

“PRESENT AND FUTURE ULTRAMODERN TRENDS FOR - CORRECTING SELENIUM TOXICANT IN ENVIRONMENT USING NATURAL BACTERIAL BIOFILMS AND NANOSTRUCTURES SYNTHESIZED BY GREEN TECHNOLOGY”

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ABSTRACT

Selenium is a rare earth element, a metalloid and occur in four different valence states in the environment such as +VI, +IV, 0 and -II. The oxyanion selenate (SeO_4^{2-}), selenite (SeO_3^{2-}) are abundant in the strata of earth crusts and spread in soil and aquatic ecosystems because of anthropogenic activities. It is a micronutrient of cells but assume toxicity at higher concentrations by interaction with glutathione and related biomolecules, these may get reduced, as a result of this reactive oxygen species such as H_2O_2 or superoxide ions that are librated lead to death of cells. Naturally occurring microorganisms easily sequester, bioconvert or biomethylate toxic oxyanions of selenium. Aerobic and anaerobic microbes either alone or together of mono and multispecies as biofilms, bioflocs and engineered SeNPs employing biofilms/microconsortia, various bioreactors invented that used fabricated nanostructures from non biological material and role in bioconversion of oxy-anions of Se to elemental selenium by bacteria has been discussed. Green technology incorporate bioremediation strategies to recover elemental Se(O) due to multitude advantages like simple, risk free, eco-friendly, low cost, easy to use, no skilled personal is required, it is a sustainable technique for all easy to manage and maintain, etc.

KEYWORDS :- Bacteria, Biogenic, SeNPs, Bioreactor, Toxicant, Biofilm .

INTRODUCTION

When the earth was formed the matter and material comprised of various inorganic elements from non-metals, metals to metalloids, which has been discovered until now, many are still to be discovered. Later due to various physical, chemical and biological processes alone or in combination resulted in the genesis of organic and inorganic compounds. This can be co-related with Azoic to the presents psychozoic era which are part of the geologic period of time scale calibrated and devised by human beings. This I would like to propose as molecular evolution. Every abiotic and biotic component respectively are

either separated or exist together in three dimensions (spatially) with respect to the time scale in this universe.

Selenium is a metalloid not homogeneously distributed on the earth's crust, its concentration ranges from 0.01 to 12.00 ppm and exists as crooksite, CuTlSe , calusthite PbSe (Haynes, W.M.,2014; Ba.L.A.,et.al.,2001; Vreins, et.al.,2014; Reilly C,2006; Chasteen, et.al.,2009; and Taylor,D.E.1999). Selenium, tellurium and sulphur are group 6 chalcogenic elements. Selenium a trace element, rarely found in elemental form comprise 0.00008% of the earth's crust. High level 100mg Se kg^{-1} has been measured in soils of USA, Ireland and India (Lenz M.,Lans P.N.L.,2009). Biological systems use Se as an essential micronutrients, glutathione peroxidases and thioredoxin reductase contain Se and Selenocysteine is 21st discovered amino acid and occur in about 25 selenoproteins of human; soil and aquatic ecosystem contain oxyanions selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}). Four valence states of selenium are (+VI,+IV,0 and -II), (Mehdi,Y.et.al.,2013). Chemical and biological methylation of Se yield dimethyl selenium a volatile compound and has been detected in soil and waters, it's very toxic due to high lipophilic nature and rapidly enters through the membranes of organisms. Selenium in concentration greater than $25\text{-}30\text{ ug/day}^{-1}$ (Lampis,S.et.al.,2014) is toxic to humans. Oxyanion of selenium from water and soil get easily absorbed into the human through food and drinking water (Barceloux, D.L,1996).Organic compound dimethyl selenide, trimethyl selenium, selenomethionine, selenocysteine and Se- methylselenocysteine and zero-valence state of Se are least toxic (Ba,L.A.et.al.,2010; Barceloux,D.G.1999 and Martens, D.A. and Suarez, D.L, 1996). Oxyanion state of Se react rapidly reducing the glutathione enzymes and similar molecules (Turner, R.J.et.al., 2012 and Spallholz, J.E, 1994) and hydrogen peroxide one of the reactive oxygen species and superoxide (O_2^-) ions the second species formed eventually prove lethal to cells of the body (Beben, M.et.al.,2002; Kassi, J and Hanselman, K.W,2004; Perez .M.J.et.al.,2007; Zannoni,D,et.al.,2008 and Halmogren A.1989). Vit E and sulphur-containing amino acid (selenocystine) carry out various functions in the metabolism of animals, it is present in glutathione peroxidase (GSH-Px) by 2010 mostly enzymes selenoproteins about 30 were identified (Hefnawi, Tortora-Perez, 2010) and 10 from these have biological roles. Mammal body contain 4-isoforms of enzymes such as classic GSH-Px (cytoplasmic peroxidase) ,plasma GSH-Px (an extracellular enzyme),gastrointestinal GSH-Px and phospholipid-hydroperoxide GSH-Px (Arthur,J.R,2000).Many selenoproteins identified include W in rat muscle (Whanger,P.D,2000),spleen, brain,etc; selenoprotein K an antioxidant in cardiomyocytes (Lu,C.et.al.,2006); the neuroprotective selenoprotein M and H(Zhang, S.et.al.,2010),selenoprotein N aid in muscle contractions (Lescure,A.et.al.,2009);T,O and I are selenoproteins whose functions are less known (Lopez-Heres,et.al.,2011).Deficiency of selenoprotein S lead to colorectal-cancer in human (Sutherland,A.et.al.,2010) because in blood of cancer patients Se occur at low levels as selenium itself occur in less amount in soil, selenium posses antineoplastic activity (Sanz-Alaejos,et.al.,2000).Many functions has been assigned to selenium, few may be enumerated:stimulates antineoplastic metabolites secretion; blocks angiogenesis and promotes apoptosis of cancer cells (Combs,G.F and Gray W.F.1998). The cytotoxic action of NK cells destroy several animal tumor growth, this proliferation may be either stimulated or inhibited by dose of selenium used (Koller,L.D.et.al., 1986).Most animal species exhibit susceptibility to a single dose of Se (1 to 6 mg/kg body weight) according to the research work of Hogue,1970 and Whanger,P.et.al.,1996. Acute selenosis occur due to ingestion of 20-30 ppm of Se

whereas sub acute/chronic toxicity result from ingestion of less than 3-5ppm of selenium (Panter,James,1990 and Nuttal,2006).Evidence exist that selenium suppress transcription factors involved in control of mitosis of cell, the anti-neoplastic role of Se is due to antioxidant effect exercised through the redox-route(Spyrou,G.et.al.,1995).The authors of this review paper suggest analysis and screening of cow-urine distillates. If selenium is present it can be to design selenium nanostructure for therapy of colo-rectal and other cancer. Biomagnification of non biodegradable heavy metal involves food chain and food web (Gary J.S.2020).Geological weathering of parent rock substratum along with eruptions from volcano add to problem of heavy metal pollution and nature of pollution depends on composition of rocks, and soil, climatology and human activities (Wuana R.A, Okieiman F.E.2011 and Techounwou et.al.,2012). Surface water for irrigating agro-biosystem cause heavy metal bioaccumulation in food crops. Heavy metal from atmosphere through rain contaminate fresh water and ground water (Adesiyani I.M,et.al., 2018). Out of 414 river water quality stations, 57 have been contaminated with 2 or more heavy metals and don't conform to permissible limits (New Delhi, Central Water Commission, 2018).Bioremediation of the selenium oxy-anions is chiefly dependent on microbe-catalyzed redox conversion to insoluble forms; not on ellectropositive - metal ligands connections between surface of bacteria and charged sites of the toxicants (McLean,J.S,et.al.,2002). Biosorption-chemiosmotic gradient across cell wall do not require ATP it is regulated by absorption process, Ion-exchange, covalent bonding in dead or living cell or non conventional alternate strategy for recovery of metal from solutions.

RESEARCH METHODOLOGY

Various review papers related to the present research paper were used to write the paper on bioremediation of selenium using bacterial biofilm. Experimental papers related to removal of selenium from aquatic ecosystems of the world were also considered in writing this paper. After going through various available research literatures the authors of this paper wonders whether any method or prior technology ever exist or will exist in future which will not alter or impact the environment. Anthropogenic activities are and will be responsible for drastic and non reversal disruption to the environment, biodiversity and human civilization. Zero waste technology can't be invented using conventional physical, chemical and biological paradigms either alone or in combination with engineering technologies. Bioremediation like other methods is not 100% efficient. Technology for 100% sustainability to save soil, water, atmosphere, energy, probably doesn't exist. Mining, industrialization, urbanization, agriculture and animal husbandry, not to mention many more practices add to the dimension of imbalance in natural environment. Altering and then searching and implementing corrective measure may or may not resolve our many of the created issues. Advancement of existing and invention of new technologies and its application should be done for sustainable development or for luxury is questionable. Many countries around the globe are already facing the dilemma of poverty, diseases, decline in and easy access to natural resources, low per capital income despite utilization of green,

blue, red, grey and multicoloured technologies.

DISCUSSION

Need for bioremediation

Bioremediation of contaminated water and soil ecosystems globally utilize various species of microorganisms and dissimilar reduction process to obtain insoluble Se (0) from Se (VI) (Gadd,2004). Similarly (Gadd, 2007) metal immobilization using microbes can be done to obtain inorganic and organic biominerals in the form of oxalates, phosphates, sulphides, oxide and carbonates.

Many methods and strategies have been invented by researchers all over the world. According to Vidali (2001) low cost effective technique- technology currently available are using fungi, microbes, green plants and their enzymes to detoxify or reduce hazardous contaminants present in environment into harmless tolerable form. Cell wall and envelope of microbes contain chemical sites such as amine, sulphate, carboxylate,etc which bind passively to metal without using energy (Gadd 2009;Volesky,2001). Carboxyl, hydroxyl and phosphyl group occur on live or dead biomass and aid in biosorption by interacting with metal cations present in contaminated and waste waters, but depend on factors like covalent bonding, ion-exchange adsorption and permits use of low cost biomass-bioabsorption as an alternative method (Marazoiti C,1998; Chen X.C. et.al.,2005; Chen J.Z. et.al.,2005; Spain A. and Alm E,2003; Errasquin E.L, and Vazquez C,2003). Biosorption and bioaugmentation are used where intrinsic bioremediation or biostimulation are ineffective and all of them are now categorized under bioremediation. Biodegradation by direct and indirect extracellular enzymes for bioremediation of heavy metals, textile dyes and associated xenobiotics have been established. Either direct or indirect extracellular enzymes singly from an organism or both mechanisms together from different organisms need to be employed for remediation of any chemical toxicants (Kulla,H.G.et.al.,1983; Fewson, C.A. 1988) and Zhau, W. and Zimmerman W, (1993). When bacteria and fungi are used for remediation it is microbial remediation. These microbes being very small have short life-cycle, easy to culture, exhibit wide distribution in nature and greatly adapted to resist high concentrations of metals are golden choice for bioremediation.

Outer membrane of gram negative bacterial cells carrying phosphoryl negative residues serve as sites for cation binding and metal precipitation from environment, other negative groups are carboxyl and hydroxyl (Beveridge, T.J and Doyl R.J,1989; Fein J.B.et.al.,1997 and Blance A, 2000) . Syntrophism is a wide spread phenomenon wherein synergism between anaerobic microbes exist for exchange of nutrients, also involve small enthalpy changes and interspecific hydrogen transfer a classical example is metabolism of 3- chlorobenzene. Thus, codominance shortens the time period of degradation for the contaminant. Such microbial cells can be cultured and used to treat effluents or polluted soil (Cookson J.T.R,1995; Nile

D.H.1992 and Ghosh A.et.al.,2005). Commercialization of patented microbial biosorbents had failed due to many factors(Tsezos,2001;Gornham,1997).Initial patenting was done in 1980's (Tsezos,2001) followed by commercialization in1990's of algal , bacterial and biofilms, etc., incorporating immobilization technology (Volesky,1990; Veglio,1997; Garaham,1997).Various algal species biosorbent biomaterials were produced in Canada(Volesky,1990).

For detoxification of soil and water containing selenium in their toxic oxidation states, aggregation of anaerobic microorganisms for bioconversion to elemental selenium was first reported by Gao,D.et.al.,2011; Oremland R.S,et.al.,(1989) through dissimilatory reduction of SeO_4^{2-} and SeO_3^{2-} to Se^0 (Macy J.M.et.al.,1989). Anaerobic methanogenic microbes in granular sludge more effectively removed high SeO_4^{2-} level by utilizing various donor compound in the experiments (Astratinej, V.Van Hullebuseh E,Lens P.N.L, 2006) employing technologies and reactors like ABMet^R biofilter system,the electrobiochemical reactor (EBR),the biofilm reactor (BSeR), the membrane biofilm reactors (MBfR) , the upflow anaerobic sludge blanket reactors (UASB) and sequencing batch reactors (SBR)(Tan L.C.et.al.,2016 and E.Piacenza et.al.,2018).

Bacterial biofilms is an aggregation of various species of bacteria present in an extracellular polymeric matrix. This matrix is composed of extracellular DNA, lipids, proteins, polysaccharides and high water content. Bacterial community in the form of biofilm survive easily in diverse unpolluted and polluted natural waters despite of differences in their physiology, morphology and behaviour conferring resistance and tolerance against Se oxyanions (Harrison,J.J.et.al.,2005; Fleming, H.C. and Wingender J,2010; Costerton, J.W.et.al.,2007; Workentine, M.L. et.al.,2011 and Zannoni, D.et.al.,2008).Precipitate of Se^0 accumulate by abiotic bioconversion of SeO_4^{2-} and/or SeO_3^{2-} as a result of sulphide (S_2) formed in the biofilm ESP containing sulphate- reducing bacteria (SRB) (Hockin,S.L, and Gadd, L. 2003). Te^0 and Se^0 precipitate in EPS and intracellularly post reduction process of compounds such as TeO_3^{2-} and SeO_3^{2-} was brought about by biofilms of *S.oneidensis* grown in anaerobic conditions (Klonowska,A.et.al.,2005). The author of this paper have observed biofilm and bioflocs of microorganisms suspended at the surface and below the surface either stationary or slowly moving biomass due to circulation of effluent in effluent treatment plant and sewage treatment plant also (D.R. Saxena, personal communication 1991 and 1997 to 2004) and lentic deep and shallow water of lake (Aarzo, N. Sheikh, Ashwini, P. Meshram, Nikita, J. Tupkar, and D. R. Saxena, 2021), ponds and sewage drain of Nagpur (M.S.). On characterization, identification and classification these biofilms and bioflocs may be aerobic and anaerobic microorganisms and can be used for bioremediation as inoculum. Immobilize biofilms on solid substrate of eitherbiopolymer, polymers and silicon in the form of chips and beads have been developed and used in various man-made reactors by many research workers. Polymer threads with fabricated attachment surface can be used preparing thread-microbial biofilm for decontamination of several types of waste-waters. These threads have longer durability than cotton thread.

Architectural design, utility, function and efficiency of various reactor system.

ABMet^R reactor system: It is cylindrical tank of varying size depending whether it is required for pilot experiment or commercial purpose. The biofilter component consist of an anoxic/ anaerobic bed made up of porous granular activated carbon (GAC) which is a substratum for growth of communities of microbes in the form of a biofilm. Influent wastewater is supplied in to the tank containing molasses solution to nourish microbes and accept electrons discharged by donor molasses during bioconversion of Se- oxyanions like SeO_4^{2-} and SeO_3^{2-} reduction to their elemental state Se^0 in the persisting anaerobic condition. Entire Se^0 can be recovered by backwash strategy and the fixed biofilm of microbial communities can be reused. The purified water effluent is obtained and other metals and NO_3^- also get removed. Efficiency of 99.3% for contaminant removal in ABMet^R biofilter system needed retention of waste water for 16 hours at the Duke Energy and Progress Energy in North Carolina using low amount of nutrient supplement(Tan, L.C. et.al.,2016; Sonstegard,J.et.al.,2010; Sonstegard,J.et.al.,2007).

The EBR system: Electro-biochemical reactor is a cylindrical tank containing microbial communities and graphite electrodes. Influent waste water loaded with SeO_4^{2-} and SeO_3^{2-} taken in the tank undergo reduction through direct interspecies microbial electron transfer received from oxidation of graphite electrodes, at the outer bacterial cell surface electrons reduce the terminal electron acceptor Se oxyanions when waste water retention is for 6 to 18 hours. Efficiency of EBR system is evident from lowest level of Se^0 ($5\mu\text{g L}^{-1}$) present in effluent water obtained after treatment of contaminated influent coal mine waste water containing $500\mu\text{g L}^{-1}$ Se-oxyanions at low temperature of 1°C (Lovely,D.R,2008 and Opara, A.et.al.,2014). The pilot experiment was done at coalmine of British Columbia (Canada).

The BSeR and MBfR systems: Research by Yang, S.E.et.al.,(2016) have provided interesting information on utilization of bacterial biofilms of multispecies like *Rhodococcus* sp., *Pseudomonas* sp., *Bacillus* sp., and *Arthrobacter* grown on granular activated carbon where survival in anaerobic condition and very efficiently bioconvert at high concentration of SeO_3^{2-} polluted waters and inorganic compounds of these oxyanions that accumulate in biofilms as elemental Se^0 submicrometer size particles, thereby proving their role in bioremediation process by virtue of their involvement in natural biogeochemical cycles. A recovery project at Garfield Wetlands-Kessler Springs (Utah USA USEPA ;2001) claim of containing 97% elemental Se^0 from agriculture drainage waste water harbouring SeO_4^{2-} and SeO_3^{2-} using this technology of BSeR (Bjornestedt,M.et.al.,1992).

Removal of selenate alone or different compounds and selenate from waste water employing the MBfR technology have been investigating by (Chung,J.et.al.,2008; Chung J.et.al.,2007; Chung J.et.al.,2010; Van Ginkel, S.W.et.al.,2011).Here on the surface of the cylindrical reactor biofilm of *Cupriavidus metallidurans* bacterial membrane present receive bubble-less H_2 gas this autohydrogenotrophic microbe biconvert very efficiently Se-oxyanions from contaminated water (Van Ginkel, S.W.et.al.,2011) . It is advantageous to

use hollow fiber membranes in the MBfR system as it provides high surface to volume ratio and withstand purging of high gas pressure also (Tan L.C.et.al.,2016) and keep the pores of hydrophobic membranes dry to facilitate rapid diffusion of gas to get bioremediation result as predicted. The multispecies autotrophic micro-biofilm grows luxuriantly in the contaminated water being treated for bioremediation. The Se-oxyanion reduction is coupled with oxidation of hydrogen (act as electron donor) molecule and retainment inside microbial biofilms of Se^0 thus achieving 94% removal of SeO_4^{2-} aided by variable hydrogen pressure maintenance in the system (Chung J.et.al.,2006) to recover crystalloid aggregates of elemental selenium (Ontiveras-Valencia, A.et.al.,2016) . According to Tan L.C.et.al.,(2016) use of pyrosequencing 16S rRNA method to confirm Denitratisoma and Dechloromas growth in biofilm, these denitrifying bacteria easily tolerated the extreme level of SeO_4^{2-} . Lay, C.Y. et.al.,(2016) preferred methane gas as electron donor in the MBfR system because of its low cost effectiveness due to easy availability of cheap methane gas from anaerobic digester and accumulation of Se-nanosphere in the bacterial biomass; one methanotrophic bacteria used methane to produce electron donating organic metabolites for other methanotrophic bacteria species to reduce SeO_4^{2-} in the biofilm; one genus Methylomonas confirmed by 16S pyrosequencing rRNA could at the same instant oxidize methane and reduce SeO_4^{2-} . Research group Bjornstedt, M.et.al.,(1992) stated reason like failure to use this system on industrial scale mainly because of prohibition on large scale manufacture and use of costly electron donors for operation of the reactors.

The USAB system : The widely and mainly used method for anaerobic treatment of industrial effluents is the up flow anaerobic sludge blanket reactor that seems a perfect way for removal of microbial biomass flocculates as well as suspended solids, where heavier particulate sludge bed deposited at the bottom provide substratum for bioconversion of Se oxyanions (Seghezzi,I.et.al.,1998),higher starting time for heavy organic anaerobic sludge can be done so that the flocculates and granular biogas formed continuously remain in contact with the bulk of influent sludge for anaerobic digester (Seghezzi,I.et.al.,1998). In San Joaquin Valley California (NAMC,2010) influent with a heavy level $500\mu\text{gL}^{-1}$ Se treated in AAADRC pilot plant efficiently decreased the Se content from 58% to 90% Lenz, M.et.al.,(2007) under methanogenic, sulphate-reducing and denitrifying conditions in several experiments and reported encouraging results to remove Se- oxyanions from SeO_4^{2-} synthetic waste waters (Lenz,M.et.al.,2008 Lenz,M.et.al., 2008). Similarly, in a selenium respiring subpopulation of bacteria and sulphate reducing bacteria (methanogenic – sulphate reducing conditions) in the UASB reactor using lactate molecules as electron donor 99% of SeO_4^{2-} removal could be achieved (Lenz, M.et.al.,2007). Remedial solutions include Se-free purified water, energy and Se^0 recovery in methanogenic condtions for Se oxyanions containing methanogenic sludges using this system is advantageous (Bjornstedt, M.et.al., 1892),efficiency of the same at thermophilic conditions (55^0C) and proper retention of reduced selenium in microbial consortia mass for recovery of more SeO_4^{2-} by sulfurosprillum barnesii and D. indicum bioconversion (Dessi.P.et.al.,2016), such operation must be done in

controlled condition to prevent elevation of effluent selenium levels by process either biomethylation or bioconversion by selenium species (Tan,L.C.et.al.,2016) .

The SBR system:- It incorporate sequential operations like the filling reaction, sedimentation, withdrawal, purging of gas and inactivity (Gali,A.et.al.,2008) to process waste water to remove Se by alternating oxic and anoxic conditions (Chan,Y.J.et.al.,2009 and Gali, A.et.al.,2008), mostly to separate dyes from textile wastewater; and reduction of both the SeO_3^{2-} and SeO_4^{2-} in waste water by denitrifying bacterial aggregate which utilize acetate as electron donor ,after 150 hour lag phase a higher reduction rate of SeO_3^{2-} then the SeO_4^{2-} have been demonstrated (Rege,M.A.et.al.,1999). Bacterial strains *Thauera selenatis* (Macy,J.M.et.al.,1993) and *Bacillus* sp. SF-1 (Kashiwa,M.et.al.,2001) for bio-remediation of SeO_4^{2-} waste water lead to SeO_3^{2-} accumulation after a time and showed its influence on the bacterial survival. Activated sludge from a waste water treatment plant along with NH_4^+ provided microbial consortium to remove SeO_4^{2-} upto 100% and ammonium upto 95% level respectively by partial nitrification and also nitrification/denitrification involving anaerobic and aerobic conditions (Mal,J.et.al.,2016),efficiency enhancement occurred by lengthening of anaerobic phase for 3 to 4.5 hours duration .Due to accumulation of greater proportion of biogenic Se^0 in the activated sludge low concentrations of both volatile and elemental selenium was detected in the effluent. Many more problems to be addressed include research information to know remedial measures for waste water simultaneously containing Se and other metal contaminants, limit of effluent discharge and disposal of the concentrated selenium solids permitted by various authorities (Tan,L.C.et.al.,2016 and Bjornstedt,M.et.al.,1992). Less research studies on Se polluted soil exist in literature but aerobic rhizobacteria species of genus *Bacillus* when tested by Parkash,N,T.et.al.,(2010) to remove SeO_4^{2-} and SeO_3^{2-} was intended to correct concentrations of selenium toxicity.

Meticulous and judicious use of green technology designed nanoparticles of Se to resolve ever increasing and persisting problems to mitigate and protect life on earth.

Nanoparticles due to its miniscule size posses higher surface energy, larger surface area, spatial confinement and less imperfectiveness (Chaudhary,S.et.al.,2016) . They have wide application in agriculture, biotechnology, biomedicine, nanobiotechnology , pharmacology, optoelectronics, etc., because of their size morphology, chemical composition, surface functionality and crystal structure (Rasouli, M,2019; Placenza, E.et.al.,2018 and Elahian, F,et.al.,2017). Multitude of physical and chemical based methods have been greatly researched to construct engineered nanoparticles and include laser ablation, co-precipitation, and hydrothermal process, solvo-thermal electrochemical techniques, sonochemistry and microwave assisted methods (Brito-Silva,A.M.et.al.,2010; Nee,C.H.et.al.,2016; Anbrasu,M.et.al.,2015; Janjua, M.R.S.A. 2019; Li,M.et.al.,2020; Clark, L.et.al.,2020; Cheng,G.et.al.,2010; Yang, S.et.al.,2010; Ricco,R.et.al.,2011; Brayner, R.et.al.,2010; Brayner,R.et.al.,2011; Starowicz,M.et.al.,2011; Armijo Garcia,D.et.al.,2020;

Yan,Q.et.al.,2019; Kumar,S.V.et.al.,2019 and Bafana,A.et.al.,2018). To prevent production of dangerous chemicals, to decline or cease use of environmentally disastrous pollutants for bioremediation natural biological systems one is bacteria is employed in metallic and metalloid synthesis of nanoparticles generally using aqueous solution to bring about bio reduction process at room or mildthermal and atmospheric pressure condition respectively (Das,S.K. and Marsili, E.A,2010; Gahlawat, G. and Roy Chaudhary,A.2019 ; Kuppuswamy P.et.al.,2016; Singh, P.et.al.,2016; Rahman,A.et.al.,2019 and Wang, D.et.al.,2019) .Biological system resources open new frontiers to prepare biogenic nanoparticles for use in clinical fields in comparison to toxic chemicals nanoparticles (Gomez- Gomez,A.et.al.,2019; Dahaoumane,S.A.et.al.,2017 and Rahman,A.et.al.,2020). Currently green synthesis of inorganic nanoparticles using microorganisms help to generate diverse shaped, size and composition, unique physicochemical and biological properties possessing for example SeNPs and TeNPs (Pearce, C.I.et.al.,2009 and Pasula, R.R.et.al.,2017).Microorganisms are nanofactories to fabricate nanostructures by virtue of their accumulatory nature to detoxify and reduce metal salts to metallic nanoparticles and do not require personal skill and sophisticated equipment but have limitations regarding composition, crystallinity , morphology size distribution and polydispersity (Xia,X. et.al.,2018 and Rajasree, R.S.R.and Gayathri,S,2015). Se posses photoconductive, semiconductive and optical properties, fabricated Se nanostructures catalyze removal or recovery of contaminant Hg^{2+} from different polluted environments by chelation process (Filippo,E.et.al.,2010; Zang,X.et.al.,2013; Om,D.et.al.,2016 and Wang, R.et.al.,2013) ,degrades many toxic chemicals trypan blue dye (Bhawani, P.et.al.,2013)is an efficient biological sensor for H_2O_2 in different matrices (Wang, T.et.al.,2010), their tremendous absorptive function antioxidant functions and biological reactivity (Turner, R.J.et.al.,2012; Ingale,A.G.et.al.,2013 and Wang, H.et.al.,2007), they guard structure integrity of DNA by blocking oxidation (Wang, H.et.al.,2007),exhibit antimicrobial, anticancer activity, high biocompatibility for non cytotoxicity against human fibroblasts and dendritic cells to treat diseases (Tran,P.A.,et.al.,2011; Piacenza, E.et.al.,2017; Ahmad,M.S.et.al.,2015; Huang,W.et.al.,2016; Zonero,E.et.al.,2015 ; Cremonini,E.et.al.,2016 and Alivisatos,A.P.1996) and disallow growth of pathogenic planktonic or biofilm bacteria like E.coli, P. aeruginosa and S. aureus in the environment.

- **Selenium nanoparticles synthesis using various bacteria**

The easy handling time, short synthesis time simple genetic modifications., etc., (Wang, T.et.al.,2019), facilitate biosynthesis of spherical, hexagonal, polygonal and triangular biogenic Se nanostructures particles (Esteven, E.C.et.al.,2017), aerobic bacteria Streptomyces minutiseleroticus MIOA62, Comamonas testosteroni , Lactobacillus sp., Bifidobacterium sp, and Streptococcus thermophilus, Enterobacter cloacae Z0206, Azospirillum brasilense and the gram + ve bacteria bacillus strains: Bacillus sp. MSh-1, B.subtilis, and B. Cereus (Ramya, S.et.al.,2015; Zheng, S.et.al.,2014; Eszenyi. S.et.al.,2011; Vogel,M.et.al.,2018; Shakihai,M.et.al.,2010 and 2013; Wang, T.et.al.,2010 and Pouri,

S.et.al.,2018). These aerobic and anaerobic bacteria by various reduction biochemical pathways bioconvert inorganic selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}) to elemental red selenite Se(0) assuming variable morphological nanostructures (Dhanjal, S.et.al.,2010; Pasula,R.R.et.al.,2017; Bajaj,M.et.al.,2012; Lampsi, S.et.al.,2017 and Estevam,E.c.et.al.,2017). For treating very effectively agriculture soil harbouring Se simple, rapidly multiplying selenium reducing bacterial species that more effectively and precisely biosynthesize SeNPs under aerobic conditions have been widely used (Tan,Y.et.al.,2018; Liu,W.et.al.,2016 and Shoebi, S.et.al.,201). Heavy metal cation include Cu^{2+} , Zn^{2+} , As^{4+} and Se^{4+} and aerobic strain of *C.testosteroni* S44 easily survive without experiencing any toxic effects of above metal ions. The sulphite reductase (Cys IG) enzymes has been believed to be the general sulphate reduction pathway for Se(VI) by aerobic organisms to SeNP (Tan,Y.et.al.,2018). Similarly, *Alishewanella* sp. WH16-1 genome contain the Cr(VI) reductase (CsrF) and act as aerobic selenite reductase (Xia,X.et.al.,2018) and resembles like flavoenzymes ChR, FerB and ArSH, CsrF reductase may have role as a Se (IV) reductase. The reductase of Se oxyanions by aerobic bacteria occur intracellularly and Se(0) SeNPs are released out by cell lysis (Tan,L.C.et.al.,2018 and Tomei,F.A.et.al.,1995) rapid expulsion route (Losi,M.E.et.al.,1997), extracellular release by vesicular transits (Kessi, J.et.al.,1999) and lysis of hypha fragmentation (Tan,L.C.et.al.,2016) appear as common expulsion pathways ,precise pathway not known. In aerobic bacteria extracellular reduction of Se-oxyanions cannot occur because electron is accepted by oxygen before that of Se(IV) (Tan,Y.et.al.,2018 and 2016) but reduction occur easily on surface of anaerobic bacterial cell first Se(VI) get reduced to Se (IV), later Se(VI) get reduced in turn to yield SeNPs (Nancharial,Y.V.et.a.,2015) by the action of *Shewanella* sp. HN-41) (Tam,K.et.al.,2010); *S. oneidensis* MR-1 (Li,D.B.et.al.,2014), *Stenotrophomonas bentonitic* (Zonaro,E.et.al.,2015), *Alishewanella* sp. WH16-1 (Xia,X.et.al.,2018), *Vibrio natriegens* (Xu,C.et.al.,2018) and the facultative anaerobic bacteria *L. casei* 393 (Xu,C.et.al.,2018). Selenium nanoparticles can be fabricated by anaerobic upflow sludge blanket reactor (Tan,L.C.et.al.,2018, Wadgaonkar S.L.et.al.,2018, Staicu,L.C.et.al.,2015 and Dessi,P.et.al.,2016). *Azoarcus* sp.CIB biosynthesized SeNPs in aerobic as well as anaerobic conditions (Fernandez-Llmosas,H.et.al.,2016). According to Tugaraova,A.V.et.al.,(2020) SeNP biosynthesis by *Aspergillus brasiliense* first transport of Se-ions into cell occurs followed by reduction to Se (0) nuclei, later after release of Se(0) nuclei in supernatant lead to extracellular formation of SeNPs. Estevam, et.al.,(2017) obtained SeNPs by using *Staphylococcus carnosus* TM300; these particles when stabilized by attaching protein cocktails did not precipitate and proved antinematocidal against nanopathogenic nematode *Steinernema feltiae* and biological active against bacteria and yeasts respectively. Wadhvani, S.A.et.al.,2017 described synthesis of spherical SeNP of 78 nm diameter post 6 hours incubation of sodium selenate using *Acinetobacter* sp. SW 30 cell suspension and its proteins (TCP) as precursors, but at 48 hours rod shaped SeNPs developed at PH value 6 to 10 and 1.5.mM and 3..0 mM precursor concentrations whereas supernatant at 4mg mL⁻¹ of TCP developed 79 nm diameter polygonal nanoparticles. A study of 47 bacterial strains by Figueroa, M .et.al.,(2018) revealed in vivo and in vitro synthesis of

Se and Te nanostructures with the help of *Acinetobacter schindleri* and *Staphylococcus sciuri*. Crude and purified protein respectively with *E. cloacae* glutathione reductase (G or A) in vitro experiments generated Se nanostructures of rod, triangular and spherical configurations respectively (Losi, M.E. et al., 1997). Multitude of biomolecules include glutathione (GSH) (Song, D. et al., 2017; Tan, Y. et al., 2016 and Kessi, J. et al., 2004), glutathione reductase (Hunter, W. et al., 2014), proteins thioredoxin reductase (Hunter, W. et al., 2014 and Zhao, G. et al., 2018). Serine ABC reductase (Kraft, T. et al., 2000) fumarate reductase (Song, D. et al., 2017 and Li, D. et al., 2014), NADH-dependent enzymes (Hunter, J.W. et al., 2014), NADH-flavin reductase (Kurdo, M. et al., 2011 and Hunter, J.W. et al., 2014) membrane bound SrdBCA amino acid sequence (Kurdo, M. et al., 2011) DMSO reductase family of molybdoproteins (Afkar, E. et al., 2003) sulphite reductase (Harrison, G. et al., 1984), Hydrogenase I (Yanke, L.J. et al., 1995), nitrite reductase (Demoll, Decker, H and J.M. Macy 1993) chromate selenite reductase flavoenzyme (CsrF) (Xia, X. et al., 2018) and other enzymes and surfactants (Ridley, H. et al., 2006 and Kessi, J. 2006) all have been explored for their role in causing the reduction of Se-oxyanions to elemental Se(0) or selenium nanoparticles. Reducing, capping, and/or stabilizing agents are some biomolecules that alter features and regulate size distribution of SeNPs according to studies conducted by Dhanjal, S. et al., (2019) and Kora, A.J. (2018). In a research done by Ruiz Fresneda, M.A. et al., (2018) extracellular flagellar proteins showed ability to biotransform the amorphous Se(0) nanospheres to crystalline and polycrystalline one dimensional trigonal Se(0) nanostructures that assumes nanowire and polygonal morphology (Ruiz Fresneda, M.A. et al., 2018). Research work of Khoei, N.S. et al., (2017) revealed that electron donors activated the cytoplasmic enzymes of aerobic *Burkholderia fungorum* that reduced the selenites to Se(0) and carbohydrates, proteins and humic substances that composed the extracellular matrix stabilizes the SeNPs because of alteration in the zeta potential. In another study by several workers colloidal SeNPs coated by microorganisms exhibited electrostatic repulsion and prevent congregation to black amorphous selenium and can be attributed to elevated negative Z- potential values and also to cap formation by binding carbonyl groups of amino acid residues and SH groups of L- cysteine to metal NPs (Sonkusre, P. et al., 2014; Lenz, M. et al., 2011; Lynch, I. et al., 2005; Xue, L. et al., 2003 and Hnain, A. et al., 2013). According to Mclean, J. S. et al., (2002) microbe catalyze redox conversions affecting biomediation of oxyanions of arsenate and selenate to obtain insoluble forms. Here binding to electropositive sites on bacterial surface or formation of metal ligand association do not occur but depend upon enzyme activity and bulk of biomass involved.

Factors influencing metalloid nanoparticle synthesis by green technology

During green synthesis of SeNPs stabilization and production requirements include type of biomass, temperature range, wide pH range, chemical substances and time, because different microorganisms have their own such requirements. Moreover size, shape and composition of metalloid nanoparticles rely on pH (Alqadi, M.K. et al., 2014 and Castro, L. et al., 2010), loss of nanoscale structure occurred at pH 1.0 due to aggregation to

form 300 nm size SeNPs, at pH 8.0 in presence of precursor epigallocatechin-3-gallate (EGCG) Wu,S.et.al.,(2013) could fabricate spherical, dispersed 60 nm diameter SeNPs. More quantity of SeNPs were generated at pH 7 to 8 Akcay, F.A.et.al.,(2020) contrary to a decline in quantity occurred at pH ranging between 6 to 9 for selenite and 7 to 9 for selenate (Kurado,M.et.al.,2011), pH range of 4 to 10 successfully helped in the process (Wadhawani, S.A.et.al.,2017) but at pH 2.0 sodium selenate solution of 1.5 mM proved insufficient to provide abundant functional groups for reduction process . Same precursor at 3.0 mM yielded spherical and rod shaped selenium nanostructures which at 1.5 mM assumed spherical configuration (Wadhawani, S.A.et.al.,2017), reduction process take place up to 40°C in presence of *Acinetobacter* sp. SW 30 but nanorods may result at 80 to 100°C temperatures (Wadhawani, S.A.et.al.,2017), temperature controls formation and aggregation of SeNPs (Ge,J.et.al.,2006) blockage of biosynthesis of SeNPs above 45°C was demonstrated for bacteria (MollAnia, N.et.al.,2015), average incubation for most bacteria lead to growth, shrinkage and aggregation of NPs(Baer,D.R.2011) altering their morphology and quality; morphology, crystalline structure, optical absorption of NPs alter after their life span is over (Sadler,D.H.et.al.,2013).

Morphology and growth of NPs depend on the strength of precursors and reducing/surfactants (Dahoumane, S.A.et.al.,2017; Vijayanandan,A. S.et.al.,2018 and Moloto,N.et.al.,2009), colour intensity and rate of change during formation depends on precursor concentration (Dahoumane, S.A.et.al.,2012; and Rahman,A.et.al.,2019). Similarly ,precursor of Se like Na₂SeO₄, Na₂SeO₃ and SeO₂ at different pH and time yield different sizes and shapes of SeNPs, initial concentration of precursor influence SeNPs size . In his experiments with actinomycete *Rhodococcus aetheriovorans* BCP1 under conditioned and unconditioned physiological states of 0.5 and 2 mM of SeO₃²⁻ ,demonstrated toxicity of Se oxyanions, bioconversion rate and yield of Se(0). The size and size evolution of SeNPs depend on initial precursor, small SeNPs formed at the lowest concentration later develop into (SeNRs) rods. On the other hand at highest concentration of precursor the longest SeNPs formed finally convert to shortest selenium nanorods. Contradictory results of Wang,T.et.al.,(2010) showed no effect of different concentrations of sodium selenite on morphology and size of SeNPs synthesized by *Bacillus subtilis*. According to Menon, S.et.al.,(2019) sodium selenite precursor at 10 to 30 mM concentrations yielded optimum bioproduction of SeNP and influence of pH and reaction time was demonstrated. Thus, precursor concentration directly regulate quantity of NP formed and at lower precursor concentration and temperature NPs of smaller size are obtained (Vide infra).

Characterization of metalloid NPs using laboratory techniques.

The bio-functional effects and toxicity of the metalloid NPs require its characterization to determine physicochemical properties (Piacenza,E.et.al.,2018; Sayes,C.M. and Warheit, D.B.,2004 and 2003; Powers, K..et.al.,2009), like shape ,size porosity, crystallinity, size distribution, dispersion pattern and surface chemistry (Kapur,M.et.al.,2018). Extensively

used techniques by researchers globally are UV-visible spectroscopy, luminescence (LS), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), and Fourier transform infra-red spectroscopy (FTIR), X-ray diffraction (XRD). Lattice structure, crystallinity, and crystallite structure size of NPs by XRD generally use Debye-Scherrer equation (Armyo, G.D.et.al.,2020 and Estevan,E.C.et.al., 2017). To determine size, shape, size distribution and elemental composition (EDX) of NPs transmission and scanning electron microscopy (FESEM) are employed according to Kapur,M.et.al.(2018). Similarly, detection of surface functional groups of NPs require repeated analyses to confirm the results, for this FTIR is the technique of choice. Functional group probably bring about reduction of metal ions and/or the NP cap formation make it a colloidal stable entity (Wadhawani, S.A.et.al.,2017 and Rahman,A.et.al.,2019). Surface charge (Z- potential), the hydrodynamic diameter obtained by dynamic light scattering regarding NPs and their stability/ aggregation that is measured by Brownian movement provide necessary information to infer the biological role of nanoparticles (Kapur,M.et.al.,2018). The tridimensional visualization of NPs become easily possible using atomic force microscopy (AFM) that yield quantitative needed information concerned with length, width, height, morphology and surface texture (Dhanjal, S.et.al.,2010). In the present paper the authors suggest a possibility that in the rocks soil, and aquatic systems respectively such NPs or biogenic NPs can be searched in nature to confirm their existence. These may be formed by weathering of parent-rocks, in volcanoes, etc; in various celestial bodies in galaxies of our universe which is a natural laboratory providing all prerequisite condition physical, chemical, biological, engineering, etc, may help in the formation of chemical biological nanoparticles. Exploration to reveal this mystery of nanoparticles generation in space will throw light and help to understand the mechanism how TEM and SEM assume size, shape, dispersed aggregated configuration, etc., of the NPs and biogenic NPs. Space observation telescope if modified to incorporate automated TEM, SEM and other techniques may open new vistas in the frontiers of science and technology to decode the mystery which remains undiscovered and unknown, meteorites reaching the earth surface must be examined by geologist for finding nanostructures which form macrostructures on the earth. The infinite nanoscale to macro scale explosions (big bang theory., etc) in the universe probably evolved many galaxies in which solar system like ours were formed. Nuclear fusion reactions in the sun and other stars and nuclear fission reaction of radioactive substances in extra terrestrial universe and crust of earth and the invented nuclear reactor where daughter elements/ compounds are formed to release tremendous energy in space and time may be generating nanoparticles. Energy obey the laws of thermodynamics, their interconversion occurs through quantum (small and large quantities). Initially reduced atmosphere favoured evolution of anaerobes, now we know many of them that perform anaerobic functions and is a part of present and future technologies for human welfare. With the evolution of aerobes oxygen molecule evolved in earth's atmosphere. Thus, the redox-reaction/potential destructive and constructive pathway initiated in earth atmosphere, hydrosphere and biosphere. Anaerobes and aerobes reached earth by meteorites, asteroids, etc. In green

technology for bioremediation of metals and metalloids and the toxic compounds natural and artificial synthesized by humans can be effectively regulated in the ecosystem to totally contain or at least minimize their toxicity to living organisms is done using biogenic NPs and biofilms according to permissible limit concept of toxicity. Biogenic nanoparticles are generated by microbes on earth and elsewhere in the universe. Researches has been done world-wide by workers already discovered through experiments in laboratory, on-site pilot plants, in the developed miniature aerobic and anaerobic reactor models have shed light to unfold mysterious role played by anaerobic and aerobic singly or in combination as monospecies or multispecies micro consortia to recover toxicants in their less toxic elemental forms. Aerobic and anaerobic mono and multispecies combination have also been utilized for bioremediation of pollutants (metal, metalloids, etc) . Thus, the story of fabrication of biogenic NPs evolved and will continue. Low-cost, effective, non-toxic, manageable, easy handling green technology for bioremediation will be invented in near future. Zero-waste generation technology probably will never be invented or exist. In the present review paper the hypothesis proposed, explained and discussed is based on past, current and future researches to come and develop variable sizes of nanostructures by synthesis in the laboratories. Selenium-Tellurium alloy synthesized intracellularly or extracellularly is one example and many more may be their. The scope of present paper being limited it is not possible to discuss here creative thinking in detail, an attempt has been done.

- **Biological applications of selenium nanoparticles/nanostructures**

Multifunctions of SeNPs like nanomedicine, nanodetoxification in industries, mines, remediation of rural and urban waste generated in agriculture, fishery sectors, etc., exist at present. According to Thanh,N.T.et.al.,(2010); Salata,O.V,(2004)and Zamora-Ledezma,C.et.al.,(2020) the core of nanobiomaterial is/are nanoparticle fabricated to attach different functional groups to design low toxic and improvised effective drugs. Moreover, the functional surface groups also helps for imaging, sensing, and delivery of drugs to target sites (Mout,R.et.al.,2012). Hyperthermia, treatment of cancer, pathogens as well as biomolecule detection efficiently involve use of as obtained NPs (Soloviev,M.2007). Selenium NPs of various sizes and properties and their easy bioavailability and lower toxicity widens scope of its application (Zhang.J.et.al.,2008), due to its reduced toxicity it is used as antioxidant in food agent and to treat cancer (Wang,H.et.al.,2007). At a very low 2 ug/mL concentration nanoselenium efficiently and specifically treat patients suffering from prostatic cancer (Sonkusere,P.et.al.,2014). SeNPs posses antimicrobial property as they are prepared using stentrophomonas maltophilia(-) and B.mycooides strains to study effects like viability and function of the antigen presenting immune and non immune cells (fibroblasts). The as-produced SeNPs was nantoxic and did not elevate release of IL2, IL4 and IL6 cytokines that function as proinflammatory and immunostimulatory biomolecules

(Cremonini, E.et.al.,2016). Immunotoxic invitro culture experiments of bacterial generated/synthesized SeNPs exhibit their ability to induce apoptosis and suppress both growth and multiplication of human cancer cells(Ahmad,M. S.et.al.,2015;Filipe, V.et.al.,2010, Prasad, K. S.et.al.,2012 and Salenius, M.et.al.,2010). A very potent antiproliferative activity against 4T1 cells, MCF-7, NIH/3T3 and HEK 293 cell lines was demonstrated for acinetobacter sp. The Sw 30 synthesized SeNPs (Wadhawani,M.et.al.,2017)and B. oryiterrae synthesized SeNPs demonstrated great anticancer activity against H157 lung cancer cell lines (Schrauzer, G.N.2000). Extreme toxicity at higher concentration to human sarcoma cell line (HT-1080) occurred in assay when challenged to Bacillus sp. MSH-1 synthesised SeNPs. HT-1080 cells exhibited anti invasive property and moderate decline in expression of MMP indicate their use for treatment and reoccurrence of tumor metastases. Similarly, MTT assay explored and assessed cell viability, proliferation and cellular toxicity of breast cancer cells (Shakibiae,M.et.al.,2010) .According to Ahmed M. S.et.al.,(2015) SeNPs act as anticancer agents they release copper bound on DNA or from intracellular cytoplasm, later this metal ion help in preoxidation process, cancer cell lines such as Hep-G2 and MCF-7 are easily destroyed by the reactive oxygen species liberated during electron shuttling from copper to selenium nanoparticles. Being a major constituent of selenoproteins , selenium may play a role in enhancing detoxification of carcinogen. Other important bioactive functions of SeNPs that need mention include elevated immune surveillance, inhibition of tumor cell invasion and angiogenesis (Schrauzer,G.M,2008;Zeng,H.et.al.,2008 and Brown,C.D.et.al.,2018).

CONCLUSION

Bioremediation serve many purposes like detoxification of land air and aquatic ecosystems (Lentic and lotic fresh water, marine and estuarine waters), allow permissible limit of selenium to serve as micronutrient for all types of animals and human for normal growth, metabolism and reproduction. It provides healthy life without suffering from cancer and teratogenic effects leading to deaths and malformations in the body. Every activity of human alter environment and zero pollution technology will never be invented, but remediation must also be done meticulous and judiciously for the same. Creation and use of technology for sustainable development is most essential according to the author.

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