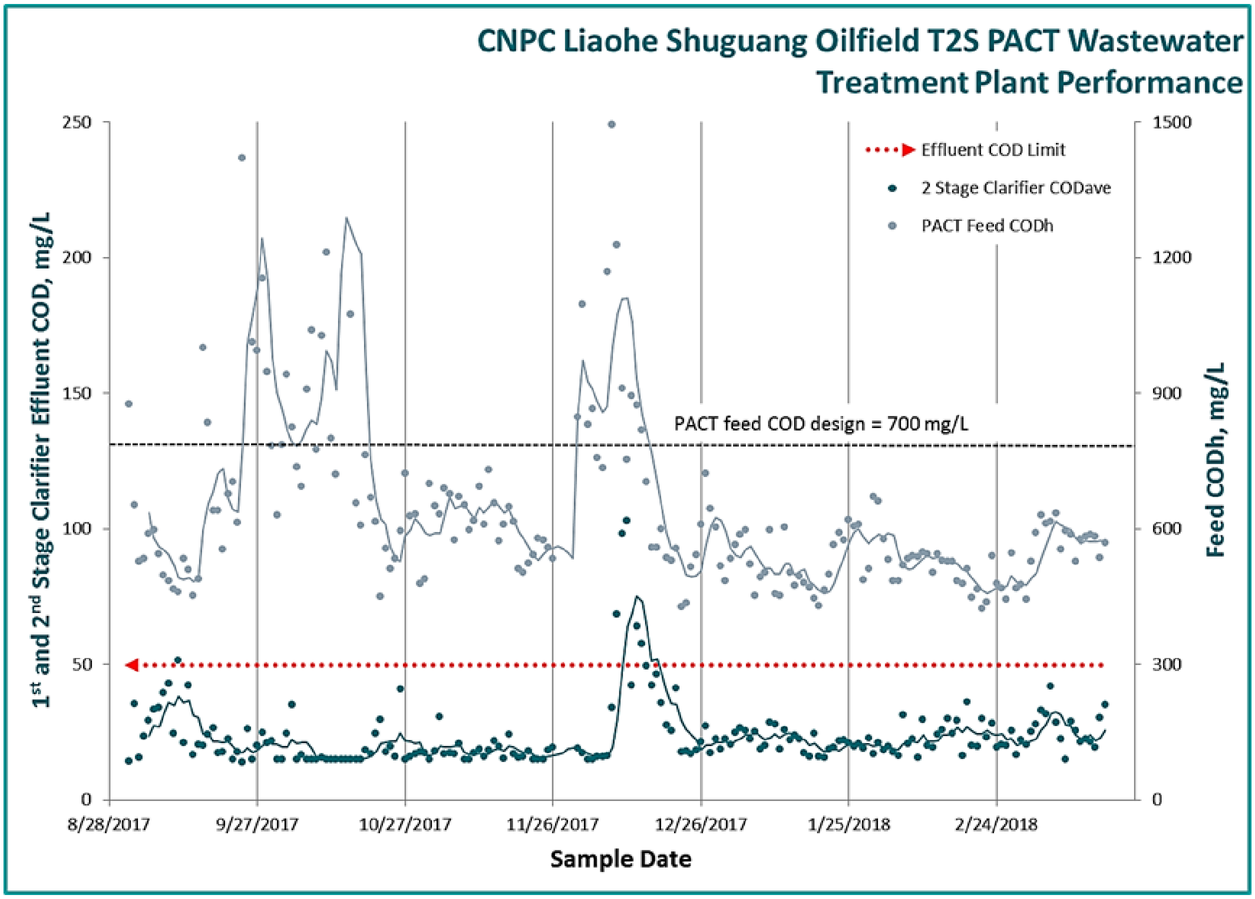

Figure 7. Liaohe T2S PACT Treatment Plant Performance Following T2S PACT® Commissioning