

Analytical approach to the waste management of nanomaterials in developing countries

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Abstract

Nanotechnology has been worldwide rapidly growing and developing scientific and industrial field since 1990s. Nanomaterials (NMs) and nanoparticles (NPs) refer the materials having thousand millionth of a meter (10⁻⁹ meter) size. NMs production and consumption increase every passing day. Different variety of consumption products as sunscreen, cosmetics, antibacterial textile, batteries, automotive industry, glass coating, medical and pharmaceutical include NMs. Some consumer products including NMs such as cosmetics, drugs etc. directly expose humans and the environment. Although nanotechnology field exhibit large scale economic and research potential, there are limited information about biological and environmental risk of nanoproducts during their “end of life” release to environment. It is very difficult to detect and prevent NMs release to the environment at their end of life. NMs have strong interaction with biological structures, due to their size, shape, chemical and bioaccumulation features. NMs are called as “nanocontaminants” or “nanowaste” when they release to environment and offer hazardous effects. Toxicological risks of nanocontaminants and nanowastes are not fully understood. NMs behaviour in the environment is fully different from regular materials and they may show more reactive and toxic effects compared to other bulk waste materials in the environment. In developed countries legislative regulations were constituted and been improved parallel to the development of the product range, however in developing countries there is wide gap about determination of nanowastes and legislative regulations are still insufficient. The goal of this article is to initiate discussion on handling of NMs containing wastes and nanowaste management in developing countries.

Introduction

The Latin word “*nano*” that means dwarf, that refers one thousand millionth of a meter (10⁻⁹ m). Nanotechnology is that rapidly progressing and multidisciplinary scientific field and has wide scope of application area [1]. Nanotechnology researches are highly attract attentions of scientists and paper on nanotechnology is being published rapidly [2]. Nanoparticles, nanoplates and nanofibers are the International Organization for Standardization (ISO) classification of nanomaterials [3]. Nanoparticles have three main classifications that based on dimensions are; one dimension (1-100 nm thin film sized) two dimension (carbon nanotubes) and three dimension (Dendrimers, Quantum Dots, Fullerenes). Nanoparticles can be characterized by advanced electron microscopy techniques as atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [1,4].

Materials that 1-100 nanometres (nm) or include nanoscale particles are termed as nanomaterials (Figure 1) [2]. It has been reported that nanomaterials production annual production amount will increase 58,000 tons by 2020 [5]. It has been reported that, global nanomaterial production is regularly increase 25% per year and [3]. Due to different research reports, global nanomaterial market growing rate will be reach to 55.0 billion USD by 2022. Prominent regulatory coordinators about nanomaterials are The United States Environmental Protection Agency (EPA), The European Chemicals Agency (ECHA), Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in the US and the EU and also the Ministry of Industry and Information Technology (MIIT) in China [6-9].

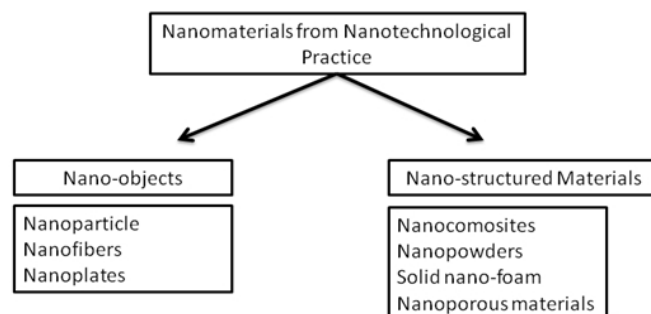


Figure 1. Summarized definition of nanomaterials (ISO, 2008) [10]

Concerning about NMs effects on human health and environment cause restrictions in global marketing. Most of NMs are toxic or include toxic solvents, release hazardous intermediate compounds during production phases. Thus governments should organize critical legislative regulations and managements [9].

Nanocontaminants and nanowaste

Particles that sized at nanoscales regularly occurs in the environment. Also increasing number of nanomaterials releasing

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to environment from market products that include cosmetics, textiles, lubricants, batteries and solar cells products, drug delivery materials, medical imaging agents and medical implants etc. regularly. Nanomaterials conducts different types of transformations dependent to their molecular specifications which sometimes resulted with hazardous residuals in the environment called as “nanocontaminants”. There are contradictory evidences in the literature about effect of nanomaterials on human and environmental health in the literature, however important issues for risk characterization of nanomaterials are size, shape, solubility, chemical parameters, biocompatibility features of the particles to qualify (specify) them as “nanowaste” [3,11].

During regular production and usage phases of nanomaterial and nanopartcles, their wastes disposed like large scale sized products commonly [3]. And also nanoproducs that reach its end of life mix waste circulation too. [12-14]. This case make monitoring and quantification of nanowastes in complex environmental matrixes a current issue for ecosystem to do hazard identification. There are several different analytical methods for the characterisation of nanomaterials in the environment as waste. These methods based on nanomaterials particle number, elemental composition, particle size, particle distribution, aggregation state, shape, structure, surface area, surface charge and surface specifications [11]. Nanowastes behaviour are not same as normal wastes in the environment and it is hard to detect these materials with nowadays technology. Legal regulations and managements have critical role on identify and control of nanowastes [15].

Toxicological risks of nanowastes

There were limited data about distribution of nanomaterials into the environment and biological systems due to their uncontrollably entrance to environment [16,17]. Environmental detection and monitoring of nanowastes are important issues. Detection, quantification and analysis of nanowastes are more difficult compared large sized bulk wastes, because of their low concentrations, large chemical variety, other nanomaterials interference which occurs naturally in the environment as Al₂O₃, CuO, SiO₂, TiO₂, or ZnO and

insufficient analytical methods. Although there are different improved imaging techniques as Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and ICP-MS, it is still impossible determination and quantification of nanoparticles in complex solid phases [11].

Nanomaterials effects on environment and biological systems are not fully understood and unclear because of their wide range physical, chemical and biological features [18,19]. And these features of nanomaterials could be enhance their spread in environment and may increase toxic effects on the biological systems. Also nanomaterials may play role as a particle carrier in water and air due to their physical and chemical characteristics [20]. While with nanotechnology it is possible to work at nano scales, this new era introduce a new waste definition as “nanowaste”. Nanowastes can be spread out during production, storage and distribution and usage phases (Table 1). Nanowaste contamination routes were shown in Figure 2 According to British Standards Guide (BSI) in the environment there are four form of nanowastes as pure, material and surfaces include nanowaste, liquid phases include nanowastes and solid matrixes include nanowastes. There were several studies about nanowastes health and toxicological effects in the literature [16,18,21,22], however limited studies on nanowaste controlling and management. Nanomaterials uncontrolled releasing into the environment may generate short- and long-term high risks of nanowaste contamination of soil, agricultural products, underground waters and air [17].

Evaluating nanowaste is not same with larger particles in case of different physical and chemical properties of nanomaterials and nanoparticles. Although toxicological properties of larger molecules well defined, conditions are different in nanoscales and it is needed re-evaluating toxicological properties of these nanomaterials. For instance, if molecule size get smaller, its surface area and also its biological activity increase [2]. There are some examples at the below how nanoparticle contamination of groundwater, soil, air and water occurs. Nanoparticle directly releasing from technical compartments for instance using for water treatment or groundwater remediation, effects groundwaters and

Table 1. Significant nanotechnology appliaiton areas [26]

Automotive	Construction	Electronics	Food-drink	Medicine	Textile	Cosmetics	Military	Energy
Catalysts Painting Sensors	Insulation Flame retardants	Displades Laser diodes Fiber optics transistos	Packaging additives	Drug delivery Coast medium Test systems Diagnositic systems	Surface coating Coloring	Sunscreen Lipsticks Creams	Neutralizator of chemical weapons	Lighting Fuel cells Solar cells

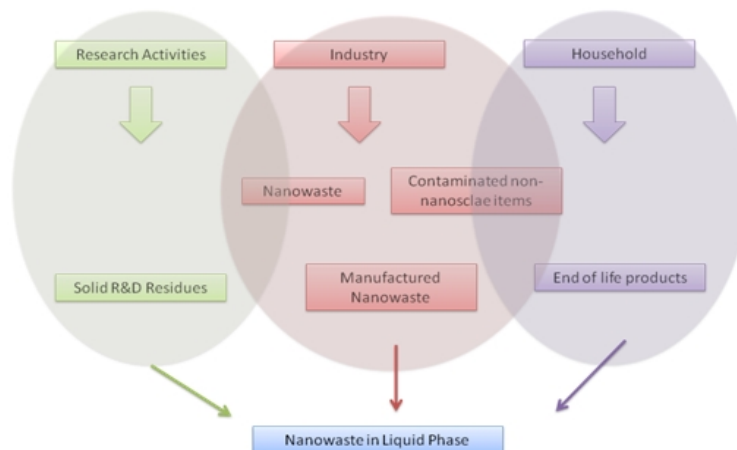


Figure 2. Nanowaste contamination routes [23]

air. Diffuse sources like fuels including CeO₂ or Paints including TiO₂ effects soil, water and air [24].

There are insufficient toxicological data from scientific studies about nanomaterials effects on mammalian and aquatic model systems in the literature that make complicate risk assessment and hazard identification of these materials. These limitations also negatively effect to arrangement of nanowaste management. While physical and chemical features are an advantage for usage of nanomaterials, same features are disadvantage for evaluate their toxicological profiles in biological systems and environment. In different areas as air, soil, water, nanowaste shows different toxicological characteristics [17]. Due to their different physical and chemical properties, nanoscales of bulk materials have higher toxicity and chemical reactivity. For instance, as a nanoparticle character asbestos was highly used without sufficient toxicity and hazardous data in the past caused several serious health impacts. Today asbestos is a banned product in many countries [10].

There are limited and contradictory data in the literature about toxic effects of nanomaterials. These data reported that some nanoparticles may pass the biological membrane barriers, transport via body fluids and may accumulate in target organs. Respiratory, cardiovascular, reproductive, central nervous system and urinary system are the main targets of nanoparticles that effects cellular molecular mechanisms of these systems. nanoparticles cause toxic effects primarily in respiratory system In case of their smaller size that enhance entrance respiratory system. Nanoparticles toxic effects are related their particle size than their molecular mass. Also nanoparticles surface encapsulation properties alter their toxicological effects in the biological system. Nano capsules, nanospheres and quantum dots are the another nanomaterials that commonly used as bio pharmacological vectors. A few toxicological data were in the literature about these types of nanomaterials. These studies reported that nanodots may release cytotoxic ions and initiate oxidative stress in cellular systems, however toxicologic data in workers of nanomaterial production were insufficient [25].

Titanium dioxide (TiO₂) nanoparticle was classified as possible human (group 2B) carcinogen by the International Agency for Research on Cancer (IARC). TiO₂ distribution to environment as waste cause disruptions and death of beneficial soil microorganisms may result with imbalance of ecosystem. Although carbon based nanomaterials have wide range production and application field in electronics, their hazardous toxic and carcinogenic effects limited their applications in biological systems. Carbon nanotubes usage in buidings initiate asbestos like toxic effects [10].

Nanomaterials usage in medicine and pharmacy

Nanotechnological improvements in medicine may lead to more effective and personalized therapy for diseases with lower adverse effects of drugs. Nanomaterials can be used as imaging with high resolution, targeting disease area, increasing bioavailability of drugs, increasing effects of the drugs and in tissue engineering. Carbon nanotubes, several nanoparticle types as superparamagnetic iron oxide nanoparticles (SPIONs), gold (AuNPs), magnetic, ferrofluidic, fluorescent, silver and copper nanoparticles, quantum dots (QD), nanogels, dendrimers and liposomes are commonly used nanomaterial types in medical applications. With further studies, nanomaterial options for medicinal applications will be increased [27,15].

Several different type of barriers plays key roles on absorption, distribution, metabolization and excretion of the drugs. Recent studies are focused on the bypass of biological barriers that decrease

drug's effectiveness in the body. Some examples that cross the biologic barriers are given in the below paragraphs. PEGylation (grafting with polyethylene glycol) one of the process that increase the hemodynamic of the drugs in the body. Micelles are the another nanodrug composing type that increase the effects of drugs with hydrophobic interaction. For instance, anticancer drugs encapsulated into the micelles and then these micelles including drugs are decomposed in the acidic environment of the tumour cells. And also nanoparticles design and use for induce immune system to initiate immune response to influenza infections through respiratory administration. Several types nanocarriers and nanocontainers are designed for DNA therapy and still investigating under in vitro studies. Thus, several from basic to complex nanomaterials and nanoparticles designed and studied for several aspects for medicinal applications. These materials enable to drugs; accessing target area by-passing the biologic barriers, decreasing the drug tolerance, escape from drug clearance, increasing drug activity [28].

Nanoparticles and nanodevices usage in medicinal applications and drug delivery are growing rapidly scientific area [29]. Some examples about nanoparticle usage in medicinal area listed below;

- Magnetic nanoparticles for quantify several parameters in polarized cells, in molecular biology studies and diagnostic purpose.
- For cancer therapy, for the purpose of transporting chemical factors in drug targeting.
- Drug biomanipulation
- Labelling biomolecules to evaluate physiological features of the cell
- Contrasting agent in imaging
- Antibacterial, biocidal and antifungal properties
- Biochemical tests and analysis [29-32]

Risk assessment of nanowaste in the environment

Automotive, cosmetic, medical, textile industries are the main nanowaste sources and different type of nanomaterials, bare or functionalized nanoparticles are released into the air, soil and water rapidly in the environment after production processes from these industries. After degradation in the environment these nanowastes may accumulate and show ecotoxicological effects.

De gradated nanowastes which released to environment have short-term effects on biological systems, however low soluble and degradable nanomaterials have tendency to accumulate in the environment and biological systems. Despite to several scientific studies and technological improvement about nanotechnology, it is stil difficult to describe toxicity and bioavailability of nanomaterials in biological systems [15].

There are two risk categories defined in the literature as "known risks" and "potential risks". Nanoparticles risks are categorized under "potential risks". Potentials risk factors have features as; it is not certain that material or chemical have danger and when this material or chemical occur is it cause a significant damage. There are several in-vitro and in vivo studies about nanoparticles toxic effects, however further studies should done to explain detailed hazard effects of these materials. Different types of nanoparticles different toxic doses and dose-response associations evaluated and revealed in different species, however it is needed comprehensive and extensive guidelines that include these studies and explain detailed toxicity and risk assessments. Due to non-

standardized testing protocols, it is difficult to clearly determine chemical properties of nano sized particles, their characteristics in the environment and biological systems, and also their adverse effects [33].

Management

In Turkey, Medical Waste Control Regulation was first put in place in 1993 from Ministry of Environment and Forestry legislators, then in 2005 this regulation revised to New Medical Waste Control Regulation (MWCR) which in align with EU Environmental Directives was published. MWCR include issues on collection, transportation, storage, disposal of medical wastes that classified into four group as municipal, medical waste which are infectious, pathological and sharps, hazardous and radioactive wastes [34].

In 1983, Ministry of Environment published Law 2872 which include regulations about improving environmental conditions in Turkey and after 20 year duration only three regulative management update became to main topic which in 1993, 2003 and 2005. This law regulation is not enough for today because of several type of waste characteristics and different disposal methods for different types of wastes. Although strict regulations about municipal solid waste regulations, wrong disposal methods of municipal solid waste like open dumping ongoing problem in developing countries.

According to The Turkish State Statistical Institute (TURKSTAT) 2014 report, municipal solid waste generation was approximately 26 million ton and this number rising each passing year. In our country, different departments and organisations work on waste management which cause interaction problems and serious implementation and administrative disruptions. In rural areas this problems increase incrementally due to controlling disruptions [35].

In Turkey there is no information or regulation about nanowaste in "Hazardous Waste Management of Turkey" and in "cosmetic management". However in the world few developed countries refers nanowaste risk in their managements or waste guidelines as shown in Table 2 [36].

Discussion

Nanotechnological scientific studies and industry improving each passing day, therefore in parallel with this, wastes releasing environment increase too. Further studies and observations needed to determination and advanced risk assessment of nanowastes in the environment. There is big deficiency about management and Nano biomonitoring of nanowastes in developing countries. It is needed to prepare regulative managements on nanowastes releasing to environment before the nanoprodukt come to marketing. With today's technology it is limited and very expensive to detect nanowastes in the environment and also evaluate their toxicological risk assessment in the biological systems. Before publish highly effective nanowaste management, it is needed to develop recent and cheaper technology strategies which faster and include easier protocols to identify nanowastes in the environment and also in biological systems. Possible remediation and deactivation techniques should be developed that incorporate with waste management [37].

Table 2. Regulations for nanosafety in major countries [24]

Country	USA	EU	JAPAN	THAILAND	AUSTRALIA	KOREA
Regulations	TSCA FIFRA FFDCA	REACH CLP RoHS CR	MOE-METI including informations	NANOTEC	NICNAS	Comprehensive plans of nano-safety (2011.10)

Within this review article we want to fill existing knowledge gaps on NMs "end of life process" in Turkish Waste Management and provide data for scientist and regulatory authorities. For this purpose, some directions and suggestions to manage safe and effective waste regulations about nanowastes were given in this paper. Developing country governments should make a nanowaste detection, elimination, recycling and prevention strategies and technologies in contact with researches works on nanotechnology before preparing legislative managements. With recent scientific researches high throughput analytical methods should be developed for detecting nanowastes during their contaminating phases and effecting biological structures. And also improved detection technologies needed which discriminate new and old nanocontaminants in the environmental and biological samples. After detection, identifying and classification of nanocontaminants, improved technologies should be developed for removal of nanocontaminants from environment, especially from waste water. Scientist should carefully work on artificial intelligence software's to predict early nanowaste release to environment from industries, medical and pharmaceutical sector.

Official and semi-official organisations should set up by related ministry and semi-official organisations should organize regular surveillance to nanotechnology producing, using and nanotechnology research places regularly about waste releasing with developed new technology strategies. Industry, universities and governments in developing countries should handle nanowaste issue and recycling of nanocontaminants to prevent pollution and adverse health effects of these materials on biological structures. During landfilling, incineration and recycling processes of nanomaterials, several amounts of nanocontaminants release to the environment. To minimize releasing during landfilling, nanocontaminants chemical properties should know clearly and storage should convenient to this chemical properties. Governments in developing countries should pay a special budget to scientific research activities on highly sensitive detection protocols and analytical equipment's which discriminate noncontaminants from their natural counterparts.

Educative conference and workshops that organized by official and semi-official organisations to universities, industries, medical sector workers about nanowaste and their adverse effects on environment and health. To high quality and enhanced detection and prevention strategies, a formal nanocontaminant and nanowaste analysing laboratories should open in every region. To limiting occupational exposure of workers on this area, health control centres and hospitals should updated for monitoring nanocontaminants exposure. And another important issue is, organizing routinely ground water analysis from government.

Conclusion

Although nanotechnology research area and industrial activities and also medical applications grow exponential, controlling, recycling and disposal management of noncontaminants and nanowaste grow more slowly. Different international organisations as OECD, IUON and developed countries seriously handle Nano contamination however developing countries have big gap about managing and controlling

on Nano contamination. These countries should seriously attain importance to Nano contamination and nanowaste management, because developed countries works is not provide worldwide efficient and effective protection about this type contamination and adverse effects.

There were few study on nanowaste from Turkey and unfortunately there is no diverse regulatory management. Immediately workshops, educations, research activities should organise in our country to prepare a detailed management. In this paper we aimed to attract attention on Nano contamination and nanowaste issue in Turkey and step by step set a course for improving nanowaste researches and organising official managements.

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