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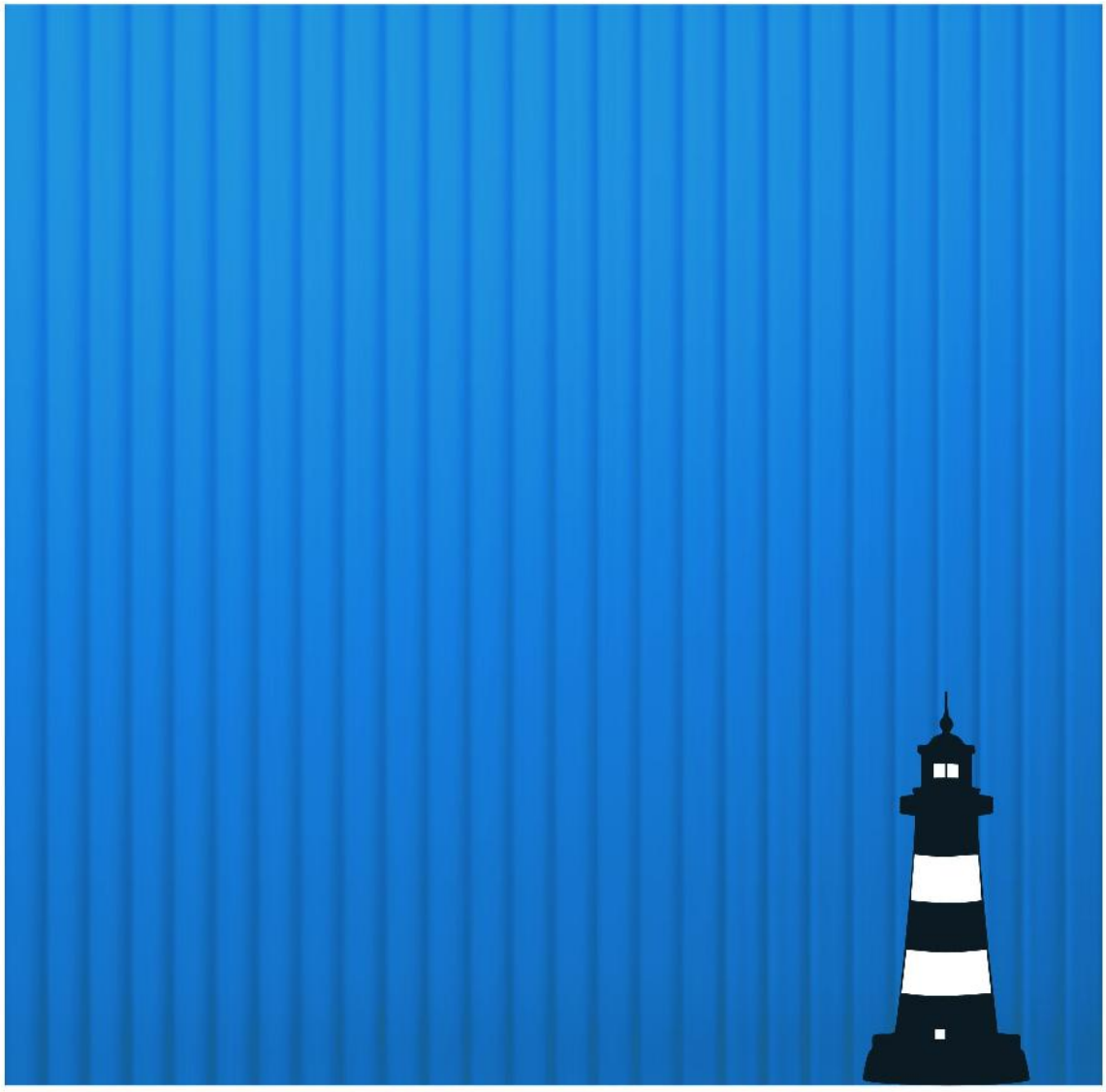

Khyber Pakhtunkhwa Higher Education Academy of Research and Training (HEART)

Message from Patron in Chief

Khyber Pakhtunkhwa Higher Education Academy of Research and Training (HEART) successfully added to the professional capabilities of Associate professors, Assistant professors and Lecturers of the Higher Education Department by imparting quality trainings on updated modules to meet the academic challenges inside the classrooms. Nevertheless, no stone is left unturned to enhance the capacity of DDOs and ministerial staff working in offices at government colleges across Khyber Pakhtunkhwa. The continuous pursuit to excel in the area of training has made HEART a topping professional training institution in KP. Despite the monumental achievements in the area of training however, was deemed unaccomplished as this august academy confronted a demand of initiation of academic research by virtue of the spirit of its act.

An effective Research Wing has been established to look into the intellectual and academic challenges in government colleges and to suggest redressal measures to the government. The Research Wing conceived the idea of *The Lighthouse*, a word suggestive of paving a way forward to the budding creative college faculty and to further glitter the bloomed researchers. The Research Wing tirelessly worked day and night to bring into light the present issues of *The Lighthouse Journal of Literature and Linguistics*, *The Lighthouse Journal of Social Sciences*, *The Lighthouse Journal of Natural Sciences* and *The Lighthouse Journal of Computational and Numerical Sciences*. This is a milestone achievement by the research wing of the academy to provide a first ever forum to the college teachers to get their quality research papers published in journals of their own. This valued contribution by the Research Wing of HEART is also the first ever distinguished endeavor among the four provinces. It is further envisioned to invite researchers from college teachers of other provinces to seek benefit from HEART by publishing their best articles and research papers in the light shedding *The Lighthouse*.

I share the pride of this moment with Ms Seema Rahman, Deputy Directress Academics and Chief Editor of *The Lighthouse* journals, and Mr. Imran Mohsin, the Managing Editor of *The Lighthouse Journal of Natural Sciences*. I am fingers crossed to seeing *The Lighthouse* comes up to gleam and twinkle from afar to the light seekers from all across the country.

Prof. Tasbih Ullah

Director HEART

Patron in Chief

Khyber Pakhtunkhwa Higher Education
Academy of Research and Training (HEART),
Sector F-2, Phase-6, Hayatabad, Peshawar.
+92-91-5863654, hetta.kp@gmail.com

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The Ethno-medicinal Study of Plants locally utilized in District Karak Khyber Pakhtunkhwa Pakistan

Roohul Amin[1], Paris Arshad[2], Sana Ullah[1], Ziarat Shah[3]

ABSTRACT

In this work, 47 plants having medicinal importance of 24 families were collected during summer and winter season. The detail about their scientific, local and family name, parts utilized and medicinal importance are discussed. These plants are not only used in specified area of district Karak but are also used throughout Khyber Pakhtunkhwa (KP) and Pakistan .The knowledge of their usage and importance is transferred to coming generations. The utilization of different medicinal plants by various age groups is tabulated and summarized. It showed that use and significance of herbal medicines by various age groups is more than 70%, as it is clear from the figure given in text. Whereas over all usage of medicinal plants is more than 50%, this showed the importance and primary health care of medicinal plants. Medicinal plants are often focused for ethno-medicinal studies as well as for primary first aid. The earlier study is the pathway towards the discovery of new medicines. Further, it is also a valuable heritage of the local population of the area which may be conserved and recognized, as they are playing a vital function for primary health safety and care.

Keywords: *Ethno-medicinal study, Medicinal Plants, Primary health care, First aid and Herbal medicine*

INTRODUCTION

The word medicinal plants are used for those plants which are used for the treatment of some particular disease. Medicinal plants play an important role for the cure of various ailments [1]. It is claimed that around 4,22,000 flower plants noted worldwide, among them 50,000 show medicinal importance [2]. These herbal assists give cultural based valuable and relevant source for initial health care for the most of people [3]. Now these indigenous medicinally important plants are known across the world for healthcare. WHO reported that conventional medicinal plants are significant sources for health care [4].Pakistan Forest Institute surveyed and according to their report about 75 unfinished

[1]Assistant Professor of Chemistry, Government College Peshawar, Pakistan, **Corresponding Author's Email: roohulamin1947@gmail.com,**
[2]Govt. Post Graduate College Karak, Pakistan
[3]Institute of Chemical Sciences, University of Peshawar, Pakistan

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herbal medicines are exported expansively and 200 plus are traded inside Pakistan. These crude herbal plants material costs round about 150 million rupees annually inside Pakistan, including majority of such plants are acquired from natural and rural areas of the country [5].

There are 6,000 plus species of privileged plants in Pakistan, including 600-700 medicinal species [6]. These herbal plants provide a greater source of structural based biodiversity in the shape of a mixture of natural bioactive products, playing an important role in drug discovery [7]. Since many plants are also utilized as food besides their medicinal worth, whereas the metal content of such plants is helpful for understanding of their suitability [8]. Most of the research in Pakistan is limited up to documentary level. However nowadays the research activities is carried out mostly in universities and some institutes based on ethno-botanical importance of medicinal plants. The local people of various areas of Pakistan have years old expertise about conventional usage of herbal plants of their regions. This native and old awareness of herbal plants is transferred to newly coming generation from their parents. Such herbal plants are utilized for the treatment of different diseases from simple headache to stomachic pain and from simple cuts to chronic infections etc. [9].

The important aim of this work is recording the significance and application of medicinal plants. Mostly for initial health care, 80% of the world people are dependent on conventional medicines [10].The local community of any area have sound awareness about the utilization of medicinal herbs and other plants. As compared to costly pharmaceutical drugs, local population usually gives preference to medicinal plants for the treatment of ailment due to its low cost and availability [11]. Modern pharmacopoeia has 25% of the drugs that come from plant origin, while more than 121 active compounds of synthetic analogue are obtained from natural precursors.

However, importance of herbal plants may not be under estimated as they have significance without major side effects [12].These herbs have significant components and the knowhow about their usage is considered as a part of cultural heritage [14]. These plants are also good source of income for the local people as well as for the business purposes however unfortunately there is no gardening of such plants in our country [15]. Medicinal plants are often focused for ethno-botanical studies while the past work has given very promising guidelines for the discovery of new medicines [16].The purpose of this work is exploration, identification and application of these natural assists, for the benefit of mankind.

Introduction about area &habitat for the accessibility of Medicinal plants

The present project of our research is based on medicinal plants in District Karak Khyber Pakhtunkhwa (KP). The Karak district is situated on west of district Bannu and Lakki Marwat and western side of Kohat. This area is 123 km from Peshawar on the main highway to Karachi. It is situated at 33.1277^{o}N and 71.0973^{o} E, comprising of total area of 3,372 square kilometer containing population of 536000 persons approximately. The climate of the area is semi-arid with very cold winter and hot summer. The rainfall in this area is insufficient and mostly uncertain.

The winter raining is usually of low concentration and long duration. The average soil temperature remains in the range of 21.87^{o}C to 26.37^{o}C in summer and low down in winter. There are three tehsils (major administrative areas) in this district including Karak, Banda Daud Shah and Takht-i- Nasrati.

The income source of the people is based on rain fed agriculture as canal system is not present in this area. The hills are dry and containing sources of valuable minerals like uranium, coal, salt, oil and natural gas etc. Oil and gas reservoirs are also found in Gorgerin, Nashpa Banda and Makori town. Besides these, irrigation resources are little, which is a constant problem; however wells (tube wells, dug wells) and manual pumps are utilized for irrigation purposes in some places, whereas most of the area is rain dependent. There is constant problem of drinking water which is brought by people from far-flung distances. The available water is salty and unhygienic as in Tarkhaal Ganda. Small storage dams are constructed at Sarki Lawagar and Zibe dam for storing rain and stream water.

The aim of this study was to identify medicinal plants and explore their uses, to enlist the indigenous medicinal plants used by local people for common ailments and to raise the plant conversation issue of the study area.

METHODOLOGY

Collection of medicinal plants

Some trips were arranged to 8 different places of district Karak (KP), Pakistan for collection of significant medicinal plants during Academic Year 2015. Almost about 40 medicinal plants were collected from different areas.

Identification and Drying

In this work various samples of medicinal plants were collected from different areas of district Karak (KP). In the second step, these plants were pressed by wooden blocks. Later on, these plants were kept inside a newspaper and pressed for dryness. After about 5-8 days they were pressed on herbarium sheet and dried.

Exploration of curative plants

The exploration of curative plants was not an easy task, for this purpose important guidance for collection of plants and location of area was gotten from related office in district Karak (KP). A performa was designed to explore the medicinal plants in particular area and different information like local and botanical name, family name of plant, portion used as medicine were tabulated as given below in results and discussion portion. These plants are not only used in specified area district Karak (KP) but these are used throughout Khyber Pakhtunkhwa and Pakistan, further knowledge of their utilization and importance is transferred from generation to generation.

DISCUSSION AND ANALYSIS

In this work, 47 plant species having medicinal significance of 24 families were collected during summer and winter season. The knowledge about their scientific, local and family name, part utilized and their medicinal importance are listed in tables 1-3.

Table1. Medicinally Important Flora (Leaves and Stem) of District (Karak)

Local Name	Botanical Name	Family	Medicinal Use for treatment
Ghaz	Tamarixarticulata	Tamaricaceae	Used for flu and tetanus and against smallpox
Spalmaka	CaltropisProcera	Asclepiadaceae	Headache, stomach ulcer, fever and cough while flower are used for throat infection
Ganderi	RhazyaStricta	Apocynaceae	Leaves & Roots used as blood purifier, A brush made from root known as **Miswak** used for the cleaning of teeth, Roots are used for treatment of snake bite and sugar disease.
Aspalagzia	Fogoniacretica	Zygophyllaceae	Blood purifier and for treatment of skin rashes during sugar disease
Velana	Menthapiperata	Lamiaceae	Dry leaves are used for treatment of diarrhea and vomiting
Bobarai	OcimumBasilicum	Lamiaceae	Flower used for ear pain and for opening of periods and for ornamental purposes
Green Tea	Comellia vulgare	Theaceae	Dry leaves are used for weight loss and for digestion
Makko	Solanum nigrum	Solanaceae	Leaves are cooked as sag type & used for treatment of sugar disease
Bhang	Cannabis Sativa	Cannabaceae	Cough & flu, the leaves of C-Staiva are mixed with green tea and used for coldness
Zergia	Aloe vera,Aloebarbadensis	Liliaceae	Leaves are used for beauty, burns cuts wound and skin care.

Table 2. Medicinally important Flora (Fruits)of District (Karak)

Local Name	Botanical Name	Family	Medicinal Use for treatment
Bare	ZizyphusJujuba	Rhamnaceeae	Used for constipation
Shopyanga	Withaniacoagulans	Solanaceae	Abdominal problem such as stomach & intestinal gas problem
Doda,Tobacco	Nicotinatobacum	Solanaceae	Cough and flue
korkaman	Curcummalong	Zingiberaceae	It is used for knee and back pain while also used for healing of wounds.
Toormrch	Piper nigrum	Piperaceae	It is used for digestion and for cough, flue during coldness

Lemon	citrus limonum	Rutaceae	Low blood pressure patient, beauty, facial care, herbal steam, herbal teas
Shoon, Zeeton	Oliaeuropia Olea cuspedata	Oleaceae	Fruit used for sugar disease and also as blood purifier, oil used for knee joint pain and for hair
Amrood	Psidium guajava	Myrtaceae	Used for constipation & diarrhea while its juice is also used for stomach problem
GadarhNali	Casia fistula	Fabaceae	Used for baby belly pan
Kareela	MomordicaChararntia	Cucurbitaceae	Juice used for sugar disease
Pamanka	Carolluma edulis	Apocynaceae	Whole plant is used for sugar disease
Palosa, Kanrh	Acacia modesta	Fabaceae	Its plant resin is used for back pain
Carrot	Daucus Carota	Umbelliferae	Used to improve eye sight also used for face care
Annar	PunicaGranata	Rosaceae	Peel is used for abdominal problem
Shawtala	Trifolium repens	Fabaceae	Seeds powder form used for vomiting
Lemon grass	Cymbopogoncitratus	Poaceae	Whole plant is used for digestion, and for Weight loss without sugar
Muli	Raphanus sativus	Brassicaceae	Seeds used for weight loss
Sponda/Syrian	Peganum	Zygophyllaceae	Its leaves and seeds are used for insecticidal effects & for tetanus
Sungara	Acacia senegal	Leguminoseae	Acacia gums are used for cough, throat problems

Table3. Medicinally Important Flora (Seeds) of District (Karak)

Local Name	Botanical Name	Family	Medicinal Use
Ispaghual	Planta Goovota	Plantaginaceae	Seeds are used for diarrhea, relieves constipation, reduce blood cholesterol, effective for acidity and stomach problem.
Sperkiye	Plectranthusrogosus	Lamiaceae	Used for Menstrual Problem and given to animal like goat after delivery.
Sonaf	Foeniculum vulgare	Umbelifers	It is used for digestion and also for baby belly pain
Kalvanjee	Nigella Sativa	Ranunculaceae	Used for weight loss
Shoon, Zeeton	Oliaeuropia Olea cuspedata	Oleaceae	Fruit are used for sugar disease and blood purifier, oil used for knee joint pain and for hair
Sharsham	Eruca Sativa Mill	Brassicaceae	Massage for body and hair and for baby massage
Ooza	Allium satium	Alliaceae	Its blub are used to reduce blood pressure
Piaz	Allium cepa	Alliaceae	Its blub is used for finger pimples
Kunzaly	Sesamum indicum	Pedaliacae	Used for urine problem
Elaichi	Elettaria Cardamomum	Zingiberaceae	Used for digestion, cough and flu
Tarkahamarabeej	Citrus Colocunthus	Cucurbitaceae	For abdominal problem or belly pain

Sharsham	Eruca Sativa Mill	Brassicaceae	Used for massage of body and hair
Elaichi	Elettaria Cardamomum	Zingiberaceae	Used for digestion, cough and flu
Tarkhamarabeej	Citrus Colocunthus	Cucurbitaceae	For abdominal problem or belly pain

In these tables 1-3 different medicinal plants were described along their local, botanical name, family, different parts of plant and their medicinal application. The usage and significance of various medicinal plants in different areas of district Karak are shown in table 4 and 5.

Table 4: Check List of people using different medicinal plants in different areas of Karak district

Botanical names	Taabaikho in sabairabad	Mashere banda	Session court	Lghrib anda	Yaqobi banda	Main karak city	Babal Khel
Tamarixarticulata	0	1	1	0	0	1	1
ZiZyphusJujuba	1	1	1	1	1	1	1
CaltropisProcera	0	0	0	1	1	0	1
RhazyaStricta	0	0	0	0	0	0	1
Withaniacoagulans	0	1	1	0	0	1	0
Fogoniacretica	1	1	1	1	1	1	1
Nicotinatobacum	1	1	1	1	1	1	1
Menthapiperata	1	1	1	1	1	1	1
OcimumBasilicum	0	1	1	0	0	1	0
Plantagoovota	1	1	1	1	1	1	1
plectranthusrogosus	1	1	1	1	1	1	1
comellia vulgare	1	1	1	1	1	1	1
Foeniculum vulgare	1	1	1	1	1	1	1
Curcummalong	1	1	1	1	1	1	1
solanum nigrum	1	0	0	0	0	0	0
Piper nigrum	1	1	1	1	1	1	1
Eruca Sativa Mill	1	1	1	1	1	1	1
Allium satium	1	1	1	1	1	1	1
Allium cepa	0	1	1	0	0	1	0
Aloe vera,Aloebarbadensis	0	1	1	0	0	1	1
citrus limonum	1	1	1	1	1	1	1
Nigella Sativa	1	1	1	1	1	1	1
Oliaeuropia Olea	1	1	1	1	1	1	1

cuspedata							
Psidium guajava	1	1	1	1	1	1	1
Sessamumindicum	0	1	1	0	0	1	0
Casia fistula	1	1	1	1	1	1	1
MomordicaCharantia	1	1	1	1	1	1	1
Carolluma edulis	1	1	1	1	1	1	1
Acacia modesta	0	1	1	0	0	1	0
Cannabis Sativa	0	1	0	0	0	1	0
ElettariaCardanomum	1	1	1	1	1	1	1
CitrullusColocynthus	0	0	0	1	1	0	0
Daucus Carota	1	1	1	1	1	1	1
PunicaGranata	0	0	0	0	1	0	0
Trifolium repens	0	0	0	0	1	0	0
Cymbopogoncitratus	0	1	1	0	0	1	0
Raphanus sativus	0	0	0	1	1	0	0
Acacia senegal	0	0	0	0	0	0	1
Peganum	1	1	1	1	1	1	1

Table 4 showed the usage of different medicinal plants by people in different areas of district Karak. It is concluded from above survey that most of the people prefer herbal medicine (medicinal plants) as first aid or primary health care. Our research showed that people of different ages use medicinal plants as primary health care or medicinal purposes. Table 5 showed various percentage ratios of different age groups and their use about some particular medicinal plants as given below.

Table.5: Percentage of people using medicinal plants

Botanical Name	Old Age People	Middle Age people	Young Age People
Tamarixarticulata	90%	80%	80%
ZiZyphusJujuba	80%	80%	60%
CaltropisProcera	80%	80%	50%
RhazyaStricta	80%	80%	80%
Withaniacoagulans	80%	80%	50%
Fogoniacretica	90%	80%	50%
Nicotinatobacum	90%	80%	50%

Menthapiperata	90%	80%	80%
OcimumBasilicum	80%	80%	80%
Plantagoovota	90%	90%	90%
Plectranthusrogosus	90%	90%	90%
Comellia vulgare	90%	90%	90%
Foeniculum vulgare	80%	80%	70%
Curcummalong	90%	90%	60%
solanum nigrum	80%	80%	70%
Piper nigrum	90%	90%	90%
Barassicacampestris	90%	90%	90%
Allium satium	80%	90%	90%
Allium cepa	90%	80%	80%
Aloe vera,Aloebarbadensis	90%	90%	70%
Citrus limonum	90%	90%	80%
Nigella Sativa	90%	90%	60%
Oliaeuropia Olea cuspedata	90%	90%	90%
Psidium guajava	90%	90%	90%
Sesamum indicum	90%	90%	90%
Casia fistula	90%	90%	80%
MomordicaChararntia	90%	90%	90%
Carolluma edulis	90%	90%	60%
Acacia modesta	80%	80%	80%
Cannabis Sativa	80%	80%	60%
Elettaria Cardamomum	70%	70%	50%
Citrus Colocunthus	80%	80%	50%
Daucus Carota	80%	80%	80%
PunicaGranata	80%	80%	80%
Trifolium repens	70%	60%	40%
Cymbopogoncitratus	80%	80%	60%
Raphanus sativus	80%	80%	80%
Peganum	90%	90%	90%
Acacia senegal	80%	60%	50%

In the table 4, use of different medicinal plants is given that is summarized in figure 1 below, which showed medicinal significance of various plants used by people in various areas as given below.

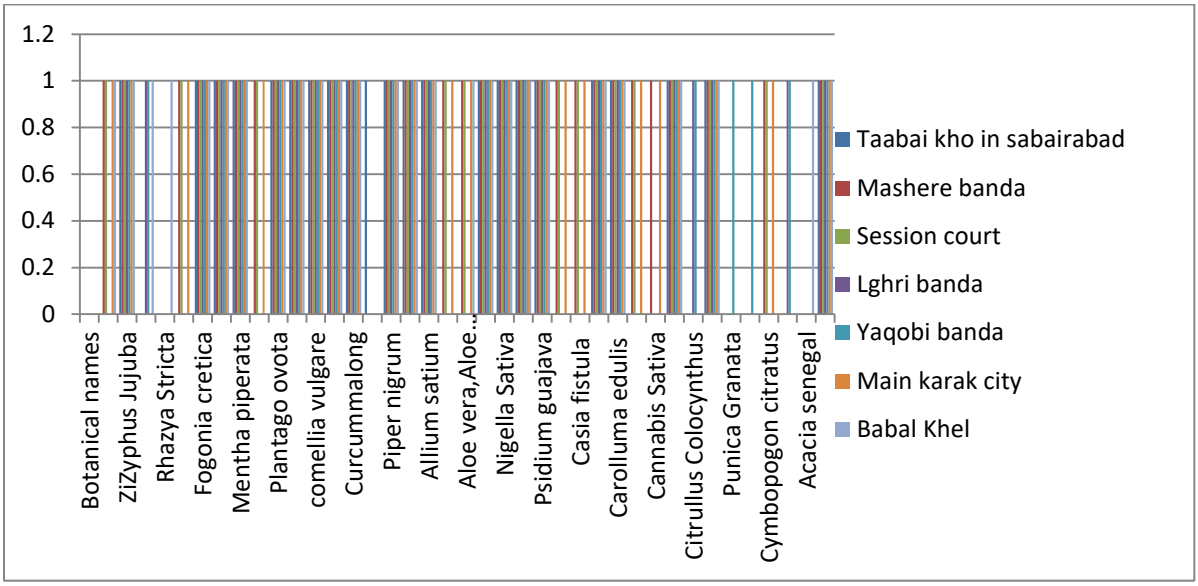

Figure 1: Ethno-medicinal significance of various plant species for seven different categories in the research area of District Karak

The use of different medicinal plants by various age groups in shown in table 5 above, which is summarized in figure 2 below. It showed that use and significance of herbal medicines and direct utilization of medicinal plants by various age groups is more than 70%, as it is clear from figure. Whereas over all usage of medicinal plants is more than 50%, this showed the importance and primary health care of medicinal plants.

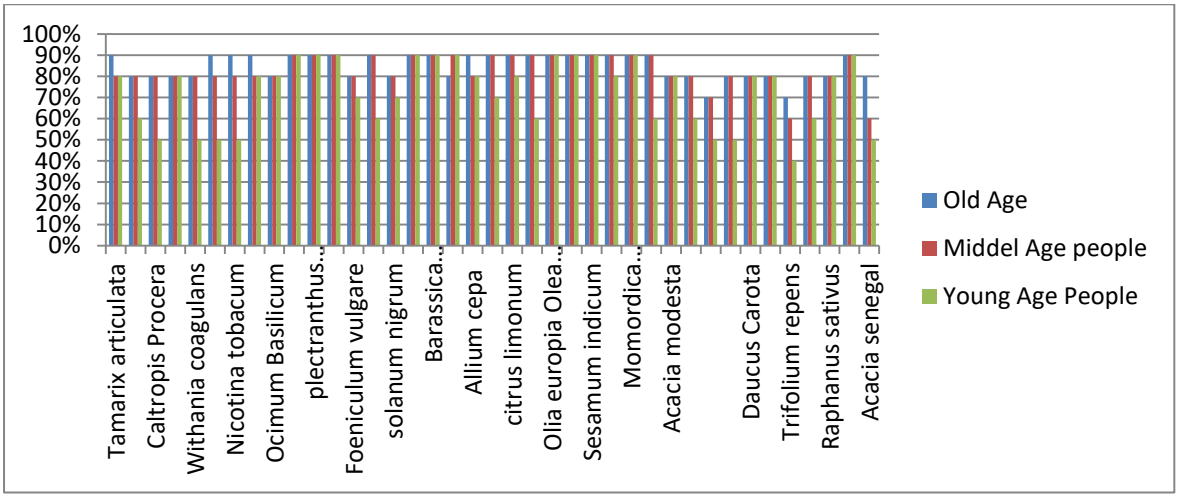

Figure 2: Ethno medicinal usage by different age groups of district Karak

This research exposed that 47 plants having medicinal importance of 24 families were known in the research area. These plants included in this work were both wild and

cultivated. Medicinal plants are often focused for ethno-medicinal studies for medicinal purposes as well as for primary first aid. Past studies in this research has given very important results in discovery of new synthetic medicines. Further, it is also a valuable heritage of the local people which is recognized as well as conserved, further these herbs are important for initial health care purposes. In this study useful conventional applications of these medicinal plants are reported given in Table 1-3 and Figure 1. The conventional experts are local people who know the importance of plants and consider that any part of the plant beneficial. However, pharmaceutical study and biochemistry based analysis is needed to verify information about the plant in local area of research. The utilization of definite parts of the desired plant recommended them as greater medicinal assets. This study is also linked that either this area have some causes for fever, respiratory infections, gastro-intestinal problems and some other health issues. The probable motive following such complaints in that specified area may be caused by presence of high pollutants in air and water, deficiency of suitable cleanliness measures, smoke habits inside houses due to fuel wood and poor quality of food.

S.NO	**Family Name**	**No of genra**	**S.NO**	**Family Name**	**No of genra**
1.	Tamaricacea	1	14.	Alliaceae	2
2.	Rhamnaceae	1	15.	Liliaceae	1
3.	Asclepiadace	1	16.	Rutaceae	1
4.	Apocynaceae	2	17.	Ranunculaceae	1
5.	Solanaceae	3	18.	Oleaceae	2
6.	Zygophyllaceae	2	19.	Myrtaceae	1
7.	Lamiaceae	3	20.	Pedaliacae	1
8.	Plantaginaceae	1	21.	Fabaceae	3
9.	Theaceae	1	22.	Cucurbitaceae	2
10.	Umbeliferae	2	23.	Cannabaceae	1
11.	Zingiberaceae	2	24.	Rosaceae	1
12.	Piperaceae	1	25.	Poaceae	1
13.	Brassicaceae	2	26.	Leguminoseae	1

Table 6: List of Families having number of genre

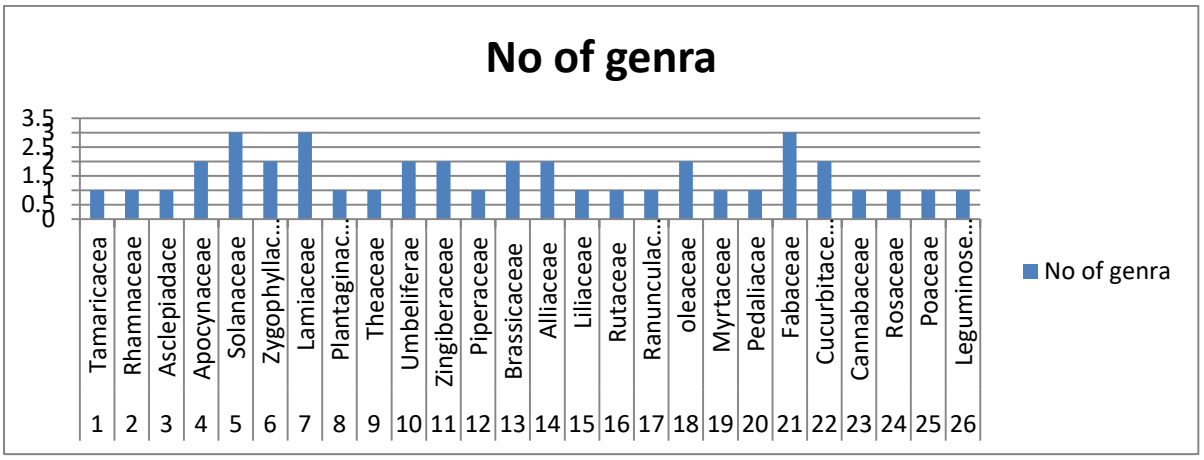

Fig 3: Ethno medicinal significance of various plant species for different genera

As, the concerned region is not developed therefore, people utilize such plants straight away for medicine. The plant species most frequently used for medicinal applications are, Fagoniacretica L., which is one the most used plants for medicinal purposes. The whole plant is used by one or another way for treatment of different illnesses. The local people believe that it is anti-diabetic due to its bitter taste and also helpful for treatment of stomach ulcer. The root and leaves extract of Solanum surattense Burm.f., is used for curing of stomach ulcer in cow and other animals. The hunting activity is common in Karak area, therefore persons involved in hunting eat more food, which causes stomach pain, which is treated by using fruit of Withaniacoagulans (Stocks) Dunals.

Table 7: Different types (Habits) of the reported species:

S.No	Herbs	Shrubs	Trees
1	Nicotinatobacum	RhazyaStricta	Tamarix articulate
2	Menthapiperata	Withaniacoagulans	ZiZyphusJujuba
3	OcimumBasilicum	CaltropisProcera	CaltropisProcera
4	Plantagoovota	Fogoniacretica	Psidium guajava
5	Eruca Sativa	plectranthusrogosus	citrus limonum
6	Foeniculum vulgare	comellia vulgare	Oliaeuropia Olea cuspedata
7	Curcumma longa	solanum nigrum	Casia fistula
8	Piper nigrum		Acacia modesta
9	Allium satium	PunicaGranata	PunicaGranata
10	Allium cepa	Peganumharmala	Acacia Senegal
11	Aloe vera,Aloebarbadensis		
12	Nigella sativa		
13	Sesamum indicum		

14	MomordicaChararntia		
15	Carolluma edulis		
16	Cannabis Sativa		
17	Elettaria Cardamomum		
18	CitrullusColocunthus		
19	Daucus Carota		
20	Trifolium repens		
21	Cymbopogoncitratus		
22	Raphanus sativus		

The fruit portion of Ziziphusjujuba Mill, is utilized for laxative and constipation, and minor cuts by people of local region as this herbal plant is simply accessible and useful. During the interview, we saw people are talking about the medicinal uses of Aloe vera (L.) Burm. People told that, latex portion of Aloe vera (L) Burmis plant is utilized more often for cuts and burns, (skin treatment purpose) and it also possesses rapid healing characteristics. Another plant Nicotina tobacum is also used for cough and flue. Mentha piperata dry leaves are used for digestion, motion and vomiting.

CONCLUSION AND RECOMMNDATIONS

The research was completed in District Karak which exhibited that less number of plant species are present as compared to the total area of this district .There are different reasons for least number of plants such as scattered population, scanty rainfall throughout the year and lack of proper irrigation system. The unavailability of modern facilities in this area, people mostly utilize different plants for curing of various illnesses. The elder persons of this area knew the medicinal significance and knowledge about these plants and they transfer to their young generation. In this research work, the medicinally important plants were collected, identified and classified on different basis. The results depicted that Karak district contains rich plant species for which proper management and conservation is mandatory. The use of different medicinal plants by various age groups is tabulated and summarized. It showed that use and significance of herbal medicines and direct use of these plants by various age groups is more than 70%, as it is clear from figure given in the text. Whereas over all usage of medicinal plants is more than 50%, this showed the significance and primary health care of medicinal plants.

REFERENCES

1. Bako, S. P., Bakfur, M. J., John, I., & Bala, E. I. (2005). Ethnomedicinal and phytochemical profile of some savanna plant species in Nigeria. *International Journal of Botany*.

2. Walter H, Hamilton A: *The vital wealth of plants UK*; Bates and Sons Ltd; 1993.

3. Hussain, J., Khan, A. L., Rehman, N., Hamayun, M., Shah, T., Nisar, M., & Lee, I. (2009). Proximate and nutrient analysis of selected vegetable species: A case study of Karak region, Pakistan. *African journal of Biotechnology*, *8*(12).

4. Azaizeh, H., Fulder, S., Khalil, K., & Said, O. (2003). Ethnobotanical knowledge of local Arab practitioners in the Middle Eastern region. *Fitoterapia*, *74*(1-2), 98-108.

5. Rahman, A. U., & Choudhary, M. I. (2003). Bioprospecting of medicinal and food plants: Pakistan. *New York: UNDP*.

6. Shinwari, Z. K. (2010). Medicinal plants research in Pakistan. *J Med Plants Res*, *4*(3), 161-76.

7. Cragg, G. M., Newman, D. J., & Snader, K. M. (1997). Natural products in drug discovery and development. *Journal of natural products*, *60*(1), 52-60.

8. Pandey, M., Abidi, A. B., Singh, S., & Singh, R. P. (2006). Nutritional evaluation of leafy vegetable paratha. *Journal of Human Ecology*, *19*(2), 155-156.

9. Taiga, A., Suleiman, M. N., Aina, D. O., Sule, W. F., & Alege, G. O. (2008). Proximate analysis of some dry season vegetables in Anyigba, Kogi State, Nigeria. *African Journal of Biotechnology*, *7*(10).

10. Hussain, J., & Khan, A. L. (2009). ur Rehman N, Hamayun M, Shinwari ZK, Ullah W, et al. Assessment of herbal products and their composite medicinal plants through proximate and micronutrients analysis. *Journal of Medicinal Plants Research*, *3*(12), 1072-1077.

11. Hussain, J., Khan, A. L., Rehman, N., Hamayun, M., Shah, T., Nisar, M., & Lee, I. (2009). Proximate and nutrient analysis of selected vegetable species: A case study of Karak region, Pakistan. *African journal of Biotechnology*, *8*(12).

12. Bhardwaj, S., & Gakhar, S. K. (2005). Ethnomedicinal plants used by the tribals of Mizoram to cure cuts & wounds.

13. Riaz, U., Zahid, H. Z. I., Javid, H., Farman, U. K., Naeem, K., Zia, M., ... & Iqbal, H. (2010). Traditional uses of medicinal plants in Darra Adam Khel NWFP Pakistan. *Journal of Medicinal Plants Research*, *4*(17), 1815-1821.

14. Qureshi, R. (2004). *Floristic and Ethno Botanical Study of Desert-Nara Region, Sindh* (Doctoral dissertation, Shah Abdul Latif University).

15. Zabta, K. S. (2010). Medicinal plants research in Pakistan. *Journal of Medicinal Plants Research*, *4*(3), 161-176.

16. Gilani, A. H. (2005). Trends in ethnopharmacology. *Journal of ethnopharmacology*, *100*(1-2), 43-49.

18. Heinrich, M., Ankli, A., Frei, B., Weimann, C., & Sticher, O. (1998). Medicinal plants in Mexico: Healers' consensus and cultural importance. *Social science & medicine*, *47*(11), 1859-1871.

19. Bhardwaj, S., & Gakhar, S. K. (2005). Ethnomedicinal plants used by the tribals of Mizoram to cure cuts & wounds.

20. Cox, A. P., & Balick, J. M. (1996). Ethnobotanical Research and traditional Health Care in Developing Countries, plants, people and culture.

Fabrication of Compact Films Butyl Ammonium Chloride Doping into $Cs_3Bi_2I_9$: Improved Film Morphology

Abbas Ali[1], Abdul Basit[1], Aleena Gul[1], Muhammad Junaid[2], Idrees Ahmed[2], Muhammad Usman[2], Sana Ullah[2], Nasir Ali[2], Sanam Attique[3]

ABSTRACT

Albeit the iconic lead-based perovskites solar cell has summited power conversion efficiency (PCE) of 23%. Lead toxicity remains a glitch for its commercialization. To replace the toxic lead, numerous alternatives have been introduced. Out of many, bismuth (Bi) was introduced as a stable alternative with isoelectronic properties to the conventional lead in perovskites (PVKs) framework. However, Bi-based PVKs also encountered several problems; for example, poor film morphology and crystallinity. The crystallization of Bi-based PVKs is abrupt and does not form any intermediate solvated phases, leading toward isolated crystals formation instead of uniform pinholes-free films. Hence, it is challenging to fabricate compact thin films of Bi-based PVKs. Herein, we attempted to fabricate compact and pinholes-free Bi-based PVKs film by incorporating butyl ammonium chloride (BACl) into the precursor solution of the Bi-based PVKs. Preliminary results indicate that the doping of BACl not only caused the improvement in the film morphology but also improved the crystallinity of the film. We believe that these results could be helpful in the material development of the Bi-based PVKs and their utilization in optoelectronic devices.

Keywords: *Bi-based perovskites, Butylammonium chloride, Thin film synthesis*

INTRODUCTION

Organometal halide perovskites are in demand because of their prodigious applications as ferroelectrics, piezoelectric, superconductors, photovoltaic, LED, LASER, etc. [1]. They are propitious ones for optoelectronic devices having high absorption

[1] Department of Physics, Government Degree College Gul Abad, District Dir Lower, Khyber Pakhtunkhwa, Pakistan.
[2] Government Degree College Thana, District Malakand, Khyber Pakhtunkhwa, Pakistan: **Corresponding Author's Email nasirphysicist@yahoo.com**
[3] Institute for Composites Science and Innovation (InCSI), School of Material Science and Engineering, Zhejiang University, Hangzhou, PR China

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coefficient, enhanced charged mobility, long charged diffusion length, and small exciton binding energy. In a very short period, lead-based perovskites PCE reaching 24.2% with low cost and low-temperature solution processibility made itself a strong contender against the mainstream state of art device silicon-based solar cells [2].

Besides these peculiar advantages, PVKs encountered many serious pitfalls like they are highly unstable against humidity, heat, and UV light. Owing to a long-standing impression of lead-based organometal halide perovskites' efficiency, its toxicity due to the presence of lead inhibits its commercialization. A lot of work has been done to solve the problem of moisture ingress using proper encapsulation and combining it with lower-dimensional PVK [3, 4]. The Down conversion technique is used to solve the problem of UV light and thermal instability is resolved by using a 2D material at the top of the PVK layer [5, 6]. Instead of all the solutions regarding the pitfalls toxification of lead is not able to compensate as there is no safe threshold value of the damage caused by lead has been reported. High levels of health risks indulge the scientific community to dig out a possible solution to replace toxic lead with nontoxic or less toxic elements [7, 8]. In this regard, many materials have been put forward by the scientific community to find out the best replacement for lead. Mostly this replacement is from group 14 and group 15 of periodic table elements.

Prominently group 14 has mainly Sn and Ge as potential candidates for replacement of the lead. Sn is prone to self-doping [9]. Ge has its problem of smaller band gaps that are not even in the range of the Shockley-Queisser limit necessary for working of the solar cell.

Group 15 ultimate choice is Bi as it shares the same electronic configuration, comparable ionic radius, similar electronic configuration, and above all Bi is nontoxic and is used in many medicines [10, 11]. As far as toxicity and stability are concerned, Bi remained a probable choice as a lead alternative [12]. Attaining charge neutrality in typical PVKs ABX_3 structure is difficult as Bi has a different oxidation state than that of lead [13, 14]. To cope with it, mixed valency approach is used to balance the charges in the structure as the lattice of Bi-based PVKs built up of distorted octahedra due to which they have structural diversity and can be easily categorized as zero, one, two, and three-dimensional structures [15]. [16-18]. Many groups inferred that for Bi-based PVKs poor film morphology is the greatest hitch in improving the device efficiency so that it comes at par with lead-based perovskite efficiency [19, 20].

The high-quality film is a necessary aid to achieve high device performance and stability. Many approaches are being practiced to solve this glitch instantly. In this regard, films were made by using single-step and two-step spin-coating deposition techniques for compact film fabrication [16, 21]. Some groups reported solvent engineering approaches for better film morphology significant improvement in device performance has been reported by improving the film quality [19]. Though Bi-based, PVKs have superior stability factors in the open air, their poor device performance is very disheartening therefore extensive research is needed to resolve the issue of film quality by understanding what is lacking to assemble green and inexpensive solar cells.

Better PV performance needed quality thin films with full coverage, improved crystallinity, and pinhole-free films. For instance, Bi-based PVKs crystalize in a very

different manner than that conventional Pb-based PVKs. It crystallizes without forming any solvated phase and grows to form an uneven isolated crystal with greater pinholes and thin films [22, 23]. Thus it's really difficult to fabricate compact pinhole-free thin films for Bi-based PVKs.

Bi has also been used as a dopant material in different materials for electrical conduction enhancement, photonic applications, etc.[24, 25]. For instance, we thought that doping may have fruitful effects on the morphology of Bi-based PVKs films. Here in this paper, we have doped $Cs_3Bi_2I_9$ with Butyl ammonium chloride followed by one-step film synthesis which gives maximum coverage on ITO substrate. Doping of Butyl ammonium chloride resulted in better compact films having excellent film morphology with improved crystallinity. These better results could be helpful in compact film fabrication and may eventually provide efficient device fabrication.

METHODOLOGY

Cesium iodide (CsI), bismuth iodide (BiI_3), butyl ammonium chloride (BACl), hydrochloric acid, dimethyl formamide (DMF), and indium tin oxide (ITO) glass substrates were purchased from McKlin China. All of the purchased reagents were of analytical grade and used as received.

Preparation of $Cs_3Bi_2I_9$ solution: CsI and BiI_3 were dissolved completely in DMF solution with 1.5 millimolar and 1 millimolar ratio respectively under constant stirring at 70 ℃ temperature for about two hours. Filtered out the saturated solution using an organic filter after the designated time.

Preparation of doping solution: For doping CBI solution 0.1milli molar amount of butyl ammonium chloride was added to the above prepared $Cs_3Bi_2I_9$ solution to ensure that dopant dissolved and chemical reaction occurred completely doped solution kept on stirring again for about six hours. After the designated time, filter out the solution using an organic filter. Now our doped solution is ready which is further used for characterization and film fabrication.

Glass cleaning: To ensure the formation of better quality films substrate cleaning is very essential to make it free from any dust and other residues which may contaminate the film or the solution. ITO glass was sonicated (10 min) in de-ionized water, acetone and ethanol. Each time after sonication, the glass substrates were dipped in hot water (~ 90 ℃) and dried with nitrogen gas. The substrates were finally treated with UV-Ozone to remove all the organic species from the surface.

Film Fabrication: One-step spin-coated thin film fabrication is now can be done using a cleaned ITO substrate. About 70 µl of the doped solution was dropped gently at the center of the glass substrate which is already spinning at 3500rpm and after one minute of rotation substrate is now removed quickly from the spin coater and placed on a hot plate on the already spinning glass substrate (3500 rpm) and allowed to rotate for 1 minute. Afterward, the substrate was quickly transferred to the hot plate and annealed at 120 C for 5 min while covered with a glass dish.

Characterizations and techniques: Photoluminescence (PL) analysis performed using Andor SR-500i-B1 spectrograph FLS-920 and Steady/Transient fluorescence spectrometer from Edinburgh Instrument having incident radiation 535 nm. Optical absorption (OA) was done by 5000 UV–VIS-NIR spectrometer by Agilent Technologies. For film characterizations, scanning electron microscope (SEM) from Hitachi S4800 was used. X-ray diffraction (XRD) analysis was done by Empyrean Alpha-681 X-Ray Diffractometer from PANalytical. Contact angle measurement was done by CAM200 optical contact-angle meter (KSV Co.Ltd.).

DISCUSSION AND ANALYSIS

Figure 1a shows the optical absorption and PL spectra of the as-prepared pure CBI films. The characteristic absorption peak (which is associated commonly with the lower dimensional perovskites) is shown at about 650 nm. The corresponding PL spectra are also shown in the same figure. The PL peak and the absorption onset are almost at the same wavelengths, indicating a lower Stoke's shift of the material. The PL peak is broader and shows a wider full-width half maxima, indicating less coverage of the substrate as well as poor crystallinity of the pure CBI film. Similarly, Fig. 1b shows the absorption and PL characteristics of the doped CBI film. In contrast to the pure CBI, the optical absorption peak of the doped CBI is of higher intensity, showing better coverage of the film. Likewise, the PL of the doped CBI is not only sharper but more intense than the pure CBI, showing better crystallinity and fewer defects sites than the doped CBI.

The improved coverage of the substrate is also vivid from the scanning electron images of the pure and doped CBI films. Figure 1c shows the SEM image of the pure CBI thin film, exhibiting dispersed sheets (parallel to the substrate) of hexagonal shape with poor coverage of the substrate. On the other side, Fig. 1d shows SEM image of the doped CBI, which has more surface coverage than the pure CBI films. Moreover, the doped CBI crystals are oriented perpendicular to the substrate, which is favorable for better charge transport in planar-type photovoltaic devices [26]. The improved coverage of the doped CBI can be attributed to the longer chain of organic cations in the structure, which usually crystallizes slowly as compared with the inorganic Cs-based perovskites [5].

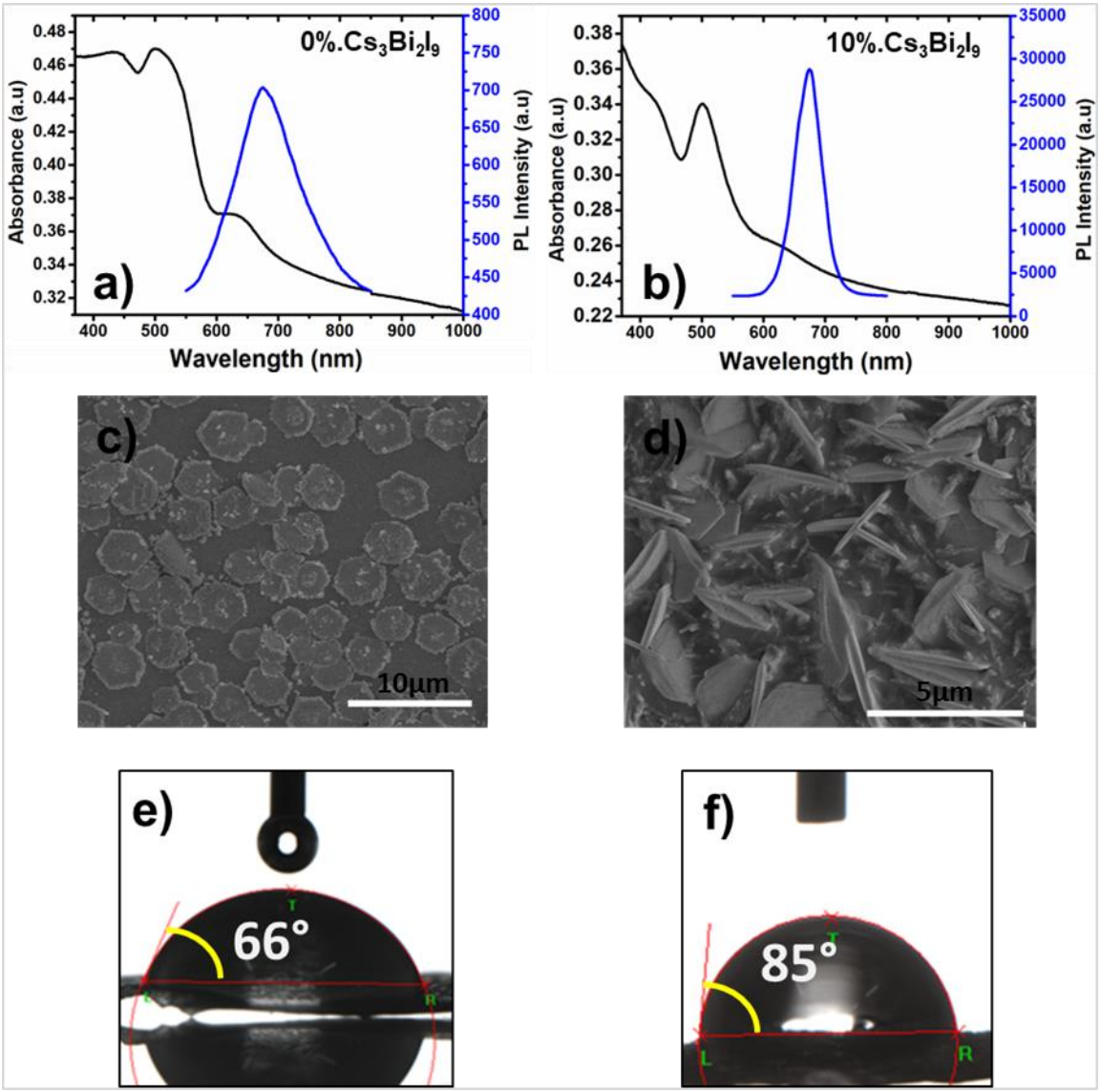

Figure 1: Optical and morphological characterization of the pure CBI and doped CBI: (**a**) absorption and PL spectra of the pure CBI. (**b**) Absorption and PL of the doped CBI. (**c**) SEM micrographs of the pure and (**d**) doped CBI thin films. (**e**) and (**f**) are the snapshots of the water contact angles respectively for the pure and doped CBI.

Additionally, to observe the surface hydrophobicity of the pure and doped CBI, water contact angle tests were performed. The water contact angle can provide information about the resistance of a material to the water ingress i.e. greater the water contact angle, the greater will be the hydrophobicity of the material and vice versa [27]. Since doped CBI exhibited better coverage; therefore, showed a greater contact angle (85°) than the pure one (66°), as shown in Figure 1e and 1d. Better surface coverage and greater hydrophobicity could not only improve the environmental stability of the material but also for minimizing the shunt resistances of the photovoltaic device.

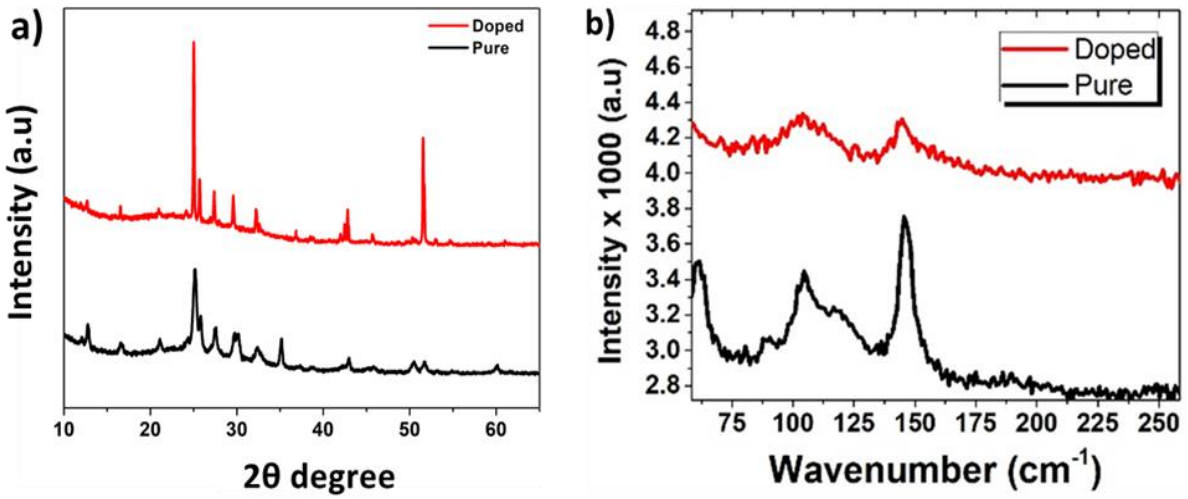

Figure 2 a) Xrd of pure and doped CBI films. **b)** Raman spectroscopy of pure and doped CBI films.

Figure 2a shows XRD spectra of pure CBI and doped CBI. Both the spectra showed a characteristic peak of hexagonal phase, i.e., Pmmc 63, which is following the previous results [28, 29]. With doping of Butyl ammonium chloride, the intensity of the XRD peaks increases. It gives more sharp peaks that are attributed to the good crystallinity of the doped CBI films. This increase in intensity is attributed to the greater film coverage, and better crystallinity as well as .pinhole-free compact films [23]. The XRD results are also in line with SEM results as well as with Raman spectra (discussed as follows).

Raman spectroscopy indicates the vibrational modes of pure CBI and doped CBI films in Figure 2b. Detailed analysis of Raman vibrational modes for CBI films has shown that $[Bi_2I_9]^{3-}$ dominates the vibrational modes in the Raman spectra. So most dominant vibrations within the structure are due to this strongly bounded anion. Major stretching in pure CBI films is shown with Bi–I mode this stretching mode is further associated with six Iodide atoms three of which are terminal iodides and the rest of the three are bridging iodides that eventually connect two Bi atoms. Peak 146 cm^{-1} for pure CBI film is the symmetric stretch whereas the two anti-symmetric stretches are shown at and two anti-symmetric stretches are shown at 127.2 cm^{-1} and 119.8 cm^{-1} [30].

Bridging iodides have a lesser force constant than that of terminal iodide atoms as they need to share their bonding with the Bi atoms to join the two Bi atoms together. The stretching peak is a high energy peak as it is related to the terminal bonds, a major peak of 146 cm^{-1} is attributed to the Bi–I terminal bonds that are associated with its anti-symmetric bonds as shown in pure CBI film [31]. Moreover, it was also attributed from Raman peaks that the presence of strong intense peaks for $[Bi_2I_9]^{3-}$ showing that still a lot of unreacted anions are still present in pure CBI film resulting in less coverage and rough film. Noticing the Raman peaks for doped CBI film showing very less intense peaks for the $[Bi_2I_9]^{3-}$ anion depicting that minute amount of anion remained unreactive and resulted in a complete chemical reaction which becomes the reason for compact and almost pin-hole free film with maximum coverage.

CONCLUSION & RECOMMENDATIONS

We have demonstrated one way to attain compact and almost pinhole-free CBI film by using the doping technique as many solvent techniques have been used to improve the quality of the film but still, poor device efficiency remained an unsolved issue because of the film quality. A comparison of pure CBI film and doped CBI film shows that organic doping has a strong impact on the quality of the film. Doping of Butyl ammonium chloride in CBI films has shown improved crystallinity, better coverage, and morphology which could be helpful in improved device efficiency. All the characterization results justify each other and are well attributed to better compact films for further utilization in optoelectronic devices.

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REFERENCES

1.Hirose, K., Sinmyo, R., & Hernlund, J. (2017). Perovskite in Earth's deep interior. *Science*, *358*(6364), 734-738.

2. Zhu, X., Lin, Y., San Martin, J., Sun, Y., Zhu, D., & Yan, Y. (2019). Lead halide perovskites for photocatalytic organic synthesis. *Nature communications*, *10*(1), 1-10.

3. Ali, N., Rauf, S., Kong, W., Ali, S., Wang, X., Khesro, A., ... & Wu, H. (2019). An overview of the decompositions in organo-metal halide perovskites and shielding with 2-dimensional perovskites. *Renewable and Sustainable Energy Reviews*, *109*, 160-186.

4. Attique, S., Ali, N., Khatoon, R., Ali, S., Abbas, A., Yu, Y., ... & Yang, S. (2020). Aqueous phase fabrication and conversion of Pb (OH) Br into a CH 3 NH 3 PbBr 3 perovskite and its application in resistive memory switching devices. *Green Chemistry*, *22*(11), 3608-3614.

5. Ali, N., Wang, X., Rauf, S., Attique, S., Khesro, A., Ali, S., ... & Wu, H. (2019). Enhanced stability in cesium assisted hybrid 2D/3D-perovskite thin films and solar cells prepared in ambient humidity. *Solar Energy*, *189*, 325-332.

6. Hou, J., Yu, Y., Attique, S., Cao, B., & Yang, S. (2021). Laurionite Competes with 2D Ruddlesden–Popper Perovskites During the Saturation Recrystallization Process. *ACS Applied Materials & Interfaces*, *13*(5), 6505-6514.

7. Attique, S., Ali, N., Ali, S., Khatoon, R., Li, N., Khesro, A., ... & Wu, H. (2020). A potential checkmate to lead: bismuth in organometal halide perovskites, structure, properties, and applications. *Advanced science*, *7*(13), 1903143.

8. Attique, S., Ali, N., Rauf, S., Ali, S., Khesro, A., Khatoon, R., ... & Wu, H. (2021). Nontoxic and Less Toxic Hybrid Perovskites: a Synergistic Strategy for Sustainable Photovoltaic Devices. *Solar RRL*, *5*(8), 2100212.

9. Huang, J., Gu, Z., Zhang, X., Wu, G., & Chen, H. (2018). Lead-free (CH3NH3) 3Bi2I9 perovskite `solar cells with fluorinated PDI films as organic electron transport layer. *Journal of Alloys and Compounds*, *767*, 870-876.

10. Hoye, R. L., Brandt, R. E., Osherov, A., Stevanović, V., Stranks, S. D., Wilson, M. W., ... & Buonassisi, T. (2016). Methylammonium bismuth iodide as a lead-free, stable hybrid organic–inorganic solar absorber. *Chemistry–A European Journal*, *22*(8), 2605-2610.

11.Turkevych, I., Kazaoui, S., Ito, E., Urano, T., Yamada, K., Tomiyasu, H., ... & Aramaki, S. (2017). Photovoltaic rudorffites: lead-free silver bismuth halides alternative to hybrid lead halide perovskites. *ChemSusChem*, *10*(19), 3754-3759.

12. Brandt, R. E., Stevanović, V., Ginley, D. S., & Buonassisi, T. (2015). Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites. *Mrs Communications*, *5*(2), 265-275.

13. Wang, Z., Shi, Z., Li, T., Chen, Y., & Huang, W. (2017). Stability of perovskite solar cells: a prospective on the substitution of the A cation and X anion. *Angewandte Chemie International Edition*, *56*(5), 1190-1212.

14. Yang, B., Chen, J., Hong, F., Mao, X., Zheng, K., Yang, S., ... & Han, K. (2017). Lead-free, air-stable all-inorganic cesium bismuth halide perovskite nanocrystals. *Angewandte Chemie International Edition*, *56*(41), 12471-12475.

15. Creutz, S. E., Liu, H., Kaiser, M. E., Li, X., & Gamelin, D. R. (2019). Structural diversity in cesium bismuth halide nanocrystals. *Chemistry of Materials*, *31*(13), 4685-4697.

16. Park, B. W., Philippe, B., Zhang, X., Rensmo, H., Boschloo, G., & Johansson, E. M. (2015). Bismuth based hybrid perovskites A3Bi2I9 (A: methylammonium or cesium) for solar cell application. *Advanced materials*, *27*(43), 6806-6813.

17. Johansson, M. B., Zhu, H., & Johansson, E. M. (2016). Extended photo-conversion spectrum in low-toxic bismuth halide perovskite solar cells. *The journal of physical chemistry letters*, *7*(17), 3467-3471.

18. Singh, T., Kulkarni, A., Ikegami, M., & Miyasaka, T. (2016). Effect of electron transporting layer on bismuth-based lead-free perovskite (CH3NH3) 3 Bi2I9 for photovoltaic applications. *ACS applied materials & interfaces*, *8*(23), 14542-14547.

19. Shin, S. S., Correa Baena, J. P., Kurchin, R. C., Polizzotti, A., Yoo, J. J., Wieghold, S., ... & Buonassisi, T. (2018). Solvent-engineering method to deposit compact bismuth-based thin films: mechanism and application to photovoltaics. *Chemistry of Materials*, *30*(2), 336-343.

20. Mali, S. S., Kim, H., Kim, D. H., & Kook Hong, C. (2017). Anti-Solvent Assisted Crystallization Processed Methylammonium Bismuth Iodide Cuboids towards Highly Stable Lead-Free Perovskite Solar Cells. *ChemistrySelect*, *2*(4), 1578-1585.

21. Ran, C., Wu, Z., Xi, J., Yuan, F., Dong, H., Lei, T., ... & Hou, X. (2017). Construction of compact methylammonium bismuth iodide film promoting lead-free inverted planar heterojunction organohalide solar cells with open-circuit voltage over 0.8 V. *The journal of physical chemistry letters*, *8*(2), 394-400.

22. Tang, M. C., Barrit, D., Munir, R., Li, R., Barbé, J. M., Smilgies, D. M., ... & Amassian, A. (2019). Bismuth-Based Perovskite-Inspired Solar Cells: In Situ Diagnostics Reveal Similarities and Differences in the Film Formation of Bismuth-and Lead-Based Films. *Solar RRL*, *3*(7), 1800305..

23. Ali, N., Attique, S., Rauf, S., Wang, X., Khesro, A., Ali, S., ... & Wu, H. (2020). The effect of dodecylammonium chloride on the film morphology, crystallinity, and performance of lead-free Bi-based solution-processed photovoltaics devices. *Solar Energy*, *207*, 1356-1363.

24. Acharya, M., & Maiti, T. (2018). Effect of bismuth doping on thermoelectric properties of Sr2 TiCoO6. *Ferroelectrics*, *532*(1), 28-37.

25. Wei, S., Ding, M., Fan, D., Luo, Y., Wen, J., & Peng, G. D. (2018). Effects of post treatments on bismuth-doped and bismuth/erbium co-doped optical fibres. *Bismuth: Advanced Applications and Defects Characterization*, *155*.

26. Bi, C., Shao, Y., Yuan, Y., Xiao, Z., Wang, C., Gao, Y., & Huang, J. (2014). Understanding the formation and evolution of interdiffusion grown organolead halide perovskite thin films by thermal annealing. *Journal of Materials Chemistry A*, *2*(43), 18508-18514.

27. Ma, Y., Cao, X., Feng, X., Ma, Y., & Zou, H. (2007). Fabrication of super-hydrophobic film from PMMA with intrinsic water contact angle below 90. *Polymer*, *48*(26), 7455-7460.

28. Park, B. W., Philippe, B., Zhang, X., Rensmo, H., Boschloo, G., & Johansson, E. M. (2015). Bismuth based hybrid perovskites A3Bi2I9 (A: methylammonium or cesium) for solar cell application. *Advanced materials*, *27*(43), 6806-6813.

29. Zhang, H., Xu, Y., Sun, Q., Dong, J., Lu, Y., Zhang, B., & Jie, W. (2018). Lead free halide perovskite Cs 3 Bi 2 I 9 bulk crystals grown by a low temperature solution method. *CrystEngComm*, *20*(34), 4935-4941.

30. McCall, K. M., Stoumpos, C. C., Kostina, S. S., Kanatzidis, M. G., & Wessels, B. W. (2017). Strong electron–phonon coupling and self-trapped excitons in the defect halide perovskites A3M2I9 (A= Cs, Rb; M= Bi, Sb). *Chemistry of Materials*, *29*(9), 4129-4145.

31. Laane, J., & Jagodzinski, P. W. (1980). Low-frequency vibrational spectra of bromo-and iodobismuthates and the observation of a trans effect. *Inorganic Chemistry*, *19*(1), 44-49.

Utilization of 0D Perovskite to the 3D Organometal Halide Perovskite: Improved Morphological, Optical, and Structural Properties

Irfan Ullah[1], Waqas Rahim[1], Muhammad Sajid[1], Muhammad Idrees[1], Aqib Javed[1], Abbas Khan[1], Arsalan Khan[1], Muhammad Asad[1], Nasir Ali[1], Sanam Attique[2]

ABSTRACT

Albeit low efficiency of lower-dimensional perovskites are still game-changer; when they are used with 3D perovskites. Numerous factors are responsible for efficient photovoltaic devices based on organometal halide perovskites. Among them, better film morphology and extended environmental stability are critical parameters, governing the photovoltaic performance of a device. The present researche has utilized lower-dimensional perovskites, i.e., $DA_{0.1}Cs_{2.9}Bi_2I_9$ (0D) into triple-cations organometal halide perovskite, i.e., $CsFAMAPbI_3$ (3D) to fabricated compact films in the ambient environment without pre-heating the substrate. It is revealed by various characterization results that the prepared 0D/3D perovskites films exhibited better film morphology, improved crystallinity, and optoelectronic properties. The 0D perovskites shield the 3D perovskites from moisture ingress consequently, the final product remains environmentally stable. This study can provide a pathway toward the ambient fabrication of high-quality perovskite thin films for highly efficient optoelectronic devices.

Keywords: *$DA_{0.1}Cs_{2.9}Bi_2I_9$; $CsFAMAPbI_3$; 0D/3D perovskites; Thin films*

INTRODUCTION

Organometal halide perovskites are emerging as a promising material for solar energy harvesting and other optoelectronic applications [1-5]. Its peculiar optoelectronic properties; including higher photoabsorption and photoemission, longer carrier diffusion length, and weaker exciton binding boosted the photoconversion efficiency of perovskites solar cells to 26% in only 9 years [1-3, 6-9]. Although their power conversion efficiency is on par with the conventional silicon-based solar cells; it is still way lower than the theoretically predicted limit for single-junction solar cells [10, 11]. Many factors govern the

[1] Government Degree College Thana, District Malakand, Pakistan, **Coresponding Author's Email: nasirphysicist@yahoo.com**

[2] Institute for Composites Science and Innovation (InCSI), School of Material Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

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performance of photovoltaic devices; for example, compact pinholes-free perovskite films, uniform surface morphology, and better crystallinity are ideal to ensure maximum efficiency. In addition, perovskite material is very sensitive to the ambient environmental condition, e.g., humidity, high temperature, and UV light.

Therefore, it is challenging to guarantee a compact high-quality perovskite thin film with a larger grain size while using simple solution processability in the ambient environment. Many techniques including spray paralysis, solvent engineering, hot costing, etc. are utilized to fabricate compact perovskites thin films with larger grain sizes [12-14]. Liang et al. [12] fabricated compact perovskite thin-film via spray paralysis under ambient conditions (with 50% humidity) without post-annealing. The prepared thin films exhibited larger grain sizes about micrometer size, which covered the substrate completely.

The heterojunction photovoltaic devices showed a power conversion efficiency of 7.89%, which was expected to further increase with post-annealing. Likewise, Gedamu et al. [13] fabricated pinholes-free perovskites ($CH_3NH_3PbI_{3-x}Cl_x$) thin films with higher substrate coverage (~99.97%) and larger crystals (> 5 µm) by utilizing solvent engineering under ambient environmental conditions. Solar cell devices based on those films demonstrated a power conversion efficiency of 14%, which was attributed to the larger grain size and denser film morphology of the film.

Lower dimensional perovskites are found to be relatively stable than their 3D counterparts; for example, 2D perovskites exhibited better environmental stability than bulk perovskites [15, 16]. Similarly, dodecylammonium chloride (DCl) utilized and enabled the fabrication of the perovskite thin films due to the formation of hybrid 2D/3D perovskites in the ambient environment [15]. The prepared films not only showed better crystallinity, optoelectronic properties, film morphology, and environmental stability than the pure 3D perovskites, but also exhibited an enhanced device performance.

The improved environmental stability of the hybrid perovskites can be attributed to the 2D perovskites being relatively more hydrophobic and longer chained organic cations acting as a shield again environmental factors [17, 18]. Moreover, along with other excellent optoelectronic properties, 0D Bi-based perovskites ($Cs_3Bi_2I_9$) also demonstrated excellent environmental stability than the conventional organolead-based perovskites. For example, the excellent environmental stability of 6 months for $Cs_3Bi_2I_9$ thin films has been reported [19].

Inspired by the above studies; the researchers herein utilized first a minute amount of dodecylammonium chloride into the 0D Bi-based perovskites ($Cs_3Bi_2I_9$) to prepare $DA_{0.1}Cs_{2.9}Bi_2I_9$ (DCBI). Subsequently, a small amount of DCBI is added to the triple cations-based 3D perovskites (i.e. $CsFAMAPbI_3$) to prepare 0D/3D perovskites i.e. ($DCBI_x.CsFAMAPbI_3$).

Thin films based on this perovskite compound are characterized by optical and electron microscopies; exhibited excellent coverage with compact grain boundaries. The films were also characterized by X-ray diffraction analysis, which revealed an improved

crystallinity of the films as compared with pure CsFAMAPbI$_3$ films. The existence of vertically-oriented 0D perovskite crystals among the 3D perovskite crystals not only endows the 3D perovskites with better environmental stability but also helps in charge transportation.

METHODOLOGY

All reagents, cesium iodide (CsI), bismuth iodide (BiI$_3$), lead iodide (PbI), dodecylammonium (DCA), hydrochloric acid (HCl, 37 wt% in H_2O), methylammonium iodide (MAI), formamidinium iodide (FAI), dimethylformamide (DMF), and indium tin oxide (ITO) glass substrates were obtained from Aladdin, China. All of the reagents were used as received.

Synthesis of precursor solutions

To synthesize dodecylammonium chloride, 1 equivalent of dodecylammonium was thoroughly dissolved in ethanol (at 0 °C) and a slightly excessive amount of HCl (i.e., 1.1 equivalent) was titrated into the above solution (with constant stirring for 2 h at 0 °C). The dried solution turned into a white powder (after evaporation). Afterward, the powder washing was done for several times using diethyl ether. The powder was then filtered followed by drying at 50 °C for 24 hours. The obtained white powder of the dodecylammonium chloride will be used as a precursor of dodecylammine.

Preparation of $Cs_3Bi_2I_9$

To prepare the 0D $Cs_3Bi_2I_9$ (CBI) precursor solution, 1.5 mM of CsI and 1 mM BiI$_3$ were completely dissolved in DMF under constant stirring for 2 hours (70 ℃). After the species in the solution were fully dissolved, a 0.45 µl organic filter was used to filter out the solution.

Preparation of $DA_{0.1}Cs_{2.9}Bi_2I_9$ and $FAMAPbI_3$

To prepare $DA_{0.1}Cs_{2.9}Bi_2I_9$, a 0.1 mM of dodecylammonium chloride was added to the CBI solution and stirred again for 6 hours. Afterward, the solution was filtered again with a 0.45 µl organic filter.

Similarly, to prepare the 3D FAMAPbI$_3$ precursor, 0.7 mM of MAI, 0.1 mM of CsI, and 0.2 mM of FAI were fully dissolved in DMF by means of stirring for 12 hours (70℃). Upon full dissolution, the precursor was filtered with a 0.45 µl organic filter.

Preparation of 0D/3D Perovskites

To synthesize mixed 2D/3D perovskites (DA.$Cs_3Bi_2I_9$ and FAMAPbI$_3$), 5% addition of $DA_{0.1}Cs_{2.9}Bi_2I_9$ to the FAMAPbI$_3$ and let it stirred for 6 hours to prepare 0D/3D perovskites. This solution will be used for film fabrication, which will be further

characterized by optical microscopes, scanning electron microscopy, and X-ray diffraction analysis.

Preparation of thin films

Before film fabrication, the ITO glass was sonicated (10 min) in de-ionized water, acetone, and ethanol. Each time after sonication, the glass substrates were dipped in hot water (~ 90 ℃) and dried with nitrogen gas. The substrates were finally treated with UV-Ozone to remove all the organic species from the surface. Subsequently, 70 µl of the precursor solution was dropped genteelly on the already spinning glass substrate (3500 rpm) and allowed to rotate for 1 minute. Afterward, the substrate was quickly transferred to the hot plate and annealed at 120 ℃ for 5 minutes while covered with a glass dish.

Characterization Techniques

Photoluminescence (PL) analysis was done by Andor SR-500i-B1 spectrograph FLS-920 and fluorescence spectrometer from Edinburgh Instrument with 535 nm laser beam as incident radiation. UV absorption were done by Carry 5000 UV–VIS-NIR spectrometer from Agilent Technologies. For the investigation of the films surface morphology; a scanning electron microscope (SEM) from Hitachi S4800 was used. X-ray diffraction (XRD) measurements were performed by Empyrean Alpha-681 X-Ray Diffractometer from PANalytical. The water contact angle was measured through CAM200 optical contact-angle meter (KSV Co.Ltd.).

DISCUSSION AND ANALYSIS

Figure 1a shows the absorption measurement plots of both 3D perovskite thin films. A strong absorption slope near 800 nm, can be attributed to the absorption characteristics of the 3D perovskites. In comparison to the pure 3D perovskite, the 0D/3D perovskites exhibited more steeper absorption slope, which is indicative of the films with fewer defects and better crystallinity [20].

An optical energy bandgap is an important parameter to efficiently absorb the sunlight and convert it into an electrical current. The present study calculated the optical energy bandgaps for both puer 3D and 0D/3D perovskites from their Tauc's plots, as shown in **Figure 1b**. The onset wavelength of the absorption slope of the pure 3D perovskites in the Tauc plot indicates a bandgap of ca. 1.51 eV, which is closer to optimum bandgap of single-junction solar cell and is consistent with the previous studies [21]. In contrast to this, the 0D/3D perovskite showed a slightly wider energy bandgap of 1.53 eV, which can be attributed to the existence of the lower dimensional (0D) perovskites [20].

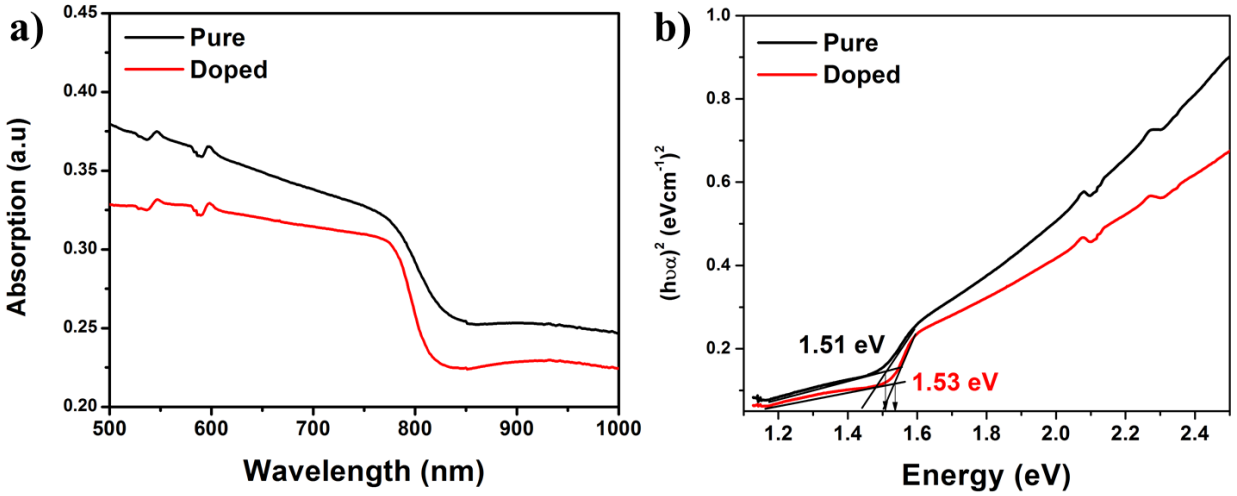


Figure 1 (**a**) Absorption plots for pure and doped perovskite thin films. (**b**) Tauc plot of pure and doped perovskite films for energy bandgap calculations.

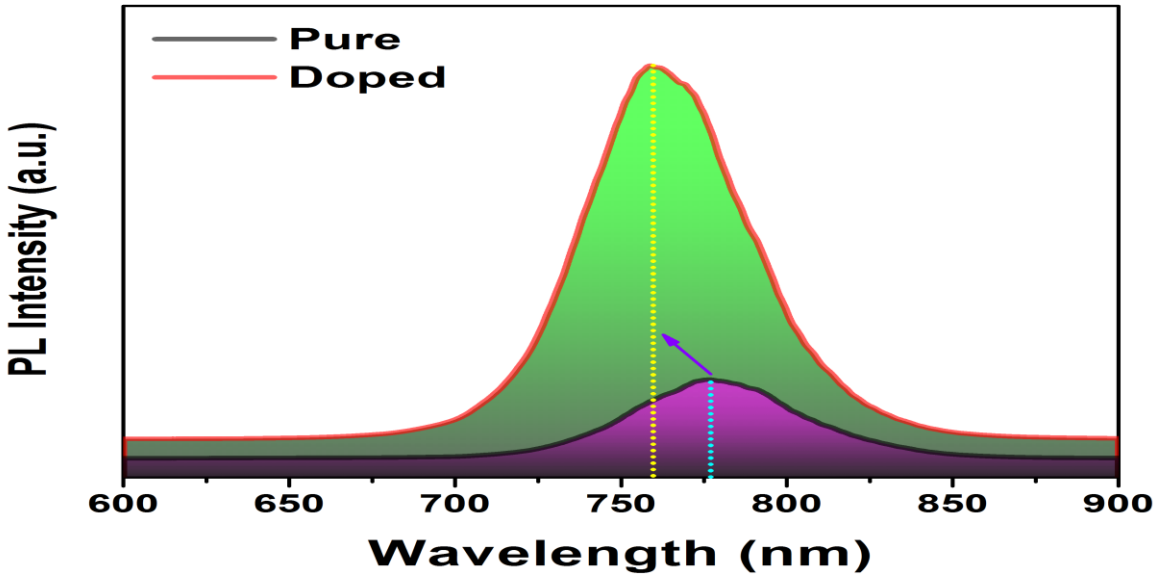


Figure 2 Photoluminescence spectra of the pure and doped perovskite thin films. The dotted lines and an arrow are the guideline to the eye to indicate the blue shift in the PL spectra.

Similarly, photoluminescence (PL) characterizations of the pure and doped samples were carried out, as shown in **Figure 2**. Pure 3D perovskite thin-film shows wider and less intense PL characteristics with a peak near 800 nm. While 0D/3D perovskites show strong and narrow PL characteristics with a peak slightly blue-shifted. The blue shift in the PL peak is consistent with increased energy bandgap (calculated from absorption spectrum) and is attributed to the existence of the lower dimensional (0D) perovskites. The PL peak exhibit

a smaller full-width maxima, indicating the better crystallinity and lesser defects sites in the 0D/3D perovskites films and is consistent with the steeper absorption slope in **Figure 1a**.

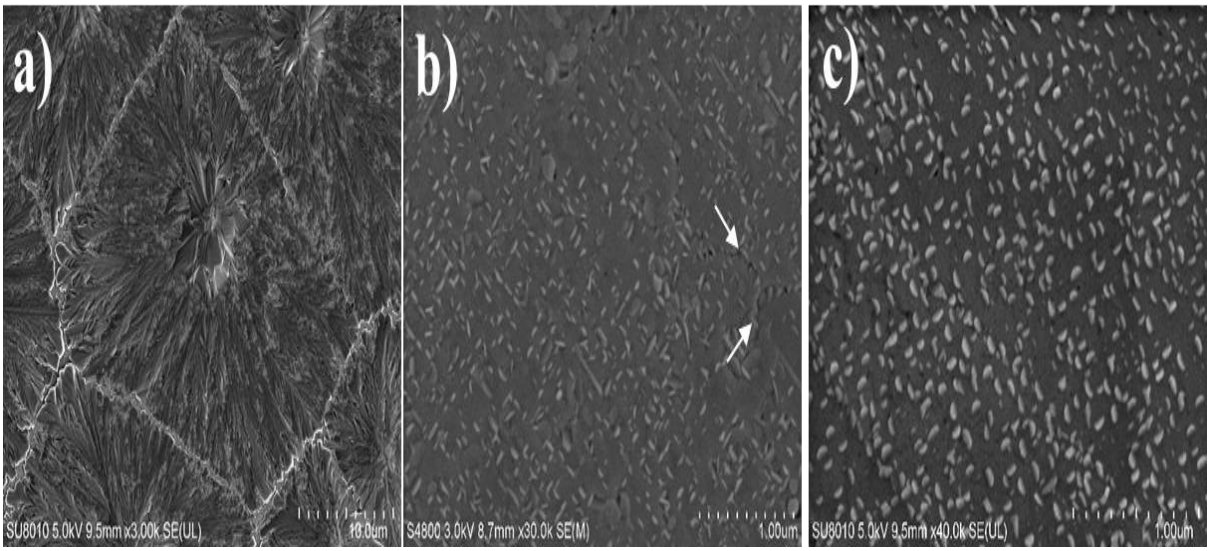


Figure 3 Scanning electron microscopic images of the pure (**a**) and (**b**, **c**) doped perovskite films. The arrows indicate the filling of the 0D perovskite sheets filled up in the grain boundaries. Scale bars: (**a**) 10 µm, (**b**) 1 µm, and (**c**) 1 µm.

To examine the surface morphology of the pure 3D and doped 0D/3D perovskites films, scanning electron microscopy (SEM) was performed, as shown in **Figure 3**. Pure 3D perovskites show large crystal domains with rough film morphology and defined domain boundaries, as shown in **Figure 3a**.

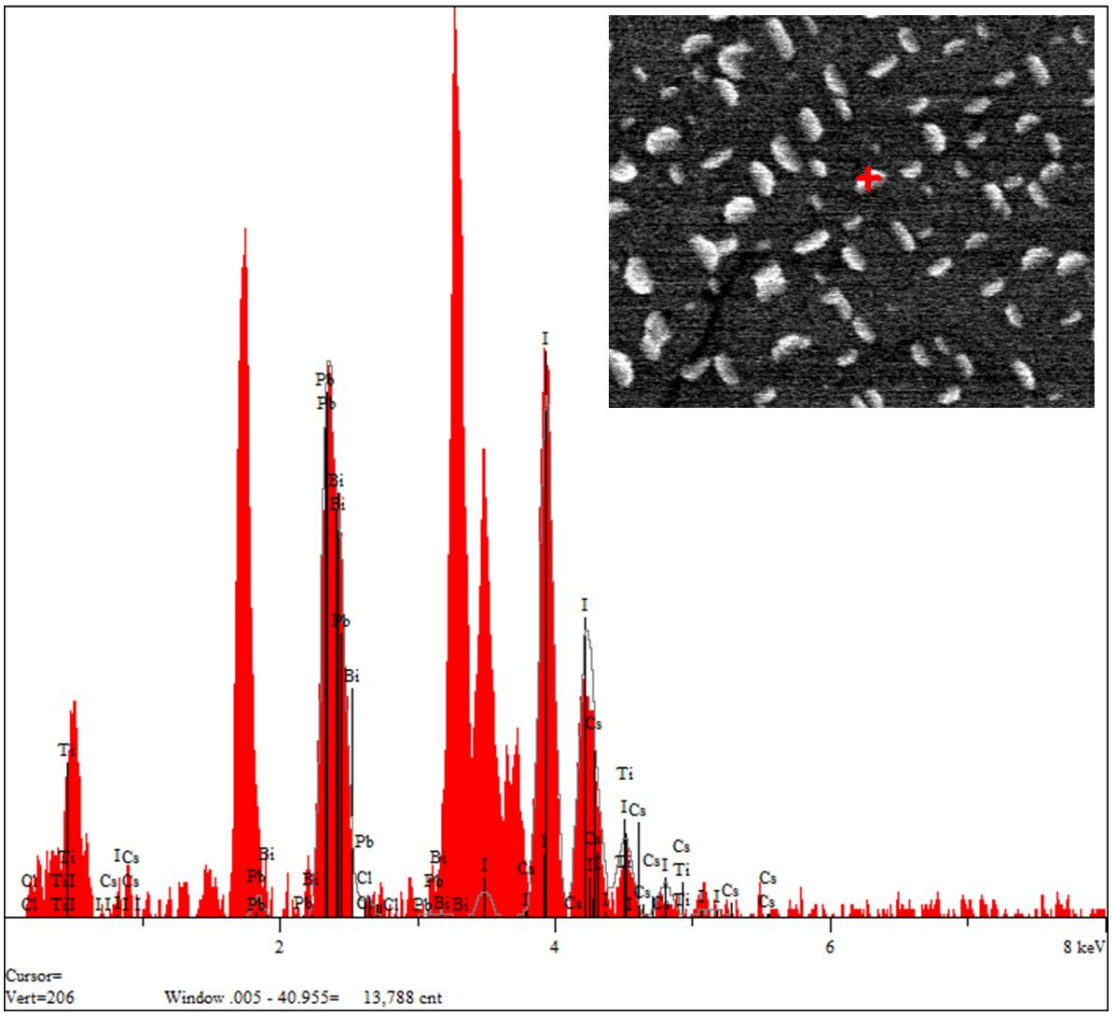
In contrast to this, 0D/3D perovskites showed smoother morphology with small hexagonal crystals vertically embedded into the 3D perovskite matrix, as shown in **Figures 3b** and **3c**. The smoother film morphology could be helpful for better contact between charge transporting material, leading toward better charge transportation. Also, the vertically oriented 0D perovskite crystals could have synergistic advantages, i.e., i. due to their hydrophobic nature, they act as shields against the moisture ingress to the main 3D perovskite matrix; ii. due to their vertical orientation to the substrate, they could fasten the charge transportation [22].

From the SEM images, larger crystal domains can be observed, which may be formed by the combination of a large number of crystallites. Such a large crystal domain could be useful to reduce the grain boundary, which leads to lesser carriers' recombination losses. Also, it provides more freedom to the exciton electron-hole pair to move across the grains and mitigates the defects in the sample. Moreover, due to their smaller surface-to-volume ratio, films with bigger domains are more environmentally stable [23].

In addition, the 0D perovskite crystals have filled up the grain boundaries (as shown in **Figure 3c**), hence minimizing the defect concentration in the film. Such high-quality

compact films are favorable for increased PV characteristics and decreased hysteresis losses [24].

To confirm whether these small vertically oriented crystals on the surface of the larger grain are 0D Bi-based perovskites or not; energy-dispersive x-ray spectroscopy (EDX) analysis was carried out. The elemental map of the EDX analysis (shown in **Figure 4**) showed a signature of bismuth and iodine along with other elements (given in table **Figure 4**).



Elt.	Line	Intensity (c/s)	Atomic %	Atomic Ratio	Conc	Units	Error 2-sig	MDL 3-sig	
Cl	Ka	.00	.000	.0000	.000	wt.%	.000	.000	
Ti	Ka	.00	.000	.0000	.000	wt.%	.000	.000	
I	La	153.18	47.172	1.0000	35.327	wt.%	2.215	1.966	
Pb	La	6.48	45.736	.9696	55.926	wt.%	24.213	30.349	
Bi	La	.64	7.092	.1503	8.746	wt.%	31.594	47.177	
			100.000		100.000	wt.%			Total

Figure 2 EDX mapping of the small sheet-like crystals (top) and corresponding elemental chart (bottom). The inset of the figure is the SEM image of the selected area, which was used for EDX characterization.

The improved crystallinity of the 0D/3D perovskite films was also justified by their XRD analysis. **Figure 5a** shows the XRD patterns of the pure 3D perovskites (bottom) as well as 0D/3D perovskites (top and middle). It can be observed from the pure 3D perovskites pattern that the peaks are very faint showing poor crystallinity and orientation of the crystals. On the other side, the XRD pattern of the 0D/3D perovskites (middle) shows significantly intense peaks, indicating its superior crystallinity and preferred orientation perpendicular to the substrate. The peaks near 14° and 28° (designated with stars and diamond symbols) are representing the reflection from the (001) and (002) planes of the cubic phased perovskite crystals [15]. All of the peaks exhibit narrow full-width maxima, indicating the larger size of the crystals. The top of **Figure 5a** shows the XRD pattern of the same sample after being exposed to the ambient environment for 2 weeks.

Almost no change is observed in the XRD pattern of the sample, indicating that the samples retained their crystallinity even after exposure to the ambient conditions. The improved environmental stability is attributed to the inclusion of the lower dimension perovskites as well as to the compactness of the film.

The existence of the small peak (**Figure 5b**, designated with a sphere) near the 8° is attributed to the formation of the 2D perovskites due to the reaction of the DACl with the leftover PbI_2. Such peaks are also previously observed for the 2D/3D perovskites [15]. The increased crystal size can also be observed from the deviation of the main 3D perovskites peaks towards lower angles, which usually occurred with the shrinkage of the crystal size.

Furthermore, the crystallites size for the doped samples is calculated using D. Scherrer's equation formula: $d = K\lambda/\beta Cos\theta$ [25]. Where d is crystallite size, K is Scherrer's constant (i.e., 0.94), λ is x-ray's wavelength (i.e., 1.5406 Å for CuKα)), β is full-width of the half maximum (FWHM), and θ is the Bragg's angle in degrees. By using FWHM = 0.07222 (calculated from the intense diffraction peak), θ = 0.9925, the crystallite size is calculated to be 2.02 nm. The crystallite size is much smaller than the crystal domains or grains that are shown in the SEM images, which indicates that the crystal domains are composed of a large number of crystallites.

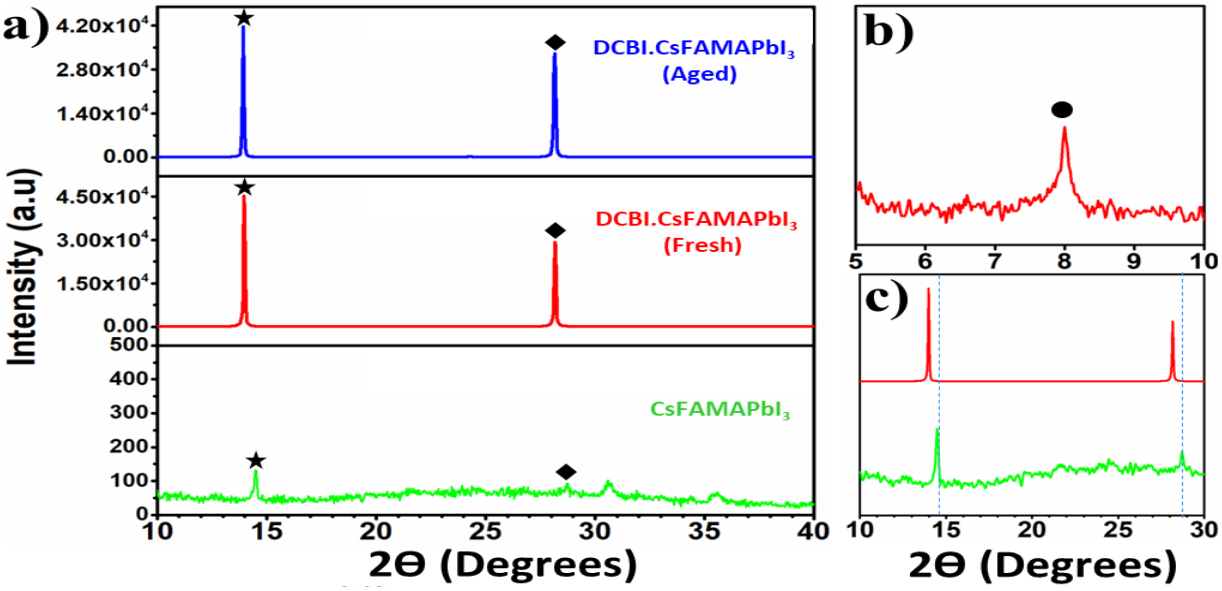


Figure 5 X-ray diffraction analysis of the DCBI doped $CsFAMAPbI_3$ perovskites thin film: (**a**) Pure $CsFAMAPbI_3$ (bottom), freshly doped with DCBI (middle), and aged doped with DCBI (top). Stars and diamonds represent the main 3D perovskite peaks. (**b**) The visualization of the peak is due to the formation of the 2D perovskites. (**c**) The deviation of the main XRD peaks towards a smaller angle.

CONCLUSION AND RECOMMENDATIONS

The researchers combined a 3D perovskite ($CsFAMAPBI_3$) with a dodecylammonium chloride doped 0D perovskite to prepare 0D/3D perovskites. Thin films based on such perovskite exhibited larger grains with compact grain boundaries. The surface morphology of the films was studied using scanning electron microscopy. The improved crystallinity of the 0D/3D perovskite films was justified by XRD analysis. Optical absorption and PL spectra showed the typical characteristics of the 3D perovskites. Along with better crystallinity, the prepared 0D/3D perovskites exhibited improved environmental stability. It is believed that these high-quality, pinholes-free, and compact perovskite films with larger grain sizes will play a vital role in the improvement of the performance of the next generation of perovskite-based optoelectronic devices.

Acknowledgment

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REFERENCES

1. Yang, W. S., Park, B. W., Jung, E. H., Jeon, N. J., Kim, Y. C., Lee, D. U., ... & Seok, S. I. (2017). Iodide management in formamidinium-lead-halide–based perovskite layers for efficient solar cells. *Science*, *356*(6345), 1376-1379.

2. Correa-Baena, J. P., Saliba, M., Buonassisi, T., Grätzel, M., Abate, A., Tress, W., & Hagfeldt, A. (2017). Promises and challenges of perovskite solar cells. *Science*, *358*(6364), 739-744.

3. Kojima, A., Teshima, K., Shirai, Y., & Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the american chemical society*, *131*(17), 6050-6051.

4. Sai Bai, Yizheng, and J.F. Gao. (2015). *Organometal Halide Perovskites for Photovoltaic Applications*, in *Advanced Functional Materials*. p. 535-566.

5. Zhang, W., Eperon, G. E., & Snaith, H. J. (2016). Metal halide perovskites for energy applications. *Nature Energy*, *1*(6), 1-8.

6. Saparov, B., & Mitzi, D. B. (2016). Organic–inorganic perovskites: structural versatility for functional materials design. *Chemical reviews*, *116*(7), 4558-4596.

7. *Best Research-Cell Efficiency Chart*.https://www.nrel.gov/pv/cell-efficiency.html.

8. Jeong, J., Kim, M., Seo, J., Lu, H., Ahlawat, P., Mishra, A & Kim, J. Y. (2021). Pseudo-halide anion engineering for α-FAPbI3 perovskite solar cells. *Nature*, *592*(7854), 381-385.

9.*Chart of Best Research-Cell Efficiencies*.Retrieved June 4, 2021 from http://www.nrel.gov/pv/assets/images/efficiency_chart.jpg.

10. Ma, L., Ju, M. G., Dai, J., & Zeng, X. C. (2018). Tin and germanium based two-dimensional Ruddlesden–Popper hybrid perovskites for potential lead-free photovoltaic and photoelectronic applications. *Nanoscale*, *10*(24), 11314-11319.

11. Reshi, H. A., & Zargar, R. A. (2018). Perovskite solar cells: the challenging issues for stable power conversion efficiency. *Recent Dev. Optoelectron. Devices*, *117*.

12. Liang, Z., Zhang, S., Xu, X., Wang, N., Wang, J., Wang, X., & Ding, J. (2015). A large grain size perovskite thin film with a dense structure for planar heterojunction solar cells via spray deposition under ambient conditions. *RSC advances*, *5*(74), 60562-60569.

13. Gedamu, D., Asuo, I. M., Benetti, D., Basti, M., Ka, I., Cloutier, S. G., & Nechache, R. (2018). Solvent-antisolvent ambient processed large grain size perovskite thin films for high-performance solar cells. *Scientific reports*, *8*(1), 1-11.

14. Nie, W., Tsai, H., Asadpour, R., Blancon, J. C., Neukirch, A. J., Gupta, G., & Mohite, A. D. (2015). High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science*, *347*(6221), 522-525.

15. Ali, N., Wang, X., Rauf, S., Attique, S., Khesro, A., Ali, S., & Wu, H. (2019). Enhanced stability in cesium assisted hybrid 2D/3D-perovskite thin films and solar cells prepared in ambient humidity. *Solar Energy*, *189*, 325-332.

16. Ali, N., Rauf, S., Kong, W., Ali, S., Wang, X., Khesro, A., & Wu, H. (2019). An overview of the decompositions in organo-metal halide perovskites and shielding with 2-dimensional perovskites. *Renewable and Sustainable Energy Reviews*, *109*, 160-186.

17. Zhang, X., Wu, G., Fu, W., Qin, M., Yang, W., Yan, J., & Chen, H. (2018). Orientation regulation of phenylethylammonium cation based 2D perovskite solar cell with efficiency higher than 11%. *Advanced Energy Materials*, *8*(14), 1702498.

18. Yao, K., Wang, X., Xu, Y. X., Li, F., & Zhou, L. (2016). Multilayered perovskite materials based on polymeric-ammonium cations for stable large-area solar cell. *Chemistry of Materials*, *28*(9), 3131-3138.

19. Khadka, D. B., Shirai, Y., Yanagida, M., & Miyano, K. (2019). Tailoring the film morphology and interface band offset of caesium bismuth iodide-based Pb-free perovskite solar cells. *Journal of Materials Chemistry C*, *7*(27), 8335-8343.

20. Ali, N., Attique, S., Rauf, S., Wang, X., Khesro, A., Ali, S., & Wu, H. (2020). The effect of dodecylammonium chloride on the film morphology, crystallinity, and performance of lead-free Bi-based solution-processed photovoltaics devices. *Solar Energy*, *207*, 1356-1363.

21. Bi, C., Shao, Y., Yuan, Y., Xiao, Z., Wang, C., Gao, Y., & Huang, J. (2014). Understanding the formation and evolution of interdiffusion grown organolead halide perovskite thin films by thermal annealing. *Journal of Materials Chemistry A*, *2*(43), 18508-18514.

22. Zhang, X., Wu, G., Yang, S., Fu, W., Zhang, Z., Chen, C., & Chen, H. (2017). Vertically oriented 2D layered perovskite solar cells with enhanced efficiency and good stability. *Small*, *13*(33), 1700611.

23. Attique, S., Ali, N., Khatoon, R., Ali, S., Abbas, A., Yu, Y., & Yang, S. (2020). Aqueous phase fabrication and conversion of Pb (OH) Br into a CH 3 NH 3 PbBr 3 perovskite and its application in resistive memory switching devices. *Green Chemistry*, *22*(11), 3608-3614.

24. Tang, Z., Bessho, T., Awai, F., Kinoshita, T., Maitani, M. M., Jono, R., & Segawa, H. (2017). Hysteresis-free perovskite solar cells made of potassium-doped organometal halide perovskite. *Scientific Reports*, *7*(1), 1-7.

25. Ali, N., Bi, G., Khesro, A., Khan, M., Lang, J., Samreen, A., & Wu, H. (2018). Hybrid AgNPs/MEH-PPV nanocomplexes with enhanced optical absorption and photoluminescence properties. *New Journal of Chemistry*, *42*(23), 18991-18999.

Assessment of Residential Water Demand and Groundwater Supply using ArcGis Tools in Mardan City, Khyber Pakhtunkhwa, Pakistan

Mohammad Ibrahim[1], Dr. Ihsanullah[2], Ghani Ur Rehman[3], Mohammad Iqbal[4]

ABSTRACT

Mardan city is facing the problem of portable water supply. Majority of the households do not have access to public water supply. The main focus of this research is to assess present residential water demand and ground water supply in the study area. To achieve this objective, baseline data was collected from Municipal Committee Mardan (MCM) and Public Health Engineering Department (PHED) Mardan. The ancillary data was collected from census reports Bureau of Statistics, etc. The results showed that the present water supply in each sampled union council is less than that of water demand. The gap between ground water supply and demand is widening due to population growth and urbanization. There is urgent need to enhance ground water supply to meet increasing water demand in the study area.

Keywords: *Water supply, water demand, Arc GIS, Portable water*

INTRODUCTION

Water is vital to human existence. Access to potable water supply is a basic human right [1]. It is significant to recognize that every individual on earth must have access to water [2]. About 1.1 billion people who are 17% of the total world population do not have access to portable water resources [3]. Out of this 1.1 billion people, 22% people live in South Asia, 30% in Sub- Sahara Africa and 39% in East Asia and the Pacific [4]. With the passage of time, these numbers will further increase due to rapid population growth. However, this situation will be more critical in South Asia, Africa and Middle East [5].

Rapid population growth, urbanization and climate change related uncertainties are the major causes of water scarcity around the globe [6]. Since 2007, urban population has exceeded rural population due economic migration [7]. A vertical growth of societies was observed in the form of multi-storied buildings to accommodate increasing population on a

[1] Assistant Professor of Geography GDC Palai, Malakand, **Corresponding Author's Email: ibrahimgeographer@gmail.com**
[2] Assistant Professor of Geography, Department of Geography, University of Peshawar
[3] Lecturer in Geography, University of Gujarat, Punjab
[4] PhD scholar, Shijiazhuang University, China

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limited area [8]. This also resulted in the physical characteristics of the household such as number of rooms, built of area and garden area. These changes in household physical characteristics have a direct effect on the household water consumption [9]. The commercial, industrial and residential water demands are assessed by water management authorities [10]. However, more emphasis is given to residential water demand because it not only consumed more than 50% of the total municipal water but also required better consistency and quality as compared to other sectors [12].

In Pakistan, the population growth and per capita water availability has a direct relationship [13]. In 1951, the per capita water availability was 5650 cubic meter and the population was 33.7 million. This availability of water was reduced to 2800 cubic meter as the population reached to 65 million in 1972 [14]. By the year 1992, Pakistan has entered to water stress country [15]. The per capita availability would decrease to 800 cubic meter by the year 2020 at the present rate of population growth [16]. Therefore, the proper understanding and management of water demand is outmost necessary to meet the needs of human for social and economic development in the future [17]. The demand of residential water is continuously increasing in the Mardan City because of rapid population growth and pace of urbanization. The rapid population growth exerts pressure on existing water supply infrastructure. As a result, water supply infrastructure is deteriorating making supply of water challenging and costly. Therefore, the main objective of this research paper is to assess residential water demand and ground water supply management in the study area.

METHODOLOGY

Study area description:

Mardan City is located from 34° 05' N to 34° 32' N latitude and 72° 3' E to 72°14' E longitude (Figure 1). It is about 60 km east of Peshawar, capital city of Khyber Pakhtunkhwa, Province of Pakistan. It is bounded on the Northeast by Buner, Northwest by Malakand, on the East by Swabi, on the West by Charsadda and on the South by Nowshera District respectively. District Mardan has extreme continental climate i.e., hot in summer and cool in winter. In summer, monsoon precipitation occurs from June to September in which August is the rainiest month, which has recorded 128.85 mm of rainfall [18]. In winters, precipitation occurs from December to March because of winter depression.

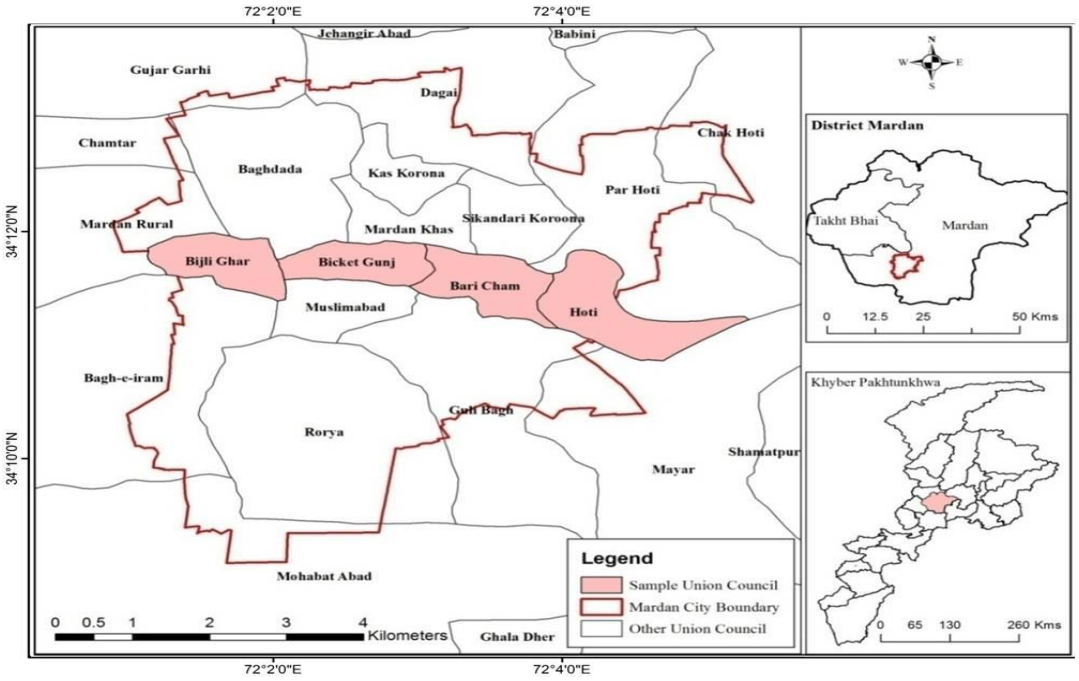

Figure 1: Location map of the study area, which is taken from Local Government and Rural Development Department, District Mardan

Existing source of water supply

Tube wells are the main ground water source of residential water supply in the study area. There are fourteen tube wells in the study area. Among these, two tube wells are in union council Bejlighar, four in union council Baricham, two tube wells in union council Bicket Gunj and six tube wells in union council Hoti respectively. These tube wells are operated once or twice a day to fill the overhead tanks. These tanks are connected with water supply pipelines. The widths of these pipelines vary in size from 2 to 8 inches as shown in figure 2.

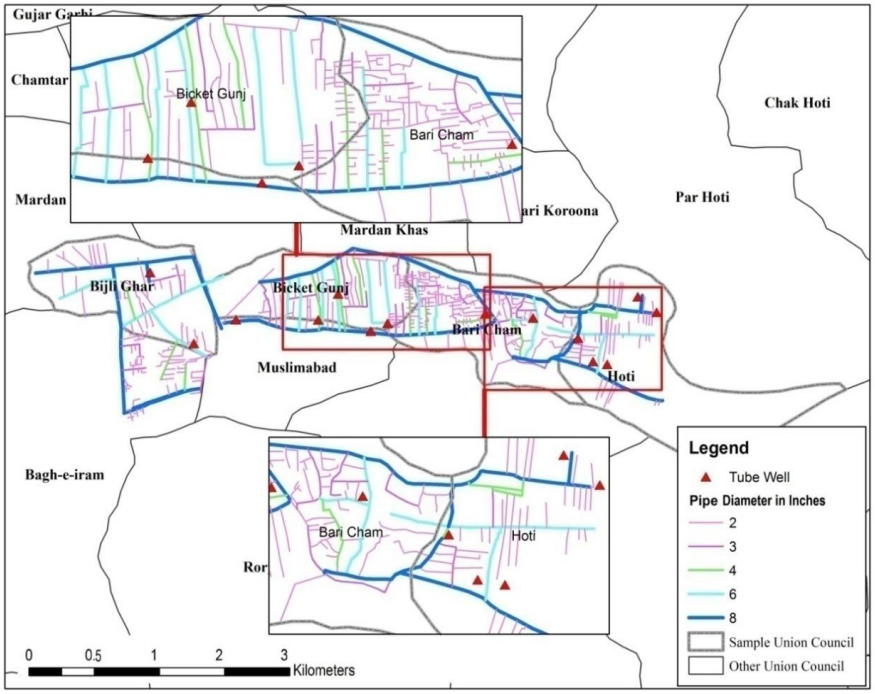

Figure 2: Density of Water Supply Pipelines and Tube Wells in the Study Area for which the source PHED Mardan (2015 has been used.

Population Growth and Distribution

Total population of district Mardan was 357 thousand in 1951. It reached to 481 thousand in 1961, 697, 881 and 1460 thousands in 1972, 1981 and 1998 respectively [19]. It is evident that the population of district Mardan has increased since 1951. For this study, union council polygon layer with attributes of population figures of 2009 were used to calculate population density layer. The analysis shows that except union council Hoti, all other sampled union councils have higher population density followed by adjacent union councils as evident from figure 3.

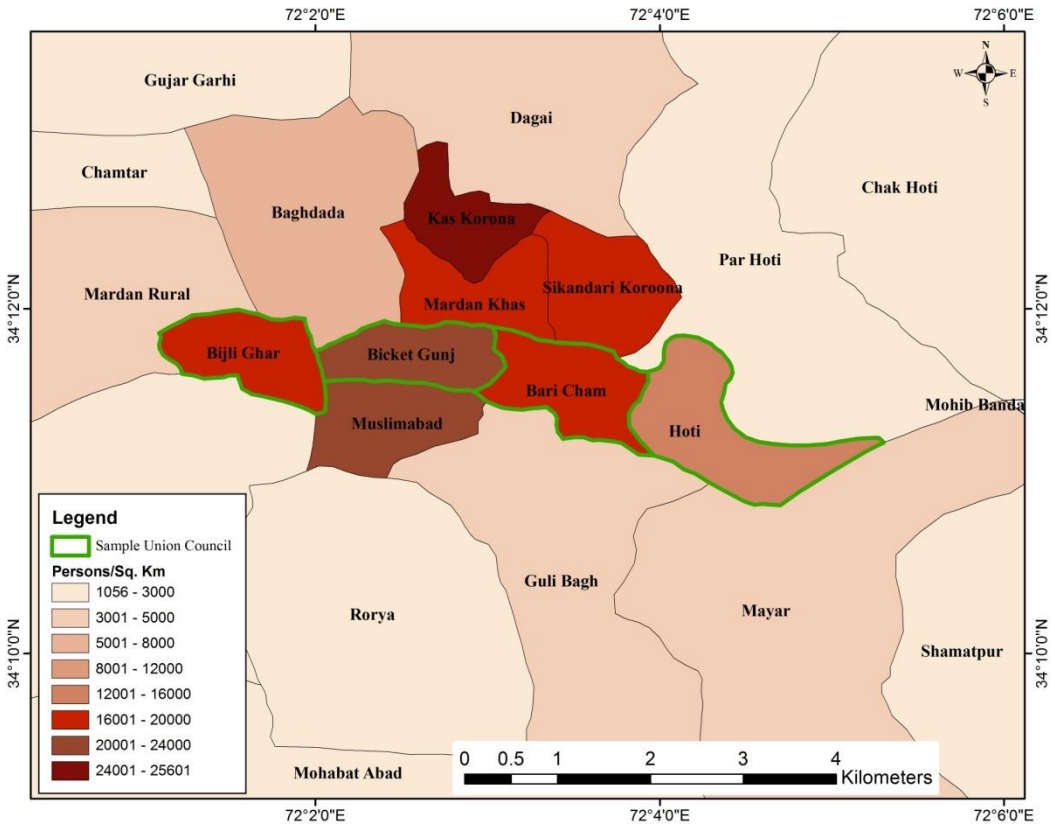

Figure 3: Population Density of the Study Area, taken from District Population Welfare Office Mardan (2009)

DISCUSSION AND ANALYSIS

The baseline data, such as maps of water supply pipelines and location of tube wells was collected from Public Health Engineering Department (PHED) Mardan and the data regarding water supply from each tube, type of machinery, number of connections, operational hours of each tube wells were collected from Municipal Committee Mardan (MCM). Map of the study area was obtained from Local Government and Rural Department (LG &RDD) Mardan. This map was later on modified in Arc GIS. The population statistics were taken from District Census Report of the study area. However, for this study, the population data of 2009 was obtained from population welfare department Mardan.

The maps of water supply pipelines, location of tube wells, overhead tanks were collected from PHED Mardan. First, these maps were scanned and were saved as jpeg files. Then these maps were geo-referenced and digitized in ArcGIS software. To find the total water demand for each sampled union council, the population figures were multiplied by 20 because MCM has taken 20 gallons as a standard of water supply for each individual in the study area. For this purpose, the population figures of 2009 were obtained from Social Welfare Department Mardan. The values of water supply per acre per day of each sampled

union council were obtained from MCM. To assess water budget, the following formula was used:

Water Budget = Water Demand – Water Supply

These values were then plotted on the study area map to show spatial distribution of water budget by using Arc GIS software.

Assessment of Residential Water Budget

Assessment of residential water budget is determined by subtracting water supply values from water demand values. The water demand values were obtained from census figures multiplied by standard of water supply fixed by water supply agency in the study area.

Union Council-Wise Per Acre Water Supply

The actual water supply in union council Bicket Gung is 75,000 gallons per day. The total area of union council is 153 acres. The per acre water supply in union council Bicket Gung is 490 gallons per day. The total public water supply in union council Hoti is 200,000 gallons per day and the total area is 538 acres, so per acre water supply is 372 gallons per acre per day. While the total water supply in union council Bari Cham is 170,000 gallons per day and its total area is 116 acres, so the total water supply per acre is 1,465 gallons per day. Similarly, the total water supply in union council Bejlighar is 170,000 gallons per day and its total area is 119 acres, so its total supply is 119 gallons per acre as shown in **figure 4**.

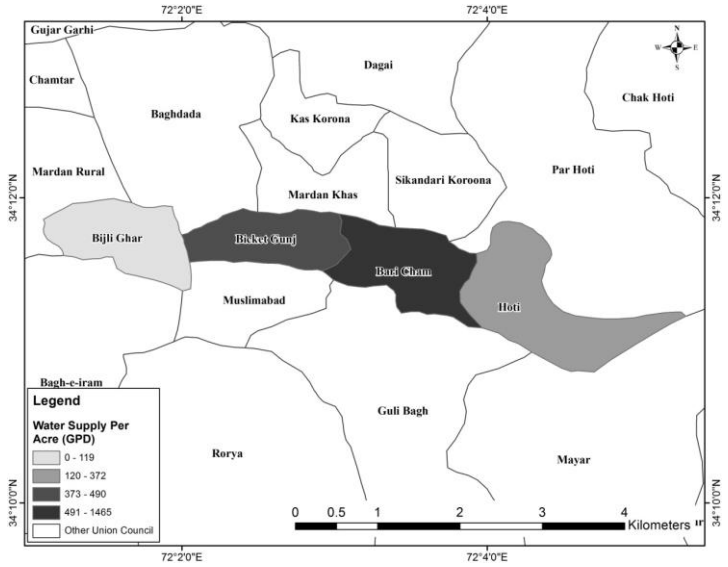

Figure 4: Union Council-Wise per Acre Water Supply, taken from MC Mardan (2015)

Union Council-Wise Per Acre Water Demand

The population density in union council Bicket Gung is 125.39 persons per acre. MCM has taken 20 gallons per day as a standard of water supply per capita in the study area. So, to find out water demand per acre in union council Bicket Gung, the population density per acre was multiplied by 20 and the result was 2,508 gallons per acre. Similarly, this water demand was 760 gallons, 3,680 gallons and 660 gallons per day in union council Hoti, Bari Cham and Bejlighar respectively as shown in **figure 5**.

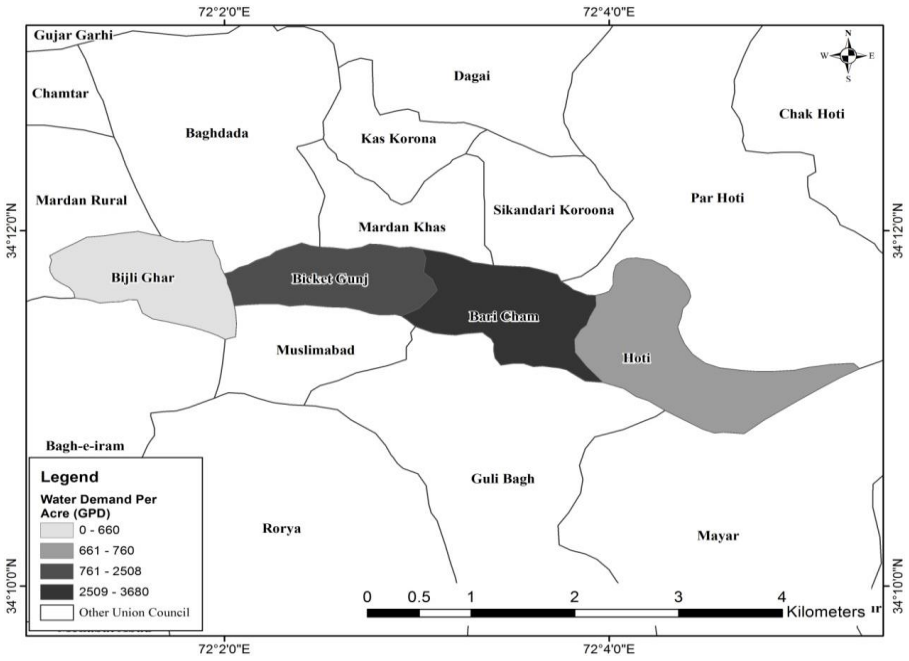

Figure 5: Union Council-Wise per Acre Water Demand, taken from MC Mardan (2015)

Water Budget Analysis Per Acre (Gallons per Day)

The present water demand per acre in union council Bejlighar is 660 gallons per day and actual water supply is 119 gallons per day. Similarly, this water demand is 2,508 gallons per day in union council Bicket Gung and its water supply 372 gallons per acre day while these figures are 3,680 gallons and 1,465 gallons per day per acre for union council Bari Cham and 760 and 372 gallons per acre per day for union council Hoti respectively. It is evident from above figures that water demands exceed more than 60% of the water supply in each sampled union council in the study area. This gap is widening with the passage of time because of rapid population growth and pace of urbanization. There is urgent need to improve the existing water supply to narrow down the gap between water supply and demand in the study area.

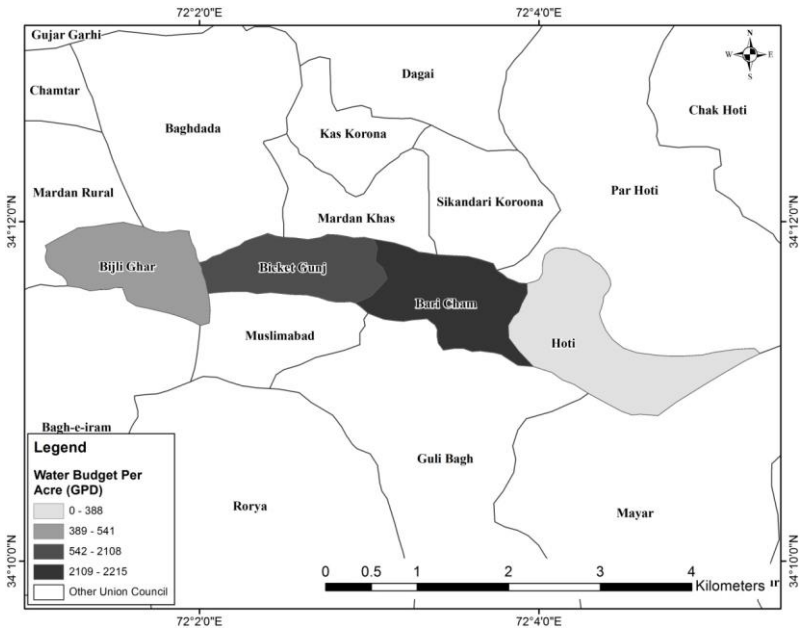

Figure 6: Water Budget Analyses per Acre (Gallons per Day) which is taken from MC Mardan (2015).

CONCLUSION AND RECOMMENDATIONS

In Mardan city, total water supply is dependent on ground water. Water is mainly supplied through tube wells. There are fourteen tube wells in four sampled union councils. Union council wise, water supply and demand budget analysis concludes that all the sampled union councils were short of water supply. Similarly, the present tube wells and water supply infrastructure is not capable of meeting the present water demand in the study area. There is an urgent need to allocate budget to upgrade present water supply infrastructure, to install new tube wells and employ skilled labor force for the maintenance of water supply pipelines and tube wells.

REFERENCES

1. Montgomery, M. A., & Elimelech, M. (2007). Water and sanitation in developing countries: including health in the equation. *Environmental science & technology*, *41*(1), 17-24.

2. Cosgrove, W. J., & Loucks, D. P. (2015). Water management: Current and future challenges and research directions. *Water Resources Research*, *51*(6), 4823-4839.

3.Onda, K., LoBuglio, J., & Bartram, J. (2012). Global access to safe water: accounting for water quality and the resulting impact on MDG progress. *International journal of environmental research and public health*, *9*(3), 880-894.

4. Cosgrove, W. J., & Loucks, D. P. (2015). Water management: Current and future challenges and research directions. *Water Resources Research, 51*(6), 4823-4839.

5. Azizullah, A., Khattak, M. N. K., Richter, P., & Häder, D. P. (2011). Water pollution in Pakistan and its impact on public health—a review. *Environment international*, *37*(2), 479-497.

6. Buytaert, W., & De Bièvre, B. (2012). Water for cities: The impact of climate change and demographic growth in the tropical Andes. *Water Resources Research*, *48*(8).

7. Novotný, L. (2016). Urban development and migration processes in the urban region of Bratislava from the post-socialist transformation until the global economic crisis. *Urban geography*, *37*(7), 1009-1029.

8. Wamsler, C., Brink, E., & Rivera, C. (2013). Planning for climate change in urban areas: from theory to practice. *Journal of Cleaner Production*, *50*, 68-81.

9. Fox, C., McIntosh, B. S., & Jeffrey, P. (2009). Classifying households for water demand forecasting using physical property characteristics. *Land use policy*, *26*(3), 558-568.

10. Kafy, A.A., Raikwar, V., Al Rakib, A., Kona, M.A. and Ferdousi, J., 2021. Geospatial approach for developing an integrated water resource management plan in Rajshahi, Bangladesh. *Environmental Challenges*, *4*, 100-139.

11. World Health Organization, WHO., & World Health Organisation Staff. (2004). *Guidelines for drinking-water quality* (Vol. 1). World Health Organization.

12. Mahmood, S., Mayo, S. M., & Mahmood, I. (2020). Spatial Quantification of Domestic Water Consumption in Rehankot, Dir Town, Khyber Pakhtunkhwa Province-Pakistan: Spatial Quantification of Domestic Water Consumption. *Proceedings of the Pakistan Academy of Sciences: A. Physical and Computational Sciences*, *57*(3), 77-85.

13 Mahmood, S., Mayo, S. M., & Mahmood, I. (2020). Spatial Quantification of Domestic Water Consumption in Rehankot, Dir Town, Khyber Pakhtunkhwa Province-Pakistan: Spatial Quantification of Domestic Water Consumption. *Proceedings of the Pakistan Academy of Sciences: A. Physical and Computational Sciences*, *57*(3), 77-85..

14. Hasnain, S. A. (2018). *An integrated approach towards identification of the barriers to implementation of rooftop Rainwater Harvesting Systems in urban residential areas of Pakistan* (Doctoral dissertation, Heriot-Watt University).

15. Hussain, A. (2020). Pakistan's Water Economy. In *Water Management in South Asia* (pp. 135-157). Springer, Cham.

16. Habib, Z. (2021). *Water availability, use and challenges in Pakistan-Water sector challenges in the Indus Basin and impact of climate change*. Food & Agriculture Org.

17. Khan, S., Guan, Y., Khan, F., & Khan, Z. (2020). A comprehensive index for measuring water security in an urbanizing world: the case of Pakistan's capital. *Water*, *12*(1), 166.

18. Pakistan, G. O. (1998). Population and housing census of Pakistan, population census organization statistics division. 2. *Census bull*.

Quality Estimation and Iodine Determination of Marketed Edible Iodized Salt at Consumer Level for Better Nutrition

Qazi Muhammad Sharif[1] Roohul Amin,[2] Jan Nisar[3]
Muhammad Sadeeq Afridi[1], Sana Ullah[2]

ABSTRACT

Six locally manufactured and one foreign manufactured marketed edible iodized salt samples are collected from super stores. These samples are analyzed for impurities like Magnesium Sulphate, Calcium Chloride, Calcium Sulphate, Magnesium Chloride, Sodium Sulphate, Potassium Chloride, Water Insoluble Matter, Acid insoluble Matter, Alkalinity, Iodine content and Trace elements. Most of the samples have purity as NaCl greater than permissible limits as per Codex Alimentarius specifications, while some samples are less pure and are not safe for human consumption. Metal load in all salt samples are in the permissible limits as per Codex Alimentarius specifications except lead (Pb), which is greater than permissible limits in one sample. Iodine content at consumer level is adequate in all salt samples and complies with standard specifications except one sample. On the basis of purity as NaCl the foreign manufactured salt sample and sample LM-5 are superior in quality and Iodine content than other locally manufactured salt samples.

***Keywords**: Salt, impurities, Codex Alimentarius, Trace elements, Iodine content*

INTRODUCTION

Salt is an essential mineral for animal life, composed chemically of sodium chloride. It is an important part of human diet as it is necessary to take a particular amount of salt in food daily for the normal functions of the human body. The UK's Scientific Advisory Committee on nutrition (SCAN) suggested that for an adult, the reference nutrient intake is 4.0gm salt per day (1.6gm or 70 mmole sodium). The FDA does not make a suggestion but refers to Dietary Guidelines for Americans 2005. They suggested that salt to be consumed per day must be less than 2,300 mg of sodium (2.3gm of sodium=5.8gm salt) per day [1]. It is also used for preventing heat cramps and other medicinal purposes. One common

[1] P.C.S.I.R Laboratories Complex Peshawar, Pakistan
[2] Assistant Professor of Chemistry, Government College Peshawar – University of Peshawar, Pakistan, **Corresponding Author's Email: roohulamin1947@gmail.com**
[3] National Center of Excellence in Physical Chemistry University of Peshawar, Pakistan

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medicinal use is for isotonic salt solutions. It is commonly used in preserving and seasoning foods such as in curing meat, other meat products, curing fish, making pickles, preserving other vegetables, canning vegetables, meat baking and many other familiar house hold uses [2].

Pakistan is one of the few countries that have been bestowed with all types of available salt in the world i.e. rock salt, sea salt and lake salt. Salt mines of salt range are the oldest mines of the sub-continent from the eastern terminal part of the salt range [3], the plugging of the salt has been out cropped at different places like Warcha, Kalabagh, Khewra, Jatta and Bahadurkhel, which produce many thousands tons of salt annually [4].

However, salt is produced in different forms i.e., unrefined salt (such as sea salt), refined salt (table salt), and iodized salt. Refined salt, which is most widely used presently, is mainly sodium chloride. The food grade salt accounts for only a small part of salt production in industrialized countries (3% in Europe [5]) although world-wide, food uses account for 17.5% of salt production [6]. Today, most refined salt is prepared from rock salt. These rock salt resources were obtained by the evaporating of old salty lakes [7].

These resources may be gotten by conventional method or via the injection process of water. Such injected water works to dissolve salt, meanwhile the salty solution may be pushed to surface where the salt is collected from brine. This raw form of salt is refined and purified. This purification is also called recrystallization process. In this method, the salty solution is also mixed with chemicals for precipitation of impurities (mostly Calcium and Magnesium salts) [8]. Several steps of evaporation are utilized for collection pure crystals of sodium chloride.

This table salt is refined after purification and mixed with a small amount of Potassium Iodide (KI), or Sodium Iodide (NaI), or Iodate, to reduce the Iodine deficiency in human beings. While keeping the important of Iodine (I), which is mandatory for the production and proper function of thyroid hormones inside the body [9]. The deficiency of causes Iodine Deficiency Disorder (IDD) which is considered a common group of diseases. This IDD varies from abortion/stillbirth to the formation of goiter or impaired mental disorder [10].

The Iodine is an important element works for the prevention of insufficient production of thyroid hormones (hypothyroidism), which produce goiter, while cretinism in children, and meanwhile myxedema in young. The Iodized common salt reduced disorders of iodine deficiency significantly in countries where it is utilized [11]. The IDD affected roundabout 30 percent of world population, where 655 million people across the world is reported with goiter [12]. This IDD affected about 50 million population in Pakistan, in which 6.5 million people are affected seriously [13].

The Pakistani Government in collaboration of UNICEF initiated a struggle to cope with the IDD by the utilization of iodized salt and advertized extensive attentiveness via

media both print and electronic sources. The marketing of iodized oil and supplementation of iodized salt during 1985-1995 was carried out among four million persons [14]. The production, and distribution of non-iodized salt is banned in Khyber Pakhtunkhwa and Baluchistan since 1994 and 1995 effective through legislation respectively. This study is little forward to our previous studies [15]. In the present work marketed salt samples were assessed for its quality parameters, purity as sodium chloride, trace metals and iodine content at consumer level.

METHODOLOGY

Chemicals used for the analysis are all of analytical grade and used without further purification. Water used was doubly distilled over alkaline $KMnO_4$.

Sample preparation

The salt samples were crushed, grinded and sieved -80 mesh and stored in appropriate air tight glass containers. Weighed 5.0gm of each samples and added slowly to a beaker containing 100 ml doubly distilled water and a magnetic stirrer. Stirred the salt solution for 5 minutes, then the residue was separated by vacuum filtration for water insoluble matter and preparing the volume of the filtrate up to 500 ml in a volumetric flask as a stock solution for further analysis as per ASTM and AOAC methods [19-20].

Separate samples were taken for the determination of iodine content and acid insoluble matter as per AOAC methods [20].

Atomic Absorption spectrophotometer

The salt samples solution were prepared by dissolving 5.0 gm of powdered sample in 10.0 ml of Nitric acid and 90.0 ml of doubly distilled water in 100 ml of volumetric flasks. These solutions were heated to ensure metal ions dissolution. The solutions were filtered to remove any insoluble matter. The trace elements were analyzed by atomic absorption spectrophotometer having specification as (Model#Z-8000, Hitachi, Japan).

DISCUSSION AND ANALYSIS

The six different local brands and one foreign brand edible iodized salt samples were collected followed analysis by conventional and instrumental methods [16-20]. These samples are analyzed for moisture content, alkalinity, water insoluble matter, acid insoluble matter, alkalinity and purity as per ASTM standard method [19]. The experimental results are given in Table-1 below.

Table-1. Solubility of salt in acid and water, alkalinity, purity and moisture contents

Salt 2samples	**Acid insoluble %**	**Alkalinity as Na_2CO_3 %**	**Water insoluble %**	**Moisture %**	**Purity* as NaCl %**
LM-1	0.146	0.067	0.152	0.078	98.75

	±0.002	±0.001	±0.002	±0.002	
LM-2	0.160 ±0.003	0.075 ±0.001	0.640 ±0.012	0.230 ±0.017	96.94
LM-3	0.130 ±0.002	0.112 ±0.0 02	0.920 ±0.016	0.170 ±0.015	96.60
LM-4	0.270 ±0.002	0.570 ±0.012	0.330 ±0.014	0.077 ±0.002	94.42
LM-5	0.140 ±0.002	0.440 ±0.018	0.400 ±0.019	0.070 ±0.001	98.20
LM-6	0.020 ±0.002	0.460 ±0.019	0.040 ±0.002	0.009 ±0.001	96.94
FM	0.320 ±0.017	0.075 ±0.002	0.380 ±0.015	0.016 ±0.001	99.38

The presence of different salts and radicals such as Potassium (K^{+}), Calcium (Ca^{+2}), Magnesium (Mg^{+2}), Sulphate (SO_4^{-2}) and Iodine are determined and the results are recorded in table 2 as per ASTM standard method [19].

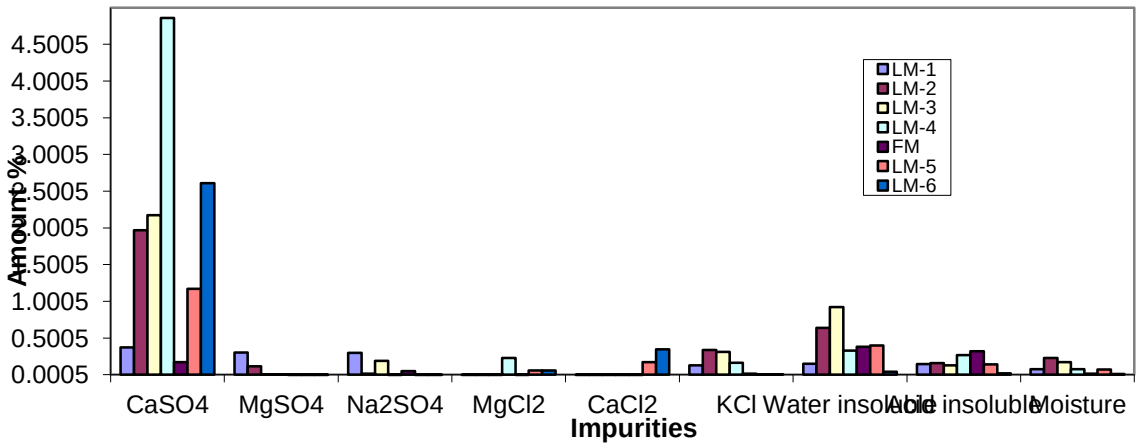


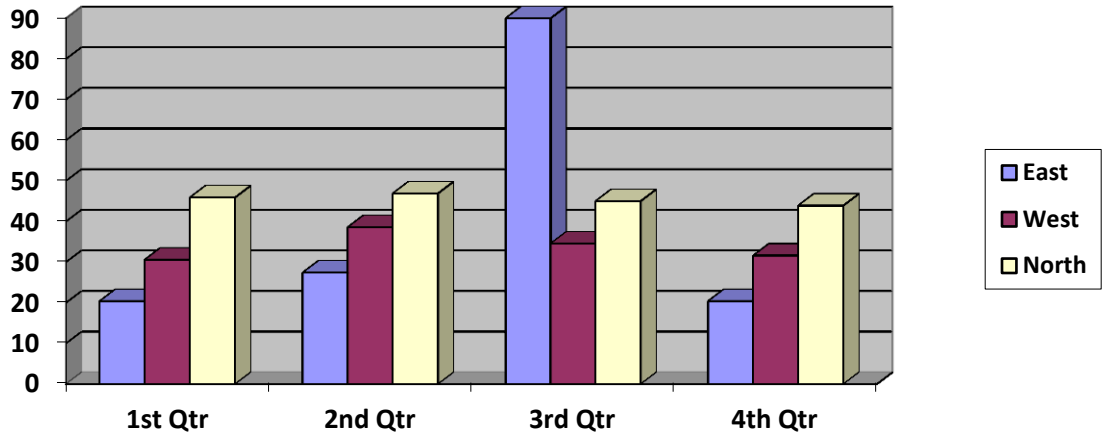
Figure.1 Composition of different Salts (as impurities in salt samples)

The table-1 shows that the moisture content ranges from 0.009% (LM-6) to 0.23%(LM-2), alkalinity as Na_2CO_3 ranges from 0.067% (LM-1) to 0.570 % (LM-4), Water insoluble matter from 0.04% (LM-6) to 0.92% (LM-3), Acid insoluble matter from 0.02% (LM-6) to 0.32% (FM), $CaSO_4$ from 0.173% (FM) to 4.86 % (LM-4), $MgSO_4$ from 0.00 (FM, LM-5 & LM-6) to 0.114(LM-2), Na_2SO_4 from 0.00 (LM-4, 5 & 6) to 0.297% (LM-1), $MgCl_2$ from 0.00 (LM-1,2,3& FM) to 0.227% (LM-4),$CaCl_2$ from 0.00 (LM1,2,3,4 & FM) to 0.347% (LM-6), KCl from 0.006% (LM-5 & 6) to 0.339% (LM-2).The presence of small

amounts of different salts in small amount (considered as impurities) in all salt samples are shown in figure-1and table 2.

Table -2 Percentage ratios of different salts (as impurities in salt samples)

Salt samples	**$CaSO_4$ %**	**Na_2SO_4 %**	**$MgSO_4$ %**	**$MgCl_2$ %**	**$CaCl_2$ %**	**KCl %**
LM-1	0.374 ±0.009	0.297 ±0.015	0.304 ±0.016	0.000	0.000	0.128 ±0.002
LM-2	1.970 ±0.024	0.014 ±0.002	0.114 ±0.013	0.000	0.000	0.339 ±0.018
LM-3	2.174 ±0.010	0.188 ±0.015	0.003 ±0.001	0.000	0.000	0.310 ±0.018
LM-4	4.860 ±0.103	0.000	0.003 ±0.001	0.227 ±0.003	0.000	0.162 ±0.013
LM-5	1.172 ±0.011	0.000	0.000	0.060 ±0.001	0.171 ±0.015	0.006 ±0.002
LM-6	2.609 ±0.054	0.000	0.000	0.060 ±0.001	0.347 ±0.014	0.006 ±0.002
FM	0.173 ±0.015	0.050 ±0.001	0.000	0.000	0.000	0.150 ±0.015



Results are given by calculating means of Six times analysis of each sample with Standard deviation.

* Purity determined as per ASTM standards E 534-98 (2002).

Salt samples LM.2, 3, 4 and 6 have purity as NaCl less than Codex Alimentarius specifications [21], and are not safe for human consumption while salt samples LM-1, 5 and FM are safe for human consumption. The purity of all salt samples are given in the figure 2

below.

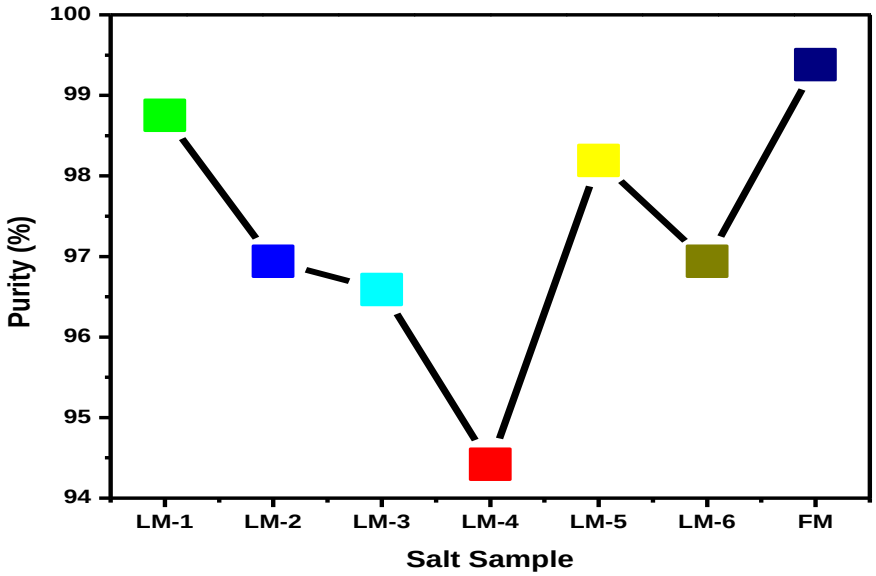


Figure-1. Purity of different salt samples LM-1 to LM-6 and FM

The Acid insoluble matter is also higher for all salt samples than ICRC standard specifications [22] except sample LM-6.The recommended alkalinity as Na_2CO_3 is with in permissible limits for sample LM-1, 2, & FM while it is higher than permissible limits for sampleLM-3, 4, 5 & 6.

Trace elements have important consequences due to their affinity to accommodate inside human organs over a prolonged period of time. The occurrence of trace metals beyond the permissible upper and lower limits is responsible for metabolic disturbance. Thus the deficiency and as well as the excess of trace metals may produce undesirable effects [23]. Trace elements (Fe, Zn, Pb, Ni, Mn, Cr, Cd & Co) were analyzed with the help of atomic absorption spectrophotometer. The results of trace elements are given in Table-2. There was no presence of trace metals (Mn, Cr, Cd and Co) in all salt samples, however Fe, Zn, Pb and Ni were found in various amounts in all samples.

Sample LM-1, 4 & FM has permissible level of iron as per RDA limit of 50-400 µg/day, while sample LM-2, 3, 5 & 6 has no iron content. Iron exhibits an important role in the metabolism inside human body. It acts as a catalyst and it is present in greater quantity than any other trace element [24]. Sample LM-2, 3 & FM has no lead (Pb) content while sample LM-4, 5 and 6 has permissible Level of lead content. Sample LM-1 has 2.95 mg/kg of lead, which is greater than codex alimentarius standard specifications. [21]

Lead is a toxic trace metal and is a cumulative poison, which is found in surface/ground water as a result of its dissolution from natural sources [25]. Lead is regarded as high hazardous for plants & animals. Long term intake or exposure may cause in accumulation of lead inside the body and may cause more severe symptoms. These include pale skin, anemia, decrease handgrip strength, vomiting, nausea, abdominal pain, and paralysis of the wrist joint, chances of miscarriage or birth defects [26].

Amount of Zinc ranges from 0.92 mg/kg (LM-3) to 4.56 mg/kg (LM-5). Zinc (Zn) is an important element playing a range of functions in the body, beside this Zn is cofactor for a number of enzymes, however no health based guidelines values has been proposed by codex alimentarius. The concentration range of Ni in the analyzed samples is from 1.84 mg/kg (LM-3) to 7.87 mg/kg (LM-1), while there is absence of Ni in sample FM. However no health based guidelines values has been proposed by codex alimentarius for nickel. Iodine was also determined in these samples and shown in figure 3. Salt containing (0-7 PPM) iodine content is low, (7-15 PPM) iodine content is moderate and from (>15 PPM) is adequate [27].

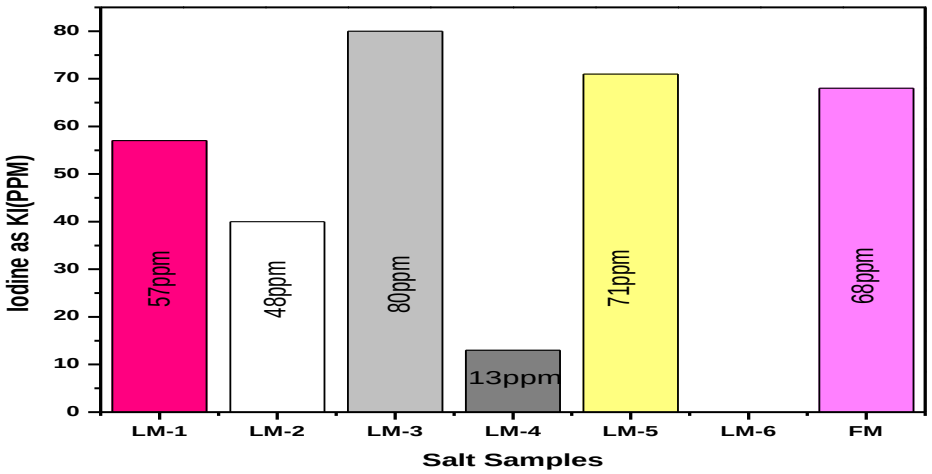


Figure 3. Iodine contents in different salt samples

It is suggested plan that the iodization level is set at a minimum of 15 PPM at customer level and 30 PPM at manufacturing level [28]. Iodine content in all samples is adequate (> 15 PPM) except Sample No. LM-4 where iodine content is moderate and sample No.LM-6, where iodine content is low. The results are given in Table-3.

Table-3. Iodine content in different salt samples including as

Salt samples	LM-1	LM-2	LM-3	LM-4	LM-5	LM-6	FM
Iodine as KI (PPM)	57	40	80	13	71	NIL	68

CONCLUSION AND RECOMMENDATIONS

From the present study, it is clear that nearly all salt locally produced are not safe for human consumption due to impurities although iodine supplementations is proper in most of the samples. The salt sample FM that is foreign brand sample is purified and safe for human consumption.

It is recommended that routine assessment of the quality of edible iodized salt at salt deposits and purifying plants at salt refineries should be undertaken by the concerned authorities and if found unsatisfactory, the manufactures should be subjected to punitive measures.

The salt is readily available in the country but will only be successful in combating dietary nutrient deficiencies if the government, health agencies and salt producers combine together.

REFERENCES

1. US Department of Health and Human Services. (2005). Dietary guidelines for Americans 2005. *http://www. health. gov/dietaryguidelines/dga2005/document/default. htm*.

2. Firestone, D. (1994). Determination of the iodine value of oils and fats: summary of collaborative study. *Journal of AOAC International*, *77*(3), 674-676.

3. Simurdiak, M., Olukoga, O., & Hedberg, K. (2016). Obtaining the iodine value of various oils via bromination with pyridinium tribromide. *Journal of Chemical Education*, *93*(2), 322-325.

4. Das S, Dash HR (2014). *Laboratory Manual for Biotechnology*. S. Chand Publishing. p. 296. ISBN 978-93-83746-22-4.

5. Miyake, Y., Yokomizo, K., & Matsuzaki, N. (1998). Rapid determination of iodine value by 1H nuclear magnetic resonance spectroscopy. *Journal of the American Oil Chemists' Society*, *75*(1), 15-19.

6. Hilp, M. (2002). Determination of iodine values according to Hanuš using 1, 3-dibromo-5, 5-dimethylhydantoin (DBH): Analytical methods of pharmacopeias with DBH: part 7. *Journal of pharmaceutical and biomedical analysis*, *28*(1), 81-86.

7. Akoh CC, Min DB. (2002). *Food Lipids: Chemistry, Nutrition, & Biotechnology* (Second Ed.). CRC Press. ISBN 978-0-203-90881-5.

8. Andersen AJ, Williams PN. (4 July 2016). *Margarine*. Elsevier. pp. 30–. ISBN 978-1-4831-6466-3.

9. C. Bellamy "Global Iodine deficiency day spectrum" *The medical spectrum*: **16:9**-10(1995).

10. Kapil, U. (2007).Health consequences of iodine deficiency. *Sultan Qaboos University Medical Journal*, *7*(3), 267.

11. Paech K, Tracey MV. (2013). *Modern Methods of Plant Analysis / Modern Methoden der Pflanzenanalyse* Vol. 2. Springer Science & Business Media. p. 335. ISBN 978-3-642-64955-4.

12. Van der Haar, F. (1997).The challenge of the global elimination of iodine deficiency disorders. *European journal of clinical nutrition*, *51*, S3-8.

13. Rafiq, M. (1996). Iodine deficiency disorders control program in Pakistan: an analytic review. *University of Leeds*.

14. Fazizi.IDD in the Middle East. *IDD News Letters* 17(3): 33-41 (2001).

15 Kuhn, T., Chytry, P., Souza, G. M. S., Bauer, D. V., Amaral, L., & Dias, J. F. (2020). Signature of the Himalayan salt. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *477*, 150-153.

16. Furman, N. H. (Ed.). (1962). *Standard Methods of Chemical Analysis: Vol. 1*.

17. M.Artho and R.kelly *Analytical Chemistry*. John Willey and Sons.Inc.New York (1998).

18. Jeffery, G. H., Mendham, J., Denney, R. C., & Bassett, J. (2016).*Text book of quantitative chemical analysis*.

19. Langer, H., & Offermann, H. (1982).On the solubility of sodium chloride in water. *Journal of crystal growth*, *60*(2), 389-392.

20. Association of Official Agricultural Chemists, & Horwitz, W. (1975). *Official methods of analysis* (Vol. 222). Washington, DC: Association of Official Analytical Chemists.

21. Codex Alimentarius Commission. (2006). The Codex Standard for Food Grade Salt. *Codex Stan 150*.

22. ICRC, *Emergency relief items Catalogue* (2002).

23. Kabata-Pendias, A. (2000). *Trace elements in soils and plants*. CRC press.

24. Hardisty, R. M., & Weatherall, D. J. (1974).Blood and its disorders.In *Blood and its disorders* (pp. 1540-1540).

25. Mohod, C. V., & Dhote, J. (2013).Review of heavy metals in drinking water and their effect on human health. *International Journal of Innovative Research in Science,Engineering and Technology*, *2*(7), 2992-2996.

26. Alloway, B. J. (1990). Heavy metals in soils, edited by: Alloway. *BJ, Blackie,Glasgow and London*.

27. Ullah, Z. (2004). Impact assessment of salt iodization on the prevalence of goiter in district swat.

28. Pandav, C. S., Arora, N. K., Krishnan, A., Sankar, R., Pandav, S., & Karmarkar, M. G. (2000). Validationof spot-testing kits to determine iodine content in salt. *Bulletin of the World Health Organization*, *78*(8), 975-980.

Guidelines for Authors

Publication Type

Full-length submissions are considered for publication that considerably improve understanding in social Sciences and closely related disciplines and are likely to have a notable impact on the relevant scientific and research communities.

Formatting & Template

It is the responsibility of the authors to ensure that the submitted manuscript follows the language standards required by the publication of the scientific journal. Authors are invited to use the language editing and proofreading services. If the manuscript is written in a second or third language, it is recommended to first contact a language reviewing service to avoid grammar and style mistakes. Authors are further advised to follow the format of the manuscripts available on our official website and OJS. The manuscripts should be in MS Word format. Use an appropriate font size (12), Times New Roman for the whole text except references, which must be 11 font size, Times New Roman. Line spacing 1 and first line needs to be indented and Title of the Paper, Authors' names, title of the Abstract & References must be centralized. Follow the template of the first issue of the Journal.

Paper length

The manuscripts submitted should have minimum 3000 to 5000 words, including abstract, notes, references, and annexures.

Structure of the Article

The manuscripts have to follow the APA and APL style of formatting (Publication Manual of the American Psychological Association, 6th edition). The article should follow the **Introduction, Literature Review, Methodology, Discussion and Analysis, and Conclusion.**

Authors are advised to submit the paper/manuscript through **OJS** along with **Title Page** including details of all the authors and **Authorship Certificate** available on the official website as well as **Open Journal System of HEART**. Only **1-10 Authors** are acceptable for a single manuscript.

Khyber Pakhtunkhwa Higher Education Academy of Research and Training (HEART)

To implement the directives of Education Policy 2009, Khyber Pakhtunkhwa Higher Education Academy of Research and Training (HEART) was established under the Approved summary of the Chief Minister Khyber Pakhtunkhwa in May 2013. HEART Act was passed by the Provincial Assembly later on in October 2016 with its defined mandate.

As per Section-4 of HEART Act 2016, aim and objectives of the Academy are to:

a) provide pre-service and in-service trainings to the academic and managerial staff of the Department, and personnel of the bodies and institutions which are directly or indirectly related to higher education with a view to develop their capacity, professional competence, research and ethical standards for efficient dispensation of knowledge and skills;
b) to conduct examination;
c) award certificates and other distinctions to the trainees and to prescribe standards of proficiency before such awards in pre-service and in-service trainings, which may also form mandatory yardstick for future promotions of such officers subject to their respective services rules;
d) hold conferences, seminars, lectures, workshops and symposia in matters relating to public policy on and the delivery of quality services in the fields of higher education, teachers' education, training and research;
e) initiate, promote and encourage research projects, publication of books, research journals, research papers and reports on important topics relating to policy, education, training and research;
f) establish liaison with research institutions, universities and other bodies of national and international repute in the field of higher education for the promotion of teachers education, training and research;
g) inculcate and promote professional and ethical values and standards of academic and managerial staff and other personnel connected with the Department;
h) formulate and prescribe courses of studies, research and training;
i) determine teaching methods and instructional strategies as well as co-curricular activities in order to ensure the most effective educational, training and other related programs;
j) undertake consultancy and advisory services;
k) serve as a research institute for Government on matters related to public policy on education and to advise the concerned authorities on matters as are referred to it; and
l) conduct such other activities as may be considered necessary in order to achieve its objectives under this Act.

Khyber Pakhtunkhwa Higher Education Academy of Research and Training (HEART)

Sector F-2, Phase-6, Hayatabad, Peshawar

Tel. +92-91-5863654

Email: hetta.kp@gmail.com

Website: www.kpheart.edu.pk