Combined Electrocoagulation, Electrolysis and Photocatalysis Technologies Applied to Ship Sewage Treatment

Yu Qing, Yu Hang, Liu Xuelei, Wang Hui, and Xu Shu

Abstract—To develop new ship sewage treatment method, an electrochemical treatment device combined technologies of electrocoagulation, electrolyzing and photocatalysis was utilized to treat the stimulated ship sewage. The experimental showed that through the treatment of the combined technologies, BOD5, COD, TSS and Thermotolerant Coliform was reduced significantly and based on the reasonable structure design and operational parameters, UV irradiation method can be an alternative and potential technology of the traditional de-Chlorine methods. All the experimental results met the requirements of IMO resolution MEPC.159(55). This new electrochemical method and device will be very competitive for sewage treatment in the future.

Index Terms—Sewage, electrocoagulation, electrolyzing, photocatalytic reaction.

I. INTRODUCTION

With the rapid development of shipping industry and of marine resources exploration, marine environmental pollution is becoming more and more serious, and people are paying more and more attention to the marine environment protection. Compared with the city sewage, sewage from ships has its own characteristics: ship sewage has higher pollution load. due to the less flush water, COD, BOD and TSS have higher values and Less organic matter in sewage is decomposed because of the shorter discharge period [1]; the generation and discharge of is more unstable and Ship domestic sewage generated and discharged more unstable, characteristic significantly and the fluctuation of hydraulic load is obvious; the space condition and ship motion limit the application of the various conventional land sewage treatment process [2].

In order to control the discharge of ships and platforms more strictly, International Maritime Organization (IMO) had made and adopted resolution MEPC.159(55) on October 2006 -- Revised Guidelines on Implementation of Effluent Standards and Performance Tests for Sewage Treatment Plants and the resolution has been implemented on or after 1 January 2010. Resolution MEPC.159(55) made the requirements on the water quality of the discharged ship sewage, Table I shows the details:

The biochemical, physicochemical, electrochemical and the combined technologies are the main treatment technologies and systems for sewage treatment in the market.

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The biochemical technology adopts the microbial degradation of organic matter to lower the BOD₅ and COD value of the sewage. Cyclic Activated Sludge Technology (CAST) and Membrane Bioreactor (MBR) are the main technologies of the biochemical treatment methods. Sewage is treated by physicochemical technology using coagulation, precipitation, filtration effect to remove the solid and disinfected by UV [3]. However most manufacturers adopt biochemical technology, electrochemical technology has gradually become the most potential technical in ship sewage treatment filed. The electrochemical method can oxide and disinfect the sewage through the electrode direct oxidation and the oxidants produced by electrolyzing the water. The electrochemical treatment system has obvious advantages: high degree of automation, same footprint, no biological culture, high hydraulic loading resistance and stable treatment effect, etc. due to the requirements to the performance and the materials of the electrode is very high, there are only few manufacturers have the commercial electrochemical treatment systems.

TABLE I: REQUIREMENTS ON THE WATER QUALITY OF THE DISCHARGED SHIP SEWAGE

SHIP SEWAGE							
Items	IMO Resolution MEPC. 159 (55)						
BOD ₅	≦25mg/L						
COD	$\leq 125 \text{mg/L}$						
TSS	\leq 35mg/L						
Thermotolerant	≦ 100 Thermotolerant Coliform /100ml						
Coliform	= 100 Thermotolerant Comorni / Toolii						
рН	6-8.5						
Residual Chlorine							
(When chlorine is used	< 0.5mg/L						
as a disinfectant)							

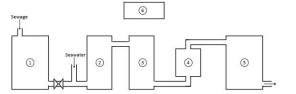
In the present work, stimulated ship sewage treatment experiments using a new type of electrochemical sewage treatment system have been investigated.

II. EXPERIMENTAL

A. Experimental Apparatus and Materials

Sunrui electrolyzing sewage treatment system. The system is composed of electrocoagulation unit, electrolysis unit and de-chlorine unit, Collection Tanks, Macerator Pump, Seawater Pump and Blower fan, etc. The details of the system are shown in Fig. 1.

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(1) Collection tank 1; (2) Electrocoagulation unit; (3) Collection tank 2; (4) Electrolysis uni; (5) De-chlorine unit, (6) Control cabinet

Fig. 1. Sunrui electrolyzing sewage treatment system.

The tank body of tanks, electrocoagulation unit, electrolysis unit and de-chlorine unit is made of Q235B and the external side is coated by anti-corrosion coating and the internal side is coated by coal tar epoxy.

The electrode of the electrocoagulation unit is aluminium

with the purity>99%. The anode of the electrolysis unit is made of titanium and coated with a special DSA coating (Dimensionally Stable Anode) and the cathode is made of titanium. The Light-source UV lamps are used in de-chlorine unit. All the other metal components which contacting the water are made of 316L stainless steel.

B. Experimental Sewage

The test water is the stimulated ship sewage which is composed of fresh sewage from office area sewer and kitchen wash water (The volume ratio is 4:1). In order to increase the pollution degree of sewage, glucose, Starch and silt had been added into the sewage. The parameters of the stimulated sewage are shown in Table II.

TABLE II: THE PARAMETERS OF THE STIMULATED SEWAGE									
Item	BOD_5	COD	Thermotolerant Coliform		TSS	Residual Chlorine mg/l			
	mg/l	mg/l	/100ml	pН	mg/l				
Value	698-76	1211-126	1.7.1.04 1.2.1.1.05	7.05-7.12	589-72	0			
	9	7	$1.7 \times 10^4 - 1.2 \times 10^5$		9				

TABLE III: TREATMENT RESULTS OF THE THREE TEST CYCLES									
Test cycle	Sampling point	BOD5 mg/l	COD mg/l	Thermotolerant Coliform/100ml	pН	TSS mg/l	Residual Chlorine mg/l		
The first test cycle	1	698	1267	1.20×10^{5}	7.05	635	0		
	2	264	562	1.45×10^4	6.87	238	0		
	3	28	137	123	7.46	111	18.6		
	4	13	78	1	7.38	15	0.02		
The second test cycle	1	769	1211	1.05×10^{5}	7.08	589	0		
	2	285	612	1.23×10^4	6.76	256	0		
	3	26	121	56	7.23	124	17.8		
	4	16	66	1	7.35	21	0.05		
The third test cycle	1	734	1232	1.7×10^4	7.12	729	0		
	2	312	548	1.03×10^4	6.85	277	0		
	3	38	146	48	7.13	96	18.9		
	4	20	87	1	7.15	15	0.1		

C. Experimental Method

As a sewage storage tank, collection tanks have the liquid level switch for controlling liquid level. The seawater pump pumps the seawater to mix with the sewage before flow into the electrocoagulation unit. The main structure of electrocoagulation unit is a cabin with Aluminum plates. The sewage treated by the electrocoagulation unit flow out of the unit and flow into collection tank 2. The sewage is pumped from tank 2 to electrolysis unit. In the electrolyzing chamber the sewage is oxidized and disinfected by electrolysis reactors and flow into the de-chlorine unit. The de-Chlorine unit adopts UV technology using UV irradiation to make the photocatalytic reactions occur and decompose the residual Sodium Hypochlorite. Finally, the Drain pump drains the treated sewage out of the system.

Three test cycles have been conducted and four sampling points was set in each cycle: 1) collection tank 1; 2) outlet of

the electrocoagulation unit; 3) outlet of the electrolysis unit and 4) outlet of the de-Chlorine unit.

D. Analysis Methods

1) Total Suspended Solids (TSS)

Revised Guidelines on Implementation of Effluent Standards and Performance Tests for Sewage Treatment Plants (MEPC. 159(55))

2) 5-day Biochemical Oxygen Demand (BOD₅)

ISO 5815-1-2003: Water quality-Determination of biochemical oxygen demand after n days (BODn) — Part 1: Dilution and seeding method with allylthiourea addition Chemical Oxygen Demand (COD)

ISO 15705-2002 Water quality-Determination of the chemical oxygen demand index (ST- COD) — Small-scale sealed-tube method

3) Thermotolerant Coliform

ISO 9308-2-1990 Water quality-Detection and

enumeration of coliform organisms, thermotolerant coliform organisms and presumptive Escherichia coli — Part 2: Multiple tube (most probable number) method pH.

GB/T 6920-1986 Water quality-Determination of pH value-Glass electrode method

Residual Chlorine

CB 3328.6-1988 Water quality-Determination of free chlorine and total chlorine.

III. RESULTS AND DISCUSSION

Table III presents the treatment results of the three test cycles.

Changes of BOD₅, COD, Thermotolerant Coliform, pH, TSS and Residual Chlorine of the four sampling points in the three test cycles are shown in Fig. 2 to Fig. 7 respectively.

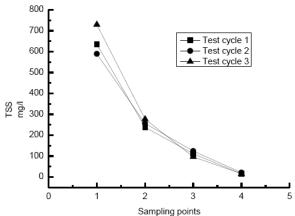


Fig. 2. BOD5 changes of the four sampling points in the three test cycles.

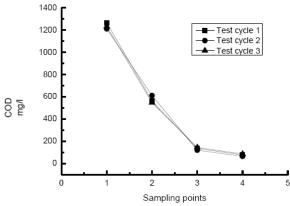


Fig. 3. COD changes of the four sampling points in the three test cycles.

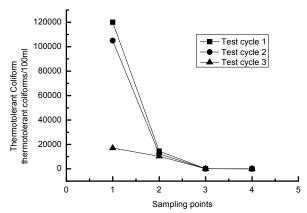


Fig. 4. Thermotolerant coliform changes of the four sampling points in the three test cycles.

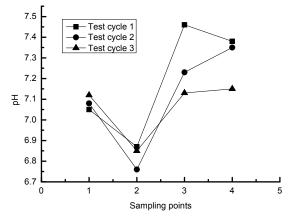


Fig. 5. pH changes of the four sampling points in the three test cycles.

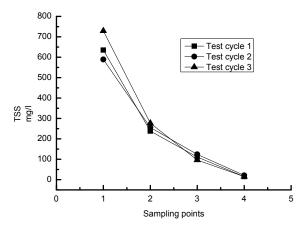


Fig. 6. TSS changes of the four sampling points in the three test cycles.

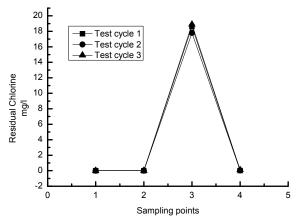


Fig. 7. Residual chlorine changes of the four sampling points in the three test cycles.

Fig. 2 and Fig. 3 show that the BOD_5 and COD decrease with the processing of the treatment. In the electrocoagulation unit, the main structure of electrocoagulation unit is a cabin with Aluminum plates. Under the effect of the current, Aluminum plates dissolved and change into aluminum ion, the aluminum ion hydrolyzes and generates flocculants, which can act on impurities and form precipitates(equation (1) - (6)) [4]-[9]. The suspended solids, insoluble organic matter and part of the oil can be absorbed by the flocculants and precipitated to the bottom of the electrocoagulation unit. Meanwhile, electrolysis will generates tiny H_2 and O_2 bubbles. On the way up, the bubbles can absorb light suspended particles and water-repellent substance. Those impurities will float on water surface and can be cleaned automatically or

manually. So the BOD5 and COD value decreased obviously.

Anode Al
$$\rightarrow$$
 Al³⁺ + 3e (1)

Cathode
$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$
 (2)

$$2H_2O \rightarrow O2 + 4H^+ + 4e \tag{3}$$

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$$
 (4)

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^{+} + H^{+}$$
 (5)

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$$
 (6)

BOD₅ and COD are further reduced on the outlet of the electrolysis unit. The anodes of the electrolysis unit are made of titanium and coated with a special DSA (Dimensionally Stable Anode) coating and the cathodes are made of titanium. The sewage flows through the space between the anodes and cathodes, under the anodes oxidation effect the organic matter is directly oxidized to CO₂ and H₂O. Meanwhile, Sodium Hypochlorite which is a strong oxidant is produced by the electrochemical reactions (7) [10], (8) and (9). Sodium Hypochlorite can also oxidize the organic matters to lower the COD and BOD₅.

Anode:
$$2Cl^{-} \rightarrow Cl_2 + 2e$$
 (7)

Cathode:
$$2H_2O + 2e \rightarrow 2OH_2 + H_2$$
 (8)

Overall reaction:
$$NaCl + H_2O \rightarrow NaClO + H_2$$
 (9)

The sewage containing certain concentration Sodium hypochlorite flows into the de-Chlorine unit. Several UV lamps quartz tubes are set in the unit and irradiate the sewage before the sewage flow out of the unit. Experimental shows that COD and BOD5 continue to be reduced in this treatment step. Two reasons may be responsible for this change: one reason is the Sodium hypochlorite continue to oxidize organic matter in de-Chlorine unit before Sodium hypochlorite was total degraded, another is under the UV lamps irradiation, photocatalytic reactions occur and decompose the residual Sodium Hypochlorite. Meanwhile an active Oxygen with high oxidation ability is produced which can also oxidize the organic matters in the water [11]. The reactions are listed below:

$$NaClO \xrightarrow{UV} NaCl + [O]$$
 (10)

$$[O]+Organic Matters \longrightarrow CO_2 + H_2O$$
 (11)

According to S. Raghu [10], OH can also be generated during the reactions and oxidize the organic compounds to CO_2 and H_2O .

Fig. 4 shows the Thermotolerant Coliform change in the whole treatment process. In the electrocoagulation unit, the produced flocculants carry some particles out of the sewage, so part of the Thermotolerant Coliform which is contained in the particles is also separated from the sewage. In electrolysis unit and de-Chlorine unit , under the combined effects of Sodium Hypochlorite oxidation, UV irradiation and active Oxygen Oxidation, the Thermotolerant Coliform is almost

killed [12].

Fig. 5 shows that the pH increases obviously after the electrolysis unit, because during the electrolysis reaction, the OH- can be produced according to reaction (8).

Fig. 6 shows the change of TSS. Due to the electrocoagulation effect of the electrocoagulation unit and the settlement effects of collection tank 2 and de-Chlorine unit, The TSS is separated and decrease gradually.

Fig. 7 shows the change of residual Chlorine. According to reaction (9), certain concentration Sodium Hypochlorite is produced in electrolysis unit. Due to its decay and especially the UV irradiation, Sodium Hypochlorite is decomposed to the allowable discharge concentration. The traditional methods to neutralize sodium hypochlorite are to add the neutralizer (sodium thiosulfate, sodium sulfite and sodium purosulfate, etc.) to the water. UV irradiation technology avoids to transport, storage and prepare the chemicals and can't bring the second pollution.

IV. CONCLUSIONS

- Based on the combined technologies of electrocoagulation, electrolyzing and photocatalytic reaction and appropriate operational parameters, the electrochemical sewage treatment system can meet the requirements of IMO resolution MEPC.159(55);
- 2) The anode of the electrolysis unit which is made of titanium and coated with a special DSA (Dimensionally Stable Anode) coating can be used for the advanced treatment of organic compounds in the water;
- Based on the reasonable structure design and operational parameters, UV irradiation method can be an alternative and potential technology of the traditional de-Chlorine methods.

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