Dynamics of Gandhi Model of Development in the Era of Liberalization, Privatization and Globalization

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Abstract: The study examines relevance of Gandhian principle of economic restructure in context of post LPG (Liberalization, Privatization and Globalization) reform in India. Study has also look into issue of use of heavy industrialization in which Gandhi was very much against. Data were analyzed using qualitative, analytical analysis i.e. various government report and documents. Study concluded that the LPG reform in India led to one directional concentration of wealth in hand of few big business houses.

Keywords: Integer programming, assignment, Lingo program

1. INTRODUCTION

The issue of Liberalization, Privatisation and Globalization impacted world both way positively as well as negatively. Maximum negative impact remained on poor population and indigenous community. The growth and development in Modern World is just in cost of human life which have been affected by Globalization reform across world. Most government across world are simply favouring capitalist growth in name of liberalization. Globalization is defined by intellectual and scholar as progression of assimilating and opening market across national borders. This process led to development of new economic zone and economic activity is highly liberalized. It is progression of cumulative interdependence in World. This free flow is related to ideas; good, service, money, value and culture across national frontier.It is shaping new era of interaction among nation, economies and people. While Globalization have positive innovative aspect it also has negatives and marginalised aspect. The whole development of globalization is highly contentious raising great concern about national sovereignty equity for world underprivileged people. It is multifaceted occurrences and its complexity is likely to increase with unfolding of process.(Pandey, 1996)

2. ALGORITHM

The Globalized world is seeking efficient institutions and respect for individuals peace through greater social justice. But humanity is going through difficulty period. Violence and terrorism have become catch word of international politics. K Joseph in 2010 argued that existing military solution were inadequate to provide security to people concerned. What happened to war in Iraq and Afghanistan led by USA military troop. A million of civilians have lost their lives and it is still going on. While Globalization have increased contact between people across national boundaries in economy and technology. It is also fragmenting productions process labour market. Now time have come to rethink about non military solution for conflict resolution and peace building in this unstable world. Once Gandhi himself said that "we do not know how to handle arm. It is our perhaps misfortune that we cannot . Richard Diet activists of non violence support argument by saying that while "non violence is as old as hill "as Gandhi said it is only in recent decades that philosophy of non violence have grasped human imagination.(Kumrappa,2008).

Satyagraha and Self rule are two core concept in Gandhi political thought. These are core value of his theory of freedom and power. Non violence developed by Gandhi is not only political development but moralistic philosophy also. Gandhi defines Satyagraha as force of truth and non violence. In Gandhi word Non violence is law of human race.

According to Gandhi, Self rule is political power to invest in control of violence and human aggression towards nature as well as their fellow individuals. It means that sovereign kingdom freedom from external control. State should not impose any coercive powers to destroy autonomy of self rule. They must be having all kinds of freedom and liberty to decide their fate of Social, Economic, Cultural and Political development. Psychologically sense change its meaning that being liberated inner and divine being free from ignorance and illusion and free to gain greater knowledge to control all kind of greed in life. If nation would follow these principles of Gandhi then there is possibility to avoid global warming as well as no one will sleep hungry? Or one will be without shelter and issue of uneven economic growth will also settle down in world(Pandey,1996) Mahatma Gandhi considered Non violence, total abstention of physical or mental torture of any living as supreme truth of God. Mahatma Gandhi suggested Non violence as mean to achieve truth. For success of any revolution, Gandhi emphasised over non violence means only. Gandhi adopted and suggested various method to apply non violence according to circumstances and

conditions in which there is a need to apply these. Truth is very important to sustain human civilisation. If all people will be selfish and organisations will hide truth then process of contemporary modernization will collapse. So even to sustain modern day development in society, it is needed to have more number of people seeking truth through different means. Mahatma Gandhi also suggested certain characteristics for practitioner of non violence such as fearless ,self suffering,truthfulness and self control etc.

Through his model of development Gandhi want to change pathetic human condition in globalized world which was full of exploitation. Even more Gandhi was not in favour of strong state who will be having brute force in form of police and army to maintain order in state. Gandhi advised path of non violence not only for individuals but also nation in general. Satyagraha not only liberate country from foreign dominance politically but also led to establishment of ideal state based on every kind of freedom like Economic Religion and Political which include Right to self rule, Freedom of Press and equal right for all. Satyagraha as techniques of political injustice was first experimented by Gandhi in South Africa and later in freedom struggle in India which was quite unique in human history. The other example of revolution inspired by Gandhian philosophy in West is American civil rights movement led by Martin Luther king and Hungarian revolution 1956. Global leader get inspired from Gandhi to liberate their country from repressive rule. Exploitive nature of state can be control by method of Non violence. (Kumar,2000) Mahatma Gandhi was against this idea of this modern development in which heavy machineries have taken place of human labour. Privatisation is eating up all national resources thus causing lot of environmental problems in world. Poor people are victim of this uneven development model in which people like farmer are forced to die from environment burden. With this structural setting in third World Country, globalization has further worsened situations of vulnerable section of society. Especially poor people are more dependent on natural resources for their survival and becoming victim of economic loot across globe. As decision are made by narrow state, poor people are marginalised, State are running big project on cost of native habitat. Large project which are taken by Government in name of development have displaced large number of people leading to unemployment depriving their source of livelihoods. Force of globalization have ravaged agricultural community leading to poverty, deprivation and lost of livelihoods. Such destitution have resulted in suicide by farmer in many parts of India.

India is a country of poor village with still 70 percent of people living in the remote village with primary source being farming. Gandhi was very much worried with degradation of village economy that Gandhi himself focused to organise village through village self development. Gandhi himself said that if village perish, India will perish too. Revival of village will be possible only when it is no longer exploited by people. Soul of people reside in village which is highly depends on natural production. Industrialisation on mass scale will led to excessive exploitation of village as problem of competing and marketing will come in. Present open market model of Development are so ruthless that in normal condition it can kill farmer and small trader. That is why after independence most of village cottages industry have died due to lack of support. If however in spite uneven support, rich do not become guardians of poor, and poor people keep on die of hunger Gandhi have suggested non violence and non cooperation as right mean. Rich cannot accumulate wealth without cooperation of poor. Poor will become stronger and learn how to free themselves by means of non violence from crushing inequality which have brought them to verge of starvation.

Since begging of of freedom strugglewhen get entered into every time advocated to save village economy to bring more development in village. Soon ideal of self sufficiency were accepted throughout India. Death kneel of British economy in India was sounded and British authorities soon realised that by attacking their self interest, Gandhi have successfully isolated their rationale behind their rule of India. Economic exploitation of the poor people is brutal repression in context of modern development. We have to concentrate on village self contain mainly for use. Provided this character of village is maintained there will be no objection to villager using modern machine tool they can make and afford to use. In this way they can improve their economic conditions in liberalized world but most of competition is coming from market .Naturally development of country depends on development of village. All good and services necessary for village member should be gone within village.

If every village allocate its surplus product then problem of poverty and starvation will be solved. Agricultural sector alone cannot solve problems of rural poverty. But agricultural sector in India is having heavy wait for providing job to rural poor.(Srivastava ,1991) Village development ÷Big market economy should be stopped to impose only they should not used as mean of exploitation in name of explosives development. India does not need industrialisation in modern sense of term. India has more than 7 lakh 5 thousand village. Vast majority are looted to soil and vast majority are dependent on the agricultural products for their survival. Agriculture does not need revolutionary change .Whatever may be said on contrary having travelled through whole length of land with eyes open and millions are living in idleness for 4 months in a year. India pleasant required supplementary industry. Most natural is introduction of spinning wheel not handloom. Later cannot be introduced in every home whereas farmer can and used it. It was driven out not by economic pressure but by force deliberately.

3. GANDHI AT ASHRAM

Gandhi resigned from Indian National Congress over difference with other leader. Gandhi established All India village industry association at wardha and devoted most of his time toward reorganisation of Indian village. Gandhi started experiment in rural lifestyle such as revival of village craft, agro based industry so that villagers could be able to live in ideal surroundings. Gandhi observes u cannot build non violence on factory civilisation but it can be built on self contained village. We need to have faith in spinning wheel. Gandhi focus on removal of untouchable also. Before moving to ashram in 1936. Gandhi have started experiment in wardha. Gandhi efforts were to train people in local workfare to fulfilled their need from national resources. Gandhi train many worker in rural construction work such as making Neera from palm tree jaggerry etc. He shifted headquarters of All India spinning associations to Wardha This development have inspired more people to go for village development projects. In ashram neera was served every morning .Gandhi believes that hand spinning hand weaving and khadi will preserve India culture. Gandhi anticipates that when nation will become free with its own efforts various experiments would be needed to prepare for economic conditions of masses Wardha remain Gandhi headquarters till his death. Gandhi who fought mightiest empire in world had also simultaneously developed and demonstrate new way of life for village mass Gandhi had organised three non cooperation movement in his whole life. First was civil disobedience movement in 1921, second was salt march in 1930 and quit India movement in 1942 India attain independence in 1947 and Gandhi ideas of economic development were given proper importance to complete other global economy. It was very much difficult to survive economy based on village economy and more modernization was needed to deal with issues of global development.(Sinha,1990).

Privatisation involved selling state owned asset to private sector. It is argued that private sector tend to rural businesses more effeciently because of profit motive. However critic argue private firms can exploit their monopoly and ignore social cost. Privatisation is often achieved through listing new private company. This article will discuss advantage and disadvantages of privatization arguments for and against privatization. Privatisation is owned by private sector whereas nationalisation is owned by governments. In privatization profit motive act as incentives for owners and managers whereas in nationalisation worker may felt motivated if they felt company belong to them. Benefit of privatization: 1. There is a lack of political interference in privatization. 2. Improved efficiency-Since privatization companies such as British airways has shown degree of improved efficiency 3. Shareholders: It is argued that private firms have pressure from shareholders to perform efficiently .If firm is insufficient then firm could be subject to take over. There is no pressure in state owned one.

Disadvantages of privatization

- Natural monopolies It occurred when most effecient of form in industry is one. For example top water have significant fixed cost. Therefore there is no scope for having competition among several forms. In this way privatization can create monopolies.
- Government lose out on potential dividend.
- Problem of regulating private monopoly.

4. GLOBALIZATION

Effect of globalization in world and how to address problem of globalization in world and how to overcome challenge of globalization by India. Globalization is process of integrating various economy of world to allow free flow of good, service and technology. India has adopted policy of globalization since 1991.Importance of liberalization and privatization and globalization have resulted in gradual withdrawal of unnecessary trade and integration of India economy. Adoption of the economic reform has resulted in the increase of economic development in country. In this report states that there have been winner and loser in India as result of globalization. Lives of rich have been enriched by globalization. Yet benefit are yet to reach majority and risk are being cropped up for loser. India war ranked 134 according to human development index. We observed that globalization bring polarisation in Indian society and fail to eliminate problem of Socio-economic sector. But India is already hooked on globalization. Globalization have other possible negative effect like destruction of domestic industry etc.(Sahey,1998)

5. PROBLEM OF GLOBALIZATION IN WORLD

Some principle of Mahatma Gandhi are

- Sustainable economic development. Gandhi economic start from fundamental composition that economic policies of colonial religion must be eliminated and new economic policies must be developed which will abolish effects of factory. Gandhi is well aware that since most of people live in villages in India if Villages economy is improved then Economy of India will improve.(Srivastava,1991).
- Eradication of poverty in India Gandhi believe that poverty can be eradicated if proper opportunity is given to all people.
- Basic education Gandhi was believer of basic education Gandhi believes that process of education is continuous throughout human life.
- Economic efficiency It refer to revival of village industry. Gandhi was very much firm believer on encouraging village firm industry cottage industry. Gandhi considers non violence and total abstention of physical or mental torture of any living as supreme truth of God.

He suggested non violence as mean toachieved truth. For success of any revolution he emphasised over method of Non violence only Gandhi suggested various method to apply nonviolence according to circumstances and conditions" in which there is a need to apply these. Truth is very important to sustain human civilisation. If all people will be selfish and organisations will hide truth then process of contemporary modernization will collapse. Gandhi also suggested certain characteristics for practitioner of non violence such as fearless, self sufficient, truth, love etc.(Singh,1995).

6. RESEARCH METHODS

The study will be qualitative and analytical in nature. Study will explore and analysed various principle of Gandhi of economic organisations of society. Shift of market economy to market economy of India has created problem and destruction to small cottage industry and farmers. Therefore study will use theoretical perspective of socio economic restructure of society in context of India to understand various tenet of social development. It will also use theoretical perspective of socio economic development of Gandhi and view to protect right of farmers and poor people in age of capitalism. Data will be collected from Primary and Secondary source. Primary source include various government report and documents, interview and press statement. Data receive from statistical bureau of government and national census will be analysed to understand quantitative change in economy in India. Data will be collected from Prominent Scholars, government programme, Research article and newspapers report based on economic development in India. Interview with the leader of leading activism and Political leaders could form source of data. Interaction with Scholars and Residents will also be part of Sources of information for this method. Studies will also secondary resources including Book, Journalists and Newspapers. Study will most use data resources available in English. It will also use other data sources and their translation in English. Field visit to search various government report and documents is essential to this study.

6. CONCLUSION

Global unequality reports 2018 show that impact of globalization and privatization is very much unequal in last 40 years. This report states that 1 percent of people in country holding more than 22 percent wealth of nation. On other hand Indian GDP is growing and showing indications of growth but on other hand inequality is increasing rapidly. On other reports by Oxfam also paint real picture of economic development in India. India was ranked 147 out of 157 countries. This report exposed development nature of India which is unequal in Nature and causing more patterns of inequality in India. Gandhi principles of development have been neglected in socio, development in India mostly after LPG reform in India. Gandhi model of development which emphasised more on cottage industry and village industry is left behind and much focus is given on big industry for development. Project of Globalization is almost going against idea of Gandhian philosophy of economic organisations. While whole world is in grip of high growth of capitalist mode of production and capitalist, so today world is more unequally equal and unstable. The growing economy concentration of wealth in hand of few is leading world poor and economic disadvantages for poorer section of society across world. Gandhi was staunch supporter of empowering rural employment through village cottages industry and agricultural based production. Gandhi was having holistic approach to reconstruct whole economy in which all will be participants of development. Gandhi develops many idea to led country to path of development. In 21 century his idea were most needed where all society are turning into selfish human and exploiting national development and claiming 21 century as era of development. But this development is very uneven and not having any kind of sympathy towards poor population. Fraud and force are diseases, truth and non violence are health. Economic exploitation of the poor people is brutal repression in context of modern development. Therefore we have to concentrate on village self contain manufacturing mainly for use. Providing this character of village is maintained there would be no objection to villager using modern machine tool they can make and afford to use. This is way they can improve their economic conditions in liberalized world but more challenge are coming from market completion in which production of cottage industry are not competent in nature.

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Physicochemical Modification and Surface Characterization of *Citrus microcarpa* Peel Wastes Nanoparticles for the Biosorption of Copper

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Abstract: The Philippine mining industry has been continuously contributing to water pollution by the improper discharge of toxic effluents. Pagatban River in Southern Negros is one of the outcomes of such, due to copper contamination. Major drawbacks presented by conventional treatment methods demand an alternative which uses waste materials in the process of biosorption. This study extended the development in the aforementioned area by producing competent biosorbent nanoparticles in Pristine (PB), Alkali (NaOH) modified (AB), and Carbonized Forms (CB) from Calamansi (*Citrus microcarpa*) peels for Copper removal. Biosorbents were prepared by drying, grinding, sieving, and modifying the peels. Assessment by batch biosorption followed 0.5g:50 ml biosorbent-to-water ratio in 60 mins of agitation; Water samples were then analyzed using Flame Atomic Absorption Spectroscopy and a pH meter. Both in biosorption (%) and pH, all biosorbents were significantly different: AB showed the best results with means of 95.70% and 6.51, respectively, followed by PB (78.57%, 4.41) and CB (76.42%, 5.77). The presence of carboxylic acid and carboxylate functional groups and the successful modification of the biosorbents were confirmed by Fourier Transform Infrared Spectroscopy. Field Emission - Scanning Electron Microscopy established the heterogeneous morphologies of quasi-spherical nanoparticles with mean sizes of 65.30 nm, 52.09 nm, and 63.46 nm for PB, AB, and CB respectively. Moreover, predominant biosorption mechanisms recognized were ion exchange and chemisorption, which are potentially reinforced by their nanoparticle-size. Thus, the biosorbents, particularly AB can be utilized for the treatment of copper-bearing wastewaters and facilitate the valorization of *C. microcarpa* peel wastes.

Keywords: calamansi peels, biosorption, copper, alkali-modification, nanoparticles

1. INTRODUCTION

The Philippines is the fifth most mineral-rich country and is home to the largest copper-gold deposit in the world. With about 40 metallic mines and 62 non-metallic mines operating as of September 2016 [1].

Mining industry generates wastes, primarily during mineral extraction, beneficiation, and processing [2]. Tailings, in particular, are byproducts left over from mining and extracting resources which may include finely ground rock particles, extraction chemicals and water with high concentrations of heavy metals [3].

Mining companies in the country have long been violating its environmental regulations which caused environmental consequences [4]. In the past, as a result of irresponsible actions of a copper mining company, Pagatban River in Southern Negros experienced a devastating long-term fishkill. It was caused by effluents that were dumped straightly into the river which lead to its deterioration, with heavy metal (copper and zinc) levels in water beyond the standard limits [5]. After three decades of no-mining activities, chemical analyses by the group of [6] confirmed that heavy metal contamination still persists in its bottom sediments. Elevated concentrations of heavy metals were also found in rivers and water bodies in Iloilo, Metro Cebu, Benguet and Manila with potential anthropogenic origins, in which some were found to be accumulating in the tissues of native aquatic organisms [7, 8 - 10]. Thus, posing an environmental threat.

Copper (Cu) is a vital component of human biochemistry but, is a potentially dangerous toxin. It is linked to various

neurodegenerative diseases (such as Parkinson's disease, Alzheimer's disease, etc.) as a factor that accelerates the aggregation of their associated toxic proteins [11]. Aquatic ecosystems are also affected by Cu directly by impairing the olfaction (sense of smell) ability of fishes [12], by reducing algal growth, thus affecting the biota's food chain ([13] as cited by [12]), and by adversely affecting the survival, growth, reproduction, biochemical functions and even cause the mortality of aquatic organisms [14].

According to [15], Conventional technologies (coagulation, oxidation, ion exchange, etc.) that are used to remove heavy metals from water have major drawbacks such as poor cost-effectiveness, high toxic sludge production, and other technical constraints. This necessitates a cost-effective and eco-friendly water treatment methods. Presenting a solution is a promising biotechnology for pollutant removal and recovery termed "Biosorption". It is a physicochemical method in which pollutants are removed by biological materials from aqueous solution. It became popular because of its efficiency, simplicity, and availability of biological materials [16].

Multiple studies have assessed different pectin-rich biomass as biosorbents where they exhibited high removal efficiency [17, 18 – 19]. Citrus peels and pectin were found to be containing carboxylic functional groups that enable their biosorption capabilities in the removal of metal ions [20]. In particular, *Citrus microcarpa* locally known as Calamansi is a hybrid plant cultivated in Southeast-Asia [21]. It is a major fruit crop of the Philippines with 28.03 thousand metric tons of produce from October to December of 2017 only, as reported by the Philippine Statistic Authority (PSA) [22]. Hence, the large-scale consumption of calamansi mostly in juice processing, food preparation, and cosmetics, results in the abundance of solid wastes which are the discarded peels. The peels were found to be high in pectin just like those of other fruits [23] making it an auspicious candidate as biosorbent material.

The new discoveries of the types of metal-binding biomass will potentially introduce very competitive and cost-effective biosorbent products. These materials can function as a basis for a novel technology for metal removal and retrieval. However, biosorption is still in progress and requires further scientific understanding with the aid of chemistry and engineering disciplines [24]. Recently, nano-sized biosorbents are also being studied due to their high surface area [25].

This study expanded the advancement in the area of biosorption by producing competent biosorbents (Pristine, Alkali-modified, & Carbonized Forms) in nanoparticle-size from Citrus microcarpa peels using various procedures. In addition, this work aimed to characterize the biosorbents instrumentally using Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Field Emission Scanning Electron Microscopy (FESEM) in order to determine the surface functional groups, particle size and distribution, and surface morphology of the biosorbents. It aimed to evaluate the copper concentration and the pH of the copper contaminated water before and after the application of the biosorbents and also their biosorption percentage (%), and it aimed to statistically investigate if there is a significant difference among the aforementioned variables in terms of the parameters considered. All of these are directed to the elucidation of the biosorptive mechanisms of the biosorbents on the removal of copper from water.

The results of this study could act as a foundation in the development of new materials in Philippine water treatment technology for metal removal and prospectively their recovery, leading to their real-world application in industrial and mining sectors. Thus, it could significantly mitigate the impending environmental and health hazards of heavy metal exposures, particularly of copper.

2. MATERIALS AND METHODS 2.1 Research Design

This study used descriptive research method in defining the physical and chemical characteristic of the prepared pristine, alkali modified and carbonized biosorbents with the use of instrumental analyses (ATR-FTIR and FESEM) in terms of their surface functional groups, particle size and distribution, and surface morphology. Whereas, experimental research method was used in order to assess and compare the prepared biosorbents in terms of their biosorption percentage (%) and, the pH and Copper concentration of the simulated copper contaminated water after their application.

A Pretest-Posttest Control Group Design was followed in the study. The concentration of the copper, pH were analyzed before and after the application of the biosorbents. The data gathered from the copper concentrations were needed for the calculation of the biosorption percentage (%). The experiment has three (3) replications for every biosorbent assessed a total of nine (9) experimental units and three (3) control units for the pretest values of the water parameters.

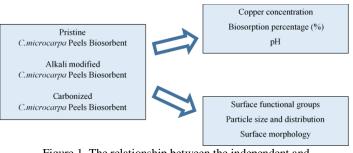


Figure 1. The relationship between the independent and dependent variables in biosorbents' assessment and characterization

*Control (Pretest) value was also be determined in the biosorption experiment

2.2 Location and Duration of the Study

Waste *C. microcarpa* peels were collected from a food establishment located at General Luna St., Brgy. Balingasag, Bago City, Negros Occidental, and samples were verified at the Bureau of Plant Industry's National Plant Quarantine Services Division, Station 15 – Port of Bacolod in Brgy. 39, Bacolod City.

The preparation of the biosorbents and water analyses for the biosorption of copper were conducted in the Sugar Regulatory Administration – Bacolod under the Research, Development and Extension Department's Agro-based Materials Laboratory it is located at Araneta St., Singcang, Bacolod City, Philippines.

Further characterizations of the *C. microcapa* biosorbents using Field Emission Scanning Electron Microscope (FE-SEM) and Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) were conducted at the Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST) located at General Santos Ave., Bicutan, Taguig City, Philippines under the Advanced Device and Material Testing Laboratory (ADMATEL) and the Standards and Testing Division.

Gathering of the materials started on July 23, 2018, while the last data gathering was on September 03, 2018.

2.3 Collection and Authentication of *Citrus microcarpa* Peel Wastes

One (1) kilogram of waste calamansi peels was collected from a local food establishment in Bago City. The fruit and peel samples were sent to the Bureau of Plant Industry (BPI), National Plant Quarantine Services Division, Bacolod City for the verification of the plant's scientific name.



Figure 2. Cleaned Citrus microcarpa peels

2.4 Preparation of Biosorbents

2.4.1 Pristine C. microcarpa Peels Biosorbent (PB)

The collected *C. microcarpa* peels were separated from the other parts (seeds & endocarp) and were washed thoroughly using distilled water to remove unwanted materials. Afterwards, it was dripped and air dried for fifteen (15) minutes. The cleaned calamansi peels obtained had a fresh weight of 800 g. The peels were dried using a Laboratory drying oven in 100°C for 12 hours to remove moisture and water. Then 200g of the dried materials were grounded using a grinder and sieved using a U.S. Standard Sieve No. 40. The biosorbent was then stored in a clean and closed container labeled as **Pristine Biosorbent (PB)**.

2.4.2 Alkali-Modified C. microcarpa Peels Biosorbent (AB)

Alkali Modification was based on the treatment methods presented by [26] and [27]. The 0.05 M aqueous solution of Sodium hydroxide (NaOH) was prepared by dissolving two (2) grams of NaOH pellets with one (1) liter of distilled water thru the aid of a magnetic stirrer.

Ten (10) grams of Pristine Biosorbent was treated by immersion with 0.05 M aqueous solution of Sodium hydroxide (NaOH) for three (3) hours at room temperature. Then, it was washed thoroughly with demineralized/distilled water until neutral pH (7) via decantation and filtration procedures, then dried in an oven at 70°C for 12 h and subsequently grinded. The biosorbent was sieved using a U.S. Standard Sieve No. 40 and stored in a clean and closed container. It was labeled as **Alkali Modified Biosorbent** (AB).

2.4.3 Carbonized C. microcarpa Peels Biosorbent (CB)

To facilitate carbonization the Pristine Biosorbent was contained in a closed ceramic container with a small opening on the top. The vessel was then subjected to heat at 60 minutes and washed using distilled water. Then, it was sieved using a U.S. Standard Sieve No. 40. It was then stored in a clean and closed container to avoid contamination with moisture, unnecessary moisture can cause the degradation of the material. It was labeled as **Carbonized Biosorbent (CB**).

2.5 Spectroscopic and Microscopic Surface Characterization of Biosorbents

2.5.1 Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy

The different pristine and modified biosorbents were sent to the Department of Science and Technology-Industrial Technology Development Institute (DOST-ITDI) at Gen. Santos Ave., Bicutan, Taguig, Metro Manila 1631. Where the Biosorbents were analyzed via Attenuated Total Reflectance -Fourier Transform Infrared Spectroscopy also known as ATR-FTIR in the range of 4,000–400 cm⁻¹ using an ABB MB3000, in order to determine the chemical and functional groups present in the surface of the materials that would help in elucidating their biosorption mechanisms.

2.5.2 Field Emission – Scanning Electron Microscopy

The *C. microcarpa* peel biosorbents were subjected to Field Emission - Scanning Electron Microscope (FE-SEM) to define its surface morphology, particle size and particle size distribution with the aid of Advanced Device and Materials Testing Laboratory (ADMATEL) of the Department of Science and Technology-Industrial Technology Development Institute (DOST-ITDI) at Gen. Santos Ave., Bicutan, Taguig, Metro Manila 1631.

Prior to the analysis, the particles were grounded using a carbon tape in relative humidity of $50\pm10\%$ and Room temperature between $+20^{\circ}$ C and $+25^{\circ}$ C. For the imaging, the instrument used was Dual Beam Helios Nanolab 600i. The samples were loaded and analyzed based on the instrument's user operation manual. The FESEM imaging was conducted using the following parameters: FESEM Accelerating voltage of 2.0 to 5.0 kV Secondary Electron - Through Len Detector (SE-TLD) and Beam Current of 86 pA.

To analyze particle size distribution, SE-TLD mode images (preferably with evident black-and-white-contrast of nanoparticles) for each sample were obtained. The nanoparticle size (image) were then analyzed using ImageJ software following the Feret diameter method. Data analysis was done by analyzing the frequency distribution of nanoparticles, in nm (using histogram). These analyses would help in expounding the behavior of the materials as biosorbents.

2.6 Biosorption of Copper using *C. microcarpa* Peel Biosorbents

2.6.1 Preparation of Simulated Copper Contaminated Wastewater

30 ppm copper solution was prepared by dissolving Copper sulfate pentahydrate crystals (CuSO4·5H2O) in distilled water with the help of a magnetic stirrer and labeled as Simulated Copper Wastewater.

2.6.2 Assessment of the Biosorbents using Batch Biosorption Experiment

Biosorption of copper were assessed using a batch experiment were the biosorbents were suspended in the water in a certain period of time. Methods are based on the work of [28].

A constant amount of 0.5 g of the biosorbents was contacted with 50 ml of simulated copper contaminated wastewater. Nine (9) plastic laboratory bottles were used to contain the materials for the reaction, and they were labeled according to the biosorbent used. Pristine, Alkali-Modified, and Carbonized Calamansi Biosorbent were placed in separate plastic bottles having three replicates in each treatment.

The plastic laboratory bottles labeled as PB contained the Pristine Calamansi biosorbent, while bottles labeled as AB were for the Alkali Modified Calamansi biosorbent and the bottles labeled CB for the Carbonized Calamansi biosorbent. The plastic containers were shaken for one (1) hour using a reciprocal shaker.

Subsequently, the samples were filtered separately using Whatman no. 42 filter paper in a glass funnel with the help of a funnel stand. Then, the filtrates were dripped inside the labeled volumetric flasks. The samples were then subjected to analysis.

2.7 Pretest and Posttest Analysis of Water Samples

2.7.1 Test for the Determination of pH

Sartorius PB-11 was used to measure the pH level of the water samples. Before the analysis the device was calibrated

using standard buffer solutions. The device read and stabilized the result. The electrode was rinsed with distilled water and was blotted dry. The electrode was then placed into a container containing a sample of 25 mL water sample and measured the sample's pH.

2.7.2 Test for the Determination of Copper concentration

Standard solutions containing a varying concentration of copper (1ppm, 2ppm, 3ppm, & 4ppm) were prepared for the air-acetylene Flame Atomic Absorption Spectrophotometer (FAAS). The spectrophotometer was turned on and was allowed to warm-up for ten (10) minutes. Afterwards, the standard solutions were read.

The pretest and posttest water samples were analyzed for copper concentration using Flame Atomic Absorption Spectrophotometer (FAAS) with air-acetylene.

2.8 Risk Assessment and Safety Precautions

Experiments were done under the supervision of a Licensed Chemist/Sr. Research Specialist. Proper laboratory attire (Lab gown, mask, rubber gloves etc.) were followed throughout the experimentation especially in handling chemicals to ensure the safety of the researcher. Various emergency apparatus were also stationed all throughout the laboratory such as Emergency eyewash and shower, First aid kit and Fire extinguisher.

2.9 Proper Disposal

The water samples were disposed of properly at the disposal unit of the laboratory with the guidance of the laboratory chemist. The leftover stock solutions were kept and stored for future use. The used biosorbents were stored in zip lock bags for further study.

2.10 Data Gathering and Analysis

The concentration or the number of copper ions in the water were expressed in part per million (ppm). The concentration of copper and pH of the water samples were measured before and after the biosorption experiments. The concentration of the copper ions in the contaminated water was analyzed using a Flame Atomic Absorption Spectrophotometer (FAAS).

The Data were subjected for the calculation to determine the biosorption percentage (%) to the equation:

$Biosorption = (C_i - C_f) / C_i \ge 100\%$

Where C_i is the initial concentration and C_f is the final concentration of Copper ions (ppm) in the contaminated water. Based on the equation used by [29].

For the ATR-FTIR Spectra, Correlation/Assignment Charts were used in order to assign the important functional groups of the biosorbents.

2.11 Statistical Data Analysis

Data gathered were analyzed using the IBM Statistical Package for Social Science (SPSS) Software 22 using the following tools:

Mean - used as a descriptive tool to establish the average adsorption efficiency and capacity of the treatments.

Standard Deviation - The standard deviation was used as a descriptive tool to find out how far the values are from the mean (Represented by error bars).

One-way Analysis of Variance (ANOVA) at $\alpha = 0.05$ – was used as an inferential tool to determine if there was a significant difference among the water samples before biosorption (Pretest) and after biosorption using the prepared biosorbents (Pristine, Alkali-modified, and Carbonized Biosorbents) in terms of their copper concentration and pH, and to determine if there are significant differences among the (%) biosorption of the biosorbents.

Duncan's Multiple Range Test (DMRT) - used as an inferential tool to determine which of the means are equal and which are significantly different.

3. RESULTS

3.1. Characterization of the *C. microcarpa* **Peel Biosorbents**

3.1.1. Fourier Transform Infrared Spectroscopy

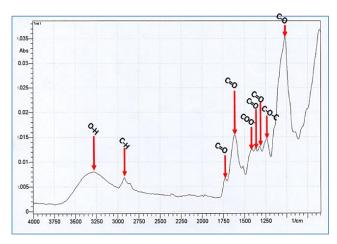


Figure 3. ATR-FTIR Spectrum of Pristine Calamansi Biosorbent

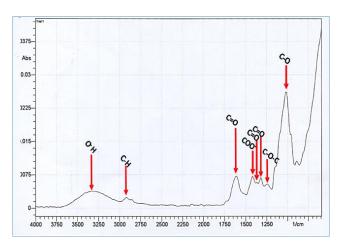


Figure 4. ATR-FTIR Spectrum of Alkali-modified Calamansi Biosorbent

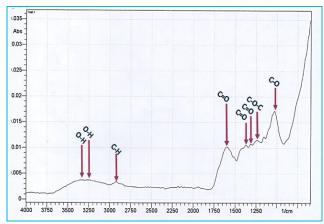


Figure 5. ATR-FTIR Spectrum of Carbonized Calamansi Biosorbent

-	Important Functional groups of the <i>C</i> . eeel Biosorbent Nanoparticles

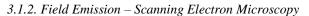
*Functional Group	Wavenumber, cm ⁻¹				
	РВ	AB	СВ		
O-H Stretching	3286	3333	3325 <i>,</i> 3248		
C-H Stretching	2924	2924	2924		
C=O Stretching (ester)	1728	-	-		
C=O (Carboxylate)	1612	1612	1597		
COO ⁻ (Pectin)	1412	1420	-		
C=O (Carboxylate)	1366, 1319	1373, 1319	1373, 1311		
C-O-C	1234	1242	1234		
C-O (pectin)	1018	1018	1018		

^{*}Assigned with reference to [30, 31 – 32]

Different Functional groups of the biosorbent were identified using Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance. The spectra of the biosorbents indicate successful modification of the *C. microcarpa* peels particles.

FTIR Spectroscopy is a technique based on the determination of the interaction between an IR radiation and a sample that can be solid, liquid or gaseous. It measures the frequencies at which the sample absorbs, and also the intensities of these absorptions. The frequencies are helpful for the identification of the sample's chemical make-up due to the fact that chemical functional groups are responsible for the absorption of radiation at different frequencies. It can be used for characterization of biomaterials used in depolluting processes, but also to characterize materials obtained after chemical modification. Particularly, ATR-FTIR is a non-destructive, reliable and robust technique in the analysis of wide-array of samples [33].

Hydroxyl (O-H) stretching was observed in wavenumbers of 3286 cm⁻¹ for PB, 3333 cm⁻¹ for AB, and 3325 cm⁻¹ and 3248 cm⁻¹ for CB. C-H stretching was detected at 2924 cm⁻¹ for all of the biosorbents. Stretching of Carbonyl (C=O) functional group of ester was observed in PB at 1728 cm⁻¹ but absent in AB and CB. For the carbonyl (C=O) functional group of carboxylate/carboxylic acid salts, peaks were found at 1612, 1612, and 1597 cm⁻¹ for PB, AB, and CB, respectively. Carboxylate (COO⁻) of pectin were observed at 1412 cm⁻¹ and 1420 cm⁻¹ for PB and AB, respectively. Again, Carbonyl (C=O) functional group of carboxylate were detected at 1366 and 1319 cm⁻¹ for PB, 1373 and 1319 cm⁻¹ for AB, and 1373 and 1311 cm⁻¹ for CB. C-O-C functional group was found at 1234, 1242, and 1234 cm⁻¹ for PB, AB, and CB, respectively. C-O of pectin was observed at 1018 cm⁻¹ for all of the biosorbents.



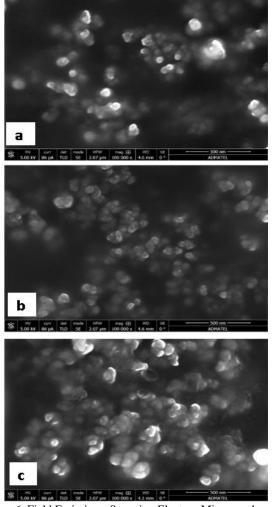


Figure 6. Field Emission - Scanning Electron Micrographs of (a) Pristine, (b) Alkali-modified, and (c) Carbonized C. microcarpa peels Biosorbent nanoparticles taken at 100 000x magnifications

Greyish clustered globules as seen in the FE-SEM Micrographs (Figure 6) of the different *C. microcarpa* peels particles revealed that the biosorbent nanoparticles have heterogeneous, irregular and quasi-spherical morphology, it was also observed that the particles are aggregated. Furthermore, particle-size measurements (Feret's diameter method) determined sizes of the pristine (Figure 6a), alkalimodified (Figure 6b) and carbonized (Figure 6c) biosorbents nanoparticles as observed at 100 000x magnification, with means of 65.30 nm, 52.09 nm, and 63.46 nm respectively (see Table 2).

Table 2. Mean Particle Size Measurement (n=20) for all C. microcarpa peel particle samples

	Calamansi peel biosorbents' particle size* (nm)			
	РВ	AB	СВ	
Mean	65.30	52.09	63.46	

*Particle size was measured using Feret's method in ImageJ software

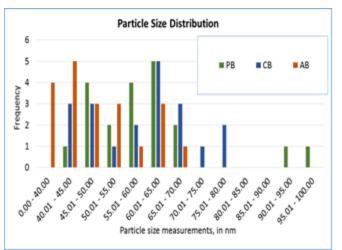


Figure 7. Particle size distribution of all biosorbent samples using Feret diameter method

Based on the data obtained (see Table 2) all estimated sizes of the samples via the Feret Diameter Method are in the nanometer size. In terms of the particle size distribution, as shown in Figure 7, the PB and CB have frequently distributed from the range of 60.01 to 65.00 nm while AB is most frequently distributed from the range of 40.01 to 45.00 nm. However, these results are only based on the selected measurements done on certain (specific areas) of each sample and the data obtained are only limited to 20 measurements.

3.2. Batch Biosorption of Copper Using the *C. microcarpa* Peel Biosorbents

3.2.1 Copper concentration of water samples

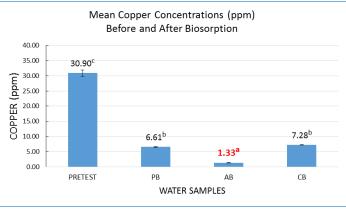


Figure 8. Mean copper concentrations of the water samples before and after the biosorption of copper using the *C*. *microcarpa* peel biosorbents

*Means with different superscripts (a, b & c) are significantly different

Table 3. One-way Analysis of Variance of the Copper
Concentration (ppm) of the Water Samples

	Sum of Squares	Df	Mean Square	F	Sig. (p- value)
Between Groups	1564.032	3	521. 344	1769. 567	.000
Within Groups	2.357	8	.295		
Total	1566.389	11			

*Further analyzed with IBM Statistical Package for Social Science (SPSS) Software 22

The simulated copper contaminated water along with the treated water samples using the different biosorbents were analyzed for copper concentration using a Flame Atomic Absorption Spectrophotometer (FAAS) with acetylene. Atomic Absorption Spectrophotometry is a technique in the quantitative analysis of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest. This is done by reading the spectra produced when the sample is excited by radiation [34]. This standard method is identified by the American Standards for Testing and Materials (ASTM) under the ASTM D1688 - 17 which is the "Standard Test Methods for Copper in Water" [35].

The biosorption of copper using the pristine, alkali modified, and carbonized *C. microcarpa* peel biosorbents were assessed using a batch biosorption experiment where a constant mass of biosorbents (0.5 g) was suspended in a constant volume of

the water sample (50 ml) and shaken for one (1) hour. As seen in Figure 8 after the batch experiment the biosorbent materials were able to reduce the concentrations of copper as compared to the mean pretest (control) value of 30.9 ppm (Cu) which did not undergo any treatment.

Results of One-way Analysis of Variance (One-way ANOVA) at 0.05 alpha value level of significance as shown in Table 3 indicates that there is a significant difference among the copper concentration of the water samples treated with the biosorbents and the pretest value (F-value = 1769.567 & p-value =0.000). As shown in Figure 8, Duncan's Multiple Range Test (DMRT) as Post hoc (alpha value = 0.05) as denoted by the superscripts revealed that there is no significant difference between PB and CB in terms of the copper concentration but they are significantly different from the Pretest and AB. The lowest value for copper (ppm) was exhibited by AB with a mean of 1.33 ppm followed by PB (6.61 ppm), CB (7.28 ppm) and Pretest (30.9 ppm).



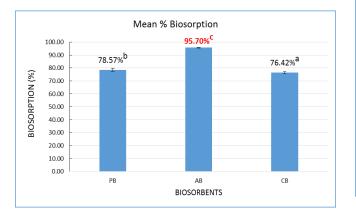


Figure 9. Mean (%) Biosorption of the *C. microcarpa* peel biosorbents in copper biosorption

*Means with different superscripts (a, b & c) are significantly different

Table 4. One-way Analysis of Variance of the (%)			
Biosorption			

	Sum of Squares	Df	Mean Square	F	Sig. (p- value)
Between	669.392	2	334.	499.	.000
Groups			696	580	
Within	4.020	6	.670		
Groups					
Total	673.412	8			

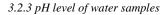
*Further analyzed with IBM Statistical Package for Social Science (SPSS) Software 22

Percentage Biosorption was calculated by subjecting the copper concentration data to the formula by [28]: *Biosorption* = $(C_i - C_f) / C_i \times 100\%$, where C_i is the initial concentration and C_f is the final concentration of Copper ions in the contaminated water used. The biosorption efficiency reflects

the percentage of copper that was removed by the biosorbents from the water.

One-way ANOVA at 0.05 alpha value level of significance revealed that the mean percentage biosorption efficiency of the biosorbents are significantly different from each other (F-value = 499.580 & p-value = 0.000) as shown in Table 4.

As shown in Figure 9, DMRT, as denoted by the superscripts, showed that Alkali modified *C.microcarpa* biosorbent exhibited the highest percentage biosorption with 95.70 %, followed by PB with 78.57 % and CB with 76.42 %. It was revealed that modification of the biosorbent using an alkali solution (0.05 M NaOH) enhanced its (%) copper biosorption which indicates that it is a better biosorbent compared to the raw form. But, the modification of the biosorbent thru carbonization showed a negative effect on its ability to remove copper from water.



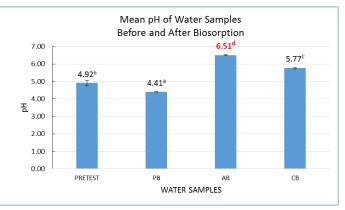


Figure 10. Mean pH value of water samples before and after the biosorption of Copper using *C. microcarpa* peel biosorbents

*Means with different superscripts (a, b & c) are significantly different

Table 5. One-way Analysis of Variance of the pH value of the
Water Samples

	Sum of Squares	Df	Mean Square	F	Sig. (p- value)
Between Groups	7.753	3	2.584	399. 654	.000
Within Groups	.052	8	.006		
Total	7.805	11			

*Further analyzed with IBM Statistical Package for Social Science (SPSS) Software 22

Figure 10 shows that there is a change in the pH values of the water samples after the biosorption of copper. One-way ANOVA revealed that the pH values of the water sample are significantly different with each other with F-value of 399.654 and p-value of 0.000 as shown in Table 5. DMRT, as represented by superscripts (Figure 10), showed that AB

displayed the highest pH value of 6.51, followed by CB with 5.77, Pretest with 4.92, and PB with 4.41.

Using only the simulated copper contaminated water in a batch biosorption experiment, only the mean pH of the water samples after the biosorption of copper using the Alkalimodified Biosorbent (AB) was able to reach the standard range for pH of Class A effluents as mandated by the Department of Environment and Natural Resources (DENR Administrative Order No. 2016-08) [36]. In contrast to the results shown in the % Biosorption, CB exhibited better values in terms of pH compared to the pristine form.

4. DISCUSSIONS

4.1 Characterization of Surface Functional Groups ATR-FTIR

The presence of functional groups on the surface of the biosorbent particles was confirmed using Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR). Hydroxyl functional group and carbonyl functional groups of carboxylic acid, carboxylates, and esters were found on the biosorbents that could have contributed in the binding of copper ions from water. The shifting of the peaks of carbonyl (from 1412 cm⁻¹ to 1420 cm⁻¹) and of carboxylates (from 1366 cm⁻¹ to 1373 cm⁻¹) after the modification of the biosorbent particularly after alkali treatment indicates interaction of the biomass to the sodium ions. Also, the peak for ester at 1728 cm⁻¹ disappeared after the alkali modification and carbonization, as mentioned by [26] alkali treatment facilitates the conversion of esters present in the pristine biosorbent into carboxylic acid in the process of base-promoted ester hydrolysis/saponification, which is then converted to carboxylate [37]. On the other hand, peak at 1412 cm⁻¹ for carboxylate disappeared only after carbonization. The alteration or/and elimination of some of the functional groups, hydroxyl groups, in particular, may have caused the variation in the water samples' pH values, where the modified biosorbents showed lower acidity compared to the output of the raw form.

4.2 Characterization of Surface Morphology and Particle Size and Distribution Using FESEM

As established by Field Emission Scanning Electron Microscopy (FESEM), biosorbent nanoparticles of *C. microcarpa* peel wastes were successfully produced and modified using Alkali modification (via NaOH) and Carbonization. Nanoparticles of the biosorbents were observed to have heterogeneous and quasi-spherical morphology. It is also evident in the micrographs that the particles are agglomerated in nature. Results of the ImageJ Analysis using Feret's method showed that the nanoparticles vary in size. Due to the modifications, the size of the particles was reduced and the particle size distributions were narrowed down as compared to the raw/pristine form. Specifically, alkali treatment with NaOH affects the lignin and holocellulose compounds on the surface of the nanoparticles resulting in a decrease in the particle size [38 – 39].

The excellent biosorption abilities of the nanoparticles may be attributed to their functional groups and their nano-size. The nanometer size of the biosorbent, even when aggregated, enhances the materials physical and chemical properties resulting in higher removal activity [40]. The smaller the sizes of the nanoparticles the higher is their surface area, which means that the material reacts better compared to materials in bulk-sizes.

4.3 Assessment of Biosorption of Copper Using the *C. microcarpa* Peel Biosorbents in Batch Biosorption Experiment

The usage of fruit peels as biosorbent is gaining attention due to their functionalities. [20] suggested that orange peels can be a cheap and effective material for the treatment of metal ions in water. The study of [41] showed that unripe calamansi peels can remove Congo red as evaluated using batch adsorption studies.

All of the biosorbents (PB, AB & CB) exhibited high biosorption percentage (%), as assessed using the batch biosorption experiment. Alkali modification using Sodium hydroxide was able to increase the (%) biosorption of copper.

After biosorption, the pH value of the water changed. The increase in the pH of the water after the treatment using the AB and CB may signify that ion exchange mechanism is one of the causes of the metal removal involving cations (Na⁺). While the pH decreased for PB, which most probably because of the acidic functional groups in the raw biosorbent, particularly the principal involvement of the hydroxyl group, via the exchange of Hydrogen ions (H⁺).

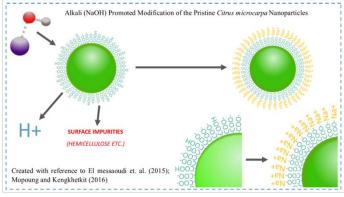


Figure 13. Graphical illustration of the Alkali-modification of the pristine nanoparticles using Sodium hydroxide (the molecule on the upper left side).

*Created with references to [37, 27]

Alkali-modification both significantly increased the (%) biosorption of copper and the pH of the water as compared to the pristine biosorbent and the carbonized biosorbent. A similar observation was obtained from the study of [26] where the alkali-treated Citrus limetta peels showed enhanced adsorption capacity in the recovery of Gallium (III). As discussed by [27], this can be explained by the removal of surface impurities present on the biosorbent particles and exposure of the active binding sites for metal adsorption after the solubilization of hemicellulose and pectin embedded in the cell walls as an effect of the treatment with Sodium hydroxide (NaOH). Furthermore, a deprotonation of the particles should have taken place and the Sodium (Na⁺) cation from NaOH could act as the counter ion to negatively charged functional groups in the modified biosorbent. These Na⁺ ions will be exchanged with the heavy metals ion during the sorption process, this modification also increases the cation exchange capacity of the nanoparticles [38]. Effects of the modification are further visualized as seen in Figure 13.

4.4 Elucidation of Biosorption Mechanisms Involved in the Biosorption of Copper Using the *C. microcarpa* Biosorbents

Biosorption mechanisms were established with the help of ATR-FTIR Spectroscopy. The carboxylic acid (RCOOH) and the carboxylate (RCOO⁻, M^+) functional groups identified from the spectra of the *C. microcarpa* biosorbents can be linked to the peels' pectin content. As reported by [22], calamansi peels were able to yield high amounts of pectin ranging from 2.99 to 4.08%. Pectic substances are high molecular weight polysaccharides widely spread in plants and can be found as an essential part of the primary cell wall and middle lamella of higher plants. Moreover, citrus pectin and peels were found to be possessing similar surface functional groups (especially Carboxylic acid), and this confirms that pectin is an important component in the biosorption process as elucidated in the study of [20].

Furthermore, the suggested mechanism in the removal of Congo red using calamansi peels is chemical adsorption or chemisorption involving valence forces through sharing or exchanging of electrons between adsorbate and adsorbent [41].

In general, the potential predominant mechanisms involved in the biosorption of copper (II) ions in water are ion-exchange and chelation/complexation due to carboxylic acid and carboxylate functional groups forming chelates/complexes to copper ions, with reinforcement from the physical properties (particle size and morphology) of the materials.

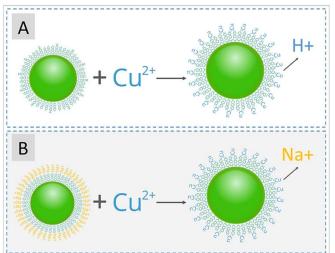


Figure 14. Graphical illustration of the possible interaction of the (A) Pristine or Carbonized biosorbent nanoparticles and (B) Alkali-modified biosorbent nanoparticles to the divalent copper ions.

Figure 14 above shows the simplified version of the interaction of the biosorbent nanoparticles to the copper ions in water.

The viable reactions would be:

1. 2RCOOH + $Cu^{2+}(aq)$ + SO₄²⁻(aq) \rightarrow (RCOO)₂Cu + H₂SO₄

2. 2RCOO' Na⁺ + Cu²⁺(aq) + SO4²⁻(aq) \rightarrow (RCOO)₂Cu + Na₂SO4

Where Two (2) carboxylic acid functional groups release hydrogen ions (Reaction 1) or carboxylates releases Sodium ions (Reaction 2), which reacts with the sulfate ion, as it binds

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the divalent copper cation to form a complex and sulfuric acid or sodium sulfate as byproducts.

In accordance with this study the researcher would highly recommend: the analysis of the biosorbents using potentiometric titration; the application of the biosorbents in the removal of other heavy metals and organic pollutants; the analysis of the biosorbent before and after the biosorption using Energy Dispersive X-ray Spectroscopy (EDX) and Xray Diffraction (XRD) for further mechanistic understanding; the kinetic and isothermal investigation of the biosorbents; and the application of the biosorbents in large-scale setting for the treatment of heavy metal-bearing wastewaters.

5. CONCLUSION

Based on the results of the study, it is evident that the C. microcarpa peels in pristine, alkali-modified and carbonized form are promising biosorbents in the removal of copper from water but, the Alkali (NaOH) modified biosorbent topped the other two. ATR-FTIR identified the existence of functional groups such as hydroxyl and carbonyl that are associated with carboxylic acids and carboxylates of pectin. The nanoparticlesize of the biosorbents were established using FESEM along with their heterogeneous and irregular morphologies, and their quasi-spherical and aggregated nature. The Biosorbents were able to decrease the concentration of copper in the water and change the pH of the water after the biosorption. High biosorption percentage were exhibited by the biosorbents. Moreover, there is a significant difference among the biosorbents in term of the copper concentration, pH and biosorption (%) percentage, where the Alkali-modified biosorbent showed the best results. Thus, the predominant biosorption mechanisms established in this study are ion exchange mechanisms along with chelation/complexation, which are potentially reinforced by the physical properties of the biosorbents. Therefore AB can be utilized in water treatment systems, especially in the mining industry, for the treatment of copper-bearing wastewaters and facilitate the valorization of calamansi peel wastes.

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Electronic Forklift by Remote Control

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Abstract: Forklifts are used in a wide variety of applications, such as manufacturing, construction, retail, meat and poultry processing, lumber and building supplies, trades, agriculture, and a variety of warehouse operations. This work mainly approaches to design and modeling of electronic forklift. Electronic forklifts are extensively used primarily for material handling in food industry. The objective of the electronic forklift is to ensure safety of the operator and to save time and money to push and pop items. In this system, five DC motors, Arduino UNO, IR remote and IR receiver are used. Four DC motors are used for moving and one DC motor is used for lifting. Arduino UNO is mainly used to control the overall system. Arduino UNO will determine whether the motors have to rotate forward or backward. Motor directions are implemented by Arduino programming management. Therefore, the system will be a foundation in implementing of the industrial forklift.

Keywords: Arduino UNO; IR remote; DC motor; forklift; lifting; moving

1. INTRODUCTION

A forklift is a small industrial vehicle with a power-operated pronged platform that can be raised and lowered for insertion under a load to be lifted and moved. They are used to lift and move cargoes in where such as airports, rail stations, harbors, industries and etc. In making design of forklift, the part of moving is powered by gasoline, diesel, gas and electrical. Hydraulic and electric are used for lifting system.

Forklifts are used in two places such as indoors and outdoors. Gas or diesel powered forklifts can never be used indoors because of their toxic emissions and fear of carbon monoxide poisoning. Electric forklifts rely on batteries to operate. Gasoline or gas forklifts are sometimes stronger or faster than electric forklifts, but they are more difficult to maintain, and fuel can be costly. Electric forklifts are greater for warehouse use because they do not give off noxious fumes like gas powered machines do. Electrics forklifts are ideal for indoor use, as they do not generate emissions, but cannot be used outside; expect on smooth paved parking lot type areas. Electric forklifts are quite, another plus for indoor use, and do not need storage areas for gas or diesel fuel.

Today is an electronic world, so everything can be replaced by electronic technology. A forklift machine can be driven by dc motors and can be controlled by a control device. In the past, gas or diesel forklifts were used widely in the required places. Before the development of electronic technology, the part of moving is powered by electrical and hydraulic is used for the lifting. The production cost of forklifts can be reduced by using electronic technology. Moreover, this kind of forklift protects environment from being damaged by pollution.

2. METHODOLOGY

Mini forklift can be operated by dc voltage and can be driven by the remote control system. In this work, five dc motors and Arduino UNO controller are needed and IR remote and IR receiver are required. Signals from IR remote are read by IR receiver. Digital signals from IR receiver are read by Arduino UNO controller. The controller will determine whether the motors have to rotate forward or backward.

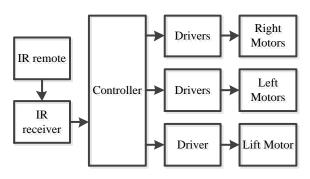


Figure 1. Block diagram of the system

3. COMPONENTS SELECTION

3.1 Arduino UNO

A microcontroller is a high integrated computer system on a chip. It is contained an integrated memory and programmable input/output peripherals.

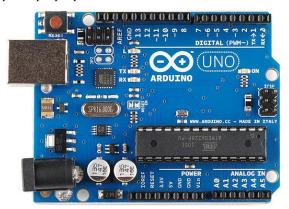


Figure 2. Arduino UNO

The Arduino Uno is a microcontroller board based on the ATmega328. It has 14 digital input/output pins (of which six can be used as PWM outputs), six analog inputs, a 16MHz crystal oscillator, a USB connection, a power jack, an ICSP header and a reset button. The Arduino Uno can be powered

via the USB connection or with an external power supply. The power source is selected automatically. External (non-USB) can come either from an AC to DC adapter or battery. The board can operated an external supply of 6 to 20 volts, if supply with less than 7V, however, the 5V pin may supply less than five volts and the board may be unstable. If using more than 12V, the voltage regulator may overheat and damage the board. The recommended range is 7 to 12 volts.

3.2 IR remote

Infrared remote control is a handheld, wireless device used to operate audio, video and other electronic equipment within a room using light signals in the infrared (IR) range. Infrared light requires line of sight to its destination. Low-end remotes use only one transmitter at the end of the unit and have to be aimed directly at the equipment. High-quality remotes have three or four powerful IR transmitters set at different angles to shower the room with signals. This little remote control would be handy for controlling a robot or other project from across the room. It has 17 buttons and a layout we thought was handy: directional buttons and number entry buttons. The remote uses the NEC encoding type. The user can use this to control something that is expecting NEC codes or the user can pair this with the IR remote receiver sensor.

Specifications:

- Mini remote control with 17 buttons
- 38KHz NEC code output, 940nm IR LED
- Runs on CR2032 battery, included
- IR receiver breakout board.



Figure 3. IR remote

3.3 DC motor and wheel

A brushless DC (BLDC) motor is a synchronous electric motor powered by direct-current (DC) electricity and having an electronic commutation system, rather than a mechanical commentator and brushes. In BLDC motors, current to torque and voltage to rpm are linear relationships. Some of the problems of the brushed DC motor are eliminated in the brushless design. DC hobby motor with a 48:1 gearbox and a 66mm wheel are selected for this system. Ideal for small robotics projects, such as a Simple Bot or other car type design. Easy to control using either N-DRIVE module or a PWM output from Arduino for single-direction variable speed, or H-Bridge shield for forward / reverse variable speed. The gearbox includes a press-fit axle that allows the wheel to be mounted on either side.

Specifications

 Working voltage: 	3-6Vdc
Gearbox ratio:	48:1
 Motor size: 	70x22x18mm
 Motor weight: 	50g
• Wheel diameter:	66mm
• Wheel weight:	12g.



Figure 4. DC motor with wheel

3.4 L298N motor driver

The L298 is an integrated monolithic circuit in a 15-lead Multi watt and powerSO20 packages. It is a high voltage, high current dual full-bridge driver de- signed to accept standard TTL logic levels and drive inductive loads such as relays, solenoids, DC and stepping motors. Two enable inputs are provided to enable or disable the device in dependently of the in-put signals. The emitters of the lower transistors of each bridge are connected together and the corresponding external terminal can be used for the connection of an external sensing resistor. An additional supply input is provided so that the logic works at a lower voltage.

Specifications:

•for Stepper Motor Dual H Bridge Control

- •Driver: L298N Dual H Bridge DC Motor Driver IC •Driven part of the terminal supply area Vs: +5 V ~ +35 V; such as the need to take power within the board, the supply area Vs: +7 V ~ +35 V
- •Driven part of the peak current Io: 2A
- •The logical part of the terminal supply area Vss: +5 $V \sim +7 V$



Figure 5. L298N DC motor driver

4. HARDWARE AND SOFTWARE IMPLEMENTATION

During the design process the hardware and software aspects were broken down and designed in smaller sections. This made testing of the system easier, as some of the smaller design components could be combined such that individual aspects of the system could be tested.

4.1 Design layout

In this design, forklift car is four wheels drive system. The left two wheels are driven by only one signal. The right two wheels are also driven by only one signal from the controller.

4.3 Process flowchart

In this system, one process acts purely without other process. So, all processes are simple.

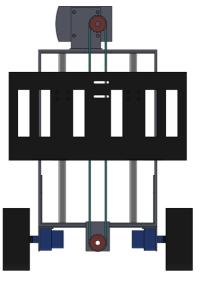


Figure 6. Front view of the system

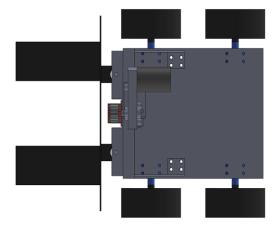


Figure 7. Top view of the system

4.2 Overall circuit diagram

In the overall circuit diagram, 6V DC is the power supply for the whole system. Seven keys from the IR remote are used to operate the system.

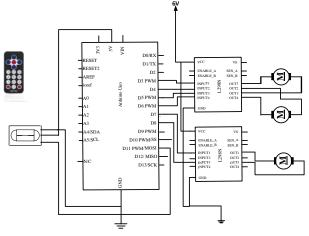


Figure 8. Overall circuit diagram of the system

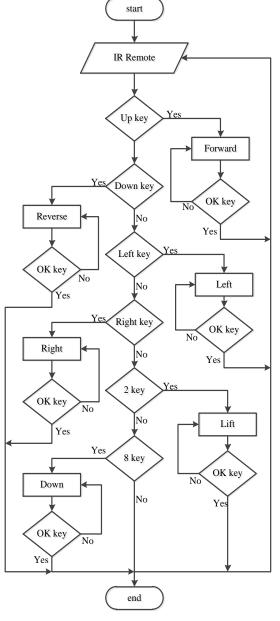


Figure 9. Process flowchart

4.4 Test and Results

Input device and actuators are tested before installation of the system. The results of the testing will be shown in details. Some are tested with the Arduino IDE and some are tested by supplying the power. After installation the system, test and results will be shown.

4.4.1 IR Remote and IR Receiver Testing

IR remote and IR Receiver are tested with the Arduino IDE. The output signal of the IR receiver is connected to the digital pin number 2 of the Arduino UNO. When the keys of the IR remote are pressed, the Arduino UNO receives the signal through the IR receiver. The results are the number value as hexadecimal. This testing is shown in figure 10.

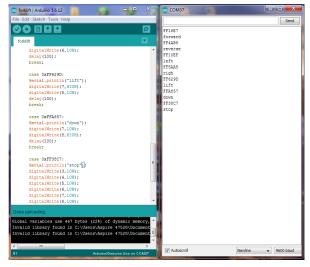


Figure 10. Testing IR remote on Arduino IDE

4.4.2 Forward and Reverse Testing

When the upper arrow key of the IR remote is pressed at once, the forklift car moves forward direction. If the OK key of the IR remote is pressed at once, the forklift car stops.

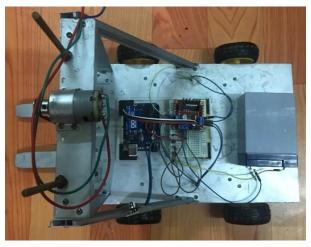


Figure 11. Testing for drive system

When the under arrow key of the IR remote is pressed at once, the forklift car moves reverses direction. If the OK key of the IR remote is pressed at once, the forklift car stops. This testing is shown in figure.

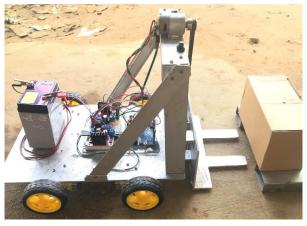


Figure 12. Testing for inserting the load

4.4.3 Lifting and Down Testing

When the 2 key of the IR remote is pressed at once, the forklift car is lifting. If the OK key of the IR remote is pressed at once, the lifting stops.

When the 8 key of the IR remote is pressed at once, the forklift moves down direction. If the OK key of the IR remote is pressed at once, the downing car stops. This testing is shown in figure.



Figure 13. Testing for lift and down

4.5 Conclusion and discussion

The safety of the operator can be improved by providing alternatives to the existing design of the standup forklift trucks. One such alternative is to provide a door to protect the operator. Design changes had to be made to prevent accidents and to protect the operator in case of an accident. In the electronic forklift, by using the electronic control system, the operator doesn't face any difficulties in the work envelope. Regular preventative maintenance is required.

Excellent performance values for acceleration, travel and lift speeds allow for maximum productivity. Electric forklifts have no exhaust emissions, and thus can provide significant air quality benefits. One benefit is that electric forklifts have lower life cycle costs when compared with ICE models. This is due to lower maintenance costs, lower fueling costs, and longer useful life for an electric forklift. These forklifts lead to higher productivity by eliminating time-consuming battery changing.

5. ACKNOWLEDGMENTS

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Secure Controls for Smart Cities; Applications in Intelligent Transportation Systems and Smart Buildings

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Abstract: Internet of Things (IoT) is an emerging concept in smart infrastructures describing a wide ecosystem where interconnected devices and services collect, exchange and process data in order to adapt dynamically to a context. IoT is tightly bound to cyber-physical systems and in this respect is an enabler of Smart Infrastructures by enhancing their quality of service provisioning. Smart infrastructure, enabled by technologies like IoT, offer numerous of advantages bringing serious cost savings and efficiencies. These kinds of data-driven environments, fueled by connected devices and network connectivity, become a new attack surface for cyber threats. Cyber security approaches develop guidance to secure IoT and Smart Infrastructures from cyber threats, by highlighting good security practices and proposing recommendations to operators, manufacturers and decision makers. In this paper, cyber security approaches are analyzed in a smart city infrastructure.

Keywords: Internet of things; Cyber security; Smart transportation; Smart city.

1. INTRODUCTION

Nowadays buildings are not only walls, floors and ceilings. By applying artificial intelligence (AI), internet of things (IOT), and in general smart technologies, building systems autonomously collect all the information from IoT devices, occupant behavior, and environment to learn from the data, analyze it, optimize the performance and eventually improve the building efficiency. As a matter of fact, by applying innovative IOT and AI embedded platforms in today smart buildings, the occupants satisfaction is improved significantly. Moreover, the new smart buildings make it possible to radically reduce costs through management, automation, and optimization of operations in a smart environment [1-7].

A comprehensive building management system leverages all aspects of building facilities; e.g., [3], [4]. In [3], the developed smart building with IOT solutions allows for monitoring all the living conditions; e.g., temperature, humidity, energy allocation, movements, etc. In [4], all the aspects related to the heating, ventilation, and cooling (HVAC) system in a smart building are managed and optimized. All the data related to the HVAC system of each zone is used to trigger the distributed control algorithms to not only detect but also predict and respond to anomalies [4]. In other words, the smart building technologies are employed to identify possible root causes, so actions can be prioritized, assigned, monetized and prevented. Recommendations that appear on dashboards or adjustments is transmitted directly to the IoT device for quick and efficient actions. Introducing smart automation infrastructures in smart buildings increases the residents convenience and reduces the labor operational costs, however, these new facilities dramatically increases the level of potential vulnerability in the smart infrastructure. Examples of these vulnerabilities are disgruntled employees, cyber criminals, cyber attackers, etc. The problem is that any control system can be attacked internally, therefore there is a need for more efficient protection in a smart environment; e.g., smart transportation system, smart building.

In this paper, we have considered different vulnerability cases in controls of smart transportation systems and smart buildings, and we have discussed and introduced some trustworthy and safe control frameworks for these environments.

The rest of the paper is organized as follows. Section 2 presents the smart building technologies and challenges.

Section 3 explains the smart transportation systems technologies and challenges. The next section introduces the failsafe SCADA networks. Sections 5, 6, 7, and 8 present the forensics, engineering, monitoring, and vulnerability management in the smart city environment. Finally, section 9 provides the conclusions and the future research.

2. SMART BUILDING AND CHALLENGES

In a smart building, after the equipment information is collected through sensors and meters, a library of benchmark data is applied, analytics are performed and potential actions toward performance improvement are identified [3]. To automate insights into actions as they optimize assets with IoT, we can utilize the predictive analytics to artificial intelligence or learning systems [4], [5]. By taking advantage of predictive algorithms, building owners can significantly cut energy consumption and achieve ambitious cost-saving targets. For example, by combining data for heating and cooling with weather forecasts, an HVAC system can deliver more efficient heating and cooling; see [4] for more information. Thus, by combining the cognitive analytics and sensors in the existing building systems, we can significantly improve occupant experience. The buildings will be flexible, adaptable and able to predict occupant needs [4]. The features in the fig. 1 can be considered in a smart building or a smart workplace.

- Energy costs and demands for smart building are on the rise.
- Companies are facing aggressive energy reduction targets.
- Increasing IOT adoption is leading to data overload.
- High pressure to address the environmental concerns.

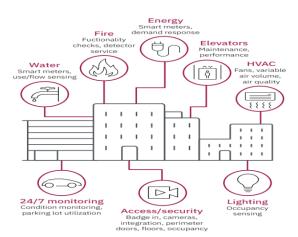


Fig. 1: Smart features in a smart building

3. SMART TRANSPORTATION SYSTEM AIMS AND CHALLENGES

All the components such as automotive, aviation, and rail systems could be considered as the foundation of transportation systems. Also different modes of transportation from land, air to water can be considered in a transportation system. Roads, bridges, parking places, kinds of stations, airports, and shipyards provide the immobilized support and sustenance to all kinds of motions. The interactions between the transportation system components also construct a partition of these systems. Video detectors, microwave detectors, radar detectors, and magneto detectors cause the monitor, control, and communication to happen within the transportation systems. Different sensors are employed in roads or bridges to improve the transportation performance. In a smart transportation infrastructures three main parts exist to provide controls, communication, and computation; the onboard units, the roadside units, and the transportation control unit. Here we have explained each of these components.

- onboard units are the devices/equipment that are installed in the vehicles. They collect the information in the vehicle and process the stored data in the unit's memory.
- The roadside units are the embedded devices along the road to increase the overall coverage of a vehicular system. The vehicles in the coverage area of the roadside units receive messages from them. These units are installed to enhance the propagation delay of messages between disconnected vehicles and eventually increase the transportation network performance.
- The transportation control units are the supporting systems for the two other mentioned units (on-board units and roadside units). The generated data transferred over these control units. These control units can provide optimal decisions and apply the optimal strategies regardless of the time, data, and resources. Fig. 2 shows the relations between the on-board, roadside and control units in a smart transportation network.

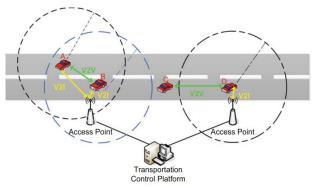


Fig. 2: Three units relation in a smart transportation network

Since the computational overhead and complications is fairly high in data analytics and controls of intelligent transportation systems, the centralized approaches is not enough in designing Fig. 2: Three units relation in a smart transportation network a management system for them. Distributed and decentralized control designs come to play for the mentioned reasons. Wireless communication networks are being commonly used in the smart transportation systems. WAVE/802.11p and ZipBee/802.15.4 are two very common communication protocols for data collection and transportation because of their improved abilities of data exchange among the vehicles and between the vehicles and the roadside infrastructures [6], [7]. Wireless sensor networks (WSNs) in also play a very important but not conspicuous role. WSNs consist of spatially distributed autonomous sensors to monitor physical conditions such as temperature, sound, pressure, and the like, and to transfer sensed data through wireless networks to sink nodes then return to the control unit. The communications in s mart transportation system are processed as in a WSN, but should concern mobility. Traditionally, there have been two types of transportation systems communications for decades: vehicleto-vehicle (V2V) communication and vehicle-to-infrastructure (V2I) communication. The third type of communication is built upon V2I and V2V based on long-distance wireless communication with the support of vehicle manufacturers or mobile service carriers (ATT, T-Mobile, Verizon, etc.). The third type of communication is known as the device-to-device (D2D) communication. Different from V2V and V2I, D2D is a multi-dimension channel that not only provides simple information exchange but also supports the interaction of images, sounds, and GPS location information. Furthermore, with the assistance of smartphone, many location-based services also benefit from the third type of communication and produce many applications (Google Map, Apple Map, etc.). Fig. 3 shows the three common types of communications in a smart transportation system.

4. FAILSAFE SCADA NETWORK

SCADA networks are commonly useful for building industrial control systems, as a prominent infrastructure. There are various vulnerabilities exist in wired or wireless communication networks of SCADAs. As a matter of fact, the communication networks can be intruded to terminate or misroute the control commands. Fig. 4 shows an SCADA networks with its local area network (LAN) and wide area network (WAN) communications. For having more safety, there can be additional layers of security in conveying commands to vital switches. For instance, a backup system can be provided in case that the system providing the confirming codes break down.

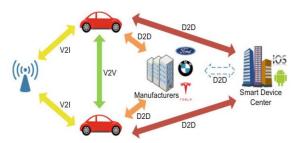


Fig. 3: Three units relation in a smart transportation network

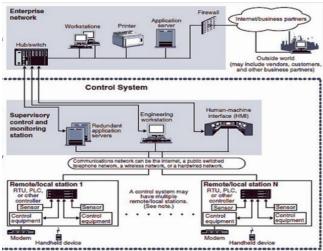


Fig. 4: Supervisory control and data acquisition (SCADA) components and communication networks

Predicting all the possible failures or malfunctions in the network equipment or communications due to the attacks or actuators faults is complicated, costly, and time consuming. This is where the human-machine interface comes to play. The human-machine interface display provides necessary information to the operators of SCADAs. HMI can send alerts to human operators when needed, or it can indicate errors. The return signals alert the malfunctions such as pipeline leaks, pumping station equipment failures, and sewage pipe blockage. The most important error signals that can be sent to the operators is the signals showing the cyber-attacks to the SCADA software. Although the artificial intelligent (AI) algorithms can be used to manage and monitor most of the SCADA alerts/errors, it is very important to quickly detect the anomalies and to quickly correct them. Therefore, it is necessary to always have human operators in the loop, along with the embedded AI algorithms. To improve the network

safety in a SCADA system, the backup communications from and to the HMI are provided. There are various types of cyber attacks in SCADA systems; database attacks, communication attacks, common protocols vulnerability, network holes, and field devices attacks. The centralized architecture is not efficient in case of cyber attacks in the SCADAs, since an anomaly may cause the vital infrastructure to shut down immediately. Thus, the decentralized structure may improve the system performance by allowing the isolation of the attacked subsystems or failed subsystems. The protective measures can be improved by considering the system operators information. The following protective measure are recommended in this paper:

- Apply technical audits of SCADA devices and networks, and any other connected networks, to identify security concerns.
- Evaluate the security level of all the remote sites connected to the SCADA network.
- Establish teams to test and evaluate attack scenarios on the SCADA.
- Define and specify the cyber security responsibilities of managers, system administrators and users.
- Provide a documents about the network architecture and systems that serve critical functions or contain sensitive information; i.e, systems that require additional levels of protection.
- Construct a rigorous, ongoing risk management process.
- Build a network protection strategy based on the defense in-depth.
- Identify cyber security requirements with specific details.
- Establish effective configuration management processes.
- Conduct routine self-assessments.
- Establish system backups and disaster recovery plans.
- Establish expectations for cybersecurity performance and hold individuals accountable for their performance.
- Construct policies and conduct training to minimize the likelihood that organizational personnel will inadvertently disclose sensitive information regarding SCADA system design, operations, or security controls.

- Implement internal and external intrusion detection systems and establish 24-hours-a-day incident monitoring.
- Establish strong controls over any medium that is used as a backdoor into the SCADA network.
- Implement the security features provided by device and system vendors.
- Do not rely on proprietary protocols to protect your system.
- Harden SCADA networks by removing or disabling unnecessary services.
- Evaluate and strengthen the security of any remaining connections to the SCADA network.
- Disconnect unnecessary connections to the SCADA network.
- Identify all connections to the SCADA network. To protect the control system in a SCADA system, four critical processes need to be done; digital forensics, engineering and architecture, operation monitoring, and vulnerability management. Fig. 5 shows the relationship between these four required processes to attain protection in the SCADA system.

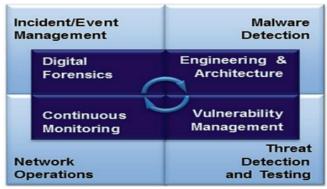


Fig. 5: Four required processes to attain protection in SCADAs

5. DIGITAL FORENSICS

The digital forensics process consists of three steps: acquisition or imaging of exhibits, analysis, and reporting. Ideally acquisition involves capturing an image of the computer's volatile memory and creating an exact forensic duplicate of the media, often using a write blocking device to prevent modification of the original. However, the growth in size of storage media and developments such as cloud computing have led to more use of 'live' acquisitions whereby a 'logical' copy of the data is acquired rather than a complete image of the physical storage device. Both acquired image (or logical copy) and original media/data are hashed (using an algorithm such as SHA-1 or MD5) and the values compared to verify the copy is accurate. During the analysis phase an investigator recovers evidence material using a number of different methodologies and tools. The actual process of analysis can vary between investigations, but common methodologies include conducting keyword searches across the digital media (within files as well as slack space), recovering deleted files and extraction of registry information (for example to list user accounts, or attached USB devices). The evidence recovered is analyzed to reconstruct events or actions and to reach conclusions, work that can often be performed by less specialized staff. When an investigation is complete the data is presented, usually in the form of a written report, in lay persons' terms.

6. ENGINEERING AND ARCHITECTURE

All the industrial infrastructures must be designed to be robust against cyber attacks databases attacks, and IT networks or communications systems attacks, either directly in real time or a later time. The hardware and software must not only be designed to protect against malware attacks, but it also must be designed with enough flexibility and modularity so that the control software and hardware can be upgraded and improved over time. The design should also be flexible so that any malware attack can be compartmentalized and contained or isolated until repairs are made and normal service is restored. Possible design elements include secret authentication features that are isolated from most system operators and are based on key functions requiring approvals from top management. There also could be delays in some execution of control commands with alerts to high level supervisors before implementation unless verified by an additional security code. Such authentication systems would be most protective against cyber criminal or techno-terrorist attack if they can be executive from a more location. The trouble with such authentication code verification can is if there is a communications or component failure or a supervisor who is suddenly unavailable, blocking a critical valid control command. Such systems require extra redundancy, and no system can ever be failsafe despite what design engineers might claim [7].

7. OPERATION MONITORING

Continuous monitoring is vital to successful network operations of any type of industrial or urban infrastructure, regardless whether this is for transportation, energy systems of all types, communications or IT systems, water and sewage systems, etc [8-10]. SCADA systems not only exercise supervisory control but also provide vital data acquisition to ensure that network operations are as they should be. Continuous monitoring must not only examine incoming data to ensure that networks are performing normally but are also built to detect spurious data providing incorrect information. Thus continuous monitoring might include random coded signals that require a proper authentication response to verify that it is live data coming through rather than faked readout such as simple repeats of previous data reports. In short, continuous monitoring at the human-machine Interface must involve more than passively awaiting problem alerts. Some form of diagnostic authentication system needs to be a part of the continuous monitoring systems of the future.

8. VULNERABILITY MANAGEMENT

Threat detection and testing of end to end systems is vital to the safe and reliable operation of a smart industrial control system. Vulnerability management includes not only executing a successful response to block an attempted intrusion but is an active process of continuous monitoring and testing to make sure that operations are indeed normal and that incoming data is not being synthesized by a cyberattacker. This verification process either involves active testing or authentication of incoming data via coded messaging, algorithms that detect abnormal data, or other testing processes. It is also important to study reports of intrusions from other operational networks and to consider case study reports concerning lessons learned from cyber attacks that have utilized new and improved techniques, software or hardware to stop cyber-attacks against parallel systems.

9. CONCLUSIONS

There are many different approaches to prevent cyber attacks. Access codes, dual authentication systems, smart algorithms that do not allow dangerous activities with regard to dams, bridges, traffic signals, power plants, energy grids and more without the highest level of authorization and multiple authentication codes can be used to prevent abuses of smart infrastructure. Defensive systems can only go so far to protect digital networks and modern urban infrastructure. At some point proactive cyber security systems will need to find the cyber criminals and techno-terrorist attackers and bring them to justice. Changes to the Internet architecture and controls on the Internet of Things (IoT) as it becomes the Internet of Everything (IoE) may be necessary. Likewise efforts to probe the dark web and bring some form of controls to electronic monetary systems such as bit coin may also become necessary. This is no simple or easy task. Personal freedom and liberty from government surveillance are keys to democratic processes. It may well be that clever technological solutions may be found to the problems that come with more and more automation in 21st century society.

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