

University of Wah Journal of Science and Technology

UNIVERSITY OF WAII
JOURNAL OF
SCIENCE AND TECHNOLOGY

NA Na 2

December 111

www.uow.edu.pk

Synthesis of Sol-Gel Silicas functionalized with Schiff Base Ligands

Shazia Naheed, Ghulam Zakria, Rana Muhammad Talal and Alina Changez

Abstract—Schiff bases containing azomethine linkage in their structure are good ligands and show great metal binding ability. In last few years sol-gel method is found very attractive for synthesis of gels due to its low cost, low operating temperature and ease of synthesis. This work presents the synthesis of Schiff base functionalized gels through sol-gel method and their use in extraction of metal ions from aqueous medium at room temperature and appropriate pH. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses of both blank and functionalized gels are presented. The analyses data show successful incorporation of the Schiff base in sol-gel matrix. Metal removal data show high efficiency of Schiff base functionalized gels.

Index Terms—Schiff base functionalized silicas, Sol-gel method, Extraction of metal ions.

I. INTRODUCTION

THE organic compounds consisting of azomethine linkage (-HC=N-) in their structure are called Schiff bases. Hugo Schiff the pioneer synthesized such compounds by the reaction of aromatic amine with aldehyde or ketone [1]. In a Schiff base nitrogen atom is connected to an aryl or alkyl group but not with hydrogen.

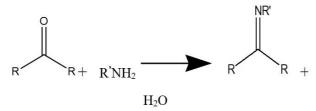


Fig. 1. Formation of Schiff base.

Manuscript received August 15, 2017; accepted January 22, 2018.

- S. Naheed (email:<u>shazia.naheed@uow.edu.pk</u>), A. Changez (email: <u>aalinakhan027@yahoo.com</u>) and R.M. Talal (email: <u>ranatilal25@gmail.com</u>) are affiliated with Department of Chemistry, University of Wah, Wah Cantt, Pakistan.
- G. Zakria is affiliated with Advanced Engineering Research Organization, Wah Cant, Pakistan. (email: zakria9613@yahoo.com) Corresponding author email: shazia.naheed@uow.edu.pk

It is a condensation reaction in which amine, acting as a nucleophile attacks at the electrophilic carbonyl carbon forming Schiff base in which (C=O) of carbonyl group is replaced by (C=N) of imine or Schiff base. A variety of compounds having amino group can be employed for the preparation of Schiff bases as shown in Fig. 1 [2-3]. Product (Schiff base) both are very low [4]. pH of the reaction mixture is to be maintained due to high basicity of aliphatic amines. Imines formed from aromatic amines are called Anils. Just like aliphatic amines, aliphatic carbonyls are also not preferred for Schiff bases synthesis as aliphatic carbonyl compounds are less stable [5-7]. Usually aldehyde is the carbonyls of choice due to their better reactivity as compare to ketones. If carbon or nitrogen of (C=N) is attached with aromatic ring, it increases the stability of the Schiff base due to conjugation [8]. Preparation of Schiff base is a reversible reaction. Therefore, the reaction can be used for the protection of amines. It takes place under basic or acidic conditions or simply by refluxing the reactants in a suitable solvent. The equilibrium can be shifted towards forward direction by dehydration with a desiccant such as TiCl₄ [9] or by azeotropic distillation [10-11]. As Schiff bases form crystals they usually show sharp melting points. They are good as ligands and form complexes with metals. Transition metal complexes form a large group in Chemistry [12].

Mechanism of Schiff base formation shows that it is nucleophilic addition reaction due to which an unstable addition product known as carbinolamine is formed. Elimination of water from carbinolamine results in the formation of Schiff base. Its elimination takes place under mild acidic conditions. This step is rate determining step in the synthesis. Therefore the reaction is often done under mild acidic conditions. Harsh acidic conditions can protonate amine diminishing their nucleophilicity and resulting backward reaction. Hydrolysis of Schiff base can be done by water under acidic or basic conditions.

Schiff bases are versatile organic ligands [13-17]. Their biomedical [18] and catalytic [19-21], analytical and other applications are well documented in literature. Previously

Schiff bases have been utilized in estimation [22-23] and separation of metals [24] and estimation of oxo groups [25-26]. They are well known for their biological activities [27]. Azomethine linkage in the structure of Schiff base is thought to be responsible for their bioactivities [28] against cancer [29], bacterial infections [30-31], AIDS [32-33], fungal infections [34-35], viral infections [36, 37], mosquito larvae [3], flamatory [39] and cancer. Entrapment of bioactive materials in a suitable matrix as support and their transport to the infected parts is an emerging field of research.

Sol-gel process was discovered in 1800. Synthesis of organic-inorganic hybrids through sol-gel process has attained much attention. Metal or semimetal alkoxides being the precursor substance of this process undergo two reactions i.e. Hydrolysis and Condensation, which leads to formation of inorganic network within which the organic moiety get entrapped due to low operating temperature. Occurrence of poly condensation reaction at low temperature is the biggest attraction and advantage of this process [40]. These reactions are shown in *Fig.* 2.

Industrial development is mainly contributing to environment pollution which is affecting the ecosystem as well as human health [41]. Un-loading of these toxic metals from environment is the urgent need of present era. Some of the previous methods for toxic metal removal are oxidation, precipitation, complexation, electrochemical treatment, filtration, distillation, application of selective membranes and sorptonetc [42-44]. Of all, Sorption is superior and more attractive method due to low cost, ecological correctness, higher efficiency and ease of operation. Chelating polymeric materials have been reported for pre-concentration and removal of metals [45-49]. Polymeric resins showed low mechanical and chemical stability, slow kinetics and irreversible adsorption [50]. Unmodified naturally occurring materials [51] and modified naturally occurring materials have also been applied for metal removal.

To overcome the problems of polymeric resins inorganic supports such as silica gel or functionalized silica gel have been applied for metal removal. They have high thermal and mechanical stability, stability to chemicals, negligible swelling, shrinking poisoning and fast sorption kinetics. To avoid some limitations of silica gel modified sol-gel materials have been used as sorbents. Porosity and surface layer composition of sol-gel materials can be tuned for specific application. The sol-gel materials can be physically or chemically functionalized with active chelating ligands for metal removal.

II. EXPERIMENTAL METHODOLOGY

A. General procedure for synthesis of Schiff bases (L1-L4)

10mmol (0.01 M) of 4, 4-oxydianiline was dissolved in methanol to get a clear solution. 20mmol (0.02 M) aldehyde/ketone was also dissolved in the same solvent. Both the solutions were mixed and refluxed. Progress of reaction was monitored through TLC in appropriate solvent

system from time to time. After reaction completion, mixture was evaporated on rotary evaporator followed by the filtration of the product. Solid obtained was weighted, recrystallized and stored in desiccator.

B. Synthesis procedure for L5

To a stirred solution of Salicylaldehyde (10 mmol, 0.01M) in 15 mL ethanol, 10 mmol (0.01M) of sulfanilamide solution in 15 mL ethanol was added slowly. The reaction was refluxed for 120 minutes. Orange precipitates were formed. The product was filtered, recrystallized with Ethanol and weighed.

Sol-Gel Reaction:

Alcohol Condensation:

Water Condensation:

Fig. 2. Sol-gel reaction.

Aldehyde/Ketone 1a-4a
$$H_2N$$

$$A,4-oxydianiline$$

$$Reflux$$

$$R_1$$

$$Schiff base/Imine (1b-4b)$$

Fig. 3. General reaction for Schiff base (L1-L5).

C. Synthesis of Organically Modified Gel

In a 100 ml container, 20 ml tetraethoxysilane (TEOS), 20 ml distilled water and 40 ml of 0.01M of ligand (L1-L5) solution in ethanol was added, followed by addition of 0.01M ammonium fluoride (NH₄F) solution as catalyst. Shaking of mixture results in immediate gel formation. It allowed the gel to dry for 4-5 days at room temperature.

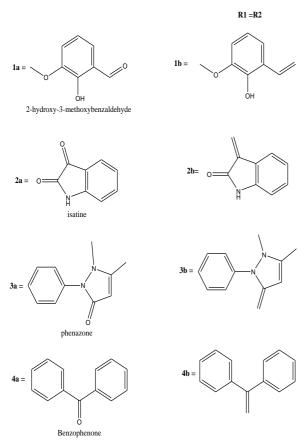


Fig. 4. Aldehydes and Ketones.

Fig. 5. Synthesis of Schiff base (L5).

Gel got dried and cracks appeared. Later it was placed in an oven at 48°C until weight became constant. After attaining the constant weight gel was crushed into fine powder and soaked in water (washed) in order to remove the undoped reagent. After washing, the gel was again dried (till constant weight by following the same method), crushed, weighed and stored in desiccator. *Fig. 3, 4 and 5* shows synthesis of Schiff base.

D. Removal of Zn^{+2} from aqueous medium using organically modified gels

10 mg/L Zn(CH₃COO)₂.2H₂O solution was prepared in distilled water. 10 ml of the solution was taken in seven different sample vials and pH was maintained at 1-6 respectively in each vial. 30 mg of functionalized gel was added in each vial and was shaken for 30 minutes at room temperature. The results are reported in *Fig. 6*.

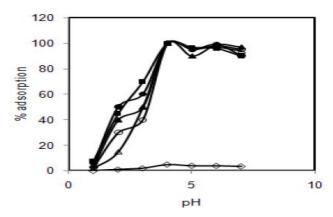


Fig. 6. Removal of metal.

Effect of pH on sorption of Zn (II) by (\lozenge) blank gel, (Δ) L1 Sol Gel, (O) L2 Sol Gel, (\bullet) L3 Sol Gel, (\bullet) L4 Sol Gel, (\bullet) L5 Sol Gel Temperature = Room Temperature, Amount of Functionalized gel=30 mg, Shaking time=30 minutes, Zn (II) Concentration=10 mg/L, Volume of suspension=10 mL.

III. RESULTS AND DISCUSSION

A. Schiff base Logands (L1-L5)

Physical properties of the ligands synthesized are reported in Table 1 while the FTIR data of L1-L5 are reported below. Disappearance of C=O stretches of aldehydes and ketones and -NH stretches of primary amines in the FTIR spectrum indicates the Imine formation while physical properties data as shown in Table 1 further confirm the ligand synthesis.

B. 2-((E)-(4-(4-((E)-2-hydroxy-3 methoxybenzylide neamino) phenoxy) phenylimino) methyl)-6 methoxy-phenol (L1)

Color: Yellow, Yield: 76%, FTIR (v, cm⁻¹, 1575, 1485 (C=C ring stretch), 3010 (sp² C-H stretch), 3450 (-OH stretch), 1200 (C-O stretch), 1620 (C=N stretch)

C. (Z)-3-(4-(4-((Z)-3-oxoindolin-2-ylideneamino) phenoxy) phenylimino) indolin-2-one (L2)

Color; Deep yellow, Yield; 65%, FTIR (v, cm⁻¹), 1590, 1459 (C=C ring stretch), 3051 (sp² C-H stretch), 1742 (C=O stretch), 3566 (-NH stretch), 1624 (C=N stretch)

D. (E)-N-4-(4-((E)-2,3-dimethyl-1-phenyl 1,2dihydrpy-razolylideneamino)phenoxy) benzeneamine (L3)

Color, Pale yellow, Yield, 68%, FTIR (v, cm⁻¹), 1585, 1460 (C=C ring stretch), 3100 (sp² CH stretch), 1200 (C-O stretch), 1624 (C=N stretch)

E. N-(diphenylmethylene)-4-(4-(diphenylmethylene-amino) phenoxy) benzamine (L4)

Color, Off-white, Yield, 70%, FTIR (v, cm⁻¹), 1550, 1478 (C=C ring stretch), 3100 (=CH stretch), 1100 (C-O stretch), 1620 (C=N stretch)

F. (E)-4-(2-hydroxybenzylideneamino) benzene sulfonamide (L5)

Color; Yellow, Yield; 78%, FTIR (v, cm⁻¹) 1540, 1453(C=C ring stetch), 3050 (=CH stretch), 3400(-OH stretch), 1320, 1140 (S=O stretch), 3350, 3400 (-NH stretch), 1620 (C=N stretch).

TABLE I DATA OF SCHIFF BASE LIGANDS

Code	Molecular Formula	M.Mass (g/mole)	M.P (°C)	Colour	Reflux Time (hrs)	% Yield
L1	$C_{48}H_{44}N_4 \\ O_9$	820.88	148- 151	yellow	10	76
L2	$C_{29}H_{20}N_4 \\ O_3$	472.49	146- 149	deep yellow	5	65
L3	$C_{40}H_{28}N_2 \\ O_3$	584.66	188- 192	Pale yellow	3	68
L4	$C_{34}H_{32}N_{6}$ O	540.66	140- 142	off- white	3	70
L5	$C_{13}H_{12}N_2 \\ O_3S$	276.31	210- 211	yellow	1.5	78

G. Organically modified gels (L1-SG to L5-SG)

Analytical data of the synthesized gels are reported in Table II. It shows that color of the blank gel was white while the organically modified gels show color similar to Schiff base ligand that indicates the silica gel is doped by the ligand. The FTIR spectra of all modified gels show a very wide band at 1100 and 470cm⁻¹ for the siloxane linkage (-Si-O-Si-) and a medium intensity band at 3300-3400cm⁻¹ for —Si-OH linkages. The siloxane band hides/masks the other functional groups of the ligands. *Fig. I* shows the FTIR spectra of the ligand (L5), blank gel (SG) and doped gel (L5-SG) as shown in Table III.

TABLE II
ANALYSIS DATA OF BLANK AND MODIFIED GELS

Product Code	Molecular Formula	Molecular Weight (g/mole)	Melting Point (°C)	Colour	% Yield
SG	-	-	Does not melt	White	2.5 g
L1	$C_{48}H_{44}N_4O_9\\$	820.88	148-151	Yellow	76 %
L1SG	-	-	-	Yellow	2.9 g
L2	$C_{29}H_{20}N_4O_3\\$	472.49	146-149	Deep Yellow	65 %
L2SG	-	-	-	Deep Yellow	2.95 g
L3	$C_{40}H_{28}N_{2}O_{3} \\$	584.66	188-192	Pale Yellow	68 %
L3SG	-	-	-	Pale Yellow	2.72 g
L4	$C_{34}H_{32}N_6O$	540.66	140-142	Off- white	70 %
L4SG	-	-	-	Off- white	2.76 g
L5	$C_{13}H_{12}N_2O_3$ S	276.31	210-211	Yellow	78 %
L5SG	-	-	-	Yellow	2.74 g

Gel modification with organic ligands is also confirmed through Scanning Electron Microscopy analysis (SEM). Data obtained from SEM studies show that porosity is decreased after modification of the xerogel. It shows the filling of the pores of the xerogel after modification with Schiff base. SEM after metal sorption shows the complete filling of pores and surface of the xerogels as indicated in *Fig. 7, 8 and 9.* XRD Spectra of the xerogels show amorphous nature of the blank and Schiff based gels.

The porosity analysis is reported in Table IV. The interpretation of results was done by getting help from reported literature. The analyses data show successful incorporation of the Schiff base molecules inside the xerogel matrix. Sorption studies further confirm the functionalization of the xerogel. Application of organically modified gel in Zn (II) sorption. The sorption studies were conducted using zinc acetate. Sorption increases with rise in pH as of 1-4, achieves its maximum value at pH 4. Insignificant sorption is examined at pH 1-2. More increase in pH above 4 decreases the sorption to a small degree as shown in Fig. 2. The reduced sorption at low pH value may be due to competition of H_3O+ ions with metallic ions for complexation with some active positions of Imines.

TABLE III
FTIR DATA OF BLANK AND SCHIFF BASE MODIFIED GELS
(KBr PELLET v.cm⁻¹)

(KDF FELLET, V CIII)				
Name	(C=N)	(Si-OH)	(Si-O-Si)	
SG	-	3300-3000	1100, 470	
L1	1620	-	-	
L1SG	1620	3300-3000	1107, 471	
L2	1624	-	-	
L2SG	1624	3400-3000	1100, 470	
L3	1624	-	-	
L3SG	1624	3300-3000	1101, 470	
L4	1620	-	-	
L4SG	1620	3300-3100	1102, 469	
L5	1620	-	-	
L5SG	1620	3100-3400	1100, 470	
•				

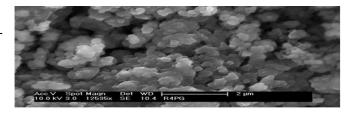


Fig.7. SEM of blank gel (SG).

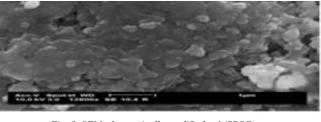


Fig. 8. SEM of organically modified gel (SBSG).

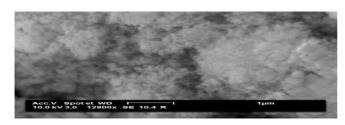


Fig. 9. SEM of modified gel after sorption of metal ions.

TABLE IV POROSITY DATA OF BLANK AND MODIFIED GELS

Xerogels	Surface Area (m/g) ²	Pore volume (g/cm) ³	Pore diameter (nm)
SG	269	0.73	17.10
L1SG	249	0.53	9.12
L2SG	235	0.54	9.09
L3SG	265	0.60	10.00
L4SG	250	0.56	11.00
L5SG	255	0.49	0.88

functionalized gels. The data shows high efficiency of the functionalized gels as compared with blank gel. The advantage of the work is that it shows high efficiency at room temperature and moderate pH.

IV. CONCLUSION

In the light of above study it is concluded that Schiff bases being good ligands for toxic metals retain metal extraction potential even after doping of silica. Sol-gel method is a good approach for synthesis of organically modified gels. The Schiff base modified gel is more promising for metal extraction than the blank gel. SEM and XRD analysis data show the successful incorporation of the Schiff base ligand into the gel. Present study confirms that Schiff base modified gels are found very promising for extraction of Zinc metal at moderate pH at room temperature as compared to blank gel.

REFERENCES

- [1] H. Schiff. Synthesis of Sciiff bases, Annual Chemical Supplement, Vol. 3, pp. 343, 1864.
- [2] S. C. Bell, G. L. Conklin and S. J. Childress. The separation of ketimine isomers, Journal of the American Chemical Society, Vol. 85, pp. 2868-2869, 1963.
- [3] H. Schiff. On some phenolic derivatives of aldehydes, Annals of Chemistry, Vol. 131, pp.118, 1864.
- [4] Dr. M. Fogiel. Staff of Research and Education Association, The Organic Problem Solver, Education Association, New York, 1987.
- [5] R. A. Mekheimer, A. M. A. Hameed and K. U. Sadek. First synthesis and isolation of the e-and z-isomers of some new Schiff bases Reactions of 6-azido-5-formyl-2-pyridone with aromatic amines, Molecules, Vol. 13, pp. 195-203, 2008.
- [6] K. N. Campbell, H. Sommers and B. K. Campbell. Organohalogenated persistent organic pollutants in American captured in eastern Canada, Journal of American Chemical Society, Vol. 66, p. 6682, 1994.
- [7] J. Hine and C. Y. Yeh. Equilibrium in formation and conformational isomerization of imines derived from isobutyraldehyde and saturated aliphatic primary amines, Journal of the American Chemical Society, Vol. 89, pp. 2669-2676, 1967.
- [8] C. Sandorfy. The chemistry of the carbon-nitrogen double bond,
- [9] H. Weingarten, J. P. Chupp and W. A. White. Ketimine syntheses use of titanium tetrachloride in a new procedure for their preparation, The Journal of Organic Chemistry, Vol. 32, pp. 3246-3249, 1967.

- [10] R. Bonnett and T. Emerson. 834 Optical rotatory dispersion Part XXII, Steroidal azomethines, Journal of the Chemical Society, pp. 4508-4511, 1965.
- [11] M.B. Smith and J. March. Advanced Organic Chemistry, 5th edition 1994.
- [12] A. O. De Souza, F.C.S.Galetti, C.L. Silva, B. Bicalho, M.M. Parma and S.F. Fonseca. Antimycobacterial and cytotoxicity activity of synthetic and natural compounds, Quim Nova, Vol. 30(7), pp. 1563-1566, 2007.
- [13] A. N. Mazidji, B. Koopman and G. Bitton. Chelating resin versus ion-exchange resin for heavy metal removal in toxicity fractionation, Water Science Technology, Vol. 26, p. 189, 1982.
- [14] Nilchi, M. R. Hadjmohammadi, S. R. Garmarodi and R. Saberi and J. Hazard. Mater Studies on the adsorption behavior of trace amounts of 90Sr2+, 140La3+, 60Co2+, Ni2+ and Zr4+ cations on synthesized inorganic ion exchangers, Journal of hazardous materials, Vol. 167, pp. 531-535, 2009.
- [15] G. V. Myasoedova and S. B. Savvin. Chelating sorbents in analytical chemistry. Critical Review Analytical Chemistry, Vol. 171, 1986.
- [16] G. Myasoedova and S. Savvin. New chelating sorbents and their analytical application, Zhurnal Analiticheskoj Khimii, Vol. 37, pp. 499-519, 1982.
- [17] A. Chow and H. Gesser. Preconcentration of trace metals from aquatic environmental samples, Hazard Assessment of Chemicals: Current Developments, Vol. 1, 1981.
- [18] J. G. Cory and A. H. Cory. International Encylopedia of Pharmacology and Therapeutics, Pergamon Press, New York, 1989
- [19] A. Llobet, A. E. Martell and M. A. Martínez. Cu (I) and Cu (II) dinuclear complexes of a new hexaaza schiff base dinucleating macrocyclic ligand and their oxygenation chemistry, Journal of Molecular Catalysis Chemical, Vol. 129, pp. 19-26, 1998.
- [20] T. Katsuki. Unique asymmetric catalysis of cis-β metal complexes of salen and its related Schiff-base ligands. Chemical Society Reviews, Vol. 33, pp. 437-444, 2004.
- [21] Lozana, P. G. Lassahn, C. Zhang, B. Wu, C. Janiak, G. Rheinwald. Dinuclear nickel (II) and palladium (II) complexes in combination with different co-catalysts as highly active catalysts for the vinyl/addition polymerization of norbornene, Zeitschrift für Naturforschung, Vol. 58, pp. 1152-1164, 2003.
- [22] R. Soomro, M. J. Ahmed, N. Memon and H. Khan. A simple and selective spectrophotometric method for the determination of trace gold in real, environmental, biological, geological and soil samples using bis (salicylaldehyde) orthophenylenediamine, Analytical Chemistry Insights, Vol. 3, pp. ACI-S977, 2008.
- [23] M. J. Ahmed and M. N. Uddin. A simple spectrophotometric method for the determination of cobalt in industrial, environmental, biological and soil samples using bis (salicylaldehyde) orthophenylenediamine, Chemosphere, Vol. 67, pp. 2020-2027, 2007.
- [24] G. K. Krishnapillai and S. J. Konnully. Removal of Fe (III) using a polystyrene anchored Schiff base, Environmental Chemistry Letters, Vol. 5, pp. 19-21, 2007.
- [25] Z. H. Chohan, M. H. Youssoufi, A. Jarrahpour and T. B. Hadda. Identification of antibacterial and antifungal pharmacophore sites for potent bacteria and fungi inhibition: indolenyl sulfonamide derivatives, European Journal of Medicinal Chemistry, Vol. 45(3), pp. 1189-1199, 2009.
- [26] L. Gibson, W. Kerr, A. Nordon, J. Reglinski, C. Robertson, L. Turnbull. On-site determination of formaldehyde a low cost measurement device for museum environments, Analytica Chimica Acta, Vol. 623, pp. 109-116, 2008.
- [27] M. Shingare and D. Ingle. Synthesis of pyrimidine schiff-bases as anticancer agents, Journal of the Indian Chemical Society, Vol. 53, pp. 1036-1037, 1976.
- [28] P. Pathak, V. Jolly and K. Sharma. Synthesis and biological activities of some new substituted arylazo schiff bases, Oriental Journal of Chemistry, Vol. 16, pp. 161-162, 2000.
- [29] A. T. Chaviara, P. C. Christidis, A. Papageorgiou, E. Chrysogelou, D. HadjipavlouLitina and C. Bolos. In vivo anticancer, antiinflammatory, and toxicity studies of mixed-ligand Cu (II) complexes of dien and its Schiff dibases with heterocyclic aldehydes and 2-amino-2-thiazoline Crystal structure of (Cu

- $\begin{array}{lll} (dien)(Br)(2a\text{-}2tzn)](Br)(H & 2 & O), & Journal & of & Inorganic \\ Biochemistry, Vol. 99, pp. 2102-2109, 2005. & & \end{array}$
- [30] M. Baseer, V. Jadhav, R. Phule, Y. Archana and Y. Vibhute. Synthesis and antibacterial activity of some new schiff bases, Oriental Journal of Chemistry, Vol. 16, pp. 553-556, 2000.
- [31] Z. H. Chohan, Hassan, H. Pervez, A. Rauf, A. Scozzafava and C. T. Supuran. Isatin-derived antibacterial and antifungal compounds and their transition metal complexes, Journal of Enzyme Inhibition and Medicinal Chemistry, Vol. 17(2), 2000.
- [32] S. Pandeya, D. Sriram, G. Nath, and E. DeClercq. Synthesis, antibacterial, antifungal and anti-HIV activities of Schiff and Mannich bases derived from isatin derivatives and N-[4-(4'-chlorophenyl) thiazol-2-yl] thiosemicarbazide, European Journal of Pharmaceutical Sciences, Vol. 9, pp. 25-31, 1999.
- [33] S. Sridhar, S. Pandeya, and E. De Clercq. Synthesis and anti-HIV activity of some isatin derivatives, Bollettino Chimico Farmaceutico, Vol. 140, pp. 302-305, 2001.
- [34] I. Cohen, N. Rist and C. Duponchel. Synthesis and antituberculosis activity of thiocarboxamide derivatives of schiff bases, Journal of Pharmaceutical Sciences, Vol. 66, pp. 1332-1334, 1977.
- [35] W. Singh and B. Dash. Synthesis of some new schiff bases containing thiazole and oxazole nuclei and their fungicidal activity, Pesticides, Vol. 22, pp. 33-37, 1988.
- [36] R. Pignatello, A. Panico, P. Mazzone, M. Pinizzotto, A.Garozzo and P. Fumeri. Schiff bases of N-hydroxy-N-aminoguanidines as antiviral, antibacterial and anticancer agents, European Journal of Medicinal Chemistry, Vol. 29, pp. 781-785, 1994.
- [37] L. Guofa, S. Tongshun and Z. Yongnian. Infrared and Raman spectra of complexes about rare earth nitrate with schiff base from o-vanillin and 1-naphthylamine, Journal of Molecular Structure, Vol. 412, pp. 75-81, 1997.
- [38] Das, T. Choudhury, G. Das, D. Chowdhury and B. Choudhury. Comparative studies on largicidal activity of some schiff bases with Correspondian Amines. Chemistry Environmental Review, Vol. 3, pp. 19-23, 1994.
- [39] F. Sparatore, G. Pirisino, M. Alamanni, P. Manca-Dimich and M. Satta. Azomethine derivatives with anti-inflammatory activity, Bollettino chimico farmaceutico, Vol. 117, pp. 638-651, 1978.
- [40] J. Wen and G. L. Wilkes. Organic/inorganic hybrid network materials by the sol-gel approach, Chemistry of Materials, Vol. 8, pp. 1667-1681, 1996.
- [41] S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian. A review of potentially low-cost sorbents for heavy metals, Water Research, Vol. 33, pp. 2469-2479, 1999.
- [42] Cochrane, S. Lu, S. Gibb and I. Villaescusa. A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media, Journal of Hazardous Materials, Vol. 137, pp. 198-206, 2006.
- [43] G. Nakhla, A. Lugowski, J. Patel and V. Rivest. Combined biological and membrane treatment of food-processing wastewater to achieve dry-ditch criteria: pilot and full-scale performance, Bioresource technology, Vol. 97, pp. 1-14, 2006.
- [44] B. E. Reed, W. Lin, M. R. Matsumoto and J. N. Jensen. Physicochemical processes, Water environment research, Vol. 69, pp. 444-462, 1997.
- [45] G. V. Myasoedova, S. B. Savvin and E. Blasius. Chelating sorbents in analytical chemistry. Critical Reviews in Analytical Chemistry, Vol. 17, pp. 1-63, 1986.
- [46] G. Myasoedova and S. Savvin. New chelating sorbents and their analytical application, Zhurnal Analiticheskoj Khimii, Vol. 37(3), pp. 499-519, 1982.
- [47] Chow and H. Gesser. Preconcentration of Trace Metals from Aquatic Environmental Samples, Hazard Assessment of Chemicals: Current Developments, Vol. 1, 1981.
- [48] R. S. Murthy, J. Holzbecher and D. E. Ryan. Trace element preconcentration from aqueous solutions on a solid phase. Reviews in Analytical Chemistry, Vol. 6, pp. 113-150, 1982.
- [49] C. Xiong and C. Yao. Study on the adsorption of cadmium (II) from aqueous solution by D152 resin, Journal of Hazardous Materials, Vol. 166, pp. 815-820, 2009.
- [50] N. V. Deorkar and L. L. Tavlarides. Zinc, cadmium and lead separation from aqueous streams using solid-phase extractants, Industrial and Engineering Chemistry Research, Vol. 36, pp. 399-406, 1997.

[51] M. Nadeem, I. Tan, M. Haq, S. Shahid, S. Shah and G. McKay. Sorption of lead ions from aqueous solution by chickpea leaves, stems and fruit peelings, Adsorption Science and Technology, Vol. 24, pp. 269-282, 2006.



Shazia Naheed is working as an Assistant Professor at the Department of Chemistry, University of Wah. She completed her PhD in Chemistry from Bahauddin Zakariya University Multan in 2016. Her research interests include Synthesis, Characterization and Applications of Organic-Inorganic Hybrid Materials.



Alina Changez received the degree of MS Chemistry from University of Wah, Wah Cantt. in 2017. Her research interests include Synthesis, Analysis and Applications of Organic-Inorganic Hybrids and Inorganic hybrid Polymeric Materials.



Rana Muhammad Talal received the degree of MS Chemistry from University of Wah, Wah Cantt. in 2016. His research interests are Organic Synthesis, Synthesis of Organic-Inorganic Hybrid Materials, Characterization and Applications.



Ghulam Zakria did PhD from the University of Science and Technology, China. Currently he is working at Advanced Engineering Research Organization, Wah Cant. His Research interests include Surface Studies of Porous Materials.



University of Wah Journal of Science and Technology

www.uow.edu.pk



Development of UAV Octocopter Based on Pesticides Spraying System

Syed Shakir Hussain Shah, Ammar Ul Hassan Khawaja, Waqas Javid, Rehan Tahir Ul Hassan, Awais Ahmad and Muhammad Ahmad

Abstract—The application of pesticides in agriculture has a leading role in increasing the per acre yield of different crops. There are a number of systems through which pesticides can be sprayed on crops. Unmanned aerial vehicles (UAVs) are being progressively used for this purpose due to their improved efficiency and high-speed characteristics. This research work mainly focuses on the construction of an octocopter based on the idea of UAVs for the agriculture sector. The implementation of octocopter for spraying chemicals is prominently increasing to minimize the wastage of pesticides while increasing the production of crops. This research also strives to minimize the spraying time, labor cost and weight of the octocopter for its better utilization and implementation in the field of agriculture. The flight test showed that the octocopter is useful, efficient and beneficial for the intended application.

Index Terms—Octocopter, Spraying UAV, Agricultural pesticides

I. INTRODUCTION

NMANNED aerial vehicle (UAV) has become less costly due to advancements in the software technology and reduction in the cost of hardware [1]. An unmanned aerial vehicle is basically a human operated vehicle through a remote control. Nowadays, the unmanned aerial vehicles are being used in many fields of daily life such as: agriculture, search, rescue operations [2], traffic surveillance, security, military and police [3], firefighting [4], and during live coverage of different outdoor events by different TV channels. UAVs have the ability to reach such places which are generally impossible for human beings [5].

Manuscript received September 8, 2017; accepted June 22, 2018.

(email:awaisahmad95@gmail.com) and Engineering, University of Wah, Wah Cantt, Pakistan.

(email:ammarkhawaja35@gmail.com),W.Javid(email:waqas.javid@wec uw.edu.pk), R.T.U Hassan (email: Tahirrehan99@gmail.com), A. Ahmad mahmed095@hotmail.com) are affiliated with Department of Mechanical

S.S.H Shah (email: Shakirshah 788@hotmail.com), A. H. Khawaja

Corresponding author Email: Shakirshah788@hotmail.com

Depending on the load to be carried, different, different amendments are made in copters. Nowadays, a multi-rotor vehicle, embedding a remote controlled system, has the ability to carry a load of about two kilograms [6]. UAVs have ability to takeoff vertically, landing, hovering and moving carefully and skillfully.

The octocopter can take off and land vertically, which relates it to the group of the multi-rotor helicopter. In helicopter, fixed-pitched blade is used with rotor, while in multi-rotor vehicle's pitches do not change as in the case of blade rotors. First multirotor dragon flyer was manufactured around 2000 [7]. The star shape configuration of an octocopter is the best to carry the maximum amount of payload [8].

This paper proposes agriculture based application through an octocopter where it is responsible for spraying chemicals on crops fields. In the agriculture sector, UAVs are mostly used for cultivation, production, protection and spraying purposes. The octocopter is generally selected because of its higher stability and maximum payload carrying ability [9]. The spraying of chemicals is controlled through wireless sensors.

The World Health Organization (WHO) estimated that every year more than one million cases of deaths while spraying pesticides are registered. The World Health Organization (WHO) estimated that every year more than one million case of deaths are register with pesticides spraying and it also effect the yield of former and economy of country as well. [9].

The main objective of this research is to reduce spraying time on crops as compared to conventional spraying systems and labor cost. This also increases the efficiency of spraying.

Basically, the idea of an octocopter was presented by Joo et al. [8] but they did not implement it practically. This research is, therefore, focused on the fabrication of a low weight octocopter and its implementation in the field of agriculture. Table I shows the overall literature study related to UAV Octocopter based on Pesticides' Spraying System.

TABLE I RESEARCH MATRIX

Reference	Researcher	Туре	Resear Purpo		The weight of Designed Copters
				sign cation	kg
[1]	Girard et. al	Quadcopter	✓	✓	3
[2]	Penga et.al	Helicopter	✓	✓	5
[3]	Pound. et.al	Quadcopter	✓		2
[4]	Mc Kerrow et.al	Quadcopter	✓	✓	4
[5]	Casbeer et.al	Quadcopter	✓		4
[6]	Rayana et.al	Quadcopter	✓	✓	3
[7]	MIT Technology Review	Quadcopter	✓	✓	4
[8]	Joo et.al	Octocopter	✓	-	5
[9]	Gandhi et.al	Quadcopter	✓	✓	4
This Research	Shah et. al	Octocopter	-	✓	3.8

II. WORKING PRINCIPLE AND SYSTEM DESCRIPTION

The Octocopter developed during research work has eight rotor propellers in which four rotates clockwise (CW) and four counterclockwise (CCW). The eight rotors produce different thrust and octocopter hovers and moves according to these motors. Basically, one motor produces a thrust of 1400g and the total thrust produced is, therefore, 11200g. Due to eight rotors plus (+) and star (*), both configurations are used in octocopter. The Octocopters have more lifting capacity and redundancy. They are very popular in carrying heavy payloads and for higher stability. According to safety aspect if copter is high in the sky carrying some expensive camera equipment it is good to have extra protection in case of crash landings.

The system, developed during this research, consists of the mechanical and electrical structures.

A. Mechanical Structure

The mechanical structure consists of frame and propellers. Frame is the basic element for any multirotor because it holds all the components together. If there is vibration or instability in the frame the flight would not be smooth and if the frame is stable and well-designed then it would be easy to move, hover and fly a multirotor.

The frame of an octocopter should be rigid and has the capacity to reduce vibrations produced by brushless motors. In octocopters, the frame is usually large as compared to quadcopter and hexacopter. The frame of an octocopter is star shaped because of its stability

requirements [8]. Its arms are made of Aluminum rods because of its higher strength and lower cost.

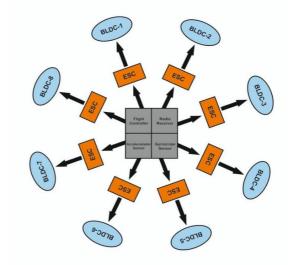


Fig. 1. The physical structure of the system.

The Aluminum is compared with steel and carbon fiber. Steel is lesser in cost but heavier in weight whereas carbon fiber is even more costly but lighter in weight. So, Aluminum is the better option for arms because of lower weight and lesser cost. The length of each rod is 38cm. Total diameter of developed octocopter is 89cm and its weight is 916g excluding electronics. Every arm is equal in length and at an angle of 45 degrees to another adjacent arm [8]. The base and motor mount are made of fiberglass because of higher stiffness and lower weight as compared to carbon fiber which is comparatively more expensive though lighter in weight. The base consists of battery pads, landing gears, controlling pads and legs.

Propellers are the type of fans which convert rotational motion into thrust. Propellers of a multirotor of quadcopter have different diameter and pitch scales; 10 (inch) * 4.7 (inch), 10 (inch) * 4.5 (inch) etc. A multirotor travel according to its pitch. An octocopter has eight propellers, four normal propellers, and four pushing propellers. For counter motor torque, octocopter use four clockwise propellers and four counterclockwise propellers. Normal propellers spin counter-clockwise and pushing propellers spin clockwise. Propellers used in the octocopter, developed here, are 10 (inch) * 4.5 (inch) which is according to the distance between its arms. 10 (inch) is the length of propeller and 4.5 (inch) is its pitch. Propellers are of low weight type made of nylon. Propellers made of nylon are of higher strength as compared to wood and carbon fiber, and also lower in cost. All the propellers used in the octocopter, developed during this research, are of the same diameter and pitch.

B. Electrical Structure

The electrical structure consists of the following components:

Transmitter and receiver having different components like the fly sky, FS-T6 transmitter with receiver, 6 channels, 2.40-2.48Hz range, 12V power DC (1.5A * 8)

and an antenna having length of 26mm. The reason of using specified transmitter is due to its higher range and ease of operation. Fly sky transmitters are lesser in cost and recommended for multirotor vehicles as shown in *Fig.* 2.

BLDC motor is also called electronically commutated motors as shown in *Fig. 3*. It is run by a DC source. It provides higher amount of torque as compared to its weight thus having: higher efficiency, lesser noise, longer battery life and higher reliability. The size of BLDC motor is compact as compared to servo and stepper motors. Also, in comparison to stepper and servo motors the BLDC motors have higher RPM, higher efficiency, lesser power consumption and produce lesser amount of vibrations. The BLDC motor used in the octocopter, developed during this research, operates at 10V or 0.4A and at 8000 rpm it produces a thrust of 1400g through propellers having dimensions of 10 (inch) * 4.5 (inch). The weight of BLDC motor used in research work is 63g.



Fig. 2. Transmitter and receiver.



Fig. 3. Brushless motor.

Electronic Speed Controller (ESC) controls the BLDC motors as shown in *Fig. 4*. Microcontroller gives signal to ESC that converts this signal to BLDC motor. In this octocopter 8 ESCs and 8 BLDC motors are installed. The signal's frequency of all ESCs changes by controlling them independently. The selection of ESC is dependent upon the selected according to motor discharge rate of the motor. It receives a maximum current of 40A and gives a burst current of 50A for 10s to the motors. The weight of the electronic speed controller used is 43g.



Fig. 4. Electronic speed controller.

Accelerometer is used to measure the acceleration as shown in *Fig. 5*. It senses the gravitational force. The octocopter, developed during this research, uses an accelerometer MPU-6050 that has different features e.g. current required for normal operating conditions is $500\mu A$, whereas other accelerometers require different amounts of current i.e. 1.25 Hz take $10\mu A$, 5 Hz take $20\mu A$, 20 Hz take $60\mu A$, 40 Hz take $110\mu A$. In addition to current requirements the other features are signaling and orientation detection, self-testing by a user, integrates 16-bit ADC and sits full-scale range is $\pm 2g$, $\pm 4g$, $\pm 8g$, $\pm 16g$. The MPU-6050 works in 6-9 axis, the input voltage is very low 2.3 V-3.4 V and also have a digital output sensor.



Fig. 5. Accelerometer sensor.

Gyroscope sensor is used to increase the stability of multi-rotors. It controls the angular velocity and angular speed. The gyro-sensor, used in the octocopter, is having a size of $36\times36\times11.5$ mm, weight of 8.6g, input voltage of 4.8-6.0V and receiver signal of 1520us (5 channels). It is used for increased stability in every axis.

The battery used here is Lipo (5000mAh-40C) which is lithium based and is therefore mostly preferred as shown in *Fig. 6*. Its energy to weight ratio is higher as compared to other types. However, before using, it should be charged properly. The battery used here has the capacity of 5000mAh with a discharge rate of 25. The weight of this Lipo battery is 520g. It gives a power output of 88 watts per hour. While operating eight BLDC motors, the 5000mAh battery takes about 15 minutes to completely discharge.



Fig. 6. Lipo battery.

III. SOFTWARE DESCRIPTION

Arduino with open source software is used for controlling the speed and direction of the motors in the developed octocopter as shown in *Fig.* 7.

Arduino is a microcontroller-based kit which basically is used for communications and controlling/operating many devices.

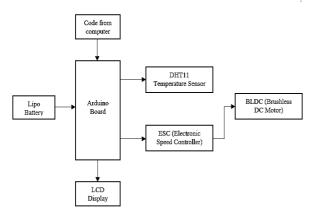


Fig. 7. Block diagram to control the motor speed.

It consists of two memories - program memory and the data memory. The code is stored in the flash program memory, whereas, the data is stored in the data memory. When the program starts it gets information, saved in the program memory, and then compiles it and gives a useful response or re-evaluates it. An LCD display, attached to the Arduino board, displays temperature and variations in speed of DC motor with respect to temperature. Temperature sensor (DHT11) is used to detect the temperature and humidity of the surroundings and display it on the LCD. DHT11 uses the temperature difference to produce a voltage signal which is processed by the Arduino to give a digital output displaying the temperature of the given surrounding. An ESC, connected with the Arduino board, is used to control the speed of the Brushless DC motor.

IV. PESTICIDES SPRAYING MECHANISM

The mechanism, developed here, uses a tank that has a capacity of 3000 ml and connected to a 12V DC pump. The pump is further connected to the battery. Also, a set of mini nozzles (switchable) is also fitted with the end pipes. Different nozzles are used for different crops, so it can be changed as per requirement. When the pump is operated, spray starts. To avoid wastage of pesticides, a balanced pressure is maintained throughout.

V. FABRICATION PROCESS

The main components used in fabrication are brushless direct current motors. The other component used is electronic speed controller (ESC), which generates different signals of high frequency. ESC is controlled to keep the motors running. It increases the power to supply enough current to motors. Aluminum rods of 38 cm are used in the developed octocopter structure. The Aluminum

is selected because of its higher strength and durability. These Aluminum rods are attached to the fiberglass frame. The total width of octocopter is 89 cm, height from the ground is 21cm and its weight is 915g. The next component used is an accelerometer sensor which measures the acceleration and gravity. It also senses the device's orientation. The other component used is the gyroscope sensor which measures the rotational speed around the 3 axes. It also controls the device and keeps the drone safe. Basically, it provides a smooth flight. Finally, a lipo battery is connected that consists of different cells (1-10) 4S1P, commonly suitable for octocopter which supplies the power of 14.8V.

MENG JOO [8] described that star shape configuration of an octocopter is best to carry a maximum amount of payload. Keeping that in view, a star-shaped octocopter is fabricated to carry maximum payload, as shown in *Fig.* 8. Basic task is to spray on a one-acre field with the help of the octocopter. To evaluate its power and performance three tests are carried out, one ground test and two flight tests. The ground test is to verify the stability of the software system, evaluate the endurance of the power system and the wireless communication range.

VI. TESTING OF DEVELOPED SYSTEM

During the ground test motors are governed to normal RPM and propellers are not installed for safety consideration. After the ground test, two flight tests are conducted to evaluate the power and performance of octocopter. The test of UAV is manually controlled by a skilled pilot. In both flight tests, the target of spraying in one-acre field is achieved easily which showed that the star-shaped design is best in all aspects of increasing payload, performance, and stability. At a minimum and maximum speed, the test results are shown in Table II.

TEST RESULTS					
Speed (m/s)	Coverage of Coverage Rate sprayer (m) (acre/ hour)				
		CR	Average CR		
4.71	1.5	6.32	6.235		
4./1	1.5	6.15	0.233		
18.8	1.5	23.25	24.18		
10.0	1.5	25.11	24.10		

TABLE II



Fig. 8. Octocopter fabricated structure.

After the flight tests, it is determined that during a minimum speed of 4.71 m/s the coverage rate is 6.235 acres/hr and at a maximum speed of 18.8 m/s, the 24.18 acres of land is sprayed in 1 hour. After these results, it is cleared that 1 acre of land can be sprayed easily within 2.5 minutes

VII. CONCLUSION

This research work has introduced the use of UAVs in the field of agriculture for the purpose of spraying pesticides on crops spread over large area of land. Based on this idea the use of UAVs can also be expanded to other aspects of life like: military, firefighting, sports etc. Another point, which can broadly be concluded from this research, is that the use of octocopter can actually save human lives by keeping them away from the harmful effects of chemicals and pesticides. By using UAVs, crops in the fields can also be saved by the beating they normally receive when the same task is completed with the help of heavier machines driven by tractors. Developed system also shows that the octocopter is useful in reducing the spraying time and labor cost when implemented in the field of agriculture.

The flight time of an octocopter is about 10 minutes on lipo battery. For future work, lipo can be replaced by a solar power to increase the timing of octocopter. The spraying of pesticides depends on the number of pesticides to be sprayed. In future, the spraying UAVs can be controlled with the help of Android mobiles. By using universal nozzles powder pesticides can also be sprayed. Carrying of the payload can be increased by changing material of UAVs.

REFERENCES

- C. Anderson. Agricultural Drones: Relatively cheap drones with advanced sensors and imaging capabilities are giving farmers new ways to increase yields and reduce crop damage. MIT Technology Review, Vol. 17, pp. 3-58, 2014.
- [2] A. Ryan and J. K. Hedrick. A mode-switching path planner for UAV assisted search and rescue. Proceedings of the 44th IEEE conference on decision and control, 2005.
- [3] A. R. Girard, A. S. Howell and J. K. Hedrick. Border patrol and surveillance missions using multiple unmanned air vehicles. Proceedings of the 43rd IEEE conference on decision and control, Atlantis, Bahamas, 2004, pp. 620-625.
- [4] D.W. Casbeer, D.B. Kingston, R.W. Beard and T.W. McLain. Cooperative forest fire surveillance using a team of small unmanned air vehicles, International Journal of Systems Science, Vol. 37(6), pp. 351–60, 2011.
- [5] K. Penga, G. Cai, B. M. Chenb, M. Dong, K. Yew Luma and T. H. Leeb. Design and implementation of an autonomous flight control law for a UAV helicopter, Automatica, Vol. 45(10), pp. 2333–2338, 2009.
- [6] P. Pounds, P. Mahony and R. Corke. Modelling and control of a quadrotor robot. Proceedings of the Australasian Conference on Robotics and Automation, Auckland, New Zealand, 2004.
- [7] P.J. McKerrow. Modelling the draganflyer four-rotor helicopter. Proceedings of the International Conference on Robotics and Automation, Orleans, 2004, pp. 3596-3601.
- [8] J. E. Meng, S. Yaun and N. Wang. Development, control and navigation of octocopter. Proceedings of the 10th IEEE International Conference on Control and Automation, 2013, pp. 1639-1643.

[9] N. Gandhi and B. E. Raj. Quadcopter UAV Based Fertilizer and Pesticide Spraying System, International Academic Research Journal of Engineering Sciences, Vol. 1(1), pp. 8-12, 2016.



Syed Shakir Hussain Shah completed his Bachelor degree in Mechanical Engineering from the University of Wah, Wah Cantt., Punjab, Pakistan in 2017. Currently, he is working with a private company as a Site Engineer.



Ammar ul Hassan Khawaja is a Ph.D. scholar at University of Engineering and Technology, Taxila. He received the degree of MS Mechanical Engineering from University of Wah, Wah Cantt., Pakistan in 2016. His research interests include high strength low alloy (HSLA) materials and Optimization of machining processes.



Waqas Javid completed his Bachelor degree in Mechanical Engineering from the University of Wah, Wah Cantt., Punjab, Pakistan in 2015. Currently, he is pursuing Masters in Mechanical Engineering from University of Engineering and Technology, Taxila. He is working as a Lab Engineer in Mechanical Engineering Department at Wah

Engineering College, University of Wah, Wah Cantt., Pakistan.



Rehan Tahir Ul Hassan completed his Bachelor degree in Mechanical Engineering from the University of Wah, Wah Cantt., Punjab, Pakistan in 2017. Currently, he is working as Mechanical Engineer in Daelim Industrial Co. Ltd.



Awais Ahmad completed his Bachelor degree in Mechanical Engineering from the University of Wah, Wah Cantt., Punjab, Pakistan in 2017. Currently, he is pursuing Masters in Engineering Management from the University of Management and Technology Lahore and also working with a private company as a Production Engineer.



Muhammad Ahmad completed his Bachelor degree in Mechanical Engineering from the University of Wah, Wah Cantt., Punjab, Pakistan in 2017. Currently, he is working with a private company as an HVAC Site Engineer.