Novel Pretreatment Enables Performance of MBR Installed to Treat Oily Wastewater

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ABSTRACT

Two new integrated systems processes, gas-energy-mixing (GEM) flotation – electrochemical catalytic oxidation (ECO) – membrane bioreactor (MBR) and ultra-filtration (UF) – ECO – MBR, were tested in industrial-scale pilots of 200L/h to 3000L/h for the treatment and reuse of steel mill cold-rolling emulsion wastewater. The operation parameters and mechanisms of each module action in the integrated process were analyzed. The influence of operation parameters of two processes on chemical oxygen demand (COD_{Cr}) and fats oil and grease (FOG) removal efficiency were comparatively investigated. The test results showed that the treated water quality could meet the requirement for reuse after treatment by either process. However, the quality of effluent treated by GEM – ECO – MBR was more stable than that of UF–ECO–MBR. Such system was more stable and economic to operate, and can therefore be used in various wastewater treatment plants used to remove emulsified oils and combination of non- and bio – degradable dissolved COD's.

KEYWORDS: Cold rolling emulsion wastewater; gas-energy-mixing (GEM); electrochemical catalytic oxidation (ECO); ultrafiltration (UF); membrane bioreactor (MBR)

INTRODUCTION

A large amount of oily wastewater is discharged during cold-rolling in the steel industry. Among such effluents, cold-rolling emulsion wastewater is the most difficult one to treat. (Chkrabarty et al., 2008). At present, the conventional treatment methods of oily wastewater are flotation, flocculation, adsorption, bio-chemical, membrane separation process, etc (Yi et al., 2004). However, these technologies still have some disadvantages, such as high operation costs, high chemical consumption, and unstable effluent quality, which make it difficult to achieve the expected treatment efficiency and limit their industry application.

Wastewater treatment plant of Wuhan Iron & Steel Corporation (WISCO) has been using the conventional combination of flocculation – sedimentation – ultra-filtration (UF) – contact oxidation – precipitation to treat the cold-rolling emulsion wastewater. Even under best conditions, CODcr of effluent still remained between 300 mg/L to 500mg/L, which was much higher than that in the Chinese Iron and Steel Industrial Water Pollutant Discharge Standards. As far as we know, there is no efficient process for treatment of cold-rolling emulsion wastewater in iron and steel industry. Researchers are trying to find some new integrated

methods to treat such wastewater. UF– ECO – MBR process has been proposed, but not tested, in iron and steel plants in China (Chakrabarty et al., 2008). Therefore, it is necessary to develop more reliable treatment methods to achieve the required effluent quality.

Among new wastewater treatment technologies such as ECO, MBR, GEM and UF, ECO is especially promising new technology. ECO systems provide energy high enough to break the chemical bonds of non-biodegradable organic matters so that those pollutants can be oxidized, decomposed, or even completely mineralized. This gives it unique advantages in treating non biodegradable contaminants (Liu et al., 2005, Panizza et al., 2000). After conversion into biodegradable materials, advanced bioreactor technologies such as MBR can then be used for residual dissolved BOD and COD removal. However, solids and emulsions (oils) have to be removed to prevent electrode fouling in the ECO systems.

GEM, an efficient novel solid liquid separation technology, can provide controlled mixing of contaminants, flocculants and air bubbles by sequentially translating liquid particles (down to molecular size) throughout a centrifugally rotating liquid layer inside liquid hydrocyclone columns. (Colic et al., 2008). Consequently, the floating ability of flocs is improved and the majority of oil and suspended solids (SS) can be efficiently removed (Colic et al., 2008)]. The resulting effluents are then comparable in TSS and oil concentrations to UF effluents.

Therefore, GEM-ECO-MBR and UF-ECO-MBR systems performance in treating cold-rolling emulsion wastewater was compared. In industrial-scale tests, these two processes had been introduced with the support of WISCO, PACT/USA, CWT and Shanghai DEPE. The test results showed that the treated water quality could satisfy the standards for recycling after using the two processes. But the GEM-ECO-MBR process was operationally more stable than UF-ECO-MBR. Therefore it is a promising technology that could be widely applied in a variety of industrial fields that produce emulsified partly non-biodegradable wastewater.

METHODOLOGY

The Water Quality Tests

Experimental wastewater was obtained from emulsion wastewater outfall of cold rolling mill in WISCO, the quality of wastewater and discharge standards are shown in Table 1. Analytical methods are shown in Table 2.

Table. 1 the quality of wastewater and discharge standard

	COD_{Cr}/(mg/L)	Total Oil/(mg/L)	SS/(mg/L)	pH
Raw Water	10000-66000	2000-5000	1000-9800	7.6
Emission limits	60	5	50	6-9

Table. 2 Analytical methods of water quality

Pollutants	Standard Names of Methods	Numbers of Methods
COD_{Cr}	Potassium Dichromate Method	GB/T11914-1989
Oil content	Infrared Spectrophotometry	GB/T16488-1996
SS	Gravimetric Method	GB/T11901-1987
pH	Glass Electrode	GB/T6920-1986

Quantity of wastewater for pilot study is between 200 L/h to 3000L/h.

Test Equipments

The test equipments are divided into four processing units, including GEM, UF, ECO and MBR and combined into an overall processing system. Equipments of each unit are provided by The Collaboration Environmental Ltd.

Treatment Processes

Cold-rolling emulsions wastewater is collected and homogenized in an equalization tank (EQ), and then pumped to GEM or UF. GEM is designed as a hybrid centrifugal – dissolved air flotation system. Gas is dissolved into the wastewater at the molecular level through the highly active liquid gas interface. The gas is rapidly entrained into 100% of wastewater stream at 120 psi. Before gas bubbles ever evolve, there is a homogeneous distribution of water, contaminants, chemicals and dissolved gas. (Colic et al., 2008).

During the simultaneous stages of nucleation and coalescence, small floccules bind together, expanding gases drive out excess water. The whole process includes gas entrainment, linearization of polymer, flocculation & mixing, nucleation & coalescence, pollutants trapping and large flocs formation and can be completed in seconds. (Colic et al., 2008) Then, the porous air filled flocs and bubble nuclei are formed throughout nucleation chamber. Those air filled flocs have a strong ability to float. As a result, the moisture content of sludge is low. The majority of oil and SS in the wastewater are removed by the two above mentioned pre-treatment systems. Then, the effluent flows into ECO unit.

The ECO is divided into two subunits which can be run independently. The electrolysis current is produced between positive and negative proprietary electrodes by the controllable DC power. The effect of multi-electrode is formed with the help of the solid catalysts filling in the inter-electrodes space, best applied as electrode coating. The majority of •OH free radicals are formed through the synergy effect of the electrolysis current and the solid catalysts in this process (Brillas et al., 2000). The organic pollutants can be oxidized and decomposed by these •OH. COD that are originally difficult to biodegrade are oxidized quickly and efficiently and the biodegradability of wastewater can be enhanced (Cui et al., 2000). Hydroxyl radicals are present next to electrodes as well as in the bulk solution.

The effluent from ECO is pumped into MBR unit. Biosolids are dosed into membrane bioreactor tank where aeration devices and packing media are installed. Two kinds of MBR are run simultaneously, one which is deployed with the built-in imported PTFE hollow fiber membrane and another with the domestic modified PVDF flat sheet membrane respectively. The activated sludge in the tank is intercepted by organic membranes so that the sludge concentration of MBR tank can be increased. The degradation of organic contaminants with the help of biological

species and MBR filtration would ensure the parameters of effluent, such as COD_{Cr}, SS and so on, to meet the designed requirements. Flow chart of the treatment processes is shown as Fig. 1.

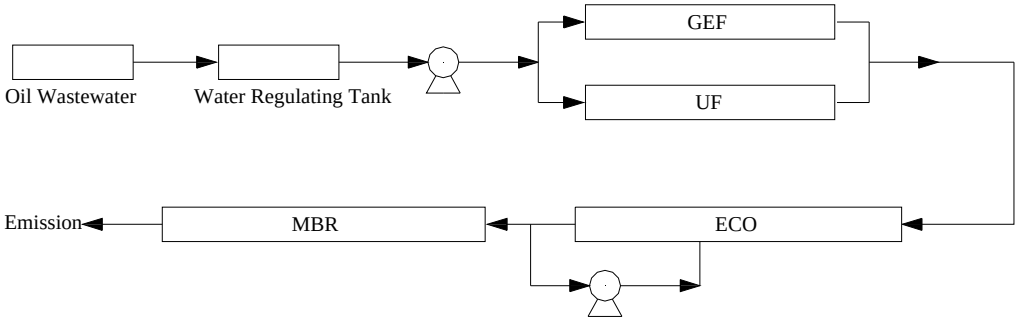

Fig. 1 Flow chart of the effluent treatment processes.

RESULTS AND DISCUSSION

Comparative Analyses of GEM and UF Units in Pre-treatment System

The pre-treatment system is needed for emulsion wastewater treatment because this kind of wastewater contains a large amount of oil and SS. Generally speaking, in order to meet the inflow requirement of follow-up processes, pre-treatment effluent must have $COD_{Cr} \leq 2000$ mg/L, TSS < 200 mg/l and oil ≤ 40mg/L. During the trial period, emulsion wastewater was pumped into GEM and UF respectively from EQ tank. Raw water and effluent of GEM and UF were analyzed and compared, and the trial results are shown in Table. 3.

Table. 3 The Performance of GEM and UF Pretreatment Systems

	COD_{Cr} /(mg/L)	Total Oil/(mg/L)	SS/(mg/L)
Raw Water	10000-66000	2000-5000	1000-9800
GEM eff.	960 -1387	10-36	100-200
UF eff.	844 -1480	10-33	5-10

Table 3 indicates that, during the pretreatment process, after flocculation with cationic polyacrylamide (PAM) in GEM, COD_{Cr}, oil and SS of effluent are similar to those of UF. However, the SS of UF effluent is lower than that of GEM. Both units can remove the majority of COD_{Cr}, oil and SS effectively and satisfy the influent quality demands of the downstream processes. UF flow rate deteriorates fast and chemical cleaning is needed 4-6 times every day. Some irreversible fouling occurs, too. UF prefilters have to be changed frequently.

To further compare the two pre-treatment techniques, a long-term monitoring of COD_{Cr} were adopted to investigate the changes of COD_{Cr} with the running time. The results are shown as

figure 2. As shown in figure 2, the effluent of GEM is more stable compared with UF.

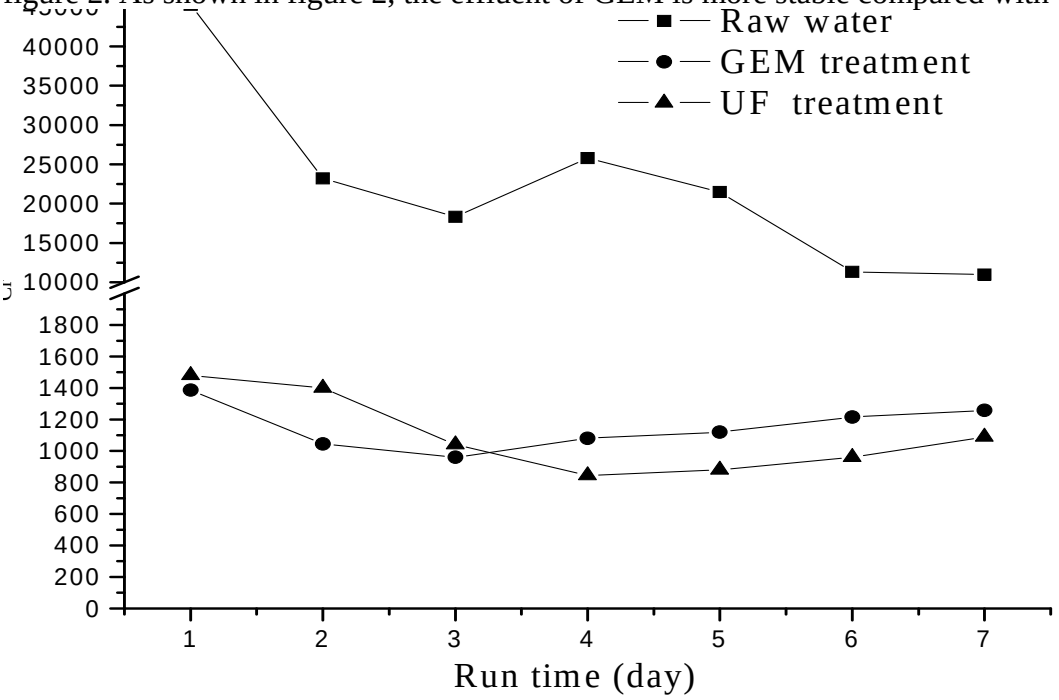

Fig. 2 Effect of run time on the COD_{Cr} of effluent

Analysis of the Final Effluent Quality

According to water reuse standards, a comprehensive analysis of final water quality was made for the combined process effluent of GEM-ECO-MBR. The results are listed in Table 4, which indicates that the effluent quality can fully satisfy the requirements of water reuse standards by using this system.

Table 4 Analyses of Effluent Water Quality of MBR

Indexes	Units	Values	Reuse Water's Requirements
pH	-	7.69	6-9
SS	mg/L	1.6	≤5
COD_{Cr}	mg/L	21.26	≤30
Oil	mg/L	0.3	≤1
Total Hardness	mg/L	140	≤450
Alkalinity	mg/L	320	≤350
Cl^-	mg/L	24.82	≤250
$SO4^{2-}$	mg/L	230.4	≤250
TFe	mg/L	0.34	≤0.3

CONCLUSIONS

The industrial-scale pilot tests of emulsion wastewater treatment at WISCO started in September, 2008 and ended on December 30, 2008. Process optimization and combination of various technologies (GEM, UF, ECO and MBR), yielded the economically feasible, effective treatment system. Influence of various parameters on process efficiency was investigated. The performance of two pre-treatment systems, namely GEM and UF are close. Both of them can remove COD_{Cr}, oil and SS effectively, COD_{Cr} of effluent is less than 200mg/L and oil less than 30mg/L, which meet the influent demands of downstream processes.

1. The integrated processes GEM-ECO-MBR, as well as UF-ECO-MBR, can treat steel mill cold-rolling emulsion wastewater effectively. The final COD_{Cr} of effluent is less than 30mg/L, which meets *Iron and Steel Industrial Water Pollutant Discharge Standards (Draft)*. Comparatively speaking, the GEM System was easier to run, more economic and produced more stable effluent flow rate and quality.
2. By adopting the integrated process of GEM-ECO-MBR, the treated water of cold-rolling emulsion can achieve the requirements of water reuse for iron & steel industry. It provides a new system for wastewater treatment and increased sustainability in iron & steel industry.

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REFERENCES

Chakrabarty, B; Ghoshal, A.K.; Purkait, M.K.(2008) Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane, *J. Membrane. Sci*., **325**(1), 427-437.

Yi , N.; Hu, W. (2004) Some treatment in the cold rolling emulsion wastewater in iron and steel plants, *J. Metallurgical Power*, **22**(5), 58-63

Liu, Fu-xing, Li ,Y. (2005) Mechanism and Development of Electrochemical Catalytic Oxidation in Degradation of Organic Pollutants, *J. SiChuan Environment*, **24**(1), 52-55.

Colic, M.; Lechter, A.; Morse, W.; Miller, J.D. The Development and Application of the Hybrid Centrifugal-Dissolved Air Flotation System for Wastewater Treatment, paper presented at *American Filtration and Separation Annual Meeting* and Expo, Valley Forge, PA (2008).

Panizza M.; Bocca ,C.; Cerisola, G. (2000) Electrochemical treatment of wastewater containing polyaromatic organic pollutants, *J. Water Res*., **34**(9), 601-2605.

Wu , K.; Zhang Cheng-zhou; Liu H. (2005) Treatment of emulsifying wastewater from cold rolling with compound flocculent, *J. Chemical Engineers*, **113**(2), 1-3.

Brillas E.; Calpe, J.; Casado, J. (2000) Mineralization of 2,4-D by advanced electrochemical oxidation processes, *J. Water Res* **34**(8), 2253-2262.

Cui, Y.; Yang, C.; (2004) Application of Electrochemical Oxidation Process in the Bio-refractory Organic Wastewater Treatment , *J. Industrial Safety and Environmental Protection*, **30**(6), 12-14.