

**CATALYTIC WET AIR OXIDATION OF EFFLUENT
CONTAINING 2, 4, 6-TRICHLOROPHENOL USING CARBON
XEROGEL BASED MONO AND BIMETALLIC CATALYSTS**

MANJARI KUMARI



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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by

MANJARI KUMARI

DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

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CERTIFICATE

This is to certify that the thesis entitled, “**Catalytic wet air oxidation of effluent containing 2, 4, 6-trichlorophenol using carbon xerogel based mono and bimetallic catalysts**” being submitted by **Ms. Manjari Kumari** 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.

Date:

Place: New Delhi

Dr. Anil K. Saroha

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

New Delhi-110016

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(Manjari Kumari)

Abstract

Chlorophenols are a group of toxic, persistent and recalcitrant chemical compounds commonly found in the effluent of various industries such as pesticides, petrochemical, pulp and paper, dye, olive oil, pharmaceuticals, etc. Since the effluent containing chlorophenol is toxic in nature, it cannot be treated by conventional biological treatment methods. The advanced oxidation process such as wet air oxidation (WAO) is a promising technology for the treatment of effluent containing toxic organic compounds which either convert them into biodegradable intermediates or completely mineralize into carbon dioxide and water. Wet air oxidation involves oxidation of pollutant at elevated temperature and pressure conditions but oxidation in presence of suitable catalyst, catalytic wet air oxidation (CWAO), can be performed at mild conditions of temperature and pressure leading to a substantial reduction in capital and operating costs. The commonly used catalysts in CWAO process are noble and transition group metals supported on various forms of alumina, silica, carbon, etc.

In the present study, efforts have been made to treat an aqueous solution containing 2, 4, 6-trichlorophenol (TCP) by CWAO under mild conditions of temperature and pressure using carbon xerogel based monometallic and bimetallic catalysts. Carbon xerogel was used as the catalyst support material due to its unique properties like high mesoporosity, specific surface area, thermal stability, mechanical strength and high content of oxygenated functional groups on its surface.

Carbon xerogels are conventionally prepared using resorcinol and formaldehyde as precursors followed by solvent exchange to replace the water content in wet organic gel with a solvent. The solvent exchange is performed to maintain the structural properties of the wet organic gel during ambient drying. In the present study, carbon xerogels were synthesized by partially replacing the costly resorcinol with natural tannic acid to significantly reduce the cost of carbon xerogel. Four different solvents (acetone, t-butanol, ethanol and toluene) were used for solvent exchange. The surface properties of the carbon xerogel obtained after the solvent exchange with the four solvents were analyzed and t-butanol was found to be the suitable solvent for solvent exchange.

The carbon xerogel, obtained after solvent exchange using t-butanol and subsequent drying at ambient conditions, was modified using an acid to further enhance its surface and textural properties. The acid modification was performed using o-phosphoric acid, nitric acid and sulphuric acid and the modified carbon xerogels were characterized using various techniques and it was found that the carbon xerogel modified with o-

o-phosphoric acid (MCXO) exhibit highest specific surface area (683 m²/g), pore specific volume (1.61 cm³/g) and oxygen content (40.77 %) among the modified xerogels and thus selected for further use as catalyst support.

The textural properties of o-phosphoric modified carbon xerogel (MCXO) were found to be comparable to those of carbon xerogel prepared using resorcinol and formaldehyde as precursors followed by solvent exchange with t-butanol (specific surface area-614 m²/g and pore specific volume-1.43 cm³/g). The cost analysis of the synthesis of carbon xerogels was performed and a 25 % reduction in the cost of preparation of modified carbon xerogel was obtained by replacing two-third of resorcinol in the precursor with tannic acid without compromising the surface properties.

The monometallic (Fe/MCXO) and bimetallic (FeCu/MCXO and FeRu/MCXO) catalysts were prepared by sonication and co-impregnation methods respectively and characterized using various techniques such as BET, EDX, XRD, SEM, TEM, FTIR, CHNS and TGA analysis. The catalysts were used in the CWAQ of an aqueous solution containing 100 mg/L TCP and the results were interpreted in terms of TCP and COD removal efficiencies. The effect of various operating parameters such as metal loading, initial pH of TCP solution, air flow rate, catalyst dose, reaction temperature and operating pressure on TCP and COD removal efficiencies were studied.

The catalytic wet air oxidation of an aqueous solution containing TCP was performed using monometallic iron catalyst (Fe/MCXO) and the optimum values of iron loading, initial pH of TCP solution, air flow rate, catalyst dose and operating pressure were found to be 4 wt. %, 4, 3 L/min, 1.6 g/L and 1 bar respectively at the reaction temperature of 75 °C. The maximum TCP and COD removal efficiencies of 74.49 % and 24.31 % respectively were obtained using monometallic (Fe/MCXO) catalyst after 3 h of reaction at the optimum value of operating parameters. No significant enhancement in TCP and COD removal efficiencies were obtained with an increase in the reactor operating pressure from 1 bar to 8 bar. It was noticed that TCP removal obtained was satisfactory due to the conversion of TCP into reaction intermediates but COD of the aqueous solution was not considerably reduced as the intermediates were not completely mineralized into carbon dioxide and water.

Efforts were made to further enhance the TCP and COD removal efficiencies by using bimetallic (FeCu/MCXO and FeRu/MCXO) catalysts. The bimetallic catalysts were found to be more active than monometallic catalyst due to the synergistic effect of the two metals on the surface of modified carbon xerogel support. The iron-ruthenium catalyst (FeRu/MCXO) was found to be more active than iron-copper catalyst (FeCu/MCXO) and the maximum TCP and COD removal efficiencies of 95.82 % and 93.14 % respectively were obtained after 3 h of

reaction at the optimum value of operating parameters. The optimum value of metal loading, initial pH of TCP solution, air flow rate, catalyst dose and operating pressure for iron-ruthenium (FeRu/MCXO) catalyst were found to be 4 wt. % iron and 0.3 wt. % ruthenium, 4, 3 L/min, 0.8 g/L and 1 bar respectively at 75 °C.

The bimetallic iron-ruthenium catalyst (FeRu/MCXO) was found to be most stable with a marginal decrease (3.11 %) in its activity after third reuse of the spent catalyst after washing and thermal treatment after each cycle. The leaching of the active metals from the catalysts into the CWAO effluent was found to be within the prescribed effluent discharge limits. The degradation of TCP followed pseudo-first order kinetics with respect to TCP concentration in the aqueous solution and the values of apparent rate constants were found to be 0.008, 0.013 and 0.019 min⁻¹ for the degradation of TCP using Fe/MCXO, FeCu/MCXO and FeRu/MCXO catalysts respectively.

The bimetallic iron-ruthenium catalyst (FeRu/MCXO) was further used for the treatment of pharmaceutical industry effluent containing complex phenolic and chlorinated compounds, collected from a nearby pharmaceutical industry. The COD of the effluent was reduced to 65 mg/L after 5 h of reaction time from an initial COD of 612 mg/L. The toxicity of the effluent was measured before and after the CWAO reaction using *E. coli* as the test organism and the toxicity of the effluent was completely removed after 5 h of reaction.

सार

क्लोरोफेनॉल जहरीले, लगातार और पुनर्नवीनीकरण रासायनिक यौगिकों का एक समूह है जो आमतौर पर कीटनाशकों, पेट्रोकेमिकल, लुगदी और कागज, डाई, जैतून का तेल, फार्मास्यूटिकल्स इत्यादि जैसे विभिन्न उद्योगों के प्रदूषण में पाए जाते हैं। चूंकि क्लोरोफेनॉल युक्त प्रदूषण प्रकृति में जहरीला है, यह परंपरागत जैविक उपचार विधियों द्वारा इलाज नहीं किया जा सकता है। गीले वायु ऑक्सीकरण (CWAO) जैसे उन्नत ऑक्सीकरण प्रक्रिया जहरीले कार्बनिक यौगिकों वाले प्रदूषण के उपचार के लिए एक आशाजनक तकनीक है जो या तो उन्हें बायोडिग्रेडेबल इंटरमीडिएट्स में परिवर्तित करती है या कार्बन डाइऑक्साइड और पानी में पूरी तरह से खनिज हो जाती है। गीले वायु ऑक्सीकरण में उच्च तापमान और दबाव की स्थिति में प्रदूषक का ऑक्सीकरण शामिल है लेकिन उपयुक्त उत्प्रेरक, गीले वायु ऑक्सीकरण (CWAO) की उपस्थिति में ऑक्सीकरण, तापमान और दबाव की हल्की स्थितियों पर किया जा सकता है जिससे पूंजी और परिचालन लागत में काफी कमी आती है। CWAO प्रक्रिया में आमतौर पर प्रयुक्त उत्प्रेरक महान और संक्रमण समूह धातुएं एल्यूमिना, सिलिका, कार्बन इत्यादि के विभिन्न रूपों पर समर्थित हैं। वर्तमान अध्ययन में, कार्बन xerogel आधारित monometallic और bimetallic उत्प्रेरक का उपयोग तापमान और दबाव की हल्की स्थितियों के तहत CWAO द्वारा 2, 4, 6-ट्राइक्लोरोफेनॉल (TCP) युक्त जलीय घोल के इलाज के प्रयास किए गए हैं। कार्बन xerogel का उपयोग उत्प्रेरक समर्थन सामग्री के रूप में किया जाता था क्योंकि इसकी सतह पर उच्च मेसोपोरोसिटी, विशिष्ट सतह क्षेत्र, थर्मल स्थिरता, यांत्रिक शक्ति और ऑक्सीजनयुक्त कार्यात्मक समूहों की उच्च सामग्री जैसे अद्वितीय गुण होते हैं। कार्बन xerogels पारंपरिक रूप से resorcinol और फॉर्मल्डाहेहाइड का उपयोग कर पूर्ववर्ती के रूप में तैयार किया जाता है जिसके बाद विलायक के साथ गीले कार्बनिक जेल में पानी की सामग्री को प्रतिस्थापित

करने के लिए सॉल्वेंट एक्सचेंज होता है। परिवेश सूखने के दौरान गीले कार्बनिक जेल के संरचनात्मक गुणों को बनाए रखने के लिए विलायक विनिमय किया जाता है। वर्तमान अध्ययन में, कार्बन xerogels कार्बन xerogel की लागत को कम करने के लिए प्राकृतिक tannic acid के साथ महंगा resorcinol आंशिक रूप से प्रतिस्थापित करके संश्लेषित किया गया था। विलायक विनिमय के लिए चार अलग सॉल्वेंट्स (एसीटोन, टी-ब्यूटानोल, इथेनॉल और टोल्यून) का उपयोग किया जाता था। चार सॉल्वेंट्स के साथ सॉल्वेंट एक्सचेंज के बाद प्राप्त कार्बन xerogel की सतह गुणों का विश्लेषण किया गया था और टी-ब्यूटानोल विलायक विनिमय के

लिए उपयुक्त विलायक पाया गया था। कार्बन xerogel, टी-बटानोल का उपयोग कर विलायक विनिमय के बाद प्राप्त किया और परिवेश परिस्थितियों में बाद में सुखाने के बाद, इसकी सतह और textural गुणों को और बढ़ाने के लिए एक एसिड का उपयोग कर संशोधित किया गया था। एसिड संशोधन ओ-फॉस्फोरिक एसिड, नाइट्रिक एसिड और सल्फ्यूरिक एसिड का उपयोग करके किया गया था और संशोधित कार्बन xerogels विभिन्न तकनीकों का उपयोग करके विशेषता थी और यह पाया गया कि कार्बन xerogel के साथ संशोधित ओ-फॉस्फोरिक एसिड (MCXO) संशोधित xerogels के बीच उच्च विशिष्ट सतह क्षेत्र ($683 \text{ m}^2/\text{g}$), पोयर विशिष्ट मात्रा ($1.61 \text{ cm}^3/\text{g}$) और ऑक्सीजन सामग्री (40.77 %) प्रदर्शित करता है और इस प्रकार उत्प्रेरक समर्थन के रूप में आगे के उपयोग के लिए चुना जाता है। ओ-फॉस्फोरिक संशोधित कार्बन ज़ीरोगेल (MCXO) के पाठ्यचर्या गुणों को पुनर्विक्रय और फॉर्मल्डाहेहाइड का उपयोग करके कार्बन ज़ीरोगेल के लिए तुलनीय पाया गया था, जिसके बाद टी-ब्यूटानोल (विशिष्ट सतह क्षेत्र $-614 \text{ m}^2/\text{g}$ और पोयर विशिष्ट) के साथ विलायक विनिमय के बाद अग्रदूत मात्रा- $1.43 \text{ cm}^3/\text{g}$)। कार्बन xerogels के संश्लेषण की लागत विश्लेषण किया गया था और संशोधित कार्बन xerogel की तैयारी की लागत में 25% की कमी सतह गुणों के समझौता किए बिना टैनिन एसिड के साथ अग्रदूत में दो तिहाई resorcinol की जगह से प्राप्त किया गया था।

मोनोमेटेलिक (Fe/MCXO) और द्विपक्षीय (FeCu/MCXO और FeRu/MCXO) उत्प्रेरक क्रमशः sonication और सह-प्रजनन विधियों द्वारा तैयार किए गए थे और बीईटी, ईडीएक्स, एक्सआरडी, एसईएम, टीईएम, एफटीआईआर, सीएनएनएस और विभिन्न तकनीकों का उपयोग करके विशेषता है। टीजीए विश्लेषण। उत्प्रेरक का उपयोग एक जलीय घोल के सीडब्ल्यूओ में 100 mg/L टीसीपी युक्त होता था और परिणाम टीसीपी और सीओडी हटाने की क्षमता के संदर्भ में व्याख्या किए गए थे। धातु लोडिंग जैसे विभिन्न ऑपरेटिंग पैरामीटर, टीसीपी समाधान के प्रारंभिक पीएच, वायु प्रवाह दर, उत्प्रेरक खुराक, प्रतिक्रिया तापमान और टीसीपी और सीओडी हटाने की क्षमता पर परिचालन दबाव का प्रभाव अध्ययन किया गया।

टीसीपी युक्त जलीय घोल के उत्प्रेरक गीले वायु ऑक्सीकरण का उपयोग मोनोमेटेलिक लौह उत्प्रेरक (Fe/MCXO) और लोहा लोडिंग के इष्टतम मूल्यों, टीसीपी समाधान के प्रारंभिक pH, वायु प्रवाह दर, उत्प्रेरक खुराक और परिचालन दबाव का उपयोग करके किया गया था $4 \text{ wt. } \%$, $75 \text{ }^\circ\text{C}$ के प्रतिक्रिया तापमान पर क्रमशः, $4, 3 \text{ L/min}$, 1.6 g/L और 1 बार । ऑपरेटिंग पैरामीटर के इष्टतम मूल्य पर 3 h प्रतिक्रिया के बाद क्रमशः 74.49% और 24.31% की अधिकतम टीसीपी और सीओडी हटाने की क्षमता monometallic

(Fe/MCXO) उत्प्रेरक का उपयोग करके प्राप्त की गई थी। टीसीपी और सीओडी हटाने की क्षमता में कोई महत्वपूर्ण वृद्धि 1 बार से 8 बार तक रिएक्टर ऑपरेटिंग दबाव में वृद्धि के साथ प्राप्त की गई थी। यह देखा गया था कि टीसीपी हटाने को प्रतिक्रिया मध्यवर्ती में टीसीपी के रूपांतरण के कारण संतोषजनक था, लेकिन जलीय घोल का सीओडी काफी कम नहीं हुआ क्योंकि मध्यवर्ती कार्बन डाइऑक्साइड और पानी में पूरी तरह से खनिज नहीं थे।

द्विपक्षीय (FeCu/MCXO और FeRu/MCXO) उत्प्रेरक का उपयोग करके टीसीपी और सीओडी हटाने की क्षमता को आगे बढ़ाने के प्रयास किए गए थे। संशोधित कार्बन xerogel समर्थन की सतह पर दो धातुओं के सहक्रियात्मक प्रभाव के कारण द्विपक्षीय उत्प्रेरक monometallic उत्प्रेरक से अधिक सक्रिय पाए गए थे। लौह-रूटेनियम उत्प्रेरक (FeRu/MCXO) लोहा-तांबे उत्प्रेरक (FeCu/MCXO) से अधिक सक्रिय पाया गया था और क्रमशः 95.82 % और 93.14 % की अधिकतम टीसीपी और सीओडी हटाने की क्षमता 3 एच के बाद प्राप्त की गई थी।

ऑपरेटिंग पैरामीटर के इष्टतम मूल्य पर प्रतिक्रिया। धातु लोडिंग का इष्टतम मूल्य, टीसीपी समाधान के प्रारंभिक पीएच, वायु प्रवाह दर, उत्प्रेरक खुराक और लौह-रूटेनियम (FeRu/MCXO) उत्प्रेरक के लिए परिचालन दबाव पाया गया। 4 wt. % लौह और 0.3 wt. % ruthenium, 4, 3 L/min, 0.8 g/L और 1 बार क्रमशः 75 °C पर।

प्रत्येक चक्र के बाद धोने और थर्मल उपचार के बाद बिताए गए उत्प्रेरक के तीसरे पुनः उपयोग के बाद द्विपक्षीय लौह-रूटेनियम उत्प्रेरक (FeRu/MCXO) अपनी गतिविधि में मामूली कमी (3.11 %) के साथ सबसे स्थिर पाया गया था। उत्प्रेरक से सीडब्ल्यूओ प्रदूषण में सक्रिय धातुओं की लीचिंग निर्धारित प्रदूषण निर्वहन सीमा के भीतर पाया गया था। टीसीपी के अवक्रमण ने जलीय घोल में टीसीपी एकाग्रता के संबंध में छद्म-प्रथम आदेश गतिशीलता का पालन किया और स्पष्ट दर स्थिरांक के मूल्यों को Fe/MCXO, FeCu/MCXO, FeRu/MCXO टीसीपी के उपयोग से टीसीपी के क्षरण के लिए 0.008, 0.013 और 0.019/min पाया गया।

द्विपक्षीय लौह-रूटेनियम उत्प्रेरक (FeRu/MCXO) का उपयोग दवा उद्योग के प्रदूषण के उपचार के लिए किया जाता था जिसमें पास के फार्मास्युटिकल उद्योग से एकत्रित जटिल फेनोलिक और क्लोरिनेटेड यौगिक होते थे। 612 mg/L के शुरुआती सीओडी से प्रतिक्रिया समय के 5 घंटे के बाद प्रदूषण का सीओडी 65 mg/L

तक घटा दिया गया था। प्रदूषण की विषाक्तता ई। कोलाई का प्रयोग परीक्षण जीव के रूप में सीडब्ल्यूओ प्रतिक्रिया से पहले और उसके बाद मापा गया था और प्रदूषण की विषाक्तता 5 h प्रतिक्रिया के बाद पूरी तरह से हटा दी गई थी।

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ABBREVIATIONS

AC	Activated carbon
AOP	Advanced oxidation process
AOX	Adsorbable organic halogen
BET	Brunauer-Emmett-Teller
BJH	Barret, Joiner and Halenda
BOD	Biochemical oxygen demand (mg/L)
C2R	Chromotrope 2R
CD	Catalyst dose
CHNS	Carbon hydrogen nitrogen sulphur
CNF	Carbon nanofiber
CNT	Carbon nanotube
CO	Carbon monoxide
COD	Chemical oxygen demand (mg/L)
CP	Chlorophenol
CWAO	Catalytic wet air oxidation
CWPO	Catalytic wet peroxide oxidation
DMFC	Direct methanol fuel cell
DNP	Di-nitrophenol
DO	Dissolved oxygen
EDX	Electron dispersive X-ray spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
GCMS	Gas chromatography mass spectrometry
GHSV	Gas hourly space velocity

HR-TEM	High Resolution-Transmission Electron Microscope
INR	Indian rupee
NTU	Nephelometric turbidity unit
OABL	Oxidative ammonium bicarbonate leaching
PEM	Proton exchange membrane
PNP	p-Nitrophenol
pH _{pzc}	pH at point of zero charge
PMOs	Polyoxometalates
RSM	Response surface methodology
SCR	Selective catalytic reduction
SEM	Scanning electron microscopy
SMX	Sulfamethoxazole
SS	Stainless steel
TCP	2, 4, 6-Trichlorophenol
TDS	Total dissolved solids (mg/L)
TEM	Transmission electron microscopy
TGA	Thermo-gravimetric analysis
TNP	Tri-nitrophenol
TOC	Total organic carbon (mg/L)
TSS	Total suspended solids (mg/L)
UV-Vis	Ultraviolet-Visible
WAO	Wet air oxidation
XRD	X-ray diffraction

NOMENCLATURE

C_0	Initial 2, 4, 6-trichlorophenol concentration (mg/L)
C_t	Final (after treatment time 't') 2, 4, 6-trichlorophenol concentration (mg/L)
$(COD)_0$	Initial COD of 2, 4, 6-trichlorophenol solution (mg/L)
$(COD)_t$	Final (after treatment time 't') COD of 2, 4, 6-trichlorophenol solution (mg/L)
CX	Carbon xerogel (Tannic acid and resorcinol derived, solvent exchange with t-butanol)
CX_R	Carbon xerogel (Resorcinol derived, solvent exchange with t-butanol)
K'	Apparent rate constant (min^{-1})
MCX	Modified carbon xerogel
MCXN	Carbon xerogel modified using nitric acid
MCXO	Carbon xerogel modified using o-phosphoric acid
MCXS	Carbon xerogel modified using sulphuric acid
R	Correlation coefficient
t	Treatment time