

**CATALYTIC OZONATION OF DYE EFFLUENT
USING MONO AND BIMETALLIC CATALYSTS
SUPPORTED ON MESOPOROUS MATERIAL**

SANTOSH P. GHUGE



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

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SUPPORTED ON MESOPOROUS MATERIAL**

by

SANTOSH P. GHUGE

DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

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CERTIFICATE

This is to certify that the thesis entitled, “**Catalytic ozonation of dye effluent using mono and bimetallic catalysts supported on mesoporous material**” being submitted by **Mr. Santosh P. Ghuge** to the Indian Institute of Technology Delhi for the award of **Doctor of Philosophy** is a record of bonafide research work carried out by him 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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(Santosh P. Ghuge)

Abstract

Textile industry effluent contains different types of dyes which are chemically stable and non-biodegradable in nature. The effluent must be treated before discharging into the aqueous ecosystem as the untreated effluent may pose serious threat to aquatic life and constitute a potential human health hazard. Various conventional methods comprising of adsorption, coagulation, flocculation, membrane filtration and biological treatments are not fully capable for the treatment of textile industry effluent. Ozone based advanced oxidation processes (AOPs) are becoming more attractive for effluent treatment as ozone is an effective oxidant which can selectively oxidize unsaturated double bonds and aromatic structures of the organic compounds present in the effluent. Additionally, ozone gets decomposed into hydroxyl radicals having higher oxidation potential than ozone and can degrade all the kinds of refractory organic pollutants.

In the present study, catalytic ozonation using monometallic (Cu/SBA - 15 (Santa Barbara Amorphous -15) and Ru/SBA-15) and bimetallic (Ru-Cu/SBA-15) catalysts was employed to degrade organic pollutants from synthetic and textile industry effluent. Mesoporous material SBA-15 was used as a catalyst support due to its unique properties like large surface area, uniform pore structure, thick pore walls and high thermal stability. All the catalysts were prepared using incipient wetness impregnation method and characterized using BET, SEM, TEM and EDX techniques. The results of catalytic ozonation were interpreted in terms of colour, COD and TOC removal efficiencies.

The degradation of reactive orange 4 (RO4) azo dye in aqueous solution was studied using oxidation with hydrogen peroxide and hydrogen peroxide in presence of UV light. A colour removal efficiency of 17.5 % and 21.1 % and COD removal efficiency of 10.1 % and 14.5 % were obtained using H_2O_2 and UV/ H_2O_2 respectively. The degradation

of RO4 azo dye in aqueous solution was further studied using ozone based AOPs such as O_3 , O_3/UV , O_3/H_2O_2 , $O_3/UV/H_2O_2$ and catalytic ozonation using 2 % Cu/SBA-15 catalyst. The colour removal efficiency of 100 % was achieved for all ozone based AOPs after 21 min. The maximum COD removal efficiency of 49 % was obtained after 60 min of catalytic ozonation.

The catalytic ozonation experiments using 2 % Cu/SBA-15 catalyst were performed for the degradation of RO4 azo dye solution. The effect of the parameters such as initial solution pH, metal loading in the catalyst and ozone dose on the efficiency of the catalytic ozonation was studied. A colour removal efficiency of 100 % was achieved after 21 min of ozonation. The maximum TOC and COD removal efficiencies of 86 % and 52.5 % were obtained after 60 min of catalytic ozonation, respectively, at optimum conditions of initial solution pH 9, metal loading of 2 wt. % and ozone dose of 5 g/m^3 .

The degradation pathway for the catalytic ozonation reaction was studied by adding radical scavenger t-butanol into the reaction. It was found that the colour removal of RO4 azo dye solution was governed by direct ozone molecular mechanism whereas TOC removal occurred by hydroxyl radical mechanism.

The catalytic ozonation reaction followed pseudo first-order kinetics with respect to RO4 azo dye concentration in the aqueous solution. The reusability of the 2 % Cu/SBA-15 catalyst was studied and no significant reduction in colour and TOC removal efficiencies was noticed after five runs of experiments suggesting negligible loss in activity of Cu/SBA-15 catalyst. The leaching test confirmed the stability of the catalyst as the concentration of leached copper in the aqueous solution was found to be within the discharge limits prescribed by statutory authorities.

Efforts were made to obtain higher COD removal efficiency for RO4 azo dye solution by performing catalytic ozonation using noble metal ruthenium (Ru/SBA-15) and bimetallic ruthenium-copper (Ru-Cu/SBA-15) catalysts. The maximum COD removal efficiency of 61.1 % and 70.4 % were obtained after 60 min of ozonation for monometallic Ru/SBA-15 and bimetallic Ru-Cu/SBA-15 catalysts, respectively, at optimum conditions of initial solution pH 9 and ozone dose of 5 g/m³.

The bimetallic catalyst Ru-Cu/SBA-15 was used for the treatment of textile industry effluent collected from a nearby dyeing industry. The effluent was characterized for various parameters such as COD, salinity, total dissolved solids and alkalinity in terms of bicarbonate and carbonate ions. A COD removal efficiency of 30.2 % was obtained after 5 h of catalytic ozonation. The low COD removal efficiency may be due to the presence of bicarbonate ions in the effluent which act as radical scavengers, thereby, reducing the availability of hydroxyl radicals generated during catalytic ozonation reaction. The bicarbonate ion concentration was reduced by lowering the effluent pH by acidification and stripping off the carbon dioxide formed during acidification. The catalytic ozonation experiment using Ru-Cu/SBA-15 bimetallic catalyst at the effluent pH 7.5 (after removal of bicarbonate ions and addition of sodium hydroxide to increase the pH) resulted in COD removal efficiency of 90 % after 4 h of ozonation.

It can be concluded from the present study that the catalytic ozonation has the potential to be employed for the degradation of organic pollutants present in the textile industry effluent.

सार

वस्त्र उद्योग प्रवाह रंजक जो रासायनिक स्थिर है और प्रकृति में गैर बायोडिग्रेडेबल हैं के विभिन्न प्रकार के होते हैं। प्रवाह अनुपचारित प्रवाह के रूप में जलीय पारिस्थितिकी तंत्र में निर्वहन जलीय जीवन के लिए गंभीर खतरा पैदा कर और एक संभावित मानव स्वास्थ्य के लिए खतरा का गठन कर सकते से पहले इलाज किया जाना चाहिए। विभिन्न पारंपरिक सोखना, जमावट, flocculation, झिल्ली निस्पंदन और जैविक उपचार के शामिल तरीकों वस्त्र उद्योग प्रवाह के इलाज के लिए पूरी तरह से सक्षम नहीं हैं। ओजोन आधारित उन्नत ऑक्सीकरण प्रक्रियाओं (AOPs) प्रवाह के इलाज के लिए और अधिक आकर्षक होते जा रहे हैं ओजोन के रूप में एक प्रभावी ऑक्सीडेंट है जो चुनिंदा असंतृप्त डबल बांड और प्रवाह में मौजूद कार्बनिक यौगिकों के खुशबूदार संरचनाओं का ऑक्सीकरण कर सकते हैं। साथ ही, ओजोन ओजोन की तुलना में अधिक ऑक्सीकरण संभावित होने हाइड्रॉक्सिल कण में विघटित हो जाता है और दुः साध्य जैविक प्रदूषकों के सभी प्रकार से नीचा कर सकते हैं। वर्तमान अध्ययन, उत्प्रेरक Ozonation का उपयोग कर monometallic (Cu / एसबीए -15 और आरयू / एसबीए -15) और द्विधात्विक में (आरयू-Cu / एसबीए -15) उत्प्रेरक सिंथेटिक और वस्त्र उद्योग प्रवाह से जैविक प्रदूषकों नीचा करने के लिए नियोजित किया गया था। Mesoporous सामग्री एसबीए -15 बड़ा सतह क्षेत्र, वर्दी संरचना, मोटी ध्यान में लीन होना दीवारों और उच्च थर्मल स्थिरता की तरह अपनी अनूठी गुणों के कारण एक उत्प्रेरक के समर्थन के रूप में इस्तेमाल किया गया था। सभी उत्प्रेरक प्रारंभिक नमी संसेचन विधि का उपयोग कर तैयार किया और बेट, SEM, TEM और EDX तकनीक का उपयोग विशेषता थी। उत्प्रेरक Ozonation के परिणामों रंग, सीओडी के मामले और टीओसी हटाने क्षमता में व्याख्या की गई। जलीय घोल में RO4 azo डाई की गिरावट हाइड्रोजन पेरोक्साइड और यूवी प्रकाश की उपस्थिति में हाइड्रोजन पेरोक्साइड के साथ ऑक्सीकरण का उपयोग कर अध्ययन किया गया। 17.5% और 21.1% और 10.1% की सीओडी को हटाने दक्षता और 14.5% की एक रंग को हटाने दक्षता क्रमशः H₂O₂ और यूवी / H₂O₂ का उपयोग कर प्राप्त कर रहे थे। जलीय घोल में RO4 azo डाई की गिरावट आगे इस तरह ओ 3, ओ 3 / यूवी, ओ 3 / H₂O₂, ओ 3 / यूवी / H₂O₂ और उत्प्रेरक Ozonation 2% Cu / एसबीए -15 उत्प्रेरक का उपयोग के रूप में ओजोन आधारित AOPs का उपयोग कर अध्ययन किया गया। 100% का रंग हटाने दक्षता 21 मिनट के बाद सभी ओजोन आधारित AOPs के लिए हासिल की थी। 49% की अधिकतम सीओडी को हटाने दक्षता उत्प्रेरक Ozonation के 60 मिनट के बाद प्राप्त हुई थी। उत्प्रेरक Ozonation 2% Cu / एसबीए -15 उत्प्रेरक का उपयोग प्रयोगों RO4 azo डाई समाधान की गिरावट के लिए प्रदर्शन किया गया। इस तरह के प्रारंभिक समाधान पीएच के रूप में मानकों का असर, उत्प्रेरक Ozonation की क्षमता पर उत्प्रेरक और ओजोन खुराक में धातु लोड हो रहा है अध्ययन किया गया। 100% का एक रंग को हटाने दक्षता Ozonation के 21 मिनट के बाद हासिल हुई। 86% और 52.5% की अधिकतम टीओसी और सीओडी को हटाने क्षमता, उत्प्रेरक Ozonation क्रमशः 60 मिनट के बाद प्राप्त किया गया प्रारंभिक समाधान पीएच 9, 2 wt की धातु लोडिंग के इष्टतम स्थितियों में। % और ओजोन 5 ग्राम / एम 3 की खुराक। उत्प्रेरक Ozonation प्रतिक्रिया के लिए गिरावट मार्ग प्रतिक्रिया में कट्टरपंथी मेहतर टी butanol

जोड़कर अध्ययन किया गया। यह पाया गया कि RO4 azo डाई समाधान के रंग को हटाने प्रत्यक्ष ओजोन आणविक तंत्र का शासन था जबकि टीओसी हटाने हाइड्रॉक्सिल कट्टरपंथी तंत्र द्वारा हुई। उत्प्रेरक Ozonation प्रतिक्रिया जलीय घोल में RO4 azo डाई एकाग्रता के संबंध में छद्म प्रथम क्रम गतिकी का पालन किया। 2% Cu / SBA- 15 उत्प्रेरक का पुनर्प्रयोग अध्ययन किया गया था और रंग और टीओसी हटाने क्षमता में कोई उल्लेखनीय कमी Cu / एसबीए -15 उत्प्रेरक की गतिविधि में नगण्य नुकसान का सुझाव दे प्रयोगों के पांच रन के बाद देखा गया था। लीचिंग परीक्षण उत्प्रेरक की स्थिरता की पुष्टि के रूप में जलीय घोल में leached तांबे की एकाग्रता सांविधिक प्राधिकारियों द्वारा निर्धारित मुक्ति की सीमा के भीतर हो पाया था। प्रयास महान धातु रूथेनियम (आरयू / एसबीए -15) और द्विधात्विक रूथेनियम तांबे (आरयू-Cu / एसबीए -15) उत्प्रेरक का उपयोग कर उत्प्रेरक Ozonation प्रदर्शन से RO4 azo डाई समाधान के लिए उच्च सीओडी को हटाने दक्षता प्राप्त करने के लिए किए गए थे। 61.1% और 70.4% की अधिकतम सीओडी को हटाने दक्षता, monometallic आरयू / एसबीए -15 और द्विधात्विक आरयू-Cu / एसबीए -15 उत्प्रेरक, के लिए Ozonation के 60 मिनट के बाद प्राप्त किया गया की प्रारंभिक समाधान पीएच 9 और ओजोन खुराक का इष्टतम स्थितियों में क्रमशः 5 ग्राम / एम 3। द्विधात्विक उत्प्रेरक आरयू-Cu / एसबीए -15 वस्त्र उद्योग प्रवाह के इलाज के लिए पास के रंगाई उद्योग से एकत्र के लिए इस्तेमाल किया गया था। प्रवाह इस तरह के सीओडी, लवणता, कुल भंग ठोस और बाइकार्बोनेट और कार्बोनेट आयनों के मामले में क्षारीयता के रूप में विभिन्न मापदंडों के लिए विशेषता थी। 30.2% की एक सीओडी को हटाने दक्षता उत्प्रेरक Ozonation के 5 घंटे के बाद प्राप्त हुई थी। कम सीओडी को हटाने दक्षता प्रवाह में बाइकार्बोनेट आयनों की उपस्थिति जो कट्टरपंथी मुर्दाखोर के रूप में कार्य है, जिससे, को कम करने हाइड्रॉक्सिल कण की उपलब्धता उत्प्रेरक Ozonation प्रतिक्रिया के दौरान उत्पन्न होने के कारण हो सकता है। बाइकार्बोनेट आयन एकाग्रता अम्लीकरण द्वारा प्रवाह पीएच कम करने और अम्लीकरण के दौरान गठन कार्बन डाइऑक्साइड बंद अलग करना द्वारा कम हो गया था। उत्प्रेरक Ozonation प्रवाह पीएच 7.5 (बाइकार्बोनेट आयनों और सोडियम हाइड्रोक्साइड पीएच को बढ़ाने के लिए के अलावा को हटाने के बाद) में आरयू-Cu / एसबीए -15 द्विधात्विक उत्प्रेरक का उपयोग प्रयोग Ozonation के 4 घंटे के बाद 90% की सीओडी को हटाने दक्षता में हुई। यह वर्तमान अध्ययन है कि उत्प्रेरक Ozonation संभावित वस्त्र उद्योग प्रवाह में मौजूद जैविक प्रदूषकों की गिरावट के लिए नियोजित किया जाना है से यह निष्कर्ष निकाला जा सकता है।

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(RO4) azo dye using Cu/SBA-15 catalyst

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ABBREVIATIONS

AOP	Advanced oxidation process
BET	Brunauer-Emmett-Teller
BJH	Barret, Joiner and Halenda
BOD	Biochemical oxygen demand (mg/l)
COD	Chemical oxygen demand (mg/l)
CRE	Colour removal efficiency (%)
CWAO	Catalytic wet air oxidation
EDX	Electron dispersive X-ray spectroscopy
NTU	Nephelometric turbidity unit
pH _{PZC}	pH at point of zero charge
P123	Poly (ethylene glycol)-block-Poly (propylene glycol)-block- Poly (ethylene glycol)
RO4	Reactive orange 4
SBA-15	Santa Barbara Amorphous-15
SEM	Scanning electron microscopy
TDS	Total dissolved solids (mg/l)
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TOC	Total organic carbon (mg/l)
UV	Ultraviolet
WAO	Wet air oxidation

NOMENCLATURE

C_0	Initial RO4 azo dye concentration (mg/l)
C_t	Final (after treatment time 't') RO4 azo dye concentration (mg/l)
$(COD)_I$	Initial COD of effluent (mg/l)
$(COD)_t$	Final (after treatment time 't') COD of effluent (mg/l)
EE/O	Electric energy consumed for pollutant removal (kW h m ⁻³ order ⁻¹)
K	Apparent rate constant (min ⁻¹)
pKa	Dissociation constant
R	Correlation coefficient
t	Treatment time
$(TOC)_i$	Initial TOC of effluent (mg/l)
$(TOC)_t$	Final (after treatment time 't') TOC of effluent (mg/l)
V	volume of effluent in the reactor (l)