



Research review paper

State of the art of biological processes for coal gasification wastewater treatment



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ABSTRACT

The treatment of coal gasification wastewater (CGW) poses a serious challenge on the sustainable development of the global coal industry. The CGW contains a broad spectrum of high-strength recalcitrant substances, including phenolic, monocyclic and polycyclic aromatic hydrocarbons, heterocyclic nitrogenous compounds and long chain aliphatic hydrocarbon. So far, biological treatment of CGW has been considered as an environment-friendly and cost-effective method compared to physicochemical approaches. Thus, this reviews aims to provide a comprehensive picture of state of the art of biological processes for treating CGW wastewater, while the possible biodegradation mechanisms of toxic and refractory organic substances were also elaborated together with microbial community involved. Discussion was further extended to advanced bioprocesses to tackle high-concentration ammonia and possible options towards in-plant zero liquid discharge.

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1. Introduction

Nowadays, coal as an important raw material has been used for producing a variety of high-value chemicals via coal gasification,

liquefaction, coking etc. The coal-derived alternative fuels have become a main energy source in addition to traditional oil and gas (Pan et al., 2012; Zhou et al., 2012). As a consequence of such rapid growth of this new business, a large quantity of wastewater has been generated from various processes, e.g. gasification, purification, water-gas shift, synthesis and distillation. The wastewater, known as coal gasification wastewater (CGW), especially the one discharged from the low/medium temperature lignite gasification unit, contains extremely complex

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high-concentration aromatic hazardous, toxic and refractory compounds including phenolics, polycyclic aromatic hydrocarbons (PAHs), nitrogen heterocyclic compounds (NHCs) and long chain n-alkanes.

The U. S. had dedicated extensive effort to the treatment of CGW due to rapid growth of coal chemical industry in the period of 1970s to 1990s. Since then, the battlefield of CGW has gradually shifted to China with increasing capacity of its new coal-to-chemical plants. Nowadays, CGW has been considered as a emerging challenge to the sustainable development of Chinese coal chemical industry. As such, extensive effort has been devoted to developing various biological processes for enhancing the removal of hazardous and refractory organics in CGW with the ultimate target of zero liquid discharge (ZLD) (Tong et al., 2010). Compared to physical and chemical/electrochemical methods, biological processes for CGW treatment appear to be more cost-effective and environmentally friendly. However, due to its highly recalcitrant nature, CGW has become a primary barrier that hampers further development of new coal-to-chemical industry in China. Therefore, this review attempts to offer a comprehensive picture about CGW generated from Lurgi or BGL gasifiers and possible biological treatment processes including anaerobic and aerobic degradation of hazardous and refractory organics in CGW.

2. Characteristics of CGW

2.1. Overview

Fig. 1 illustrates various water flows in a coal-to-gas demo-plant, including supply water (light blue), saline water (dark blue), wastewater (brown), saline wastewater (grey) and brine (black). Furthermore, Fig. 2 displays the wastewater streams from the slag flushing, ammonia stripping & phenol extraction and low temperature methanol-washing processes which have been known as the main contributors to CGW.

The characteristics of CGW are mainly determined by coal quality and gasifier types. For instance, in cases where lignite and bituminous

coal are used as raw materials in the Lurgi or British Gas/Lurgi (BGL) gasification process, highly recalcitrant CGW with complex composition is often expected due to low grade of coal metamorphism and incomplete combustion within the gasifier. In contrast, gasification of high-grade anthracite generates relatively low-strength wastewater in Shell or Texaco gasifiers. It should be noted that Lurgi and BGL gasification processes currently have a broad market due to their high production capacity and gas calorific value. So far, the conventional biological processes, e.g. sequencing batch reactor (SBR), Anaerobic/Anoxic/Oxic (A2O) have been employed for treating CGW (Chen et al., 2012). In the literature, CGW usually refers to as the effluent produced after phenol and ammonia recovery by extraction and stripping respectively.

In order to achieve ZLD of CGW, integrated physiochemical and biological treatment processes have been employed, which are the combination of flotation, anaerobic and aerobic, advanced oxidation, ultrafiltration, high efficiency reverse osmosis (HERO), evaporation and crystallization (Fig. 3). Although biological processes have been believed to be essential towards ZLD, the recalcitrant or toxic nature of CGW has posed the serious challenges to biodegradation of CGW (Ji et al., 2015). Ammonia stripping as a pretreatment is helpful for recovering or removing a large portion of organic substances (Gai et al., 2008), but the concentrations of residual recalcitrant organics are still too high, seriously affecting the performance of subsequent biological treatment.

2.2. Hazardous and refractory substances in CGW

The chemical oxygen demand (COD) and total phenols (TPh) in raw CGW are often in the range of 5000 to 20,000 mg/L (Gai et al., 2007; Yang et al., 2006). Even after effective ammonia-stripping and phenol extraction, the concentration of residual recalcitrant organic compounds in the influent into CGW treatment plant (CGWTP) still remains at high side (Table 1). In fact, >28 kinds of organic compounds had been detected in CGW, among which phenol, cresol isomers, 5-methyl, 5-ethylhydantoin and 5,5-dimethyl-hydantoin were identified as the

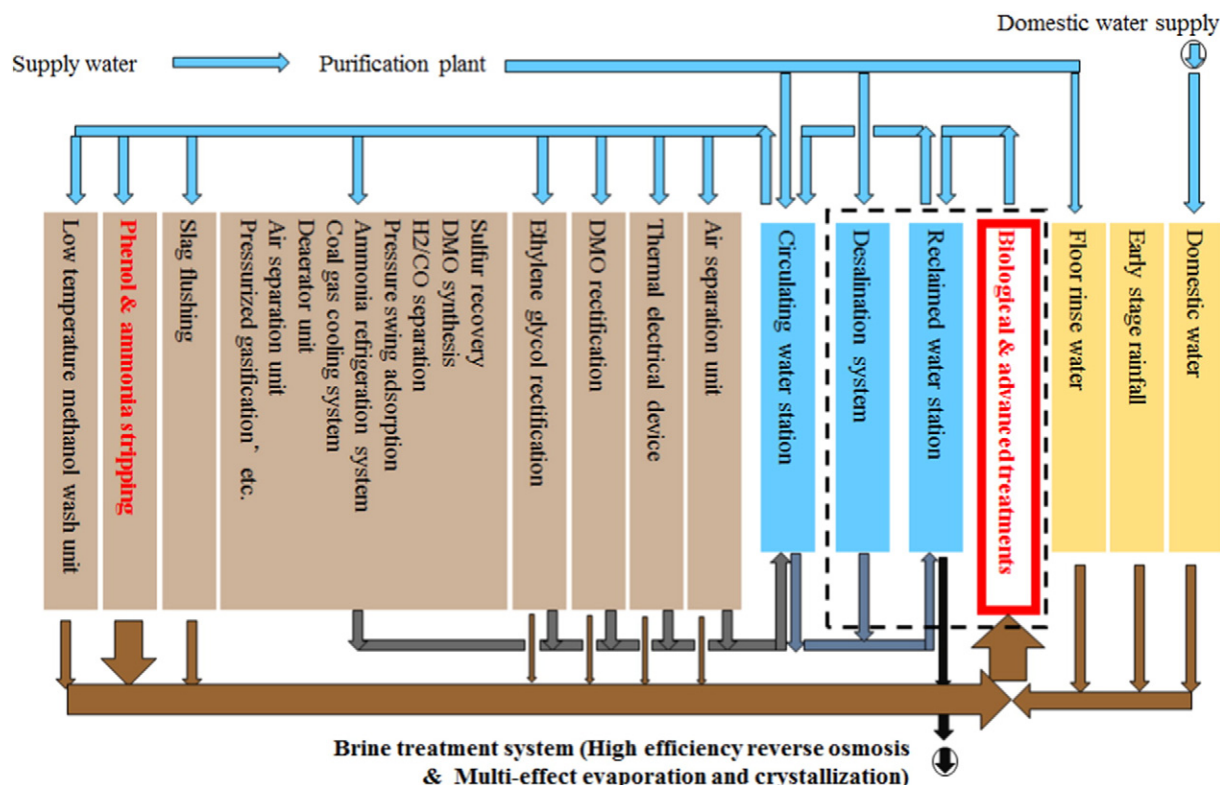


Fig. 1. Flowchart of supply water and wastewater in a coal-to-gas demo-plant (data not published).

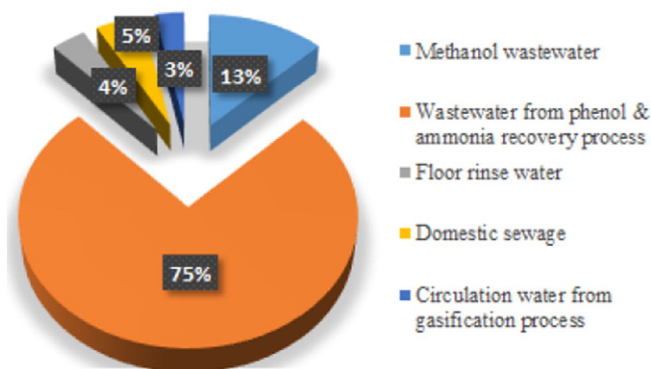


Fig. 2. Distributions of different streams in CGW (Wang et al., 2013; Ramakrishnan and Surampalli, 2013; Luthy, 1981).

major constituents of CGW. Moreover, phenolic compounds account for 40–50% of the total COD in CGW, whereas phenolic compounds with various substituted groups (e.g., methyl, dimethyl, trimethyl, methylethyl, hydroxy and methoxy), pyridines, anilines, quinolines, PAHs, dibenzofuran and aldehydes were also present at lower concentrations (Gai et al., 2008). Apart from easily biodegradable VFA, phenols, long-chain alkanes, PAHs and NHCs have all be considered highly recalcitrant. As the result, the typical BOD_5/COD ratio of CGW is generally below 0.3, suggesting that CGW is not readily biodegradable (Table 2).

In addition to phenol, long chain n-alkanes (e.g. tetracosane, octadecane and heptacosane) are also commonly present in CGW. Due to their inhibitory property to microorganisms (Liu et al., 2013), these long-chain alkanes cannot be effectively removed in conventional biological treatment processes, thus advanced treatment units would be needed with increased capital and operation costs. In addition, dodecamethyl cyclohexasiloxane as a typical surfactant may cause highly undesirable bio-foaming during biological treatment of CGW, while 2,5-furandicarboxaldehyde is highly toxic to activated sludge microorganisms.

Some compounds in Table 2 are the intermediates produced from the synthetic or gasification process, such as bicyclo[3.3.1]nona-3,7-diene-2,9-dione, 5,5-dimethyl-2,4-Imidazolidinedione, 5-ethyl-5-methyl-2,4-Imidazolidinedione, 3-methyl- 2(3H)-Benzofuranone.

Their fates in CGWTP and impacts on biological treatment of CGW stay unclear so far. On the other hand, some unidentified highly polar compounds may also exert an adverse impact on the biological treatment of CGW even at low concentrations.

3. Anaerobic treatment of CGW

3.1. Conventional anaerobic processes

In 1980s–1990s, conventional anaerobic processes had been widely employed for treating CGW, but the overall performance was not satisfactory in terms of COD removal and process stability (Chen et al., 2008). Phenolics and complex organics with high molecular weight were poorly removed during anaerobic treatment (Zhang et al., 1998). However, anaerobic treatment led to an improved biodegradability of CGW, which favored subsequent nitrification, and also served as carbon source for denitrification. Thus, it is reasonable to consider that anaerobic process may serve as a pretreatment of CGW prior to aerobic process. In fact, strong evidence shows that the operation of CGWTP eventually failed if anaerobic unit was not present or malfunctioned (Kuschek et al., 2010; Park et al., 2008; Zhao et al., 2010).

In general, anaerobic bacteria are very sensitive to the presence of toxic pollutants in CGW, and serve microbial inhibition had been commonly observed in conventional anaerobic processes (Vidal et al., 1999). To mitigate such inhibitory effect, use of granular activated carbon and dilution of CGW had been proposed (Nakhla et al., 1990). Obviously, these two options are not economically viable and environmentally friendly due to the needs for a large amount of granular activated carbon and fresh water.

3.2. Modified anaerobic processes for CGW treatment

Modified anaerobic processes (e.g. two-phase anaerobic system) had been developed for high-efficiency treatment of refractory wastewater, e.g. 55–60% and 58–63% of COD and TPh were removed respectively in a step-feeding anaerobic system at an influent COD concentration of 2500 mg/L (Fezzani and Cheikh, 2010; Xu et al., 2015a; Wang et al., 2011). Anaerobic co-metabolism has been considered as an alternative for improving the treatability of CGW (Chen et al., 2008). For instance, the removal of phenol was significantly

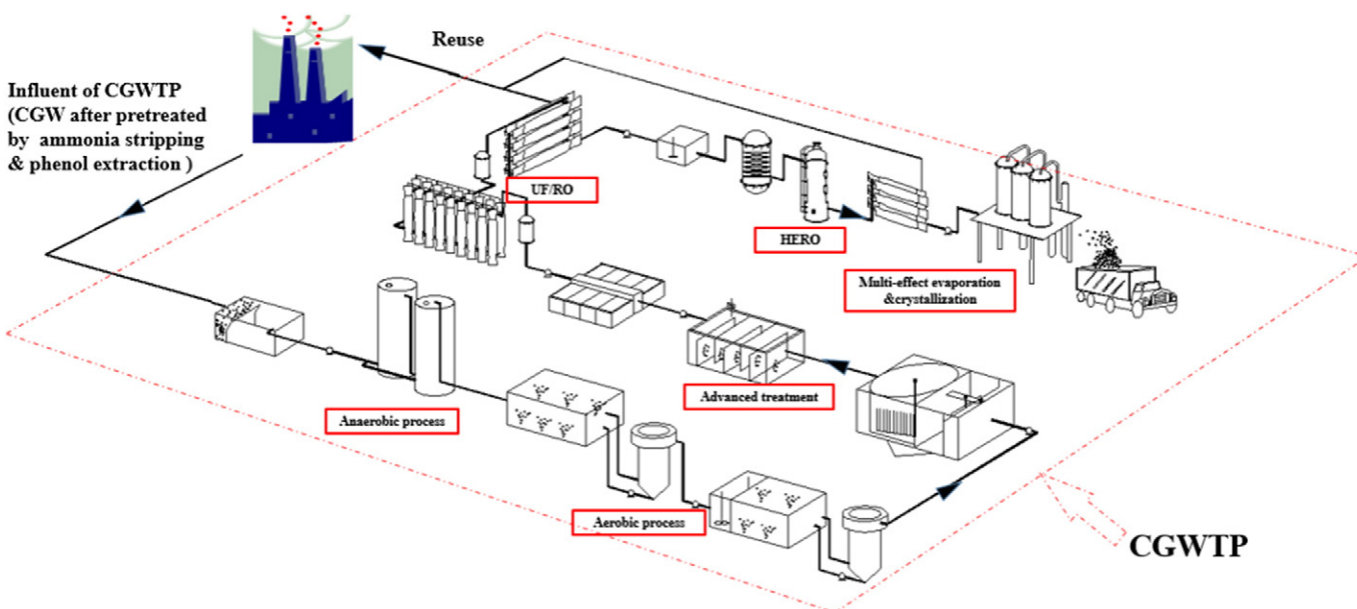


Fig. 3. Overview of a CGW treatment plant towards ZLD (Jia et al., 2016; Su et al., 2014; Tong et al., 2010; Wang et al., 2011; Zhao et al., 2013; Zhuang et al., 2014a).

Table 1
The CGW characteristics in 3 typical new coal-to-chemical plants.

Items	CGWTP in Heilongjiang (Wang et al., 2011)	CGWTP in Inner Mongolia (Jia et al., 2016)	CGWTP in Xinjiang (Data not published)
COD (mg/L)	2500–3500	3500–4500	4000–4500
BOD ₅ (mg/L)	700–1100	800–1000	1000–1200
TPh (mg/L)	450–750	650–750	700–900
Volatile phenols (mg/L)	80–200	300–450	400–600
Volatile fatty acid (VFA, mg/L)	2–10	50–100	200–300
Ammonia-N (mg/L)	100–150	100–250	280–350
Sulfide (mg/L)	20–50	20–45	13–35
Cyanide (mg/L)	0.2–5	ND	ND
pH	6.5–8	6–7.5	6.5–7.5

Note: ND, not detected.

enhanced through addition of glucose to batch cultures (Tay et al., 2001), while the biodegradation of quinoline by an indigenous mixed culture of microorganisms isolated from a full-scale CGWTP was accelerated by addition of glucose as co-substrate and the quinoline utilization rate was found to be positively correlated with the glucose concentration (Xu et al., 2015c). In fact, the influent to CGWTP contains the stream from the low temperature methanol-washing process (Fig. 1), i.e. in-plant methanol could be available to serve as co-substrate for enhancing anaerobic treatment of CGW. For example, 71% and 75% of COD and phenol were removed respectively in the presence of methanol at the concentration of 500 mg COD/L (Wang et al., 2010). Thermophilic condition had also been found to be effective for improving anaerobic biodegradation of refractory compounds. For example, 50–55% of COD and 50–60% of TPh could be removed in the thermophilic reactor at an organic loading rate of 2.5 kg COD/(m³·d) and HRT of 24 h, while only about 20–30% achieved in the mesophilic reactor treating CGW. Obviously, it is necessary to further optimize anaerobic process for CGW treatment with the focus on sustainable plant operation.

3.3. Anaerobic metabolism of hazardous and refractory organics in CGW

Hazardous and refractory compounds can be utilized, mineralized or transformed into readily biodegradable compounds via anaerobic reactions (Wang et al., 2012a). It had been reported that anaerobic process could completely remove fatty acids (hexanoic acid, heptanoic acid, butanoic acid, hexanoic acid), some phenolic compounds (resorcinol,

3,4-dimethyl-phenol, hydroquinone, 4,5-dimethyl-1,3-benzenediol, 2-methyl-1,4-benzenediol, 2-methyl-1,3-benzenediol), some long chain n-alkanes (tetracosane, heptacosane, hexacosane, eicosane) and a number of PAHs or NHCs (5,5-dimethyl-2,4-imidazolidinedione, trimethylsilyl ester, 2,5-furandicarboxaldehyde, 6-azathymine, 4,6-dimethyl-2,3-2 h-benzofuran-2-one, dodecamethyl-cyclohexasiloxane, 3,4-dihydro-6-methyl-2h-1-benzopyran-2-one, 2-methyl-1-naphthalenol, 3-methyl-2(3 h)-benzofuranone, 4-methyl-3-phenylpyrazole, trimethyl (2-methylbutoxy)-silane). Moreover, other phenolic compounds (phenol, 4-methyl-phenol, 3,5-dimethyl-phenol, etc.), long chain n-alkanes (octadecane, tricosane), ester (trimethylsilyl ester-pentanoic acid, trimethylsilyl ester-2-methyl-propanoic acid) or PAHs (2,6-bis(1,1-dimethylethyl)-naphthalene) could be largely or partly degraded anaerobically (Wang et al., 2011).

The aromatic compounds can be mineralized or transformed to readily biodegradable intermediates via enzymatic reduction under anaerobic conditions (Fig. 3). Monocyclic aromatic organics are transformed to benzoyl-CoA or benzoyl-CoA substituted with different functional groups (e.g. halide, methyl, hydroxyl or amino substitutes) (Fuchs et al., 2011). Fig. 4a further shows that aromatic compounds with hydroxyl groups at different structural positions could be converted to various intermediates prior to reductive dearomatization (Boll et al., 2014; Philipp and Schink, 2012). PAHs (e.g. naphthalene) could be biodegraded via the corresponding intermediates, e.g. 2-arylcarboxyl-CoA (Meckenstock and Mouttaki, 2011). As can be seen in Fig. 4b, the catabolism of benzoyl-CoA, arylcarboxyl-Co esters and 2-arylcarboxyl-

Table 2
Main organic composition in the influent to CGWTP (Wang et al., 2011).

Organic compounds	Inlet	Organic compounds	Inlet
Phenol	7.05	2H-1-Benzopyran-2-one, 3,4-dihydro-6-methyl-	0.43
Phenol, 4-methyl-	6.08	Pyrazole, 4-methyl-3-phenyl-	0.26
Phenol, 3,5-dimethyl-	2.94	Propanoic acid, 2-methyl-, trimethylsilyl ester	0.89
Phenol, 2-[(trimethylsilyl)oxy]	4.95	Silane, trimethyl (2-methylbutoxy)-	5.15
Resorcinol	5.00	1-Naphthalenol, 2-methyl-	0.29
Phenol, 3-[(trimethylsilyl)oxy]	2.46	6-Azathymine	0.21
Phenol, 2,3-dimethyl-	0.41	Tetracosane	0.42
Phenol, 3,4-dimethyl-	0.31	Octadecane	0.46
Hydroquinone	0.73	Heptacosane	0.28
1,4-Benzenediol, 2-methyl-	0.64	Hexacosane	0.28
Phenol, 2,3,6-trimethyl-	0.19	Tricosane	0.32
1,3-Benzenediol, 4,5-dimethyl-	0.32	Eicosane	0.21
1,3-Benzenediol, 2-methyl-	0.76	Heneicosane	0.37
Pentanoic acid, trimethylsilyl ester	5.54	2,3-2H-Benzofuran-2-one, 4,6-dimethyl-	1.28
Naphthalene, 2,6-bis(1,1-dimethylethyl)-	1.71	Cyclohexasiloxane, dodecamethyl-	0.18
2,4-Imidazolidinedione, 5,5-dimethyl-	0.63	2,5-Furandicarboxaldehyde	1.51
2(3H)-Benzofuranone, 3-methyl-	0.68	2,4-Imidazolidinedione, 5-ethyl-5-methyl-	0.47
Hexanoic acid	4.85	Bicyclo[3.3.1]nona-3,7-diene-2,9-dione	0.23
Heptanoic acid	2.15	4a,9a-Methano-9H-fluorene	0.47
Butanoic acid	4.62	Others	30.87
Hexanoic acid, trimethylsilyl ester	3.40		

Note: Values represent the relative percentage of total peak area.

CoA indeed are driven by different dearomatizing reductases with VFA, CO₂ and H₂O as the final products (Carmona et al., 2009; Fuchs et al., 2011; Holmes et al., 2011; Kuntze et al., 2008).

In general, anaerobic degradation of long chain n-alkane is a slow process compared to aerobic degradation by alkane-degrading strains. The mechanisms of anaerobic n-alkane degradation with various anaerobic isolates and consortia are illustrated in Fig. 4c. Two different pathways have been identified for the n-alkane carboxylation involved in the activation of long chain n-alkanes. With sulfate-reducing strain Hxd3, C-3 position of C16 is carboxylated and the two subterminal carbon atoms are eliminated subsequently, therefore C-odd and C-even alkanes would produce C-even and C-odd fatty acids, respectively (Aeckersberg et al., 1991). And with some other sulfate-reducing strains, C-even and C-odd fatty acids could be produced from C-even and C-odd n-alkanes (Aeckersberg et al., 1998; Cravo-Laureau et al., 2005; So and Young, 1999). The other possible pathway for anaerobic activation is the hydrocarbon addition to fumarate, leading to the formation of n-alkane-derived alkyl substituted succinates (Rios-

Hernandez et al., 2003), and subsequently β-oxidation took place with a rearrangement of carbon skeleton (Callaghan et al., 2006; Wilkes et al., 2002).

4. Aerobic treatment of CGW

4.1. Overview of aerobic processes

The effluent from anaerobic unit contains substantial amounts of hazardous and refractory organics (Zhao et al., 2013). As such, anaerobic effluent has to be treated further with one or multiple-stage aerobic process in CGWTP. Given highly recalcitrant nature of anaerobic effluent, the conventional activated sludge process has been ruled out due to its inefficiency in removing hazardous refractory substances and high-strength ammonia.

Activated sludge coupled with carries or activated carbon adsorption has been considered as a promising method to mitigate the toxicity and inhibition of anaerobic effluent. In a lab-scale moving bed biofilm

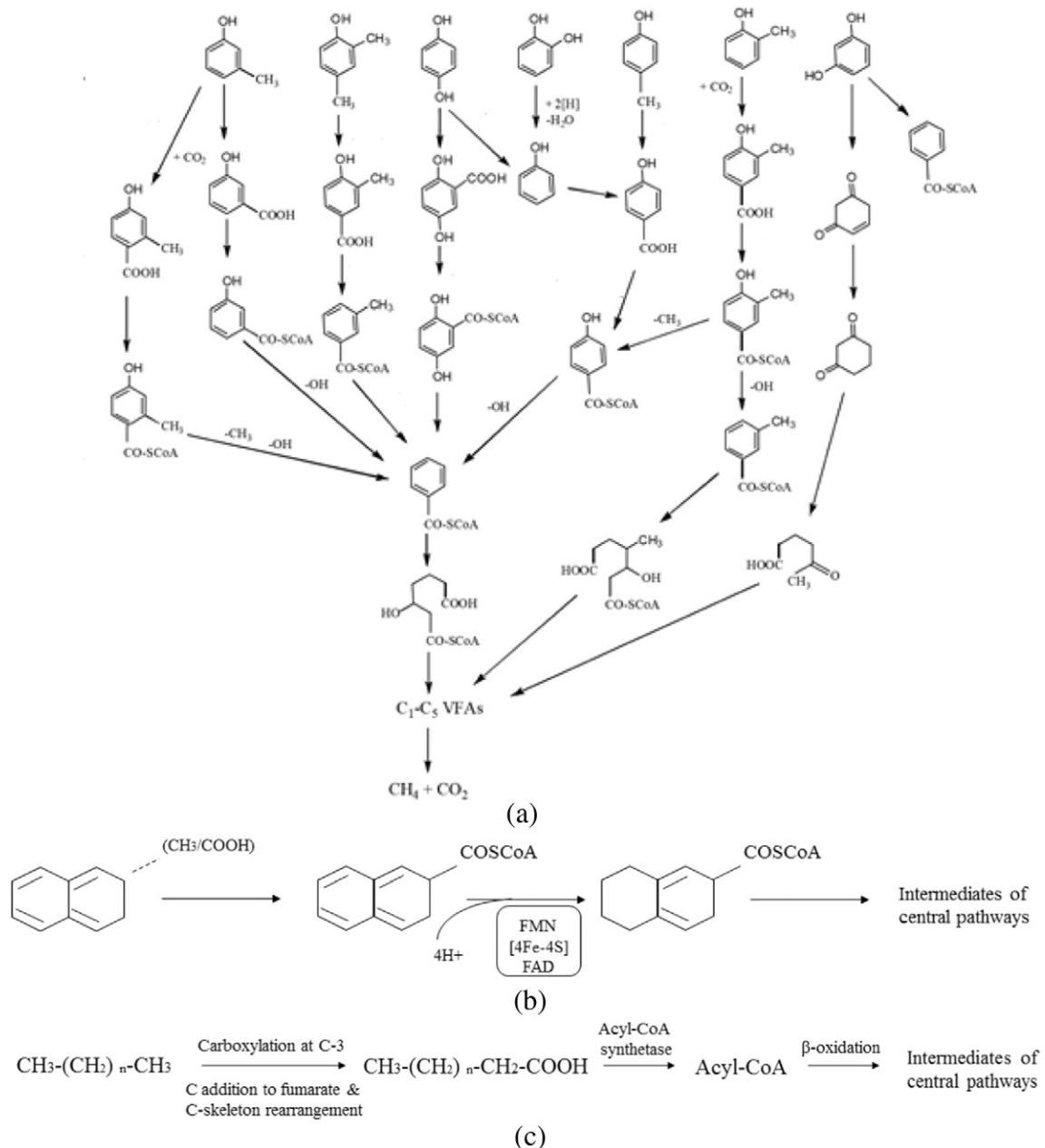


Fig. 4. Anaerobic degradation pathways of phenols (a), naphthalene compounds (b) and long chain n-alkanes (c) (Fuchs et al., 2011; Holmes et al., 2011; Heider and Fuchs, 1997).

reactor (MBBR) treating CGW, about 80% and 90% of COD and TPh were obtained respectively (Li et al., 2011a). Activated sludge dosed with powdered activated carbon (PAC) was also found to be effective for removing aromatic compounds in CGW (Cansado et al., 2012; Zhao et al., 2013, 2014, 2015). With addition of 4 g/L PAC to a laboratory-scale membrane bioreactor treating CGW, 93%, 99% and 63% of COD, TPh and ammonia-N could be removed, respectively (Jia et al., 2014), while NHCs with chromophores (e.g. indole, indanol, oxole, pyridine etc.) could also be remarkably reduced by PAC.

Bioaugmentation is another alternative for improving the removal of recalcitrant organic compounds from CGW. A quinoline-degrading bacterium, known as *Burkholderia picketti*, was used to bioaugment an A2O system treating CGW (Wang et al., 2002). It was found that pyridine, quinoline and benzene could be completely removed in a *E. aurantiacum* (a pyrene degrader)-bioaugmented three-stage rotating biological contactor treating synthetic biomass gasifier wastewater (Hansa and Suparna, 2012), together with 85–96% removal of phenol, naphthalene, phenanthrene, fluoranthene and pyrene. In addition, Fang et al. (2013) found that phenol degrading bacteria (PDB) could significantly improve the performance of biological contact oxidation process treating CGW.

After consecutive anaerobic and aerobic treatment, the amount and types of hazardous substances in CGW decreased dramatically with a final COD concentration of about 80 mg/L and a BOD₅/COD ratio of 0.06, indicating extremely low biodegradability of the aerobic effluent (Zhuang et al., 2014b). The organics remaining in the aerobic effluent mainly include NHCs (e.g. quinoline, 5-hydroxyindole, 1H-imidazole, 2-amino-3-picoline, 6-amino-2-methylquinoline, 1-methyl-4-nitro-1H-pyrazole, 2,3-dihydroindole) and alkanes (e.g. Eicosane, Docosane, Heptacosane) etc. (Zhao et al., 2013; Zhuang et al., 2014a). If further removal of these compounds was needed, advanced physico-chemical methods should be considered instead of biological means, e.g. heterogeneous catalytic ozonation, TiO₂ photocatalysis oxidation, catalytic ultrasound oxidation etc. (Xu et al., 2015b; Jia et al., 2015; Zhuang et al., 2014b). Recently, high efficiency reverse osmosis (HERO) has been explored for removing refractory COD from biologically-treated CGW.

4.2. Effect of residual toxic substances on biological nitrogen removal

CGW often contains 100–350 mg/L ammonia-N, which should be removed biologically via nitrification and denitrification. However, the residual toxic organics in the anaerobic effluent may inhibit nitrifying and denitrifying activities, e.g. phenols, PAHs and NHCs are highly inhibitory to nitrifying bacteria (Kim et al., 2008; Ramos et al., 2007; Wang et al., 2012b; Li et al., 2011b) (In a CGWTP, ammonia is usually removed in the last stage of aerobic treatment after most toxic organics have been removed (Zhao et al., 2013, 2014).

4.3. Aerobic metabolism of refractory compounds in CGW

So far, a wide spectrum of aromatics and NHCs has been reported to be transformed via different peripheral pathways to some key intermediates. In the typical aerobic catabolism, the oxidative attack of alkyl substitutes, the hydroxylation and oxygenolytic cleavage of aromatic ring can be realized by a variety of hydroxylating monooxygenases and ring-cleavage dioxygenases (Díaz et al., 2013). Fig. 5a shows that under aerobic condition, catecholic substrates undergo ortho or meta cleavage (i.e. o-cleavage and m-cleavage). Via o-cleavage the substrate is converted to instable enollactone and further hydrolyzed to oxoadipate. Oxoadipate, the dicarboxylic acid is further converted to the important intermediate-CoA, followed by the thiolytic cleavage to acetyl-CoA and succinate. The metabolic m-cleavage yields 2-hydroxybutyric semialdehyde. Oxygenolytic ring cleavage, isomerization and hydrolysis were achieved by pseudomonads and rhodococci after hydroxylation (Fetzner, 2012; Grishin et al., 2011; Rather et al., 2011).

As for the aerobic degradation pathways of long chain n-alkane, alkanes oxidation can be considered to be terminal or subterminal. In most cases, n-alkane can be oxidized to the primary alcohol by substrate-specific terminal monooxygenases/hydroxylases (Fig. 5b), whereas the subterminal oxidation may also be possible with alkanes with up to C16. As the result, a secondary alcohol and subsequent ketone are formed. Different kinds of hydroxylases may be involved in aerobic metabolism of long-chain n-alkane (van Beilen and Funhoff, 2007). The alcohol generated from the initial oxidation is further oxidized to aldehyde or carboxylic acid in the presence of relevant dehydrogenase. Catalyzed by the synthetase, the carboxylic acid could be converted to acyl-CoA, which finally enters the β -oxidation pathway.

5. Microbial diversity in CGWTP

Abundant microbial strains with different functions have been isolated or identified in CGW treatment processes. Generally, these strains have strong capacity of degrading various phenolic compounds, PAHs and long chain n-alkanes (Kurzbaum et al., 2010; Xiao et al., 2012; Xia et al., 2014; Ghosh et al., 2014). PDB and naphthalene-cultivated bacteria isolated from coking wastewater (e.g. *Burkholderia cepacia* PW3, *Pseudomonas aeruginosa* AT2, *Arthrobacter* sp. W1) had been shown to have high biodegradation activity and strong tolerance to refractory organics (El-sayed et al., 2003; Shi et al., 2014). In fact, most coal chemical degrading bacteria belong to *Proteobacteria* and *Acetivobacteria* (Ma et al., 2015). A specific strain isolated from acclimated activated sludge in a CGWTP, known as *Streptomyces* sp. (QWE-35), can effectively degrade naphthalene (Xu et al., 2015a, b, c, d), while Liu et al. (2013) also reported an alkane-degrading strain-*Acinetobacter* sp. (KC21 1013) isolated from the aeration tank treating CGW. The core genera found in CGWTP, coking wastewater, municipal wastewater treatment plants are summarized in Table 3.

It appears from Table 3 that *Proteobacteria* were identified as the most abundant phylum in four different types of wastewater treatment plants (Zhang et al., 2012). In Different from coking or domestic wastewater treatment plants dominated by β -*Proteobacteria*, high abundance of α -*Proteobacteria* in the range of 10.92% to 30.71% were found in CGWTP (Jia et al., 2016). Apparently, this seems contradictory to the generally accepted argument that many phenol-degrading species are affiliated with members of β -*Proteobacteria* commonly detected in various biological processes treating phenol-bearing wastewater (Adav and Lee, 2008). In addition, the major class- *Firmicutes* has also been found in CGWTP, which have been known to be highly resistant to phenolic compounds. Hierarchical clustering and canonical correspondence analysis for each stage in CGWTP also revealed that *Comamonas* was closely associated with anaerobic process, while *Thermomonas* and *Phycisphaera* would enhance the overall performance of biological process, while genera *Methylococcus*, *Denitratisoma*, *Truepera* and *Nitrospira* were highly involved in biological nitrogen removal. It should be noted that bacterial community structure in a CGWTP is largely associated with wastewater characteristics and operation conditions, such as COD, TPh and ammonia loading rate as well as DO, pH, MLSS and temperature etc. (Jia et al., 2016).

6. Should the hazardous substances be completely removed?

As discussed above, biologically-treated CGW exhibits low biodegradability with a BOD₅/COD ratio of 0.06 and 80 mg/L COD (Zhuang et al., 2014a, 2014b). In order to further minimize the concentration of hazardous organics in such effluent, extensive effort has been devoted to exploring different kinds of advanced treatment methods (Li et al., 2016). Currently, advanced oxidation and BAF or MBBR) have been employed as a polishing stage of the biologically treated CGW prior to membrane separation. However, some evidence suggests that HERO membrane could tolerate COD concentration up to 300 mg/L. Therefore, a fundamental question is if it is still necessary to further reduce the

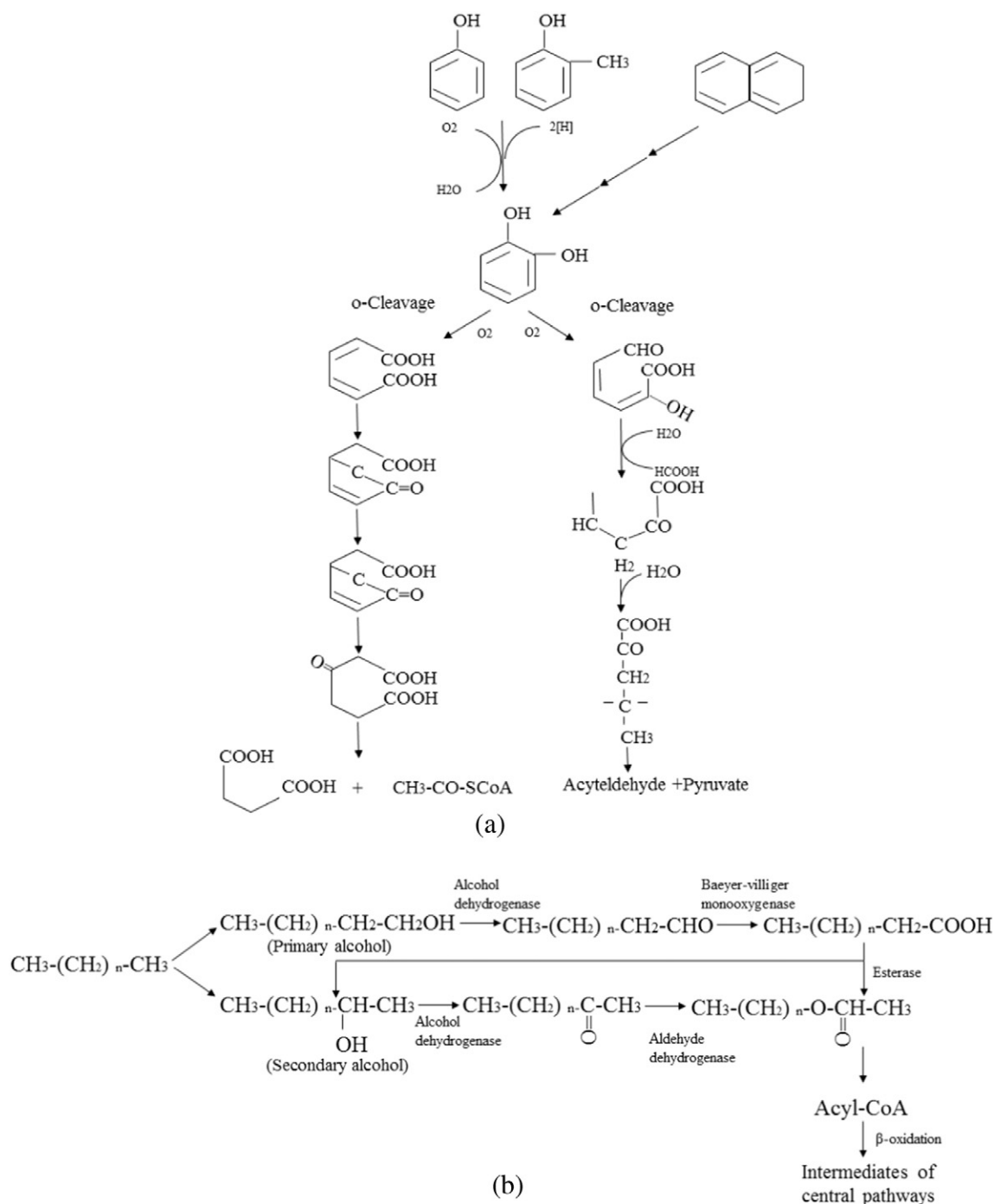


Fig. 5. Aerobic degradation pathways of phenols, naphthalene compounds (a) and long chain *n*-alkanes (b) (Díaz et al., 2013; Grishin et al., 2011; Rather et al., 2011; Whyte et al., 1998).

refractory organics in the biologically treated effluent prior to HERO. However, it should also be realized that in case where advanced treatment is not in place, residual refractory organics in biologically treated effluent eventually may all end up as salts or sort of minerals after multi-effect evaporation and crystallization, which inevitably result in increased amount of hazardous waste for further disposal. Therefore, it is a reasonable consideration that recalcitrant and refractory compounds in CGW should be reduced to a reasonable level in order to ensure the operations of downstream processes (e.g. membrane separation, evaporation and crystallization more economically viable and environmentally friendly. Obviously, future study should more focus on system integration and life cycle analysis.

7. Concluding remarks

This review sheds light into various biological processes for treating CGW. Given highly complex recalcitrant nature of CGW, it appears still challenging to handle this type of wastewater in a cost-effective and environmentally friendly manner even after decades of effort, especially when zero liquid discharge has been set to be the ultimate target. Various combinations of anaerobic and aerobic processes have been successfully applied for removing phenols, PAHs, NHCs and long chain *n*-chains from CGW at industrial scale. In order to achieve the targeted zero liquid discharge from CGWTP, biological treated effluent should inevitably be further concentrated via HERO, evaporation and crystallization, while likely by their combinations which are all considered as

Table 3
Composition of bacterial communities in CGWTP and other types of plants.

CGWTP (Jia et al., 2016)	Coking wastewater treatment plants ¹ (Ma et al., 2015)	Domestic wastewater treatment plants ² (Wang et al., 2012a, 2012b)	Sewage treatment plants ³ (Zhang et al., 2012)
Proteobacteria 58.36%	77.5%	Average 76.14%, 65.18–90.38%	36–65%
Planctomycetes Average 7.91%, 1.2–16.2%	13.8%	Average 1.84%, 0.27–7.80%	ND
Firmicutes Average 7.15%, 2.35–20.53%	<2%	Average 2.40%, 0.10–5.79%	Average 8.1%, 1.4–14.6%
Acidobacteria Average 5.69%, 0.35–13.17%	ND	Average 2.35%, 0.33–10.05%	ND
Bacteroidetes Average 4.63%, 2.78–6.23%	1.6–10%	Average 6.79%, 0.87–13.63%	Average 7.0%, 2.7–15.6%
Chlamydiae Average 3.36%, 1.16–7.54%	ND	ND	ND
Actinobacteria Average 1.05%, 0.37–1.76%	ND	Average 4.32%, 0.18–14.74%	Average 6.5%, 1.3–14.0%
Chloroflexi Average 0.98%, 0.09–1.95%	ND	ND	ND

Note: 1. 9 coking wastewater treatment plants in steel industry in China; 2. 14 domestic wastewater treatment systems located in Wuxi, Shenzhen, Beijing and Harbin in China; 3. 14 sewage treatment plants of located in mainland China, Hong Kong, and Singapore, Canada and the States; ND: Not detected.

highly-energy intensive operation. So far, most studies on biological treatment of CGW have a narrow focus on biological performance, but without attention to looking into integrated engineering system for properly handling CGW. In fact, an integrated biological and advanced treatment system is urgently needed for in-plant zero liquid discharge by coal gasification and related industry globally. Moving forward, the design, operation and optimization of biological processes for CGW treatment should be considered together with downstream advanced treatment units in a more holistic approach. Only such integrated effort may ultimately lead to a total solution for zero liquid discharge from CGWTP. Also, it is necessary to conduct a comprehensive cost-benefit and system life cycle analysis to ensure a good sustainability without sacrificing the environment.

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