TREATMENT OF INDUSTRIAL ORGANIC RAFFINATE CONTAINING PYRIDINE AND ITS DERIVATIVES BY COUPLING OF CATALYTIC WET AIR OXIDATION AND BIOLOGICAL PROCESSES

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by

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Dedicated to my
Husband & family

CERTIFICATE

This is to certify that the thesis entitled, **"Treatment of industrial organic raffinate containing pyridine and its derivatives by coupling of catalytic wet air oxidation and biological processes"** being submitted by **Ms. Sushma** to the Indian Institute of Technology Delhi for the award of **Doctor of Philosophy** is a record of bonafide research work carried out by her under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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Place: New Delhi

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(Sushma)

Abstract

Pyridine and its derivatives are nitrogenous heterocyclic compounds used as industrial solvents and intermediates in manufacturing pesticides, pharmaceuticals, dyes, explosives etc. Pyridine compounds are recalcitrant in nature and pyridine itself is listed as a priority organic pollutant by the United States Environmental Protection Agency (USEPA). The chemical industries manufacturing pyridine compounds utilize various organic compounds and ammonia at high temperature and the effluent generated from such industries is toxic in nature and has high pH due to presence of nitrogenous compounds. Therefore, it is difficult to treat effluent containing pyridine compounds by conventional biological processes.

The catalytic wet air oxidation (CWAO) is a promising technology for the degradation of refractory and nitrogenous organic compounds present in the industrial effluent. The CWAO is mainly used for achieving two objectives: (i) for complete oxidation of organic compounds into carbon dioxide and water (ii) for enhancing the biodegradability and decreasing the toxicity of the effluent by conversion of toxic compounds to biodegradable intermediates thereby allowing the use of biological methods for its further treatment. The conversion of complex organic compounds to biodegradable intermediates is much cheaper compared to complete mineralization as complete oxidation requires more energy.

Therefore, in the present study, the CWAO of industrial organic raffinate containing pyridine compounds and ammonical nitrogen was carried out at atmospheric pressure using alumina based platinum catalysts. The effect of ceria as promoter on the efficiency of CWAO was investigated. The Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts were prepared with incipient wetness impregnation method and characterized by different analytical methods such as surface

area, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermo-gravimetric analysis (TGA). The feasibility of the CWAO process was investigated by optimizing the various operating parameters such as air flow rate, metal loading, catalyst dose and temperature. The optimum values of air flow rate, platinum loading, ceria loading and catalyst dosage were found to be 1 L/min, 1 wt. % Pt, 10 wt. % CeO_2 and 3 g/L respectively and maximum COD removal of 45 % and 61 % were obtained at the optimum conditions at reaction temperature of 70^oC for Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts respectively. The effect of the operating pressure on the performance of the CWAO was investigated. The stability of the catalysts was studied to determine its potential for long run applications and it was observed that both catalysts were quite stable after 3 cycle run and no significant loss in COD removal was observed even after 3rd cycle run. The CWAO experimental results were found to be in agreement with the lumped kinetic model. The biodegradability and toxicity tests of the CWAO effluent were performed. The toxicity of the CWAO effluent decreased considerably while the BOD/COD ratio of the CWAO effluent was found to increase significantly. The CWAO effluent was treated by biological aerobic and anaerobic techniques to achieve the discharge limits prescribed by statutory authorities.

The low cost alternative such as metal oxide catalyst (MnO_x/Al_2O_3) has been studied to compare the results obtained with noble metal Pt/Al_2O_3 catalyst. The catalysts were prepared using impregnation method and characterized using various techniques. The CWAO operating parameters such as manganese loading, catalyst dosage and reaction temperature were optimized. The effect of the operating pressure on the performance of the CWAO was investigated. The catalyst stability tests were performed by repeating the CWAO experiment thrice with same

catalyst to explore reusability of the catalyst. The leaching test was performed to determine the metal (manganese) leaching from the catalyst into the CWAO effluent. The effect of ceria as a promoter on biodegradability enhancement, catalyst recycling and metal leaching was studied. The biodegradability and toxicity tests of the CWAO effluent were carried out. A significant increase in the biodegradability and complete removal in the toxicity of CWAO effluent obtained at 70^{o}C using ceria promoted MnO_x/Al_2O_3 catalyst was observed. The biological aerobic treatment of CWAO effluent obtained at 70^{o}C using ceria promoted MnO_x/Al_2O_3 catalyst resulted in COD removal of 98.36%. Therefore, it can be concluded that the integration of CWAO using ceria promoted MnO_x/Al_2O_3 catalyst and biological treatment can be employed for the degradation of industrial organic raffinate containing pyridine and its derivatives. The ceria promoted MnO_x/Al_2O_3 catalyst showed good results in terms of catalyst activity, stability and biodegradability enhancement of industrial organic raffinate and can replace the costly noble metals such as Pt/Al_2O_3 catalyst.

सार

Pyridine और उसके डेरिवेटिव नाइट्रोजिनियस हैट्रोसाइक्लिक कम्पाउंडस है, जो औद्योगिक सोलवेंट्स और कीटनाशक, फार्मासूटिकल, रंजक, विस्फोटक बनाने वाली औद्योगिकी में इंटरमीडिऐट्स के रूप में इस्तेमाल किए जाते हैं। Pyridine कम्पाउंड्स प्रकृति से recalcitrant हैं और United States Environmental Protection Agency (USEPA) ने Pyridine को एक प्राथमिक कार्बनिक प्रदूषक के रूप में सूचीबद्ध किया है। रसायनिक उद्योग Pyridine कम्पाउंड्स और अमोनिया को उच्च तापमान पर दूसरे organic कम्पाउंड बनाने के लिए इस्तेमाल करते हैं तथा इस प्रकार ऐसे उद्योग से प्रदूषित पानी उत्पन्न होता है जिसकी pH नाइट्रोजिनियस कम्पाउंड्स के कारण ज्यादा होती है। इसलिए इस प्रकार के प्रदूषित पानी जिसमें Pyridine कम्पाउंड्स होते हैं, को बायोलॉजिकल प्रौद्योगिकी द्वारा साफ करना बहुत मुश्किल है,

प्रदूषित पानी जिसमें रिफरेक्टरी और नाइट्रोजिनियस आर्गेनिक कम्पाउंड्स होते हैं को एक बहुत ही अच्छी विधि उत्प्रेरक गीली हवा ऑक्सीकरण (CWAO) औद्योगिकी से साफ कर सकते है। CWAO के दो मुख्य उद्देश्य हैं: 1. आर्गेनिक कम्पाउंड्स का कार्बनडाइआक्साइड और पानी में पूरा आक्सीडेशन 2. प्रदूषित पानी में टॉक्सिक कम्पाउंड्स का बायोडिग्रेडेबल इंटरमीडिएट्स में टूटकर उसकी बायोडिग्रेब्लिटी बढ़ाना और उसकी टॉक्सीसिटी को कम करना। इसके बाद बायोलाजिक्ल प्रयोग से उसको दोबारा साफ करना। कॉम्पलेक्स आर्गेनिक कम्पाउंड्स को बायोडिग्रेडेबल इंटरमीडिएट्स में तोड़ना ज्यादा सस्ता है बजाय उसका पूरा आक्सीडेशन करना क्योकि उसमें ज्यादा ऊर्जा की जरूरत है।

इसलिए इस स्टडी में औद्योगिक आर्गेनिक रेफिनेट जिसमें Pyridine कम्पाउंड्स और अमोनिकल नाइट्रोजन हैं, को CWAO से वायुमंडलीय दबाव पर प्लेटिनम बेस्ड एलुमिना उत्प्रेरक का उपयोग कर साफ किया है। Ceria प्रोमोटर का प्रभाव CWAO की क्षमता पर देखा गया है। Pt/Al_2O_3 और ceria प्रमोटेड Pt/Al_2O_3 उत्प्रेरक incipient wetness impregnation तरीके से बनाए गए और अलग–अलग विश्लेषक तरीकों जैसे Scanning Electron Microscope, Surface Area, Energy-dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), transmission Electron Microscopy (TEM) और Thermo gravimetric analysis (TGA) से characterize किए गए। CWAO की साध्यता उसके विभिन्न परिचालन मानक जैसे air flow rate, metal Loading, catalyst dose और तापमान से किया गया। Air flow rate, metal loading, catalyst dose और तापमान का सर्वोत्तम मान 1 L/min., 1 wt. % Pt, 10 wt. % CeO_2 and 3 g/L पाए गए और इन मानों पर Pt/Al_2O_3 और ceria promoted Pt/Al_2O_3 उत्प्रेरक से 70^oC पर अधिकतम COD रिमूवल 45% और 61% पाए गया। परिचालन दबाव का प्रभाव CWAO के प्रदर्शन पर देखा गया है। उत्प्रेरक की स्थिरता को लंबे समय तक प्रयोग के लिए देखा गया है और दोनों उत्प्रेरक पूर्णतया स्थिर पाए गए तथा COD रिमूवल में तीसरे प्रयोग चक्र चलाने के बाद भी कोई कमी नहीं आई। CWAO प्रयोग परिणाम lumped kinetic model के साथ समझौते में थे। बायोडिग्रेडिब्लिटी और टॉक्सिसिटी टेस्ट CWAO effluent पर किया गया। CWAO effluent की टॉक्सिसिटी कम पाई गई और BOD/COD ratio काफी बढ़ गया। CWAO effluent बायोलोजिक्ल एरोबिक और अनऐरोबिक विधि से साफ किया गया तथा उसका परिणाम सांविधिक प्राधिकारी की डिस्चार्ज लिमिट के अंदर पाया गया।

कम लागत वाले उत्प्रेरक विकल्प जैसे metal oxide catalyst (MnO_x/Al_2O_3), noble metal Pt/Al_2O_3 के परिणाम की तुलना करने के लिए स्टडी किए गए। उत्प्रेरक इम्पप्रिग्नेशन तरीके से बनाए गए और विभिन्न तरीकों से characterize किए गए। CWAO परिचालन मानक जैसे manganese loading, catalyst dosages and reaction temperature ऑप्टिमाइज किए गए। परिचालन दबाव का प्रभाव CWAO के प्रदर्शन पर अनुसंधान किया गया। उत्प्रेरक की स्थिरता का टेस्ट CWAO प्रयोग को तीन बार एक ही उत्प्रेरक से करके उत्प्रेरक के पुनर्प्रयोग का पता लगाने के लिए किया गया। लिचिंग टेस्ट manganese का उसके उत्प्रेरक में से लिचिंग हो जाने का पता लगाने के लिए किया गया। ceria प्रमोटर का प्रभाव बायोडिग्रेडिब्लिटी के बढ़ने, उत्प्रेरक को दोबारा प्रयोग करने और मेटल लिचिंग की जांच के लिए देखा गया। बायोडिग्रेडिब्लिटी और टॉक्सिसिटी टेस्ट CWAO effluent के लिए किया गया। CWAO effluent का बायोडिग्रेडिब्लिटी मे बढ़ाव और टॉक्सिसिटी का समाप्त हो जाना ceria promoted MnO_x/Al_2O_3 से 70^oC पर मिला। Manganese उत्प्रेरक से 70^oC पर प्राप्त CWAO effluent का बायोलॉजिकल एरोबिक उपचार से 98.36% COD रिमूवल प्राप्त हुआ। इसलिए यह निष्कर्ष निकाला गया कि CWAO के साथ ceria प्रमोटेड manganese उत्प्रेरक और बायलॉजिकल उपचार का एकीकरण pyridine और उसके डेरिवेटिवस वाला औद्योगिक आर्गेनिक रेफिनेट के उपचार के लिए किया जा सकता है। ceria प्रमोटेड manganese उत्प्रेरक ने उत्प्रेरक प्रक्रिया, स्थिरता और औद्योगिक आर्गेनिक रेफिनेट की बायोडिग्रेडिब्लिटी को बढ़ाने में बहुत अच्छा परिणाम दिया है जो महंगी nobel metal जैसे Pt/Al_2O_3 उत्प्रेरक को बदल सकता है।

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ABBREVIATIONS

BOD – Biochemical oxygen demand (mg/L)

COD – Chemical oxygen demand (mg/L)

EDX – Electron dispersive X-ray spectroscopy

FTIR – Fourier infrared transform spectroscopy

GC-MS – Gas chromatography mass spectroscopy

HPLC – High pressure liquid chromatography

SEM – Scanning electron microscopy

TDS – Total dissolved solids (mg/L)

TOC – Total organic carbon (mg/L)

TSS – Total suspended solids (mg/L)

XRD – X-ray diffraction spectroscopy

NTU – Nephelometric turbidity unit

NOMENCLATURE

LST - Liquid space time

ST - Space time

LHSV - Liquid hourly space velocity

HRT - Hydraulic retention time;

SR - Batch or semi-batch operated stirred-tank reactor with slurry;

FBR - Continuously operated fixed-bed reactor;

PBR - Continuously operated packed bed reactor

TBR- Trickle bed reactor

TOS- Time on stream

CNF- Carbon nano fibers

CNT- Carbon nano tubes

OSC- Oxygen storage capacity