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A REVIEW ON ROLE OF IONIC LIQUIDS IN GREEN SYNTHESIS OF METAL NANOPRTICLES (MNPs)

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Abstract: Metal nanoparticles (NPs) are a subject of global interest in research community due to their diverse applications in various fields of science. The stabilization of these metal NPs is of great concern in order to avoid their agglomerization during their applications. There is a huge pool of cations and anions available for the selection of ionic liquids as stabilizers for the synthesis of metal NPs. Ionic liquids are known for their tunable nature allowing the fine tuning of NPs size and solubility by varying the substitutions on the heteroatom as well as the counter anions. However, there has been a debate over the stability of metal NPs stabilized by ionic liquids over a long period of time and also upon their recycling and reuse in organo-catalytic reactions. ionic liquids covalently attached to solid supports have given a new dimension for the stabilization of metal NPs as well as their separation, recovery, and reuse in organo-catalytic reactions. The stabilization of metal nanoparticles and their applications as a function of their metal cations and counter anions.

Key words: *Ionic solutions, Metal Cations, Green synthesis, Plant extracts, Nanoparticles*

I. Introduction

The way we see, feel, and touch things is about to change. In fact, the change has already begun and though it has not touched our lives in any significant manner, the day when that happens is around the corner. From self-cleaning windows to super energy efficient lighting, nanotechnology is revolutionizing the way we live. Lighting has been an important aspect of our lives, of our existence. There is hardly any doubt that nanotechnology is very beneficial to man. With all the applications this new frontier of knowledge has been seen from the human body to industries and chemicals; thus far, nanotechnology has lived up to its name in enhancing the wealth of knowledge possessed by man. In science and technology, one among the rapidly developing concepts in the latest years is nanotechnology, which has brought tremendous development. the nanomaterial which comprises distinctive physicochemical properties has the potential to develop new systems, structures, devices, and nanoplatforms with impending bids in extensive variety of disciplines(H. Mirzaei & M. Darroudi, 2017 and Arruda 2015). Nanomaterials are particles that are in nanoscale size, and they are very small particles with improved thermal conductivity, catalytic reactivity, nonlinear optical performance, and chemical stability due to their large surface area-to-volume ratio (H. Agarwal 2017) This quality has attracted many researchers to locate novel techniques for their synthesis. Though conventional techniques (physical and chemical methods) use less time to synthesize bulk amount of nanoparticles, they require toxic chemicals like protective agents to maintain stability, which leads to toxicity in the environment. Keeping this in mind, green technology by using plants is rising as an eco-friendly, nontoxic, and safe option, since plant extract-mediated biosynthesis of nanoparticles is economically advantageous and offers natural capping agents in the form of proteins(H. A. Salam, 2014). To regulate chemical toxicity in the environment, biological synthesis of various metal oxide and metal nanoparticles through plant extraction is used, which is a marginal technique for regulating chemical synthesis, and it permits a distinct shape and size of nanoparticles with a meticulous synthesis (Anastas, 2000).Nanotechnology is one of the most active of area-research in modern material science. This field which is developing day by day is making an impact in spheres of humans' life and creating a growing excitement in the life science, especially biotechnology and biomedical science(S. Prashanth, 2011). Nanoparticles exhibit completely new properties based on specific characteristics such as shape, size and distribution. Nanocrystalline particles have found tremendous application in the field of high sensitivity bimolecular detection and diagnostics, therapeutics and antimicrobials(. Sridhara 2012) catalysis and microelectronics(B. N. Veera, 2012) . However there is still need for commercially viable as well environmentally clean biological route to synthesized nanoparticles(N. C. J. P. Lekshmi ,2012) . A number of approaches are available for the synthesis of nanoparticles for example, reduction in solution, photochemical and chemical reaction in reverse micelles thermal decomposition of nanoparticles compounds(M. Akl, Awwad, 2012) , radiation assisted, electrochemical, microwave assisted process and recently via green chemistry route(B. M. Ravindra, 2012), **Figure:1** have shown scheme of green synthesis of nanoparticles. The use of environmentally benign material like plant extract (leave, flower, bark, seed, peels etc.), fungi, bacteria, and enzyme for the synthesis of nanoparticles offers numerous benefits of ecofriendliness and compatibility for pharmaceutical and other biomedical applications as they do not use toxic chemical for the synthesis protocol(R. Gokulakrishnan, 2012) .Nanoparticles have long been recognized as having inhibitory effect on microbes present in medical and industrial process(A. Nasrollahi ,2011) .

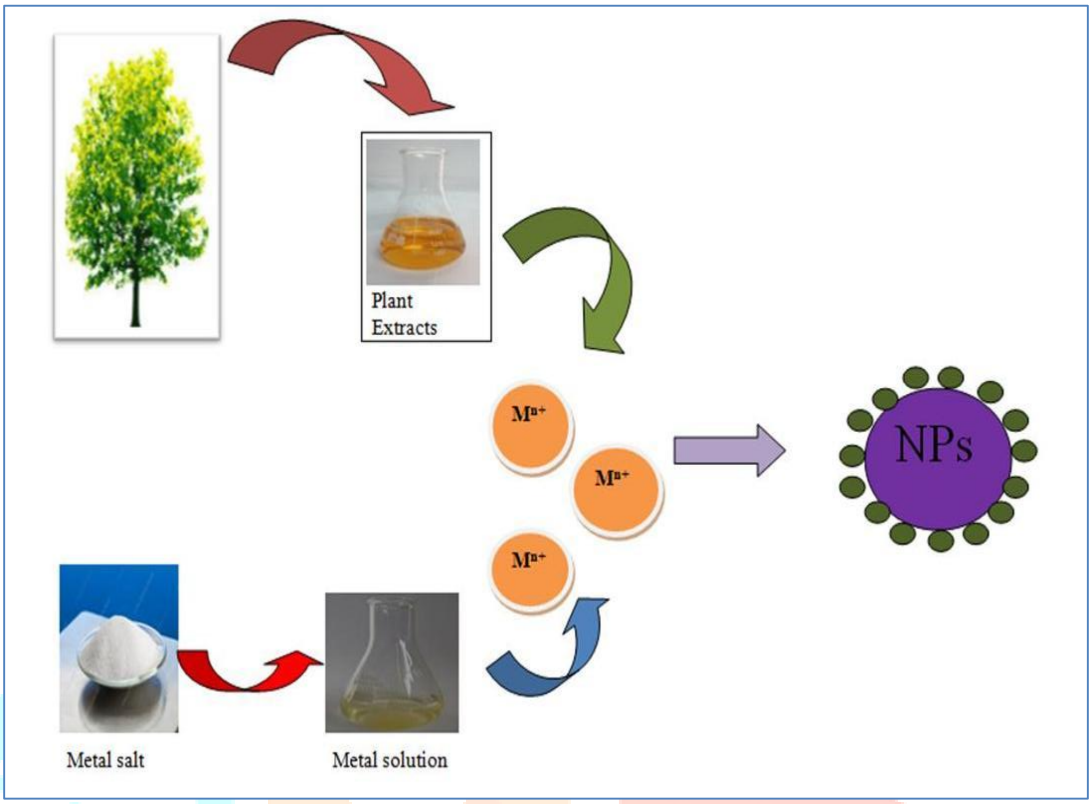

Figure:1 Scheme of green synthesis of nanoparticles

II. MECHANISM OF GREEN SYNTHESIS OF NPS BY PLANT EXTRACTS

The mechanism of green synthesis of NPs, by plant extracts in vitro Figure 2 schematically describes the formation of metallic NPs from the corresponding metal ions. When metallic salt dissociates into cation and anion, cations will be saturated to form hydroxyl complexes [$M(OH)^n$]. Immediately after the supersaturation of hydroxyl complexes, crystillite growth of metal with oxygen species starts to originate. This results in the formation of crystalline planes with different energy levels. Heat plays a key role in providing energy to the reaction system. The process continues until activation of the capping agent from the plant extracts, which will ultimately arrest the growth of high-energy atomic growth planes.

This results in the formation of specific type NPs. Generally, during the synthesis, the reducing agents donate electrons to the metal ions and convert them to NPs. These NPs exist at a high-surface energy state and tend to convert to their low-surface energy conformations by aggregating against each other. Thus, the presence of higher amounts of reducing agents and stabilizing agents prevents the aggregation of nanoparticles and promotes production of smaller NPs. Additionally, proteins can trap metal ions on their surface and convert them to their corresponding nuclei, which could further aggregate and, consequently, form NPs. Amine groups of proteins, hydroxyl and carboxyl groups of polyphenols and amino acids, hydroxyl groups of polysaccharides, and carboxyl groups of organic acids chelate metal ions and suppress the superoxide-driven Fenton reaction (which is believed to be the most important source of ROS), catalyzing the formation of metallic NPs . Although it is essential to form a protein-metal ion complex for the vacuolar sequestration of metal ions during in vivo accumulation of NPs, the role of proteins upon in vitro green synthesis is not clear. Interestingly, plant extracts possess the capacity to reduce metal ions and produce NPs even after boiling(mith,2009: Khalil,2012: MubarakAli, ,2011: Suman, 2014). Although boiling could denature proteins by altering their secondary and tertiary structures, the peptide bonds of the primary structure between the amino acids are left intact. Because all structural levels of the protein determine its function, the denatured protein can no longer be fully functional. It has been stated that the protein can bind to Au NPs, either through free amino groups or cysteine residues; the surface-bound protein lead to the stabilization of the NPs(Gole, A 2001).

Table:1 Ionic solution with plant extracts

S.No	Strong Electrolyte	Metal cations	Plants species	Extracts	MNPs	Reference
1	$MgSO_4.6H_2O$	Mg^{2+}	Chromolaena odorata	leaf	MgNPs	Enobong 2020
2	$Mg(NO_3)_2$	Mg^{2+}	Nephelium lappaceum L	peels	MgNPs	Suresh 2014
3	$Al(NO_3)_3$	Al^{3+}	1. Aerva lanta 2. terminalia chebula	Seed	AlNPs	Duraisamy 2018
4	$BiNO_3$	Bi^{+}	mentha pulegium	leaves	BiNPs	Kazemia 2020
5	$Ca\ (NO_3)_2.\ 4\ H_2O$	Ca^{2+}	Papaya	leaves	CaNPs	Ashwini 2016
6	$K_2Cr_2O_7$	Cr^{3+}	Allium sativum	garlic	CrNPs	Satgurunathan 2018
7	$Co(NO_3)_2.6H_2O$	Co^{2+}	Punica granatum	Fruit peel	CoNPs	Ismat Bibi 2017
8	$Co(NO_3)_2.6H_2O$	Co^{2+}	Populus ciliata	leaves	CoNPs	Hafeez 2020
9	$CuSO_4.5H_2O$	Cu^{2+}	tea leaf	leaves	CuNPs	Mohindru 2017
10	$CuCl_2$	Cu^{2+}	papaya extract	Fruits	CuNPs	Suresh 2014
11	$CuSO_4.5H_2O$	Cu^{2+}	Ocimum sanctum	leaves	CuNPs	Vasudev 2013
12	Cu(OAc)2	Cu^{2+}	Eclipta prostrata	leaves	CuNPs	Ill-Min Chung 2017
13	$CuCl_2$	Cu^{2+}	Aegle marmelos	leaf	CuNPs	Vasudeo Kulkarni, 2014
14	$HAuCl_4.3H_2O$	Au^{3+}	Abelmoschus esculentus	Seeds	AuNPs	Jayaseelan 2013
15	$HAuCl_4.3H_2O$	Au^{3+}	olive	leaf	AuNPs	Mostafa 2012
16	$FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ (1:2 molar ratios)	Fe^{3+}	Glycosmis mauritiana	leaves	FeNPs	Amutha 2018
17	$FeCl_2\ .4H_2O$	Fe^{3+}	Citrus medica	Hund Fruit.	FeNPs	Esam J. AL-Kalifawi 2015
18	$Fe(NO_3)_2.6H_2O$	Fe^{3+}	Rambutan	fruit peel	FeNPs	Yuvakkumar, 2014
19	$FeSO_4$	Fe^{3+}	Musa ornata	Flower Sheath	FeNPs	Saranya 2017
20	$FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ (1:2 molar ratios)	Fe^{3+}	Azadirachta Indica	leaves	FeNPs	Nurul Izza Taib 2018
21	$(NH_4)2$ Fe $(SO_4)_2.6H_2O$ and 0.1 M NH_4 Fe $(SO_4)_2$ $.12H_2O]$ in 1:2 ratio	Fe^{3+}	Euphorbiaceae Phyllanthus	Niruri	FeNPs	Viju Kumar 2018
22	$FeCl_3.6H_2O$	Fe^{3+}	Carica papaya	leaf	FeNPs	Bhuiyan 2020
23	$TiO(OH)_2$	Ti^{4+}	Ocimum basilicum	leaves	TiNPs	Prathyusha 2018
24	$TiO(OH)_2$	Ti^{4+}	Sonchus asper	leaves	TiNPs	Neelesh 2019
25	$TiO(OH)_2$	Ti^{4+}	Psidium guajava	leaves	TiNPs	Thirunavukkarasu 2014
26	$TiO(OH)_2$	Ti^{4+}	Nyctanthes arbor-tristis	leaves	TiNPs	Sundrarajan 2011
27	$TiO(OH)_2$	Ti^{4+}	Glycyrrhiza glabra	root	TiNPs	Zahra Madadi 2020
28	$TiO(OH)_2$	Ti^{4+}	Kniphofia foliosa	root	TiNPs	Bekele 2000
29	$Mg(NO_3)_2.6H_2O$	Mg^{2+}	Lepidium sativum	Seeds	MgNPs	Ashwini 2016
30	$Mg(NO_3)_2.6H_2O$	Mg^{2+}	Arabic Gum	Plant Gum	MgNPs	Saeid Taghavi Fardood 2018
31	$Mg(NO_3)_2.6H_2O$	[illegible]	Azadirachta indica)	leaves	MgNPs	Krishna Moorthy

						2015
32	$(NH_4)_6Mo_7O_{24}$	Mo^{6+}	Citrus Limetta	Fruit Pith	MoNPs	Abhimanyu 2014
33	$NiSO_4$	Ni^{2+}	Thespesia populnea	leaves	NiNPs	Dhivya 2019
34	$NiCl_2$	Ni^{2+}	Coriandrum sativum	leaves	NiNPs	Vasudeo 2016
35	$NiSO_4.6H_2O$	Ni^{2+}	Betel	leaves	NiNPs	Ravindra 2018
36	$Ni(NO_3)_2.6H_2O$,	Ni^{2+}	Ageratum conyzoides L.	leaf	NiNPs	Miessya 2019
37	$Ni(NO_3)_2$	Ni^{2+}	Rhamnus triquetra	leaves	NiNPs	Javed Iqbal 2020
38	$PdCl_2$	Pd^{2+}	Anogeissus latifolia	Gum ghatti'	PdNPs	Aruna 2015
39	$PdCl_2$	Pd^{2+8}	Pimpinellatirupatiens is	leaves	PdNPs	Palajonna 2017
40	$H_2PtCl_6.6H_2O$	Pt^{4+}	Quercus glauca	leaves	PtNPs	Karthik 2016
41	$H_2PtCl_6.6H_2O$	Pt^{4+}	Jatropa Gossypifolia And Jatropa Glandulifera	leaf	PtNPs	Jeyapaul , 2017
42	$H_2PtCl_6.6H_2O$	Pt^{4+}	Lantana Camara	leaves	PtNPs	Musthafa 2016
43	$NaHSeO_3$	Se^{4+}	fenugreek	seed	SeNPs	Ramamurthy 2013
44	$AgNO_3$	Ag^+	Olive	leaf	AgNPs	Mostafa 2014
45	$AgNO_3$	Ag^+	Manihot esculenta	leaves	AgNPs	Velayutham 2016
46	$AgNO_3$	Ag^+	Rhizophora mucronata	leaves	AgNPs	Gnanadesigan 2011
47	$Sr(NO_3)_2$	Sr^{2+}	Ocimum sanctum	Leaf	SrNPs	Apsana, 2018
48	$SnCl_2•2H_2O$	Sn^{2+}	Ficus Carica	Leaf	SnNPs	Junjie Hu 2015
49	$Y(OAc)_3$	Y^{3+}	Azadirachta Indica	Fruit	YNPs	Hamadneh 2019
50	$Zn(OAc).2H_2O$	Zn^{2+}	Moringa Oleifera	Leaf	ZnNPs	Sukanta Pal 2018
51	$Zn(OAc).2H_2O$	Zn^{2+}	Hibiscus subdariffa	leaf	ZnNPs	Niranjan Bala 2014
52	$Zn(NO_3)_2•6H_2O$	Zn^{2+}	C. halicacabum		ZnNPs	Nithya 2019
53		Zn^{2+}	Jatropha curcas	latex	ZnsNPs	Hudlikar 2012
54	$Zn(OAc).2H_2O$	Zn^{2+}	Passifloraceae	leaves	ZnNPs	Santhoshkumar 2017
55	ZnSO4.7H2O	Zn^{2+}	Sesamum indicum	Seed	ZnNPs	Sara Zafar 2020
56	$ZrOCl_2·8H_2O$		E. globulu	leaves	ZrNPs	Balaji 2017
57	$Zr(OAc)2.2H_2O$		Citrus aurantifolia	Fruit	ZrNPs	Ali Majedi 2015
58	$Pb(NO_3)_2$	Pb^{2+}	Cuminum cyminum	seeds	PbNPs	Gandhi 2018
59	$Hg(OAc)_2$	Hg^{2+}	Callistemon viminalis	flower	HgNPs	Amlan 2015
60	$Na_2S_2O_7.5H_2O$		F. benghalensis	leaves	SNPs	Tripathi 2018
61	$BaCl_2·2H_2O$	Ba^{2+}	Kiwifruit, Tomato, Orange,		BaNPs	Chen 2016

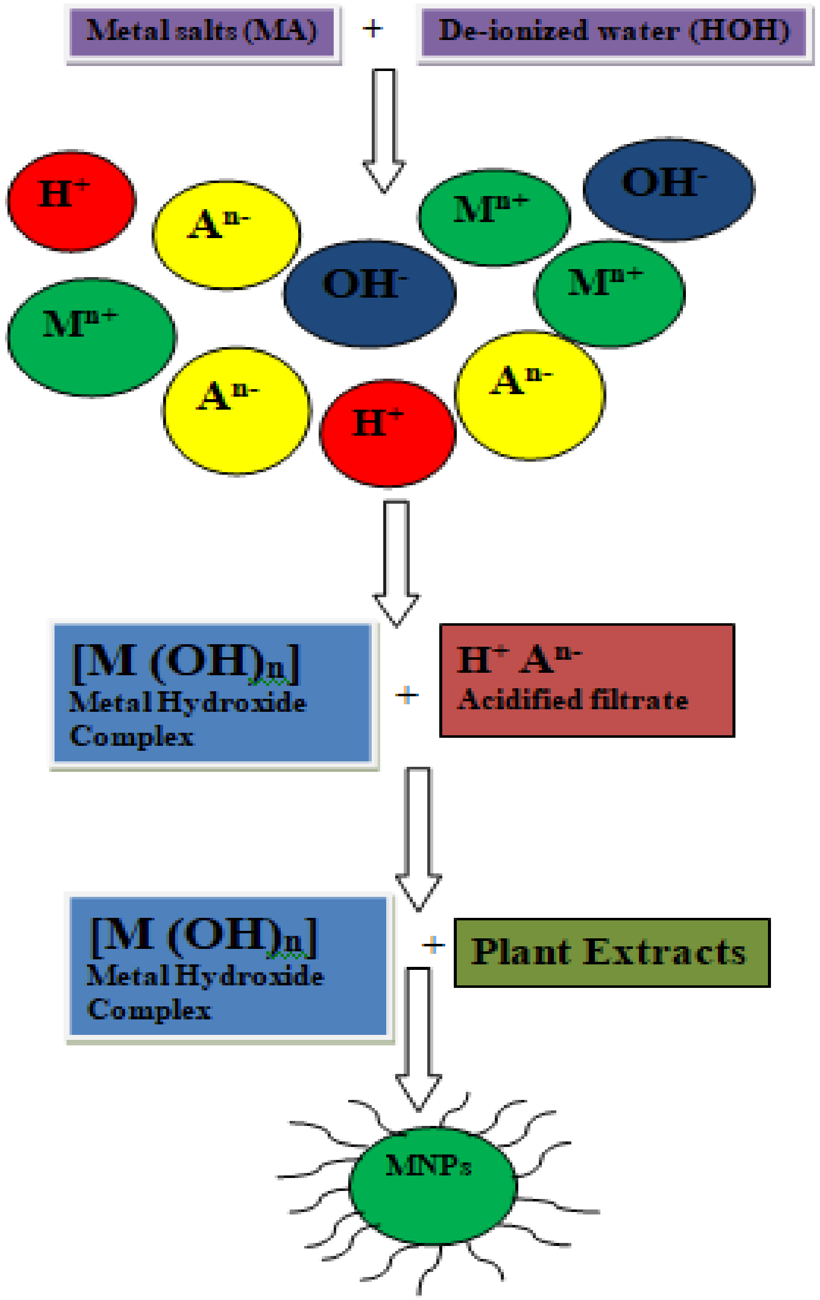

Figure: 2 Mechanism of nucleation of metal cations with plant extracts

III. CONCLUSIONS

Nanotechnology is improving our everyday lives by enhancing the performance and efficiency of everyday objects. It provides a clean environment by providing safer air and water, and clean renewable energy for a sustainable future. Nanotechnology has gained a wide attention where more investment is made for the research and development by top institutions, industries and organizations. Nanotechnology has established to be an advanced field of science where extensive research is carried out to implement the technology. Ionic solutions are very important role in the synthesis of the nanoparticles (MNPs). It is being tested for various new applications to increase the efficiency and performance of the object or process and subsequently reduce the cost so that it is accessible for everyone. The nanotechnology has a great future due to its efficiency and environmental friendly property

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