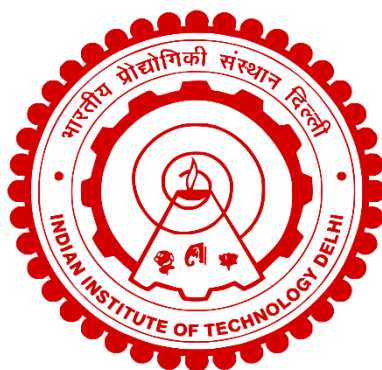


BIPYRIDINE BASED POROUS COORDINATION POLYMERS FOR ENVIROMENTAL REMEDIATION

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February 2024

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By

SHIVANI GOYAL

Department of Materials Science and Engineering

Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy
to the



Indian Institute of Technology Delhi

February 2024

Dedicated to

My Parents

In-Laws

&

Devansh

CERTIFICATE

This is to certify that the thesis entitled “**Bipyridine based porous coordination polymers for environmental remediation**” being submitted by **Ms. Shivani Goyal** to the Indian Institute of Technology Delhi, New Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Ms. Shivani Goyal** has worked under my guidance and supervision and has fulfilled the requirements for the submission of her thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any other degree or diploma.

Prof. Josemon Jacob

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(Shivani Goyal)

ABSTRACT

Extensive research has been conducted on bipyridine-based ligands for their ability to effectively bind to metals, thanks to their strong resistance to oxidation and ability to be modified easily. The compound 2,2'-bipyridine is a neutral, bidentate-donor ligand that can form coordination complexes with metal ions by contributing two pairs of electrons. It is a colourless solid, soluble in organic solvents but insoluble in aqueous media. This property has led to its widespread use in inorganic chemistry, particularly as a catalyst, where many transition metal complexes have extensively been designed for several chemical reactions, such as oxidation, reduction, and cross-coupling reactions. Its unique electronic and steric properties also make it a useful building block for synthesizing novel materials, such as chelating polymers, metal-organic frameworks, hydrogels and organogels. It has a wide range of applications in various fields, including chemistry, biology, and materials science. For environmental remediation, 2,2'-bipyridine-derived polymers open new possibilities for separation science applications. Several bipyridine-derived chelating polymers have been developed to selectively remove heavy metals from contaminated water sources by forming stable metal complexes.

2,2'-Bipyridine-based porous coordination polymers (PCPs) have also been investigated for their potential use in catalysis. These catalysts have shown high activity and selectivity to adsorb or degrade various pollutants, making them attractive alternatives to traditional homogeneous catalysts. In this context, 2,2'-bipyridine-based novel chelating polymers and PCPs have been developed to remove contaminants such as metal ions, organic dyes and antibiotics from aqueous solutions.

In the first section, a new chelating monomer N-([2,2'-bipyridine]-4-yl) methacrylamide (BpyMA) was synthesized from precursor 4-amino-2,2'-bipyridine by reacting it with methacryloyl chloride in the presence of triethylamine as a base, in order to introduce the polymerizable group. Several optimizations were done to synthesize its corresponding polymer, poly-N-([2,2'-bipyridine]-4-yl)methacrylamide (PBpyMA), using the free radical polymerization technique. The highest molecular weight was achieved at $M_w \sim 43.9 \text{ kg mol}^{-1}$ at 65 °C for 24 h using the free radical initiator AIBN (0.25 mol%). Thermal analysis was done to analyze the stability of the polymer (PBpyMA), and it was found to be stable up to 285 °C. FESEM studies revealed porous three-dimensional crosslinked network structure formation due to metal-polymer complexation with 80-120 nm pore size. UV-vis spectroscopy was used to establish the stoichiometry between polymer and metal ions. PBpyMA was further tested for its potential application as an adsorbent in removing metal ions from organic solvents. The polymer was found to work well in commonly used solvents such as THF, DMSO, and DMF. A simple and straightforward procedure was used to remove Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} metal ions and established from UV-vis and ICP-MS studies. Metal ion extraction reached its peak within one hour at room temperature in THF solvent, as indicated by kinetic studies. Exceptionally high metal uptake was achieved for Zn^{2+} and Cd^{2+} , respectively, by using UV-vis and ICP-MS techniques. Our findings indicated that bipyridine-based polymers are potential candidates for removing heavy metal ion contamination often seen in organic synthesis.

In the second section, two novel porous coordination polymers (PCPs) were synthesized to contribute to one of the most critical sustainable development goals of ensuring the availability of clean water. Two novel linkers, DBTA and TBTA, having two and three bipyridine units, were synthesized by reacting precursors 4-amino-2,2'-bipyridine with terephthaloyl dichloride and 1,3,5-benzene tricarboxyl trichloride, respectively in the presence of triethylamine as a

base. The solvothermal reaction generated PCPs using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a metal source. Under optimal reaction conditions, these novel PCPs were found to have a macroporous morphology with the highest surface area for Co-DBTA-5 ($296.5 \text{ m}^2 \text{ g}^{-1}$) and Co-TBTA-7 ($441.1 \text{ m}^2 \text{ g}^{-1}$). The PXRD diffractogram data validated the successful synthesis of Co-PCPs. Also, the results from the TGA analysis showed high thermal stability for PCPs. The catalytic activity of Co-PCPs to degrade various dyes from water, including cationic (MB and RhB) and anionic dyes (MO and OII), was investigated using a very straightforward approach. It was found that anionic dyes were selectively degraded with up to $\sim 99 \%$ efficiency within an hour. Co-DBTA-5 demonstrated maximal degradation efficiency for MO ($\sim 98 \%$) and OII (94.8%) in 50 and 36 min at 25°C , respectively. GC-MS analysis further confirmed the reduction of MO into small molecules, all of which could be structurally identified. Studies on regeneration and reusability reveal that the PCPs can be utilized repeatedly for up to 5 cycles with no change in degrading efficiency. The simplicity of the proposed technique suggests that Co-PCPs could be used as a catalyst in water purification applications.

In the subsequent section, macroporous bimetallic PCPs were designed to test their potential application as a photocatalyst to degrade AMX from aqueous solution. DBTA was used as an organic linker to synthesize a series of PCPs by varying $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ molar ratios. These PCPs were labelled as PCP-2 (Co: Cu-(80:20), PCP-3 (Co: Cu (67:33), PCP-4 (Co: Cu (50:50), PCP-5 (Co: Cu (33:67), and PCP-6 (Co: Cu (20:80), respectively. Two single-metal PCPs, PCP-1 (Co-DBTA) and PCP-7 (Cu-DBTA) were prepared by adding Co^{3+} or Cu^{2+} metal ions under the same reaction conditions. The surface areas of the PCPs were determined using the BET technique. The highest surface area was achieved, up to $970.70 \text{ m}^2 \text{ g}^{-1}$ for PCP-4 containing a 1:1 ratio of Co^{3+} : Cu^{2+} metal ions. From thermal analysis, a variable degradation pattern was observed by changing the molar ratio of metal ions. For the photocatalytic degradation of AMX, PCP-4 showed the highest degradation efficiency within

70 min at room temperature. The GC-MS analysis confirms the breakdown of the antibiotic into smaller and less harmful molecules. Additionally, the ability of the PCPs to be regenerated and reused for multiple cycles with minimal loss in degradation efficiency highlights their practicality and cost-effectiveness.

सार

बाइपिरिडीन-आधारित लिगेण्ड्स का उनकी मजबूत रेडॉक्स स्थिरता और क्रियाशीलता में आसानी के कारण धातु-चेलेटिंग लिगेण्ड्स के रूप में बड़े पैमाने पर अध्ययन किया गया है। 2,2'-बिपिरिडीन एक बाइडेंटेट, तटस्थ लिगेण्ड है जो दो इलेक्ट्रॉन जोड़े दान करके धातु आयनों के साथ स्थिर समन्वय परिसरों का निर्माण करता है। यह एक रंगहीन ठोस है, जो कार्बनिक विलायकों में घुलनशील है लेकिन जलीय मीडिया में अघुलनशील है। इस गुण के कारण अकार्बनिक रसायन विज्ञान में इसका व्यापक उपयोग हुआ है, विशेष रूप से एक उत्प्रेरक के रूप में, जहां कई संक्रमण धातु परिसरों को बड़े पैमाने पर कई रासायनिक प्रतिक्रियाओं, जैसे ऑक्सीकरण, कमी और क्रॉस-युग्मन प्रतिक्रियाओं के लिए डिज़ाइन किया गया है। इसके अद्वितीय इलेक्ट्रॉनिक और स्टेरिक गुण इसे नवीन सामग्रियों, जैसे कि चेलेटिंग पॉलिमर, धातु-कार्बनिक ढांचे, हाइड्रोजेल और ऑर्गेनोजेल को संश्लेषित करने के लिए एक उपयोगी बिल्डिंग ब्लॉक बनाते हैं। रसायन विज्ञान, जीव विज्ञान और सामग्री विज्ञान सहित विभिन्न क्षेत्रों में इसके अनुप्रयोगों की एक विस्तृत श्रृंखला है। पर्यावरणीय सुधार के लिए, 2,2'-बाइपिरिडीन-व्युत्पन्न पॉलिमर पृथक्करण विज्ञान अनुप्रयोगों के लिए नई संभावनाएं खोलते हैं। स्थिर धातु परिसरों का निर्माण करके दूषित जल स्रोतों से भारी धातुओं को चुनिंदा रूप से हटाने के लिए कई बाइपिरिडीन-व्युत्पन्न चेलेटिंग पॉलिमर विकसित किए गए हैं।

उत्प्रेरक में उनके संभावित उपयोग के लिए 2,2'-बिपिरिडीन-आधारित छिद्रपूर्ण समन्वय पॉलिमर (पीसीपी) की भी जांच की गई है। इन उत्प्रेरकों ने विभिन्न प्रदूषकों को सोखने या विघटित करने के लिए उच्च गतिविधि और चयनात्मकता दिखाई है, जिससे वे पारंपरिक सजातीय उत्प्रेरकों के लिए आकर्षक विकल्प बन गए हैं। इस संदर्भ में, जलीय घोलों से धातु आयनों, कार्बनिक रंगों और एंटीबायोटिक्स जैसे दूषित पदार्थों को हटाने के लिए 2,2'-बाइपिरिडीन-आधारित उपन्यास चेलेटिंग पॉलिमर और पीसीपी विकसित किए गए हैं।

पहले खंड में, एक नया चलेटिंग मोनोमर एन-([2,2'-बाइपिरिडीन]-4-वाईएल) मेथैक्रिलामाइड (बीपीईएमए) को मेथैक्रोलाइल क्लोराइड के साथ प्रतिक्रिया करके पूर्ववर्ती 4-अमीनो-2,2'-बाइपिरिडीन से संश्लेषित किया गया था। पॉलिमराइजेबल समूह को पेश करने के लिए, आधार के रूप में ट्राइथाइलमाइन की उपस्थिति। मुक्त रेडिकल पोलिमराइजेशन तकनीक का उपयोग करके इसके संबंधित पॉलिमर, पॉली-एन-([2,2'-बाइपिरिडीन]-4-वाईएल)मेथैक्रिलामाइड (पीबीपाइएमए) को संश्लेषित करने के लिए कई अनुकूलन किए गए थे। मुक्त रेडिकल सर्जक AIBN (0.25 mol %) का उपयोग करके 24 घंटे के लिए 65 °C पर $M_w \sim 43.9 \text{ kg mol}^{-1}$ पर उच्चतम आणविक भार प्राप्त किया गया था। पॉलिमर (पीबीपाइएमए) की स्थिरता का विश्लेषण करने के लिए थर्मल विश्लेषण किया गया था, और यह 285 डिग्री सेल्सियस तक स्थिर पाया गया था। एफईएसईएम अध्ययनों से पता चला कि 80-120 एनएम छिद्र आकार के साथ धातु-बहुलक जटिलता के कारण छिद्रपूर्ण त्रि-आयामी क्रॉसलिंकड नेटवर्क संरचना का निर्माण हुआ। पॉलिमर और धातु आयनों के बीच स्टोइकोमेट्री स्थापित करने के लिए यूवी-विज़ स्पेक्ट्रोस्कोपी का उपयोग किया गया था। कार्बनिक सॉल्वेंट्स से धातु आयनों को हटाने में एक अधिशोषक के रूप में इसके संभावित अनुप्रयोग के लिए PBpyMA का और परीक्षण किया गया। यह पाया गया कि पॉलिमर आमतौर पर इस्तेमाल होने वाले सॉल्वेंट्स जैसे टीएचएफ, डीएमएसओ और डीएमएफ में अच्छा काम करता है। Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} और Cd^{2+} धातु आयनों को हटाने के लिए एक सरल और सीधी प्रक्रिया का उपयोग किया गया और यूवी-विज़ और आईसीपी-एमएस अध्ययनों से स्थापित किया गया। काइनेटिक अध्ययनों से पता चला कि धातु आयनों का अधिकतम निष्कर्षण टीएचएफ विलायक में कमरे के तापमान पर एक घंटे के भीतर हासिल किया गया था। यूवी-विज़ और आईसीपी-एमएस तकनीकों का उपयोग करके, क्रमशः Zn^{2+} और Cd^{2+} के लिए असाधारण रूप से उच्च धातु ग्रहण प्राप्त किया गया था। हमारे निष्कर्षों से संकेत मिलता है कि बाइपिरिडीन-आधारित पॉलिमर कार्बनिक संश्लेषण में अक्सर देखे जाने वाले भारी धातु आयन संदूषण को हटाने के लिए संभावित उम्मीदवार हैं।

दूसरे खंड में, स्वच्छ पानी की उपलब्धता सुनिश्चित करने के सबसे महत्वपूर्ण सतत विकास लक्ष्यों में से एक में योगदान करने के लिए दो नवीन छिद्रपूर्ण समन्वय पॉलिमर (पीसीपी) को संश्लेषित किया गया था। दो नए लिंक्स, डीबीटीए और टीबीटीए, जिनमें दो और तीन बाइपिरिडीन इकाइयां हैं, को ट्राइथाइलमाइन की उपस्थिति में क्रमशः टेरफ्थालोयल डाइक्लोराइड और 1,3,5-बेंजीन ट्राइकार्बोनिल ट्राइक्लोराइड के साथ पूर्ववर्तियों 4-अमीनो-2,2'-बाइपिरिडीन पर प्रतिक्रिया करके संश्लेषित किया गया था। सॉल्वोथर्मल प्रतिक्रिया ने धातु स्रोत के रूप में $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ का उपयोग करके पीसीपी उत्पन्न किया। इष्टतम प्रतिक्रिया स्थितियों के तहत, इन नवीन पीसीपी में Co-DBTA-5 ($296.5 \text{ m}^2 \text{ g}^{-1}$) और Co-TBTA-7 ($441.1 \text{ m}^2 \text{ g}^{-1}$) के लिए उच्चतम सतह क्षेत्र के साथ एक मैक्रोपोरस आकृति विज्ञान पाया गया। पीएक्सआरडी डिफ्रेक्टोग्राम डेटा ने सह-पीसीपी के सफल संश्लेषण को मान्य किया। इसके अलावा, टीजीए विश्लेषण के परिणामों ने पीसीपी के लिए उच्च तापीय स्थिरता दिखाई। इसके अलावा, टीजीए विश्लेषण के परिणामों ने पीसीपी के लिए उच्च तापीय स्थिरता दिखाई। धनायनित (एमबी और आरएचबी) और आयनिक रंगों (एमओ और ओआईआई) सहित पानी से विभिन्न रंगों को विघटित करने के लिए सह-पीसीपी की उत्प्रेरक गतिविधि की जांच एक बहुत ही सरल दृष्टिकोण का उपयोग करके की गई थी। यह पाया गया कि आयनिक रंगों को एक घंटे के भीतर ~99 % दक्षता के साथ चुनिंदा रूप से विघटित किया गया। सह-डीबीटीए-5 ने क्रमशः 25 डिग्री सेल्सियस पर 50 और 36 मिनट में एमओ (~98 %) और ओआईआई (94.8 %) के लिए अधिकतम गिरावट दक्षता का प्रदर्शन किया। जीसी-एमएस विश्लेषण ने एमओ के छोटे अणुओं में कमी की पुष्टि की, जिनमें से सभी को संरचनात्मक रूप से पहचाना जा सकता है। पुनर्जनन और पुनः प्रयोज्यता पर अध्ययन से पता चलता है कि पीसीपी को 5 चक्रों तक बार-बार उपयोग किया जा सकता है, जिससे दक्षता में कोई बदलाव नहीं होता है। प्रस्तावित तकनीक की सरलता से पता चलता है कि सह-पीसीपी का उपयोग जल शोधन अनुप्रयोगों में उत्प्रेरक के रूप में किया जा सकता है।

अगले अनुभाग में, मैक्रोपोरस बाईमेटेलिक पीसीपी को जलीय घोल से एएमएक्स को नीचा दिखाने के लिए एक फोटोकैटलिस्ट के रूप में उनके संभावित अनुप्रयोग का परीक्षण करने के लिए डिज़ाइन किया गया था। DBTA का उपयोग $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ और $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ मोलर अनुपात को अलग करके पीसीपी की एक श्रृंखला को संश्लेषित करने के लिए एक कार्बनिक लिंकर के रूप में किया गया था। इन पीसीपी को पीसीपी -2 (Co: Cu (80:20), पीसीपी - 3 (Co: Cu (67:33), पीसीपी -4 (Co: Cu (50:50), पीसीपी -5 (Co) के रूप में लेबल किया गया था। : Cu (33:67), और पीसीपी -6 (Co: Cu (20:80), क्रमशः। दो एकल-धातु पीसीपीस, पीसीपी -1 (Co-DBTA) और पीसीपी -7 (Cu-DBTA) द्वारा तैयार किए गए थे। समान प्रतिक्रिया स्थितियों के तहत Co^{3+} या Cu^{2+} धातु आयनों को जोड़ना। पीसीपीस के सतह क्षेत्रों को BET तकनीक का उपयोग करके निर्धारित किया गया था। पीसीपी -4 के लिए $970.70 \text{ m}^2 \text{ g}^{-1}$ तक उच्चतम सतह क्षेत्र प्राप्त किया गया था, जिसमें 1:1 का अनुपात था। $\text{Co}^{3+} : \text{Cu}^{2+}$ धातु आयन। थर्मल विश्लेषण से, धातु आयनों के दाढ़ अनुपात को बदलकर एक परिवर्तनशील गिरावट पैटर्न देखा गया। एएमएक्स के फोटोकैटलिटिक क्षरण के लिए, पीसीपी-4 ने कमरे के तापमान पर 70 मिनट के भीतर उच्चतम क्षरण दक्षता दिखाई। जीसी-एमएस विश्लेषण एंटीबायोटिक के छोटे और कम हानिकारक अणुओं में टूटने की पुष्टि करता है। इसके अतिरिक्त, पीसीपी को पुनः उत्पन्न करने और क्षरण दक्षता में न्यूनतम हानि के साथ कई चक्रों के लिए पुनः उपयोग करने की क्षमता उनकी व्यावहारिकता को उजागर करती है।

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LIST OF ABBREVIATIONS

CPs	Coordination polymers
MOCNs	Metal-organic coordination networks
MOF	Metal organic framework
PCPs	Porous coordination polymers
Bpy	Bipyridine
Pyz	Pyrazine
Phen	1,10-phenanthroline
Tpy	2,2':6',2''-terpyridine
DCC	N,N'-Dicyclohexylcarbodiimide
AIBN	Azobisisobutyronitrile
BPO	Benzoyl peroxide
PEBTA	Poly(6-(ethoxybenzothiazoleacryl- amide)
BOD	Biochemical oxygen demand
SS	Soluble solid
COD	Chemical oxygen demand
ROSs	Reactive oxygen species
ARGs	Antibiotic-resistance genes
ARB	Antibiotic-resistant bacteria
CB	Conduction band
VB	Valence band
AMX	Amoxicillin
DMF	N,N-Dimethylformamide
THF	Tetrahydrofuran

DMSO	Dimethyl sulfoxide
TEA	Triethylamine
DCM	Dichloromethane
FESEM	Field emission scanning electron microscopy
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
GPC	Gel permeation chromatography
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
GCMS	Gas chromatography–mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
NMR	Nuclear magnetic spectroscopy
T _g	Glass transition temperature
T _c	Crystallization temperature
T _m	Melting temperature
dTG	Differential thermogravimetric analysis
PBpyMA	poly-N-([2,2'-bipyridine]-4-yl)methacrylamide
BpyMA	N-([2,2'-bipyridine]-4-yl) methacrylamide
TCI	Terephthaloyl dichloride
MACl	Methacryloyl chloride
NaBH ₄	Sodium borohydride
CT transitions	Charge transfer transition
BHT	Butylated hydroxytoluene
MO	Methyl orange

MB	Methylene blue
OII	Orange-2
RhB	Rhodamine B
CR	Congo red
DBTA	N ₁ ,N ₄ -di([2,2'-bipyridin]-4-yl)terephthalamide
TBTA	N ₁ ,N ₃ ,N ₅ -tri([2,2'-bipyridin]-4-yl)benzene-1,3,5-tricarboxamide
AMX	Amoxicillin
AOP	Advanced oxidation process
PFX	Perfloxacin
OFX	Ofloxacin
CIP	Ciprofloxacin
ENR	Enrofloxacin
LEV	Levofloxacin
NOR	Norfloxacin
E _g	Bandgap energy
α	Absorption coefficient
ν	Frequency
h	Plank's constant
RT	Retention time
IPA	Isopropanol
M _n	Number average molecular weight
M _w	Weight average molecular weight
Đ	Dispersity

LIST OF CHEMICAL FORMULAE

CDCl_3	Deuterated chloroform
DMSO-d_6	Deuterated dimethyl sulfoxide
CO_2	Carbon-dioxide
H_2O_2	Hydrogen peroxide
$\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$	Hydrazine monohydrate
$\text{Fe}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$	Ferric nitrate hexahydrate
$\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Nickel nitrate hexahydrate
$\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Copper nitrate Hexahydrate
$\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Cobalt nitrate hexahydrate
$\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Zinc nitrate hexahydrate
$\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$	Cadmium nitrate tetrahydrate
NaOH	Sodium hydroxide
H_2O	Water
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid
NO_2	Nitrogen dioxide
Pd/C	Palladium on carbon
$\cdot\text{OH}$	Hydroxide radical
$\cdot\text{O}_2^-$	Superoxide anion