

**AMINO ACID-BASED HYDROGEL COMPOSITES FOR
ATMOSPHERIC WATER HARVESTING AND
PURIFICATION APPLICATIONS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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**AMINO ACID-BASED HYDROGEL COMPOSITES FOR
ATMOSPHERIC WATER HARVESTING AND
PURIFICATION APPLICATIONS**

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



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Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled " **Amino acid-based Hydrogel Composites for Atmospheric Water Harvesting and Purification Applications**" being submitted by Mr. Sandeep Kumar Sahoo to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of Bonafide research work carried out by him. Mr. Sahoo has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my 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 other University or Institute for the award of any other degree or diploma.

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ABSTRACT

The growing global freshwater scarcity demands the development of sustainable and decentralized water production strategies. Sorption-assisted atmospheric water harvesting (SAWH) has emerged as a promising approach for capturing moisture from air and generating clean water, irrespective of geographic constraints. To empower the sustainable approach, suitable sorbent materials such as hydrogels, metal-organic frameworks (MOFs) and their composite structures have gained significant attention at the advent of their unique surface features like tunable porosity, high surface area, stimuli-responsiveness, and absorption-desorption channels through functional sites. In chapter 2, we have presented a composite sorbent material consisting of alanine amino acid-based hydrogel and Al-MOF. Stressing upon the fine-tuning of two individual sorbents, we designed several hydrogel-MOF composites and optimized the concentration of Al-MOF with 7.5 wt % of 0.5AHN with the best water uptake, moisture sorption, and desalination efficiency. The synergistic combination of inherently zwitterionic amino acid-based hydrogels with MOF opened up extended water uptake channels for the overall composite. As a result of such irreversible interaction, 0.5AHN-ALM(7.5) exhibited the highest sorption capacity of 2.21 g g^{-1} at 90% RH, whereas 0.26 and 0.47 g g^{-1} moisture uptake was measured at humidity levels of 40% RH and 60% RH, respectively. Moreover, with an evaporation rate of $0.79 \text{ kg m}^{-2} \text{ h}^{-1}$, 3.4 g of saline water was converted into freshwater within 3.5 h of solar irradiation to demonstrate its desalination efficiency. Building on this work, in chapter 3, a super-hygroscopic composite gel was developed using valine, 2-hydroxyethyl methacrylate (HEMA), and N-isopropyl acrylamide (NIPAM)-based thermoresponsive hydrogel, integrated with NH_2 -MIL-53(Al) MOF and hygroscopic CaCl_2 salt. The composite leverages the synergistic hygroscopic properties of its components, achieving a water generation capacity of 4.48 g g^{-1} at 25 °C at 90% humidity. The molecular level integration of the MOF's photothermal activity along with thermo-responsive PNIPAM polymer, which exhibits a reversible hydrophilic and hydrophobic phase transition, enables efficient photo-thermal responsiveness, resulting in

complete water release within 30 min. The porous architecture and hygroscopic design facilitate efficient moisture capture, in situ water liquefaction, and effective water storage and release under varying weather conditions. Furthermore, the material exhibits promising desalination performance with an evaporation rate of $2.98 \text{ kg m}^{-2}\text{h}^{-1}$. This study not only addresses water scarcity but also highlights the potential for developing advanced porous composite materials for AWH and broader environmental applications. To further expand the application potential, in chapter 4, a bimetallic Cr/Al MOF (BMOF) was incorporated into the thermoresponsive valine-HEMA-NIPAM hydrogel system, along with CaCl_2 salt, resulting in a multifunctional composite ($\text{VHN}-(\text{Cr}_d\text{Al})_M/\text{CaCl}_2$). This material combined the high surface area and hydrophilicity of BMOF, the swelling–deswelling behavior of the hydrogel, and the hygroscopic nature of CaCl_2 . The composite exhibited outstanding atmospheric water sorption under 90% RH, with a capacity of 4.9 g g^{-1} . Upon solar exposure (1 kW m^{-2}), the material rapidly heated to $\sim 46^\circ\text{C}$ within 2 minutes, enabling fast water desorption at a rate of $0.8 \text{ g g}^{-1} \text{ h}^{-1}$. The composite maintained stable performance across multiple sorption–desorption cycles, indicating excellent reusability. Notably, even under low to moderate humidity conditions (20–80% RH), effective uptake values of 0.85, 1.01, 1.53, and 3.04 g g^{-1} were recorded, demonstrating adaptability to varying environments and practical applicability in real-world AWH systems. In addition to freshwater generation, in chapter 5, we also explore the application of amino acid-based gel materials and membranes for oil–water separation. A thermoresponsive organogel was synthesized using amino acid-derived monomers and tested for organic solvent and oil extraction. The organogel showed significant swelling in a range of solvents, with maximum absorption of $\sim 1100\%$ for nonpolar and $\sim 850\%$ for polar solvents. Kinetic studies revealed pseudo-second-order absorption behavior, with excellent reusability maintained over 40 absorption/desorption cycles and $\sim 95\%$ retained efficiency. When applied as an organogel membrane for oil-in-water emulsion separation, it achieved $>96\%$ separation efficiency and a separation flux of $2.4 \times 10^2 \text{ L m}^{-2} \text{ h}^{-1}$, with 87.5% flux recovery after 10 cycles. Its favorable porous morphology, hydrophobicity, resilience, and durability

across different aqueous media make it a viable material for environmental remediation. Overall, this thesis presents a strategic platform for developing multifunctional and sustainable materials for atmospheric water harvesting, desalination and oil–water separation. The integration of responsive hydrogels, photothermal and porous MOFs, and hygroscopic salts delivers high performance across a broad range of environmental conditions. These findings advance the field of water resource management and demonstrate strong potential for real-world deployment in sustainable water and environmental technologies.

सारांश

बढ़ती वैश्विक ताजे जल की कमी सतत और विकेंद्रीकृत जल उत्पादन रणनीतियों के विकास की मांग करती है। सोर्षन-सहायित वायुमंडलीय जल संचयन (SAWH) एक प्रभावशाली दृष्टिकोण के रूप में उभरा है जो भूगोलिक बाधाओं की परवाह किए बिना हवा से नमी को पकड़ने और स्वच्छ जल उत्पन्न करने के लिए सक्षम है। इस सतत दृष्टिकोण को सशक्त बनाने के लिए, हाइड्रोजेल्स, मेटल-ऑर्गेनिक फ्रेमवर्क्स (MOFs) और इनके सम्मिश्रण जैसी उपयुक्त सोर्बेंट सामग्रियाँ, उनके अनूठे सतही गुणों जैसे ट्यून योग्य पोरसिटी, उच्च सतह क्षेत्रफल, उत्तेजना-प्रतिक्रियाशीलता, और कार्यात्मक साइट्स के माध्यम से अवशोषण-विमोचन चैनलों की उपस्थिति के कारण, महत्वपूर्ण ध्यान आकर्षित कर रही हैं। अध्याय 2 में, हमने एलानिन अमीनो एसिड-आधारित हाइड्रोजेल और Al MOF से युक्त एक मिश्रित सोर्बेंट सामग्री प्रस्तुत की है। दो व्यक्तिगत सोर्बेंट्स की सूक्ष्म ट्यूनिंग पर बल देते हुए, हमने कई हाइड्रोजेल-MOF संयोजन डिज़ाइन किए और 0.5AHN के 7.5 wt % Al-MOF सांद्रता के साथ सर्वश्रेष्ठ जल ग्रहण, नमी सोर्षन और विलवणीकरण दक्षता के लिए अनुकूलित किया। स्वाभाविक रूप से ज़्विटरआयनिक अमीनो एसिड-आधारित हाइड्रोजेल्स और MOF का सहयोगात्मक संयोजन कुल मिश्रण के लिए विस्तारित जल ग्रहण चैनलों को खोलता है। इस तरह की अपरिवर्तनीय अंतःक्रिया के परिणामस्वरूप, 0.5AHN_AIM(7.5) ने 90% RH पर 2.21 g g⁻¹ की उच्चतम सोर्षन क्षमता प्रदर्शित की, जबकि 40% RH और 60% RH आर्द्रता स्तरों पर क्रमशः 0.26 और 0.47 g g⁻¹ नमी ग्रहण मापा गया। इसके अतिरिक्त, 0.79 kg m⁻² h⁻¹ की वाष्पीकरण दर के साथ, 3.4 ग्राम खारे पानी को 3.5 घंटे की सौर विकिरण के भीतर ताजे पानी में परिवर्तित किया गया ताकि इसकी विलवणीकरण दक्षता प्रदर्शित की जा सके। इस कार्य के आधार पर, अध्याय 3 में, वैलीन, 2-हाइड्रॉक्सीएथिल मेथाक्रिलेट (HEMA), और N-आइसोप्रोपाइल एक्रिलामाइड (NIPAM)-आधारित थर्मो-प्रतिक्रियाशील हाइड्रोजेल का उपयोग करके एक सुपर-हाइड्रोस्कोपिक संयोजित जेल विकसित किया गया, जिसे NH₂-MIL-53(Al) MOF और हाइड्रोस्कोपिक CaCl₂ लवण के साथ एकीकृत किया गया। यह मिश्रण अपनी संघटक सामग्रियों की सहयोगात्मक हाइड्रोस्कोपिक गुणों का लाभ उठाता है, और 25°C पर 90% आर्द्रता में 4.48 g g⁻¹ की जल उत्पादन क्षमता प्राप्त करता है। MOF की फोटोथर्मल गतिविधि और PNIPAM पॉलिमर की रिवर्सिबल हाइड्रोफिलिक और हाइड्रोफोबिक चरण संक्रमण को जोड़ने वाला आणविक स्तर का एकीकरण कुशल फोटो-थर्मल प्रतिक्रियाशीलता को सक्षम करता है, जिससे

30 मिनट के भीतर पूर्ण जल विमोचन होता है। सच्छिद्र वास्तुकला और हाइग्रोस्कोपिक डिज़ाइन प्रभावी नमी पकड़ने, स्थल पर जल द्रवीकरण, और विभिन्न मौसम स्थितियों के तहत कुशल जल भंडारण एवं विमोचन को सुविधाजनक बनाते हैं। इसके अतिरिक्त, यह सामग्री $2.98 \text{ kg m}^{-2} \text{ h}^{-1}$ की वाष्पीकरण दर के साथ प्रभावशाली विलवणीकरण प्रदर्शन भी प्रदर्शित करती है। यह अध्ययन न केवल जल संकट को संबोधित करता है, बल्कि AWH और व्यापक पर्यावरणीय अनुप्रयोगों के लिए उन्नत सच्छिद्र संयोजित सामग्रियों के विकास की संभावना को भी उजागर करता है। अनुप्रयोग संभावनाओं को और अधिक विस्तारित करने के लिए, अध्याय 4 में, थर्मो-प्रतिक्रियाशील वैलीन-HEMA-NIPAM हाइड्रोजेल प्रणाली में द्विधात्विक Cr/Al MOF (BMOF) को CaCl_2 लवण के साथ शामिल किया गया, जिसके परिणामस्वरूप एक बहुक्रियाशील मिश्रण ($\text{VHN}(\text{Cr}_d\text{Al})_m/\text{CaCl}_2$) प्राप्त हुआ। इस सामग्री में BMOF की उच्च सतह क्षेत्र और हाइड्रोफिलिसिटी, हाइड्रोजेल का सूजन-सिकुड़न व्यवहार, और CaCl_2 की हाइग्रोस्कोपिक प्रकृति सम्मिलित है। इस मिश्रण ने 90% RH पर 4.9 g g^{-1} की क्षमता के साथ उत्कृष्ट वायुमंडलीय जल सोर्षन प्रदर्शित किया। सौर विकिरण (1 kW m^{-2}) के तहत, यह सामग्री 2 मिनट के भीतर $\sim 46^\circ\text{C}$ तक तेजी से गर्म हुई, जिससे $0.8 \text{ g g}^{-1} \text{ h}^{-1}$ की दर से तेज जल विमोचन संभव हुआ। यह मिश्रण कई सोर्षन-डिसोर्षन चक्रों में स्थिर प्रदर्शन बनाए रखता है, जो इसकी उत्कृष्ट पुनःप्रयोज्यता को दर्शाता है। विशेष रूप से, निम्न से मध्यम आर्द्रता स्थितियों (20-80% RH) में भी क्रमशः 0.85, 1.01, 1.53, और 3.04 g g^{-1} के प्रभावी ग्रहण मान दर्ज किए गए, जो विभिन्न पर्यावरणों में अनुकूलनशीलता और वास्तविक विश्व AWH प्रणालियों में व्यावहारिक उपयोगिता को दर्शाते हैं। ताजे जल उत्पादन के अतिरिक्त, अध्याय 5 में, हमने ऑयल-वाटर पृथक्करण के लिए अमीनो एसिड-आधारित जेल सामग्री और झिल्लियों के अनुप्रयोग का भी अन्वेषण किया। एक थर्मो-प्रतिक्रियाशील ऑर्गेनोजेल को अमीनो एसिड-व्युत्पन्न मोनॉमर्स का उपयोग करके संश्लेषित किया गया और कार्बनिक सॉल्वेंट्स और तेल निष्कर्षण के लिए परीक्षण किया गया। ऑर्गेनोजेल ने विभिन्न सॉल्वेंट्स (डाइइलेक्ट्रिक स्थिरांक 2.25-46.7) में महत्वपूर्ण सूजन दिखाई, जिसमें गैर-ध्रुवीय सॉल्वेंट्स के लिए अधिकतम $\sim 1100\%$ और ध्रुवीय सॉल्वेंट्स के लिए $\sim 850\%$ अवशोषण हुआ। गतिज अध्ययन ने द्वितीय-आदेश सोखने के व्यवहार को दर्शाया, जिसमें 40 अवशोषण/डिसोर्षन चक्रों में उत्कृष्ट पुनःप्रयोज्यता और $\sim 95\%$ की बनी हुई दक्षता पाई गई। जब तेल-इन-वाटर इमल्शन पृथक्करण के लिए ऑर्गेनोजेल झिल्ली के रूप में लागू किया गया, तो इसने $>96\%$ पृथक्करण दक्षता और $2.4 \times 10^2 \text{ L m}^{-2} \text{ h}^{-1}$ का पृथक्करण फ्लक्स प्राप्त किया, तथा 10 चक्रों के बाद 87.5% फ्लक्स पुनःप्राप्ति हासिल की। इसकी अनुकूल सच्छिद्र

संरचना, हाइड्रोफोबिसिटी, लचीलापन, और विभिन्न जलीय मीडिया में टिकाऊपन इसे पर्यावरणीय उपचार के लिए एक व्यवहार्य सामग्री बनाते हैं। समग्र रूप से, यह शोध प्रबंध वायुमंडलीय जल संचयन, विलवणीकरण, और तेल-जल पृथक्करण के लिए बहुक्रियाशील और सतत सामग्रियों के विकास के लिए एक रणनीतिक मंच प्रस्तुत करता है। प्रतिक्रियाशील हाइड्रोजेल्स, फोटोथर्मल और सच्छिद्र MOFs, और हाइग्रोस्कोपिक लवणों का एकीकरण विभिन्न पर्यावरणीय परिस्थितियों में उच्च प्रदर्शन प्रदान करता है। ये निष्कर्ष जल संसाधन प्रबंधन के क्षेत्र को आगे बढ़ाते हैं और सतत जल एवं पर्यावरणीय प्रौद्योगिकियों में वास्तविक दुनिया की तैनाती की प्रबल संभावनाएं प्रदर्शित करते हैं।

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LIST OF ABBRIVIATIONS

1

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC)

2

2-hydroxyethylmethacrylate (HEMA)

2-amino terephthalic acid [NH₂-BDC]

2,2,2- Trifluoroacetic acid (TFA)

4

4-dimethylaminopyridine (DMAP)

A

Atmospheric Water Harvesting (AWH)

Attenuated total reflectance (ATR)

Aluminium based metal organic framework (Al_M)

Ammonium persulfate (APS)

Aluminium chloride hexahydrate (AlCl₃·6H₂O)

Atmospheric water generator (AWG)

B

Barrett-Joyner-Halenda (BJH)

Brunauer-Emmett-Teller (BET)

Bi-metallic MOF (BMOF)

C

Chemical Vapor Deposition (CVD)

Covalent organic framework [COF]

Cross-polarization/magic-angle spinning (CP-MAS)

Chromium based metal organic framework (Cr_M)

Chromium doped aluminium metal organic framework [(Cr_dAl)_M]

Calcium chloride (CaCl₂)

Carbon nanotubes (CNTs)

D

Dichloromethane (DCM)

dimethylformamide (DMF),

Dimethyl sulfoxide (DMSO)

Differential scanning calorimetry (DSC)

Deuterated chloroform (CDCl₃)

E

Energy-dispersive X-ray spectroscopy (EDX)

Ethanol (EtOH)

Ethyl Acetate (EtOAc)

F

Field Emission Scanning Electron Microscope (FE-SEM)

Fourier transform infrared (FTIR)

G

Graphene oxide (GO)

H

Hydrochloric acid (HCl)

Humidification and dehumidification (HDH)

I

Inductively coupled plasma mass spectrometry [ICP-MS]

Infrared (IR)

Interpenetrating polymer network (IPN)

L

L-Alanine-hydroxyethyl methacrylate-co-N-isopropylacrylamide (AHN)

L-Valine-hydroxyethyl methacrylate-co-N-isopropylacrylamide (VHN)

Lower critical solution temperature (LCST)

Lithium Chloride (LiCl)

Large fog collectors (LFC)

M

Metal organic framework (MOF)

N

N-isopropylacrylamide (NIPAM)

nanofiltration (NF)

Nanoparticle (NP)

Nuclear magnetic resonance (NMR)

N,N,N',N'',N'''-
pentamethyldiethylenetriamine (PMDETA)

N,N'-methylenebisacrylamide (MBA)

Nickel based metal organic framework
(Ni_M)

O

Oil permeation percentage (OP%)

Organogel (GEL)

P

Polydimethylsiloxane (PDMS)

powder X-ray diffraction (PXRD)

Polyurethane (PU)

Polypyrrole (PPy)

Polyaniline (PANI)

Polyvinyl caprolactam (pVCl)

Poly propylene (PP)

R

Relative humidity (RH)

Room temperature (RT)

S

selected area electron diffraction (SAED)

Solar assisted atmospheric water harvesting
(Sol-AWH)

Saturation ratio percentage (SR%)

Soluble fraction (SF)

Small fog collectors (SFCs)

Sodium bicarbonate (NaHCO₃)

T

Thermogravimetric analysis (TGA)

transmission electron microscopy
(TEM)

tert-butoxy carbonyl (BOC)

Tetrahydrofuran (THF)

tert-butoxy carbonyl- L-Alanine-
hydroxyethyl methacrylate (Boc-Ala-
HEMA)

tert-butoxy carbonyl- L-Alanine-
hydroxyethyl methacrylate (Boc-Val-
HEMA)

Total organic carbon (TOC)

Tetramethylsilane (TMS)

Thermoelectric cooler (TEC)

U

Ultraviolet photoelectron
spectroscopy (UPS)

Ultraviolet-Visible (UV-Vis)

Ultrafiltration (UF)

V

Vapor compression refrigerator
(VCR)

W

World Health Organization (WHO)

X

X-ray diffraction (XRD)

X-ray absorption spectroscopy (XAS)

X-ray photoelectron spectroscopy
(XPS)

Z

Zinc based metal organic framework
(Zn_M)

List of Symbols

e_s	saturated water vapor
T_a	environmental temperature
P	radiative power
T_s	surface temperature
σ	Stefan-Boltzmann constant
ε	emissivity
J_o	oil separation flux
J_{ro}	recovered oil flux
θ	weight of the swollen gel at time t
θ_{max}	weight of the swollen gel at equilibrium
k	rate of absorption
t	time
A	area
M_w	weight of the sample after moisture uptake
M_i	initial mass of the composite
M_t	weight of the sample at a specific time
Q_e	Equilibrium adsorption capacity of solute
K_F	Freundlich constant indicative of adsorption capacity
C_e	Equilibrium concentration of solute in solution
$1/n$	Freundlich exponent indicative of adsorption reliability
V	Volume
ρ	density