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## **Religious Beliefs, Employee Training and Green Performance**

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**Abstract**. The main aim of the study is to discover the connection between the dependent and the independent variables. Regardless of whether there is a positive, negative connection between them or there is no impact. Additionally, the point of this study was how the climate can be spared from more harms and how the issues of contamination, carbon emissions, the steady increase in temperature, and global warming can be tended to and solved for this purpose, the exploration has been done in a way to find out to what extent the organizations are using green performance. Secondly, by testing the variables and finding their correlations, and finding what are the best practices that can amplify the green performance. The results suggest that there is a positive relationship between employee training and green performance, which means that if the employees in an organization can be trained effectively on green performance. They can easily adapt the green practices and behaviors and contribute to the different environment-friendly practices. The second relation which is religious beliefs and green performance also show a positive effect, which means that employees at a large scale are attached to their religions.

Keywords: Religious Beliefs; Training; Green Performance.

#### 1. Introduction

It is an alarming situation that the climate of the whole world is changing drastically. The change that is taking place is destroying the climate. The pollution is increasing at a very alarming rate alongside carbon emissions (Amato, 2010). The main reason for this pollution is the industrial sector. In the industrial sector, there are a lot of SMEs, MNC's, MNE's. Alongside it, the pollution is caused by the vehicles due to carbon emissions, according to a report a vehicle emits 4.6 metric tons of carbon dioxide each year (Myles. Allen, 2009).

This huge amount of pollution is damaging several things that are related to human lives, animals, and other species, moreover the earth. Pollution contributed to nearly 9% of the global deaths every year. It is the leading risk factor for death, the number of deaths is 5 million annually (Luís Ferreira Braga, Zanobetti, & Schwartz, 2001). As this situation is

getting worse day by day and getting out of hand, some serious actions should be taken to keep this issue limited and as minimum as possible.

If the actionable steps are not taken, then the consequences that are waiting to arrive are serious and disastrous enough that they can't be handled. These consequences include constant increasing global warming and worst climate change all this leads to the melting of thick layers of ice and glaciers around the world, which causes sea level to rise and that is a nightmare for the low-lying countries. In the list of low-lying countries, there is Norway, Alaska, Bangladesh, Namibia, Maldives, Netherlands, etc. (Locke, 2009).

If humans want to save the environment and all these countries and the world, then they should start from the roots of pollution which is industrial pollution. They have to seriously work on how they can stop it or take it to a minimal level (Snowden-Swan, 1995). This the main purpose of writing this report, for this there are three variables selected that are religious beliefs, employee training, and green performance. The independent variables are religious beliefs and employee training and the dependent variable is green performance. The effect of the independent variables i.e., religious beliefs, employee training on dependent variables i.e., green performance can be checked.

After checking and interpreting results that what effect does independent variables have on the dependent variables. Whether it has positive, negative, or no effect. And most importantly how they contribute to saving this environment.

#### 1.1. Religious Beliefs

Religious beliefs are properly defined by defining religions. If religion can be seen as a whole it is a collection of beliefs, practices, and values. A religious belief is a critical part of the religion. And it is far away different from religious practice (Kirkpatrick, 1990). In religious beliefs, it is how one can perceive the religion they follow. What is their thinking regarding the religion and to what extent they follow it? An example of this is taken as that a person is very spiritual and has firm beliefs but does not practice it all. On the other hand, there is a person who does not follow a religion with that much motivation or spatiality but practices it much better.

By having a look at every religion that exists in this world, there is much common in all these religions. For example, where, when, and how this all started, when it all ends a prophecy about it and there is a brief set of ethics, rules, and laws to live life according to them. There is no doubt that religious beliefs present their undeniable importance in human societies (Weber, 2000).

#### 1.2. Employee Training

By studying the employee training and looking deep

into it that training is an ongoing process. As the world is changing continuously and there is advancement in technology at every blink of an eye, the way of working is evolving and the competition is increasing (Nuria. Esteban-Lloret, 2016). So, management and employees must stay updated and continuously acquire new skills to perform well. Different kinds of pieces of training are used for the employees some are for acquiring a new skill set or knowledge, some are for how to perform well and some are how to perform in a different way to achieve some goals and objectives (Maimuna Muhammad Nda, 2013).

Training is a very costly and time-consuming process, sometimes it shows acceptable results and sometimes not (Blomberg, 1999). Several training programs failed badly, that costs too much. The objective behind this is to find out how if the employees are trained in a way that they can change their way of working to save the environment then what is the effect of it.

#### 1.3. Green Performance

The green performance or green environment is related to the preservation and conservation of the environment. It includes different practices that are helpful in this process, like investments in renewable energy sources and informed consumptions, etc. (Douglas Renwick, 2013). It is also about introducing new trends on how to improve green performance, how to keep this trend going on the global level. So, the world can have the advantage of it as a whole (Olson, 2008).

# 1.4. Relation of Religious Beliefs, Employee Training with Green Performance

This is the main objective of the study to find out the relation between the above mentioned independent and dependent variables. By doing a little pre-research the conclusion is drawn that there is no sufficient study, work, or research is done in this regard. It is wrong to say beforehand that what is the exact and actual relation of religious beliefs, employee training with green performance whether it has positive, negative, or no effect because there is no such sufficient data available. It is assumed that the results should be positive because it is beneficial for the environment.

#### 1.5. Global Warming and Pollution

Global warming is a subset of climate change. In recent decades the average global temperature increased at an alarming rate. The very main reasons for this are the emission of different dangerous gases and pollutant directly into the atmosphere without treatment and the different types of pollution that are caused by mankind (Crabbe, 2008).

Pollution is caused when different dangerous and undesirable containments are added to the natural environment and have the worst effect on the environment and climate (Potters, 2008). For example, when the toxic gases from different factories and vehicles are released without changing their nature. And different waste from the factories, households, and other industries whether it is in solid or liquid form thrown directly and openly into the environment.

#### 2. Problem Statement

The major problems that today's world is facing are climate change, excessive pollution, global warming and carbon emissions, etc. Which is affecting biodiversity and the overall world badly. Everyone that is living on this planet earth is facing its consequences in many ways like bad air quality, many diseases that are related to pollution such as lung cancer, myopia, etc. There is a need to change the world, so it becomes a better place for all living creatures.

#### 3. Research Question

The research question is that what are the effects of

independent variables i.e., religious beliefs and employee training on the dependent variable i.e., green performance. In this way, an idea can be generated whether it is worth working on these variables in saving or contributing to saving the environment or not.

#### 4. Scope and significance of the study

The scope and significance of the study have many aspects like conservation of natural resources, ecological aspects, controlling the pollution, etc. these all aspects can be seen as a whole and a broad view of all these can be taken. Moreover, this study contributes to the existing and future research that is done or going to happen. For this purpose, different variables are selected to fulfill the gap between them.

#### 5. Objective

The main objective of the study is to find out the relation between the dependent and the independent variables. Whether there is a positive, negative relation between them or there is no effect. It is also known as the result of the study. Moreover, the aim of this study is how the environment can be saved from more damages and how the issues of pollution, carbon emissions, the constant rise in temperature, and global warming can be addressed and solved.

#### 6. Methodology

The data which is required is collected through the structured questionnaire. The questionnaire is distributed to related personnel, moreover, it is a selfadministered questionnaire. The questionnaire is divided into different sections. Sections one consists of the general demographic information of the respondent and the firm such as gender, age, qualification, position, number of employees, years of experience, etc.

The second section consists of the already

implemented green performance and green human resource policies in an organization. This section will measure up to what extent the organization uses these policies to empower and encourage green environmental/ performance behavior. Respondents have to answer the question that: "To what extent use the following methods to uplift the employees to adapt or behave in a pro-environmental way?" response actions are divided into six groups categories.

The third section consists of the environmental performance of the organization. It is to measure the influence of environmental commitment on the organization's performance. Respondents have to answer the question: "How moving towards green performance adaptability has allowed the organization to get the following results". Forth section consists of three questions that are related to the religious beliefs of a person.

Then the collected data is analyzed carefully, the questionnaire which is up to the mark is selected for further research. For the analysis of data, we used SPSS. To examine the collected data in various ways and find out the relationship between questionnaire elements.

#### 7. Literature Review

#### 7.1. Introduction

In recent years, the concept of working on environmental management has grown to many folds, provoked our ability to act naturally mindful, and set up a typical worldwide basic to react to important issues that emerge from overall climate and environmental change and regular resources preservation (Robert, 1996). Climate change, global warming, carbon emissions have become regular terms heard on news and science repeatedly. All things considered, but these have not come to light in most organizations, declarations to the venture network, or at investor gatherings.

The world is facing much environmental damage and its cynical outcomes consist of climate changes, deforestation, water pollution, soil erosion, natural disasters, rising sea levels, and so on. Environmental challenges are increasing and also affecting governments, organizations, and individuals across the globe (Warner, 2010). Developing countries are now also paying attention to environmental issues. It would be more understandable by an example like Asia Pacific Economic Cooperation (APEC) that consist of 21 countries as members, they all came on the same page to cut the different taxes and tariffs on some 54 products which are considered and categorized as eco-friendly with the target to improve existing advances and encouraging the sustainable power source use in the area (Gleick, 2020).

To come over these problems efforts as a whole are required, to come over the negative impact of environmental challenges. In this need of the hour, there is a need of introducing the concept of green performance (Pratima Bansal, 2017). The concept of green performance is all about plotting different HRM practices and training employees in such a manner that overall different HR functions hold up the organization's environmental management activities and helps in improving the current environmental condition (Douglas Renwick, 2008).

Different organizations and governments have to take different initiatives consist of using green human resource management. It is observed as essential and important for the effective utilization and implementation of eco-friendly management practices to deal with these issues. The results of green performance comprise the better performance of firms in case of the environment, employee's greener behavior, and attitude towards the environment

#### (Ahmad, 2015).

Proper employee training is direly needed to aware and train the employees in a way that they would contribute more evenly to preservation and conservation of the environment, it has to be checked whether it is worth it or not (Douglas Renwick, 2013). Secondly, research also has to check whether religiosity or religious beliefs play a significant role in saving the environment or not. To get the answer to all these questions three variables are selected, in the bracket of independent variables there is employee training and religious beliefs and in the dependent variable, there is green performance. After checking and interpreting results that what effect does independent variables have on the dependent variables. Whether it has positive, negative, or no effect. And most importantly how they contribute to saving this environment.

#### 7.2. Green Performance

The green performance or green environment is all related to the preservation and conservation of the environment. It includes different practices that are helpful in this process, like investments in renewable energy sources and informed consumptions, etc. (Benefits of Renewable Energy Use, 2017). It is also about introducing new trends on how to improve green performance, how to keep this trend going on the global level. So, the world can have the advantage of it as a whole.

Organizations are changing in manners that improve the climate, and that change is quickening, yet not many organizations have set up an enterprise-level green strategy (Masurel, 2006). Numerous undertakings that advantage the climate attempted by companies in the past were the consequence of new legislations, network weight, or client wellbeing concerns. Truth be told, gigantic advancement has been made through legislation in numerous countries to decrease vehicle exhaust outflows, lower contamination through the exchanged carbon credit program, and improve wellbeing by taking out the utilization of toxic paint (Tord Kjellstrom, 2006).

Nonetheless, with the proof that science is demonstrating to us about the increasing speed of global warming, there is a developing agreement that changes to secure the climate should be more unavoidable and bigger and serious actions are required (Scientists Agree: Global Warming is Happening and Humans are the Primary Cause, 2017). However, building up an enterprise-level green strategy is simpler to imagine, and numerous organizations are now headed toward that path. A green strategy enables an enterprise to settle on choices that positively affect the climate. The rules that structure the premise of a green system should lead a business to settle on choices dependent on the strong business rationale and bode well (MadsGreaker, 2003).

#### 7.3. Employee Training

Training and improvement are a constant process in improving the bore of workers. It is an endeavor to improve their current and future exhibition yet the organization should keep track of their performance after granting them training, it implies training needs evaluation it is a precise process of changing the conduct of employees toward a path to accomplish the organization's objectives (Mozael, 2015).

A training program is an effort by the organization to give chances to the employees to gain work interrelated aptitudes, perspectives, and information. To meet the ever-growing needs of training the area needs to get dynamic and refreshed in the present-day situation and to take up this sector to the statures of worldwide greatness requires the best level of innovation and capable, skillful employees (Chopra, 2015). The objective behind this is to find out how if the employees are trained in a way that they can change their way of working to save the environment then what is the effect of it.

Since training includes time, efforts, and funding by a firm, an organization ought to be cautious while planning a training program. The objectives and requirements for training ought to be recognized and the strategy or kind of training ought to be picked by the necessities and targets set up (Beach, 2016). When this is done precisely, an organization should take feedback on the training program from the trainees in the form of a well-developed questionnaire to know whether the money and time put on training have transformed into an investment or it was an expenditure for the organization (Andriotis, 2019).

#### 7.4. Religious Beliefs

Religion is a social and cultural factor that is one of the most general and compelling social institutions that affects the conduct, perspectives, and values of an individual and the general public all in all Researchers acknowledge religion as a salient influencer of human behavior (Fasching, 2002). A religious belief is a critical part of the religion. And it is far away different from religious practice.

In religious beliefs, it is how one can perceive the religion they follow. What is their thinking regarding the religion and to what extent they follow it? Religious beliefs serve a social capacity in human groups, giving a common personality of where individuals originated from and where they are likely going after death (Kenneth. Pargament, 2009). Each individual who has strolled the earth has presumably considered What is my motivation throughout everyday life? What or who is up there in the sky?

In a regularly chaotic world, loaded with apparently

odd viciousness and unexpected calamities, religious beliefs can fill the gap and give importance and solace. At the point when a child out of nowhere dies, people need answers. At the point when the dry season ruins the main food crop for the fifth year straight, people need to feel like they can change the course of nature by participating in ceremonial penances or religious practices (Rapley, 2017).

Religious beliefs as well as spiritual practices could make a consequential difference in an employee's behavior and performance, besides contributing to the organizations in attaining competitive advantage. Realizing this, numerous organizations have initiated yoga and meditation in their training programs and seek to increase connectedness among employees (George Mathew, 2018). These are the estimable and effective factors that can accelerate job satisfaction, employee commitment, and employee performance.

#### 7.5. Employee Training and Green Performance

Writing in the context of this report the relation between training and green performance is yet to be discovered. The main goal is to find if employees are trained specially and specifically to adopt green behavior and contribute to saving the environment by working green. There is a big question mark whether the employees accept this change or not and how they perceive this training. There is a gap that has to be fulfilled, in this study the employee training is taken as an independent variable and green performance is taken as a dependent variable. To find the relation between them a questionnaire-based study is going to happen and after interpreting the results there is a clear vision that what is the effect of an independent variable on the dependent variable i.e., positive, negative, or no effect. And whether it is worth researching in this context or not.

#### 7.6. Religious Beliefs & Green Performance

Religion plays an important role in the life of a person who follows the religion, it doesn't matter to what extent. Religious beliefs can shape a person into several forms like some people reach extremism while following religious beliefs while some people become mild and nice following the same religious beliefs. In the context of this study, the aim is to find out what role does religious beliefs play in saving the environment is it is used as a tool for driving the employees towards green performance. Firstly, what is the effect of it, secondly to what extent it is useful, and how much percentage of the results can get by it?

#### 8. Data Analysis & Results

#### 8.1. Questionnaire Analysis

To get the objectives of the research, descriptive analysis methods are used to get the relevant data that characterizes the study sample; at a 95% confidence interval, p values not exactly or equivalent to 0.05 are viewed as critical. Internal consistency of a survey is done by a method which is Cronbach alpha (Table 1).

Table 1. Cronbach's Alpha: The following tables
show the amount of Cronbach alpha for all the
components

Item	Items Number	Cronbach's Alpha
Organizational Culture in Management	5	.876
Selection and Recruitment	5	.971
Development and Training	5	.931
Appraisal and Performance Management	5	.954
Compensation and Rewards	3	.933
Participation and Employee Empowerment	5	.913
Environmental performance	8	.982

Religious beliefs	3	.943
Total	39	0.976

#### 8.2. Population Study

This segment portrays the outcome populace utilizing the frequency tests.

#### 8.2.1. Gender

The gender of the respondents consists of 80.4% male and 17.6% female. And 2% prefer not to say (Fig. 1).



Fig. 1 Gender distribution

#### 3.2.2. The Sector of the Organization

The sector in which the respondent's works are written further. 76% percent of the respondent works private sector and 24% of the respondents work in the public sector (Fig. 2).



Fig. 2 Sector of Organization

#### 3.2.3. The number of employees

The data collected from the respondents shows that the ratio of employees in there is as further, the organizations that have 1-9 employees are 23.5%, 10-

19 employees are 9.8%, 20-49 employees are 25.5%,50-99 15-7% and 100+ employees are also 25.5% (Fig. 3).



Fig. 3 Number of Employees in Organization

#### 3.2.4. Position in the organization

The data collected from the respondent shows that 17.6% of the respondents are at GM/ CEO position, 23.5% at the HR Manager position, 13.17% at the Quality manager position, and 45.1 at Other positions.



Fig. 4 Position in the Organization

#### 3.2.5. Education level

The data collected from the respondent shows that 60.8% of the respondents have a bachelor's degree, 29.4% of the respondents have a master's degree, 7.8% of the respondents have a diploma or below and 2% are other (Fig. 5).



Fig. 5 Education Level

#### 3.2.6. Experience in the Organization

The data collected from the respondents shows that 58% of the employees have less than 2 years' experience, 26% have 2-5 years' experience, 14% have 6-10 years' experience and 2% have greater than 15 years' experience (Fig. 6).



Fig. 6 Experience in the organization

#### 3.2.7. Environmental management

The data collected against the question: "Does your company have a formal environmental management system (EMS) (such as ISO 14001)" is as follow 31.4% said that it currently exists, 19.6% said no plans to implement, 27.5% said plans to implement within 12 months and 21.6% said they are unsure (Fig. 7).



Fig. 7 Environmental Management

# 3.2.8. Human Resource Management has direct involvement in green practices

The data collected against this question shows that 78% of the respondents said yes and 22% said no.



Fig. 8 HRM Involvement

3.2.9. Green Human Resource Practices assessment To find out the GHRM practices respondents have to rate as per the level of their agreement going how much the organizations, they work in execute GHRM. To distinguish the level of each practice, reactions were grouped into five degrees and the results are shown in Table 2.

Table 2. GHRM Assessment

Interval	Degree
Less than 20%	Much low
Less than 20%-40%	Low
Less than 40%-60%	Average
Less than 60%-%80%	High
80% and more	Much high

The implantation of GHRM in organizations is analyzed by using the descriptive analysis. Mean, standard deviation, and percentage were utilized to recognize the practice of application for each degree.

3.2.10. Degree of Application for best GHRM Practices

Rank	Innovation and practice	Standard Deviation	Percentage	Applications
1	Organizational culture for Green Management	.85350	65.4%	High
2	Appraisal and Green performance Management	.03655	56.5%	Average
3	Selection and Green recruitment	.98626	55.4%	Average
4	Development and Green training	.93688	54.7%	Average
5	Participation and Green employee empowerment	.99811	51.4%	Average

#### Table 3. Degree of Application for best GHRM Practices

6	Compensation and Reward	1.12839	48.6%	Average
	Total	.89910	55.8%	Average

The conclusion that is obtained from the above results is that the implementation of Green Human Resource Management practices is 54.9% which contemplates as moderate.

3.2.11. Environmental performance

Environmental performance	Standard deviation	Percentage
Improvement of corporate reputation	.75121	82.3%
Reduce emissions of toxic chemicals in air and water	.73774	80.6%
Improved product quality	.70134	79.9%
Waste reduction and process of recycling the materials	.76176	78.1%
Improved plant performance	.60507	78.2%
Reduction in the utilization of electricity	.71379	76.3%
Helped the company design/ produce superior products	.68692	74.1%
Expansion in the utilization of renewable energy and imperishable Power	.61410	72.5%

**.**... . . . 1 . .

The result we get from the analysis and data is that the "Improvement of corporate reputation" comes on top as environmental performance. Then at the second there is "Reduce in emissions of toxic chemicals in air and water". The third is "improved product quality", fourth one "reduced waste of recycling of the materials during the production process", on fifth there is "improved plant performance". At number six there are "reductions in the consumption of electric energy", at seven "helped our company design/ develop better products" and at the number eight and the lowest is "increased use of renewable energy and sustainable fuels".

#### 3.2.12. Religious Beliefs

#### **Table 5. Religious Beliefs**

Religious beliefs	Mean	Standard deviation
Religion is one of the most important philosophies of life	3.90	1.555
Religion forms an important basis for the kind of person	3.73	1.4833
Often think about religious matters	3.74	1.454

#### 9. Recommendations

The study that is done shows that environment can be benefitted if the organizations use Green Human Resource Practices if the organization can use better Human Resource Management practices to support

and motivate the initiatives towards green performance and better environmental performance. Different recommendations help organizations to improve green performance and contribute to the practices of saving the world.

The organizations have to make a strategy that asses the environmental concerns to make solid improvements, moreover, they have to add the environmental preferences into their business strategies to clarify their environmental concerns. The organizations have to dig deep and add green performance factors in their vision, mission, and goals. There should also an internal and external audit related to green performance.

Organizations have to develop a pro-environmental culture at the workplace for this purpose different policies are needed to be designed that emphasize adapting green behaviors. They have to consider the green performance in their all tasks through characterizing diverse green practices, qualities, activities, and rules.

The top management should be well aware and welltrained of the green performance and practices, so they can actively participate in the implantations of environmentally friendly policies. If the management is well aware and educated about this scenario, they cannot resist the change of going green. Moreover, they can also help to implement these policies down through the employees.

There should be proper training and development programs for all employees in the organization, so they can better understand this behavior and more aware of the advantages and disadvantages of going green. In the recruitment and selection, there should be proper environmental criteria and the applicant who knows about green performance can be given preference. There will be environmental criteria in the organization appraisal system which can have a track of the employee's green behavior and performance. Employees that actively participate in adopting green behaviors should be given rewards and compensation to keep them motivated. There should be employee empowerment and involve them in the decision making that will lead to greater duty and commitment to embracing the new culture of green performance.

The government should make new rules, laws, and regulations to ensure environmental safety and security. There will be strict check and balance on the organizations that how much there are affecting the environment and to what extent they are playing their role in saving this world and environment. If any of the organizations found guilty, then there should be a heavy penalty for this.

#### **10. Limitations**

Future researches can also face limitations, the current study also faces limitations. The limitation that is faced in this study is that the organizations, management, and employees are not much familiar with the green performance, environment friendly, green behavior, green practices terms.

#### 11. Conclusion

The main aim of the study is to discover the connection between the dependent and the independent variables. Regardless of whether there is a positive, negative connection between them or there is no impact. Additionally, the point of this study was how the climate can be spared from more harms and how the issues of contamination, carbon emissions, the steady increase in temperature, and global warming can be tended to and solved for this purpose, the exploration has been done in a way to find out to what extent the organizations are using green performance. Secondly, by testing the variables and finding their correlations, and finding what are the best practices that can amplify the green performance.

The results suggest that there is a positive relationship between employee training and green performance, which means that if the employees in an organization can be trained effectively on green performance. They can easily adapt the green practices and behaviors and contribute to the different environment-friendly practices. The second relation which is religious beliefs and green performance also show a positive effect, which means that employees at a large scale are attached to their religions. If religious teaching and preaching about saving the environment can be used in different training and development programs, then definitely employees can learn more and contribute more to green performance and practices.

By concluding the results, it has been sorted out that organizations appear to utilize green human practices at a normal level to work up environment-friendly well-disposed endeavors in their employees. The aftereffects of the analysis show that the practice is which is most ideally done to raise the mindfulness and commitment of the employees toward green performance is the "green management of organizational culture" and the base practice that was utilized is "green reward and compensation".

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## **Professional Competence of Women Police in Pakistan**

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Abstract. Based on technology driven world, the sustainable development goal is a multi-dimensional concept. It demands planning with pragmatic policy to grasp its interconnectedness of the already designed policies. The purpose of this study is to examine the professional competence of Pakistani women police. Stratified sampling technique by draw was used: the entire population was divided into different strata; then finally random sample of 150 was drawn from the designed strata. A questionnaire was developed and micro-tested on other than the stratified sample. The data analysis involved the qualitative techniques. The findings reflect a gloomy picture: the development of competence is not the purpose of the training; the male dominated police suppress the potential; educational and professional qualities are not counted. And the basic remedies suggested are to raise public awareness, introduce and support for investigative training, acquire modern equipment and professional competence.

Keywords: Professional; Competence; Additional Inspector General; Female Police; Male Police.

#### 1. Introduction

Based in a technology driven world, the sustainable development goal is a multi-dimensional concept. It demands planning with pragmatic policy to grasp its interconnectedness of the already designed policies.

Some researchers view "competence" as a mixture of knowledge, skills and behavior for progress enactment; or excellence of adequately or well eligible, having the capability to perform a precise role.

It has four general areas: (i) Meaning Competency, (ii) Relation Competency, (iii) Learning Competency and (iv) Change Competency. Competencies are the capabilities that one keeps and can often be separated into domain-general and domain-specific skills. These usually entail certain environmental stimuli and circumstances to assess their level being exposed and used.

#### 2. Literature Review

Natarajan (2000) concluded in the study that the

depiction of women in the Asia region fluctuates between 2.2 to 19.1 percent. There is no evidence regarding the ranks held by these women or their responsibilities.

In USA the research conducted on the problem of Equality Denied: The Status of women in Policing: 2000 and 2001. This research study comprises the status of females in policing that the number of females in law enforcement agencies remains trivial and the stride of upsurge very deliberate. Furthermore, females and males are equally skilled of police work prevalent bias in police hiring, selection practices and recruitment strategies keeps the statistics of women in law enforcement artificially low. Female frequently deals with discrimination, harassment, bullying, and are viciously thwarted (Lonsway, 2001 and 2002).

Lonsway and National Centre for Women and Policing (2002) launched a new research called "Men, Women, and Police Excessive Force: A Tale of Two Genders". It presented that women officials were significantly less prospective than their male counterparts to be intricate in hitches of excessive force. Women officials are dramatically underrepresented in excessive force occurrences. Police officials should hire more female officers for the purpose that cost substantially less than their male counterparts in terms of civil liability disbursements for excessive force lawsuits; female officers are also knowingly under-represented related to male officials in both citizen complaints and continued accusations of excessive force.

Jamal (2010) conducted study on "Police Organizations in Pakistan" with Human Rights Commission of Pakistan/Commonwealth Human Rights Initiative. It has specifically given the theme of Women in the Police and has reported that historically, women in Pakistan police have had limited influence.

Ahmad (2012) conducted a survey on "Male Police Perception of Women Police in Pakistan". The objective of this survey was to evaluate the perception of the male police in terms of image, performance of their women colleagues. The adopting of a career by a female is considered unconventional, harsh, unsafe and unfavorable. Ahmad (2012) also conducted a research study on Women Police in Pakistan with the support of Royal Norwegian Embassy, Islamabad – Pakistan. She concluded that the rising cases of violence against women and the conflict engulfing many parts of the country, requires an immediate consideration towards emerging a gender wideranging and citizen responsive police.

#### 3. Theoretical Perspective

The following theories covers the Philosophical sights of Women Policing performance in term of shouldering their social responsibilities:

#### 3.1. Social Role Theory

In this theory behavioral sex variances helix from the

variance in social roles settled by female and male. Over all, because of Social, economic, ecological and technological pressures, male and female were owing to labor duties that were reliable with their physical traits. Hence, men were more apparent to complete responsibilities that required speed, strength, and the skill to be away from home for extended periods of time. On the other hand, females were primarily responsible for childbearing, female were more apparent to achieve responsibilities associated to home and family. Therefore, men are likely to accomplish the masculine gender role that duplicates agentic potentials and women are likely to accomplish the feminine gender role that emulates collective qualities (Eagly, Wood, & Diekman, 2000).

#### 3.2. Role Theory

Mead (1934) work on Mind, Self and Society, Linton (1935) was work on study of Man and Moreno (1934) work on "Who Shall Survive?", all studies are considered as the instigators of Role Theory.

The Role Theory arguments to the commodious and pied body of analyses examining the connotations between the social organization, enactments and culture that humans give while involved in interaction (Martin – Wilson, 2005: 651). Role Theory are casually indicated institutions, and the established the ways of rendezvous predictable from repositories of certain positions. It is plausible to track athwart term role paradigm which is hypothetical to concealment various approaches and fractional terms used in the capacity of role theory. The role theory does not appear by itself as a foremost thought but rather is likely to apparent the self, groups, institutions, role taking (Biddle, 2000).

#### 3.3. Preference Theory

Catherine (2007) elucidate and visualizing divergence of work-lifestyles, as outcome of the assortment in

women's sex-role preferences and the three accompanying models of family roles. Theory claims well-off modern societies, that in women's preferences become a dominant element of life in accurate the choice between selections, prominences on activities connected to children and family life or an emphasis on competitive and employment activities in the public sphere. The economic environment and social structural still constrains women's selections to some extent, but social structural influences are of deteriorating importance most particularly social class.

#### 3.4. The Politics of Presence

Phillips (2006) says that it does in fact matter who is a representative, and not only what is represented. Phillips claims for an amalgamation of politics of presence and politics of ideas and gives four main explanations for the need of women representatives. The first is the symbolic representation that the enclosure of formerly excepted groups is important by showing these groups that they are well-thought-out as equals, irrespective of the outcomes. The second is that there are numerous issues that have not been deliberated before the election of representatives, which makes the individual characteristics of the representative a significant factor to the choices the representative will make on these matters once they are discoursed. The third argument is that in order to alteration the pattern of representation, there is a need for belligerent spokespersons for the previously excluded groups in the public arena to be able to alteration the existing power hierarchies.

#### 4. Objective of the study

The purpose of this study is to examine the professional competence of Pakistani women police in gender equality.

#### 5. Methods

This study followed the quantitative research design which includes the followings:

#### 5.1. Case Study Method

This is a case study methodology. According to Ruzzene (2014), in case studies scholars espouse a more generous view and try to reeducate that the case study method is the arena of scientific methods.

#### 5.2. Conceptual Framework

It comprised the following components of conceptual framework (Fig. 1).



Fig. 1 Hierarchy for Conceptual Framework of Research Design (Manzoor, 2021)

#### 5.3. University of the Study

Total strength of the Pakistan Police was selected as the universe of this study.

#### 5.4. Sampling

The stratified random sampling method was used in this study. The strata were designed on participants' collective qualities. Then a random sample from a piece stratum was taken in a number proportional to the stratum's size when related to the population. These subgroups of the strata were then pooled to form a random sample.

The sample measured the cross-section of Police Officials: the 05 Additional Inspector Generals of Police involved in policy making; 80 males Police Officers and 65 females Police Officers. It included senior and junior Police Officers. These Police Officials were randomly drawn from this Universe of the Police of Pakistan. The size of the sample was 150 as shown in Table 1.

Table 1. S	Sample	Size (	Manzoor,	2021
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S. No	Designation	Number of Respondents	
		Male	Female
01	Additional Inspector General of Police	05	-
02	Deputy Inspector General of Police	05	-
03	Senior Superintendent of Police	05	-
04	Superintendent of Police Assistant Superintendent of	10	05
05	Police/ Deputy Superintendent of Police	10	05
07	Inspector	10	05
08	Sub- Inspector	15	20
09	Assistant Sub- Inspector	15	20
10	Head Constable and Constable	10	10
	Total	85	65

#### 5.5. Date Collection Tool

The nature of the tools used comprised of the openended questionnaires. A Questionnaire is based on professional competences of Women Police and comprising 04-open-ended-funnel-type Questions were developed: one for the Women Police and the other for the Male Executive Staff. Then for improving version, served to the sample for microtesting other than the stratified sample.

#### 5.6. Procedure of Administering the Questionnaire

In this study Police Stations were visited, met the police officials and provided the Questionnaires to respond. Some police officials took time to respond the questionnaires, while others were sent back by post and others were emailed.

Interview was taken as a discussion between two or more individuals where questions were probed by the interviewer to prompt truths or statements from the interviewee. It remained a standard part of this research and was employed to the Additional Inspector Generals of Police, Deputy Inspector General of Police (DIGP), Senior Superintendent of Police (SSP), Superintendent of Police (SP), Assistant Superintendent of Police (ASP), Deputy Superintendent of Police (DSP) and Inspectors (male and female) were contacted personally, through their emails, and those who consented.

#### 6. Methods

# 6.1. Sample's Responses for Skill Development through Trainings

To find out skill / competencies' echelons, all the groups of the sample were asked which competencies the training course of Women Police inculcated to let them grow into a competent Police Officer. The retorts are given below.

#### 6.1.1 Additional Inspector General of Police

Almost same training was being given to female police trainees in the ranks of constable and ASI. Training was separated into three parts: (a) physical, (b) Academic and (c) practical. Physical part encompassed exercises, armed and unarmed drills, and unarmed combats. Academic training encompassed laws like Pakistan Penal Code (PPC), Criminal Procedure Code (Cr.PC), Evidence Act and Local and Special Laws (LSL). Practical training was given at the police station, police lines, police office branches and visit of the court and hospital for postmortem procedure. Anti-terrorism was also a subject.

#### 6.1.2 Male Police Officers

Basically, it is not the competencies, but it is the will which is deficient. Women are not deficient due to their incapability, but they are often dragged-down by manly chauvinism and corrupt system.

Women officers are proficient and can handle situations. Women Police officers acquired routine training as overall restructuring of police department is required. Aims (not the competencies developed) of Female Training are physical fitness, mental alertness, basic knowledge of fire arms, knowledge about Laws, Police Rules, job descriptions, limits, challenges and respect for chain of command/orders.

#### 6.1.3 Female Police Officers

Mostly skill acquire through education of Criminal and police related laws perhaps physical skills in the form of parade, musketry and to some extent firing. The focus is to build the skills how to obey the commands of seniors and way of applications is humiliating manners with junior officer's trainees. The instructors of Law are those officers who are posted in training centers as punishment. They are scared of the ASI Probationers (Selected through Public Service Commissions of Pakistan), and always degrading that trainees are raising stupid questions about practicing Laws, emphasized that there is no need to understand the implications, try rattafication (route memorization) techniques, make "Rata" of Articles word by word, that is the method of all successful Police Officer. Instructors of junior training

institutions are unaware of New Technologies, they only making money from trainees.

The physical instructors are those who have lack of knowledge to speak in front of Educated Women, and then how they trained Women Police? They always feed them about subordination, that women are the subordinate of the Kings and the godfathers. Women are appointed just to obey the orders of Rulers; they have no brain to choose what is wrong and what is right; they are just order obeying machines.

In positive side through drilling activity women become strong and patient (how to face odd situations). They have developed their confidence and can guide others as well. These physical activities developed authoritative skills as compared to civilian female.

Some Female officer's look considers trainings as a routine course just to qualify, not to train themselves. For them, it is just a formality of physical activities. During training period, they developed the tactics of disregarding the general duties: whenever they want to absent from the duties used what type of channel to ignore the duties.

Hardworking, patience and tackling of worst situations are learnt by women police officer because in Junior Officers Training Institution there is no living facility for them, they live in old barracks which fall in pieces time by time.

Instructor teach them that investigation starts from "shaak" (suspiciousness) and deal with humiliating behavior through training patterns, techniques and order to do every cheap work without any guilt and thus discontinuity self-respect of being a human. On other hand male Police officers look to female officers with suspicious behavior.

#### 6.1.4 Drawbacks of the Training Courses

Training courses for Women Police in Pakistan do not

inculcate in them to become a good police officer. Appointment in training institution in Pakistan is wellthought-out a stigma; so, instructor posted there either remain busy in their private matters or keep on politicization to get rid of these institutions. In this situation most, pretentious class is the under-training officers whether they are men or women. Based on that most of instructors near to the retirement, always speaks on the practical implications that those officers who are the most mundane trainees always become the experienced officer in the field of police.

Police academies are not proficient of inculcating competencies in Police Officers in both Junior and Senior Officers. But they are inculcating the bad habits and practices for the instantaneous gains.

Our training centers teach them how to tolerate pressure? But here in police they must face too much stress which sometimes is intolerable for female. Women can well give empathy to the aggrieved individuals; so, they can work well on police stations.

No essential to adhere any other supplementary course, they should be given equal opportunity and need to be encouraged. The courses being taught during training are not much useful for field duties for Women Police Officer. Women Officials should especially be trained about problems related to women at preliminary stage because we don't have appropriate atmosphere for Women Police Officials to work in all fields.

#### 6.2. Participation in the Courses during Service

To embed skills/competencies the other characteristic is the involvement in various courses during the service; it was thus enquired which courses the Women Police had participated during their service. The responses are given below.

#### 6.2.1 Additional Inspector General of Police

All the same courses that a male police officer has to

endure for promotion, like Criminal Laws, Police Rules, basic investigation skills, use of force including firearms.

At the subordinate level all course participated by male, for constable there are examination for promotion like A list, B list and C List. Once a constable is competent and entered in C List, he/she is entitled to become Head Constable after undertaking his lower course. Same conditions are for D list.

#### 6.2.2 Male Police Officers

All courses like male; anti-terrorist's course (Elite), all kinds of Investigation course, recruit Course/ Lower/ Intermediate/ Upper/ PSP courses, short term specific courses under different nomenclature, only a knowhow of criminology, laws, forensic science, first aid, weapon handling, physical fitness.

#### 6.2.3 Female Police Officers

Department mostly does not allow the Women Police to anticipate in courses except the promotional courses. Unnecessary rules and regulations only and in their job time period they are not learnt about these courses and are disregarded being female.

Women Police participated in the courses are recruitment courses, elite courses, lower course, intermediate course, probationer course, upper course, special training program of PSPs and promotional course of PSPs.

#### 6.3. Lines of Projection for Women Police

It was thus queried "On what lines did the Female Police come to be projection through these courses?" The responses are given below.

#### 6.3.1 Additional Inspector General of Police

These are the same as the men police officials have: seniority cum fitness. As for as lady ASPs are concerned, there is no discrimination between men or women officers. They are trained conjointly at National Police Academy (NPA) in physical, academic and in districts for practical work. Then there are short courses organized at National Police Academy Islamabad and at NIPA. There is no discrimination between male or female PSP officer. Both are sent overseas like USA, Canada and England for Anti-terrorist courses. On reaching seniority for promotion in 19, 20 and 21 grades both have to join courses at Staff College and NIPA. There is undeniably no discernment in training. However, they should be given equivalent chance by posting as District SP, SSP, DIGP and Addl. IGP.

Firstly, it is not the precedence of provincial polices; secondly, courses are not advised to all concerned due to which they get lapsed. Thirdly, female police officers themselves at times are not concerned to undergo these courses due to assortment of reasons.

They are skilled enough which is understandable from their accomplishments with UN Peace Forces. They are courageous and can work with bravery and potential, but education and training must be enhanced. Support and conveniences must be providing to them for healthier performance. For giving projection these are mandatory: result oriented activities, sound character and discipline and overall capabilities, but alas! These are tumble-down. Courses regarding their own rights as "women" and "women employees" is needed. The sorry state of the matter is that these are not there.

#### 6.3.2 Male Police Officers

Even the originators, implementers of these courses have belief that these are just unreal ideas that are not feasible. None of the courses attended make available any projection to the Office; it is only the political influence that tallies. Women policing is at a factual preliminary stage in our country and Women Police Officers are not assumed "full ostentatious exposure of policing"; this is instigating damage to Women Police.

Pakistan does not pave way to Female Police to flourish; government policies and implementation procedure is still far away for the anticipated results; some INGOs (International Non-Government Organizations) and NGOs can contribute their role to train these Women Police officers. So, government minimum show piece like authorities for Media coverage and reporting only.

#### 6.3.3 Female Police Officers

There is no projection for appearing in these courses; it is on the record that the Women Police Officers got the first, second and third positions in Law and Parade activities in the training centers BUT nothing had come out of "this nothingness". This is the state of affairs that prevails in the Police Department; only the politics/briber/sex gratification rules the roost. Training institutions project females in forward-facing of media that Police Department is not male dominating but in the field no projection is given because male dominion generates hurdle to contribute women as fecund co-partners.

#### 7. Discussion

Under discussions are the actualities that the inculcation of competencies in the Female Police were queried, but the goals of the training programs had been given and several drawbacks were recognized, finally conjecturing that the courses do not entrench the competencies claimed to be imbued. The responses made it vibrant that the Women Police are not equipped for the job they are allocated to. Stress is the most controlling factor, and nonentity is done to retain it to the minimum manageable level.

These discussions are validated by the police

department. Pakistan Police have so far not established an operative system of internal accountability. The process of dealing with grievances against Police personnel have not been stream lined yet. The received complaints are dealt with in most humdrum manner (Shah, 2001). In addition to it is said that individuals posted as instructors at Police Training Schools/ Colleges served with lifethreatening challenges. The moment an officer is dispatched on instructional assignments, he makes every conceivable effort: administrative, political, compassionate etc., to have his posting orders negated. Posting orders to the training institutions are thoughtout as the blank warrants of Policing. The state of mind of such officer, who attains at training center as an instructor, can be evidently visualized. He senses that he has been discriminated against. He is dissatisfied and in a pitiful frame of mind. With this mental state, these instructors generate an environment of a penal institution in the training centers (Shah, 2001).

#### 8. Conclusions

The findings of this study reflect grizzly picture:

- i. The advancement of competence is not the purpose of the recent trainings.
- The male dominated police officers overpowered the potential of the Women Police officers.
- iii. Women police officer's professional and educational qualities are not calculated and wherever these are, they reflect competence as an accomplishment. Then how the change will emerge.
- The facts projected are the gloomy state of affairs; it is all a stereotype bustle without any profit, neither being generous to the department

nor to the community from which these ladies have been drawn.

 v. San Francisco News Letter of November 30, 1895, under the caption "Women in The Police Department is pertinent: "The time has come and the need pressing for the cooperation and heroic aid of women." This is also the decision of history.

#### 9. Discussion

#### 9.1. Short Range

Raise public awareness of the changes introduced in policing system. Support for investigative training especially for women police to help in acquiring modern equipment's. Professional competence of Women Police in clinching sustainable goal of gender equality in society.

#### 9.2. Medium Range

Police department launched victim-centered the programs. approaches through training Satisfactorily keeping decision making role of women police especially in sexual harassment affairs. Eradicating gender discrimination, improved strategies for recruiting women police.

#### 9.3. Long Range

Safeguarding of chastity of Women Police Officers as one of the permanent values in cultural behavior (Manzoor, 2002).

Establishing gender balance in Varsities, Colleges and Educational Institutes of Pakistan. Maintaining gender responsive policing in Pakistan.

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## Power, Sexuality, Politics and Gender in the Middle Eastern Resistance

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Abstract. In the Middle East, wars and conflicts have had a significant effect on women and gender. This research essay aims to call attention to the current oppression and war in the Middle East affect the responses of women in the Middle East. In particular, the cases I use the context of Iraqi, Palestinian, and Kurdish women. What is discussed is the resistance of the Iraqi, Palestinian, and Kurdish women of Turkey, outside the 'Orientalist' rhetoric that portrays Middle East women in armed wars as purely powerless and helpless victims. The nuanced reality of Arab cultures, particularly how women's experiences differ over time and place and the methods they employ to negotiate themselves, has not been helped by simplistic generalizations such as this. As Michel Foucault says, where there is power, there will be conflict, and because resistance is a focus in this essay, I will define power, including the empowerment of women.

Keywords: Feminism; Masculinity; Femininity; Middle East; Politics; misogyny.

#### 1. Introduction

For generations, the role of women in state-building and armed conflicts have been remained highlighted in Middle East especially after the involvement of UK and US which showed the armed presence of women as female suicide bombers who killed themselves on the name of their region. As in uprising revolts in Israel showed that women of Palestine participated in violent acts too to protect their interests and it was assumed that Palestinian women stabbed over Israeli soldiers to show their political strength (Burhan, Habib, Tariq and Asghar. 2016).

Globally, the status of women is always lost due to polygamy and misogynist attitude of men towards women. This essay is about the representation of women and her rights in Islamic world. It is a common perception that Islamic women are, marginalized and under oppression since Islamic invasion but the scenario is quite different. As previously women were not even allowed to drive cars in Saudi Arabia but right now, they are allowed. Egyptian women can lawfully divorce their husbands legally after slight amendments. Women are enjoying their social and political rights in Tunisia as well where she can abort and polygamy is also considered illegal there due to the social, political and Islamic status given to women of Middle East. Women served as Vice President in Iraq and also served as Ministers in many territories of Muslim nations like Jordan, Iraq, Syria and Egypt. Power dynamics in Muslim nations has thus been shifted from being ruled to be independent in certain aspects of life by removing all the strongly embedded stereotypical notions of women subjectivity (Tariq, 2017).

According to Michael Foucault and Judith Butler,

Queer theory is basically based upon the notion of everyone where sexual minorities, oppressive nations, constitutional identities, subjectivity of any gender, and resistance to oppression occurs and discussed worldwide. The dynamics of Gender and women in Islam is misinterpreted as the caretakers of home, family and should be bounded within four walls of home. But the reality is different and women are allowed to do certain things within their boundaries. Western misinterpretation depicted a wrong image of Middle Eastern women as veiled and vulnerable having no right and liability to take decisions. In fact, women of third world countries are also participating on the same level of progress.

# 2. Pre-Imperialism and Middle East Since Past

British Imperialism dates back to 1798 in Middle East when Napoleon invaded in Egypt which affected British policies in the mid of 20th century and interplayed Great Power Rivalries to balance the political and economic structure of nation. It has been divided into four interactions when Imperialism affected Middle East:

- After the conquest of Egypt by Napoleon, political and economic stability occurred and seen in Middle East.
- Official infringement occurred which leads towards World War I after the invasion of Egypt.
- After World War II period when in 1948 Israel emerged from the region of Palestine and Israel-Arab Wars took place also started Palestinian refugee problems (Hariri, 2015).

#### 2.1. Orientalism

Edward Said explained orientalism in his own words by saying that Middle East is a Eurocentric term and derived from British proximity. British and French are considered to be the invaders of Middle East. It started in a sense when they setup their business ties and influencing their region and religion which is now even implemented in 21st century. Orientalism is basically the belief based upon the concept of exaggeration for looking over the distorted differences between the people of Arab and British. They have their biased beliefs about Arabs and call them exotic, backwards, uncivilized and sub-humans people having no education or sense to accept western influence or change (Ward, 2018).

#### 2.2. People of Lot

The slogan used in Middle East for people who belong to homosexuality or trans-sexuality as they are misinterpreted with the teachings of Quran. Middle East don't use words like gay or lesbians for those people rather they sue certain words having no meaning in dictionary. In Middle East, Islam and misinterpretation of Islam is considered to be the logical and religious explanation for the arrest, exile and detention of homosexuals. It is allowed in United States and in many other western nations but in Middle East, people are fighting still for their same sex love then murdered thousands of people. Iraqi women portrayed their public and political interests related to equality took on International channel as well along national level lobbying or campaigns and they made reports as well against state flared violence against women by proposing certain reports made in NGO's (Olney, 2017).

## 3. Middle Eastern Women between Oppression and Resistance: State Uprising Revolts against Women

Due to limited visibility of literature on women in Middle East has led many Western nations to make a belief that women in Middle Eastern nations are always oppressed, vulnerable, inferior, excluded, marginalized, deteriorated, financially and emotionally dependent and imprisoned by the dominant male members of society. After the critical analysis done by many scholars, it has been noted that poor status and marginal inferior level has been given everywhere while it is depicted wrongly too. Women in Middle East since their invasion are fighting and stepping back to violence, state oppression, patriarchal norms and misogynist social and political agendas. Here I'm going to reflect the images of women during ongoing conflict and war situation in Middle East related to Iraqi, Turkish Kurdish women, Palestinian and Egyptians who are facing such deteriorated resistant approaches on the name of Islamic misinterpretations to subjugate them in all walks of life. The emergence and involvement of socalled Islamic States (IS) have led to a massive increase in enslavement and rape of many young girls and also the life expectancy of women have been decreased to 66 from 85 due to violence, domestic violence, rape, mortality of mother while childbirth and many more. The role of Orientalist discourses and the reaction of Iraqi, and Turkish women over the state regulated oppression in certain shapes has been enlisted here (Khodary, Salah and Mohsen, 2020).

#### 3.1. Turkey

In turkey, the Kurdish women are fighting against so called formal state oppression on women by becoming part of certain non-peaceful activities of armed forces. These women become active members of Kurdistan Worker's Party (KWP) and they are actively showing their political strength by involving in many leadership roles like men.

Women have also made progressive claims under the umbrella of Secularization or Islamization where they became members of militant forces or peaceful nonarmed forces to activate their own rights. Historical Kurdish struggle showed very clearly that women dismantled strongly embedded anti-feminist women participation in armed and resistant forces by defining its subjects under the umbrella of opposition to patriarchal, colonialist and capitalist order of male captivity over women (Holt and Jawad, 2013).

#### 3.2. Iraq

In Iraq, Libya and Syria, women have been affected negatively by many Civil wars and displacement activities resulted in so called massive movements like Arab Spring which resulted the involvement of women in certain civil societies aiming for their own individual rights. While Palestinian women relied upon non-conventional or peaceful resistance towards male oppression and dominance of men over women in certain areas of life. Iraqi women are still perceived as peace-makers within and outside the home who can compromise their own wishes and desires to maintain peace in family. Middle Eastern women are fighting their fight unlike than western feminist movements where they are challenging orientalist point of view which says that women should be veiled and bounded within the four walls of home. The concept of "Everyday Resistance" was introduced by James Scott who conceptualize certain strategies of resistance by women against their own status. He said that we can use culture as a tool of resistance and ensure that women incorporate positive role in the uplifting of cultural norms.

#### 3.3. Arab Spring

It has shown the stereotypical image of women being shown in western agenda and said that women are fighting and even risking their sexual assault to restore democracy and demonstrate inhumane activities against women.

#### 4. The Future of Women in Middle East

It is a common perception that either you belong to traditional, modern, western or eastern state, if you're a woman you aren't supposed to enjoy the same liabilities as given to males and you're considered to be the most disadvantaged group of your society. The Global Gender Gap Index published a report on Gender gaps between different countries which showed that Turkey, Iraq or Palestine are the nations still among those deprived and marginalized portions of society where women are still fighting armed or peaceful fights with state or misogynist ideas to represent their identity and individuality.

Women are breaking the stereotypical boundaries in Gulf Countries and removing cement ceiling. Iran, Turkey and Palestinian nation. For example, if a researcher talks about Iran, it has long history dating back to 1905 during the constitutional revolution when popular political and social parties demanded a quality check on Monarchy of Qajar. During 1920 to 1979, the regime of Pahlavi made women some influential progressive moves in the field of education, employment, and political participation along with the right to be enrolled in universities and right to give vote to their favorite political party or leader. But still their certain legal constraints which hinder women to become equal participants of any organization. Suppose if a driver hits any woman pedestrian then penalty amount to that victim will be paid half. And a married woman may not be allowed to travel internationally without the written permission of her husband. But since 2005, Iranian women have launched a campaign named "One Million Signatures Campaign" where young boys and girls are trying their hard to remove discriminatory practices against specific gender.

# 5. Politics and Men is of no Significance for Women

Since the inception of international politics and international relations among male and women, Gender is ignored because certain theories were

proposed by male dominated western scholars who excluded the basic notion of gender in this mainstream. Many feminists have argued on this stance as by saying that this international politics and relations is masculine in its nature and thus gender-biased when we approach over issues concerning women or deteriorated status given males. Theorists were males thus they ignored the concept of other gender in fact ignored the concept of gender itself. After World War I, scholars argued that it is the time to get all genders in mainstream to promote research and topics teaching on cooperation and involvement of both genders in the time of war and peace. Scholars have made explicit statements about gender-based exclusion of women from politics and this issue was addressed by few feminist scholars.

J. Ann Tickner argued that many theories are male originated and male centered and these theirs address that in the attainment of enlightenment, autonomy and rationality, women are not capable enough or strong enough to take part in international relations and politics paradigms as they are not emotionally stronger to take decisions on their own. Thus, these western based theorists ignore the overall concept of gender while drawing theories on the inclusion of feminine or masculine nature of any gender. The basic misunderstanding between International politics and Feminism is divided in three main sub-sections by Tickner:

- First, it is manifested that gender is a more personal issue rather than a public one. Thus, it should not be incorporated in international realms.
- Secondly, there are different opinions and ontologies of feminist and non-feminist people which aren't going to be incorporated in international political dynamics.

International politics is considered a male domain in ways that both genders have different emotional and physiological appearance and nature. Thus, politics is something take care of nation's borders and it would be difficult for a female gender to take decisions boldly for the protection of its state. These questions were raised by J. Ann Tickner.

- i. Why can't I see a gender equality index in my discipline and why I'm seeing few women in global relations and politics?
- ii. If this field has been defined as a conventional subject, then why there are few writings and readings produced by women?
- iii. Why the absence and explicit removal of women has been so apprehensive in the world of diplomacy, peace-keeping, military foreign world politics?

#### 6. Conclusions

Marginalization of women in fields like global politics is not going to be changed easily as it incorporated experiences of males only written and spoken by masculine voices. Tickner wanted to eliminate gender hierarchies and addressed how world look like if they add experiences, knowledge and stances of women in world politics and international affairs. But this is a total male centered approach held responsible for the coverage of male dominated beliefs about the security and foreign concerns of country. Politics and masculinity have strong ties with each other by ignoring gender as a category and flared up more gendered stereotypes which marginalized more women over the edges. The problem is not with women gender only rather the problem is with the exclusion of gender as an entity from world politics. These words and writings have been drawn by males where they addressed masculine concerns and never allowed women to attend any foreign policy meeting on the view that she will be focused on issues related to Human Approach only instead of being focused on male asserted problems.

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## Methods and Techniques of Criminal Investigation Used by Women Police in Pakistan

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Abstract. Methods and techniques are advancing with prompt rate that the information must be inquire in the context of advanced technology and practices attuned as appropriate. The purpose of study is to analyze the methods and techniques in crime investigations used by the Women Police. A stratified sampling technique by draw was used. A questionnaire was developed, administered, then procedure of data analysis of "yes/no/neutral" and finally formed the propositions by qualitative method. The findings of the study are that majority of the sample agreed that women are not aware to use methods and technologies in investigations of crime. The actual work of Women officials must do in the Police Stations is neglected. It is the defective training that makes the crime bloom in the grass-roots of the society. The basic remedies suggested are to educate and train for crime investigation acquiring modern methods, and techniques in the criminal investigation services.

Keywords: Techniques; Criminal Investigation; Additional Inspector General; Women Police; Male Police.

#### 1. Introduction

Technology is going forward with such a prompt rate that the truth must be examined in the framework of current techniques, methods and practices attuned as suitable.

#### 1.1. Forensic and Technical Principles

When dealing allocating with technology and techniques, the following forensic and technical principles are practical:

- Arrangements taken to protect and accrue the evidence and do not alternate that evidence.
- Bustle concerning to the confiscation, investigation, storing, transference of electronic evidence is entirely documented, well-presented and manageable for review.
- Specialized training is compulsory for the inspection of devices described.
- Appropriate personnel are accessed prior to conducting any investigation (Haque, 2021).

#### 1.2. Investigative Assistance

Due to the nature of technological progress, mainly crimes are committed on the Internet, criminal behavior often befalls across jurisdiction restrictions. It is, therefore, for the Police Officers to work in partnership with other law enforcement agencies at all the level to efficaciously investigate these types of crimes and criminals.

#### 1.3. Information Gathering

Information of fact-finding significance is collected from the diversity of the sources including individuals, places, and things. These information are composed through the interviews, crime scene analysis, location searches, publicly available information, Police department databases, and legal procedure.

#### 1.4. Encryption

Encryption is used to defend or hide noteworthy or implicating data or communications. Interviews and crime scene searches are the best methods for gaining the passwords to decrypt data. With the numbers of passwords that operators are compulsory to remember, an option exists that passwords may be stored on paper or other electronic devices (Haque, 2021).

#### 1.5. Validity of Digital Evidence

RAM and ROM are forms in which digital data stored, hard drivers and additional magnetic or optional media are focused to unintended alternation, degradation or loss. Powering up or shutting down are the example of the practical activities which complete on a device, whether unintended or premeditated (Haque, 2021).

#### 1.6. Electronic Communications

Online chat, e-mail, text messaging and picture messaging which may be available from ISPs (Internet service providers), cellular phone services, wireless phone services providers, Internet cafes, academic institutions, pager cooperation, wireless hotspots, telecommunications, cell tower data or cell side data, answering machines, portable devices for communications and voice mail services are the examples of the electronic communications.

#### 1.7. Video Surveillance

The proliferation system of video surveillance is progressively probable because of community demeanor will be caught on video. Video safety system put in place by businesses, private citizens and government entities.

#### 1.8. Consensual Monitoring

It is the monitoring system of wire, oral or electronic communications with the information and consensus of at least one intricate party. It may comprise the followings:

- Telephonic conversations, e.g., Wire,
- Personal Communications, e.g., parabolic microphones, body wires,
- Computer communications, e.g., keystroke monitoring, sniffer output (Manzoor, 2014).

#### 1.9. Criminal Investigation Methods

Initially Criminal Investigation methods were rudimentary process, depends on eyewitnesses, inferences, confessions mined under torture. Now compartment of an investigation is administrated by information attained from people, records, and physical evidences. Witnesses and victims still make available the bulk of facts as to when, where, how, why, and by whom the crime was committed (Mazoor, 2014).

The following advanced methods are used by Police for criminal investigations:

- Evidence Preservation,
- Interviewing,
- Computer Forensics,
- Records Collection,
- Records analysis,
- Investigation and Search Warrants,
- E-mail Pen/Trap and Trace,
- Undercover Activity,
- The Apprehension,
- Post Arrest Investigation.

There are several methods of gathering information and generally all or an amalgamation of the following methods is used:

- Organization Charts,
- Observation,
- Interviewing,
- Questionnaires,
- Existing Documentation,
- Record Searching,
- Sampling and Manuals or Handbooks.

The exact tool applied in the right circumstances can make a substantial involvement to the efficiency and effectiveness of an investigation (Manzoor, S., 2014).

#### 2. Objective of the Study

The purpose of study is to analyze the methods and

techniques in crime investigations used by the Women Police as one of the burning challenges.

#### 3. Literature Review

Jamal (2010), POLICE ORGANIZATIONS IN PAKISTAN is a research report conducted by Human Rights Commission of Pakistan/Commonwealth Human Rights Initiative. It has exactly given the theme of Women in the Police and has conveyed that historically, women in Pakistan police have had inadequate influence. Ahmad (2012) conducted a survey on Male Police Perception of Women Police in Pakistan. This survey evaluated the perception of the male police in terms of image, performance of their female contemporaries. The nonappearance of women in the police department can be interrelated to the general image of the police and the challenging profession nature. The espousing of an occupation by a woman, especially a profession which is wellthought-out unconventional, harsh and even perilous, is not observed on auspiciously.

Another research conducted on Women Police in Pakistan, the objectives of the mapping are to (a) establish the number of female police within the provincial police departments and Center (b) mature an insight of their work performance (c) study meticulously the state of women police stations and their performance and (d) to determine the challenges and accomplishments of women police. It concluded that the increasing cases of violence against women and the conflict overwhelming various parts of the country, entails an instantaneous attention towards developing a gender inclusive and citizen responsive police. Commendations were also made, that were articulated based on the argument given in the report. These areas are mandatory to be focused if the involvement and contribution of women within the police department has to be enlarged and improved. It has also recommended certain procedures on the basis of Departmental, infrastructural, and attitudinal characteristics (Ahmad, 2012).

Babakhel (2013) Gender-sensitive Policing is a news article reported that the earliest history of Women Police in Pakistan is initiate during 1939 in British Rule when there erupted a Farmer's Movement in Punjab; it encompassed female agitators as well. In command to deal with this Movement and maintain law and order, the established order recruited seven constables and a head constable. The next substantial recruitment was commenced when twenty-five constables, two head constables and one ASI were appointed in 1952, however, there appearances to be no reference of women policing in the Police Act of 1861 and Police Rules of 1934. It is only the Police Order 2002 that documented the necessity and importance of women in policing.

#### 4. Methods

This study followed the mixed method research design, which includes the followings:

#### 4.1. Conceptual Framework

It included the following instruments of conceptual framework (Fig. 1):



Fig. 1 Hierarchy for Conceptual Framework of Research Design (Manzoor, 2021)

#### 4.2. Universe of the Study

Total strength of the Pakistan Police was designated as the universe of this study.

#### 4.3. Sampling

A stratified sampling technique by draw was used: the
entire population was divided into different strata by designation like Additional Inspector Generals of Police, Male and Female Police Officers; then finally a random sample of 400 was drawn by draw proportional to the designed strata (Table 1).

<b>Fable 1. Sample</b>	e Size	(Manzoor,	2021)	1
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Additional IGP	Male Police Officers	Female Police Officers	Total
05	195	200	400

#### 4.4. Data Collection Tool

A questionnaire was developed, micro-tested and served to the sample other than the stratified sample.

#### 4.5. Data Analysis Mechanism

In this study, data analysis indicates quantitative and qualitative methods. Mostly the qualitative data analysis approaches were used in this study. The following six steps were used for data analysis:

- The data analysis of "yes/no/neutral" represented that weightage of responses in percentages.
- ii. Involved the creation of data repository.
- iii. Initial codes, expanded codes and rationalized codes. Analysing the coded data and, finally, formed the propositions qualitatively, the narratives were transcribed in verbatim.

### 5. Results of Methods and Techniques

This study was conducted to recognize the level of methods and techniques the women police officers use for investigating the cases. Therefore, to probe this phenomenon of methods and techniques in investigation of crime, a question was enquired to reflect methods and techniques of High order competencies women police have acquired. The responses from all segments of the sample are given in Table 2. Fig. 2 shows that from the point of view of all the segments of sample, the Women Police do not reflect the techniques and methods of higher order competencies.

<b>Fable 2. Sam</b>	ple Size	(Manzoor	, 2021)
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S. No	Respondents		Respo	ises
-	-	Yes	No	Neutral
01	Addl. IGP	-	100	-
02	Male Police Officers	-	83	17
03	Female Police officers	28	72	-



Fig. 2 Respondents Responses (%) Reflected Over Techniques and Methods of Higher Order Competencies

# 5.1. Reasons for Lack of Methods and Techniques

Then they were further encouraged to identify the root causes of this phenomenon. The responses are reproduced below:

#### 5.1.1 Additional Inspector General of Police

They are largely not interested in doing courses away from their families, lack of resources and social support. The techniques and competencies remain same except that they should have better knowledge of social environment in which we are living. This profession especially for women, is highly negligible in front of society as well as Provinces. Highly deprived ladies come in this profession. So, they have not any aptitude to get advancement in technology, on the other hand in advanced countries with woman police partnerships proactive problem solving can achieve efficiently to address crime.

#### 5.1.2 Male Police Officer - For No Response

Women just do common jobs that can be handled by even civilian without police training. Female police officers have no higher order competencies methods and techniques in watch and ward and crime investigation. It's because women officers are neglected in training courses.

# 5.1.3 Female Police Officers - For "Yes" Response

There was one such example; it said: "I investigated many cases like male colleague and also faced all the difficulties which my male colleagues faced; it was because of non-availability of modern techniques in Pakistani Police culture".

#### 5.1.4 Female Police Officers - For "No" Response

Women Police officers are weak in Police Investigation Techniques and Methods, although they achieve positions in laws but in practical field of investigation, they are a failure. Mostly Women Police Officers have no knowledge how to write FIR, investigation dairies, crime scene reports, statements, interrogation reports, evidence collection from crime scene, search reports, final Challan reports, interimchallan reports, Case Paper of FIR, even they don't know how to write NC (non- cognizable offence) reports, how to maintain Police Station 25 registers which are most necessary; it helps to curb the crime. Police practical work is the most neglected areas of the Women Police and government and Police Bureaucracy show negligence on that basic issue which was the basic cause of Failure of Female in Police and Women Police Stations. And there is no

concept of Modern techniques, Scientific Investigation techniques and methods in the entire Police Department.

Women Police are commonly used to trap the criminal phonic calls: she calls at specific place for dating; this involves life risk for women police chastity. Women Police are not competent because our training institute does not educate us properly, I worked with Women Elite Force of Karachi in Prime Minister Duty, I experienced that they have no knowledge about security plans and security duties, responsibilities of Women Elite Force, cordon (inner and outer), they are unable to make inner cordon at the stage to protect VVIP from lady's interaction, even they have no knowledge to make hand chain. It's surprising for me being Women Elite Force they have no skills they are just statue in the uniforms and batches of Elite Force. That was the fault of their trainings and heads of Elite Force.

### 6. Discussions

The outcomes of this study may or may not be mathematically exact, but it can be specified that this only reproduces a general mindset of the male and female police personnel in the usage of methods and techniques in criminal investigation. The Female Officers have become progressively outspoken criticizers and have voiced razor-sharp remarks against government and Police Bureaucracy. And worldwide usage of methods and techniques in investigation of criminal cases by Women Police are advancing day by day, but in Pakistan policing is still a male-dominated profession and owed to social taboos women are reluctant to join the advanced methods and techniques in investigation of criminal cases (Manzoor, 2014).

## 7. Conclusions

Concluded from this sample's opinions is a hanging

position of the Women Police in the quest of methods of crime investigation. The authentic work these Women have to do in the Police Stations is ignored. It is the defective training that makes the crime bloom and blossom in the grass-roots of the society and hardly any segment of the sample has control of the emerging narrative in the law enforcement apparatus. This reflects a gloomy picture of training institutes. On other hand, women's experiences of higher educational institutes are often marked by anxiety, fear and negotiation with varying degrees of harrowing sexual-slurring experiences: scrawling across, mocking and shouting, sense of safety being snatched away, rape culture leading to rape, hate speech against women being trivializing etc. The good is that women are now resisting in quiet individual fights in front of harassment committees, and in collective action based on shared experiences of being sexualized, objectified and violated. They have also vocalized the gendered impact of many student issues. With women's voices becoming louder, the hope is that Varsity experiences will entail solidarity, support and safety to respect the women-folk, and to safe-guard chastity that ALLAH TWT ordains in the Qur'an as a permanent value (Haque, 2002).

#### 8. Recommendations

The basic remedies suggested are:

Enlightening women police education and training to reinforce and upsurge investigative dimensions in criminal investigations. Applied usage of advanced professional methods and techniques of investigations, including the practice of forensic knowledge and skills in the procedure of criminal investigations. Provision for the conception of mechanisms to guarantee a suitable response to the Women Police by the Criminal Justice System towards vulnerable groups, especially Women and Juveniles. Enhancement of the organizational performance of the Forensic Science Labs.

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# Role of Metacognition in Jealousy and Self-Esteem among Married Adults

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Abstract. The aim of the present research was to investigate the impact of Metacognition on Jealousy and Selfesteem among married adults. For present survey design, Data was collected through Purposive sampling using Metacognition questionnaire (MCQ-30; Wells & Cartwright-Hatton, 2004), Self-esteem Scale (RSS; Rosenberg, 1965), Multidimensional Jealousy Scale (MJS; Pfeiffer & Wong, 1989). Results indicated significant negative correlation between self-esteem and metacognition (r = -.25\*\*) and also between metacognition and jealousy (r = -.54\*\*) and significant positive self-esteem and Jealousy (r = .30\*\*). Regression analysis showed metacognition to be a significant predictor of both self-esteem (B = -.54) and jealousy (-.25). Thus, metacognition is a significant therapeutic variable in regard to treating low self-esteem and jealousy among married adults. This is the first study of its nature and further studies are needed to generalize findings.

Keywords: Metacognition; Jealousy; Self-esteem; Adults.

#### 1. Introduction

Metacognition states to "considerations about musings" (Sun et al; 2017) stating "worrying about worries" that metacognition is the mindfulness individual has possessed thought techniques (singular musings). It is singular ability to resistor individual musings strategies through various techniques, for example, displaying, watching, and acclimating. In addition, it is singular ability to uncover upon the errands or techniques individual begin and to decision and utilize the best possible designs fundamental in individual intercultural associations. Jealousy is a troublesome vibe that involves sentiments fluctuates from fear of renunciation to temper and disgrace. Jealousy assaults the two people and is high typically prompted in light of the fact that when an individual watches a terrorizing to an acknowledged relationship from a third assembling. The terrorizing might be genuine or watched. It isn't some level of two sentimental connections yet additionally can develop among relative opponent for parent cognizance or in harmonies. Desire is outstanding from Jealousy in that Jealousy constantly incorporates a third assembling seen as a going after affection. Jealousy happens among two people and is most prominent summed up as "I require what you have" (Pines, 2016). Selfesteem may be depicting similarly as constructive or in adverse point of view close identity (Rosenberg, 1965). Self-esteem can likewise be expressed that as the familiarity with certainty, or the level to which an individual benchmarks, rewards, or rises the character. Self-esteem is the thoughtful an individual makes of his or her esteem, established on emotions and sentiments about how he or she ready to or accomplishes in some predetermined condition in lifespan. Self-regard once in a while said to as selfassurance or self-esteem, can be a critical bit of accomplishment. Likewise, mild level of Self-esteem can stop person's feeling most exceedingly bad or troubled. It can likewise demonstrate people to make malicious determinations, drop into unhelpful relations, or unsuccessful to living their filled plausible.

#### 2. Problem Statement

Numerous past examinations have centered on relationship there is an absence of research examination the job of Self-esteem in desire and metacognition among Adults and there is couple of open research in Pakistan that has explored connection among metacognition and Jealousy. Self-esteem was observed to be connected with desire and metacognition yet no announced writing demonstrates coordinate connection among Jealousy and metacognition. Not very many inquiries about examination have contemplated that two factors yet not straightforwardly. Hence, there is a critical need to study about these constructs in this manner with this foundation this exploration will be directed to consider connection among Jealousy and metacognition and role of Self-esteem in this relationship among married adults of our population.

#### 3. Hypothesis of the Study

- There will be a significant relationship between Metacognition and Jealousy among married adults.
- There will be a significant relationship between Metacognition and Self-esteem among married adults.
- iii. There will be a significant relationship between Self-esteem and Jealousy among married adults.
- Metacognition will predict self-esteem and jealousy among married adults among married adults.
- v. Metacognition, self-esteem and jealousy will vary on gender among married adults.

#### 4. Method

#### 4.1. Instruments

4.1.1 Metacognition Questionnaire (MCQ-30)

Metacognition Questionnaire (MCQ-30; Wells & Cartwright-Hatton, 2004) is a 4-point Likert scale (1 = do not agree -4 = agree very much) and self-report measure for metacognitive thinking. The total score can be obtained by adding scores on all items lower the score, lesser the metacognition and vice versa. The five sub-scales assess the following extents of metacognition: (1) positive feelings about stress; (2) negative feelings about worry about uncontrollability and danger; (3) cognitive Self-esteem; (4) beliefs about the essential to jurisdiction opinions; and (5) cognitive self-consciousness. The scale has incredible inside consistency and great convergent and predictive validity in usual populations. For the present study scale was translated into Urdu language with psychometric properties established.

#### 4.2. Rosenberg Self-esteem Scale (RSS)

This tool (Rosenberg; 1965) is a 10 items onedimensional scale that estimates self-esteem worldwide. All items are responded using a 4- point Likert scale fluctuating from highly agrees to highly disagree. Items 2, 5,6,8,9 are reversed scored. Allow "Strongly Disagree" 1 Point, "Disagree" 2 points, "Agree" 3 points, and "Strongly Agree" 4 point. Total scores are total of ten items. Higher score demonstrates higher Self-esteem and vice versa.

#### 4.3. Multidimensional Jealousy Scale (MJS)

The MJS (Pfeiffer & Wong, 1989) is 24 items scale which involves three subscales (cognitive, emotional and behavioral) made up of 8 items each. The cognitive and Behavioral subscales are evaluated on a 7-point Likert scale, from 1 (never) to 7 (all the time). The emotional subscale is evaluated from 1 (very pleased) to 7 (very upset). All items in Cognitive subscale are reversed. The scale has incredible inside consistency and great convergent and predictive validity in usual populations. For the present study scale was translated into Urdu language with psychometric properties established.

### 4.4. Procedure

Participants were informed about the reason of the study, with consent taken and briefed about ethics of research process. They were given protocol consisted of demographic sheet and above three scales. They were requested to score each of the scales as per the given directions. The information acquired was then utilized for the quantitative investigation. All participants were thanked for their contribution and interested one's were also discussed about sharing research detections with them.

#### 5. Results

The basic intent of analysis of examine was to hypothesize the relationship between Meta-cognition, Jealousy and Self-esteem. Basically, descriptive analysis of demographic variables was found out along with reliability evaluation of scales on current sample. Correlation coefficient and regression analysis was done to examine analysis basic hypothesis.

Table 1 demonstrates the descriptive statistics of the sample, with mean age of 40.50(7.73). The number of males (225) (52.3) are greater as contrast to females (205) (47.7).

Table 1. Descriptive analysis of demographic variables of sample (N = 430)

		<b>I I I I</b>	
Variables	F	(%)	M (SD)
Age	-	-	40.50 (7.73)
Gender	-	-	-
Male	225	(52.3)	-
Female	205	(47.7)	-

Table 2 demonstrates that descriptive statistics for all

variables. Significant greater negative relationship (p < .000) was found among SES and MCQ (r = ..25\*\*), Results reveals that positive relationship were found among SES and MJS (r = .30\*\*), and other results shows that there is negative relationship found among MCQ and MJS (r=..54\*\*).

Table 2. Correlation among SES, MCQ and MJS (N=430)

Variables	1	2	3
SES	-	25**	.30**
MCQ MJS	25** .30**	54**	54** -
М	25.96	72.44	1.10
SD	2.66	29.32	42.80

Note. SES= Rosenberg Self-esteem Scale, MCQ = Metacognition Questionnaire, MJS = Multidimensional Jealousy Scale, \*\*p<0.00.

Table 3 demonstrates that there is significant gender difference in level of Metacognition among male and female adults. The mean differences demonstrates that female adults (M = 96.62, SD = 18.78) have significantly high (p < .093) than male adults (M = 50, 41, SD = 17.39). While, the Cohen's d values propose medium effect size of SES and larger effect size of MCQ and MJS on the scores. Results indicate that Metacognition significantly predict the development scores of jealousies. The model was significant (F (175.44, p< .000). Total R2 explains the variation in the development predicting scores reveals are .067% effect on jealousy due to metacognition as shown in Table 4.Results indicated that Metacognition significantly predict the development scores of selfesteems. The model was significant (F 28.30, p<.000). Total R2 explains the variation in the development predicting scores reveals are .014% effect on self esteem due to metacognition as can be seen in Table 5.

-	Ma	ale	Fen	nale			<u>95 %</u>	6 <u>CI</u>	-
Variable	M	SD	M	SD	t (198)	Р	LL	UL	Cohen's d
SES	26.52	2.79	25.34	2.36	4.70	.000	.69	1.67	0.46
MCQ	50.41	17.39	96.62	18.78	-26.49	.093	-49.64	-42.78	2.55
MJS	1.30	26.64	88.40	46.22	11.72	.000	35.12	49.27	2.30

Table 3. Independent sample t -test for gender difference in SES, MCQ and MJS

Note. CI = Self-esteem interval. LL = lower limit. UL = upper limit. \*p<.000.

Table 4	Table 4. Simple regression analysis for Metacognition in predicting Jealousy $(N=430)$						
<b>T</b> 7 • 11		Coefficients					
variable	В	В	SEB	Р	LL	UL	
Intercept	167.51	-	4.64	.000	158.38	176.64	
Jealousy	79	-54.06	-	-	-	-	
F	175.44	-	-	-	-	-	
$R^2$	.29	-	-	-	-	-	

Note.  $\beta$  = standardize coefficient of regression. *SEB* = standard error of beta. *LL* = lower limit. UL = upper limit. *R* = .54, p< .000.

Table 5. Simple regression analysis for Metacognition in predicting Self-esteem (N=430)

Variabla		95% CI				
variable	В	В	SEB	Р	LL	UL
Intercept	27.59	-	.33	.000	26.94	28.25
Self-esteem	02	25	.00	-	-	-
F	28.30	-	-	-	-	-
$R^2$	.06	-	-	-	-	-

Note.  $\beta$  = standardize coefficient of regression. *SEB* = standard error of beta. *LL* = lower limit. *UL* = upper limit. *R* = -.25, *p*< .000.

#### 6. Discussion

The first hypothesis has been accepted by showing significant negative correlation between Metacognition and Jealousy, the person with high worrying about worries will be so obsessed about his worries that he will be less likely to be focusing on his/her partner, thus reducing in jealousy (Leahy, 2018). The second hypothesis has been accepted by showing significant negative correlation between Metacognition and self-esteem. Negative metacognitive beliefs concerned the uncontrollability of self-critical rumination and its negative impact on mood, motivation and perception of self-worth (Kolubinski et al; 2016). The third hypothesis has been accepted by showing significant positive correlation between self-esteem and jealousy. the person who values himself high will also expect high from his partner and those expectations delayed or not met will lead towards being jealous (Chin et al; 2017). The fourth hypothesis has been accepted by showing metacognition to be a significant predictor of selfesteem and jealousy. The person, who is focusing on the content of his thoughts in addition to the thoughts, will be critical about himself and his partner and his activities (Tortoriello et al; 2017). The fifth hypothesis has been accepted by showing metacognition, selfesteem and jealousy to be significantly differing on both genders. Low self-esteem in females can be directly linked to cultural value given to female gender, as preferred birth of a male (Rizwan et al; 2017). Higher Metacognition and jealousy in females can be attributed to their different thinking patterns and expectations out of the relationship (Dimaggio et al; 2017).

# 7. Conclusions

From the current study, it can be concluded that metacognition is a significant therapeutic variable in regard to treating low self-esteem and jealousy among married adults. This is the first study of its nature and further studies are needed to generalize findings.

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# Do Financial Liberalization Affect Environmental Degradation (CO<sub>2</sub> Emission and Ecological Footprints)? Evidence from South Asian Economies

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Abstract. The aim of this study is to explain the effect of financial liberalization on environmental degradation  $(CO_2)$  emissions and ecological footprints in the South Asian Economies using data over the period from 1980 to 2017. Fully modified ordinary least square (FMLOS) and dynamic ordinary least square (DOLS) technique used to examine the effect of financial liberalization on environmental degradation  $(CO_2)$  emissions and ecological footprints and ecological footprints and it is found that financial liberalization has no effect on carbon dioxide emission, however positive and significant effect on ecological footprints. Financial liberalization is driving factor for economic growth but it is not better for environmental sustainability. This paper has significant contribution for the region and also have important policy implications in promoting sustainable environment in the South Asian Economies.

Keywords: Financial liberalization, CO<sub>2</sub> emission, Ecological footprints, South Asian economies.

#### 1. Introduction

After the Second World War, a lot of pressure has put on national resources and an idea of free trade, economic growth, and urbanization was developed (Munir & Ameer, 2018). Meanwhile, over the last few decades, globalization has opened the door of international trade, this intensively less restricted trade between countries and concentration on manufacturing sector have influenced environment quality (Hultberg, 2018). Furthermore, Association of Southeast Asian Nations (ASEAN) have expended trade and investment activities under free trade agreement and most of these countries rely on fossil energy which causing environmental degradation (Akbar, Alam Rehman, Zeeshan, & Afridi, 2020). Hence, the volume of trade is increasing globally but especially in Asia due to lower cost and cheap natural resources which attract the investors (Ling, Ab-Rahim, & Mohd-Kamal, 2020). However, developed

countries focusing in reforming the trade liberalization policies, and shifting towards cleaner industries by observing environmental regulations but the developing countries, those are practicing of open economy, are facing environmental degradation (Ling et al., 2020).

Financial liberalization is the relief on rules and regulations as given by government and regulatory authority to its institutions or removal of ban on foreign trading (Tancho, Jermsittiparsert, & Chienwattanasook, 2021). "Trade liberalization is the removal or reduction of restrictions or barriers on the free exchange of goods between nations. This includes the removal or reduction of tariff obstacles, such as duties and surcharges, and, nontariff obstacles, such as licensing rules, quotas and other requirements" (Mahrinasari, Haseeb, & Ammar, 2019). Thus, the control on financial liberalization is essential for the human development and present study financial liberalization is the predictor of the study.

Ecological footprints was firstly introduced in 1990s as the use of land and water for production consumed by humans and wastage elimination generated by population (Hassan, Xia, Khan, & Shah, 2019). On the other hand, since 1990s, trade liberalization was gain considerable attention by the world to promote economic growth but it escalates the volume of CO2 emission Akbar et al. (2020) and also influence ecological footprints (Al-Mulali & Ozturk, 2015). Energy Information Administration (EIA) had predicted that carbon emission of developing countries will increase 127% by 2020 as compare to the developed countries.

Economic development largely depends upon natural resources (Hultberg, 2018). Key indicator of any country is the economic growth and high standard living Shahbaz, Shahzad, Ahmad, and Alam (2016) but it should be associated with protection of environment which should also persuasively be addressed in near future (Tamazian & Rao, 2010). South Asian economies have low and cheap cost labor and natural resources, and due to that these resources are being utilized for fostering their economic development but on account of heavy expense of environmental quality. Especially, South Asian economies have very less restricted trade without the enforcement of strict environmental regulations and mismanagement consequently resulted in this environmental degradation (Ling et al., 2020).

Since two decades, many researchers have examined relationship between environmental issues and macroeconomic variables (Jamel & Maktouf, 2017). Evidences are available that there is positive relationship between economic growth and environmental degradation in developing countries (Scott, McFarland, & Seth, 2013). Scientists, economists, environmentalists, and policy makers is paying attention on this issue and argued that trade liberalization systematically influencing the national resources. Simply, an increase in trade will also increase the consumption of fuel and transportation to generate energy. However, in advanced countries, environmental quality is better than Asian region (Ahmed, Kousar, Pervaiz, & Shabbir, 2021) due to better regulations system (Hussain & Dogan, 2021).

However, previous studies could be divided into two aspect with financial liberalization and environmental degradation; some researchers argued that financial liberalization boost up the carbon emission, other argued that financial liberalization increases the investment in energy efficient technology that improve the environmental quality and mitigate the consumption of energy (Tancho et al., 2021). However, several protection environment policies have already been developed by almost all countries but environmental degradation is increasing. Countries must imposed environmental regulations Azam, Liu, and Ahmad (2021), where liberalization in trade is increasing economic growth, and this growth leads to environmental degradation (Le, Chang, & Park, 2016). According to the best of our knowledge, previously financial liberalization was not studied specifically with environmental degradation carbon emission and ecological footprints for South Asian economies. Therefore, this study investigates the effect of financial liberalization on environmental degradation in the witnessing region of South Asian economies to reduce environmental pressure.

Therefore, this study has significant contribution to the existing literature by testing the effect of financial liberalization with environmental degradation with different tests which to produce reliable results. It also helps the economists, environmentalists, and policy makers in designing policies especially for Asian region.

# 2. Literature Review

# 2.1 Financial liberalization and carbon emissions

Many researchers have examined the contributions of financial liberalization to carbon emissions. For example, (Ling et al., 2020) investigated the effect of trade openness on environmental degradation in ASEAN-5 countries during the period from 1995 to 2014 by using Panel unit root test, Pedroni Cointegration test, Panel Granger Causality test and found that trade openness and carbon dioxide emissions have a positive relationship among studied countries. Similarly, (Akbar et al., 2020) have investigated effect of trade liberalization on carbon dioxide emission in Southeast Asian countries for the period from 1991 to 2018 and used structure equation modelling (SEM). The empirical results reveal a nexus between trade openness, energy consumption, CO2 emissions, and health expenditure in Southeast Asian countries. Both these researchers, concluded that positive and significant impact of trade on environmental degradation. Likewise, Tancho et al. (2021) have investigated financial liberalization on environmental quality in ASEAN countries for the period from 2001 to 2018 and used GMM estimator and found that financial liberalization has negative link with environmental quality of ASEAN countries. In contrast, Khan, Weili, Khan, and Khamphengxay (2021) have investigated trade openness and environmental degradation in carbon emission in the world developing and developed countries by employing static, dynamic and long run estimators. Trade openness has been found to have a decreasing effect on carbon emission in developed countries while degrading the quality of environment in developing countries. Here, regulations play important role for environmental degradation. Similarly, Shahbaz, Tiwari, and Nasir (2013) also investigate the effect of trade openness on CO2 emissions in South Africa using time series data 1965 to 2008 and used error correction method (ECM) and found that financial openness and liberalization reduces environmental degradation and suggested to increase spending on energy conservation R&D which results in energy efficiency and lower emissions.

Some researchers, investigated these factors with short run and long run. For example, Oktavilia and Firmansyah (2016) have investigated the relationship between environmental degradation and trade openness in Indonesia by employing the error correlation model (ECM) for the period from 1976 to 2014 and found that in short run CO<sub>2</sub> emission is partially influenced trade liberalization. Similarly, (Le et al., 2016) investigated trade openness and environmental quality and used a panel data set over a period from 1990 to 2013 of 98 countries and found that in long run trade openness causes environmental degradation, however, countries of middle and lower income level, this effect is very harmful. Hua and Boateng (2015) investigated long run relationship between financial openness carbon dioxide emissions across 167 countries over a period from 1970 to 2007 and used Dynamic GMM technique and found a financial openness reduces CO2 emissions for all countries, it is further found that countries of North get more benefit from trade than countries located in South side of the world.

Jamel and Maktouf (2017), investigated the nexus between economic growth, financial development, trade openness, and  $CO_2$  emissions in 40 European countries by using panel data from 1985 to 2014 and utilize Cobb-Douglas production function to examine causal link and found a positive connection between  $CO_2$  and trade liberalization. Hultberg (2018) investigated the effect of trade openness on environmental degradation by using panel data set of Asian economies from 1986 to 2013 and found that trade openness and economic growth intensify  $CO_2$ emissions.

Despite of huge environmental pressure on South Asian Economies, many scholars did not pay much attention on this issue for the region, in spite of availability of a large number of literature and investigated factors that contribute the environmental damage. Previously, trade openness was studied with carbon emissions in South Africa Shahbaz et al. (2013), on environment of Asian economies Munir and Ameer (2018), on environmental quality Le et al. (2016), on carbon emissions of European countries Jamel and Maktouf (2017), with environmental degradation Asian countries Hultberg (2018), with environmental degradation ASEAN-5 Countries (Ling et al., 2020), with environmental degradation of MENA region Al-Mulali and Ozturk (2015), with carbon emissions Asian countries Akbar et al. (2020), with environmental degradation developed and developing countries (Khan et al., 2021).

Some researchers focus on financial liberalization with environments of North-South Hua and Boateng (2015), economic growth, natural resources and ecological footprints evidence from Pakistan Hassan et al. (2019), economic freedom with carbon emissions Carlsson and Lundström (2001), energy and trade with carbon emissions Indian economy (Boutabba, 2014), financial development with environmental degradation Adams and Klobodu (2018), financial development with carbon emission emerging economy Abbasi and Riaz (2016), environmental degradation with trade openness Indonesia Oktavilia and Firmansyah (2016), financial liberalization and environmental quality ASEAN Countries, Tancho et al. (2021), energy usage and environmental degradation N-11 countries, Sinha, Shahbaz, and Balsalobre (2017), carbon emission and trade openness Kuwait (Wasti & Zaidi, 2020).

In contrast to these studies and to the best of our knowledge, no prior study has tested the relationship of financial liberalization on environmental degradation  $CO_2$  emission in South Asian economies.

# 2.2 Financial liberalization and ecological footprints

Many researchers have examined the contributions of financial liberalization to ecological footprints. For example, Hassan et al. (2019) have investigated the economic growth, natural resources of Pakistan and ecological footprints and used ARDL technique for long run estimation and found that natural resources has positive effect on an ecological footprints that deteriorates the environmental quality. Al-Mulali and Ozturk (2015) investigated the trade openness on environmental degradation (ecological footprints) in 14 MENA countries over a period from 1996 to 2012 and utilized Pedroni co-integration and FMOLS technique and found that trade openness increases environmental damage. Moreover, Granger causality test found that used variables have short run and long run causal relationship with the ecological footprint. Makhdum, and Kousar (2021) have Usman,

investigated the effect of energy utilization accelerate ecological footprints in 15 highest emitted countries over the period from 1990 to 2017 and used AMG estimation approach and found that unidirectional causality is running from non-renewable energy and trade openness to ecological footprints. Zambrano-Monserrate, Ruano, Ormeño-Candelario, and Sanchez-Loor (2020) have investigated Global ecological footprint and spatial dependence between countries and found that bio capacity, trade openness and GDP increase the Ecological Footprint of countries.

In contrast to these studies and to the best of our knowledge, no prior study has tested the relationship of financial liberalization on environmental degradation ecological footprints in South Asian economies.

#### 3. Methods

3.1 Data and sample:

Variable	Observations	Mean	Std. Dev.	Min	Max
CO <sub>2</sub> emissions	228	0.502	0.384	0.028	1.783
E-Footprints	228	1.428	1.365	0.443	5.071
FL	228	47.859	24.536	12.219	116.549

#### Table 1. Descriptive statistics

This study empirically explores the effect of financial liberalization on environmental degradation carbon dioxide emission and ecological footprints in South Asian economies such as Bangladesh, Bhutan, India, Nepal, Pakistan, Sri-Lanka. Whereas, Afghanistan and Maldives are excluded from the study due to non-availability of the sufficient data. In this study, the data of carbon dioxide emission (metric ton per capita) and financial liberalization (trade % of GDP) are collected from the World Bank over the period from 1980 to 2017 whereas the data of ecological footprints (gha per person) from Global Footprint Network of the same period of time. Description and measurement of the

#### **3.2** Econometric Techniques

variables are shown in the Table-A.

#### 3.2.1 Cross-sectional dependence

For better understanding of the results, it is necessary

to check the cross-section dependence among variables (Baltagi & Hashem Pesaran, 2007). Breusch and Pagan (1980) and Pesaran (2004) tests are used for cross-sectional dependence see Table2.

#### 3.2.2 Panel Unit root:

To determine the stationarity of the panel data, panel unit root test is used. Both, first and second generation Table 1. Descriptive Statistics unit root tests are utilized to check the stationarity assumption. This study uses Breusch and Pagan (1980) and Pesaran (2004) tests and finds cross-sectional dependence among the variables. Therefore, in this study, crosssectional Im-Pesaran-Shin (CIPS) test are used to check the stationarity of the data.

#### Table 1: Descriptive Statistics

#### 3.2.3. Cointegration tests

Cointegration tests are used to examine the long-run relationship among the variables. In this research, Pedroni (1999), Kao (1999), and Westerlund and Edgerton (2007) tests are used of cointegration to examine the long-run relationship among the variables.

#### 3.2.4. Estimation techniques

In this study, fully modified ordinary least squares (FMOLS) and dynamic ordinary least squares (DOLS)

models are used. These approaches are useful, even in the presence of the heterogeneity and endogeneity. Kao and Chiang (2001) illustrated that FMOLS can deal with these problems because the FMOLS estimator is developed after making the corrections for serial correlation and the issue of endogeneity in the estimator of ordinary least squares (OLS).

Variables	Level	First-Difference			Order of
	Constant	Constant and trend	Constant	Constant and trend	megration
E-Fprints	4.3711	-0.869	-8.700***	-9.049***	I(1)
CO2	10.238	3.085	-7.307***	-8.448***	I(1)
FL	0.211	-0.928	-8.203***	-8.230***	I(1)

#### Table 3. Cross Sectional Im Pesara and Shin (CIPS) Unit Root

#### 4. Results

#### 4.1 *Descriptive Statistics:*

Table 1 mentioned below of descriptive statistics shows the results for all the variables used in the study. Our results reveal that the mean of financial liberalization (FL) is 47.859 with ranging from 116.549 to 12.219.

The mean value of Ecological footprints is 1.428, with a maximum and minimum of 5.071 and 0.443, respectively. The mean of carbon dioxide emissions is 0.502, with a maximum and minimum of 0.028 to 1.783, respectively.

# 4.2 Cross-sectional dependence:

The results of the Table 2 are showing that test of Pesaran CD 2004 which are applied to test the crosssectional dependency of all the variables and found significant results, as the null hypothesis of crosssectional independence for all the variables is rejected at the 1 percent level of significance.

#### Table 2. Cross-sectional dependence

Variable	Pesaran CD 2004	Decision
CO <sub>2</sub> emission	21.770***	Cross sectional dependence exists
E-footprint	10.100***	Cross sectional dependence exists
F-Liberalization	3.270***	Cross sectional dependence exists

#### 4.3. Unit-root test

Below Table 3 describe the results of stationarity test for all variables by using CIPS unit-root test at the level and first difference for the constant effect and trend. The test has a null hypothesis of nonstationary series. The results of all these variables are nonstationary at the level. Hence, the null hypothesis of nonstationary series is rejected, because the variables become stationary at the first difference are significant and integrated of order 1.

#### 4.4. Cointegration

Cointegration results are showing in Table 4. The study uses different cointegration tests like Pedroni (1999), Kao (1999), and Westerlund and Edgerton (2007). Further, these tests are conducted separately with carbon dioxide emission and ecological footprints. The results of the Pedroni (1999) indicates that the null hypothesis of the test is rejected. Philips Perron (PP) and Augmented Dicky Fuller (ADF) are significant for the CO2 emission. Similarly, the statistics of another dependent variable that is ecological footprints are also significant at 1%. From

these results, it is concluded that long-run relationships exist among the variables. Meanwhile, the results of the Kao (1999) cointegration test also indicating the presence of a long-run association among the variables. However, the results of the Persyn and Westerlund test reveals that a long run relationship among variables are not exist. Based on the results of all these cointegration tests, it is concluded that a long-run relationship exists among  $CO_2$  emission, Ecological Footprints, and Financial Liberalization.

DV=CO2				DV= E-Footprints						
		РР		ADF		РР		ADF	Decision	
Statistics	6.6	596***		6.888***		3.574**	*	3.451** *	Cointegration exists	
<i>p</i> -value	0.000		0.000	)	0.000		0.000			
Kao (1999) Cointegration										
DV=CO2				DV=E-Footprints						
	ADF					ADF			Decision	
Statistics	5.4790***			-1.367***			Cointegration exists			
<i>p</i> -value	0.0000					0.0857				
Westerlund (2007) Cointegration										
	DV=CO2			<b>DV=E-Footprints</b>			Decision			
	Gt	Ga	Pt	Pa	Gt	Ga	Pt	Pa		
Statistics	-0.140	- 0.709	1.315	1.486	- 0.802	-3.867	3.017	-3.879	Cointegration exists	not
p-value	1.000	0.998	1.000	0.999	0.996	0.930	0.703	0.577		

Table 4. Panel Co-integration: Pedroni (1999) Cointegration

#### 4.5. Results of FMOLS and DOLS

Fully modified ordinary least square (FMOLS) and Dynamic ordinary least square (DOLS) used to estimate the long-run coefficients as shown in Table 5 and 6. These tests are separately used for both dependent variables (CO2 emission and Ecological Footprints). The results of FMOLS with respect to first dependent variable (CO2 emission) explain that the coefficient (0.003) of financial liberalization (FL) is positive but insignificant. Similarly, the results of Dynamic ordinary least square (DOLS) are also positive but insignificant. These results show that increase or decrease in financial liberalization of any country in South Asia have no effect on carbon dioxide emissions. The results of financial liberalization with CO2 emission of this study are different from the opinion of Tancho et al. (2021)

who divide the different researchers in two categories, some researchers are with financial liberalization due to its positive role for environmental degradation ( $CO_2$ emission), others researchers found its negative impact.

However, the results of financial liberalization with ecological footprints are positive and significant. In

#### 5. Discussions

Among three pillars of sustainability, the environmental sustainability is very important and essential for achieving sustainable development (Díaz de Otálora, del Prado, Dragoni, Estellés, & Amon, 2021). The present study, examines the effect of financial liberalization in environmental degradation (CO2 emission and ecological footprints). As the environmental quality in South Asian region is worse than other region of the world (Ahmed et al., 2021) due to better regulations system (Hussain & Dogan, 2021). This study is based on the South Asian countries from 1980 to 2017. Two countries (Afghanistan and Maldives) are excluded from the study due to data unavailability of the data in different years. Furthermore, FMOLS and DOLS models are this study, FMOLS and DOLS approaches are also used to test the impact of financial liberalization on ecological footprints. The results of FMOLS shows that an increase in 1% of financial liberalization of any country in South Asia will increase 4% ecological footprints.

Table 5, FMOLS and DOLS (DV=Carbon Dioxide Emission)							
	FMOLS		DOLS				
Variable	DV:CO2	p-value	DV: CO2		Decision		
	Coefficient		Coefficient	p-value			
FL	0.003	0.194	0.001	0.452	Daiaatad		
R2	0.027		0.059		Rejected		

	FMOLS		DOLS		
Variable	DV: CO2		DV: CO2	Decision	
	Coefficient	p-value	Coefficient	p-value	
FL	0.045	0.000	0.041	0.000	
R2	0.512		8.951		Accepted
Adjusted R2	0.509		-29.541		

utilized to examine the empirical results. Based on the results of these approaches, there are some interesting findings.

First, the study found that financial liberalization has no effect on carbon dioxide emissions. However, the studied countries are largely depends upon natural resource exploitation to increase economic growth as these resources are cheap and low cost in the region Ling et al. (2020), further lot of free trade agreements (Akbar et al., 2020) causing environmental degradation. Whereas, number of researchers have positive and negative opinion (Tancho et al., 2021) about financial liberalization factor (Murshed, Rahman, Alam, Ahmad, & Dagar, 2021). Secondly, the effect of financial liberalization on ecological footprints is positive and significant. Hence, it is concluded that financial liberalization is not good for environmental sustainability.

This study has a few implications. First, the financial liberalization uses of advanced technologies for natural resources exploitation minimize the environmental degradation. Secondly, improved could institutional quality be helpful in implementation of transparency and regulations and fighting against corruption. Policy makers should focus on extensive trade in South Asian economies as free trade without regulations causing environmental damages. So, trade policies must be redesigned and formulate in accordance towards the betterment of environmental quality. Otherwise, this extensive free trade and financial liberalization could influence in achieving the objective of SDGs 2030.

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# Manufacturing of Bricks from Pumice, Fly Ash and Waste Lime from Fertilizer Industry Multan

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Abstract. Lime has been used for construction for centuries in Mughal Era. Today for the brick making has been incorporated in the policies for the low-cost houses, lime use for bricks has been increased globally due to its availability from the industrial waste, in Multan from Fertilizer Company. One of the largest components of the Lime from Multan Fertilizer waste is "Lime chalk calcium carbonate (CaCO<sub>3</sub>, 87.5%)", reuse of refused Lime from Multan Fertilizer waste for the production of bricks is suitable solution. This project is focusing to utilize lime for making bricks. "Lime chalk, calcium carbonate (CaCO<sub>3</sub>, 87.5%)", was mixed with sand replacement Pumice and fly ash in fixed proportions. Those mixes were then used to cast the cylinder  $10\times3$  inches. Compressive strength, heat resistance, and water absorption tests were performed on those blocks and results were analyzed and compared with those of conventional concrete block and clay brick. Conventional concrete blocks absorb about 9.5% of the water while water absorption of the Lime from Multan Fertilizer block is only 0.24%.

Keywords: Fly Ash; lime chalk; Multan Brick; Pumice, Brick; Sugarcane Bagasse

# 1. Introduction

The objective of the research is to develop a methodology for making of lime from Multan Fertilizer using Lime from Multan Fertilizer waste. The author aims to simulate the compressive strength, heat resistance, and water absorption of Lime from Multan Fertilizer bricks. To compare properties of blocks made of lime from Multan Fertilizer with conventional concrete block. The scope of this project is to utilize lime from Multan Pak Arab Fatima Fertilizer for manufacturing of blocks. Only Lime from Fertilizer industry is used in this project, no other type of Lime is used. This Lime from will be mixed with pumice, fly ash Sanawa sugarcane Bagasse Fly Ash and Cement in different ratios.

#### 2. Literature Review

This section elaborates the literature review for

making blocks out of Lime from Fertilizer industry. The aim of the literature review is to highlight the usage of Lime from Fertilizer mixed with the Fly Ash and Pumice materials to manufacture different blocks and to test their respective properties. Fertilizer industry have been growing remarkably in terms of diversity, quality, and production volume in recent (Caruso et al. 2021). Mechanical characterization. Due to the extensive amount of Fertilizer Lime availability over the year in Multan, it is considered as one of the most important block fillers in the present Multan Nshimiyimana et al. (2021). Nshimiyimana studied Durability simulations of Compressed Earth/ Clay Blocks Stabilized with Agricultural By-Product Binders which included Rice Husk Ash, Lime from Multan Fertilizer is semi-crystalline and semitransparent, it has higher tensile strength, chemical resistance, and suitable thermal stability. Huge

quantities of Lime are used in the filling sites. The company is producing 320 million tons of Lime from Multan Pak Arab Fatima Fertilizer every year and same at the Sanawa Industrial Area. 8 billion tons of Lime from Multan Pak Arab Fatima Fertilizer has been produced since 1950 Abbas et al (2017) described. Out of 8 billion, only 9% is recycled, the total production capacity of Lime is 64,400 kilo tons per year in 2018. Lime from Multan Fertilizer accounted 30.3% of the total production of Lime unlike natural lime this is a non-degradable lime in the natural environment, leading to environmental pollution when it is discarded after use Siuda et al. (2021). Some common characteristics of lime are high strength and durability. Most of the Lime from Multan Pak Arab Fatima Fertilizer is disposed of at landfill sites which also lead to serious environmental issues (Liu et al. 2021).

#### 2.1. Experimental Program simulation procedure

The methodology follows a sequence of activities to achieve the desired objectives. At first, the block specimens were cast and then tests were performed on it. The casting of the blocks involves the number of activities i.e., mixing, pouring in mold, de-molding, and testing. Moreover, the block specimens were tested for water absorption, heat resistance and compressive strength (Fig. 1).

Table 1. Comparative analysis of cylinder								
Water Absorption (%)								
		Type 1	Type 2	Type 3	Type 4	Type 5		
Mean	_	9.13	9.18	9.35	9.2	9.3		
	SD	9.1	9.85	9.9	9.8	9.9		
		10.5	10.25	10.8	10.95	10.7		



Fig. 1 Prepared Specimens using Various Materials

#### 3. Lime from Multan

The collected waste Lime from Multan Fertilizer, Pumice and Fly Ash are taken in a proportion of 1: 1:1.5 (1 Lime from Multan Pak Arab Fatima Fertilizer: 1 Pumice: 1.5 Fly Ash) by weight and mixed to get a homogenous mix and then poured into the molds of 12 inch high and 6-inch diameter cylinder size. After setting in for 12 hours in the mold, the simulated specimens were demoded and immersed in water for 28 hours before being removed for testing Doğan-Sağlamtimur at el. (2021).

# 3.1. Pumice

The Collected Lime from Multan Fertilizer is brought at the site and plant of Sothern University of Punjab. The Lime from Multan Fertilizer, fly ash from Sanawa power plant and pumice from Chaghi (Baluchistan) are taken in a proportion by weight and Fly Ash is added and mixed thoroughly using rod and trowel before it hardens.

#### 3.1.1 Fly Ash

The mixture is then homogeneously poured into the cylindrical mold and then is compacted with the aid of steel rod and surface is finished using trowel. Before pouring the mix into the mold, the walls of the mold are oiled for smooth removal afterword, Gupta (2021), as shown in Table 1 and Fig. 2.



(a) Deformation profile Pumice

(b) Deformation profile Fly Ash

Fig. 2 Model output training data for the comparative analysis of cylinder casted on 1st May 2021

			1 1		
Block Type	No. Of Samples	Lime Weight	Sand Weight	Fly Ash Weight	Pumice Weight
Sand	4	1.96 kg	5.6 kg	-	-
Fly Ash (15%)	4	1.96 kg	4.76 kg	0.84 kg	-
Fly Ash (20%)	4	1.96 kg	4.48 kg	1.12 kg	-
Fly Ash (25%)	4	1.96 kg	4.2 kg	1.4 kg	-
Pumice (15%)	4	1.96 kg	4.76 kg	-	0.84 kg
Pumice (20%)	4	1.96 kg	4.48 kg	-	1.12 kg
Pumice (25%)	4	1.96 kg	4.2 kg	-	1.4 kg

 Table 2 Mix proportion for trials

# 4. Conclusions

The first objective of this research was to develop a methodology for making of Lime from Multan Fertilizer block using Lime from Multan Pak Arb Fatima Fertilizer waste. From the experimental results presented following conclusions have been summarized: Proper methodology for making of Lime from Multan Fertilizer block was formulated in an economical manner. Work was been done considering different ratios of lime Fly Ash Sanawa and Pumice from Chaghi in order to compare their properties with each other and to opt the best result generating ratio. The second objective as mentioned above of this project was to determine the compressive strength, heat resistance, and water absorption of Lime from Multan Fertilizer block: The mix lime and 25% replacement of aggregate with pumice Fly Ash generates best result in compressive strength i.e., 2027 psi. The mix of lime and 25% replacement of aggregate with pumice by Fly Ash give most resistance to heat. The mix of lime and 25% replacement of aggregate with pumice by fly ash absorb least waster i.e., 0.24%.

The third objective as mentioned above of this project was to compare the properties of

manufactured Lime from Multan Fertilizer block and conventional concrete block: The compressive strength of conventional concrete block is about 725 PSI. Compressive strength of Lime from Multan Fertilizer is thrice of that of conventional concrete block. Conventional concrete blocks absorb about 9.5% of the water while water absorption of the Lime from Multan Pak Arab Fatima Fertilizer block is only 0.24%. After analyzing the results in terms of compressive strength, water absorption and heat resistance, following are the recommendation. It is recommended to use these blocks instead of concrete blocks in construction of houses. The use of these blocks will help reducing 'carbon foot print' and it will also help to reduce Lime waste. Since the surface of the block at 40% Lime from Multan is quite smooth which does not require any plaster but just a finishing polish required to be utilized as tiles. With some variation in its properties, it can be used for making. Water absorption behavior of the Lime from Multan for block was closely observed, it is concluded That Lime from Multan Pak Arab Fatima Fertilizer block can also be used for constructing UGWT and OHWT.

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# Importance of Coordination Chemistry and Role of Sulfonamide Derived Compounds in Biological Activity – A Review

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Abstract. Coordination compounds have been playing an important role in our daily life due to their complex structures and magnetic properties. In coordination chemistry, we mostly discuss the Schiff bases which are prepared through condensation process between the amine group and an aldehyde (RCH=O) or ketone ( $R_2C=O$ ) group. These compounds possess many sites to coordinate with the metal atoms that enhanced their bioactivity. Aromatic Schiff bases are pharmaceutically more important. Metal-based Schiff base compounds have become more popular for treating illnesses that are hard to treat with traditional methods. Pharmaceutical researchers took use of unique characteristics of metal chelates as an intermediary between organic and inorganic molecules. (Synthesized, published, and evaluated in the past 10 years) that exhibit antiviral, antimicrobial, antioxidant, and other biological properties such as antitumor and anthelmintic.

Keywords: Coordination chemistry; biological properties; Metal-based compounds; Schiff bases; pharmaceutical

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#### 1. Introduction

Infectious diseases created by microorganism's impact millions of people globally, resulting in deaths (Sumrra and Chohan 2013). The pathogenic microorganisms that produce bacterial infections are responsible for a number of deadly illnesses (Ebrahimi et al. 2016). At the moment, the most widely used antibiotics are Daptomycin, Torezolid, and Solithromycin (Swain et al. 2020). Despite the fact that antimicrobial agents are intended to kill or restrict the growth of harmful bacteria, there is the possibility that bacteria will develop a resistance to antibacterial/antibiotics over time (Abu-Dief et al. 2020). Emergence of drug-resistant bacteria has impacted the treatment of infectious illnesses in several ways (Mondal et al. 2015).

The condensation reaction for Schiff bases typically works as bi-, tri- and polydentate ligands as well as form coordination compounds with metal transition (Amjad et al. 2016). The Schiff bases demonstrate their numerous uses in different organic compound synthesis as well as in carbonyl compound analysis and characterization, as in the preparation of the fluorescent adsorbents and in the pharmaceutical field (Rahim et al. 2015).

The Schiff bases have been thoroughly analyzed as ligands as the HC=N azomethine form stable chelates with several metal ions, accompanied by many electron donors' groups. Thanks to their high synthetic versatility, different ligands and complexes can be synthesized, some of which are listed below (Yasmeen et al. 2017). A number of sulfonamides are well-

known for their antibacterial and anticancer actions, as well as their diuretic and anti-carbonic anhydrase properties. Metallic compounds have altered pharmacological and toxicological potentials for several medicines (Sumrra et al. 2020). Cobalt, copper, nickel, and zinc are the most researched metallic ions in this regard because they produce low-molecularweight complexes that have been shown to be more helpful against a variety of illnesses (Zafar et al. 2021). In the field of metal-based sulfa medicines, the sulfonamides received a lot of interest (Arjmand et al. 2019).

Metal-based compounds of sulfadiazine were introduced successfully to treat and prevent bacterial infections (Sharaby et al. 2017). It is the ease with which the metal ion and ligand connection may be disrupted that determines the biological characteristics of metal complexes in biological systems, it is consequently important to understand the coordination behavior and interaction between metals and ligands (Jain and Mishra 2016). To better understand the coordination characteristics of sulfonamides, we have initiated a program to synthesize and design metal-based sulfonamides, and to study their structural and biological behavior as a result (Mounika et al. 2010).

Pathogenic resistance together by drug resistance has displayed scientists a severe risk to project and improve such bioactive compounds (Shalini et al. 2014). Synthesis of such compounds is seen exponentially since last two decades. Schiff base compounds as biologically active candidates are widely employed as antifungal, antibacterial, insulin mimics, and enzyme inhibitors etc. (Apostolidis and Lee 2010). Schiff base compounds derived from sulfonamides are and area of interest for the synthetic scientists. For studies with regard one and the same, the major goal of this review is to highlight that transition metal chelates display strong bioactive properties, which are controlled by the minerals and their various oxidation states, and the kind of ligands employed in the chelation procedure (Khalid et al. 2020). In addition, this study focuses on and discusses the biological actions of certain metal-based sulfonamide-derived Schiff base compounds. The pharmacological study of different sulfonamide derived Schiff bases and their respective metal complexes have signified the biological properties of metal ions. Metal complexes have exhibited efficient cleavage of DNA in the control experiments, whereas the actual DNA showed no cleaving activity (Fig. 1) (Jarrahpour et al. 2007).



Fig. 1 Important applications of sulfonamide Metalbased compounds

Paul Gelmo (1908) have synthesized the first sulfonamide, while working on azo dyes (Pervaiz et al. 2020). Different types of sulfonamide drugs hold many donor sites that facilitate the chelation process with different metal ions. Nitrogen and sulfur containing ligands and their metal complexes are being widely studied since their strong and efficient medicinal potentials. Substitution on the sulfa groups have enhanced the bioactivity of sulfonamide drugs. Carbonic anhydrase having the highest inhibitory effect of sulfonamides used to treat the various diseases such as epilepsy, mountain illness, cancer and acts as anti-inflammatory, anti-convulsant, and antitubercular agents. Compounds having sulfonamide groups are used in different fields such as potentially they are used as coating and as separation membrane in fuel cells. Sulfonamide antibiotics also possess many other features as they are stable in structure, can be easily stored, anti-bacterial properties and having low price. Therefore, sulfonamides and their bio esters are clinically more important. Some sulfonamide compounds show many applications in hypoglycemia as phosphodiesterase-5 inhibitor. The main aim of this review paper is the present of biological activity of sulfonamide ligands and their complexes (Fig. 2) against the bacterial and fungal species (Alaghaz et al. 2014).



Fig. 2 The chemical structure of a Schiff base

# 2. Medicinal Importance

According to the literature, aryl sulfonamide compounds (1a-1f) having are essential in industrial and medicinal science. Drug-like properties are displayed by aryl sulfonamide derivatives that include heterocyclic moieties. Idemudia et al. (2015) and his colleagues reported the synthesis of new Schiff base ligands and their metal complexes. Analytical and spectroscopic methods were used to characterize the synthesized compounds. The results of spectroscopic and thermal analysis have confirmed the octahedral geometry of the transition metal complexes. All the newly synthesized compounds were screened against Bacillus pumilus, Proteus vulgaris, Staphylococcus aureus and Aeromonas hydrophila for anti-bacterial activity and against free radical 1, 1-diphenyl-2picryl-hydrazyl (DPPH) for antioxidants activity (Fig. 3). The results showed the low biological activities of these compounds against the bacterial strains.



M = Mn(II), Ni(II), Co(II), and Cu(II)1a: R = CH<sub>3</sub>; 1b: R C<sub>6</sub>H<sub>5</sub>



Fig. 3 Structures of bioactive sulfanilamide ligand and its complexes

In the last several decades, metal-based compounds have been studied as potential therapeutic agents for a variety of illnesses. Metals in proteins that provide therapeutic effects can react with various atoms of numerous amino acid residues. Alsafee (2015) reported the synthesis of transition metal complexes of benzene sulfonamide (2a-2e). All the compounds were characterized by elemental analysis, NMR and mass spectroscopy. Molar conductance of the compounds was also measured. The synthesized compounds were ability to act as antimicrobial, antiinflammatory, and antibiotics. The purity of synthesized compounds was checked by thin layer chromatography (TLC). According to the physicochemical measurements it was observed that the ligand coordinated through thiadiazols nitrogen and sulfonamide oxygen atoms. The octahedral geometry of mostly complexes was confirmed after spectral study of the compounds (Fig. 4).



Cr(II), Fe(II) and Co(II)

Fig. 4 Structures of ligands and complexes of octahedral geometry

Sulfonamides are a type of biologically active compound that originates in a variety of arrangements.

During preset investigation, a pyrazole-based sulfonamide (3a) that has carbonic anhydrase (CA) inhibitory properties from ethyl-1-(3-nitrophenyl)-5phenyl-3-((5-sulfamoyl-1,3,4-thiadiazol-2-yl)

carbamoyl) and its metal complexes with Ni(II) (3b), Cu(II) (3c), and Zn(II) (3d) have been synthesized (shown schematically in Fig. 5). The elemental analysis, <sup>1</sup> H NMR, IR, UV-Vis, and MS spectral data were used to determine the structures of metal complexes. Utilizing hydratase and esterase bioassay, the inhibition of two human carbonic anhydrase (hCA, EC 4.2.1.1) isoenzymes I and II, as well as 1 and synthetic complexes (2-4) and acetazolamide (AAZ) as a control compound, was evaluated in vitro. The inhibition constants for hCA-I and hCA-II were 0.1460-0.3930 mM for hCA-I and 0.0740-0.0980 mM for hCA-II, respectively, and they had expressively extra inhibitory activity on hCA-I and hCA-II than the relating free ligand (3a) and standard (AAZ) (Büyükkidan et al. 2017).



Fig. 5 Biologically active sulfonamide derived nickel, copper and zinc complexes

The Schiff bases and their metal complexes include vast applications including chemical, biochemical, pharmaceutical and medicine industries. The metal complexes having different oxidation states were stabilized by forming metal complexes with these synthesized Schiff bases. Anandakumaran et al. (2017) synthesized a Schiff base of benzene sulfonamide and its metal complexes (4a-4e). The synthesized compounds were characterized through different analysis. The spectral data of compounds confirmed the bidentate coordination of ligand (Fig. 6). The nonelectrolytic nature of the complexes was confirmed through molar conductance. The crystalline nature of ligand, Cu and Mn complexes were confirmed through X-ray powder diffraction after showing the sharp peaks. While the broadening of peaks in other complexes confirmed their amorphous nature. The synthesized compounds were also tested on malignant cell line growth to check their anticancer effects. The results showed good anticancer activity of metal complexes. The antifungal activity of synthesized compound was performed against Candida albicans and Aspergillus niger. It was concluded that all the complexes show good inhibition activity towards the fungal strains.



Fig. 6 Structure of anti-cancer metal complexes

1,4-Dihydropyridine (DHP) products are widely utilized therapeutically in the management of hypertension and cardiovascular conditions, as L-type calcium channel blockers (CCBs). Ebrahimi et al. (2016) synthesized new sulfonamide derivatives (5a and 5b) as antibacterial agents and their metal complexes (5c-5f). All the compounds were characterized by detailed analytical, structural and spectroscopic methods. The physical properties such as color, melting point and stability were also checked. Thermal analysis was done to find out the thermal stability and coordinated water molecules of metal complexes. The electronic properties and computational studies were carried out to characterize the newly synthesized sulfonamide derivatives. To the check the antibacterial potency, all the compounds were screened against Gram positive bacteria such as Staphylococcus aureus as well as Gram negative Pseudomonas bacteria including aeruginosa, Escherichia coli and Proteus mirabilis (Fig. 7). All the compounds were found to be biologically active and as drug candidates for bacterial pathogens.



Fig. 7 Schiff base ligands and their metal complexes as anti-bacterial agents

Bacsar et al. (2016) synthesized novel sulfonamide derivatives (6a-6k) which have ability to treat the glaucoma. And human carbonic anhydrase II [HCAII] is the isozyme that is used for the management as well as treatment of glaucoma. It was confirmed from kinetic studies that these compounds have inhibitory effect on esterase and hydratase activities of hCAII. All these compounds were characterized by spectral data such as NMR, FT-IR, and HRMS (Fig. 8). The results of *in vitro* studies showed that newly synthesized products possess influential inhibitory properties.



4-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>- (6e); 2-naphthyl (6f) 2,4,6(CH<sub>3</sub>)C<sub>6</sub>H<sub>2</sub> (6g) 3,5-diCl (6h), 2-OCH<sub>3</sub>C<sub>4</sub>H<sub>2</sub>- (6i) C<sub>6</sub>H<sub>5</sub>- (6j); 4Br-C<sub>6</sub>H<sub>4</sub>- (6k)

Fig. 8 Structures of sulfonamide derivatives having enzyme inhibition activity

Compounds that include sulfur have been used as medicines and for treating wounds for a long time. The inhibitors of tumor cells, anti-thyroid, antidiabetic, diuretic and many other actions are now employed as antibiotics employed to treat infectious illnesses. Therefore, research in this area is beneficial. Salehi et al. (2016) synthesized the new series of Schiff base ligands (7a-7c) and their metal complexes (7d-7f). All the synthesized sulfonamide derived compounds were characterized by spectroscopic analysis including FT-IR, UV-Vis along with the X-ray diffraction analysis. Biological studies were done to determine the minimum inhibitory concentrations (MIC) and minimal bactericidal concentration (MBC). The antibacterial properties of all the compounds were determined against Gram-positive bacteria including *Staphylococcus aureus* and *Klebsiella pneumoniae* in addition to Gram-negative bacteria such as *Escherichia coli* and *Enterococcus faecalis* (Fig. 9). The results showed the higher activity of the complexes against bacteria as compared to the Schiff base ligands.



Fig. 9 Structural elucidation of sulfonamide ligands and related complexes

The increasing occurrence of multi-drug-resistant (MDR) strains of diverse pathogens attracts considerable interest to the development of antibiotic resistance with unique mechanisms of actions against distinct biological targets. Tahriri et al. (2017) synthesized two new sulfonamide Schiff base compounds (8a and 8b). Elemental and spectral data was used for the structure elucidation of all the sulfonamide derived compounds (Fig. 10). Two different methods such as minimum inhibitory concentration (MIC) and disc diffusion method were used to study the antibacterial activity of the synthesized compounds against Staphylococcus epidermidis, and Proteus mirabilis pathogens. To study the antifungal activity of the compounds against Aspergillus clavatus, Aspergillus fumigates the same method was used. During this miconazole was used as antifungal standard.



Fig. 10 New sulfonamide derivatives with efficient antifungal activity

containing sulfanilamides Drugs have been investigated as possible chemotherapeutic agents. Their method of action is to prevent folic acid production in bacteria, resulting in cell death. Sulfa medicines have received a great deal of interest since their discovery. Rani et al. (2017) narrated the synthesis of sulfanilamide derived Schiff bases (8a-8c) and their metal complexes (8d-8o). The octahedral geometry of the metal chelates with bidentate ligands were confirmed after spectral and elemental analysis of the compounds. All the newly synthesized products were screened against many bacterial pathogens such as Pseudomonas aeruginosa, Salmonella typhi, Escherichia coli, Staphylococcus aureus, Bacillus

*subtilis*, and many fungal pathogens such as *Fusarium solani*, *Candida glabrata*, and *Candida albicans*. The results showed that the activity against pathogens increased upon chelation as compared to free ligands (Fig. 11).



Fig. 11 structures of sulfonamide ligands and complexes having antimicrobial activity

Bioactive compounds, such as sulfa drugs, typically exhibit increased activity when chelated with metals. Such compounds have also been shown to have a variety of biological and pharmacological properties. Khan et al. (2018) described the synthesis, characterization, and biological evaluation of the sulfonamide-based Schiff base (10a) and its metal complexes (10b-10f). All the compounds were characterized through elemental, physical and spectral analysis that confirmed the nature of ligand as bidentate. The octahedral geometry of all the complexes were also confirmed after these studies. The results of antibacterial activity of these compounds against Staphylococcus aureus and Escherichia coli showed that the complexes exhibited good activity against these pathogens as compared to the free Schiff base ligand (Fig. 12).



M= Mn(II), Co(II), Ni(II), Cu(II), Zn(II)



Sulfonamides have long been used as powerful antibacterial agents against Gram+ and Grambacterial strains linked to a variety of infectious illnesses. These synthetic pharmacological compounds compete with and block the adsorption of p-amino benzoic acid (PABA) at the active site of dihydropteroate synthase (DHPS), interacting with the essential bacterial dihydrofolic acid production pathway. Saleem et al. (2018) reported the synthesis of three new sulfonamide derivatives (11a-11c). All spectroscopic techniques such as NMR, FT-IR and elemental analysis was done for structural characterization of all the synthesized compounds. Molecular docking studies were also done to examine the functional and structural basis of antibacterial activity of newly prepared sulfonamide compounds. The antibacterial actions of these derivatives were tested against both types of bacteria such as Bacillus subtilis, Escherichia coli, Brevibacterium linens, and Bacillus licheniformis (Fig. 13). The results showed that all these newly synthesized compounds having better potency and efficiency against these microbes. These derivatives also have ability to act against resistant pathogens.



# Fig. 13 Structures of some new sulfonamide derivatives having antimicrobial activity

Aryl/heteroaryl sulfonamides are versatile chemicals with important synthetic and biological characteristics. The production of different sulfonamide derivatives has piqued the interest of many researchers since several of them exhibit excellent anticancer activity in vitro and in vivo against that variety of cancer cell lines. El-Mekabaty and Awad (2020) prepared some new sulfonamide derivatives (12a-12e). These synthesized compounds were characterized by several techniques such as NMR, FT-IR, mass spectroscopy and elemental analysis. These derivatives were examined in vitro for their cytotoxic activities against two human cell lines normal retina pigmented epithelium cells and breast adenocarcinoma cells. The results of this activity showed the significant potential of these compounds on McF-7 and less effect on RPE-1 cells. It was concluded that these compounds may be used as anticancer drugs (Fig. 14).



Fig. 14 Chemical structures of some biologically active drugs having sulfonamide moiety

The sulfonamides are physiologically significant substances with minimal toxicity, many bioactive components, and relatively low cost. Isik et al. (2019) synthesized some new sulfonamide derivatives (13a-13d) and described their effects on *AChE* enzymes. Different analysis such as FT-IR, NMR were performed to characterize the sulfonamide derivatives. To check the enzyme inhibition activity of sulfonamide derivatives docking studies were performed. The results showed that the derivatives of sulfonamide exhibited different types of inhibition (Fig. 15). They have many biological effects such as protease inhibitor activity, anti-diabetic, anti-tumor, anti-bacterial, anti-carbon anhydrase and also beneficial for the treatment of Alzheimer's disease by inhibiting the formation of amyloid- $\beta$  which is the starting material.



Fig. 15 Structures of sulfonamide compounds having inhibitory effect on AChE

Sumrra et al. (2020) reported the synthesis of novel sulfonamide derived Schiff bases. The synthesized ligands and their metal complexes were characterized through physical, spectral and analytical techniques. Both the ligands were also investigated by theoretical exploration using density functional theory (DFT). The results of natural bond orbital (NBO) analysis have revealed the greater stability and less reactivity of ligands. All the prepared compounds were evaluated for antimicrobial activities against bacterial such as *Escherichia coli, Klebsiella pneumoniae* and *streptococcus aureus* species and fungi such as *Aspergillus flavus* and *Aspergillus niger*. The compounds were also screened for their antioxidant activity such as radical scavenging activity, total phenolic contents and enzyme inhibition properties (Fig. 16). The results showed the bioactive nature of these new sulfonamide derivatives.



Fig. 16 Chemical structures of sulfonamide-based compounds

Mustafa et al. (2019) synthesized the new sulfonamide derivatives (15a-15d). All the synthesized compounds were characterized by different techniques such as NMR, FT-IR, LC-MS and elemental analysis. Different methods were used to check the antioxidant activity of the newly synthesized compounds such as radical scavenging and FRAP assays. Moreover, the prepared compounds showed better results for enzymes inhibition particularly against hCA II isozyme. As a result, this activity could be beneficial to treat the neurodegenerative disorder such as Alzheimer's disease (Fig. 17).



Fig. 17 Structures of some new sulfonamide derivatives

Hassan et al. (2021) reported the synthesis of new ligands (16a and 16b) and their metal complexes (16c-16n) having sulfonamide moiety. All the newly synthesized products were evaluated through FT-IR, NMR, mass spectrometry and elemental analysis. The octahedral geometry of mostly complexes were confirmed after studying the electronic spectra. Molecular electrostatic potential (MEP) and chemical

descriptive properties of the compounds were also studied. All the compounds were screened against some bacterial species such as *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and some fungal species such as *Aspergillus flavus* and *Aspergillus niger*. The strong bioactive nature of metal complexes was confirmed after studying the antioxidant and enzyme inhibition properties of ligands and their metal complexes (Fig. 18).



Fig. 18 Sulfonamide ligands and their metal complexes having antimicrobial activity

Alyar et al. (2021) reported a new Schiff base (17a) synthesized from the reaction of sulfonamide with salicylaldehyde along with its Pd(II), Cu(II) complexes (17b and 17c). These compounds were characterized by spectroscopic analysis, magnetic susceptibility and conductivity measurements. The single crystal X-ray diffraction technique was done to explore the molecular structure (Fig. 19). For biological evaluation of all the compounds their effect evaluated on carbonic anhydrase II.



Fig. 19 Sulfisoxazole Schiff base and its metal complexes

To check the Pd/Cu complex-hcAII enzyme interaction docking study was performed. The results showed that the metal complexes (18c and 18d) having the best activity against carbonic anhydrase II enzyme as compared to the ligands. All these compounds also exhibited cytotoxic activity against McF7, breast (Fig. 20).





Taslimi et al. (2020) reported the synthesis of benzene sulfonamide derivatives (19a-19h). Analytical and spectral data was used to characterize the sulfonamide derived compounds. To calculate the binding free energy of the compounds molecular docking study was done. These derivatives showed high biological activity. The newly synthesized sulfonamide derivatives exhibited stronger inhibition against many enzymes such as acetyl cholinesterase (AChE), glutathione s-transferase (GST) and  $\alpha$ -glycosidase ( $\alpha$ -GLY). Alzheimer's disease which is caused by AChE. The inhibition effect of products on AChE was determined by Michaelis-Menten and Lineweaver-Burk kinetics. The results showed the higher AChE inhibitory potential of sulfonamide derivatives (Fig. 21).



Fig. 21 Sulfonamide derivatives having enzyme inhibition activity

Chelation is effective to improve the therapeutic destiny of new bioactive compounds. Its function in several bioactive pharmacophores has developed a

potential role in combating pathogenic susceptibility. Sulfa drugs are pharmacologic entities that include sulfonamide core moiety including such sulfanilamide,
sulfathiazole, or sulfadiazine. Hassan et al. (2021) reported two novel sulfonamides Schiff base ligands and their corresponding complexes with the first-row transition metals (Fig. 22). They were characterized by spectral and elemental data.

The density functional theory optimized their molecular geometries at their ground-state energies.

against Antimicrobial bacterial activity Staphylococcus aureus, Bacillus subtilis, Escherichia coli and Klebsiella pneumoniae) and fungal species (Aspergillus niger and Aspergillus flavus) has been investigated in vitro. There was considerable bioactivity in all of the synthesized compounds that improved during chelation due to the phenomena of charge shifting between metal to ligand.



 $X = H_2O$  or 0 for 20c and 20j

Fig. 22 Sulfonamide derivatives having enzyme inhibition activity

#### 3. Conclusions

Schiff base ligands and their resultant transition metal chelates are attaining massive attention in different fields owing to their ease of preparation, chemical versatility and numerous applications. In this regard, sulfonamide ligands and their metal complexes are playing their significant role in various pharmacological applications. The present review focus on some important sulfonamide ligands with their complexes having microbial activity against different types of bacterial and fungal pathogens. Metal-based compounds having established chemical properties have been evaluated for their pharmacological effects. When it comes to developing and designing promising

pharmacological agents for the treatment of severe ailments that are difficult to treat with conventional methods such as chromium and manganese-based metals, this review article suggests which transition metals such as vanadium, chromium, manganese, nickel, copper and zinc, as well as cobalt, platinum and palladium could be useful. Even though it has been shown that metal-based compounds are more efficient in biological activities than ligands, very little is known about their modes of resistance.

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# Exploring the Effects of Washing Treatments on Storage Potential of Various Potato Cultivars

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Abstract. Potato (Solanum Tuberosum L.) is one of the most important crops worldwide and grown in tropical and temperate zones. It belongs to the family Solanaceae. Potato is a rich source of starch, proteins, amino acids, vitamins, minerals, colorants and antioxidant phenols. In this experiment two potatoes varieties were stored at 7°C with 85% relative humidity after washing treatments. The main objective of this experiment to compare the results of both treatments and checked the effect. Various analysis was performed for evaluation of different quality attributes after 30 days interval during 90 days of storage. Finally, data obtained was subjected to statistical analysis. Analysis showed that ascorbic acid decrease and dry matter, weight loss, sugar, total phenolic contents, sprouting, texture and specific gravity increased with increase in storage days. In washed potatoes variety Lal Moti (V1) showed better storage stability as compared to unwashed.

Keywords: Potato, washed, storage.

## 1. Introduction

Potato (Solanum Tuberosum L.) is one of the most important crops worldwide. It belongs to the family Solanaceae (Saraiva et al., 2004). Potato has relatively higher amount of starch (about 75% of potato dry matter), and better quality of protein (2.8-14.6% of potato dry matter) with substantial essential amino acids (e.g., lysine, methionine, tryptophan) (Kwon et al., 2008). It is rich in micronutrients such as vitamins (C and B-complex), minerals (potassium, magnesium, calcium, phosphorus, and iron), colorants (carotenoids anthocyanins), antioxidant and and phenols (Burlingame et al., 2009).

Due to its rich nutrients, potato as a basic food has been consumed widely in the Western world and is increasingly becoming a staple in developing countries (Ek et al., 2012). Potato.is.one of the most vital crops as carbohydrate sources in human diets and as industrial commodities for the starch production and potato-based foods (Simkova et al., 2013). 200g of boiled potatoes in usual meal add to our daily diet with 6% energy, 0.3% of fat, 11% of carbohydrates, 9% of protein, 11% 0f dietary fibres, 28% of potassium and 47% of vitamins (Hasse, 2007). Coloured potato varieties contain phytonutrients, like polyphenolic compounds. Polyphenols prevent from certain diseases like cancer, cholesterol accumulation in blood, macular degeneration and risk of coronary heart disease (Lachman and Hamouz, 2005; Jansen and Flamme, 2006).

Potatoes are widely grown in temperate and tropical zones (Scanlon et al., 2006). Potato is grown on approximately 22 million hectares worldwide, and the annual potato consumption of an average global citizens is approximately 33kg. The total world potato production is assessed at 364,808,768 tons in 2012

### (FAO, 2012).

Potato is number one non-grain food crop in the world and one third of the total production is being harvested in densely populated developing countries, like China and India, and thus alleviates the food crisis in third world countries (PIC, 2008). It is ranked top most important crop in South American continent, second most important crop in Europe and fourth on the Globe after wheat, rice and maize (Messer, 2000). The overall estimated yield of potato in the world is about 320.67 million tons and China being the major contributor produces 72 million tons followed by Russian Federation and India with yield of 35.7 and 26.2 million tons respectively. The demand for potato in the international market is one the rise and all the major exporting countries are trying to increase the yield and as a reciprocal increase their share in world market (FAO, 2007).

Processing quality of potato tubers is evaluated by high dry matter, phenol contents and low reducing sugar (Abong et al., 2009). High dry matter content rises crispy-consistency, chip yield, and decreases oil absorption during cooking (Pedreschi et al., 2005; Rommens et al., 2010). Dry matter and chip color of potato are genetically controlled and subjective by environmental conditions during storage temperature and growing season (Kawchuk et al., 2008).

Potatoes produce sprouts for fresh market and industrial processing during long term storage (Saraiva et al., 2004). During storage increases alteration of starch to sugars and cause the sweetening which carries critical browning of potato fries during processing because of Millard reactions (Teper-Bamnolker et al., 2010; Saraiva and Rodrigues, 2011). During frying acrylamide is a carcinogenic which can be produced, increases significantly when sugar is high (Matsuura-Endo et al., 2006). Tuber stored at 20C in which acrylamide chances ten times greater during processing of potato as compared to 200C which also associated with both fructose and glucose levels (Chuda et al., 2003).

## 2. Materials and methods

### 2.1. Raw Material

Two potato varieties Lal Moti (V1) and Sante (V2) were selected from different farms in Faisalabad. Selected potatoes were free from cuts, bruises, mechanical damage, insect/pest infestation and other physical defects. The best selected potato was brought to the laboratory of NIFSAT (National Institute of Food Science and Technology), University of Agriculture Faisalabad, Pakistan.

Samples were washed under tab water to remove dust and dirt particles, especially to remove mud that on the potato varieties during harvesting. Potatoes were sorted on the basis of size, shape, and outer look of potato. Washed, sorted and graded potatoes were subjected to air drying technique to get clean, good quality and properly dried samples. After drying, varieties were packed in net bags and stored at 70C in electric chamber with 85% relative humidity.

#### 3. Analysis

#### 3.1. Ascorbic Acid determination

Ascorbic acid content will be determined by indophenol's titration method described by AOAC (2006).

### 3.2. Dry matter

Dry matter will be determined by using the hot air oven method which includes weighing, ashing, desiccation and then drying in oven at 100±5 0C for 48 hrs. Till constant weight is obtained. (Abbasi et al., 2011).

## 3.3. Weight loss

The weight loss (%) in different experiments at specified storage interval was determined by weighing the samples with digital balance (OHAUS, Model TS4KD Florham Park, NJ, USA) and reported as percent loss in sample weight based on its initial weight (Bassetto et al., 2005).

# 3.4. Sugar

Total sugar contents were determined by using Fehling solution as described by AOAC (2000).

# 3.5. Sprouting

Sprouting (SPRT) percentages in potato tubers (sprout length > 3mm) were calculated by the equation described by (AOAC, 2007).

Sprouting (%) = No. of eyes sprouted  $\div$  Total no. of eyes  $\times 100$ 

### 3.6. Total Phenolic contents

Total phenolic contents were analyzed by Folin Ciocalteu method described by Ghafar et al. (2010)

## 3.7. Texture analysis

Potato texture analysis in term of penetration force was done at texture analyzer according to the method of Taniwaki et al. (2010).

# 3.8. Specific Gravity

The specific gravity was determined by the following equation as described by AOCS (2006).

Specific Gravity = Weight in air / Weight in air – Weight in water

## 3.9. Statistical analysis

The obtained data for each parameter was interpreted by applying three-way factorial design. Level of significance (P $\leq$ 0.05) was determined (ANOVA) as described by (Steel et al., 1997).

#### 4. Result and Discussion

Means regarding the effect of physical and chemical parameters (Ascorbic acid, Dry matter, weight loss, sugar, total phenolic contents, sprouting, texture and specific gravity) showed significant differences at P<0.05 for treatment, varieties and days and nonsignificant effect on their interaction. Fig. 1. According to results Maximum contents of vitamin C (18.31) was measured in V2' of unwashed potatoes while minimum vitamin C contents (3.70) was calculated in V2' of unwashed potatoes. Vitamin C of washed and unwashed potatoes decrease with increase in storage days due to their degeneration under prolonged storage. Variation in vitamin C contents is more in unwashed (T2) as compare to washed (T1) potatoes. These results go parallel with the findings of (Nourian et al., 2003) who concluded that the ascorbic acid contents decreased with the increase in storage temperature and storage duration. (Blenkinsop et al., 2002) also reported that decline in ascorbic acid with the progression in storage time. Figure 2. Maximum value of dry matter (26.30) was measured in V2 of washed potatoes while minimum dry matter value (15.20) was calculated in V2' of unwashed potatoes. Dry matter of washed and unwashed potatoes increases with increase in storage days. Variation in dry matter value is more in washed (T1) as compare to unwashed (T2). These results go parallel with the findings of (Casanas et al., 2002) who concluded that dry matter of potatoes changed during storage. Figure 3. Maximum weight loss (6.58) was measured in V1 and V2 of washed potatoes while minimum weight loss (1.98) was calculated in V1' of unwashed potatoes. It is evident from our result that weight loss of washed

and unwashed potatoes increases with increase in storage days due to respiration and sprouting. Variation in weight loss value is more in washed (T1) as compare to unwashed (T2) potatoes. Present study coincides well with (Tester et al., 2005) studies who reported that the loss of water activates the series of complex metabolic activities thus considered as an important stability index for the storage life assessment in fruits and vegetables. The weight loss in potato is attributed to the water loss through peel tissues due to physiological processes like respiration and sprouting. (Raghami, 2009) also reported direct relationship between storage temperature and weight loss (%) in potato tubers. Figure 4. Maximum value of sugar (10.55) was measured in V2 of washed and V2' of unwashed potatoes while minimum value (2.25) was calculated in V1 of washed and V1' of unwashed potatoes. Total sugar of washed and unwashed potatoes increases with increase in storage days due to starch degredation. Variation in total sugar value is more in washed (T1) as compare to unwashed (T2). Similar observations were recorded by (Kyriacou, 2009), (Kazami et al., 2000) and (Herman et al., 1996) who estimated inverse relationship between total sugar contents and temperature in potato tubers under storage. Figure 5. Maximum sprouting (3.01) was observed in V1 of washed while minimum (1.00) was calculated in V1' of unwashed potatoes. Sprouting of washed and unwashed potatoes increase with increase in storage days. Variation in sprouting is more in washed (T1) as compare to unwashed (T2) potatoes. Sprouting during the post-harvest storage results in extensive economic losses due to increased weight loss and reduced tuber quality. Sprouting reduces air flow through the piles under storage thus elevates the average temperature consequently increases the chances of disease attack and reduced storage life

(Sonnewald, 2001). Figure 6. Maximum of total phenolic contents (197.31) was measured in V2 of washed potatoes while minimum total phenolic contents value (150.48) was calculated in V1' of unwashed potatoes. Total phenolic contents of washed and unwashed potatoes increase with increase in storage days. Variation in total phenolic contents value is more in washed (T1) as compare to unwashed (T2) potatoes. Similar results were reported by Vitti et al. (2011) that total Phenolic contents increases during the post-harvest storage of potato however found susceptible to the activities of enzymes like polyphenol oxidases and peroxidase. Jung et al. (2011) determined losses in phenolic compounds in potatoes after different methods of home processing. Maximum losses were reported to occur during boiling followed by deep-frying, steaming and minimum losses occurred during microwave baking. Cooking alters the content as well as composition of polyphenols. Figure 7. Specific gravity of washed and unwashed potatoes increases with increase in storage days due to increase in dry matter. Variation in specific gravity is more in unwashed (T2) as compare to washed (T1) potatoes. Specific gravity is one of the most important tools for the quality evaluation of potato variety and is largely associated with the presence of its dry matter or total solid contents. The correlation between specific gravity and processing quality of potato is eminent (Komiyama et al., 2007), and the potato processing industry for the production of chips and French fries mostly depends on the specific gravity for the acceptable quality of processed products (Haynes, 2001). Potato varieties with a high specific gravity have been revealed to produce a high yield of chips with low oil uptake (Kita, 2002). Figure 8. Maximum value of texture (29.43) was measured in V2 of washed potatoes while minimum (19.74) was

calculated in V1 of washed potatoes. Texture changes of washed and unwashed potatoes decrease with increase in storage days. Variation in texture value is more in unwashed (T2) as compare to washed (T1) potatoes. Similar results were reported by Singh et al. 2008; Prado et al. 2005 that texture changes increases with increase in storage days due to weight loss and sprouting.



Fig. 1. Effect of washing treatments on Vitamin C of potatoes during storage



Fig. 2. Effect of washing treatments on dry matter of potatoes during storage



Fig. 3. Effect of washing treatments on weight loss of potatoes during storage



Fig. 4. Effect of washing treatments on total sugar of potatoes during storage



Fig. 5. Effect of washing treatments on sprouting of potatoes during storage



Fig. 6. Effect of washing treatments on total phenolic contents of potatoes during storage



Fig. 7. Effect of washing treatments on specific gravity of potatoes during storage



Fig. 8. Effect of washing treatments on texture of potatoes during storage

### 5. Conclusions

Results showed that parameters (Dry matter, Weight loss, Total sugar, sprouting, total phenolic contents, specific gravity and texture) increase with increase in storage days but ascorbic acid decrease. Maximum variations were observed in unwashed potatoes as compared to washed because unwashed potatoes were spoiled more quickly during storage due to presence of more dust particles on the surface of unwashed potatoes. During storage physicochemical changes were observed more rapidly because in dust particles microorganisms also present which carried these changes. It was concluded on statistical basis that in washed potatoes variety Lal Moti showed better storage stability.

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# Binuclear Metal Complexes of Symmetrical Phenylenediamine Schiff Base: Synthesis, Characterization, Computational Simulation and Biological Studies

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**Abstract**. Coordination compounds with bioactive ligands are currently being studied in detail for their increased biological activity and potential application to be used in the advancement of promising metal-based drugs. Within this research theme, a symmetrical Schiff base ligand, 2,2'-{benzene-1,4-diylbis[nitrilomethylylidene]}bis(6-methoxyphenol) (L) was synthesized and characterized. The computational based calculations of ligand (L) were performed using DFT/B3LYP/6-31+G (d,p) approach. Both the experimental results as well as computational findings agreed well with the structure of ligand (L). The phenylenediamine ligand was used to synthesize its binuclear VO(IV), Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. Moreover, the synthesized compounds were also estimated using DPPH assay. The results of these studies have shown that the metal complexes exhibited a greater antibacterial and antioxidant efficiency in contrast to free ligand, and the activity of metal complexes was high due to chelation process.

Keywords: Symmetrical phenylenediamine Schiff base ligand, binuclear metal complexes, DFT, antibacterial, antioxidant

## 1. Introduction

Advances in the coordination chemistry through designing and developing metal endowed compounds has also led to improvements in both bioinorganic and pharmaceutical chemistry [1-3]. Schiff bases are considered as privileged ligands as they can be readily synthesized by the condensation reaction between primary amines and carbonyl compounds (aldehydes and ketones) under specific conditions [4]. Schiff bases are of great importance due to their characteristic properties of coordinating with metal ions having various oxidation states along with their contribution in widespread biological activities [5]. Schiff bases form stable metal complexes because of the lone pairs of azomethine-nitrogen and adjacent electronegative atoms (S, O, and N) present in their structure [6]. In biological systems, the azomethine linkage of Schiff base play leading role and act as a binding site for the attachment of metal ions with different bio-molecules such as amino acids and proteins for bioactivities [7].

Microbes have developed multiple resistances against various antibiotics, thus causing infectious diseases with increased mortality rates [8]. And this increase in the frequency of systemic microbial infections is life threatening [9]. Therefore, to overcome this situation, the exploration and development of new antibacterial drugs is the key requirement of modern era [10]. In the recent times, metal-based compounds having oxygen and nitrogen as the electron donors are evidencing themselves as the promising drug candidates for replacing the conventional organic based antibiotics [11]. Schiff bases and their derived metal complexes are excellent antibacterial agents as they are more toxic on microbial species because of the existing lipophilic groups (CH3CH2CH, OCH3, and C6H5) in their structure [12]. Particularly all the metal complexes were found to more toxic as compared to their corresponding ligands. Chelation increases the permeability of metal complexes to pass through the microbial lipid layer resulting in their enhanced antimicrobial activity [13]. Together with the synthetic chemistry, the theoretical study is also playing advantageous role in describing chemical scaffolds for various medicinal applications with enhanced efficacy [14]. In this regard, density functional characteristic features have attained great attention in order to optimize the molecular structures to analyze and describe their geometrical design, biochemical activity, active sites as well as molecular interactions [15]. With this perspective, DFT based computational calculations have attained more attention, as it is an extensively employed tool in developing a close relationship between experimental findings and theoretical data. As a result, this technique has been acknowledged as reliable tool for predicting the molecular structure and electronic properties with great precision [16].

Schiff bases of phenylenediamine derivatives are considered as promising candidates for a variety of applications including clinical, analytical and biological [17]. Schiff bases derived from phenylenediamine can be used as substrates for the synthesis of many metal-based compounds with biologically active profiles. [18]. Considering the promising bioactive nature of metal based phenylenediamine compounds and the deciding character of chelation in enhancing their bioactivity, we intend to extend our ongoing interest to synthesize and explore some more bioactive metal based phenylenediamine Schiff base compounds [19]. All the synthesized and well-characterized compounds were evaluated for their antibacterial activity against selected bacterial species along with antioxidant activity.

### 2. Experimental

All of the chemicals and solvents used in our study were of analytical reagent grade and used without purification. Chemical reactants including 2-hydroxy-3-methoxybenzaldehyde and p-phenylenediamine were purchased from Merck and Sigma Aldrich and utilized directly for the synthesis of ligand. Whereas the ethanol was doubly distilled prior to its use in the synthetic reactions. The melting points of synthesized compounds were determined by using Stuart melting point apparatus. FT-IR spectra were documented on Shimadzu FTIR-8400S spectrophotometer. UV-Vis analysis was performed on a high-tech Shimadzu UV-4000 spectrophotometer using solutions of all the compounds in DMF solvent. The molar conductivity measurements were carried out using Inolab Cond 720 conductometer at room temperature. The magnetic moments were determined by using Magnetic Susceptibility Balance (MSB Mk-1 model).

# 2.1. Synthesis of Symmetrical Phenylenediamine Schiff Base Ligand (L)

The phenylenediamine ligand (L) was synthesized by the reaction of 2-hydroxy-3-methoxybenzaldehyde with p-phenylenediamine in 1:2 molar ratio (Scheme 1) by utilizing previously reported method [20]. For the synthesis of ligand, 10 mM (1.52 g) ethanolic solution of 2-hydroxy-3-methoxybenzaldehyde was prepared in 10 mL ethanol. Then, it was gradually added in the magnetically refluxed 5 mM (0.54 g) ethanolic solution of p-phenylenediamine in double bottom flask. The reaction mixture was continuously refluxed. Meanwhile, orange-colored precipitates were formed in the flask indicating the formation of product. The progress of reaction was examined by taking comparative TLC. After obtaining a single spot of the [2,2'-{Benzene-1,4ligand divlbis[nitrilomethylvlidene]} bis(6-methoxyphenol)], the precipitates were allowed cool down to room temperature, then filter, washed three times with hot

ethanol and finally dried. The produced ligand was recrystallized using an equimolar mixture of dioxane and acetone.

# 2.2. '-{Benzene-1,4diylbis[nitrilomethylylidene]} bis(6methoxyphenol)

Orange solid; Yield: 78%; m.p. 230-232°C; IR (KBr, cm–1): 3370 (OH), 2963 (-OCH3), 1638 (HC=N), 1374 (C-O);  $\lambda$ max (nm): 368 n $\rightarrow$  $\pi$ \*, 337  $\pi$   $\rightarrow$  $\pi$ \*; Anal. calcd. for C22H20N2O4 (376.40) (%): C (70.20), H (5.36), N (7.44); Found: C (70.14), H (5.31), N (7.38).



Scheme 1. Synthesis of symmetrical phenylenediamine Schiff base ligand (L)

#### 2.3. Synthesis of Metal Complexes (1)-(6)

The complexes of divalent, trivalent and tetravalent transition metals were synthesized in equimolar ratio (Scheme 2) by employing the already published method [21]. For the synthesis, 10 mM solution of ligand was refluxed in double neck flask using 10 mL of ethanol. After refluxing the reaction mixture for 30 minutes, the solution of respective metallic salt

prepared in 10 mL ethanol was added in the ligand solution. Then, the resulting reaction mixture was constantly refluxed for 8 hours resulting in the precipitation of the metal complex. The filtered product was thoroughly washed with warmed ethanol. After drying, product was further purified by recrystallization in an equimolar mixture of dioxane and acetone.



Scheme 2. Synthesis of metal based phenylenediamine Schiff base compounds (1)-(6)

# 3. Computational Methodology

The ligand was initially optimized and after that the optimized structure was analyzed by means of Gauss View program. Density functional theory (DFT) is considered as the most reliable method for theoretical calculations. DFT based computations were accomplished by using GAUSSIAN 09 program [22]. The theoretical calculations were carried out using B3LYP functional with 6-31+G (d,p) basis set for C, N, O and H atoms.

## a. Antibacterial Activity

The phenylenediamine ligand and its derived metalbased complexes were scrutinized for antibacterial activity against two types of bacteria including Gram negative (Halomonas halophila, Neisseria gonorrhoeae, Salmonella typhimurium) as well as Gram positive (Bacillus subtilis) by the disk diffusion approach as per already reported protocol [23]. The material to be used in antibacterial activity containing nutrient broth, petri-dishes as well as discs of filter papers were autoclaved at 121°C for 30 minutes. After cooling the media to ambient temperature, the semiliquid broth media was uniformly poured into the petri dishes and it was kept in fume hood for solidification. After that, the bacterial inoculum was spread on solidified media by the help of glass loop spreader. Then, the sterilized filter paper discs were positioned over the resulting mixture settled in petri plates. Same concentrations (2 mg/mL) of sample and standard solutions were prepared in dimethyl sulfoxide (DMSO). In this activity, DMSO was used as negative control, while the standard drug (augmentin) was used as positive control. By using the micropipette, 10 µL of respective solution (sample and standard) was added on the discs by micropipette. Later on, the petri dishes were kept in incubator at 37°C and finally the inhibition area (clear zone) was measured in millimeters (mm) after 24 hours.

### b. Antioxidant Activity

Anti-oxidant activity of as-synthesized compounds was evaluated by the help of DPPH assay.

i. DPPH Antiradical Scavenging Activity Antioxidant activity of phenylenediamine ligand and its derived metal-based complexes was performed using DPPH by recommended process [24]. Butylated hydroxytoluene (BHT) was used as reference agent for the comparison of antioxidant activity of synthesized compounds. Antioxidant potential of all the compounds was checked by taking the sample solutions (sample and standard) in two different concentrations; 1 mg/mL and 2 mg/mL. The test solutions were prepared by mixing the 1 mL solution of DPPH, 4 mL methanol and 100 µL sample solution in test tubes. After that, the test tubes were kept in dark for 30 minutes. Then, the absorption was measured at 517 nm for all the resulting solutions using UV-Vis spectrophotometer. The percentage of inhibition for DPPH was calculated by using the given formula;

Percentage (%) inhibition =  $\frac{Blank-Sample}{Blank}$  ×

# 100

### 4. Results and Discussion

The phenylenediamine based Schiff base ligand (L) was synthesized by the reaction of pphenylenediamine with 2-hydroxy-3methoxybenzaldehyde in 1:2 molar ratio using ethanol as solvent. The synthesized ligand was made to react with the salts of tetravalent, trivalent and divalent metals [VO(IV), Cr(III), Co(II), Ni(II), Cu(II) and Zn(II)] to derive their 3d-transition metal complexes using equimolar ratio of ligand and metal salt in ethanol. The change in color has shown the interaction of ligand with 3d-metal cations. The а phenylenediamine ligand and its metal complexes were obtained in solid form with good yield having specific color and definite melting/decomposition temperatures. The as-synthesized 3d-metal complexes had higher range of decomposition points in contrast to its uncompleted ligand, signifying stronger bonding between ligand and 3d-metal ions. All the synthesized compounds showed strong ability to maintain their stability in air as well as in moisture. The solubility of synthesized compounds was checked in a series of different solvents. They are soluble in dioxane, ethanol, methanol, and N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The synthesized compounds were characterized based on their micro-analytical, physical and spectral results. While the metal complexes were also analyzed for their conductivity nd magnetic moment measurements. The molecular formula of phenylenediamine Schiff base and its derived metal complexes were suggested based on results of elemental analysis together with spectral findings. Furthermore, the magnetic moments confirmed the suggested geometrical arrangement of phenylenediamine Schiff base around the 3d-metal ions. Physiochemical data of the metal complexes of phenylenediamine Schiff base (1)-(6) are depicted in Table 1.

Table 1. Physical and analytical measurements for all the synthesized compounds

	Yield (%)	<b>M.P (°C)</b>	MW (gmol <sup>-1</sup> )	С	Н	Ν	Μ
 (L)	Orange	230-232	$C_{22}H_{20}N_2O_4$	70.14	5.31	7.38	-
	78		376.40	(70.20)	(5.36)	(7.44)	
(1)	Black	[VO(L)] <sub>2</sub>	$C_{44}H_{36}N_4O_{10}V_2$	59.81	4.05	6.29	11.47
	80	205-210	882.59	(59.87)	(4.11)	(6.35)	(11.54)
(2)	Black	$[Cr(L)]_2(Ac)_2$	$C_{44}H_{36}N_4O_8Cr_2$	61.94	4.17	6.51	12.13
	79	210-217	852.77	(61.97)	(4.26)	(6.57)	(12.19)
(3)	Brown	[Co(L)] <sub>2</sub>	$C_{44}H_{36}N_4O_8Co_2$	60.92	4.16	6.38	13.54
	83	255-261	866.645	(60.98)	(4.19)	(6.46)	(13.60)
(4)	Brown	[Ni(L)] <sub>2</sub>	C44H36N4O8Ni2	60.95	4.11	6.43	13.47
	75	239-243	866.165	(61.01)	(4.19)	(6.47)	(13.55)
(5)	Black	[Cu(L)] <sub>2</sub>	$C_{44}H_{36}N_4O_8Cu_2$	60.26	4.08	6.37	14.49
	75	211-217	875.871	(60.34)	(4.14)	(6.40)	(14.51)
(6)	Orange	[Zn(L)] <sub>2</sub>	$C_{44}H_{36}N_4O_8Zn_2$	60.01	4.07	6.32	14.83
	86	200-210	879.59	(60.08)	(4.13)	(6.37)	(14.87)

 $Ac = CH_3COO^{-1}$ 

# 5. FT-IR Spectral Analysis

The promising FT-IR vibrational bands for the phenylenediamine Schiff base (L) have been summarized in the experimental section. The ligand formation was evidenced by the disappearance of bands at 3343 and 1713 cm<sup>-1</sup> indicating the absence of amine (NH<sub>2</sub>) group of phenylenediamine and carbonyl (C=O) group of aldehydes, respectively. Instead, a sharp band was observed at 1638 cm<sup>-1</sup>, signifying the presence of azomethine linkage (C=N)

together with a broad band at 3370 cm<sup>-1</sup> for hydroxyl group [25]. Furthermore, the appearance of two bands at 2963 and 1374 cm<sup>-1</sup> were attributable to the methoxy (O-CH<sub>3</sub>) group and (C-O) bond. The experimental FT-IR spectrum of ligand was compared with computed spectrum, indicating a close agreement between them. Figure S1 and S2 shows the experimental and computed IR spectra of ligand, respectively. The theoretical computed data was calculated at DFT/B3LYP/6-31+G (d.p) level.

The comparative analysis of the FT-IR vibrational assignments (Table 2) of the synthesized transition metal complexes with the free ligand was used for evidencing the involvement of coordinating sites of the ligand for complexation (Figure S3-S5). The downward shifting of azomethine nitrogen (C=N) from 1638 to 1627-1604 cm<sup>-1</sup> signified the synthesis of metal complexes by the coordination of azomethine-nitrogen to the metal ions [26]. In comparison to the free ligand, the vibrational broad band owing to hydroxyl group at 3370 cm-1 was not observed in the spectra of its resulting metal complexes evidencing the coordination of ligand with the transition metal ions by deprotonating the hydroxyl (OH) group. The absence of vibrational band of hydroxyl (OH) group accompanied by the downward shifting of (C-O) stretching vibrations from 1374 to 1363-1352  $cm^{-1}$  confirmed the coordinating action of ligand with metal ions through deprotonated hydroxyl (OH) group present in the ligand [27].

Furthermore, the vibrational band of methoxy (O-CH3) group also observed lowering in its frequency from 2963 to 2954-2937 cm<sup>-1</sup> signifying the involvement of methoxy group in the complexation for all the metal complexes except vanadium complex (1) [28]. The appearance of new bands at the comparatively lower frequencies indicated the bonding of metal ions with nitrogen and oxygen atoms. The bands observed in the range of 542-470 cm<sup>-1</sup> were attributed to (M–O-Ph) stretching vibrations signifying the coordination and bonding of ligands with the metal ions by oxygen atoms after deprotonation of hydroxyl (OH) group. Similarly, the bonding of ligand with metal ions through nitrogen of azomethine was confirmed by the presence of bands at 521-545 cm<sup>-1</sup> due to (M-N) vibrations [29]. In addition to other vibrational bands, the vanadium complex (1) has also exhibited the typical band for (V=O) asymmetric stretching vibration at 972 cm<sup>-1</sup> [30].

Compounds	$\Omega_{\mathrm{M}}$ $(\Omega^{-1}~\mathrm{cm}^2~\mathrm{mol}^{-1})$	µeff (B.M)	v (cm <sup>-1</sup> )
(1)	21.3	1.69	2961 (-OCH <sub>3</sub> ), 1607 (C=N), 1352 (C-O), 972 (V=O), 546 (V-N), 525 (V-O).
(2)	81.7	3.73	2948 (-OCH <sub>3</sub> ), 1618 (C=N), 1357 (C-O), 552 (Cr-N), 531 (Cr-O).
(3)	15.1	3.81	2944 (-OCH <sub>3</sub> ), 1623 (C=N), 1363 (C-O), 570 (Co-N), 545 (Co-O).

 

 Table 2. Molar conductivity values, magnetic moments and FT-IR spectral data for metal complexes (1)-(6)

(4)	23.5	2.79	2937 (-OCH <sub>3</sub> ), 1619 (C=N), 1362 (C-O),
			559 (Ni-N), 527 (Ni-O).
(5)	12.7	1.71	2954 (-OCH <sub>3</sub> ), 1627 (C=N), 1358 (C-O),
			542 (Cu-N), 521 (Cu-O).
(6)	14.6	-	2939 (-OCH <sub>3</sub> ), 1604 (C=N), 1360 (C-O),
. ,			549 (Zn-N), 528 (Zn-O).

#### 6. UV-Vis Spectral Analysis

The electronic spectra of all the compounds including ligand and its metal complexes were recorded in DMF (0.001 M). In the electronic spectrum of the ligand (L), the peak observed at 368 nm was attributed to the  $n \rightarrow \pi^*$  electronic transitions of the azomethine (C=N) linkage. While the peak observed at 337 nm was assigned to  $\pi \rightarrow \pi^*$  electronic transitions of the aromatic ring system. In the spectra of metal complexes, these peaks are shifted to lower wavelength, signifying coordination of ligand with metal ions. In addition to these peaks, emergence of new peaks owing to d-d electronic transitions were also observed in their electronic spectra. In the electronic spectra of vanadium complex (1), the peaks were obtained due to B2 $\rightarrow$ E $\pi$ , B2 $\rightarrow$ B1 and B2 $\rightarrow$ A1 excitations at 381, 549 and 742 nm, respectively. While the peak emerging at 354 nm was because of the charge transfer process from metal to ligand (MLCT). These absorption bands are accredited to the electronic transition inside the square pyramidal arrangement [31].

Chromium complex (2) displayed absorption bands at 427 and 581 nm because of  $4A2g(F) \rightarrow 4T1g(F)$  and  $4A2g(F) \rightarrow 4T2g(F)$  electronic excitations, correspondingly specifying their octahedral geometry

[32]. Cobalt complex (3) has displayed the low energy absorption bands at 531 and 749 nm for  $4T1g \rightarrow 4T1g(P)$  and  $4T1g \rightarrow 4T2g(F)$  electronic excitations, respectively together with a high energy band at 342 nm, validating their high spin octahedral geometrical structure. The electronic spectrum of nickel complex (4) was appeared with three absorption bands at 384, 557, 789 nm for  $3T1g(F) \rightarrow 3A2g(F),$  $3T1g(F) \rightarrow 3T2g(P)$ and  $3T1g(F) \rightarrow 3T2g(F)$ electronic excitations, correspondingly. In addition to these, the emergence of a new peak was also obtained at 337 nm because of transfer of charge from metal to ligand. The position of these electronic bands confirmed its octahedral geometry [33]. Copper complex (5) demonstrated two transitions due to  $2B1g \rightarrow 2Eg$  and  $2B1g \rightarrow 2A1g$ electronic excitations at 507 and 678 nm along with a high energy band at 346 owing to charge transfer from  $M \rightarrow L$ , approving its octahedral geometry. Zinc complex (6) has shown strong absorption at 334 nm for transfer of charge from metal to ligand. No other band was observed for zinc complex validating its diamagnetic character [34].

### 7. Magnetic Moments

Magnetic moments provide valuable information that can be significantly used to determine the number of unpaired electrons and stereochemistry of metal cations, validating the proposed geometrical arrangement of metal complexes. Table 2 shows the magnetic moments for all the metal complexes. All the metal complexes have exhibited different magnetic moments based on their number of unpaired electrons. The obtained magnetic moments (for per metal ion) were found to be consistent with their dimeric structure and agreed well with the fact that the magnetic moments for binuclear metal complexes are slightly less than that of mononuclear metal complexes due to spin coupling [35].

For vanadium complex (1), magnetic moment of 1.69 BM was obtained suggesting the presence of only one unpaired electron and validating its square pyramidal configuration [36]. Chromium and cobalt complexes (2) and (3) have exhibited magnetic moment of 3.73 and 3.81 BM, respectively designating them as paramagnetic complex owing to the presence of three unpaired electrons having octahedral geometry [37]. The obtained magnetic moment for nickel complex (4) as 2.79 BM was assigned owing to the existing two unpaired electrons and octahedral arrangement of ligands around nickel ions [38]. Likewise, paramagnetic copper complex (5) also exhibited 1.71 BM attributing to one unpaired electron and certifying

its octahedral configuration [39]. Whereas, the diamagnetic nature of zinc complex (6) was confirmed by its zero magnetic moment value.

### 8. Molar Conductance

Molar conductivity measurements were performed using 10–3 M solutions of all the complexes in DMF solvent at room temperature and the conductance values are listed in Table 2. All the divalent and tetravalent metal complexes have shown low conductance values in the range of 12.7-23.5  $\Omega$ –1cm2mol–1, confirming these metal complexes as non-electrolytes and ruling out the existence of any counter ion in the outer sphere, whereas the trivalent chromium complex (2) has exhibited conductance value of 81.7  $\Omega$ –1cm2mol–1, evidencing its electrolytic nature and presence of acetate ion in the outer sphere.

# 9. Computational Investigation

DFT based computational calculations were executed to optimize the structure of synthesized ligand (L) and to determine its atomic arrangement using B3LYP/6– 31 G (d, p) basis set. The DFT-optimized structure of ligand (L) with atomic numbering is shown in Fig. 1, whereas Figure S6 illustrates the DFT-optimized structure of ligand along with optimized bond lengths.



Fig. 1. DFT-optimized structure of ligand (L)

The structure optimization, HOMO and LUMO distributions, energy and frequency calculation for synthesized ligand (L) were executed from the absolute minimal level of neutral molecular system employing the same level of theory. The optimized molecular structure of the ligand was used to perform NBO, MEP and MAC analysis.

# 10. Frontier Molecular Orbitals (FMOs) of Ligand (L)

As an electron acceptor, the LUMO denotes its competency to accept electrons, whereas the HOMO denotes the ability to donate the electrons. Smaller HOMO-LUMO gap facilitates the electrons to readily excite from the HOMO and makes it uncomplicated for LUMO in accepting the upcoming electrons [40]. These two orbitals provide the information about the interaction of studied molecular system with different types of species. The negative values of  $E_{LUMO}$  and  $E_{HOMO}$  signified that the studied molecular systems have greater stability. And the difference in their bond energy specifically describes the chemical stability as well as chemical reactivity of the active molecular systems. The smaller value of EHOMO-LUMO indicates that the studied molecular system has high chemical reactivity and less chemical stability. On the other hand, molecular system having greater value of EHOMO-LUMO will have more chemical stability and less chemical reactivity. The FMO study effectively enlightens the chemical stability and chemical reactivity together with the identification of the active sites in the investigated molecular system. The energy values for the HOMO and LUMO orbitals and their energy difference also elucidates the charge transfer (CT) interaction [41]. The energies of the FMOs, HOMO-LUMO band gap and global reactivity descriptors were calculated using the B3LYP/6-31+G (d,p) level of theory and the results are depicted in Table 3.

Table 3. Energies of frontier molecular orbitals (FMOs) and global reactivity

descriptors	(GRD) for	ligand (L)
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Descriptors (eV)	Ligand (L)	<b>Descriptors (eV)</b>	Ligand (L)
E <sub>LUMO+2</sub>	0.359	Ionization Potential (IP)	5.244
E <sub>LUMO+1</sub>	-0.779	Electron Affinity (EA)	4.324
ELUMO	-1.674	Global Hardness $(\eta)$	0.460
E <sub>HOMO</sub>	-5.244	Chemical Potential (µ)	-4.784
E <sub>HOMO-1</sub>	-5.681	Global Softness ( $\sigma$ )	1.087

Еномо-2	-5.777	Electronegativity $(\chi)$	4.784
$\Delta E_{HOMO \rightarrow LUMO}$	-0.920	Electrophilicity index $(\omega)$	24.877

From the FMO analysis of synthesized ligand (L), the negative values of  $E_{LUMO}$  and  $E_{HOMO}$  were obtained as -1.674 and -5.244 eV, respectively, which showed the greater stability of synthesized ligand (L). The energies of other orbitals LUMO<sup>+1</sup>, LUMO<sup>+2</sup>, HOMO<sup>-1</sup> and HOMO<sup>-2</sup> were obtained as - 0.779, 0.359, -5.681 and -5.777 eV, respectively.

FMOs including LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, and HOMO-2 for studied ligand (L) are shown in Figure 2. In the LUMO+1, LUMO, HOMO and HOMO-2 of ligand (L), the electronic charge density is spread over the whole structure of ligand, [2,2'-{benzene-1,4diylbis[nitrilomethylylidene]}bis(6-

methoxyphenol)], with the exclusion of methoxy groups. And in In LUMO+2 of the ligand (L), the charge density in is just accumulated on the aromatic ring of the *p*phenylenediamine part of the ligand. Whereas in HOMO-1 of ligand (L), the charge density is mainly populated on the 2hydroxy-3-methoxybenzaldehyde.

# 11. Molecular Properties of Ligand (L)

The DFT calculated chemical reactivity

descriptors including global softness ( $\sigma$ ), global hardness ( $\eta$ ), ionization potential (IP), electron affinity (EA), global electrophilicity index ( $\omega$ ), chemical potential ( $\mu$ ) and electronegativity ( $\chi$ ) have been calculated from the HOMO-LUMO energy values as depicted in Table 3 by using the equations S1-S6.

In the FMO studies, the E<sub>HOMO</sub> and E<sub>LUMO</sub> of the studied molecular systems explained the reactivity parameters. EHOMO is global associated with the ionization potential, whereas E<sub>LUMO</sub> is related to electron affinity. The lower value of electron affinity (4.324 eV) in comparison to ionization potential (5.244 eV) showed that the ligand readily forms bonds by accepting the electrons. The electronegativity ( $\chi$ ) defines the capability of an atom for attracting the electrons in a chemical bond which is also described as the negative values of chemical potential  $(\mu)$  in DFT. Likewise, the chemical hardness determines the resistance confronted during the process of charge transfer [42]. The ligand has negative chemical potential (-4.784  $e^{V}$ ), suggesting that its weaker tendency to decompose and convert into its

components. The value of global hardness is  $[(\eta) 0.460]$  found to be less than that of global softness;

$$[(\eta) 0.460 e^{V} < (\sigma) 1.087 e^{V}].$$



Fig. 2. Frontier molecular orbitals (FMOs) and their energies for ligand (L)

The greater chemical softness ( $\sigma$ ) for the studied ligand (L) specifies its greater reactivity and less stability. Figure 3 shows the graphical comparison of DFT calculated chemical reactivity descriptors. The electrophilicity index ( $\omega$ ) signifies the energy of stabilization for any investigated chemical system and defines its tendency for accepting the electrons. It also measures the decay of binding energy caused by maximum flow of electrons between donating and accepting groups [43]. The electrophilicity was obtained as a positive quantity with a value of 24.877 eV, indicating its ability for accepting the electron from the surrounding.



Fig. 3. DFT calculated chemical reactivity descriptors for investigated ligand (L)

# 12. Molecular Electrostatic Potential (MEP) of Ligand (L)

Molecular electrostatic potential (MEP) is considered as an important property to characterize intra as well as inter molecular electrostatic interactions owing to the reason that it offers significant information regarding the chemical reactivity of the investigated molecular systems with reference to their interactions occurring between different molecules. The dispersed charge over the surface of the studied molecular systems can be utilized to determine the type of chemical bond. MEP play significant role in structural biology for determining the enzyme-substrate, ligandsubstrate and drug-receptor interactions [44].

The 3D MEP plot can also be used for predicting the reactive molecular sites in studied molecular systems. The regions of positive and negative electrostatic potentials along with the molecular properties associated with these potentials are detected and explored by their specific color codes. The green color indicates the neutral zone, red color shows the area having negative values of electrostatic potential whereas the blue color displays the region having positive values of electrostatic potential. Furthermore, the red region specifies the strongest repulsion while on the other hand, the blue color directs the strongest attraction. MEP surfaces are very advantageous for the qualitative interpretation of hydrogen bond interactions together with chemical reactions by nucleophilic and electrophilic species [45].

The total electron density plot mapped with electrostatic potential has been constructed on the

surface of synthesized ligand (L) employing B3LYP/6-31+G (d,p) level is displayed in Figure 4. The blue colored area of positive potential (electron deficient zone) is spread over the hydrogen and some carbon atoms, suggesting this zone as more favorable site for nucleophilic attack. Whereas, the red colored area of negative potential (electron rich zone) is positioned over the oxygen atoms of methoxy and hydroxyl groups in addition to the nitrogen atoms of azomethine linkage, specifying this zone as leading site for the electrophilic attack on the ligand.





# 13. Mulliken Atomic Charges (MAC) of Ligand (L)

The Mulliken atomic charges are directly associated with the chemical bonds together with vibrational properties of studied chemical systems. Mulliken atomic charges are capable of affecting the characteristic properties, electronic structure, polarizability and dipole moment of molecular system [46]. Table S1 and Figure S7 shows the atomic charge distribution of the studied ligand while the histogram is given in Figure 5. All carbon atoms have negative atomic charges with the exception of C1, C2, C19 and C19 that were directly bonded with oxygen atoms (O7, O9, O26 and O27) and C10, C13, C14 and C25, which were directly attached with nitrogen atoms (N17 and N18). The reason behind their atomic charges is that more electronegative atoms such as nitrogen and oxygen bonded with these carbon atoms, which have withdrawn the partial charges from these carbon atoms. Consequently, these carbon atoms are positively charges. Whereas, all the hydrogen atoms have positive atomic charges.



Fig. 5. Histogram for the atomic charge distribution of the investigated ligand (L)

# 14. Natural Bond Orbital (NBO) Analysis of Ligand (L)

The NBO analysis is a useful approach to explore the interactions taking place among different bonds as well as for examining the transfer of charge owing to the conjugative interactions in bio-molecular compounds. The NBO analysis was performed to obtain information regarding the delocalization of electronic charge and energy density of atoms.

The energy values for these hyper-conjugative interactions are calculated using the second-order perturbation approach. The stabilization energy E(2) accompanying the delocalization can be estimated considering the acceptor (j) and a donor (i) by using following formula;

$$E^{(2)} = qi \frac{\left(F_{i,j}\right)^2}{\varepsilon_j - \varepsilon_i}$$

Here  $q_i$  denotes the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_j$  are orbital energies (diagonal elements) and F(i, j) shows the offdiagonal NBO Fock matrix element.

The strength of donor to acceptor interaction depends on the value of stabilization energy. Stronger interaction will be due to greater value of stabilization energy [47]. Table  $\underline{S2}$  summarizes the leading orbital interactions having highest values or energy stabilization between of bonding and antibonding orbitals. In general, any

chemical compound exhibit four most important transitions including LP $\rightarrow \sigma^*$ , LP $\rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$ . The  $\sigma \rightarrow \sigma^*$ transitions are exhibit least values of stabilization energy,  $LP \rightarrow \sigma^*$  and  $LP \rightarrow \pi^*$ transitions have moderate values for stabilization whereas  $\pi \rightarrow \pi^*$ energy, transitions are having highest stabilization energy. The  $\pi \rightarrow \pi^*$ transitions;  $\pi(C_{5} C_6$ ) $\rightarrow \pi^*(C_1-C_3)$ ,  $\pi(C_{14}-C_{16}) \rightarrow \pi^*(C_{11}-C_{12})$ ,  $\pi(C_2-C_4) \rightarrow \pi(C_1-C_3),$  $\pi(C_{11}-C_{12}) \rightarrow \pi^*(C_{13}-$ C<sub>15</sub>),  $\pi(C_{19}-C_{21}) \rightarrow \pi^*(N_{18}-C_{25}),$  $\pi(C_1 C_3) \rightarrow \pi^*(C_2 - C_4)$ π(C20and C22) $\rightarrow \pi^*$ (C19-C21) orbitals result in the stabilization energies of 20.38, 19.62, 19.28, 17.90, 17.84, 17.82 and 17.82 kcal/mol correspondingly. In resonance, the LP $\rightarrow \pi^*$ transition were found as LP(O<sub>9</sub>) $\rightarrow \pi^*(C_2-C_4)$ ,  $LP(O_{26}) \rightarrow \pi^*(C_{19}-C_{21}), LP(O_7) \rightarrow \pi^*(C_1-C_3)$ 

and LP(O<sub>27</sub>) $\rightarrow \pi^*(O_{20}-O_{22})$  with stabilization energies 32.89, 32.89, 28.51 and 28.51 kcal/mol respectively.

# 15. Computed UV–Vis Analysis of Ligand (L)

The UV-Visible spectral study of ligand was done by TD-DFT/B3LYP/6-31+G (d,p). The computed excitation energies, absorption maxima, oscillator strengths together with major and minor contributions of studied ligand are depicted in Table 4. The computed maximum absorption wavelength was obtained at 375.47 nm having an oscillator strength of 1.5324 (Figure S8). This transition was accompanied by major contribution of 97% by HOMO $\rightarrow$ LUMO excitation together with minor contribution of 2% by HOMO-2 $\rightarrow$ LUMO excitation.

Table 4. Excitation energies, wavelengths, oscillator strengths, major and minorcontributions of ligand (L)

Na	Energy	Wavelength	Oscillator	Major	Minor
INO.	(cm <sup>-1</sup> )	(nm)	Strength	contributions (%)	contributions (%)
1	26633.42	375.47	1.5324	H→L (97)	H-2→L (2)
2	28765.96	347.63	0.0	H-3→L (92)	H-4→L+1 (7)
3	29348.30	340.74	0.0011	H-4→L (89),	
				H-3→L+1 (10)	

H = HOMO, H-2 = HOMO-2, H-3 = HOMO-3, H-4 = HOMO-4, L = LUMO, L+1 = LUMO+1

# 16. Antibacterial Study

The antibacterial action of the phenylenediamine Schiff base together with its corresponding metal complexes was determined against four bacterial species; three Gram negative (N. gonorrhoeae, H. halophila and S. typhimurium) in addition to one Gram positive (B. subtilis) by disc diffusion method as mention in the experimental section. The results of antibacterial activity revealed that all the compounds exhibited moderate to significant contribution regarding their bacteriostatic activity (Table 5). The antibacterial results of all the synthesized compounds were compared with augmentin as shown in Figure 6. The recorded inhibition zones for all the synthesized compounds were obtained less than those of the augmentin (26-32 mm). Overall, all the synthesized compounds have shown antibacterial activity for all bacteria in the following decreasing order; Ν. gonorrhoeae (16.28 mm) > B. subtilis (13.43)mm) > S. typhimurium (12.57 mm) > H. halophila (11.86 mm). The ligand (L) has shown significant antibacterial activity with inhibition zone range of 12-20 mm against all

the four bacteria.

For all the synthesized compounds, the overall descending order of inhibition activity against B. subtilis was obtained as; (6) > (L) > (2) > (5) > (3) > (4) > (1). The compounds have exhibited antibacterial activity against N. gonorrhoeae in the following descending order; (3) > (L) = (6) >(1) > (2) > (5) > (4). While the overall descending order of inhibition zone against H. *halophila* was found as; (2) > (1) > (6) = (L)> (5) > (4) > (3). The overall order of antibacterial activity for the synthesized compounds measured for S. typhimurium was in the following decreasing order as; (1) > (L) = (2) > (6) > (5) > (4) > (3). The increased antibacterial activity of metal complexes than that of free ligand could be as a result of chelation. Among all the synthesized compounds, zinc complex (6) was concluded as most active with highest inhibition zone of 23 mm against B. subtilis. Whereas, complex cobalt complex (3) exhibited least activity with inhibition zone of 06 mm against S. typhimurium.

Table 5. Antibacterial activity of ligand (L) and its derived metal complexes (1)-(6)

Compounds		Zone of Inhibition (mm)			
	B. subtilis	N. gonorrhoeae	H. halophila	S. typhimurium	

(L)	18	20	12	14
(1)	07	19	13	20
(2)	15	17	20	14
(3)	10	21	07	06
(4)	09	08	09	10
(5)	12	09	10	11
(6)	23	20	12	13
Augmentin	27	32	30	26



Fig. 6. Antibacterial activity of ligand (L) vs its derived metal complexes (1)-(6)

# 17. Antioxidant Study

The antioxidant activity was estimated as the DPPH antiradical (%) activity. Table 6 display the antioxidant profile of all the synthesized compounds and butylated hydroxytoluene (BHT) with reference to their scavenging ability (Figure 7). Maximum activity was shown by reference drug (BHT). Using 1 mg/mL concentration, the synthesized compounds exhibited antioxidant action in the following decreasing order; (5) > (6) > (2) > (1) > (L)

> (4). While in 2 mg/mL concentration, the descending order of antioxidant activity for all the compounds was obtained as; (2) > (6)
> (1) > (3) > (4) > (5) > (L). All the compounds have shown greater antioxidant

activity when used in high concentration (2 mg/mL). Overall, zinc complex (6) was found to be most active as it has shown significant activity in both concentrations.

Compounds	Inhibition (%)		
—	1 mg/mL	2 mg/mL	
(L)	24	51	
(1)	36	77	
(2)	37	86	
(3)	29	69	
(4)	12	59	
(5)	46	55	
(6)	38	84	
Butylated hydroxytoluene (BHT)	58	94	

Table 6. Antioxidant activity of ligand (L) and its derived metal complexes (1)-(6)



Fig. 7. Antioxidant activity of ligand (L) vs its derived metal complexes (1)-(6)

# 18. Conclusion

In this study, a new series of binuclear metal complexes of symmetrical phenylenediamine Schiff base ligand was synthesized. The synthesized phenylenediamine derived ligand act as tridentate ligand for coordination with tetravalent, trivalent and divalent transition metals ions (VO, Cr, Co, Ni, Cu, and Zn) via oxygen of the deprotonated hydroxyl group from the phenyl group and nitrogen of azomethine linkage. The magnetic moment measurements of all the complexes recommended their octahedral geometry with the exception of the vanadium complex (1) that was characterized having the square pyramidal geometry. The conductance values also confirmed all the metal complexes as non-electrolytes excluding chromium complex (2) that was validated as an electrolyte having acetate ions in the outer sphere. The structural properties, vibrational and electronic spectra, frontier molecular orbitals and noncovalent interactions were also studied for ligand using DFT/B3LYP/6-31+G (d,p) level. From the FMO analysis of synthesized ligand (L), the negative values of ELUMO and EHOMO were obtained as -1.674 and -5.244 eV, respectively, which showed the greater stability of synthesized ligand (L). The electrophilicity was obtained as a

positive quantity with a value of 24.877 eV, indicating its ability for accepting the electron from the surrounding. The ligand has negative chemical potential (-4.784eV), suggesting that its weaker tendency to decompose and convert into its components. reactivity predictions, the Under 3D molecular electrostatic potential plot showed that the oxygen atoms of hydroxyl and methoxy group and nitrogen of azomethine linkage are the possible sites for electrophilic The results of antibacterial and attack. antioxidant have evidently displayed that the ligand was significantly active but its activity was further improved upon chelation with 3*d*-metal ions.

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