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A high efficiency biological system for treatment of coal gasification wastewater-key depth technology research

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ABSTRACT

Coal is the main energy resource in China hence pollution caused by coal gasification wastewater has been severe for decades. A three stage system was adopted to treat the coal gasification waste water as anaerobic hydrolysis acidification (333 days), aerobic oxidation (300 days) and ozonation-aerobic fluidized bed process (220 days) with the lowest HRT of 45h. After, more than a year of trial high efficiency and stability of the treatment process has been achieved the results showed that when average influent (COD 4400 mg/L, total phenol 950 mg/L, volatile phenol 530 mg/L, $\text{NH}_4^+\text{-N}$ 300 mg/L, volatile acids 120 mg/L and chromaticity 1000 times), the effluent COD could decrease to <60 mg/L, total phenol, volatile phenol, $\text{NH}_4^+\text{-N}$, volatile acids were not detected, and chromaticity 10 times) showing average removal efficiency of COD, total phenol, volatile phenol, $\text{NH}_4^+\text{-N}$ and volatile acids of 96%, 99.9 %, 99.9%, 99.9% and 99.9%, respectively. The pollutants removed were converted to biogas; organic transformation in the system was analysed by GC/MS equipment. The power consumption and the amount of sewage sludge reduced 30%. The wastewater treatment cost is 0.135 \$/m³. This study can be used to build a test to simulate future engineering applications of small scale technology platform as it is a short, simple processing unit, low energy consumption, low sludge production and easy management and maintenance.

Keywords: Coal gasification wastewater, COD, phenol, anaerobic, aerobic, sludge

1. Introduction

The stresses of environmental pollution, fossil-fuel depletion, water and other resource shortage are driving intensive efforts towards more sustainable treatment and utilization of wastewater. Indeed, while abating contamination continues to be an important task of wastewater treatment, sustainability is gradually becoming a pivotal criterion and driven to its further advancement¹. One of the most difficult wastewater pollution control task for coal gasification industry around the world is the Coal gasification wastewater (CGW) treatment².

CGW is discharged mainly from the gas washing and condensing operations of the coal gasifier, which contains high concentration of organic pollutants³. Basically, treatment of CGW mainly includes a series of biological treatment after a physico-chemical pre-treatment^{4, 5} in order to reduce the concentration of phenols, ammonium^{6, 7} and refractory organics; most of them have been reported to be carcinogenic and mutative^{8, 9}. But still this dual process confront with several problems, like unsatisfactory effluent, complicated technology, high handling costs, large occupation of area¹⁰. As well as absolute degradation of volatile phenol, total phenol and ammonia nitrogen is challenging. Even, the reduction of effluent COD to a level below 200 mg L⁻¹ remains difficult¹¹. Furthermore, one of the particular concerns is an increasing amount of sewage sludge generated by biological wastewater treatment plant,

which would result in a serious problem for the environment in case of inappropriate disposal¹².

For the treatment of CGW certain traditional biochemical treatment processes had been deeply investigated such as conventional activated sludge (CAS), sequencing batch reactor (SBR), anoxic-aerobic (A-O) and anaerobic-anoxic-aerobic (A-A-O) process¹³⁻¹⁶. The growth of nitrifying bacteria and specialized microbes in the aeration basin is restricted due to the presence of toxic and refractory compounds¹⁷. Hence, the effluent concentrations of COD, nitrogen compounds and so on are difficult to meet the discharge standards¹⁸⁻²¹. Therefore, it is of great importance to enhance the CGW treatment process to pursue clean production.

It is very difficult to treat CGW by conventional biochemical treatment as the existing treatment process are long, complex processing unit, high energy treatment system, production of sludge, maintenance of the processing system. It is a challenge to treat CGW around the globe²². Nonetheless, coal gasification wastewater treatment does have the potential to become a sustainable process if suitable technologies can be applied that are operated at less energy, low operating cost and low investment.

In recent years, the use of aerobic granular sludge (AGS) technology i.e. a special kind of biofilm structure composing of self immobilized cells has been used for aerobic system^{23, 24}. But it has some drawbacks that have restricted the development of AGS

technology from lab scale to pilot scale^{13, 25, 26}. The present study overcomes the weaknesses of AGS.

Anaerobic reactors that were sold worldwide during the last decade 34% were Upflow Anaerobic sludge blanket (UASB) reactors and Expanded Granular Sludge Blanket (EGSB) were 52%²⁷⁻²⁹. Both have some advantages over each other³⁰. The present study combines the advantages of UASB and EGSB technology.

Anaerobic and aerobic biological treatment technologies have their advantages and disadvantages, and anaerobic - aerobic treatment process can play the advantages of separate processing technology, especially in the refractory wastewater treatment.

In the current study we combine and extend the recent work of our lab^{31,32}, we build a high efficiency coal gasification wastewater treatment process in our laboratory that utilizes two patented water treatment technologies of our group AnaEG (A state-of-the-art advanced anaerobic expanded granular sludge bed)^{31, 33} and BioAX (A novel environmental biotechnological aerobic process with internal circulation)^{32, 34} along with a ozonation-aerobic fluidized bed (ABO+AF) system. A more elaborate efficiency of the whole system is employed that efficiently meets final effluent standards^{18, 21} in spite of great fluctuation of water quality and the presence of bio-refractory organic pollutants. COD, phenols and ammonia removal were monitored at each stage of the treatment. Estimation of energy consumption and processing cost was also evaluated. The current study will become competitive in future industrial

applications in terms of a technically and economically feasible method for the treatment of CGW.

2. Materials and method

2.1 Characteristics of coal gas wastewater

As seen in Table 1, CGW is highly contaminated which in turn have an inhibitory effect on the treatment. So, the treatment should need to be deal in depth. The coal gasification wastewater was received from the Coal Long Hua Harbin Coal Chemical Industry Co. Ltd, Harbin, China. COD conc. 3800-4400mg/L, BOD conc. 500-700 mg/L, Total phenol 850-950 mg/L, ammonia 230-300 mg/L, BOD/COD ratio between 0.13-0.16; so poor biodegradability and strong inhibitory effect on biological wastewater.

For microbial growth certain trace elements were added in anaerobic influent like K_2HPO_4 (20mg/L), KH_2PO_4 (10mg/L), $CaCl_2 \cdot 2H_2O$ (20mg/L), $FeSO_4 \cdot 7H_2O$ (15mg/L), $MgSO_4 \cdot 7H_2O$ (50mg/L), $MnCl_2 \cdot 4H_2O$ (0.5mg/L), $ZnCl_2$ (0.5mg/L), $CuCl_2$ (0.5mg/L), $(NH_4)_2MoO_4 \cdot 4H_2O$ (0.5mg/L), $AlCl_3$ (0.5mg/L), $CoCl_2 \cdot 2H_2O$ (0.5mg/L), $NiCl_2 \cdot 2H_2O$ (0.5mg/L).

2.2 Coal Gasification Wastewater Treatment Process System Setup.

The setup of anaerobic-aerobic-ozone oxidation and aerobic fluidized bed combined process flow diagram is shown in Figure 1. Coal gasification wastewater after phenol and ammonia recovery pumped into anaerobic reactor AnaEG (Plexiglas,

cylindrical, effective volume (EV) 13.4L, inner diameter 100 mm, height 1500mm, operated under mesophilic conditions 35°C. It undergoes hydrolysis acidification. The purpose of this unit is to remove volatile phenol and some total phenol; refractory organic pollutants are decomposed to smaller organic pollutants by the microorganism in AnaEG. Now, effluent enters into aerobic biological treatment reactor (BioAX) (8.0L; inside diameter 0.15m; Height 1m; operating temperature 15-20°C, it was designed on the principle of central tube air lift reactor. It added internal recycle in the bio-contact oxidation. It is an improvement of original biological contact oxidation process. The aerobic metabolism treatment of anaerobic effluent take place in the aerobic reactor, most of Volatile phenol (VP) & Total phenol (TP) will be removed by aerobic heterotrophic bacteria.

Now aerobic effluent enters into ozonisation reactor. In this process remained TP will be removed, biodegradability will further enhance. Now ozonized effluents enters into subsequent aerobic fluidized bed (EV 18L Plexiglas, Inside diameter 0.15m; Height 1m; Operating temperature 15-20°C) The circulating fluidized bed is design acc. to the principles of centre pipe airlift reactor. The reactor structure and flow channel enhanced the carrier in a fluidized state in a fluidized bed, i.e. solid phase (biofilm), liquid (wastewater), gas (air). Violent collisions occurred constantly between particles, biofilm surface gets renewed constantly. Wastewater in the reactor continuously circulating in a cycle is having full contact with the microorganism (sludge), where

further decomposition of the organic matter by aerobic heterotrophic bacteria take place. After this process the final discharged effluent meets National emission standard^{19, 20, 35}

2.3 Seed Sludge and Inoculum.

AnaEG anaerobic reactor:

Inoculated anaerobic granular sludge was made in our own Laboratory (Digested sludge inoculum anaerobic reactor effective volume of 40%). The anaerobic effluent, adjusted to pH 8 with sodium bicarbonate before the inlet into aerobic reactor.

BioAX aerobic reactor and aerobic fluidized bed (AFB reactor):

Seed sludge for aerobic reactor was collected from aeration tanks treating municipal wastewater. The initial SS and VSS of aerobic inoculated sludge were 4,530 mg/L and 3,220 mg/L, respectively. The VSS/SS ratio of the seed sludge was about 0.71.

2.4 Operational Strategies

By shaker test³⁶ and chromatographic analysis it was concluded that the appropriate time for anaerobic hydrolysis acidification was 45 hr. For anaerobic (AnaEG) and aerobic (BioAX) reactor the operational strategies were same as described in our recent study^{31, 32}.

Anaerobic reactor start-up stage operation was run for 330 days, whole process takes place in three stages as start-up (run for 87 days, HRT 96h), Loading or stability (run for 110 days, HRT was reduced from 96hr to 48hr) and second start-up (anaerobic reactor

was stopped for 10 days; start-up again and operated for 133 days with HRT 48hr) as shown in Figure 2a when HRT was high than loading rate was low and vice versa based on effluent COD and phenol conc. HRT was controlled (loading rate max.806 mg COD/L-d and mini. 338 mg COD/L-d).

Considering, effluent quality (volatile) from the anaerobic reactor in the start-up stage, so aerobic reactor HRT was set at 125 hr. (Figure 2b). After, the successful completions of start-up phase in anaerobic reactor. Loading of aerobic reactor was increased with reduction in HRT from 94hr to 63hr. Reactor was intentionally stopped on 200th day, a second start up was given, HRT maintained at 64 h (loading rate max.447.62 mg COD/L-d and mini. 120.58 mg COD/L-d).

2.5 Advanced treatment process

The aerobic effluent needs advanced treatment in order to reach the national standard requirement (COD < 60 mg/L). So a technically and economically feasible treatment process is required. The feasibility of two methods such as PAC (Poly Aluminum Chloride) coagulation & sedimentation or Ozonation+ fluidized bed is discussed.

PAC is a group of highly effective coagulants³⁷. Generally, coagulation method is used to remove colloid, subtle suspended substances and refractory organic matter. In this study, coagulation is adopted initially to treat the aerobic effluent to study the removal effects of coagulation on refractory organic compounds in the aerobic effluent, thus

knowing whether coagulation process should be adopted in practical engineering applications.

2.5.1 PAC coagulation & sedimentation

To achieve the optimum pH, when PAC (Poly Aluminum Chloride $\text{Al}_2\text{O}_3 \geq 28\%$) dosage is 200mg/L, a series of coagulation experiments are conducted while the pH of aerobic effluent is 4, 5, 6, 7, 8, 9, 10. To get the optimum PAC dosage, when pH is 7, a series of coagulation experiments are conducted while the PAC dosage is 100, 200, 300, 400, 500mg/L.

2.5.2 Ozonation + aerobic fluidized bed test

60 minute ozonation experiments are conducted when ozone flow rate 2L/min and pH 9. Intermittent aerobic biological treatment tests are carried out on ozonation effluent (pH adjusted to 8) after 10, 20, 30, 40, 50 and 60min, with additional 5000mg/L aerobic activated sludge, investigating the treatment effect of ozonation-aerobic fluidized bed (reaction time 24hr).

2.6 Analytical Methods.

The following parameters were analysed: COD, BOD, alkalinity, ammonia nitrogen, and kjeldahi nitrogen, were determined according to the standard procedure³⁸. Elemental composition was analysed with inductively coupled plasma (ICP) emission spectrophotometry (Thermo Electron, USA) using standard operating conditions and

parameters³⁹. Volatile acid was analysed with HP5890 series II gas chromatograph (HP, USA). To further understand the nature of wastewater GCMS 2.0 (Shimadzu, Japan) was used. Ozone generator: OZWAVE ND-OZS30 type.

Biogas production was daily measured with a wet glass flow meter making correction for atmospheric pressure and temperature. Methane concentration were determined by GC2010A gas chromatography (shimadzu, Japan) with stainless steel column (300cm x 0.3 cm) packed with active carbon (30-60 mesh) using thermal conductivity detection (TCD).

GC-MS analysis condition:

Wastewater samples for GC/MS analysis were firstly filtered by a 0.45 μ m membrane filter and extracted by CH₂C₁₂ into neutral, basic and acid phases (repeated three times for each phase) and then concentrated by evaporating in a water bath at 40 °C. The concentrated samples with a volume of 0.2 μ L were analysed by Angilent 7890-5975 GC/MS equipment. The analytical conditions were described in the previous paper⁴⁰

GC/MS analytical conditions were as follows: a capillary column made of quartz with inner diameter of 0.25 mm and length of 50 m was packed with OV-101; temperature for the gasification compartment was maintained at 280 °C ; the temperature control program was followed by retaining at 70 °C for 3 min and then

increasing to 280 °C with an increment of 3 °C/min; temperature for MS ion source was 200 °C and electron energy was 70 eV.

SEM analysis condition:

SEM was carried out using a Hitachi TM3000 Tabletop Microscope. The pre-treatment steps of sample are as follows:

(1) Sampling and fixation: Take 2 to 3 mL of samples, fix in 2.5% glutaraldehyde for 12h at pH 6.8

(2) Dehydration: Dehydration was done in steps of 50%, 70%, 80%, 90%, 95% and 100% ethanol concentration for 30 min each, dehydration was done twice for each conc. Then the sample soaked in 100% ethanol for 12 h

(3) Freeze drying: Using freeze-dryer machine to dry samples at -50 °C, until the ethanol volatilized completely from sample;

(4) Gold Sputter coating: With Ion sputtering coating machine, the surface of the sample is coated with a layer of metal film;

(5) Observation: Samples are observed with the SEM (scanning electron microscopy) and desired photographs were taken.

3. Results and discussion

3.1. Degradation Performance in Anaerobic and Aerobic Reactor.

As can be seen from Figure 3a, 3b and 3c in start-up stage I (1-87days; water flow rate 3.4L/d) in anaerobic reactor, after successful completion of stage I the effluent COD conc. is 680mg/L and removal efficiency 50%, total phenol conc. is 170mg/L and removal efficiency 44%, volatile phenol conc. is 61mg/L and removal rate 57%. In stage II, (88-200 days) TP conc. was maintained at 170-200mg/L, VP conc. at 80-130mg/L; in the latter half TP conc. maintained at 150mg/L, VP 20-40mg/L, removal rate (TP 50%, VP 70%). In stage III; Second start-up (201-222 days), as the anaerobic treatment system uses a hydrolysis acidification process, therefore in second start time, did not reduce the load, but to maintain original load, HRT was still 48 h. After a successful and stable operation of the second start-up we undergo stable operation of anaerobic reactor for the 110 days (223-333 days) COD effluent remaining at 500mg/L with removal rate 50%. TP maintained at 100mg/L, removal rate TP over 50%, effluent VP remain at 20mg/L or less, removal rate above 80%. With the lowest HRT 48 h the average COD removal rate was 276.74 (mg COD/L-d).

Wang et al.⁴¹ investigated that the CGW was treated by the mesophilic UASB reactor, with methanol addition and hydraulic retention time of 24 hr. During the study, the maximum COD and phenol removal rates were 71% and 75%, respectively. But it is important to note that the start-up period of the UASB reactor was as long as 227 days, and in the whole experiment period (359 days) the UASB requires the addition of the methanol.

In another study, Wang, et al.⁴² investigated that the CGW was respectively treated by the mesophilic UASB and thermophilic UASB reactor, with hydraulic retention time of 24 hr. After start-up period, the removal of COD and total phenols by the thermophilic reactor could reach 50–55% and 50–60% respectively. But the COD and phenol removal rates of the mesophilic UASB reactor were both only 20–30%. And it is important to note that the start-up period of the thermophilic and mesophilic reactors were both 120 days.

In the present study, after the first start-up period, when the HRT was 48h, without methanol or glucose addition, COD, TP and VP removal rate could reach up to 50%, above 50 %, above 80 %, respectively. The first and second start-up period of the AnaEG reactor was only 90 days and 20 days, respectively. Compared with the other studies^{41, 42}, AnaEG reactor showed advantages with respect to shorter start-up period and less methanol or glucose, which is important for implementation of a large-scale coal gasification wastewater treatment.

In aerobic reactor the treatment efficiency of aerobic influent depends on effluent of anaerobic reactor, when anaerobic reactor run in stable operational phase, aerobic reactor showed a stable and efficient treatment effect. Aerobic reactor total operation takes place in 302 days. In phase I (1-88 days; HRT 125), amount of sludge in system was higher due to new sludge dosing, therefore higher removal of COD about 70% (Figure 4a & Figure 4b). The aerobic reactor showed a fairly stable removal due to

anaerobic hydrolysis acidification, its biodegradability increases, and so aerobic organisms through a short acclimation period exhibit high activity. In second and third operational phase, COD removal basically stable around 70-80 %, effluent COD concentration stabilized at 200mg/L. Aerobic microbial removal of phenolic compounds was also superb as shown in Figure 4b, basically maintained at above 80%; aerobic effluent had undetectable VP (removal rate 100%). During stable secondary start-up of aerobic reactor, aerobic influent $\text{NH}_3\text{-N}$ conc. 80-100mg/L, effluent $\text{NH}_3\text{-N}$ conc. 15-30mg/L, removal efficiency 70-80 %. The removal rate appears to follow a linear relationship with the organic loading rate in the aerobic reactor ($R^2 = 0.82795$), (SI Figure S1). High loading rate shows high removal of COD and supports a 355.64 mg COD/L-d removal of COD with a load of 412.57 mg COD/L-d. With the lowest HRT 64 h the average COD removal rate was 24.43 (mg COD/L-d). Detailed description regarding the working of anaerobic (AnaEG) and aerobic (BioAX) can be seen in our recent study^{31, 32}

3.2 Advanced treatment process results

3.2.1 PAC coagulation and sedimentation test result

PAC coagulation and sedimentation test result were conducted on anaerobic-aerobic effluent. The best effect of coagulation process was seen when pH 7 and coagulant dosage 400mg/L, respectively. COD removal efficiency was 9.1% as seen in Table 2(a) and 2(b). In this study, the effect of PAC coagulation and sedimentation process on the

chromaticity removal for CGW was poor. During the whole experiment process, the removal rate of chromaticity was about 36% (average).

However, coagulation process does not have removal effect on chromaticity, which is similar to those results of some researcher⁴³. Therefore, coagulating sedimentation process does not show a good treatment effect on SNG biochemical effluent. The final effluent still can't meet the standard.

3.2.2 Ozonation + aerobic fluidized bed test result

When ozone flow is 2L/min and pH is 9, ozonation has obvious removal effect on refractory substances such as phenols in the aerobic effluent. As shown in Table 2(c), after 10 minutes of ozonation, total phenols are completely oxidized by ozone, and COD removal efficiency reaches 36%. Afterwards, COD removal efficiency continually increases. After 60min, it reaches 79%, and COD in the effluent is below 60mg/L.

As it is reported in literature that pH affects the double action of ozone on the organic matter, that may be a direct or an indirect (free radical) ozonation pathway^{44, 45}. At low pH, ozone solely reacts with compounds with specific functional groups through selective reactions as electrophilic, nucleophilic or dipolar addition reactions (i.e. direct pathway)⁴⁶. However, at basic conditions, ozone decomposes yielding hydroxyl radicals, which are high oxidizing species⁴⁷ that react in a non-selectively way with a wide range of organic and inorganic compounds in water (i.e. indirect ozonation)⁴⁸.

Normally, under acidic conditions ($\text{pH} < 4$) the direct ozonation prevails, in the range of $\text{pH} 4-9$ both are present, and above $\text{pH} > 9$ the indirect pathway prevails.

It is also reported that the degradation of chlorophenols is favored at high pH ⁴⁹. Phenolic compounds are the main pollutants in the effluent of BioAX reactor. The pH of the BioAX reactor effluent is usually 7-8. In the light of the above consideration the $\text{pH} 9$ was chosen for BioAX reactor effluent for performing ozone oxidation experiments. The purpose is to improve the wastewater treatment effect by ozone oxidation.

Ozonation is technically feasible but expensive in treating aerobic effluent. Therefore, in this test, ozonation is followed by aerobic biological treatment to furthest reduce operational cost.

3.3. Degradation Performance in Advanced Treatment Process.

Aerobic effluent, after intermittent ozonation process enters aerobic fluidized bed. Ozonation-aerobic fluidized bed ($\text{O}_3 + \text{AFB}$) run for 220 days, divided into three stages as shown in Figure 5 Phase I, the ozonisation process carried out under ozone flow rate 2L/min, reaction time 30min, the effluent enters into AFB, operating for 100 days (HRT 125hr); Phase II, ozone flow 1L/min, reaction time 30min, effluent follows into AFB running for 20 days (HRT 125 hr.); Phase III, ozone flow 1.5L/min, reaction time 30min, enters AFB, run for 100 days (HRT 86 hr) as shown in Table 3(a).

Since the aerobic effluent conc. was 200mg/L which cannot meet the effluent standard (less than 60 mg/L). It was necessary to treat the effluent deeply. O₃+AFB 220 days of operation, the use of ozone oxidation unit operates intermittently (batch); continuous operation was done in AFB. As can be seen from Table 3 (b), when ozone flow rate 2L/min, COD removal efficiency 40%; ozone flow rate 1L/min, COD removal 30%; ozone flow rate 1.5L/min, COD removal efficiency 30-40%; effluent COD stable at 150mg/L. TP conc. 30mg/L or less, and after 30min of ozonation, TP was undetected in the effluent. As can be seen from Figure 5 in first 10 days, the microbes exhibit inadaptability, COD removal rate dropped to about 30%. But after 27th day domestication of microbe's takes place, COD removal ratio gradually increases. COD removal gradually picked up in first 37 days its removal efficiency reached higher than 60% , and effluent COD dropped to 60mg/L in AFB it's probably that after ozonation wastewater directly enter into the fluidized bed. The water still contains some ozone after 30 min.

If ozone is brought into the fluidized bed after aerobic decomposition, it would produce toxic effects on aerobic microorganisms and inhibit degradation performance⁵⁰.⁵¹. In this study, as the ozone oxidation reactor was operated by intermittent mode. The effluent of Ozone oxidation reactor was sent into the buffer tank ('12' in FIG. 1), and the hydraulic retention time is 1 h (as we know the half-life period of ozone is very short, usually less than 1 h). It is to ensure that the residual ozone in the wastewater mostly broken down. Therefore, it would not produce toxic effects on aerobic

microorganisms in the fluidized bed reactor. Therefore, after ozonation, wastewater should be placed for some time, and then enter into fluidized bed.

In stage II, COD conc. (effluent) was very unstable, and cannot be decreased to 60mg/L after 20 days running observation. Hence, in stage III, ozone flow rate was adjusted to 1.5L/min, as anaerobic-aerobic effluent shows good effect; COD conc. (effluent AFB) was basically stable below 60mg/L, removal rate higher than 60%.

During stable running of O₃+AFB reactor, NH₃-N conc. was determined results are shown in Table 3(c), concentration of NH₃-N was less than 30mg/L, in effluent NH₃-N conc. was below 1mg/L, NH₃-N level meets the national effluent standards^{18,21}. After the parameter of optimization of anaerobic and aerobic treatment process, the waste water treatment by ozonation-aerobic fluidized bed experiment can provide a key depth technology research in microalgae breeding. With the lowest HRT 86 h the average COD removal rate was 62.80 (mg COD/L-d). As can be seen in Figure 2c. HRT was higher than it is decreased, due to conc. of COD and ammonia, OLR was high so HRT was low (loading rate max. 116.79 mg COD/L-d and mini. 50.54 mg COD/L-d)

After the ozonation process, the phenol was oxidized into hydroquinone and catechol which were degraded into acids and carbon dioxide without high molecular weight byproducts⁵². The ozone oxidation intermediates are generally more biodegradable than the original molecules⁵³. The water quality in each stage is shown in Table 4 and the water quality of the final effluent and related standards are shown in Table 5.

3.4. Characterization of Anaerobic Sludge.

By SEM analysis Figure 6.it revealed that different types of microorganisms intertwined randomly throughout the cross section. A large population of filamentous long-chain micro-organism were observed. In addition, many colonies consisting of cocci and bacillus were also observed, representing the typical shape of acid producing bacteria and they were linked together. The methanogenic bacteria were dominant. SEM illustrates that the granules had porous and multiple cracks on the surface. These pores were likely to facilitate the passage of nutrients and substrate⁵⁴.

3.5. Estimation of Energy Consumption and Processing Cost

Evaluation of Energy consumption during ABO+AF treatment (excluding ozone oxidation) is done

$$E = n * P / q$$

Where, E = Electricity consumption; n = number of pump or blower;

P = Power; q = quantity of wastewater flow

If water flow rate 400m³/hr., TP conc. 300mg/L, COD 1500mg/L. For the anaerobic reactor influent pump P1 (Fig. 1):

Pump selection CHD 545-250B, flow: 420m³/hr, Head: 22m, power 45kW, 1 units energy consumption will be:

$$E_1 = n * P / q = 1 * 45 \text{ kW} / 400 \text{ m}^3/\text{h} = \mathbf{0.1125 \text{ kW}^*\text{h}/\text{m}^3}$$

For the blowers in the aerobic system P3 and P6 (Fig. 1):

Energy Consumption if fan selection: FSR 300 Roots blower, flow: 110m³/min, power 160kW, 2 units then:

$$E_2 = n * P / q = 2 * 160\text{kw} / 400 \text{ m}^3/\text{h} = \mathbf{0.8 \text{ kW}^*\text{h}/\text{m}^3}$$

Then total cost of electricity consumption = Price * (E₁ + E₂)

$$= 0.13\$/(\text{kW}^*\text{h}) * (0.1125 + 0.8) \text{ kW}^*\text{h} / \text{m}^3 = 0.119\$/\text{m}^3$$

In anaerobic process we add trace elements, which costs about 0.016 \$/m³ of wastewater. Therefore, the cost of the wastewater treatment process is

$$0.119 \text{ \$/m}^3 + 0.016 \text{ \$/m}^3 = \mathbf{0.135 \text{ \$/m}^3}$$

The cost estimate for treating CGW is closely related to the wastewater quality, effluent quality, wastewater treatment process and so on. Literature reported^{55, 56}, that the industrial scale coal gasification wastewater treatment process cost roughly from \$0.4 - \$0.7 / m³. In this study a lab scale attempt has been made to obtain the total treatment cost of CGW **0.135 \$/m³** (without ozonation).

3.6. Sludge Volume

There is no discharge of surplus sludge during 1 year of running. In each reactor unit the change is compelled between the pre-treatment and final treatment. During 1 year of running amount of sludge in each reactor has no significant change excluding the need

of experiment when anaerobic/aerobic batch experiment certain volume of domesticated sludge from respective reactors were extracted.

As, sludge production is closely related to the process involved. It is well known that the sludge production of anaerobic process is less than aerobic process, and the sludge production of aerobic biofilm contact oxidation process is less than activated sludge process. In this study the advanced anaerobic expanded granular sludge bed (AnaEG) and the advanced bio-membrane technology aerobic reactor (BioAX) were used to treat the CGW, which is the foundation of the less sludge production of ABO+AF system.

Secondly, less sludge production for ABO+AF system could be explained from the perspective of carbon balance. The conversion pathways of the COD in the CGW includes sludge growth, biogas, VOCs (aeration blowing off) and residual COD in CGW. In this study, the total COD removal rate of AnaEG was 50%, and part of the removal COD was transformed into biogas³¹.

The COD removal by BioAX only accounts for 30-35% of the total COD removal in the ABO-AF system. Due to the long and complex biological chain of BioAX biofilm, and also the BioAX reactor was run in sections with dominant bacteria respectively³², therefore the sludge production of BioAX was less than the conventional bio-contact oxidation process.

Moreover, it should be noted that during the aerobic aeration, there is part of COD, such as VOCs, directly escaped from CGW into the air, which was not degraded by microorganism. Furthermore, about 10% of the total COD removal was degraded by

ozonation. Therefore during this study sludge generated is very less, we can ignore it which is a big advantage of this technology. This process will become competitive in future industrial applications.

Conclusions

A laboratory scale AnaEG-BioAX-Ozonation+Aerobic Fluidized bed (ABO+AF) system was used to treat coal gasification wastewater. The biggest characteristic of the treatment process are: it exhibit high dispose capability for treatment of highly contaminated and toxic coal gasification wastewater. Although the removal of ammonia along with the other pollutants from coal gasification wastewater is a complicated process but our system treated it efficiently, effectively and simultaneously with excellent removal efficiency of COD 96%, Ammonia 99%, total phenol 100%, volatile phenol 100% and Volatile acids 100%, respectively. This process has obvious technical advantages: as in the whole treatment process do not have reflux of effluent, short residence time, low energy consumption, low sludge production easy management and maintenance. Both the opportunities and the limitations of ABO+AF technology meet the multiple criteria of water sustainability. So it should have a negligible environmental and ecological impact.

A simplified processing unit AnaEG reactor was used in this study that focused on enhancing the wastewater biodegradability. The anaerobic reactor primarily converted refractory and inhibitory compounds into biodegradable organic substances, hence wastewater toxicity is reduced³¹. BioAX reactor used in this study has its own advantage

as maintenance is negligible, shortcut flow does not exist, air distribution is uniform, plug flow with overturning, growth of biofilm is not disturbed by aeration, higher oxygen transfer efficiency, faster start up: shorter microorganism cultivation time, lower power consumption: lower blower capacity, no need for replenishment of microorganism.³²

This paper presents a laboratory attempt to explore the possibility of applying ABO+AF as a sustainable technology for wastewater treatment and to guide its future development on industrial scale. This technology will be star in the future industrial wastewater treatment.

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Figure Captions

Figure 1. Coal gasification wastewater treatment process flow diagram: (1) storage tank, (2) influent dosing pump, (3) anaerobic reactor, (4) gas absorbing liquid, (5) gas flow meter, (6) anaerobic effluent, (7) aerobic intake pump, (8) aerobic reactor (package film), (9) oxygen inject pump, (10) aerobic effluent tank, (11) ozone reactor, (12) storage tank, (13) pump, (14) aerobic fluidized bed, (15) air compressor, (16) storage tank

Figure 2. Start-up and operational strategy for (a) anaerobic reactor (b) aerobic reactor (c) aerobic fluidized bed

Figure 3. Anaerobic reactor degradation trends and removal efficiency (a) COD (b) Total phenol (c) Volatile phenol

Figure 4. Aerobic reactor degradation trends and removal efficiency (a) COD (b) Total phenol

Figure 5. Aerobic fluidized bed degradation trends and removal efficiency of COD.

Figure 6. Scanning Electron Microscopy analysis of anaerobic sludge

Figure S1. Removal rate versus loading rate in aerobic reactor