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Review of bio-hydrogen production and new application in the pollution control via microbial electrolysis cell

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ABSTRACT

Breaking through the "fermentation barrier" bottleneck of conventional biological hydrogen production technology, achieving the depth use of carbon source, and obtaining the higher hydrogen production, bioelectrocatalysis technology assisted fermentation process has vast prospective of applications. The main technical route is the microbial electrolysis cell (MEC). Based on the cutting-edge researches carried out by worldwide scholars, this paper focuses on the comprehensive discussion of MEC design, substrate selection, electrode materials, performance optimization, microbiology, as well as the main problems of the corresponding research. The review also presents recommendations and solutions accordingly. Finally, the prospects of microbial electrocatalysis assisted technology in the field of environmental pollution control and energy recovery application have been disclosed.

Keywords: Microbial electrolysis cell (MEC); Bio-hydrogen production; Fermentation barrier; Pollution control

1. Introduction

Hydrogen gas as a single element having 2.8 times energy content as the combustion of gasoline makes it environmentally friendly [1]. Bio-hydrogen production from industrial and agricultural organic wastewater is a promising technology, which is completed by the metabolism of micro-organisms [2]. This technology integrates both pollution treatment and energy production, and so it has the advantages of cleanness, energy saving, and waste utilization [2].

At present, bio-hydrogen production technology includes photo-fermentation and dark-fermentation. Photo-fermentation produces hydrogen via algae and photosynthetic bacteria under the role of solar energy, so that the reaction is limited to light condition and intensity makes it slowly progress in application [3]. Dark-fermentation produces hydrogen by microbial degradation of organic materials in an anaerobic environment with the maximum hydrogen yield of 12 mol/mol·glucose theoretically, but the "fermentation barrier" makes it only 2–3 mol in practice [4]. The problems mainly reflect on: (1) low rate of carbon source utilization and incomplete substrate conversion

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which means the intermediate products cannot be spontaneously converted to H_2; and (2) accumulation of volatile fatty acids (VFAs) such as acetic acid, propionic acid, and butyric acid make the system instable [5].

Microbial electrolysis cell (MEC) based on the technology of bioelectrocatalysis could solve the problem of "fermentation barrier." In the MEC, organic materials are used as the electron donor and degraded by the exoelectrogenic bacteria at the anode with the release of electrons and protons. Hydrogen is evolved when the proton and electron meet at the cathode. Under the drive of the applied voltage, the VFAs can be further degraded and thus the hydrogen yield has been greatly improved [4]. The MEC reactor mainly includes anode chamber, cathode chamber, membrane, and DC power supply. The schematic diagram is shown in Fig. 1.

The concept of the MEC for hydrogen production was put forth since 2005, but the relevant researches were published in 2007 [4]. These studies were mainly based on the results of microbial fuel cell (MFC) including reactor design, substrate selection, electrode materials, performance optimization, and microbiology. These parameters play important roles on hydrogen yield and operation stability, but they have apparent inadequacy. This paper summarizes the latest research progress of MEC, analyses main problems, and puts forward reasonable suggestions and countermeasures. In addition, the present review outlooks the MEC technology in the environmental pollution control and energy recovery field for new application as well. Therefore, this study has an important significance in MEC hydrogen production.

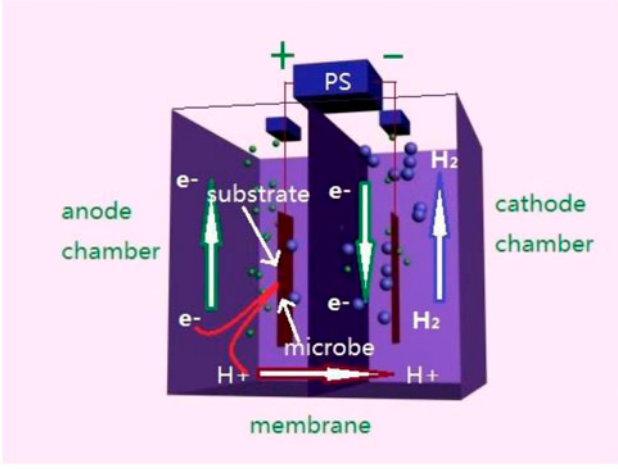

Fig. 1. Schematic diagram of MEC reactor.

2. Reactor design

As the body of MEC is concerned, the structure of the reactor directly affects the current density and hydrogen yield via internal resistance. According to the presence of ion exchange membrane, they could be divided into membrane and membraneless reactor; while according to the chamber numbers, they could be divided into single-chamber and two-chamber. The advantages and disadvantages compared to the diverse reactors are noted in Table 1.

Ion exchange membranes include cation and anion. With the barrier of ion exchange membrane, H_2 and O_2 are separated, so that H_2 oxidation at the anode is decreased. Meanwhile, anion exchange membrane could improve the MEC performance and increase the H_2 yield up to $1.1\,m^3\,m^{-3}\,d^{-1}$ [6]. When the applied voltage is around 0.6 V, the performance of cation and anion exchange membrane shows close; but above 0.6 V, the cation exchange membrane performance will be superior to the anion exchange membrane [7]. Previous studies also show that membrane not only increases the internal resistance of the reactor, but leads to the imbalance in the oxidation process at the anode [6,8].

Decreasing the internal resistance, achieving higher hydrogen production, decreasing the gradient of pH [9], reducing the energy loss [10], increasing the energy recovery rate [11], and decreasing the cost of the system [8], membranless MECs demonstrate great potential. Alternative to membrane, high permeability of synthetic fabric used to separate the electrodes could reduce the internal resistance and increase the current density, but enhance the oxidation of H_2 by hydrogen-consuming micro-organisms and consequently decrease the hydrogen concentration [12]. In order to reduce the oxidation of H_2, research carried out by Ren Nanqi demonstrated that in a single-membranless MEC, with the fermentation effluent as feed, the overall hydrogen capture rate could be 96% at the applied voltage of 0.6 V [13]. Some other researchers also found that maintaining appropriate spacing of electrodes has important implications for cathodic hydrogen generations [14]. Constructed single-chamber MEC with applied voltage below 0.6 V could reduce the electrode spacing and consequently lead to improvement in hydrogen yield. They also found that when the spacing is controlled at 0.2 cm, the current density and hydrogen yield could be up to the maximum [15]. In the following research, the inhabitation of hydrogen-consuming micro-organisms and optimal spacing of electrodes should be the research trends. The examples are: (1) setting baffles into the single-chamber MEC to separate the hydrogen and

Table 1
Comparative advantages and disadvantages of different structures of MEC

Structure	Characteristics	Advantages and disadvantages
H-type	Two bottles separated by a membrane	Structure is simple and the separated chambers could prevent the mixing of oxygen and hydrogen; but the electrodes space cause the large system resistance
Cube-type	Single chamber without membrane	Significantly increase the current density and hydrogen recovery rate, enhance the reaction performance; but the hydrogen could be used by the methanogens
Rectangular-type	Reaction be separated by a membrane into two chambers	Membrane could prevent the mixing of oxygen and hydrogen gas; but increase the pH gradient

methane phase prevent hydrogen to be utilized by hydrogen-consuming microorganisms as to the two-chamber reactor and (2) low resistance of novel membrane should be exploited to reduce internal resistance for increasing the current density and consequently the hydrogen production rate.

3. Substrate of MEC

In the MEC, when the complex carbohydrate is hydrolyzed into monosaccharide, then it is converted into pyruvate by microbes through the glycolytic pathway; subsequently redoxed into the balance mechanism of coenzyme NAD+ or NADP+; and finally equilibrated the energy production and reaction process. During the pyruvate oxidation and reduction, the end products of VFAs under the drive of applied voltage could be further oxidized spontaneously and thus overcomed the "fermentation barrier." Consequently, the substrate is vital to MEC as it determines the reaction process and hydrogen yield. Research about the format [16], acetate [17], livestock wastewater [18], fermentation effluent [19], industrial wastewater [20], protein [21], and glucose [9] have been carried out. According to the different substrates, the comparisons of hydrogen production results are presented in Table 2.

Different types of substrate lead to the different rates of organic degradation and proton release, and hence result in various hydrogen yields. In anaerobic conditions with sodium acetate as substrate, hydrogen production is higher than other substrates such as sodium acetate can directly enter into the biochemical reaction. While with protein [22] and polysaccharide [9] as substrates, microbes must first convert them into acetic acid through glycolytic pathway, and subsequently entering the biochemical reaction to generate electrons and protons, so that they affect the columbic efficiency. However, fermentation effluent as substrate could achieve more hydrogen in lower extra voltage comparable to other substrates [19].

In order to increase the hydrogen yield of the MEC, different types of processes should be coupled. At present, the main coupling processes include: (1) conventional fermentation process coupled with MEC [23]; (2) conventional fermentation process coupled with MFC and MEC [19]. Ethanol–H_2-coproducing fermentation is the advantage of fermentation bio-hydrogen technology and the main trend of future [14]. As to MEC, making full use of high concentration organic wastewater and strengthening the acetic acid content of the acidogenic fermentation process effluent as the feed of MEC may be the focus of future research.

4. Electrode materials

4.1. Anode materials

In the MEC, microbes attach on the anode to degrade organic materials and release electrons, and therefore affect the current density of the system. Thus, the compatibility of electrode materials and microbial, electron mobility, the stability, and catalytic properties should be taken into account during the selection of anode materials. Carbon fibers, graphite, active carbon, conductive polymer material, and metal compound materials are mostly used in practice [24].

The conventional conductive materials such as carbon cloth and carbon paper [6] due to high conductivity, high performance stability, convenient source, and low-cost are more widely used. However, the carbon cloth and carbon paper are easy to scatter along with the reaction and have a low energy conversion rate [25]. Because of large porosity and specific surface, graphite materials such as graphite granules, graphite felt, and graphite brushes obtain high current density in MEC [26]. Especially, the graphene applied in MFC, which obtain the higher power generation efficiency and energy conversion rate than carbon cloth [25]. As a good conductor of electricity, activated carbon has the advantages of structural strength in

Table 2
Process operating parameters and hydrogen production effects of the typical substrate of MEC

Types	Concentration (mg/L)	Cathodic H_2 recovery efficiency (%)	Coulomb efficiency (%)	Gas production rate (%)
Acetate	100	46.4 ± 8.5	56.0 ± 10.2	2.6 ± 0.5 L m^{-2} d^{-1} [17]
Acetate	1,000	93	–	17.8 m^3 m^{-3} d^{-1} [15]
Acetate	1,500	88 ± 7	87 ± 4	1.1 ± 0.2 m^3 m^{-3} d^{-1} [22]
Swine wastewater	2,000 (COD)	58 ± 1	48 ± 9	0.9–1.0 $m^3m^{-3}d^{-1}$ [9]
Bovine serum albumin	700	35 ± 3	100 ± 8	0.54 ± 0.05 $m^3m^{-3}d^{-1}$ [21]
Peptone	700	20 ± 0	66 ± 1	0.09 ± 0.01 $m^3m^{-3}d^{-1}$ [21]
Fermentation water	–	58	–	0.48 m^3 m^{-3} d^{-1} [19]
Potato waste water	1,500–2,000 (COD)	–	80	0.74 m^3 m^{-3} d^{-1} [20]
Glucose	1,000	88 ± 5	105 ± 10	1.87 ± 0.3 m^3 m^{-3} d^{-1} [9]

application. For its porous structure with a high specific surface area, studies demonstrated that it obtains three times the power output than carbon cloth [27,28]. The research conducted by Wang Aijie has also emphasized that activated carbon as anode material not only reduced the internal resistance but also increased the columbic efficiency and hydrogen conversion rate. The creation of conductive polymer and metal compound material such as the application of titanium plate coating could enhance the anodic oxidation performance and generate higher power output [24]. In the future, the focus of the researches will be about the conductive polymer and metal compound materials.

Considering the compatibility of electrode materials and microbial, improving the adhesion of microbe at the anode is another important factor. Therefore, pretreatment of anode materials is commonly used, such as high temperature ammonia or nitrogen gas pretreatment [23].

4.2. Cathode materials

To improve the cathode hydrogen evolution, overpotential should be reduced. The catalyst can make it possible, and therefore enhance the cathode hydrogen recovery rate [29]. The cathode materials include carbon cloth, carbon paper [6], stainless steel [30], and biocathode [31].

Recently, studies have shown that using stainless steel cathode not only reduce the cathode overpotential but also produce greater current density [32] and power efficiency [33], which can obtain more stable performance than Pt catalyst [34]. Biocathode, proposed by Rozendal, causes enriching of hydrogen-oxidizing bacteria on the anode and then reverse the polarity of the electrode to achieve the anode and cathode catalytic at the same time [35]. But the current density, it produced only 1.2 Am^{-2} at −0.7 V cathode potential compared with 4–10 Am^{-2} produced by Pt catalyst [30].

With low overpotential, stable performance, and high hydrogen recovery rate, Pt catalyst is widely used [6]. However, its high cost and sensitive toxic limit the use of Pt catalyst [36]. While a study demonstrated that Pt catalysis was not obvious to solar-drive MEC when the applied voltage was up to 0.7 V [37]. However, without catalyst, the performance of the cathode was found poor than the catalyst cathode [7]. Thus, there has been a trend towards using alternated catalyst to replace Pt because of its low cost and advantages to enhance the cathode hydrogen recovery rate. The examples of the catalyst are: Co/FeCo catalysts [7], NiMo/NiW catalysts [36], Ni powder catalyst [38], MoS_2 catalyst [39], and nanoscale Pd catalyst [17]. Especially, the catalyst of metal alloy [40] could achieve better catalysis as compared to pure metal. Simultaneously, increasing the superficial area of cathode could achieve the higher efficiency [37] and three-dimensional electrode could overcome the problem of low current density [36].

In the following research, materials and construction of cathode should be focused. As the cathode materials should be low cost to obtain the superior economic efficiency, three-dimensional electrode through the particle electrode should decrease the internal resistance and increase the current density to enhance the yield of hydrogen production, such as the construction of graphite particle bed. But in practice, particle electrodes should avoid the phenomenon of short circuit.

Table 3
Comparison of hydrogen production under the different process parameters of MEC

Type	Concentration (mg/L)	Temperature (℃)	Buffer solution	Extra voltage (V)	Cathodic H_2 recovery efficiency (%)	Coulomb efficiency (%)	Gas production rate (%)
Fermentation water	–	25	NBS	0.43	58	–	0.48 $m^3 m^{-3} d^{-1}$ [19]
Acetate	1,500	25	50 mM PBS	0.6	88 ± 7	87 ± 4	1.1 ± 0.2 $m^3 m^{-3} d^{-1}$ [22]
Acetate	1,000	30	100 mMPS	1.0	93	–	17.8 $m^3 m^{-3} d^{-1}$ [15]
Glucose	1,000	30	50 mMPBS	0.9	88 ± 5	105 ± 10	1.87 ± 0.3 $m^3 m^{-3} d^{-1}$ [9]
Peptone	700	25	NPBS	0.8	20 ± 0	66 ± 1	0.09 ± 0.01 $m^3 m^{-3} d^{-1}$ [21]

5. Performance optimization

In the MEC, the parameters including pH, temperature, and extra voltage affect the hydrogen yield and production. Being the key factors to the growing of micro-organisms, pH, and temperature through the metabolic activity affect the hydrogen production. While the applied voltage through the energy efficiency and columbic efficiency affects the hydrogen yield. The comparison of main parameters used in various processes is shown in Table 3.

5.1. pH

In order to ensure the growth of micro-organisms, pH control is the key factor. Based on pH and the concentration of buffer effects of micro-organisms, different buffers are studied such as bicarbonate and phosphate buffer. Some studies demonstrated that 50 mm mol L^{-1} phosphate buffer obtains higher current density than 30 m mol^{-1} bicarbonate buffer [41]. When the pH value is controlled at 6.5–7.0, the anode biological membrane works normally; but when the pH value is below 6.0, the hydrogen production is decreased obviously [42]. Also, the research shows that pH affects the hydrogen production is restricted to the applied voltage. As the applied voltage is kept at 0.6 V with pH of 5.0, the MEC could achieve higher hydrogen production than the values of 7.0 and 9.0 [43]. Therefore, to control the value of pH should take the applied voltage into account so that micro-organisms grow well.

5.2. Temperature

The effect of temperature on micro-organisms reflects in: (1) the growth of exoelectrogenic bacteria, (2) the transfer rate of mass, (3) the activity of the substrate, and (4) the potential of the electrode. The appropriate temperature directly influences the hydrogen yield. The way of temperature control includes an invariable temperature room or temperature-control system. In the research, it is found that keeping the temperature at 30℃ could achieve current density two times as that of at 20℃ [43]. While Kyazze found that the optimal temperature of MEC is 30.4℃, but if the temperature is increased up to 49.3℃, it might inhibit the growth of micro-organisms.

5.3. Applied voltage

Theoretically, microbes could oxidize the organic materials at the anode and produce −0.3 V, while hydrogen evolution reaction needs −0.41 V at the cathode. Hence, it is needed at least additional 0.11 V to produce hydrogen. In the laboratory-scale of MEC, the voltage is generally applied by the DC power supply such as a voltage regulator to control the anode potential [22] or solar power [37]. In order to realize the industrialization of MEC, the way of real-time monitoring for controlling voltage is needed [44].

Though it needs at least 0.11 V, the applied voltage usually keeps at 0.2–0.8 V [4] in practice. The researches demonstrate that applying the lower voltage obtains the lower hydrogen yield. Especially, when the applied voltage is maintained below 0.3 V, the hydrogen production is low. If the applied voltage is increased to 0.8–1.0 V, the hydrogen production is noted maximum [6]. The widely applied voltage value appears to be 0.5 V [18,23]. In the research carried out by Wagner, kept the temperature at 30℃ using the undiluted wastewater which makes the effective wastewater treatment and hydrogen production as a whole [18]. And in the research carried out by Elodie, coupled the fermentation with hydrogenolysis into the

two-stage hydrogen production system achieved 9.95 mol H_2/mol glucose [23]. Using an ethanol–H_2-coproducing fermentation with applied voltage of 0.5–0.8 V, the overall hydrogen recovery rate could achieve 96%; while using the effluent as the feed of MEC and keeping the applied voltage of 0.6 V, 83% of the overall hydrogen recovery rate was achieved [14].

As to the research of a voltage regulator for increasing anode potential, Nam found that in a single-MEC when the anode potential was controlled on −0.2 V, both the overall hydrogen production and gas production were higher than those for the same conditions with 0.6 V applied voltage [22]. No matter the fermentation hydrogen production or MEC, with the applied voltage of 0.2–0.8 V, temperature of 25℃, and pH of 7, both of them could achieve superior hydrogen yield. At the same time, lower anode potential without current limitation could decrease the energy loss of anode [10].

6. Micro-organisms

In the MEC, the degradation efficiency of organic materials and hydrogen yield are affected by the anode electronic generation and extracellular electron transmission process. The key to increase the efficiency is the enrichment of cytochrome gene and exoelectrogenic bacteria [45]. The way to inhibit hydrogen-consuming micro-organisms could also improve the cathode hydrogen recovery [46].

Ways of enriching predominant bacteria are as follows: (1) inoculating with different kinds of bacteria. Pure or mixture cultures vaccination will directly affect the distribution of flora. Studies have shown that the predominant pure bacteria include four genuses, such as *Shewanella*, *Pseudomonas*, *Geobacter*, and *Bradyrhizobium* [47]. The source of inoculate includes municipal wastewater [14], soil [4], livestock wastewater [18], or industrial wastewater [23]; (2) using different types of anode materials [48]. *Geobacter* is the predominant flora in granular active carbon and carbon material; while in the graphite particles is *Azospira*; and (3) using different types of substrates [49]. *Geobacter* is the predominant flora in the sodium acetic substrate while in the butyric acid is *Firmicutes*.

The MFC mode is the most widely used ways to enrich the anode biofilm. When the maximum voltage reappears for at least three circles, transferred the anode into MEC [50]. During the process, the anode biofilm is predominated by *Geobacter Sulfurreducens* [20]. While the research indicated that the columbic efficiencies by inoculated the electricigens could be three times than sludge in the MEC [51].

Assisted with the molecular biological technology, the results demonstrated that the main exoelectrogenic bacteria include: (1) Dissimilatory metal-reducing bacteria (DMRB) such as *Geobacter sulfurreducens*, *Desulfuromonas acetoxidans*, *Shewanella putrefaciens*, *Rhodoferax*, and *Geothrix*; (2) *Desulfuromonas*; (3) *Pseudomonas*; (4) *Enterobacter cloacae*; and (5) *Rhodopseudomonas*. Among them, DMRB could use the non-soluble electron acceptor such as metal oxides (Fe^{3+}); while non-DMRB could use the MEC/MFC anode as electron acceptor. The mechanism of extracellular electron transfer in DMRB and *Pseudomonas* includes cell contact transfer, electronic intermediary transfer, and nano-wire transfer, but unknown in other exoelectrogenic bacteria. Thus, it is realized the symbiosis of exoelectrogenic bacteria and hydrogenogens is the trend of MEC.

7. New application of MEC in pollution control

Assisted with electrochemical catalysis, the persistent organic pollutant such as cyanide [52], phenolic aldehyde [53], polycyclic aromatic hydrocarbon [54], and glycerin wastewater [55] could be degraded into CO_2 or other small molecule compounds via the hydroxyl radicals which was produced through the water hydrogenolysis. Especially to the industrial pollutants, electrochemical catalysis proved successful in the field of environmental pollutant control including leachate [56], tannery wastewater [57], dye wastes [58], sugar industry [59], and olive mill wastewater [60]. Meanwhile, MEC could be applied in the following fields:

(1) Development of the combined bioelectrocatalysis process with hydrolysis acidification. As to the nonbiodegradable pollutants, the pretreatment of the hydrolysis acidification process is the main technology. The bottleneck problem of this technology is to strengthen the effect of fermentation. Therefore, hydrolysis acidification coupled with bioelectrocatalysis process is the trend of the field.
(2) Development of the anaerobic–bioelectrocatalysis system to degrade the recalcitrant toxic compounds. It has been found that anaerobic process is superior to aerobic for most recalcitrant toxic compounds, but the toxic inactivation causes the low efficiency. Building the integrated system and importing the biocathode into the anaerobic reactor and collaborate its bioelectrocatalysis with the anaerobic reduction process, and strengthen the anaerobic reductive mechanism to degrade the recalcitrant toxic compounds effectively.

(3) Application of the bioelectrocatalysis process in dechlorination and denitrification [61]. In anaerobic conditions, microbial hydrolysis acidification based on the principles of reductive dechlorination could realize the removal of chlorinated organic in the wastewater [62]. As to be the rate-limiting step, the removal of chlorine substitutes will be the research focus to improve the dechlorinat speed.

As confronting the world's energy and environmental pollution problems with energy production is imperative. Therefore, it is needed to focus on the problems including: (1) performing further research about the principles of the bioelectrocatalysis process coupled with anaerobic biological treatment; (2) building the coupled process with structural optimization and performance; (3) demonstrating the mechanism of bioelectrocatalysis for nondegradable organic; and (4) further investigaing the collaborative metabolic behavior of exoelectrogenic and anaerobic bacteria.

8. Problems and prospects

In conclusion, researches about structural design, substrate selection, electrode materials, and microbe of MEC have promoted the development of MEC technology. But these researches are all limited to the MFC mode without breakthroughs and innovations. Compared with photo-fermentation and dark-fermentation, MEC on hydrogen production proves to be a potential technology. The focus of future research could concentrate on the following factors:

(1) Exploitation of new reactors, such as low resistance of membraneless reactor with tiny dead areas and high effective mass transfer. On account of that, the resistance of the reactor influences the current density, and therefore influences the hydrogen recovery rate.
(2) Selection of appropriate substrate. In the MEC, the type of substrate directly influences the hydrogen yield. Especially, the coupled process of fermentation and MEC, with the fermentation effluent as the feed of MEC could achieve higher production of hydrogen and efficient of waste water treatment.
(3) Exploitation of low-cost electrode materials. For the optimization of cathode performance, it is needed to concentrate on the catalysis effect and cost to exploit the novel low-cost cathode materials.
(4) Amplifying oxidation of hydrogen at the cathode. With the appropriate process parameters, it is required to control the conditions of MEC for inhibiting the growth of methane-consuming micro-organisms.
(5) Selection of different types of efficient exoelectrogenic bacteria and further investigation about the mechanism of exocellular electronic transfer.
(6) Expansion of the application of bioelectrocatalysis technology in environmental pollution control. With the advantages of exoelectrogenic bacteria to overcome the thermodynamic constraints, it could be coupled with anaerobic technology to expand the application in pollution control.

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