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POSSIBLE USE OF LASERS FOR CLEAVAGE OF PHENOLS TILL BASE SUBSTANCES (REVIEW)

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Abstract. *The purpose of this review article is to explain the hazards of phenol and phenol compounds to human health and the environment. To describe where and how phenol and its compounds occur, especially in industrial effluents. To study the possibility of using laser technologies for phenol cleavage, as well as for the treatment of industrial wastewater from phenol compounds.*

Removal of phenol and its compounds using biological wastewater treatment process is widely used worldwide. This method is cost-effective and environmentally friendly. On the other hand, exceeding the tolerable phenol concentration, which is individual for each biological treatment plant, may result in severe intoxication and lead to death of activated sludge system. Thus, the biological treatment process of industrial wastewater is halted until the phenol concentration is reduced to an acceptable level and the microorganisms have time to recover. Such a procedure can be time consuming and unpredictable due to the susceptibility of microorganisms to changing conditions. Based on this, sources of literature have been studied that could help to understand which laser equipment can be used to cleave a phenolic compound or benzene ring to simpler compounds.

Keywords. *Bacteria, laser technology, phenol, wastewater.*

Introduction

Due to industrial and agricultural revolutions, potentially carcinogenic and mutagenic halogen-substituted aromatics tend to accumulate in environment. Phenol and its higher molecular homologues are hazardous environmental contaminants. Due to their toxic nature, these molecules tend to accrue in water and soil after discharge without appropriate treatment. [1]

The use of bacteria to treat wastewater is one of the most effective and environmentally friendly methods for treating toxic waste from the environment. The limitation of this method is the strict control of the composition of the wastewater. The presence of various chemicals, even in small concentrations, can adversely affect bacteria and other microorganisms and affect their function. For example, phenol and its compounds are such chemicals.

Phenol is important in environmental research because it is often chosen as a hazardous pollutant. As a result, a lot of data is available on its removal or disposal, especially for wastewater treatment. Over the last decade, the treatment of wastewater contaminated with phenol and phenol groups has attracted a great deal of attention due to the toxicity and low biodegradability of these organic compounds. In the chemical industry, phenolic compounds are very challenging to treat by traditional treatment methods, such as activated sludge cleavage, solvent extraction, chemical treatment, adsorption, etc. [2]

Materials and methods

The phenol flash point is only 79 degrees Celsius, it is necessary to choose a laser device that does not emit a large amount of heat, the beam does not exceed the phenol flash point. In addition, phenol vapors are corrosive to the skin, eyes and respiratory tract. Aqueous phenol solutions react

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with oxidants which may lead to fire or explosion [18].

UV laser marker, which has a wavelength of around 355nm, offers a lower power for marking heat-sensitive materials such as plastic and glass. Because UV laser markers and other machines in the "cold laser" category emit less energy, they are great solutions for many organic or soft products, as they are less likely to burn the material. A fiber laser, on the other hand, operates at 1070nm, delivering significantly higher power [19].

Aromatic hydrocarbons are not as readily biodegradable as the normal and branched. But alkanes, they are somewhat more easily degradable than the alicyclic hydrocarbons. Many of these compounds are toxic and some are known or suspected carcinogens. The presence of phenol in drinking water and irrigation water represents a serious health hazard to humans, animals, plants and microorganisms. to some form of aquatic life and ingestion of 1gm of phenol can be fatal in human beings. Continuous ingestion of phenol for a prolonged period causes mouth sore, diarrhea, excretion of dark urine and impaired vision at concentrations levels ranging between 10 and 240 mg/L. Lethal blood concentration for phenol is around 4.7 to 130 mg/100mL. Phenol affects the nervous system and key organs, i.e., spleen, pancreas and kidneys. [1]

Hazards of phenol

Phenol is classified as a priority pollutant owing to their high toxicity and widespread environmental occurrence. Various regulatory authorities have imposed strict limits to phenol concentration in industrial discharges. Many countries regulate phenol released into the environment. For drinking water, a guideline concentration of 1μg/L, has been prescribed.

The impacts of pollution on the environment have led to intense scientific investigations. The removal of phenol from industrial effluents has attracted researchers from different fields. The increasing awareness on the environment in both developed and developing countries has initiated more studies of possible solutions for treating phenol.

Different treatment methods are available for reduction of phenol content in wastewater. Phenolic wastes are treated by several physico-chemical methods like Chlorination, Advanced oxidation process, Adsorption, Solvent Extraction, Coagulation, Flocculation, Reverse osmosis, Ozonisation, Photo catalysis and Electrolytic oxidation. [1]

Biodegradation of phenol

Phenol, or hydroxybenzene, is both a synthetically and naturally produced aromatic compound. Microorganisms capable of degrading phenol are common and include both aerobes and anaerobes. Many aerobic phenol-degrading microorganisms have been isolated and the pathways for the aerobic degradation of phenol are now firmly established. The first steps include oxygenation of phenol, by phenol hydroxylase enzymes to form catechol, followed by ring cleavage adjacent to or in between the two hydroxyl groups of catechol. Phenol hydroxylases ranging from simple flavoprotein monooxygenases to multicomponent hydroxylases, as well as the genes coding for these enzymes, have been described for several aerobic phenol-degrading microorganisms. [3]

The bacteria degrading phenols are divided into two types: the first type can use phenols as the sole source of carbon. These bacteria contain enzyme systems degrading phenols, which often live in a bad environment with phenol contamination. This type of bacteria mainly include staphylococcus, micrococcus, corynebacterium, arthrobacter, acinetobacter and alcaligenes. The second type must rely on other carbon sources to degrade phenols. This type of bacteria mainly decomposes phenols through co-metabolism pattern, which usually needs two or more bacteria working together [4, 6]. The phenol-degrading bacteria generally have their unique properties, inducement of phenol degradation ability, diversity of the matrix degradation and synergistic of phenol degradation. The inducement of phenol degradation ability suggests that the degradation ability of phenol can be improved greatly after adaptive mutation in bacteria. There are two ways to mutate phenol-degrading bacteria: increasing the concentration of phenol and increasing the dosage one time. The results show that the strains which are screened by gradually increasing the concentration of phenol had the strongest degradation ability

of phenol. Adaptive mutation of phenol-degrading bacteria is a result of inducing and selecting. In the process of adaptive mutation, the phenol-resistant strains are screened out by increasing the concentration of phenols, which greatly shortens the adaptation period of the bacteria and improves the degradation efficiency [5, 6]. The diversity of matrix degradation means that isolation and screening of phenol-degrading bacteria with a single phenolic substance as carbon source can degrade other phenolic substances and refractory organics. For example, Bacillus coagulans, separated from single carbon source, can also grow with diphenyl dichloride and naphthalene as carbon source. The synergistic of phenol degradation indicates that the degradation ability of mixed strains is significantly higher than that of single strain. The mixed strains even have strong degradation ability when the phenol concentration is high [6, 7].

Phenol biodegradation and its effect on the nitrification process

Nitrobacteria – any of several genera of bacteria in the soil that participate in the nitrogen cycle by oxidizing ammonium and organic nitrogen compounds to more soluble nitrites and nitrates [8]. Nitrifying bacteria convert the most reduced form of soil nitrogen, ammonia, into its most oxidized form, nitrate. Nitrifiers also contribute to other important processes, including nitrous oxide production, methane oxidation, degradation of organic compounds, and carbon monoxide oxidation [9].

Phenol is a toxic compound present in wastewaters from many different industries, such as petrochemical industries, chemical industries and resin producing industries. In some cases, nitrogen may be present as well. Therefore, the biological treatment of these wastewaters requires the simultaneous removal of phenol and nitrogen, which can be done in an activated sludge reactor in two successive steps. During the nitrification step, ammonium is oxidized to nitrate under aerobic conditions; and during the denitrification step, nitrate is reduced to molecular nitrogen in the presence of a carbon source under anoxic conditions. Nitrification is commonly the rate-limiting step of the overall nitrogen removal. In the presence of toxic compounds as phenol, even at low concentrations, the nitrification process may be inhibited [10].

Based on the information provided by the studied literature, it was found that phenol inhibits the performance of wastewater treatment (chemical oxygen demand (COD) removal). The kinetics of wastewater treatment based on the Michael-Menten enzyme equation were considered. The anti-competitive kinetic equation was appropriate (Equation 1)[17]:

$$V = \frac{V_{max} \cdot S}{\left(1 + \frac{I}{K_I}\right) \cdot K_m + S} \quad (1)$$

V is the COD removal rate (mg/L/h);
V_{max} is the maximum COD removal rate (mg/L/h);
S is the COD concentration (mg/L);
K_m is the half-saturation factor (mg/L);
I is the phenol concentration (mg/L);
K_I is the inhibition factor (mg/L).

Results and discussion

Favorable conditions for nitrobacterium

Nitrifying bacteria are traditionally considered to be obligate aerobes; they require molecular oxygen for reactions in the N oxidation pathways and for respiration. They are reputed to be microaerophiles, however, who thrive best under relatively low oxygen conditions. Microaerophile may be important in interface environments such as the sediment water interface and in the oxygen minimum zones of the ocean. The role of oxygen in sedimentary nitrification and coupled nitrification/ denitrification is discussed above in the section on nitrification in sediments [11].

While net nitrification and growth at the expense of inorganic N occurs only under aerobic conditions in autotrophic nitrifiers, both NH_3^- and NO_2^- - oxidizing nitrifiers are apparently capable of partial or even complete denitrification [11].

Nitrifying bacteria oxidize aerobic biological ammonia (NH_3) to nitrate (NO_3^-) in a two-step process: (1) oxidation of ammonia to nitrite (NO_2^-) by oxidation of ammonia by bacteria (AOB) and (2) oxidation of nitrites to nitrate (NO_2^-). nitrate caused by nitrite oxidizing bacteria (NOB). The molar stoichiometry of ammonium based AOB ($NH4^+$) is:

$$NH_4^+ + 1.382\ O_2 + 1.982\ HCO_3^- \rightarrow$$
$$\rightarrow 0.0182\ C_5H_7O_2N + 0.982\ NO_2^- + 1.036\ H_2O + 1.891\ H_2CO_3$$

For NOB with NO_2^- based molar stoichiometry is:

$$NO_2^- + 0.00256\ NH_4^+ + 0.0104\ H_2CO_3 + 0.00226\ HCO_3^- + 0.487\ O_2 \rightarrow$$
$$\rightarrow 0.00244\ C_5H_7O_2N + 0.00767\ H_2O + 1.0\ NO_3^-$$

The total reaction for complete nitrification is:

$$NH_4^+ + 1.856\ O_2 + 1.979\ HCO_3^- \rightarrow$$
$$\rightarrow 0.0205\ C_5H_7O_2N + 0.979\ NO_3^- + 1.041\ H_2O + 1.876\ H_2CO_3$$

Oxidation of ammonia is optimal between pH 7.5 and 8.0 and between 25 and 30 ° C. AOB has a low growth rate and yield because the oxidation of ammonia results in a small energy gain and a high energy input required to reduce inorganic carbon, resulting in a generation time ranging from 8 hours to several days [12].

Denitrification, in combination with nitrification, is widely applied for removal of inorganic nitrogen from nitrogen-polluted waste and drinking waters. Biological nitrogen removal by means of this combined process is often hampered by the accumulation of nitrite, an intermediate product in both nitrification and denitrification. Nitrite accumulation has received considerable attention, as this inorganic form of nitrogen is toxic to aquatic life and to humans when it is present in drinking water [13,15]. In denitrifies, various environmental factors were found to underlie nitrite accumulation, among them being the type and quantity of organic substrate, oxygen, pH, nitrate availability, and temperature [14, 15].

NOB activity could be selectively retarded by blue light – it can be used as the main influencing factor of mainstream partial nitrification for energy-saving wastewater treatment. [16].

Conclusions

Based on this information, it has been decided to use a marking laser with an approximate power of 20 W for further research. Operation with such a device is without consumable materials, without pollution. The marking laser is energy efficient and meets environmental protection requirements in accordance with European environmental standards.

The creation of artificial streams and the generation of phenolic vapors, which are dangerous to human health even at low concentrations, could be a problem. It is possible that the cleavage of phenolic compounds into simpler chemicals and its combination with biological wastewater treatment will achieve good results. This could lead to optimal treatment of water contaminated with high phenol concentrations. It would also promote the stable functioning of the microorganisms and prevent bacterial poisoning.

Bibliography

1. Chandana Lakshmi M.V.V., Sridevi V., A review on biodegradation of phenol from industrial effluents. https://www.icontrolpollution.com/articles/a-review-on-biodegradation-of-phenol-fromindustrial-effluents-.pdf
2. Mohammadi S., Kargari A., Sanaeepur H., Abbassian K., Najafi A., Mofarrah E. Phenol removal from industrial wastewaters: a short review. Pages 2215-2234. http://dx.doi.org/10.1080/19443994.2014.883327
3. Paula M. van Schie, Lily Y. Young. Review Article. Biodegradation of Phenol: Mechanisms and Applications. Pages 1-18 https://doi.org/10.1080/10588330008951128

4. Solyanikova I. P. and Golovleva L. A., “Bacterial degradation of chlorophenols: pathways, biochemica, and genetic aspects,” J Environ Sci Health B, vol. 39 (3), Pages 333-351
5. V. Bucci, S. Hoover and F. L. Hellweger, “Modeling Adaptive Mutation of Enteric Bacteria in Surface Water Using Agent-Based Methods,” Water Air & Soil Pollution, vol. 223 (5), Pages 2035-2049
6. Zhao L., Wu Q., Ma A. Paper: Biodegradation of Phenolic Contaminants: Current Status and Perspectives https://iopscience.iop.org/article/10.1088/1755-1315/111/1/012024
7. J. Rao, B. Nair, A. Rathinam, A. Giridhar and N. Nagiah, “Synergistic effect of pseudomonas aeruginosa and escherichia coli in the biodegradation of phenolic compounds,” Journal-American Leather Chemists Association, vol. 103 (7), Pages 222-226
8. https://en.wiktionary.org/wiki/nitrobacterium
9. Prosser J.I., in Encyclopedia of Soils in the Environment, 2005 https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/nitrifying-bacteria
10. Amor L., Eiroa M., Kennes C., Veiga M.C. Phenol biodegradation and its effect on the nitrification process. DOI: 10.1016/j.watres.2005.05.019
11. Ward Bess B., in Nitrogen in the Marine Environment (Second Edition), 2008 https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/nitrifying-bacteria
12. Wahman D.G., Pressman J.G., in Comprehensive Water Quality and Purification, 2014 https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/nitrifying-bacteria
13. Gensen O M. Nitrate in drinking water and cancer in Northern Jutland, Denmark, with special reference to stomach cancer. Ecotoxicol Environ Safety. 1982;6:258–267.
14. Wilderer P A, Jones W L, Dau U. Competition in denitrification systems affecting reduction rate and accumulation of nitrite. Water Res. 1987;21:239–245.
15. Barak Y., Tal Y., Van Rijn J. Light-Mediated Nitrite Accumulation during Denitrification by Pseudomonas sp. Strain JR12. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC106331/
16. Kim K., Park Y. G., Light as a Novel Inhibitor of Nitrite-Oxidizing Bacteria (NOB) for the Mainstream Partial Nitrification of Wastewater Treatment https://doi.org/10.3390/pr9020346
17. Siripattanakul S., Phenolic Based Pharmaceutical Contaminated Wastewater Treatment Kinetics by Activated Sludge Process, 2014 https://www.researchgate.net/publication/270768522_Phenolic_Based_Pharmaceutical_Contaminated_Wastewater_Treatment_Kinetics_by_Activated_Sludge_Process DOI:10.7763/JOCET.2014.V2.111
18. International Chemical Safety Cards (ICSCs). Phenol. [online] [reference to 10.05.2022.] Available: https://www.ilo.org/dyn/icsc/showcard.display?p_card_id=0070&p_edit=&p_version=2&p_lang=en
19. Laser applications. Laser marking. [online] [reference to 10.05.2022.] Available: https://www.mecco.com/application-laser-marking#:~:text=%E2%80%8BWhat%20is%20Laser%20Marking%3F&text=In%20simplest%20terms%2C%20laser%20marking,a%20wide%20variety%20of%20applications.