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# A REVIEW OF METAL NANOPARTICLES INCORPORATED IN POLYMER MATRICES FOR WATER DISINFECTION

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### ABSTRACT

The existence of microorganisms in water sources poses a threat in both environmental aspects and human health. With this, nanotechnology is of great importance nowadays because of their properties such as catalytic activity. optical and electronic properties, and antimicrobial magnetic activity activity. Moreover, the use of polymer matrices for the incorporation of metal nanoparticles takes commercial а advantage to enhance the property of the material. In this context, synthesis such as ex-situ and in-situ of metal nanoparticles together with their antimicrobial activity, and their impregnation in polymer is discussed further matrices to understand the possible approaches in the study. Also, results from several related studies were elaborately compared to recognize the potential of the methods and materials used. These

studies explore the chemistry behind the interaction between metal nanoparticles and the compositions of the polymer matrices. A close scrutiny on the relationship of the properties of metal nanoparticles and the morphology of polymer matrices will allow better understanding on the vet-to-be potential of discovered metal nanoparticles incorporated in different polymer matrices as an antibacterial water filter.

*Keywords:* Synergistic Property Polymer/metal nanocomposite Antibacterial activity Water disinfection Polymer Modifications Adsorption Nanotechnology Morphology

### **Highlights**:

- Different chemical modification s of polymer matrices significantly influences the adsorption capacity of the polymer towards different metal ions
- Comparison of *ex-situ* and *in-situ* synthesis of metal nanoparticles
- Formation of new bonds between the adsorbate material and the functional groups present as composition/component of the polymer matrix
- The morphological structure of the formed nanoparticle was significantly influenced by the type of polymer used and the type of synthesis
- Different antimicrobial assay for qualitative and quantitative analysis such as: disk diffusion method, and colony forming method.

### Vocabulary:

**Adsorption** – the process by which materials or substance are accumulated at an interface between the solid surface and the bathing solution. Solute molecules present in the solution is usually removed and attach to a solid surface.

**Cellulosic Materials** – composed of all materials that are derivatives of cellulose. Synthetic or semi-synthetic materials that are characterize by major constituent which is cellulose.

**Ex-situ synthesis** – a process by which pre-synthesized nanoparticles are dispersed to the layers of matrix. In this process, the matrix used only serves as a dispersion medium and the synthesis of nanoparticles are externally done.

**Incorporation** – is a process of inclusion of one material into a surface which it is being incorporated.

**In-situ synthesis** – a process by which the synthesis of nanoparticles is done internally upon dispersion in a matrix and addition of reducing agents. The nanoparticles are thoroughly dispersed and produced beneath the deepest part of the matrix.

**Natural Fibers** – fibers that are produced by plants, animals and geological process by which it is commonly used as a component composite material that exhibits distinct properties.

**Nanoparticle** – it is a microscopic particle by which at least one of its dimension ranges below 100 nm.

**Polymeric Matrix** – a composite material by which organic polymer matrix bound together short and continuous fibers.

**Synergistic effect** – the results of combination of two materials creating a synergy that enhances effect to another force or agent.



**Graphical Abstract** 



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In the several past years, contaminated sources of water have been a major environmental problem that affects every community around the world. The demand for clean drinking water increases exponentially as а response for the yearly increased in world population. One of the challenging problems that arise from this increase, is the clean water shortage and the concerns over the access to safe drinking water.<sup>37</sup> The presence of microorganisms in different sources of water drastically cause different health problems and hazards. environmental Since microorganisms grow exponentially, their existence in water streams spread the contamination thus making them a major hazard to the lives of many. Estimates suggest that, there are 1.8 billion of that consumes contaminated people drinking water and causing different health problems and death.<sup>7</sup> Through this statistical result it can be concluded that the existence of microorganisms in the water sources poses a significant hazard to human health. In this regard, different studies were conducted in development of different disinfection agents and

processes which were able to produce bacteria-free drinking water. In the recent years, many classifications of disinfection agents were introduced and were studied to determine its efficiency and capability.

Nanotechnology is an important field of research which have developed different innovative methods, processes, design, characterization and synthesis of different particles structure ranging from approximately (1-100 nm). It primarily deals with the distinct characteristics of nanomaterials such as their improved physical, chemical, biological properties and functionalities because of their improved reactivity that lies from the structure and surface area of the nanoparticles. It is known that when a material was significantly small, its surface area increases thus the reactivity of the surface and- related effects also This increases. shows that the characteristics of materials in nanoparticles form can be significantly different from the properties of the same material in a bulk form. The synthesis of nanomaterials is growing rapidly in the research area with a great potential to make technologically advanced and useful understanding materials. thus, their

behavior and properties will be of great importance. New applications of nanoparticles and nanomaterials are increasing rapidly, and some of these nanoparticles have actually proven to be good catalysts that also show bactericidal effects.<sup>24</sup> This introduces the key idea of synthesis of metal nanoparticles. The metal is known to have biocidal abilities which makes it efficient in different disinfection processes however its synthesis into nanoparticles form drastically elevates its property.

current years, In the metal sighted nanoparticles are to have numerous beneficial importance because of their properties such as catalytic activity, optical and electronic properties, magnetic activity antimicrobial and activity. According to studies of Plaza, nonessential metals have been а significant disinfection agent because of biocidal activities even in low its concentrations. Different non-essential metals were found to have the capability to inhibit the growth and simultaneously enter the cell membrane of microorganism disrupting the cell cycle. Their presence even in low affect the microbial concentrations

activity thus making them a potential disinfection agent. Essential metals also exhibit significant efficiency as a biocidal agent at certain amounts despite their relevance in biochemistry of organisms. Because of this capability of metals acting as biocidal agents, metals have been used for centuries in different applications as an antimicrobial agent in agriculture, healthcare and industry in general. However, the applications of these metals as a biocidal agent have limitations which originate from the metal itself. Even though they have significant antimicrobial effect, their usage was limited in being an additive for other biocidal agents thus making them less efficient and recognized. These limitations rooted in the nature and form of the metals itself. Synthesis of metal nanoparticles have greatly enhanced the biocidal ability of the metal. Different studies states that the morphological structure of metals in nanoparticles have elevate its efficiency in disrupting the cell membranes causing toxic effects to the microorganisms. However. upon contact of these nanoparticles with flowing water poses a threat of leaching of metal ions. The migration of these metal ions due to shear dissolution different or my cause

environmental problems. This is the limitations of past studies in the synthesis of metal nanoparticles and its application in disinfection processes.

Recently, different applications in material science extended the ability of metals through their incorporation in different matrices. One of the innovative synthesis routes for of metal nanoparticles is its incorporation into composites. This polymer method emerges as a new route in further extending the applications of biocide metals in various disciplines. The properties of nanocomposite materials do not only depend on the individual property of each component but also on the morphological and interfacial characteristics arising from the combination of distinct materials.<sup>14</sup> The synthesis of metals in a nanoparticle form and its incorporation to matrices of cellulose, activated carbon and other composites have paved the way for enhancing their microbial behavior. In this regard, polymer composites emerge effective route for further as an developing the applications of biocidal metals. For instance, the incorporation of metals in polymer matrices such as

starch, cellulose, alginate, carrageenan, chitosan and among others have gain significant relevance in the efficient biocidal activity of metals.<sup>32</sup> The incorporation of metal nanoparticle into a polymer composites regulates the possibility of loss of particle or ions that could migrate into flowing water. That is why different parameters are needed to be considered in the incorporation of metals into polymer matrices. The impregnation process extended the functionality of the metal nanoparticles and significantly improved its efficiency as a biocidal agent. It is known that the antimicrobial properties of the metal nanocomposite do not only rely on the individual capabilities of each component but also considers the morphological and interfacial interactions arising from the combination of distinct materials.<sup>32</sup>

In the recent years, natural cellulose fibers with Nano porous surfaces features were reported to be incorporated in the *in-situ* synthesis of noble metal nanoparticles. The metal ions were impregnated into the cellulose fibers by the usage of their advantage of having their inherent porosity and followed by the reduction of metal ions into nanoparticles. Studies states that the high oxygen density of the cellulose and its Nano porous structure makes it an effective Nano reactor which stabilizes the in-situ synthesis of different metal nanoparticles.<sup>10</sup> Cellulose has critical importance namely because is the most abundant and widespread biopolymer on Cellulose Earth. is an abundant biopolymer that can be found in numerous plants, algae and some cvanobacteria. The association of cellulose with metal nanoparticles offered functionalities and intrinsic further of antimicrobial development the capability of biocidal metal nanoparticles.

Synthesis of metal nanoparticles and its impregnation into the polymer matrices such as cellulose fibers have been greatly developed throughout the years. Synthesis of metal nanoparticles such as copper, silver, gold, titanium oxides and zinc oxides were further developed by incorporating them into a polymer producing matrix а nanocomposite which contains significant biocidal characteristics. However. synthesis of some of these metals require a costly procedure and the availability of the metal itself possess limitations which

hinders the production of a noble metal polymer nanocomposite. Thus, different studies were conducted in the synthesis of combination of two metal nanoparticles and their synergistic antimicrobial activity. The morphological structure of the combination of two metal examined nanoparticles were and analyzed to determine the different significant factors which proves their efficiency. Previously, few studies have been carried out with a combination of two metals such as silver and copper and their incorporation with activated carbon. Different ratio of the combined metals was analyzed by determination of their efficacy as an antimicrobial agent and whether their combined distinct characteristics improved the capacity of the nanocomposite as a whole.7

For the past years, different types of polymeric matrices were used for the impregnation and synthesis of metal nanoparticles. Ag-Cu nanoparticles were already incorporated into matrices such as chitosan. activated carbon and cellulose. incorporation For its in cellulose. different types and classifications were considered for the efficient synthesis of metals. However,

one problem of cellulosic matrices is its low absorptivity and retention prior to its modification. In this regard, studies states that modification of the cellulose polymer matrices is necessary to achieve a level of high capability to adsorb and synthesize metal nanoparticles. Abaca Fiber or Manila Hemp is one of the excellent sources for the cellulose that can be applied as a matrix for the impregnation of metal nanoparticles. At present, the various applications of this fiber are limited into its usage in cordages, textiles and handicrafts. Abaca fibers are natural fibers that are primarily formed by combination of three basic polymers such as cellulose, hemicellulose and lignin. The proportion of cellulose in the chemical composition of abaca fibers ranges from 63% to 68%.

At present, the various applications of this fiber are limited into its usage in cordages, textiles and handicrafts. Studies have states that cellulosic matrix can be a viable matrix for the incorporation of metal nanoparticles. it is known that the natural cellulose preset in abaca fiber is a potential substrate for the in-situ synthesis of metal nanoparticles. The incorporation of metal nanoparticles into

conducting polymers such as cellulose present in Abaca fiber provides enhanced performance for both the "host" and the "guest, and this can lead to interesting physical properties and important potential applications.<sup>21</sup> This shows that Abaca fiber serves а beneficial functionality for the synthesis and impregnation of Ag-Cu Nanoparticles. The treatment of Abaca fiber enhances its ability to adsorb these metals thus preventing the possibility of leaching. With that, Abaca fiber widens its usage and applications and exceeds from the common limitations of its functionality.

Water disinfection agents were developed for the purpose of reviving polluted water sources. Water is precious to all living things because it is essential for survival. However, because of the growing community the rapid spread of pollution poses a significant threat to the lives of many. This shows that their removal aside from reduction process are essential and already a necessity.<sup>37</sup> In this regard, different researches were conducted the filtration for and disinfection of water sources. Usage of chlorinated agents. UV radiation. antimicrobial filters, and others are

already a trend and shows efficiency and potential. But the usage of chemicals in the disinfection process alters and react with the composition of the flowing water along the process. Thus. these antibacterial agents were not recommendable for the disinfection of infected water sources. In this case, the reliability towards the application of some metals as a biocidal agent take the interests of different studies. The toxic effects of metals towards the cell membrane of the bacteria were taken advantage for its application in disinfecting water. Several experiments were conducted in the efficiency of this metal to disrupt the growth and existence of different microorganisms in water samples. Although, the effectivity was found to be successful another limitation was determined such as the possibility of metals to leach and flow with the water sources. Some metals like silver, copper, zinc, iron, lead, aluminum, and gold have proved to be an efficient disinfectant but some of them are toxic for human. Thus, the advent of nanotechnology made potential nanocomposite а water decontaminator and replacement to current chemical disinfectants.<sup>37</sup> Incorporation of Ag-Cu nanoparticles into

the matrix of abaca fiber suggests a potential and viable water decontaminator that could replace efficient chemical agents without generating harmful by-products.

This review aims to elaborate the functionalities and vital roles and contributions of both nanotechnology and polymer science in the widening demand of scientific researches for its combined application. And also. to give а background and information about its in the field application of water disinfection. How essential its synergistic further property that extend its antibacterial effect to certain pathogenic bacteria. Moreover, this review focuses in interpreting the chemistry behind the interaction of the metals and the components of the matrices. How these interactions significantly influence the morphological synergistic property, features of structures and the nanocomposite.

### 2. Methodology

### 2.1 Adsorption Capacity of Cellulosic Matrices

2.1.1 Alkali-Treatment of Polymer Matrices

Different chemical modifications of different cellulose matrices for the entrapment of metal ions were studied by various researchers. In which in both studies of Qin et.al. 2005; and Amin et.al. 2016, alkali-treatment with the usage of alkali hydroxide, NaOH, was executed to their respective cellulosic fibers.<sup>34,3</sup> This type of chemical modification primarily conducted alter the surface to modification of the respective cellulosic fiber for better adsorption of metals such as: copper, silver, and lead. Both studies focused on the effect of the alkalitreatment in the adsorption capacity of the cellulosic fiber with metal ions in aqueous solution. The two studies also difference investigated the in the morphological feature of the treated and untreated cellulosic fiber. Both studies inferred the significant effect of the alkali treatment of the fiber in its adsorption property.

### 2.1.2 Carboxylation and Chlorination of Polymer Matrices

Other chemical modification such as chlorination was the main method of modification that, Donia et.al. 2013,

performed in the cellulose to elucidate its effect in the adsorption of mercury (II) in aqueous solution.9 The modified an cellulose shows great adsorption capacity towards the metal ion. Moreover. carboxylation and sulfonation are some of the most widely performed chemical modification of cellulosic materials. In the previous work of Bergh, 2011, he carboxylation conducted the and sulfonation of cellulose and investigated its significant influence in its adsorption property. Same carboxylation method was executed by Sehagui et.al. 2014, with the use of 2,2,6,6-tetramethyl-1piperidinyloxy (TEMPO) as its modifying agent. Both carboxylated cellulose material show great adsorption capacity with respect to each metal used as adsorbate material. This efficient effect of chemical modifications the in optimization of the adsorption property of cellulosic matrices somehow became the subject of most researchers.

### 2.1.3 Electrospinning of Polymer Matrices

Some studies focus in the reinforcement of matrices thru surface modification such as electrospinning. In the 2014 work of Kampalanonwat, and Supaphol, reinforcement of Aminated Polyacrylonitrile was executed. The said study subjected the polymer in electrospinning and mainly evaluated its effect in its adsorption property towards the metals silver, copper, lead, and iron. The final material exhibits highest adsorption towards silver and copper metal. Further elucidation and investigation of the chemistry behind these promising characteristics have been considered as an unexplored field - a yetto-be discovered science.





Figure 1. Adsorption of metal ions in polymer matrix2.2 Synthesis of Metal Nanoparticles

### 2.2.1 In-situ and Ex-situ Synthesis

Different ways of synthesis of metal nanoparticles were introduced by different studies. Continuous

development in this area is the main focus of researches in providing chemical routes that suggests the most efficient, cost-effective and reliable process. In this sense, there are two major ways in the synthesis of metal nanoparticles. Namely, *in-situ* synthesis and *ex-situ* synthesis shows reliable generation of numerous ways in reduction of different metals to metal nanoparticles. *Ex-situ* synthesis takes advantage of the process in which metals are synthesized externally and then incorporated in the layers of a matrix which serves as a dispersion medium only. Different studies states that this process efficient ensures the production of metal nanoparticles before it is introduced in a matrix to further widens its range of applications and usage. However, this kind of process is not cost-effective because of its time requirement and usage of various chemicals. In this regard, the process of *in-situ* synthesis gains the interests of the scientific community. In-situ synthesis of metal nanoparticles takes advantage of capability of different natural the polymers to both impregnate and reduced metals. In this way the time consumed in experimentation is being minimized while the efficiency is being maximized. In the

study of Palza, *in-situ* synthesis is much preferred because of its ability to stabilize and disperse the metal because of the presence of macromolecules of different functional groups.<sup>27</sup> The process of *in-situ* synthesis considers the ability of polymer matrices as a reaction medium. In this way, the usage of the distinct properties of the polymer matrix are being maximized.



Figure 2. ex-situ synthesis of metal nanoparticles





### 2.2.2 Bottom to Top and Top to Bottom

Aside from *in-situ* and ex-situ synthesis of metal nanoparticles, in the review study conducted by Ahmed et.al, two general approach for synthesis of nanoparticles was introduced.<sup>1</sup> These approaches are known as bottom to top approach and top to bottom approach. Although this concept is sometimes neglected, the study clearly demonstrates a significant difference in the produced nanocomposite in each approach. In the (1) bottom to top approach, nanoparticles are being synthesized through selfassemble of atoms to new nuclei using chemical and biological methods that could result into nanoscale particles. While in (2) top to bottom approach, bulk materials undergo size reduction which results to breaking down of the material intro fine particles with various lithographic techniques such as milling, grinding and thermal ablation. The difference in these approaches is the nanoparticles produced after the process. Although method (2) employs an efficient method for production of nanoscale materials, the by-products and the product itself exhibits toxicity. This is the same with some of the methods that is employed in method (1) which includes processes such as pyrolysis, vapor deposition and electrochemical However, the precipitation. green synthesis suggested by different studies lies in the concept of bottom to top approach which have demonstrated a much better process for synthesis of nanoscale materials. The green synthesis of metal nanoparticles includes the usage of plant extract, bacterial cellulose and fungus. These processes are recommended for the materials produced are non-toxic.

studies concerning biomedical applications suggests that natural

polymers are much more efficient in providing reliable metal nanocomposites. In this regard, the incorporation of metals starch, into alginate, chitosan and cellulose as a matrix for composite emerges as polymer for effective route widening developing its biocidal applications.<sup>32</sup> different Among these matrices, cellulose and chitosan are studied the most. According to (Zhang et.al., 2005), silver containing chitosan fibers are highly antimicrobial. In the study, the chitosan fiber

2.3.1 Metal *Nanoparticles* Natural Impregnated in

In the *in-situ* synthesis of metal

nanoparticles, different studies showed

metals into the matrices of a polymer may

it be natural or synthetic. However,

impregnation

2.3 Impregnation of Metal Nanoparticles in

Polymer

**Polymer Matrices** 

numerous

carrageenan, an and polymeric undergo deacetylation of 85 %.34 The chitosan fiber was treated in aqueous solution of 2% acetic acid and 5% NaOH solution. The chitosan fibers were heated in a water bath before they are washed and

of

process

dried. For cellulose fibers, two distinct methodologies using two distinct substrates are being studied by.<sup>31</sup> In the study, the antibacterial property of silver nanoparticles incorporated in cellulose fibers namely bacterial cellulose and vegetable cellulose were observed. In the procedure experimental the silver nanoparticles were grown in the matrices through direct reduction of AgNO<sub>3</sub> with simultaneous addition of reducing agent such as NaBH<sub>4</sub>. under vigorous stirring. This procedure was both done in the incorporation of Ag nanoparticles into bacterial cellulose (BC) and vegetable (VC). The difference cellulose in substrates used affect the morphological structure of the nanocomposite produced. In the SEM analysis, the Ag nanoparticles in VC shows a continuous film covering the layers of cellulose while there are discrete Ag nanoparticles with an average size of 38 nm was observed when BC is used as a substrate. Thus, (Pinto et.al., 2009) concluded that both BC and VC shows a desirable result for the incorporation of Ag nanoparticles.<sup>31</sup> Significant antibacterial activities were demonstrated in both distinct cellulosic matrices thus it is concluded that cellulose/silver nanocomposite is

anticipated to have significant biomedical applications.

### 2.3.1.1 Vegetable and Bacterial Cellulose

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The incorporation of Ag in vegetable cellulose and bacterial cellulose shows significant antibacterial activity against microorganism. In the study of (Pinto et.al., 2013) the incorporation of copper nanofillers in bacterial cellulose and vegetable cellulose shows significant results.<sup>30</sup> difference in In the experimental method, CuSO<sub>4</sub>·5H<sub>2</sub>O and sodium citrate solution were mixed and stirred for an hour. A dropwise of NaBH<sub>4</sub> and NaOH is then added and vigorously stirred. This process was both done in a vegetal cellulose and bacterial cellulose. It was then concluded in the study that vegetal cellulose fibers results into a more effective and efficient matrix with copper of nanoparticles for production antibacterial materials. However, results are different in the study of (Araujo et.al., 2017) which stated that copper nanoparticles incorporated in bacterial cellulose is a more efficient matrix to avoid copper surface oxidation.<sup>4</sup> The difference in effectivity relies on the morphological structure of the metal

nanocomposite produced. Ag nanoparticles have distinct structure when it is incorporated into a bacterial cellulose compared to vegetal cellulose. In this regard, studies also show that copper nanoparticles incorporated in either type of cellulosic matrix produced a metal polymer nanocomposite with a significant difference in antibacterial activity.

The impregnation of metal nanoparticles into the polymer matrix under in-situ synthesis usually used direct reduction of metal salts through electrostatic assembly process. However, Li et.al., developed a different approach by using hydrothermal method as a green synthesis for Cu from CuO using cellulose as the reducing agent. In this regard, a study conducted by (Araujo et.al., 2017) shows the hydrothermal synthesis of bacterial cellulose/copper nanocomposite.<sup>4</sup> In the experimental method, Cu(NO<sub>3</sub>)<sub>2</sub> solution was added into a bacterial cellulose membrane in a PTFE cup. The mixture was stirred for an hour then NH<sub>4</sub>OH was added. The solution is then introduced inside a steal stainless reactor. The thermal treatment for the bacterial cellulose/copper nanocomposites were done in varying

heating times. It is concluded in the study that varying heating times of the solution in hydrothermal method affects the copper content in each nanocomposite. The different BC-Cu nanocomposites also showed significant antimicrobial activity against tested microorganisms. The study hydrothermal shows that synthesis effective route merges an for as production of copper nanoparticles in cellulosic matrices.

### 2.3.2 Influence of Solvents in Impregnation

Conventional methods in synthesis of metal nanoparticles usually involves usage of solvents. This is applicable in synthesis and hydrothermal green synthesis conducted in the studies of Pinto et.al. and Araujo et.al.<sup>4,30,31,32</sup> However, in the study of Eisa at.al. the incorporation of metal nanoparticle to cellulose nanocrystals are done through solid-state synthesis. In the experimental methods, cellulose nanocrystals were milled together with the metal salt precursor in an agate mortar without addition of solvent. The samples were then kept for 24 h allowing the adsorption of metal ion into the surface of cellulose nanocrystals. A 0.1 g of ascorbic

acid powder is then added before washing the mixture and drying for 24 h. Results demonstrates that the addition of ascorbic acid induced the reduction of metals showing that cellulose nanocrystals alone is not enough to act as the reducing agent. In the study, it showed that solid-state synthesis is a possible method for synthesis of metal nanoparticles. However, the antimicrobial property of the synthesized metal cellulose nanocrystals hybrid is not studied instead its catalytic activity was measured.

### 2.3.3 Chemically Modified Polymer Matrices

Chemical modification of the polymer is а significant process prior to impregnation and synthesis of metal nanoparticles. According to Alfredo, chemical modification of polymer can be done by the addition of synthetic polymers into the surface.<sup>2</sup> However, the difference of this method lies in the effect of the polymer to microorganisms. The modified polymer surface can only repel the microorganisms in contact. Thus, different studies employed methods that chemically modified polymer surfaces to strengthen the impregnation of metal

nanoparticles. In the study of Zhang et.al., the chitosan fiberswere treated first in an acetic acid solution and sodium hydroxide solution before washing and drying.<sup>34</sup> This aims to deacetylate the chitosan fibers to chemically modified its structure. The study of Palza states that cellulose modification can be done by periodate-induced oxidation followed by covalent attachment of the biopolymer chitosan.<sup>27</sup> Even though treatment of polymeric matrices bv chemical modification is a trend, there are still experimental procedures that resorted for a direct synthesis and reduction of nanoparticles. In the study of Pinto et.al. and Araujo et.al., the cellulosic polymer used did not undergo modifications instead the experimental procedure is a direct reduction of copper nanoparticles by subsequent addition of the reducing agent.<sup>4,30,31,32</sup> In this sense, chemical modification varies depending on the procedures of heating the metal nanoparticles synthesis. However, it is undeniable that through chemical modification the morphological structure of the metal nanocomposite produced shows a significant difference.

### 2.4 Release of Metal ions

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One important property of an antimicrobial material is its stability and permanence of the antibacterial activity over time when it is introduced and made contact into aqueous solution. In this regard, several studies suggest that methods concerning the measurement of the release of metal ions over period of time is a necessity. As metal polymer nanocomposites are used in antibacterial applications it is appropriate to tests its efficiency and permanent activity by monitoring the release of metal ions over a period of time. In the study of Pinto et. al., a stable and prolonged release of ions at suitable concentration is crucial. It is demonstrated that too slow or too fast release of metal ions can be a drawback in its main applications. Thus, in the study selected nanocomposites was prepared through cutting disc shape silver bacterial cellulose composite and silver vegetal cellulose composite. These composites were then immersed in a saline solution at 37°C for a short period of time and measured at various times. Data reports shows that Ag ions are released through diffusion from the nanocomposites to the saline solution. For a short period of time, all nanocomposites were able to released more than 10% of all the silver content in

24 h. This results primarily shows that

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the morphological structure and the position of silver nanoparticles in the layers of polymeric matrices greatly affects the release. The preparative methods and chemical modification of the polymer matrices also considered as a determining viable factor in the possibility of release of metal ions. Studies states that the presence of metal nanoparticles in the layers of polymeric matrices are not enough. Methods should be developed entrapment of nanoparticles in the structure itself of polymeric surfaces. In this regard, according to Maneerung et.al., increase in molar ration between reducing agent such as NaBH4 and metal precursor enables the impregnation of silver into the deeper structures of the bacterial cellulose.<sup>22</sup> Thus, the study suggests that there is a significant difference in addition of more amounts of reducing agent.

Title	<b>Bacterial Strain</b>	Preparative Methods	Authors
Solid-state synthesis of metal nanoparticles supported on cellulose nanocrystals and their catalytic activity	-	Incorporation of metal nanoparticle to cellulose are done through solid-sate synthesis where solvent is not used in the mixture.	Eisa, W.H., Abelgawad, A., and Rojas, O. (2018)
Plants Extract Mediated Synthesis of Silver Nanoparticles for Antimicrobial Applications: A Green Expertise	Numerous bacterial strains were included in the study	Two approach was introduced namely (1) top-to-bottom approach and (2) bottom-to-top approach	Ahmed, S., Ahmad M., Swami, B.L., Ikram, S. (2015)
Antimicrobial Polymers with Metal Nanoparticles	Staphylococcus aureus and Escherichia coli	In-situ synthesis is preferred because it enables metal nanoparticles to stabilize and disperse in matrices	Palza, H.(2015)
The Absorption and Release of Silver and Zinc Ions by Chitosan Fibers	E. coli., Staphylococcus aureus (S. aureus) and Bacillus subtilis (B. subtilis)	Chitosan fibers undergo 85% deacetylation through treatment of aqueous solution of acetic acid and Na0H	Zhang, C., Chen. Y., Chen, J., Zhu, C., and Qin, Y.(2005)
Antibacterial activity of nanocomposites of silver and bacterial or vegetable cellulosic fibers	B. subtilis, S. aureus and K. pneumoniae	Silver nanoparticles were incorporated in two kinds of cellulosic fibers namely bacterial and vegetable cellulose	Pinto, R.J.B., Marques, P., Neto, C., Trindade, T., Daina, S., and Sadocco, P.(2009)
Antibacterial Activity of Nanocomposites of Copper and Cellulose	S. aureus and K. pneumoniae	Copper nanoparticles were incorporated in two kinds of cellulosic fibers namely bacterial and vegetable cellulose	Pinto, R.J.B., Neto, C., Trindade, T., Daina, S., and Sadocco, P.(2013)
Hydrothermal synthesis of Bacterial Cellulose– Copper oxide nanocomposites and evaluation of their antimicrobial activity	S. aureus, S. enterica, E. coli, and C. albicans	Thermal treatment for the bacterial cellulose/copper nanocomposites were done in varying heating times.	Araujo, I. et.al., (2017)

**Table 1.** Selected studies concerning different preparative methods and synthesis of metal<br/>nanoparticles/nanocomposites(Unavailabledatawereleftblank)

### 2.5 Antibacterial Assay

2.5.1 Application of Polymer/Metal nanocomposite for Water Disinfection

Metal nanoparticles incorporated in the matrix of various polymers are distinguished to have significant purpose and usage especially in water purifications. In the process of biological treatments, the usage of metal nanoparticles in the layers of water filters are one of the major applications of separations in biological water purification methods. Studies suggests that the presence of metal nanoparticles in different biomedical tissues and fabrics plays an important role in the disruption of cell membranes of microorganisms. In this regard, development of water filters is one method in providing efficient biological water treatment process. In the study of Singh et.al., tabulations of different methods of purifications shows the advantages and disadvantages. One of the methods is the microbial treatment of water using a polymer nanocomposite as a water filter. In the study, microbial treatment using this kind of material is an efficient and ecofriendly process but is a

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slow type of method. Thus, development of appropriate polymer nanocomposites that exhibits an efficient water treatment is a necessity. Cellulose acetate fibers embedded with Ag nanoparticles were found to be effective against bacteria such as Escherichia Coli (E. coli). The process done to determine the efficiency of the metal-polymer composite be can determined through two distinct methodologies such as disk diffusion method and colony forming count method.

### 2.5.2 Colony Count Method

In the study of Araujo et.al., the BC-Cu nanocomposite produced through hydrothermal synthesis were subjected in antimicrobial assay using the process of disc diffusion method in agar. The experimental procedures include the cutting of the nanocomposite into a disc shape with a diameter of 1 cm. The diskshaped nanocomposite then was autoclaved for several hours before introduction into The agar plates. bacterial inoculum to be used were uniformly spread into the agar plates using sterile cotton swabs and the nanocomposite discs are then introduced. After incubation for about 18 h, the zones

of inhibition around the discs were then measured. The process of disk diffusion method is important in qualitatively determine the efficiency of the nanocomposite against strain of microorganisms. However, different studies primarily resort into the colony forming count method which involves contact of nanocomposite with different serial dilutions of microbial suspensions. This kind of process is favored due to the fact that it is able to distinguish quantitatively the effect of the nanocomposite towards the microbial growth.

colony forming count In the method, a microbial suspension is being passed through the polymer nanocomposite in a specified time. The treated solution is then subjected into pour plating and then undergo bacterial incubation for 24 hours. The effectivity is then determined by the number of colonies forming units in each agar plates. In the study of (Pinto et.al.2009), the antibacterial activity of the cellulose/silver nanocomposite produced was tested based on the standard methodology used in textiles in verifying the antimicrobial additives included in

The the fiber structure. bacterial suspension prepared was added into the fiber structure and subjected into vigorous shaking which ensures the contact of the polymer nanocomposite to The the suspension. bacterial concentration is varied and the time it for each takes solution is being monitored. At 0 and 24 h, the bacterial concentration in the suspension were determined through the process of plating untreated and treated serial dilutions in an agar plate. This process was done to obtain the overall number of bacteria thus is an important method in the effectivity determining of the produced metal nanocomposite. According to the study of (Pinto et.al., 2013), in the antimicrobial assay of copper cellulose nanocomposites, the nanocomposites samples were also subjected to contact with the microbial liquid suspensions. The colony forming units are then determined by plating serial dilutions on plate count agar and then incubated for specified times to determine the reduced microbial growth.

### 2.5.3 Disk Diffusion Method

In the antimicrobial activity studies of Maneerung et.al., both disk

diffusion method and colony forming count method was used to determine the effectivity of the silver nanoparticlesimpregnated bacterial cellulose. The disk diffusion method was conducted through freeze-dried silver cutting the nanoparticle-impregnated bacterial cellulose into disk shapes like other studies. The diameter of the disc shapes nanocomposite was measured 1.5 cm and autoclave for 15 minutes only. After sterilization autoclave in an the nanocomposite was then placed on an agar plate containing the cultures of E. coli and S. aureus and incubate for 24 h. For the colony forming count method, the nanocomposites were also cut into disc shape and eight pieces were packed into a small column. Two groups were prepared for experimental set-up, the first group is seeded with a sterile solution while the other seeded bv microbial was suspensions of the E. coli and S. aureus. The columns were incubated in a shaking incubator for 24 h. This method was employed in the study to determine the difference in viable count of the microbial growth in 0 and 24 h. Results in the study shows that the nanocomposite exhibit an inhibition zone which measures an inhibition ring of 2 mm for E. coli and 3.5

mm for S. aureus. These results were obtained from the disc diffusion method employed in the study. Through the use of this method, it is possible to qualitatively determine the capacity of а nanocomposite to inhibits bacterial growth. This method is also efficient since in the study no inhibition zone was observed when pure bacterial cellulose was used as a control. Supporting the claims of the biocidal ability of silver nanoparticles. In the colony forming count method, results show that there is a 99.7% and 99.9% reduction in viable count of E. coli and S. aureus after incubation 48 h of incubation. This shows that the method used was an effective process to demonstrate antimicrobial property of the silver nanoparticleimpregnated bacterial cellulose. Several studies that includes water disinfection as application of metal the polymer nanocomposite prefers the colony forming count method. Studies found this method much efficient than the disc diffusion method. Since water disinfection process involves contact of water into the metal polymer composite the decrease of viable count of microorganisms are clearly demonstrated. Although disc diffusion is not usually applicable for

demonstrating water disinfection ability of metal polymer nanocomposite, it is still an effective antimicrobial assay method. In this regard, studies still find disc diffusion method and colony forming count method as an effective process for demonstrating antimicrobial property results of metal polymer nanocomposite.

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Title	Bacterial Strain	Antimicrobial Assay Methods	Authors
Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing	Staphylococcus aureus and Escherichia coli	Antimicrobial assay includes both disc diffusion method and colony forming count method	Maneerung, T., Tokura, S., and Rujiravanit, R. (2007)
Antibacterial activity of nanocomposites of silver and bacterial or vegetable cellulosic fibers	B. subtilis, S. aureus and K. pneumoniae	Bacterial suspension was added into BC-Ag and VC-Ag nanocomposites and subjected into vigorous shaking at 0 and 24h. The difference in number of bacterial growths was determined through pour plating of treated and untreated bacterial suspension.	Pinto, R.J.B., Marques, P., Neto, C., Trindade, T., Daina, S., and Sadocco, P.(2009)
Antibacterial Activity of Nanocomposites of Copper and Cellulose	S. aureus and K. pneumoniae	Copper cellulose nanocomposites were subjected to contact with microbial suspension and determine the reduced microbial growth.	Pinto, R.J.B., Neto, C., Trindade, T., Daina, S., and Sadocco, P.(2013)
Hydrothermal synthesis of Bacterial Cellulose– Copper oxide nanocomposites and evaluation of their antimicrobial activity	S. aureus, S. enterica, E. coli, and C. albicans	The hydrothermal synthesized BC-Cu nanocomposite were subjected into disc diffusion method to determine zone of inhibition.	Araujo, I. et.al., (2017)

Table 2. Selected studies concerning antimicrobial assay methods

### 3. Results and Discussion

## 3.1 Adsorption Capacity of Polymeric Matrices

3.1.1 Carboxylated and Sulfonated Polymer Matrices

Chemical modification such as: alkali treatment. acetylation, carboxylation, and sulfonation of cellulose are some of the widening cellulose modification in the recent years. In 2011, Magnus Bergh conducted two modifications of cellulose. He primarily investigated the effects of carboxylation and sulfonation of cellulose to its adsorption and retention properties. And according to his study, both two modification of the cellulose were done straight forward. Herein, both the adsorption and retention properties of the cellulose were significantly influenced by the two modifications. In his study he also emphasizes that the carboxylated fiber shows greater adsorption and retention property than the sulfonated fiber.

## 3.1.2 Alkali-Treated Polymer Matrices

Another cellulose modification is alkali-treatment, in which the effects of alkali compounds in the adsorption and morphological properties of the fiber were the main subjects of different studies. The 2017 study of Malenab et.al., focuses in the reinforcement of waste abaca fiber, and assess its tensile strength and morphological features. Showing the tensile strength of the alkali treated abaca fiber increase, due to the effect of the altered morphological surface of the fiber; increased the roughness of the surface of the fiber.

In the 2012 study of Punyamarthy et.al., and 2009 study of Ozturk et. al. the two studies both investigated the effect of alkali treatment in the adsorption property of fiber. Both studies inferred that the adsorption capacity of the fiber increases as the concentration of the alkali hydroxide, NaOH, increases. From the results of the study of Punyamarthy et.al., the treated abaca fiber shows lower moisture adsorption than the untreated fiber. While in the study of Ozturk et. al., they inferred that as the concentration of the alkali hydroxide, NaOH, increases the number of swollen and splitted cellulose fiber also increases. And this increase in the swelling and splitting of the cellulose fiber significantly affects its adsorption and interaction with the complexed heavy metals such as Fe<sup>3+</sup> and Cu<sup>2+</sup>. Additionally, they have mentioned that the formation of metal anchors as fixed complexing sites on the polysaccharide substrate, and the sorption of heavy metals from water on polysaccharide materials are can be attained with an alkali-treated cellulose

fiber. The aforementioned statements were justified by the 1996 study of Lin and Hsieh, and the 2005 study of Qin et.al.

According to both studies, the fibers adsorption capacity of the significantly increases as the concentration of the adsorbate solution increases. Yielding in a greater amount of metal ions adsorbed by the fiber. The Lin, and Hsieh study also give emphasize to the influence of the temperature of the system to the adsorption efficiency of the fiber. While the study of Qin et.al., highlighted the effects of the treatment time to the adsorption capacity of the fibers.

Both studies of Sun et.al. 1998, and Punyamarthy et.al. 2012 characterized the composition of abaca fiber. In tables 1 and 2, cellulose, hemicellulose, and lignin are the found to be the main compositions of abaca fiber in both studies.

Table 3. Chemical composition of abaca fiber (Sun et. al., 1998; Punyamarthy et. al., 2012) (Unavailable data

Composition	% Weight	Comments		
Sun et.al., 1998				
Cellulose	68.32	-		
Hemicellulose	17.32	-		
Lignin	8.50	-		
Moisture Content	0.76	-		
Ash Content	5.10	-		
Punyamarthy et.al., 2012				
Extractives	0.8	-		
Ethanol soluble	0.6	-		
Hot water soluble	4.9	-		
Pectic polysaccharide	0.8	-		
Lignin	12.4	-		
Hemicellulose	20.8	Major constituent		
Cellulose	60.4	Major constituent, predominant polysaccharide		

are left blank)

The vast applications of cellulosic fibers in the material industry and its promising characteristics being а biopolymer caught the attention of most researchers in scrutinizing and evaluating its morphological features, physical and chemical properties. In which researchers have primarily elucidated the effects of its modifications in terms of its adsorption, retention, and thermal properties, and tensile strength. Fractionization and characterization of its composition have become more vital to further understand the chemistry behind its distinct properties, and interaction with other materials.

5.

Authors	Polymer	Modification	Adsorbed Metals	Major Achievements
Wang et.al. (2012)	Polystyrene- supported trimercaptotriazine resi	-	Ag (I)	Adsorption equilibrium was reached at 360mins. Produced a highly selective chelating resin.
Ramya, and Sudha (2013)	Chitosan composite*	Silk fibroin fiber reinforcement	Cd (II) and Cu (II)	The produce composite was an effective adsorbent for the removal of Cu <sup>2+</sup> and Cd <sup>2+</sup> in an aqueous solution.
Yurtsever, M., and Sengil, A. (2012)	Valonia tannin resin*	-	Ag (I)	VTR was able to be utilized for an efficient and simple way of recovering Ag+
Donia et.al. 2013	Cellulose*	Chlorination	Hg (II)	The produce adsorbent was able to show high adsorption capacity towards Hg (II) in aqueous solution
Kampalanonwat, and Supaphol (2014)	Aminated Polyacrylonitrile	Surface modification (electrospinning)	Ag (I), Cu (II), Pb (II), and Fe (II)	highest adsorption capacity towards Ag <sup>+</sup> and Cu <sup>2+</sup> in ions mixture system
Sehaqui et.al. (2014)	Cellulose* and Chitin nanofiber*	Chemical modification with 2,2,6,6- tetramethyl-1- piperidinyloxy (TEMPO)	Cu (II), Ni (II), Cr (III), and Zn (II)	Adsorption of Cu <sup>2+</sup> was correlated with both pH and carboxylate content of the two polymers. Both polymers effectively adsorbed each metal.
Karnitz et.al. (2006)	Sugarcane bagasse*	Chemical modification	Cu (II), Pb (II), and Cd (II)	The modified SBs were able to give a good adsorption capacity for each metal. The adcorption
Amin et.al. (2016)	Palm fibers* and orange peel*	Alkali-treatment (NaOH)	Cu (II), Pb (II), and As (II)	equilibrium was reached after 150mins. And both adsorbent result in higher adsorption of Cu <sup>2+</sup> than Pb <sup>2+</sup> .
Qin et.al. (2005)	Chitosan fibers*	Alkali-treatment (NaOH)	Ag (I), and Zn (II)	Chitosan fibers were able to adsorbed both metals efficiently.
Gregorio, M., Montejo, J., and Porras, B. (2015)	coconut sawdust (Cocosnucifera Linn)	Alkali-treatment (NaOH)	Cu (II)	The adsorptive property of sawdust is accounted to the presence of sterol compounds.

Table 4. Selected studies concerning the adsorption capacity of different polymer, respective modification,

and metal ions (adsorbate). \*=Biopolymer (Unavailable data were left blank)

### 3.2 In-situ Synthesis of Metal Nanoparticles

One of the most facile methods in synthesizing nanoparticles is through in*situ* synthesis. In which, a metal precursor salt is subjected into a medium matrix, then subsequently reduced with the aid of reducing agents such as sodium borohydride, and citric acid. While some studies undergo bioreduction, wherein, a biopolymer is set as the medium matrix and reduction of the adsorbed metal ions occur without the use of external reducing and stabilizing agents. The biopolymers compositions act as effective reducing and capping agent for the synthesis of NPs.

The study of Jyoti et.al., in 2015 uses *Urtica dioca* Linn. leaves as their biopolymer in synthesizing Ag NPs. Wherein the study of Bolaños et. al., in 2014, uses Duguan (*Myristica philippensis Lam.*) extracts as their biopolymer medium for the synthesis of Ag NPs. Both studies inferred the plausible reduction of the silver ions with the absence of an external reducing agent is can be attributed to the hydroxyl groups present in the cellulosic composition of each

The biopolymer. aforementioned statement was given justice by the 2012 article of Pinto et.al. Discussing the vital role and contribution of the organic moieties present in the cellulose of biopolymers for the synthesis of NPs. Carboxylic and aldehyde groups were accounted for the reduction of the silver ions, while the ether and hydroxyl groups act as nanoreactor for the in-situ synthesis of Ag NPs (Pinto, et.al., 2012). Both studies of Amin et.al., 2016 and Bolaños et. al., 2014, concluded the essential\_role of the hydroxyl groups present in the cellulosic composition of biopolymers in stabilizing the formed NPs.

The ability of biocompatible polymer to act as reducing and stabilizing agents in the synthesis of nanoparticles were given emphasize in the 2015 study of Debuy, et.al. Using a biocompatible polymer, they were able to synthesize Ag NPs without the use of external reducing agent, and were able to stabilized the formed Ag NPs by use of the polymer solution itself only. Some studies that uses reducing agents in in-situ synthesizing Ag NPs (Montazer et.al., 2012; Maneerung et.al., 2007; and Kang

et.al., 2017), were able to synthesize monodispersed and uniform in size Ag NPs. However, in the 2015 dissertation of Dikeledi Selinah More, the capping agent he used for the stabilization of the formed Ag NPs, bind too strongly into the NPs making it difficult to isolate from the



solution. In his study, he reasoned out that the nanoparticles formed is possibly too small that they cannot be isolated.

**Figure 4.** Scheme for the formation of Ag NPs from the precursor AgNO<sub>3</sub> solution. The white and black blobs signify the reducing and stabilizing agents present in the natural polymer. **Top:** the reduction of  $Ag^+$  to its elemental form – Ag. **Bottom:** stabilization of the formed Ag NPs.

**Figure 5.** Scheme for the formation of Cu NPs from the precursor CuSO<sub>4</sub> solution. The white and black blobs signify the reducing and stabilizing agents present in the natural polymer. **Top:** the reduction of  $Cu^{2+}$  to its elemental form – Cu. **Bottom:** stabilization of the formed Cu NPs.

Author	Medium	<b>Reducing agent</b>	Major Achievements
Montazer, A., Keshvari, A., and Kahali, P. (2016)	Cotton	Tragacanth gum	The cellulosic chains of cotton, polymeric chains of <i>Tragacanth gum</i> and citric acid have reducing activities to reduce Ag <sup>+</sup> and involve in synthesis of Ag NPs.
Maneerung, T., Tokura, S., and Rujiravanit, R. (2007)	Bacterial Cellulose	Sodium borohydride	Silver ions were readily penetrated into the bacterial cellulose through their pores, and was able to reduce to Ag NPs with the subsequent addition of NaBH <sub>4</sub>
Kang, C., Ahn, D., Roh, C., Kim, S.S., and Lee, J. (2017)	<i>p</i> -aramid fiber	GTAC (quaternary ammonium salt)	Surface of <i>p</i> -aramid became relatively rough after the treatment with GTAC/AgNPs.
Debuy, P., Bhushan, B., Sachdev, A., Matai, I., Kumar, S., and Gopinath, P. (2015)	poly(ethylene oxide)	B	Polymer solution itself acted as the reducing and stabilizing agents.
Jyoti, K., Baunthiyal, M., and Singh, A. (2015)	<i>Urtica dioca</i> Linn. Leaves (Extracts)		The presence of proteins, phenols diterpenes, and phytosterol may be responsible for the capping and stabilizing of the formed AgNPs.
Bolaños, R., Evangelista, R., and Munsayac, J.J. (2014)	Duguan ( <i>Myristica</i> philippensis Lam.) Extracts	-	Duguan ( <i>Myristica</i> <i>philippensis Lam.</i> ) was able to reduce silver ions, and subsequently stabilized the formed Ag NPs.
Bernarldo, B., Icalla, M., and Trinidad, S. (2015)	Super activated carbon	-	The super activated carbon successfully reduced silver ions and synthesized Ag NPs.

**Table 5.** Related Studies of *in-situ* Synthesis of Silver nanoparticles in Different Mediums (Unavailable datawere left blank)

- 3.3 Characterization of Polymer/Metal Nanocomposite
  - 3.3.1 Interaction Between Polymers' Composition and Metal ions

Fourier-transform infrared spectroscopy is one of the techniques that is most carried out in characterizing the chemistry and the possible surface functional groups present in the matrix of the sample that may interact with the metal or can be accounted for its adsorption. Some studies utilize different materials for the adsorption of specific metals such as: Cu, Pb, Zn, Ag, and As. In which they, elucidated the relevance of the composition of the adsorbent material they used; owing primarily to particular functional groups the efficient adsorption of each metal. The studies of Amin et.al., 2016; Sehaqui et. al., 2014; Donia et.al., 2013; Yurtsever and Sengil, 2012; Karnitz et.al., 2006; and Ramya and Sudha, 2013, primarily highlighted the adsorption of biopolymers. properties And characterized the main composition of their specific adsorbent responsible for the adsorption. Having the same extrapolation base on the results of their studies. The main functional groups that is evidently present in biopolymers were

the -OH, -C=O, -CH, C-C, and C-O-C groups. With the comparison of the IR spectrum of the treated and untreated biopolymers, an alteration in the band peaks of each group were revealed. Concluding with a plausible formation of new bond between the metal adsorbed and the main functional groups. The shifting and vibration of bonds between certain peaks attributed were for the efficient adsorption of the adsorbent material. Both studies of Ramya and Sudha, 2012; and Amin et.al., 2016, obtained a disappearance of strong peaks in esters and hydroxyl groups with their treated adsorbent material. Inferring that the disappearance of certain peaks is due to the formation of new bonds between the adsorbate material and adsorbent.

### 3.3.2 Role of Functional Groups in Metal Nanoparticle Incorporation

While some studies deal with the interaction of adsorbate solution and adsorbent. some researchers take advantage of the emerging interest of incorporating metal nanoparticles in different polymer matrices. and evaluating its morphological features. In the previous works of Mallick et.al., 2005; and Lv et.al., 2009, the incorporation of metal nanoparticles in their respective polymer matrices were held. Both studies extrapolated the significant role of the amide functional group present in the matrix of their polymer. Attributing the trapping of the metal ions within the matrix of each polymer, and formation of bonds via electrostatic interaction between the cationic metal and the amide groups. The work of Karnitz et.al., 2006 also justify the vital contribution of the amine and amide functional groups. In his study, he emphasizes the deformation of amide functions is the indication of the interaction of the adsorbed metal from the adsorbate solution; forming a new bond between the function and thus, weakening the band stretching and shifting in the vibration frequencies.

However, in the recent study of Jyoti et.al. 2015, they extrapolated the non-interaction of the amide linkage of the proteins present as biomolecule in the matrix of his medium into the metal ions or nanoparticles. He primarily attributed the capping/stabilizing property of the polymer into its hydroxyl and aromatic compounds. As well as the study of Vimala et. al. 2008, highlighted the essential contribution of the ester groups present in the matrix of their polymer; owing the bond formation between the surface of the polymer and cationic metal.

**Table 6.** Main IR spectrum bands observed inMSBs Samples 1, 5, and 6 (Karnitz et.al., 2006)

Modified	Main bands observed
Sugarcane	(cm <sup>-1</sup> )
bagasse	
Sample 1	1740, 1726
Sample 5	1745, 1650, 1635, 1575,
	1423, 1060
Sample 6	1738, 1651, 1635, 1560,
	1400, 1159, 1060

### 3.3.3 Morphology of Synthesized Metal Nanoparticles

Characterization of particle size is can be done through the use of scanning electron microscopy (SEM), that produces fine images by using electrons as a light source. It can also be used for the determination of the morphological features of the formed NPs. The emerging interest in the study of the promising characteristics of nanomaterials became the main subject of most researchers. Evaluating the relationship between the morphological surface of the matrix and the interacting metals.

Previous studies of Lv et.al. 2009; Maneerung et. al. 2007; Jyoti et.al. 2015; Debuy et.al. 2015; Kang et. al. 2017; and Vimala et.al. 2008, have successfully synthesized well-dispersed and spherical in shape Ag NPs using their respective matrices. The incorporation of the Ag<sup>+</sup> ions in the matrix of the polymer and subsequent reduction and synthesis, aid the formation of well-dispersed and spherical in shape nanoparticles. researchers Furthermore. the also emphasized the significant role of the organic moieties and free hydroxyl groups present in the matrix of their The respective polymer. distinct properties of biopolymer were primarily owed to the natural occurring biomolecules present in the matrix of the polymers.

A more sophisticated results were attained in the recent works of Motazer et. al. 2016; Matei et. al. 2015; and Morones et. al. 2005. In which the formed nanoparticles were highly pure crystalline, and in cuboctahedral and multi-twinned icosahedral and (Morones et. decahedral al. 2005) morphological structure. The promising structure of the formed NPs was achieved TEM when the electron beam is condensed in the NPs agglomerates; wherein some of the NPs that weren't embedded in the matrix of the used

polymer were subsequently released – yielding in an interesting structural form.

The ability of the matrix to hold the formed NPs was also mentioned in the previous works of Morones et. al. 2005; Matei et. al. 2015; Debuy et. al.2015; and Maneerung et. al. 2007. Giving off a theoretical claim to the significant effects of the matrix to the morphological features of the formed NPs. Moreover, the characteristic of the polymer constituents to stabilize and cap the formed NPs, is one important well-known characteristics that significantly influence the stability of the NPs: preventing them from aggregating and immediate release into the polymer matrix. It was mentioned in the studies of Basri et. al. 2010; and Ramva and Sudha 2013, that the molecular weight of the used polymer evidently influences the adsorption of the metal into the matrix surface - confirming aforementioned the statement. Furthermore, the surface area of the polymer matrix gives relevant impact into the size of the NPs to be formed, and an evidence to that is the study of Zain et. al. 2014. In which it was mentioned that as the concentration of the polymer composite increases the mean particle

size of the NPs (Ag and Cu) decreases. And this statement was given credit to the protective action of the matrix which prevent the growth of the NPs by adsorbing it into its surface.

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Authors	Composite	Functional Group	Absorption Location (cm <sup>-1</sup> )
Montazer, M., Keshvari, A., and Kahali, P. (2016)	Nano silver hydrogel-Cotton	0-H; C=O; C-H; C-C	3447; 1750; 2897; 1632
Mallick, K., Witcomb, M., Dinsmore, A., and Scurell, M. (2005)	Polymer nanofiber	N-H; C-H (aromatic); C-N	3439-3222; 3022-2855; 1318
Lv et.al. (2009)	Ag NP-decorated porous ceramic	N-H; CH <sub>2</sub>	3356-3298; 2977-2885
Ramya, R., and Sudha, P.N. (2013)	Chitosan	O-H and NH; C-H; C-O-C and C-O; CH <sub>3</sub>	3454; 2923; 1151 and 1098; 1384
Yurtsever, M., and Sengil, A. (2012)	Valonia tannin resin	O-H; (aromatic)C-H; (aliphatic) C-H; C=C; C-O- C	3200-3600; 3000-3200; 2900-3000; 1600-1650; 1190
Araki, J., and Hida, Y. (2017)	Cellulose nanowhisker	C=O (carboxylate groups); C=O (carboxyl groups)	1610; 1730
Amin, M.T., Alazba, A.A., and Amin, M.N. (2016)	Palm fibers and Orange peel	O-H; C-O (alcohols and carboxylic acids); C-O-C; C=O	3325, 1013 and 1033; 1014- 750; 1739
Jyoti, K., Baunthiyal, M., and Singh, A. (2015)	<i>Urtica dioca</i> Linn. Leaves	O-H; C-H; C-C; C-N; N-H; N=O	3422; 2921-2856; 1631; 1450; 1377
Debuy et.al. (2015)	poly(ethylene oxide)	C-H; CH <sub>2</sub> (scissoring, wagging, twisting, rocking); C-O-C (stretching, vibrating, bending)	2876; 1466, 1360 and 1341, 960; 1104, 960, 528
Vimala et.al. (2008)	poly(acrylamide)	N-H; C=O (ester groups); O-H	3430 and 1664; 1644, 1603, and 1655; 324, 3432, and 3454

**Table 7.** A summary of the main functional group, and absorption location characterized for each composite.

Authors	Morphology	Particle size	Crystallinity
Montazer, M., Keshvari, A., and Kahali, P. (2016)	Cubic white point	77.55 nm*	FCC
Lv et.al. (2009)	Well dispersed	10-20 nm	FCC
Shahverdi et. al. (2007)	-	22.5 nm*	-
Maneerung, T., Tokura, S., and Rujiravanit, R. (2007)	Spherical, and well dispersed	6.31 nm* 2.68 nm* 2.20 nm*	FCC
Matei et.al., 2015	Highly pure crystalline	30 nm*	FCC
Jyoti, K., Baunthiyal, M., and Singh, A. (2015)	Spherical in nature	20-30 nm	FCC
Debuy et. al. (2015)	Crystalline and well- dispersed	15 ± 2 nm**	FCC
Kang et. al. (2017)	Uniformly dispersed	11.43 ± 2 nm**	-
Morones et. al. (2005)	Cuboctahedral and multi- twinned icosahedral and decahedral	21 nm**	-
Vimala et.al. (2008)	Spherical in shape	10-15 nm	-
Gangadhara et.al. 2010	Uneven size and shape	< 5 nm	-
different studies. *=av	verage size; **=mean	size (Unavailable d	ata are left blank)

Table 8. A summary of morphology, particle size, and crystallinity of synthesized Silver nanoparticles from

Microbial contamination of water poses a major threat to public health. With the emergence of microorganisms resistant to multiple antimicrobial agents, there is increased demand for improved disinfection methods. The antimicrobial properties of silver ions were known since ancient times and silver ions are widely used as bactericide in catheters, burn wounds and dental work. Researchers have also recommended the use of silver and copper ions as superior disinfectants for wastewater generated from hospitals containing infectious microorganisms. However. residual copper and silver ions in the treated water may adversely affect human health. The emergence of nanoscience and nanotechnology in the last decade presents opportunities for exploring the bactericidal effect of metal nanoparticles (Kolar, Urbanek, & Latal, 2001). It is well known that Ag ions and Ag-based compounds have strong antimicrobial many researchers effects and are interested in studying other inorganic including nanoparticles Cu as antibacterial agents.

Several tests are conducted to evaluate the copolymer beads containing silver nanoparticles for water disinfection. In case of E. coli, the zone diameter is found to be 19 mm when subjected to plate method. On the other hand, using test tube test (batch method) shows that the mass of the copolymer beads containing silver nanoparticles has a direct effect on the percent reduction of E. coli, P. aeruginosa, and S. aureus in contrast with B. subtilis where the reduction percentage remained 99.9% for 100, 200 and 300 mg of silver bound copolymer beads. B. subtilis being a spore forming bacteria shows little resistance to the silver nanoparticles bound copolymer beads. This may be due to the presence of amines and carboxyl groups on their cell wall (Gangadharan et. al., 2010).

### 3.4.1 Effects of Metal Nanoparticle Concentration

Antibacterial activities were found to be increased with the increasing concentration of Ag nanoparticles. In a study, zone of inhibition was found to be highest (27 mm) against S. marcescens and lowest (18 mm) against K. pneumonia while against E. coli, the zone diameter was found to be 19 mm, similar to the preceding research (Jyoti, Baunthiyal & Singh, 2015). Moreover, another experimental result demonstrated that the concentration of silver nanoparticles that prevents bacteria growth is different for each type, the P. aeruginosa and V. cholera being more resistant than E. coli and S. typhus. However, at concentrations above 75 µg ml<sup>-1</sup> there was no significant growth for any of the bacteria. On the other hand, a research (Ruparelia et. al., 2008) shows a contrast with some studies reporting negligible inhibitory effect of silver nanoparticles on E. coli up to 100  $\mu$ g ml<sup>-1</sup>. However, these studies employed silver nanoparticles of larger size (12-40 nm) higher initial concentration of and bacteria in the batch cultures  $(10^5-10^8)$ CFU ml<sup>-1</sup>). For E. coli at initial concentration of 10<sup>6</sup> CFU ml<sup>-1</sup> suspended in distilled water, Li et al. reported the MIC of silver nanoparticles ( $\sim 20$  nm) as 40 μg ml<sup>-1</sup>. The relatively low Minimum concentrations inhibitory (MIC) is possibly due to suspension of the cells in distilled water compared to suspension in nutrient media as employed in the said study. For studies conducted on agar plates, the MIC of silver nanoparticles for E. coli was reported as 75 75  $\mu$ g ml<sup>-1</sup>

(Morones et. al., 2005). In batch studies with E. coli and colloidal silver nanoparticle (size range 2-25 nm), MIC was reported to be in the range of 3-25 µg ml<sup>-1</sup> for initial bacterial concentration 10<sup>5</sup>–10<sup>8</sup> CFU ml<sup>-1</sup>. Due to the fact that the parameters used in every study is different from another such as, the variation of E. coli strain employed, variation in the size of the nanocomposite, its initial concentration and the like, direct comparison between studies is not feasible.

# 3.4.2 Intracellular Effect of Metal Nanoparticles

Further studies demonstrated that the nanoparticles may not only be found on the surface of the cell membrane but also inside the bacteria after their interaction. In the study conducted, the product is a powder of Ag nanoparticles inside a carbon matrix, which prevents coalescence during synthesis. The nanoparticles were found distributed all throughout the cell; they were attached to the membrane and were also able to penetrate the bacteria. This was confirmed by an elemental mapping analysis using the x-ray energy dispersive spectrometer (EDS). The mechanism by

which the nanoparticles are able to penetrate the bacteria is not totally understood, but a previous report by Salopek suggests that in the case of E. coli treated with silver nanoparticles the changes created in the membrane morphology may produce a significant increase in its permeability and affect proper transport through the plasma membrane (Morones et. al., 2005).

### 3.4.3 Antibacterial Effect of Silver and Copper Nanoparticles

Ag and Cu nanoparticles were synthesized using ascorbic acid as reducing agent in chitosan solutions using an efficient microwave heating method. It was shown that nanoparticle size could be controlled by manipulating the concentrations of chitosan and silver and copper nitrate used in their synthesis. Minimum inhibitory concentrations (MIC) and minimum bactericidal concentration (MBC) testing showed potent а bactericidal effect with Ag nanoparticles showing a greater killing effect when compared to Cu nanoparticles at the same particle size. The mean greatest antimicrobial effect was seen when Ag and Cu are combined during synthesis to

form alloyed particles (Zain, Stapley & Shama, 2015).

Few researches focus mainly on the synergistic effect of Ag-Cu nanoparticles as an antimicrobial agent but studies show the efficiency of this bimetallic nanoparticle on E. coli and other bacteria that may be present in contaminated water. This capability of Ag and Cu is beneficial in water disinfection as it enhances the death rate of bacteria particularly E. coli.



**Figure 6. From left to right:** the bacterium is being exposed with metal nanoparticles, interaction of metal nanoparticles with the bacterium, then death of bacterium due to cell wall rupture.

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**Table 9.** Selected Studies Concerning the Antibacterial Effect of Silver nanoparticles in Different BacterialStrain

Title	Bacterial Strain	Major Achievements	Authors
Silver nanoparticle- decorated porous ceramic composite for water treatment	Escherichia coli	No bacteria detected in the treated water	Lv, Y., Liu, H., Wang, Z., Liu, S., Hao, L., Sang, Y., Liu, D., Wang, J., and Boughton, R.I. (2009)
Synthesis and effect of silver nanoparticles on the antibacterial activity of different antibiotics against <i>Staphylococcus</i> <i>aureus</i> and <i>Escherichia</i> <i>coli</i>	Staphylococcus aureus and Escherichia coli	The antibacterial activities of each antibiotic increase in the presence of Ag NPs against both strains	Shahverdi, A., Fakhimi, A., Shahverdi, H., and Minaian, S. (2007)
Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing	Staphylococcus aureus and Escherichia coli	99.7% and 99.9% reduction for <i>E.coli</i> and <i>S.aureus</i>	Maneerung, T., Tokura, S., and Rujiravanit, R. (2007)
Polymeric microspheres containing silver nanoparticles as a bactericidal agent for water disinfection	E. coli, P. aeruginosa, B. subtilis, and S. aureus	The produced copolymer beads with silver shows no bacterial adhesion/adsorption, making it as an effective water disinfectant.	Gangadhara, D., Harshvardan, K., Gnanasekar, G., Dixit, D., Popat, K.M., and Anand, P.S. (2010)
Controlled silver nanoparticle synthesis in semi-hydrogel networks of poly(acrylamide) and carbohydrates: A rational methodology for antibacterial application	Escherichia coli	The controlled-sized Ag NPs exhibited antibacterial activity against the bacterial strain.	Vimala, K., Sivudu, K., Mohan, Y., Sreedhar, B., Raju, K. (2008)
The Bactericidal Effect of Silver Nanoparticles	E. coli, S. typhus, P. aeruginosa, and V. cholerae	The synthesized NPs were able to penetrate inside the bacteria that causes its death.	Morones, J.R., Elechiguerra, J.L., Camacho, A., Holt, K., Kouri, J., Ramirez, J., and Yacaman, M.J. (2005)
Silver-nanoparticle- incorporated composite nanofibers for potential wound-dressing application	Escherichia coli	Ag NP incorporated in the nanofibers show great antibacterial activity against the bacterial strain.	Debuy, P., Bhushan, B., Sachdev, A., Matai, I., Kumar, S., and Gopinath, P. (2015)

Title	Bacterial Strain	Major Achievements	Authors
Green synthesis of silver and copper nanoparticles using ascorbic acid and chitosan for antimicrobial applications	Bacillus subtilis and Escherichia coli	Highest antibacterial activity was obtained with bimetallic Ag/Cu nanoparticles	Zain N.M, Stapley, A.G., and Shama, G., (2014)
Synergistic antibacterial activity of a combination of silver and copper nanoparticle impregnated activated carbon for water disinfection	Escherichia coli	Combined Ag-AC and Cu- AC shows significant enhancement in antibacterial activity	Biswas, P., and Bandyopadhyaya, R. (2017)
Individual and Combined Effects of Copper and Silver ions on Inactivation of <i>Legionella</i> <i>Pneumophila</i>	Legionella Pneumophila	Both copper and silver ions are bactericidal agents and that synergism exists under certain conditions	Lin, Y., Vidic, R., Stout, J., and Yu, V. (1996)
Evaluation of Synergistic Antibacterial Activity of Silver and Copper Nanocomposite	Staphylococcus aureus and Escherichia coli	The ratio of 30:70 Ag-Cu nanocomposite yields the greatest antibacterial effect than the other ratio.	Lim, D., Roslin, H., and Vilela, J.D. (2017)
Different Pathogens			

### Table 10. Selected Studies Concerning the Antimicrobial Assay of Combined Silver and Copper Against

### 4. Conclusion

The combination of metal nanoparticles and different cellulosic fiber further extended their distinctive which properties. In the final morphological features of both metal nanoparticles and cellulosic fiber are influenced by the type of modification and preparative methods that these materials Inclined with the had undergone. methodologies employed to the materials, their synergistic property took the great advantage of the combination of the materials. This review has shown the widening application of nanocomposite in disinfection. In water which the significant synergistic effect of the nanocomposite had caught the interest of most researchers to further develop the field of this study. The promising characteristics and properties of the nanocomposite further concern its physico-chemical interactions. In which most studies delved the deeper chemistry behind these promising characteristics and properties. Upon the great attention given for this field of research, relevant optimization of the material properties for multi-functional its application haven't developed yet and still scarce

despite of its enormous potential. As the demand in the utilization of combined nanotechnology and polymer science widens. the application of the polymer/metal nanocomposite as a water filter was found to be promising. Its efficient antibacterial effect in different pathogenic bacteria continuously broadens the study for its application in both biomedicine and water disinfection. Hence, further elucidation in this field of research extends its significance in the scientific community and in the water disinfection industry.

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