CHAPTER 1

Introduction

1.1. The backdrop

Nanomaterials are formed naturally during processes like volcanic eruption, ocean spray, forest fires etc; they are inadvertently produced through some industrial processes (coal fire, welding, diesel engine exhaust etc); nanomaterials are also meaningfully synthesized for specific purposes (drug delivery, cosmetic, and household products etc) [1,2]. Hence, nanotechnology deals with synthesis of useful and commercially viable nanoscale materials. The technology allows for the control, modification, study, and manufacture of chemical substances in 1-100 nanometer size range [3]. Some workers termed the chemically synthesized nanomaterials as "engineered nanomaterials" (ENMs) [4]. These materials can greatly mimic and/or change biological and natural processes owing to their low hydrodynamic diameters and unique structures. Under the perspectives of rapid growth of manufacturing industries, nano-technology is one of the most widely used avenues due to certain useful properties of nanoparticles than their bulk materials [5]. The ever-increasing demand for novel nanomaterials has expanded their synthesis and utilization to great extent. Consequently, that has led to severe increase in their release into the environment, causing pollution [6,7].

According to Keller et al. [8], about 9 - 37% of ENMs have been released directly into the atmosphere, while the remaining 63 - 91% has been land filled. Such huge and persistent rate of land disposal should contaminate the terrestrial ecosystems through leaching, accumulation or some other processes [8]. The release of these materials in soil must also have some impacts on soil environment and subsequently on plant health. However, very little is known about the impact of these nanomaterials on soil qualities. Use of silver based nanomaterials in industrial processes is common. Eventually, land and water resources are greatly exposed to silver nanomaterials [9]. On the other hand, anthropogenic engineered Fe_3O_4 and Fe_2O_3 nanomaterials are extensively used in varied consumer products, despite of serious ecotoxicological concerns [10]. Although there are numerous reports on environmental impacts of silver nanoparticles, in-depth research on engineered iron oxide nanoparticles are rare in the literature. Moreover, there is dearth of adequate research with respect to the interactions among nanomaterials and soil physicochemical properties; their accumulation-dissolution dynamics in soil-plant systems; and their long term influence on soil health.

Under these perspectives, the present study was carried out to understand the impacts of two engineered nanomaterials (silver and iron oxide) on soil environment and plant health. Silver nanoparticles are one of the most widely utilized engineered nanoparticles due to its potential antimicrobial activity against all classes of microorganisms even at very low concentrations also and utilized in various sectors viz. biomedical, agriculture, textile industries etc [11]. Whereas, iron based nanomaterials can also be useful nutrient source for agricultural crops because iron is an essential micronutrient that helps for plant growth and plays an important role in the photosynthetic reactions [12]. Iron activates several enzymes and contributes in RNA synthesis and improves the performance of photo systems [13]. Iron oxides are magnetic nanoparticles and attracted attention of researchers because of several properties: small size, high magnetism and low toxicity.

1.1.1. Beneficial role

Owing to their profound role as an antimicrobial and antifungal agent silver nanoparticles have been utilized in different areas such as health industry, biomedical, drug delivery, cosmetics, food industries, agriculture, textile industries, and water treatment [11, 14, 15, 16, 17]. In medical industry AgNPs have an ample application including topical ointments and creams containing Ag to prevent the infections of burns and open wounds [18] in coating or embedding [19].

Iron oxide nanoparticles have been showing great application potential in different technological areas such as catalysts [20], clinical uses [21, 22], magnetic storage [23], bioseparation [24] etc. Their catalytic application has got massive popularity due to low cost, easy handling and ecofriendly nature. Recently iron oxide catalysts have been largely utilized in different laboratory, industry and chemical process in order to accelerate some chemical process [25].

1.1.2. Nanofertilizer: a new concept

With the increase of the population at the current alarming rate it is quite certain that there is demand for food in a similar manner. But however, there is limited land and even this quantity gets reduced day by day as the concrete jungle expands. Hence, it becomes necessary for people to determine ways to increase the yield and productivity of plants but within a desired cost and limit because ultimately it has to be affordable by the producer families otherwise it would remain as a technology invented but unused. Here, comes the need of fertilizers; but whatsoever the use of chemical fertilizers may seem beneficial at the moment but will show its ugly head with the advent of time and hence to be hazardous for the environment.

As promising as the branch of nanotechnolgy is, the emergence of nanofertilizers was just a matter of time. According to Rai et al. [26] in order to make nanofertilizers encapsulation of fertilizers within a nanoparticle can be done in either three ways a) the nutrient can be encapsulated inside nanoporous materials, b) coated with thin polymer film, or c) delivered as particle or emulsions of nanoscale dimensions. Moreover, De rosa et al. [27] reports that to synchronize the release of fertilizer-N and P with their uptake by plants nanofertilizers, nanodevices should be used, thereby reducing the nutrient losses to the air, water, soil via direct internalization by crops and their interaction with these three factors along with microbes. Veronica et al. [28] suggests for nanosized formulation of mineral micronutrients which might be able to improve solubility and dispersion of insoluble nutrients in soil, thereby reducing soil absorption and fixation and increasing the bioavailability leading to increased nutrient uptake efficiency. According to Naderi et al. [29] nanotechnology has provided the feasibility of exploiting nanoscale or nanostructured materials as fertilizer carriers or controlled-release vectors for building of so-called "smart fertilizer" as new facilities to enhance nutrient use efficiency and reduce costs of environmental protection. The ability to regulate the release of fertilizers depend on the type of nanofertilizer whether it is coating or binding of nano composites. It has been shown that application of a nano-composite consists of N, P, K, micronutrients, mannose and amino acids which help in enhancing the uptake and use of nutrients by grain crops. However, the major challenge in regard to agricultural use is to optimize the large scale synthetic routes of nanomaterials. In general, it is apprehended that the large scale production of nanomaterials may cost their beneficial roles as determined through lab scale experimentations. As a result, the impact assessment studies are also needed to be so designed that the outcomes could be drawn on a lager canvas.

In recent time, green approaches for preparation of nanoparticles are highly attaining significance in research area. We have lately described the utilization of various bio-resources for preparation of nanoparticles. In this context, we have tried to explore yet another phyto-resource- *Thuja occidentalis* (family Cupressaceous) for the preparation of poly (ethylene glycol) assisted silver (PEG@Ag) nanoparticles. Oxalate capped iron oxide nanoparticle was also prepared from ferrous sulphate salt and oxalic acid following green chemistry method. In this respect, we were interested in assessing the ecological effect of the prepared silver and oxalate capped iron oxide nanoparticles upon soil heath status, earthworm response (*Eisenia fetida*), and leaching behaviour of ions in soil and aqueous media and plant effect.

1.2. Major research gap and the research questions

Although chelated (e.g., EDTA, DTPA etc) Fe fertilizers are used to increase the utilization efficiency, the soil pH often interfere with the stability of chelated compounds [30]. In this context, Fe-(ox) nanoparticles may efficiently and steadily supply nutrient to plants grown in varied soil. On the other hand, AgNP are reported to alter bacterial community structure in rhizosphere soil thereby greatly pacify soil enzymatic activity and significantly alter carbon use [31]. Moreover, AgNP suppress soil nitrification rate and greatly affect earthworm health in soil [32,33]. Whereas, there are reports on beneficial impacts of AgNP on soil health and crop growth as discussed earlier, which implies that there are considerable dilemma in regard to the holistic impacts of AgNP on soil-plant system. Hence, the identified research gaps are identified as follows:

1. The response of soil physico-chemical properties to the exposure of silver and iron based nanomaterials and vice-versa are rarely been studied.
2. There are dilemmas on the impacts of silver and iron oxide nanomaterials on earthworms and soil borne microorganisms; the effects dose and decay of nanomaterials within soil systems on soil biological environment are yet to be studied thoroughly.

3. To the best of my knowledge, the potency of organically capped iron-oxide nanomaterials as alternative to commercially established source of iron in agriculture has not been verified.
4. So far, no effort has been undertaken to standardize large scale synthetic route of iron oxide nanomaterials for agricultural application.
5. Finally, reports on large scale field based impact assessment of silver and iron oxide nanomaterials are scanty in the literature.

On the basis of the identified research gaps, the following research questions have been derived:

1. How the silver nanomaterials influence soil properties in regard to soil structure, ionization status, and soil reactions (acidity and/or alkalinity)?
2. Are the effects of silver and iron oxide nanomaterials vary on dose basis?
3. How the agglomeration/aggregation dynamics of nano exposed soils shall vary?
4. Is it feasible to scale-up the synthetic route of oxalate capped iron-oxide nanomaterials without compromising their properties and agricultural benefits?
5. Are the oxalate capping and the orthorhombic structure of the synthesized Fe-oxide nanomaterials renders beneficial impacts on soil quality? If so, then why? The effects of Fe based nanoparticles on availability of N and P in soil are not identified till now as well as their micronutrient values are needed to be tested on field levels.

And, hence the major objectives of this research were as below:

1.3. Aims and objectives

1. To study the impact of synthesized silver nanomaterial and oxalate capped iron oxide nanomaterial on soil health.
2. To study the leaching and solubility patterns of ions in the nanomaterial inoculated soil and aqueous media.
3. To study the impact of these nanomaterials on health and reproduction of soil borne earthworm.
4. To evaluate crop responses to silver and oxalate capped iron oxide nanomaterials exposure.

1.4. Thesis organization

The thesis has been organized in six different chapters. A brief discussion of the contents of different chapters is given below:

Chapter 1: Chapter 1 describes the prime research objectives of this study along with the key questions or research problems based on which the research plan has been organized.

Chapter 2: Chapter 2 presents the surveyed literatures of related works done by various workers before the commencement of this research work. Literature review had provided the base information which in turn helps in the formulation of research plan and to rationalize of the study.

Chapter 3: Chapter 3 describes briefly the various methods and methodology which were adopted to achieve the targeted objectives of this study. Quality assurance and quality control exercises which were conducted throughout the work period has also described in this section.

Chapter 4: The significant results recorded under different experimentations of silver nanoparticles are represented in particulars in this section. The results obtained from the different experiments conducted to achieve the targeted objectives are arranged in different sections. Representation of the data was done in tables and /or figures.

Chapter 5: The relevant and considerable results obtained under various experiments of OCIO are presented in details in this section. Figures and/or tables were arranged to represent the recorded data.

Chapter 6: This is the final chapter describes the major findings or outcome of this research work. The hypothesis of this study has also described in this section. In this chapter the scope and future prospects of this investigation has also been described

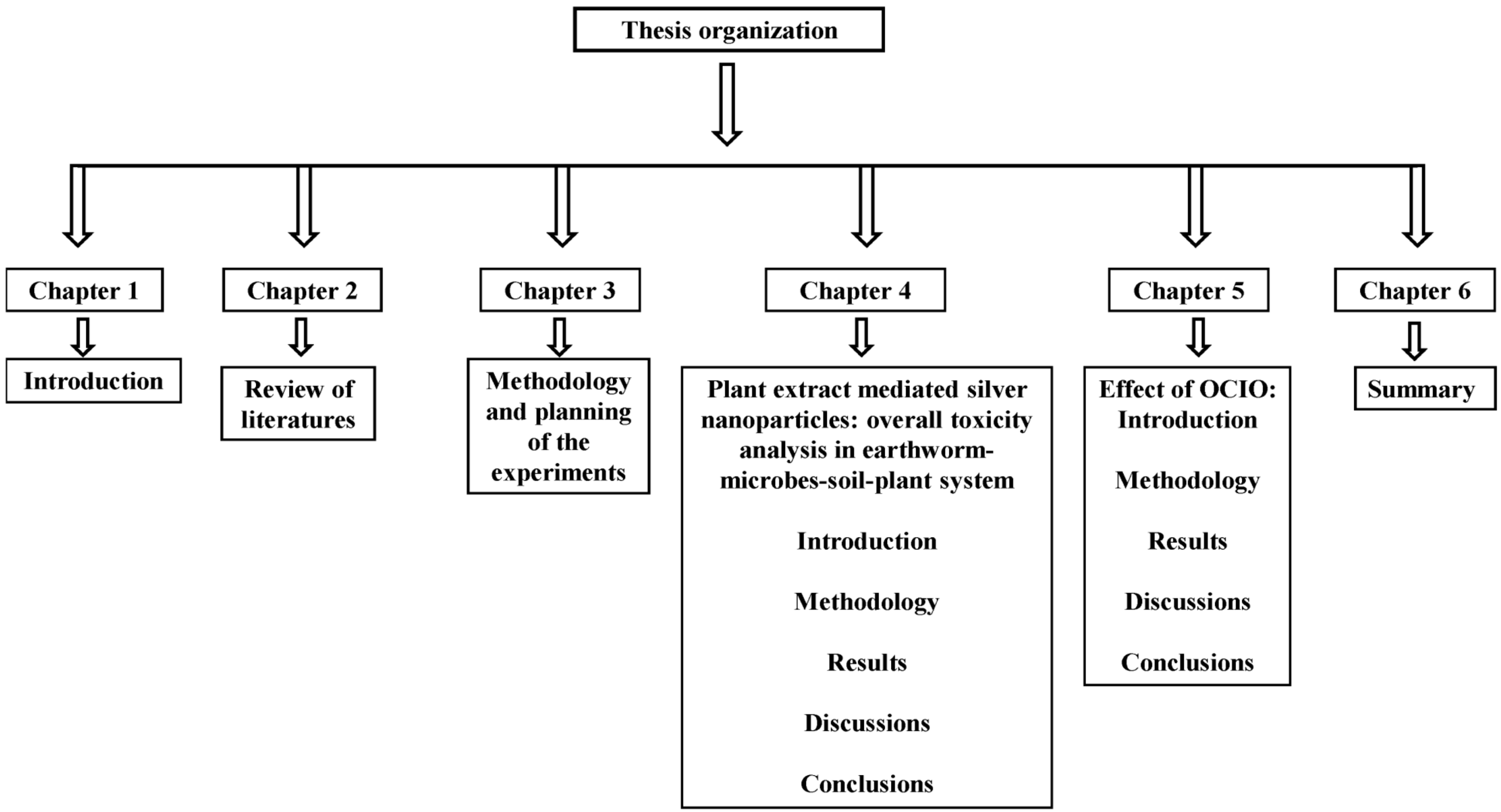

Fig. 1.1: Schematic representation of the thesis organization

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