Environmental Engineering

Enhancement of Elemental Sulfur Recovery from Wastewater Biogas Using Nickel (II)-(5,10,15,20)-tetrakis-phenylcarboxylporphyrin

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Abstract

Sulfide control is a vital issue affecting the regional air quality and operational safety in sewage treatment processes. The conventional sulfide removal techniques are sophisticated industrial processes which require large operational footprint or are related to hazardous chemicals. In this study, the performance of elemental sulfur recovery from a simple micro-aeration process with metal-TCPP ((5,10,15,20)-tetrakis-p-carboxyphenylporphyrin) was investigated through laboratory experiments. Significant enhancement of elemental sulfur recovery was achieved from sulfide dissolved wastewater with the addition of nickel (II) TCPP, which demonstrated the highest among seven various types of transition metal-porphyrin complexes in the 3d block elements. The optimized reaction conditions resulted in over 70% sulfur recovery with the addition of only 4.5ppm nickel into the solution. The catalyst significantly improves the recyclability and life-cycle of the water-based absorbent and provides benefits to odor control and resource recovery.

Keyword : Partial Oxidation, Sulfide species, Elemental sulfur recovery, Nickel(II)-TCPP, Micro-aeration

1. Introduction

Odor and toxic gas control is a critical unit operation in wastewater treatment plants (WWTPs). This exercise is especially critical in highly populated cities like Hong Kong due to high sensitivity to residential environment and limited space. The unique sewage treatment process in this metropolis has resulted in an urban-specific and extreme problems, of which the related studies may have pioneered in water purification research and works. Hong Kong applied seawater for toilet flushing in 1960s. The high concentrations of sulfate in the influent wastewater has resulted in ten to thousands times higher hydrogen sulfide content in the sewer headspace or biogas generated in the anaerobic digesters. While pipe corrosion problems can be overcome by proper selection of piping materials, complaints to unpleasant odor and frequent accidents to related workers have been frequently reported with the application.

Hydrogen sulfide is a problematic gas responsible to corrosion damages of co-generation system and wastewater related infrastructures, such as sewer pipes and cement structures. It increases the financial burden for maintenance and operational costs in the WWTPs and sewer system. In addition, sulfide in aqueous systems can affect the health of marine organisms, and hence impact the reaction kinetics of biological processes. It is also a well-known poisonous gas which can interfere the ability of red blood cells in transporting oxygen by increasing the acidity of blood. The strong odor of hydrogen sulfide affects operators' judgement on its toxicity (if proper sensor is not equipped) and damage living quality in the neighborhood. There is an urge to eliminate hydrogen sulfide from the environment.

In industrial scale, hydrogen sulfide removal has been carried out through many well-established technologies. Scrubbers are the most common methods for treating combustible gases generated from anaerobic digesters and oil-mining industries. (Nishimura et al., 1997; Pokorna et al., 2015) Basic solutions like sodium hydroxide (Molnár et al., 2017) or Methyl diethanolamine (MDEA) (Shoukat et al., 2019) are commonly applied chemicals in the scrubbers, which can effectively eliminate the hydrogen sulfide existing in the gas streams. In line with the used chemicals various strategies have been developed to treat the absorbed sulfide species in the solutions. For example, regeneration of MDEA absorbent has been carried out by heat treatment. Lo-Cat method has been adopted widely by using Fe-EDTA as the catalyst to treat the sulfide species in aqueous solution, which convert it to sulfoxide species through oxidation. (Kazemi et al., 2014) However, the catalyst is not reusable after 3 to 5 times. Iron will be lost when the catalyst was extracted from the treated liquid. The treatment efficiency decreases drastically as the catalyst is reused. Finding an alternate material which able to hold the metal more strongly for the absorption and oxidation of sulfide species in aqueous solutions has become critical to regenerate water solvent and improve the treatment performance. The use of a metal porphyrin complex on treatment of sulfide species while simultaneously recover the valuable elemental sulfur through micro-aeration provides new thinking to solve the hydrogen sulfide issue at low cost.

Porphyrin is a heterocyclic molecule of which the pyrrole molecules are linked together by methine bridges. Porphyrins have been confirmed with many different applications like as a photosensitizer (Kou et al., 2017, Meshkov et al., 2017), catalysts (Dar et al., 2019) and drug carrier (Wang et al., 2018). Porphyrins are also known as a green chemical which has been widely seen in nature, *i.e.*, the major constituent of heme group in hemoglobin and chlorophyll. Recent researches have been carried out on broadening the applications of porphyrins in photosensitizers and catalysis, *i.e.*, the properties of high quantum yield and the ability to absorb and emit visible light in catalytic reactions (Yang et al., 2019). The changes in charges and the protection of metal center by the porphyrin ring allowed metal-porphyrins to show catalytic reactions on the carbon-halogen cleavages in aryl halide compounds (Qian et al., 2015). In this study, investigation of metal porphyrins on elemental sulfur recovery was carried out by adding metal-(5,10,15,20)-tetrakis-p-carboxyphenylporphyrin (MTCPP)(Fig.1) by micro-aeration technique, of which the schematic approach of the reaction of this study was shown in Fig.2.

2. Materials and Methods

2.1. Synthesis of (5,10,15,20)-tetrakis-carboxyphenylporphyrin(TCPP)

The synthesis of TCPP was performed based on the method in literature previously mentioned. 3g (20mmol) 4-carboxybenzaldehyde was added into a 250mL round-bottomed flask. 0.35g pyrrole (5.22mmol) was added dropwise into the reaction mixture. The reaction was undergone for 4 hours and monitored by thin-layer chromatography. The reaction mixture was allowed to react for 6 hours under reflux at 200°C, then cooled down to room temperature before adjusting the pH to 3 by 1M HCl. The mixture was placed into a 4°C fridge for precipitation overnight. The solid was obtained by vacuum filtration and dried in oven overnight.

2.2. Synthesis and identification of nickel (II)-TCPP

2g TCPP(2.53mmol) and 1.5g nickel (II) chloride hexahydrate(6.32mmol) were added into a 100mL pear-shaped flask. 60mL dimethylformamide (DMF) was added into the flask. The reaction was undergone under reflux conditions with a reaction temperature of 200°C for 6 hours. The reaction mixture was allowed to cool down to room temperature. Acetone was added into the reaction mixture in order to precipitate the product. The solids were obtained from vacuum filtration and washed by acetone. It was dried in oven for 24 hours. The solid were re-dissolved in pH 9 NaOH solution. 2.2M HCl was added into the solution until pH 1 for recrystallization. The solid remained were filtered and washed by acetone and placed under 55°C oven for 3 days.

2.3. Sulfur recovery using metal-TCPP

The recovery of sulfur was performed using a 1L reactor (Fig. 3). Phosphate (3.99g PO_4^{3-}) buffer was added into the solution with sulfide concentration of 0.23g/L. A very fine bubble diffuser (bubble diameter < 1mm) and an air pump from was used to supply oxygen from air into the solution as dissolved oxygen. The reaction mixture was allowed to react for 24 hours. The solution was filtered by vacuum filtration and washed by 0.3M NaOH solution first to remove the remaining metal-TCPP on the residual. The residual was then washed by 1M HCl to remove the excess sodium hydroxide added. The solid was washed by water until the pH of filtrate reaches around 7. The solid obtained were extracted and dried in 55°C oven for 3 days. The solid were then weighed to evaluate the yield.

3. Results and discussions

3.1. Performance of recovery by adding different metal-TCPP

The effect of different metal ions added to TCPP was analyzed by using 3d transition metals as transition metals can have more than 1 stable charges. Metal concentration of 0.47ppm were added into the system for each test. The transition metals used for this study are manganese, iron, cobalt, nickel, copper and zinc. The solid synthesized were shown in Fig. 4. From Fig. 5, Zinc-TCPP did not show any enhancements in the yield of elemental sulfur but the amount of elemental sulfur produced has been suppressed. Yield enhancements were found using the other metal ions. Along the 3d transition metals, the elemental sulfur recovery increased from manganese to nickel, where it reached the highest recovery among the 6 transitional metals investigated.

3.2. Difference in oxygen content given to the system

Oxygen gas is crucial in this reaction as it is the oxidant in this process. Oxygen content provided to the system was vital to the optimization of yield as this oxidation process is a partial oxidation process. The oxygen gas transfer coefficient increases as the air flow rate provided increases. Although the reaction time may be reduced, more problems might be arisen. As the gas transfer coefficient of oxygen increases, the amount of oxygen dissolved into the reaction mixture increases. The rate of increase of dissolved oxygen concentration increases, which will lead to the over-oxidation of sulfide species to other sulfoxide species like sulfite and even sulfate. Elemental sulfur will not be formed if they are oxidized to these species. Moreover, hydrogen sulfide transfer through the gas-liquid film will increase in rate if the gas inflow increases. An increase in gas inflow indicates the increase in amount of gas bubbles entering into the solution, which in turn increases the surface area of gas in contact with liquid, leading to the reduction of concentration of sulfide species in aqueous solution for oxidation as more hydrogen sulfide gas can leave the aqueous phase through diffusion into gas bubbles. Fig. 6 showed the change in elemental sulfur yield with the oxygen content pumped into the solution. There was a decrease in elemental sulfur production as the gas flow rate increased. Highest yield was attained at oxygen gas pumping rate of 21mL/min with a yield of 72.53%. As the oxygen gas pumping rate increased, a decline in elemental sulfur yield was observed. This proved the inverse relationship between oxygen pumping rate and elemental sulfur yield. A higher oxygen pumping rate did not favor the formation of elemental sulfur. Fig. 6 also showed the enhancement in elemental sulfur formation after addition of nickel(II) porphyrins. The yield of elemental sulfur has increased even at a high air flow rate.

3.3. Difference in metal content added

From Section 3.1, it was shown that the addition of metal porphyrin could effectively increase the yield of elemental sulfur during the oxidation reaction in solution. The investigations on the addition of metal content into the solution was conducted in order to conduct researches on the increase of metal content added affecting the production of elemental sulfur. Fig. 7 showed the changes in elemental sulfur production changes in metal content added into the solution for the reaction. The production of solid sulfur has been enhanced from 14.75% to 72.53% from the addition of 0 ppm nickel(II) content to 4.5 ppm nickel(II) content. The increase in nickel(II) porphyrin concentration has enhanced the recovery of elemental sulfur from a sulfide-rich solution. The highest yield is 72.53% when 4.5 ppm nickel(II) content was introduced into the solution. However, the increasing trend flattened as more Ni^{2+} is added into the solution. A decrease in elemental sulfur recovery was also observed when more than 4.5 ppm nickel(II) ion was added into the solution. An excess of nickel(II) porphyrins limited the oxidation of sulfide species to sulfur.

3.4. Elemental analysis of the product formed

The solids obtained were analyzed to investigate on the purity of solid obtained. Elemental analyses were done to investigate the purity of solid obtained. Table 1 showed the elemental analyses results of the solid samples being produced with different metal porphyrin being added.

Table 1 showed the solid obtained is higher than 90% when manganese (III) and nickel(II)-TCPP were added into the solution. However, the purity of sulfur was found to be lower than 90% when copper(II)-TCPP was used.

4. Conclusion

Sulfide removal from aqueous solution was successfully performed in a 1-L reactor filled with synthetic wastewater with a concentration of 0.23g/L sulfide species through partial oxidation reaction with micro-aeration. The elemental sulfur recovery has been enhanced with the aid of various metal-TCPP. The highest enhancement in product yield was observed when nickel-TCPP was applied. Utilization and optimization of metal contents and varying the rate of oxygen resulted in outstanding elemental sulfur recovery at a maximum of 72.53% when the nickel content was 4.5ppm with the oxygen pumping rate of 21mL/min. This research provided a simple technique, for which the addition of an innovative catalyst chemical, to perform sulfide removal from wastewater. As the solvent is at low cost and most of the chemicals are green and recyclable, the process may be applicable in decentralized system of which space and operational barriers of concerns. The high purity elemental sulfur may be collected and sold as new resources to support the circular economy and sustainable development.

5. Acknowledgement

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7. Figures and photographs

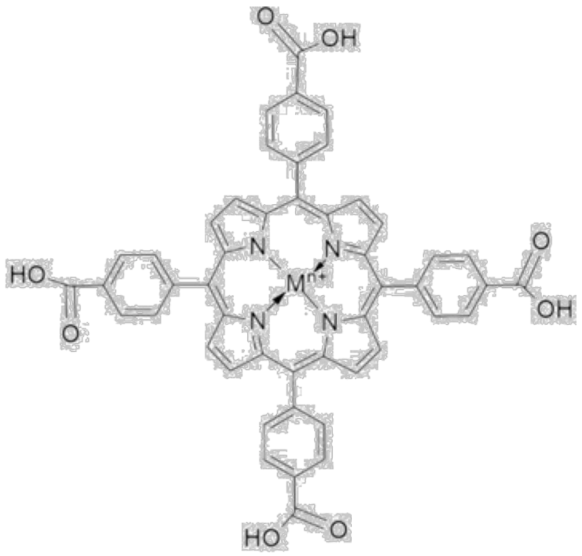

Fig. 1 Structure of Metal-TCPP

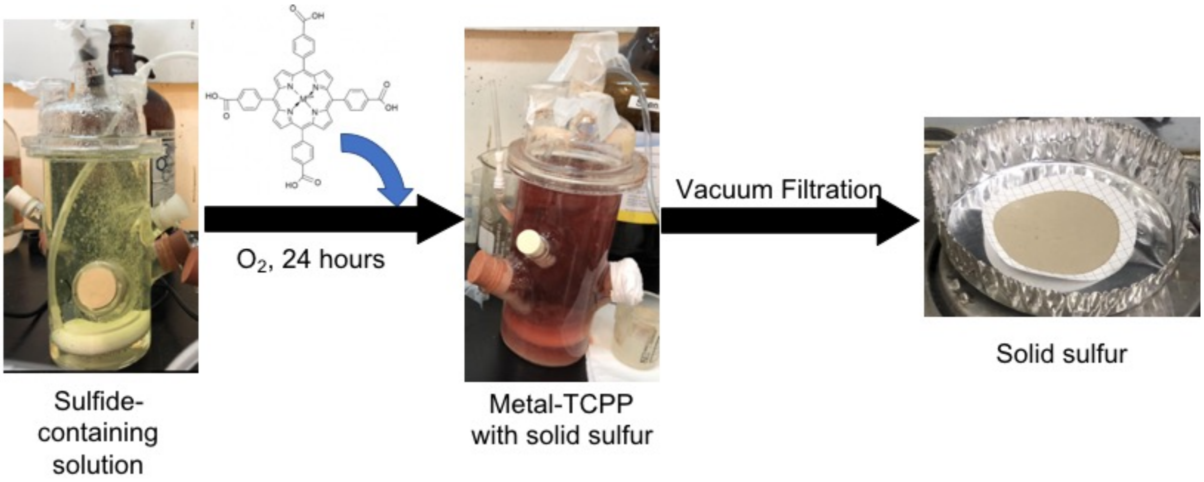

Fig. 2 Schematic approach of elemental sulfur recovery by metal-TCPP

Fig. 3 Lab-scale reactor for the recovery reaction by metal-TCPP

TCPP Mn-TCPP Fe-TCPP Co-TCPP Ni-TCPP Cu-TCPP Zn-TCPP

Fig. 4 Appearances of different metal-TCPPs synthesized in this work

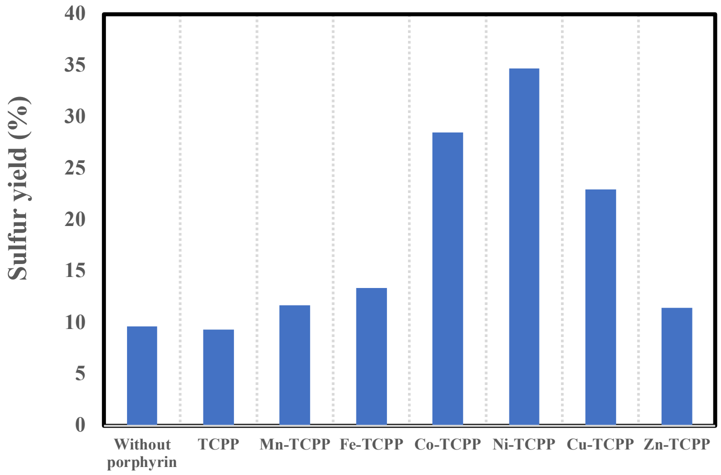

Fig. 5 Sulfur recovery percentage with different metal-TCPP catalysts

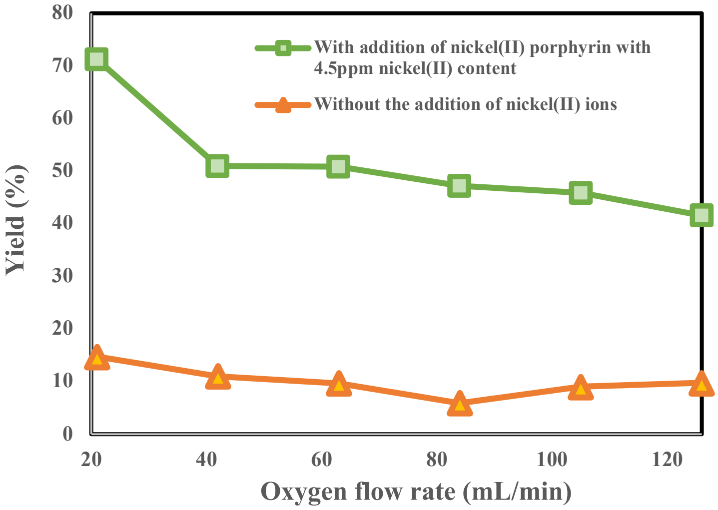

Fig. 6 Percent recovery of sulfur with and without Ni-TCPP in changing air flow rate

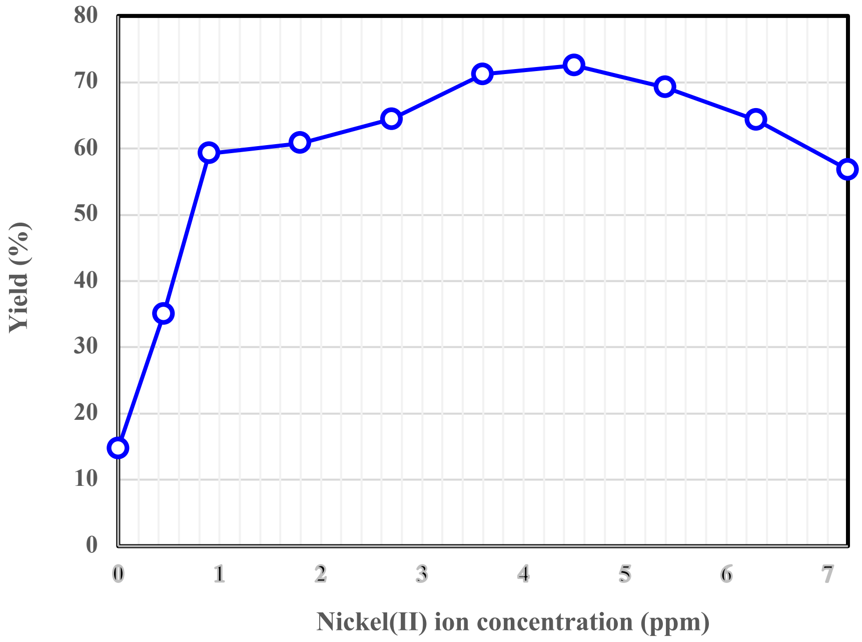

Fig. 7 Sulfur recovery percentage under different nickel(II) contents

8. Tables

Table 1 Elemental analysis results of solid obtained from 3d metal-TCPP

Metal porphyrin added	Sulfur purity(%)
Mn-TCPP	95.3 ± 1.3
Ni-TCPP	96.0 ± 1.5
Cu-TCPP	88.2 ± 2.1