Understanding bioenergy production and optimisation at the Nano-scale – A Review

[1]K M Rahman, [1]L Melville, [2]S M Imamul Huq and [3]S K Khoda

[1]Centre for Resilient Environments, Faculty of Computing, Engineering and Built Environment, Birmingham City University, Curzon Street, Birmingham, B4 7XG, UK

[2]Bangladesh-Australia Centre for Environmental Research, Department of Soil, Water and Environment, University of Dhaka, Bangladesh

[3]School of Environment and Technology, University of Brighton, UK

Abstract

Nanotechnology has an increasingly large impact on a wide range of biotechnological, pharmacological and pure technological applications. Its current use in bioenergy production from biomass is very limited. This paper examines the potential interrelationships between nanotechnology and bioenergy production through a comprehensive literature review and analysis of data from biomass characterisation studies. The aim of this review is to indicate how nanotechnology can be applied in biomass to bioenergy conversion. This study shows currently nanotechnology has been applied in the production of only two types of biomass i.e. sludge and algae. Hence interaction of nanomaterials with active sludge and algal cells were examined. Our extensive literature review indicate that: anaerobic digestion process in sludge can potentially be enhanced by using magnetite nanoparticles which gives higher methane yields. On the other hand nanosilver reduces growth and causes adverse effects on the morphology of green algae. This process for bioenergy generation has already been successfully applied to sludge and algae biomass. Our study confirms that the process can also be used in the production of bioenergy from the other biomasses, such as agricultural wastes, industrial residues. Outcomes this work will be an important tool for implementing of nanotechnology in bioenergy research.

Keywords: Nanotechnology, Biomass, Bioenergy, Sludge, Algae

1. Introduction

This paper reviews a range of studies on nanoparticles, nanomaterials, biomass and bioenergy. It examines the potential impact of nanotechnology on microorganism in bioenergy yield. The entire approach of this work was to develop a critical understanding of nanomaterials, defining them according to the EU commissioning recommendation, biomass characterisation and evaluate the impact on bioenergy process efficiency.

1.1 Definition of nanomaterials (NMs)

There is no uniformly accepted definition of what in fact constitutes a ‘nanomaterial’. In 2008 and 2010, the International Standardization Organization (ISO) has provided overarching technical definitions for nanotechnology related terms: ‘Nanomaterial’ is defined as material with any external dimension in the nanoscale or having internal or surface structure in the nanoscale, with ‘nanoscale’ defined as the size range from approximately 1 nm to 100 nm (ISO/TS 27687, 2008; ISO/TS 80004-1, 2010). All definitions of a ‘nanomaterial’ include the size range from approximately 1–100 nm, and none of the definitions take into account actual concerns in respect to the materials’ adverse effects on human health or the environment. The EU definition (EU Commission, 2011) is the only definition that includes natural or accidentally occurring nanoparticles, whereas all other definitions are restricted to ‘intentionally produced, manufactured, or engineered NMs’. According to the EU recommendation (2011/696/EU) on the definition of a nanomaterial is - ‘‘A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm”. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50 %.

The different definitions are not consistent in regard to their mentioning of the state of aggregation or agglomeration of the nanoparticles. Current level of available information on the presence of nanomaterials and products containing nanomaterials on the market is insufficient. Since the EU definition is based on the size distribution of the constituent particles of a material expressed in number metrics (EU Commission, 2011), nearly every powder can be considered a nanomaterial. However the EU has already announced the revision of its definition that was established in 2011: the definition been reviewed in the light of experience and of scientific and technological developments. The review should particularly focus on whether the number size distribution threshold of 50% should be increased or decreased (EU Commission, 2011).

All available definitions are based on material properties. While they are conceived and applied to found regulatory provisions for safety assessment, the definitions are not derived from toxicological evidence of a step-change in toxicity at 100 nm or any other single overarching material property applicable to all ‘nanomaterials’. Specific concerns that have been recognized for specific types of NMs do not relate to their nanosize, but, to their respective chemical composition or shape. There is no evidence of a novel ‘nano-specific hazard’. Instead, there is likely to be a more gradual magnification of the intrinsic hazard of increasingly small particles, e.g. in relation to surface area (Donaldson and Poland, 2013).

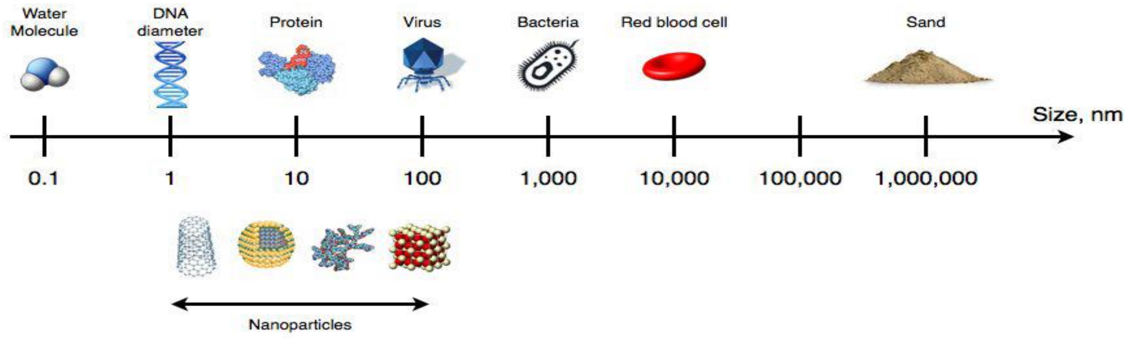

Figure1.1: A basic concept on nano sized particles (from Nguyen, 2013)

1.2 Characteristics of nanoparticles

The characteristics of NPs depend greatly on their chemical origin, which affects their fate and behaviour in environment (Stone et al., 2010; Farré et al., 2011). There are four classification groups of NPs: Carbon, Inorganic, Organic and Composites NPs. Nanoparticles have special optical, physical and chemical characteristics. Properties of particles at nanoscale change in unpredictable ways that makes them different with same substance at bigger size. Special characteristics with high reactivity of nanoparticles make them become ideal for variety of fields, such as energy, electronic, medical and consumer products. Nanoparticles can contribute to produce stronger, lighter, cleaner, smarter and more efficient materials and products (US Nanoscale Science, 2014).

Nanoparticles are interesting because their chemical and physical properties are different from their macro counterparts (e.g., sand/sugar). The sugar example is interesting- if we want to make tea sweet faster we use granules instead of cubes, but serves little real application. For example, a cube of sugar, reacting with water as the water dissolves the outside of the sugar. Now the same cube of sugar cut into many little pieces - each cut makes new outer surfaces for the water to dissolve. For smaller particles of sugar, the same volume of sugar now has much more surface area. A particle with a high surface area has a greater number of reaction sites than a particle with low surface area, and thus, results in higher chemical reactivity (Nanotechnology Centre for Learning and Teaching, 2015). Another prime example of surface area to volume ratio at the nanoscale is gold (Au) as a nanoparticle. At the macroscale, gold is an inert element, meaning it does not react with many chemicals, whereas at the nanoscale, gold nanoparticles become extremely reactive and can be used as catalysts to speed up reactions (Nanotechnology Centre for Learning and Teaching, 2015). This increased reactivity for surface area to volume ratio is widely taken advantage of in nature, one biological example being the human digestive system. Having the similar microorganism's active on both digestion (human digestion and AD) system - the surface area to volume ratio of biomass cause impact on anaerobic digestion process.

1.3 Interaction of nanomaterials with biomass

Nanoparticles can play a crucial role with liquid biomass in water purification (Stoimenov *et al*., 2002) as many of them have antibacterial properties. It is now used for detection and removal of chemical and biological substances include metals (e.g. Cd, Cu, Zn), nutrients (e.g. Phosphate, ammonia, nitrate), cyanide, organics, algae (e.g., cyanobacterial toxins) viruses, bacteria, parasites and antibiotics. Basically four classes of nanoscale materials that are being evaluated as functional materials for water purification: e. g., metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. Carbon nanotubes and nanofibers also show some positive result.

Nanomaterials reveal good result than other techniques used in water treatment because of its high surface area (surface/volume ratio) (Tiwari et al, 2008). Current and potential applications of nanotechnology in water and wastewater treatments are: Adsorption, membrane processes, photocatalysis, disinfection, microbial control, sensing and monitoring (Xiaolei et al., 2013). But knowledge on toxicity of nanomaterials is still in infancy (Colvin, 2003). Antibacterial activities of NPs depend upon two main factors: (i) physicochemical properties of NPs and (ii) type of bacteria. It is also found that the coliform bacteria treated with ultrasonic irradiation for short time period before Ag nanoparticles treatment at low concentration, enhanced antibacterial effect. Many studies have also shown an important activity of silver nanoparticles against bacterial biofilms. The correlation between the bactericidal effect and AgNP concentrations is bacterial class dependent (Chernousova and Epple, 2013). A research finding showed that, *Pseudomonas aeruginosa* and *Vibrio cholera* were more resilient than *E. coli* and *Salmonella typhi*, but at concentrations above 75 μg/mL, the bacterial growth was completely abolished (Zhang et. Al., 2014). In this perspective, Sweet et. Al., (2012) studied Ag NPs antimicrobial activity against *E. coli* and *S. aureus* showing that *E. coli* was inhibited at low concentrations, while the inhibitory effects on the growth of *S. aureus* were less noticeable (Wu et. Al., 2014). Silver nanoparticles have also significant adverse effects on growth and morphology of filamentous green algae (Anjali Dash et al., 2012).

In order to understand the importance of the role of nanomaterials on bioenergy research figure 1.2 is given to show the pathway of biomass to bioenergy conversion and the interaction of functionalised nanoparticles. The biomss to bienergy conversion could be either thermal, chmical or biological process. Molicular size, inorganic contaminants of ornanic biomass cause impact on the conversion process. Functionalised nanoparticles could come from either or both natural and synthetic (manmade) sources. Due to the existance of this multi-faceted interation within the process a numbeer of issued which could arise and therefore need to be addressed appropriately.

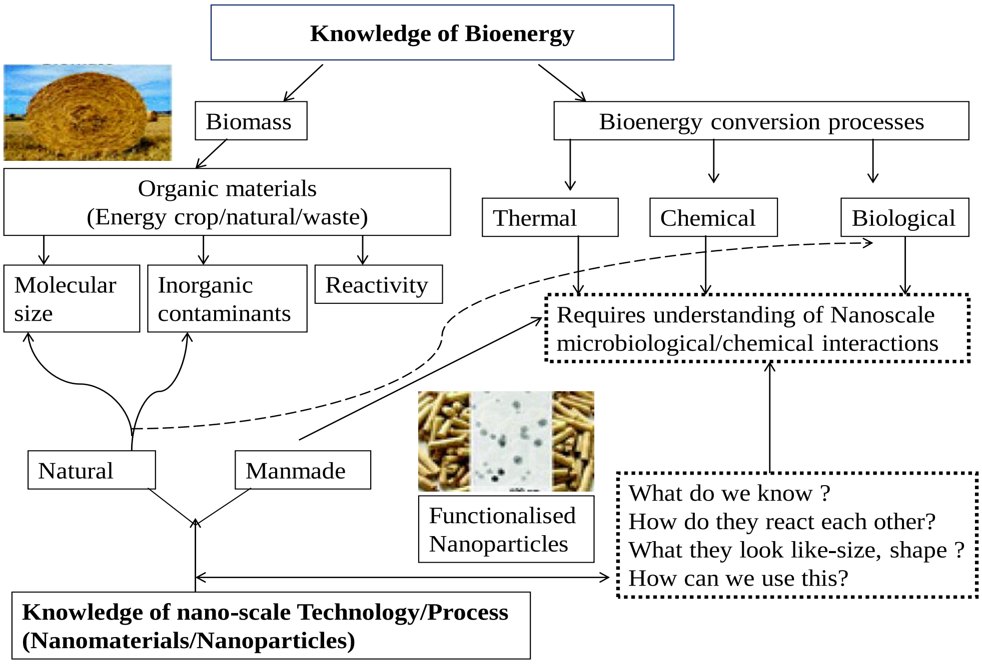

Figure1.2: Diagram showing the pathway of biomass to bioenergy conversion and the interaction of functionalised nanoparticles

The impacts of nanoparticles on biomass energy conversion are described in two types of biomass e. g., a) Waste sludge and b) Algae. The aim of this paper is to examine the impact of NPs on activated sludge systems and algal biomass systems, including the inhibitory impacts, phyto-toxicity and mechanisms by which bioenergy processes are enhanced or inhibited.

2. Review of this work/methodology

The paper has evaluated the potential applications of nanoparticles to enhance the efficiency of bioenergy production from organic material.

2.1. An understanding of nanotechnology

A comprehensive review of current nanotechnology research has been undertaken to understand the key characteristics and applications and evaluate how particle size, composition and reactivity may impact on biomass to energy conversion.

2.2. An understanding of biomass and their characteristics

Various biomass resources were studied in terms of their source and key physical, biological and chemical composition. The impact of particle size of biomass was evaluated in relation with biomass to bioenergy conversion in both biochemical and bio thermal aspect. Particle size and pre-treatment of different types of biomass were studied.

Different pre-treatment methods produce different effects on the biomass in terms of its structure and composition (Kumar et al, 2009). For example, the hydrothermal and acidic pre-treatments conceptually remove mainly the biomass hemicellulose fraction and alkaline pre-treatments remove lignin, whereas the product of a milling-based pre-treatment retains its initial biomass composition. The main objective of milling pre-treatment is to reduce particle size in order to increase the biomass-specific surface during biomass fibrillation and to reduce cellulose fibre organization, which is measured by a decrease in crystallinity.

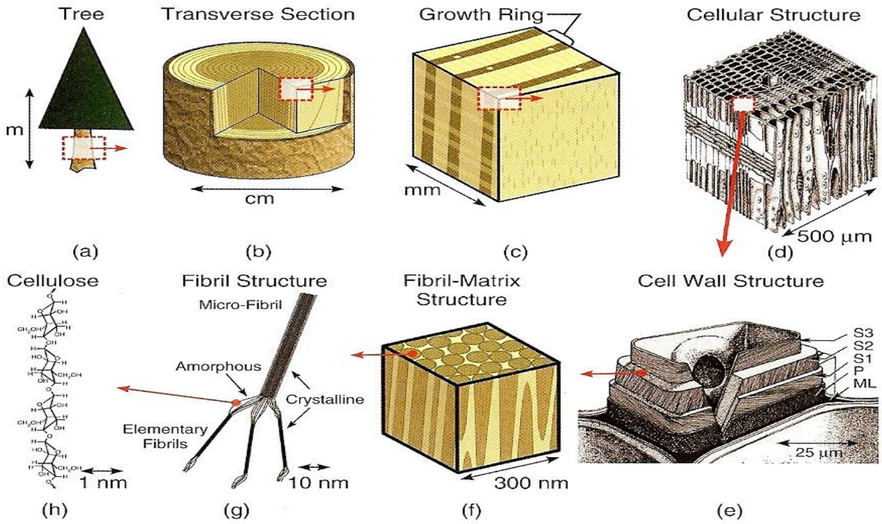

Figure 2.1: Plant biomass to nanoparticle -A journey of tree to cellulose (from Moon, 2006)

2.3 Impact on process efficiency

Evaluated the potential interaction between traditional (or new/novel NPs) and biomass substrates and its impact on process efficiency and energy production (and potentially waste from the process).

3. Results and discussion

Nanotechnologies could enhance energy efficiency across all branches of industry and economically leverage renewable energy production. It has the potential to enhance the conversion of biomass for fuels, chemical intermediates, speciality chemicals and products. Nanotechnology is an important tool that can improve the efficiency of bioenergy. The interactions of nanomaterials were found either with active sludge and few species of algal biomass. The impact was found in the form of: inhibitory (Nguyen, 2013), adverse or enhanced yield (Víctor and Ferrer, 2011) in aspect of bioenergy production. The variation in the severity of impact on the basis of particles surface area to volume ratio was also assessed. These results are described here on the basis of two biomass feedstock which was found to give significant response to nanoparticles. These are active sludge and noble feedstock algae.

3.1. Impact of NPs on activated sludge systems

The results on impact of nanoparticles in activated sludge are presented under few relevant characteristics of NP and Active Sludge. This emphasizes on concentration, size of nanoparticles and the response of microorganisms on its bioenergy yield.

3.1.1 Nanoparticles with microorganism

Microorganisms actively respond to nanoparticles and can cause a significant effect. An overview of antimicrobial properties of NPs suggests the potential adverse effect they could exert on wastewater microorganisms (Figure 3.1). This has significant negative implications although at present, information on NPs effect on wastewater microorganisms during AS and AD is rather limited (Batley *et al.*, 2012; Krysanov *et al.*, 2010). It is therefore, difficult to make specific assertions regarding the toxic effect of NPs on wastewater microorganisms. There is a possibility that NPs in contact with a microbial community may lead to reduced efficiency of AS and AD processes, complete failure of treatment and/or environmental pollution through discharge of contaminated effluent and use of biosolids for soil amendment (Hoffmann and Christoffi, 2001). The silver ion has been known to be effective against a broad range of microorganisms. Today, silver ions are used to control bacterial growth in a variety of medical applications, including dental work, catheters, and the healing of burn wounds (Klasen, 200). The mechanism of action attributed to release of ions from Ag was demonstrated with *E.coli* and found to be dependent on concentration and contact time. Adverse effects included the leaking of reducing sugars and proteins, enzyme inhibition; cell disruption, and scattered vesicles which slowly dissolve thus inhibiting cellular respiration and cell growth (Wen-Ru *et al.*, 2010).

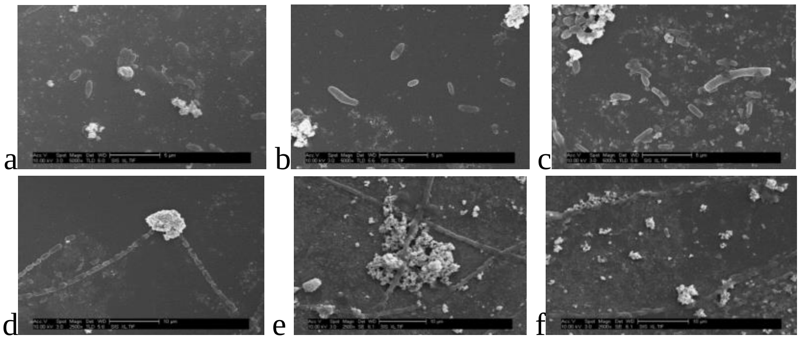

Figure 3.1: Scanning electron microscope (SEM) images showing ENPs sorption to cells (a,b), damage to microbial cell (c,d) and aggregation to biomass (e,f) in AS (Eduok, 2013)

3.1.2 Concentration of nanoparticles

Nanoparticles could come from both natural and anthropogenic sources. It could be accumulated to a very high concentration in the waste sludge. However, impact and toxicity of NPs on sludge treatment stream is still an abandoned area of research (Nguyen, 2013). Nguyen (2013) conducted a research to determine the effects of CeO_2 and ZnO NPs on sludge anaerobic digestion process, sludge dewatering process, and toxicity of sludge to bacteria and plants. The result showed that CeO_2 and ZnO NPs could cause inhibition to the biogas production of anaerobic digestion system. The exposure concentration of ZnO at 1,000 mg/l caused the greatest inhibition to the biogas volume (65.3%) and the methane composition (40.7%), as compared with controlled sample. In addition, at tolerable exposure concentration of ZnO, the system could overcome the inhibition effect after 14 days of incubation. On the other hand, CeO_2 at low concentration of 10 mg/L could increase the generated biogas volume by 11%. The positive effect of CeO_2 at low concentration was also observed on bacterial toxicity test. The ZnO NPs was more toxic to bacteria than CeO_2 NPs at the same exposure concentration (Nguyen, 2013). However, the bacterial toxicity of both nanoparticles was reduced when they were applied rather than naturally occurring to the sludge. Moreover, at the end of anaerobic digestion process, the bacterial toxicity was again lessened. Additionally, required time to dewater the digested sludge was increased proportionally with the exposure concentration of nanoparticles.

The bacterial toxicity of nanoparticles could be greatly reduced when nanoparticles was applied in the sludge. Sludge before anaerobic digestion was more toxic than sludge after the digestion process. The sludge with exposure of 1,000 mg/L of CeO_2 NPs before anaerobic digestion caused 47.5% of inhibition to bacterial viability. However, the same sample after anaerobic digestion just had 30.4% of inhibition toward bacteria viability. Similarly, sample with 1,000 mg/L of ZnO NPs induced up to 92.3% of inhibition before anaerobic digestion, while after digestion process, this value was just 34.8% (Nguyen, 2013).

The effects of metal oxide particle size on biogas and methane production during anaerobic digestion of cattle manure was studied by Luna del Risco, M. *et al*, 2011). In the experiment nanoparticles of CuO showed higher influence on biogas production than the other test compounds. The concentration of 15 mg/l of CuO nanoparticles resulted in a reduction of 30% of the biogas production from the total biogas produced in the control at day 14. Biogas production in the presence of microparticles of CuO was less inhibited whereas concentrations of 120 and 240 mg/l of bulk CuO caused a reduction by 19 and 60%, respectively. The statistical analyses have validated the differences between the 2 groups of particles tested (bulk and nanoparticles) of CuO ($p<0.05$). As reported by Heinlaan (2008), Neal (2008) and Kasemets *et al*. (2009) nanoparticles are toxic to bacteria due to the release of bioavailable metal ions that causes cell membrane damage, and therefore, the inhibition of biogas production can occur.

Biogas production in test samples containing nanoparticles of ZnO was compared with bulk ZnO. Concentrations of 120 and 240 mg/l of ZnO nanoparticles presented an inhibition of 43 and 74% of the biogas yield respectively, while test bottles containing bulk ZnO presented a reduction of 18 and 72% of the total biogas produced at day 14. However, no significant difference of biogas inhibition from bulk and nanoparticles of ZnO was found (Luna del Risco, M. *et al*, 2011). From this section it can conclude that particle size and concentration of nano-sized CuO and ZnO affects biogas yield.

The addition of Nano iron oxide (Fe_3O_4 NPs) can enhance the methane production due to the presence of the non-toxic Fe^{3+} and Fe^{3+} ions. Fe_3O_4 NPs (7 mm) were added with a concentration of 100 ppm to anaerobic waste digester at mesophilic temperature (37^0C) for 60 days and the results showed a 180% increase in biogas production and 234% increase in methane production which is could be considered the greatest improvement to biogas production using NPs (Casals et al., 2014). The new delivery system based on Fe_3O_4 (magnetite) nanoparticles leads to enhanced anaerobic digestion, and consequently to higher methane production and organic matter processing (Figure 3.2). The improved performance is due to the presence of Fe^{+2}/Fe^{+3} ions, introduced into the reactor in the form of nanoparticles in a similar way to controlled drug delivery systems. Because Fe plays an important role in transporting electron, simulating bacterial growth and increasing hydrogen and methane production rate by promoting enzyme activities (Wencheng et al., 2015). Fe_3O_4 nanoparticles are the most prevalent materials because they have low toxicity, good biocompatibility (Lie et al, 2011)

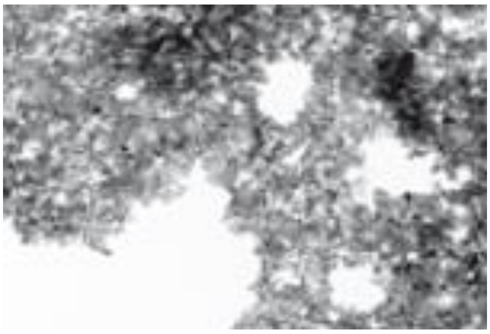

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Figure 3.2: Nanoparticles of Iron Oxide (Fe_3O_4-Magnetite) (Víctor and Ferrer, 2011)

3.1.3 Phyto-toxicity/Eco-toxicity effect of NPs

The inhibition effect of nanoparticles on performance of anaerobic digestion needs to be investigated. Moreover, the digested sludge after anaerobic digestion is usually dewatered and then applied as soil conditioner, compost and other applications. However, nanoparticles accumulated in sludge can make the sludge become toxic and inappropriate to apply as biosolid. Therefore, information about phytotoxicity and bacterial toxicity of digested sludge contaminated with nanoparticles is essential to have insights about the reusability of waste sludge. In addition, the effect of nanoparticles to the dewaterability of digested sludge is still unknown. So whether or not nanoparticles in sludge can hinder the sludge dewatering process, toxicity of nanoparticles in sludge is eliminated during anaerobic digestion or it causes inhibition effect on bacteria and plants, these are still questions that need to be answered (García et al., 2012).

In terms of ecotoxicity, there has been significantly greater focus on aquatic rather than terrestrial species, and very little work has focused on terrestrial plants. Some studies have reported the toxic effects of nanoparticles on the germination and/or root growth of some plant species (Lin and Xin, 2007). Study focuses on comparing the effects of five types of commonly used nanoparticles (Multi Walled Carbon Nanotubes-MWCNTs), Ag, Cu, Si, and Zn oxide) to their corresponding bulk material counterparts on germination, root elongation, and biomass of the agricultural plant *Cucurbita pepo* (zucchini). In this preliminary nanotoxicology study, initial concentrations of 1000 mg/L were chosen to ensure observation of relevant phytotoxic responses. In addition, the effect of nanoparticle or bulk Ag concentration (0-1000 mg/L) on zucchini biomass, transpiration, and Ag content was determined in a dose-response study. Assessing the impacts of nanoparticles on agricultural plants will provide insight into the risk of ecological exposure to these materials, as well as to the potential for human exposure through food chain contamination (Dimitrios Stampoulis, 2009).

3.1.4 Engineered NPs and particle size

Due to the rapid expansion of nanotechnology, engineered nanoparticles (ENPs) have been manufactured and applied widely in many industries. This fact leads to the constant discharge of ENPs to the environment that their possible impacts to human health and environment remain a controversial topic. There are a massive amount of natural NPs in the environment, far more than the relatively small releases of CNTs, Ag nano particles etc. Since the generation of natural nanoparticles is uncontrollable, many of studies on characteristics and impacts of nanoparticles has been focused on engineered nanoparticles. In most of study, the term “engineered nanoparticles” (ENPs) is referred shortly as nanoparticles (NPs). The effect of a mixture of engineered nanoparticles (ENPs) consisting of silver oxide, (AgO, 20 nm), titanium dioxide, (TiO_2, 30-40 nm) and zinc oxide, (ZnO, 20 nm) compared with their bulk metal salts was evaluated against unspiked activated sludge (control) using 3 parallel pilot-scale treatment plants (Eduok et al, 2013). The introduction of both nanoparticles and bulk metals mixtures in the wastewater treatment plants induced a 2-fold increase of the microbial specific oxygen uptake rate (SOUR) compared with the control plant. The scanning electron microscopy (SEM) showed that there was selective damage on some microbial cells. Further to this, activated sludge floc size was reduced in the presence of the ENPs while the sludge volume index (SVI) was unaffected. The fate and behaviour of nanoparticles in the environment are affected by various environmental factors (e.g. light, pH, ionic strength, natural organic matter, etc.) (Klaine et al., 2008). Various influences can affect the physical, chemical or bioavailable properties of released nanoparticles in the nature. In order to assess the risks of nanoparticles and nanomaterial, we must scrutinize the possible mobility, transformation, and interaction with other materials of nanoparticles (Farré et al., 2011).

The Particle size and shape of a NP is known to impact upon its behaviour/reactivity in aquatic and terrestrial media (Pelletier *et al*., 2010). For instance, NPs of < 30 nm was cytotoxic to *E. coli* and *S. aureus* (Martinez-Gutierrez *et al*., 2010) compared with 80 – 90 nm particle size (Martinez-Castanon *et al*., 2008). This suggests that silver oxide (AgO) of particle size greater than 30 nm could be non-inhibitory to microbial processes. Of particular interest is the size less than 5 nm in suspension capable of inhibiting nitrification in AS (Choi *et al*., 2008). Apart from particles size, their shape has been reported to play a role as shown for AgO which can exist in a triangular, spherical or rod-shaped form. Comparing the effects of the three distinct shapes, the truncated triangular form of AgO was found to exert the strongest bactericidal effect on *E. coli* in both agar plate and broth cultures (Pal *et al*., 2007). A direct extrapolation of this observation from pure culture to complex wastewater is unclear because wastewater components can attenuate or enhance NP contact and interaction with microbial cell.

3.2 Impact of NPs on algal biomass systems

Algal biomass has soon been started to be widely anticipated as the next energy storehouse for meeting the world’s energy needs. Algae are also important as a potential resource for bioenergy production as well as for the extraction of high value and platform chemicals and extractives. These are low trophic-level members of aquatic systems and are critical in photosynthesis and as food sources. The results on effect of nanoparticles on micro and macro algae are presented here.

3.2.1 NPs impact on microalgae

Silver in natural fresh water can be found in the form of silver chloride (AgCl), silver sulfide (Ag_2S) and the silver ions. The most toxic form of silver nanoparticles is the silver ion (Ribeiro *et al.*, 2014). Concentration of these nanoparticles is increasing in aquatic environment and can strongly affect and damage the biota (Angel *et al*., 2013; Batley *et al*., 2012). For instance, Ag NP concentrations above 5 g/L have already been found for groundwater, surface water and drinking water (WHO, 2003). There are many possible reasons for the high toxicity of silver nanoparticles, including its high surface area/volume ratio, which greatly increases its rate of dissolution (Angel *et al*., 2013). Coating of Ag NP with organic materials such as polymer-based stabilizer may also influence its toxicity (Kwok et al., 2012). Another important factor that influences nanoparticles toxicity is the bioavailability related to the aggregation behaviour (Angel *et al*., 2013). Becaro *et al* (2015) investigated toxic effects of silver nanoparticles stabilized with PVA (polyvinyl alcohol) for aquatic microalgae, such as *P. subcapitata* algae, *A. salina* and *D. similis*. According to dynamic light scattering measurements, the Ag NPs in solution are well dispersed, with size range 2–18 nm. Among the organisms studied, Ag NP showed lower toxicity to *A. salina* and *P. subcapitata* organisms and showed higher toxicity to *D. similis*.

Pithophora oedogonia and *Chara vulgaris* are predominant members of photosynthetic eukaryotic algae, which form major component of global aquatic ecosystem. Das *et al* (2012) reported that nanosilver has significant adverse effects on growth and morphology of these filamentous green algae in a dose-dependent manner. Exposure of algal thalli to increasing concentrations of silver nanoparticles resulted in progressive depletion in algal chlorophyll content, chromosome instability and mitotic disturbance, associated with morphological malformations in algal filaments. SEM micrographs revealed dramatic alterations in cell wall in nanoparticle-treated algae, characterized with cell wall rupture and degradation in Pithophora

3.2.2 NPs impact on macroalgae/aquatic plant

Nanoparticles have a significant effect on macro algae e. g., sea weed, water hyacinth. Zada *et al*., (2013) demonstrate that fermentative production of ethanol and hydrogen from water hyacinth is a commercially viable and sustainable process. Iron nanoparticles significantly affect hydrogen and ethanol production. Iron nanoparticles enhance fermentative hydrogen production. Ethanol production is also enhanced by iron nanoparticles. For fermentative hydrogen production optimum iron nanoparticles concentration is 250mg/L and for ethanol production optimum iron nanoparticles concentration is 150mg/l. These concentrations are besides that already present in dry biomass of plant. Maximum hydrogen yield is 57mL/g of the plant biomass which is 85.50% of theoretical maximum hydrogen yield. The maximum ethanol yield is 0.0232g/g of the plant biomass which is 90.98% of maximum theoretical yield. This study indicates that water hyacinth accumulate different types of nanoparticles.

3.3 Mechanisms by which bioenergy processes are enhanced or inhibited

With the rapid development of nanotechnology in the last decade, the safety of manufactured nanomaterials has been studied more rigorously by scientists. Owing to its large surface area per unit volume, nanoparticles are much more active than that particle at bulk or particulate size. NPs on sludge made the digested sludge become unsuitable to be used as biosolid, since the contaminated digested sludge caused great inhibition on root growth and seed germination of plants. They made digested sludge become difficult to dewater. For any types of enhanced or inhibited nature caused by nanoparticles with AS and Algae biomass there is a consistent mechanism behind it.

3.3.1 Mechanism microbial activity

Nanoparticles possess the properties, which cause toxic to living organism and human. Because of its nano-scale, nanoparticles are easily to be exposed to human and organism bodies through inhalation, ingestion and dermal contact. A number of authors have published literature on characterization, behaviour, and toxicological information of nanomaterials (Brar *et al*., 2010). Most of the research findings are focused on commercialized nanomaterials that were manufactured and applied widely, such as carbon nanotubes (CNTs), fullerene and metal oxides. This is important when considering the application of these NPs to large scale commercial plants also it is important in terms of fate of any NPs in the environment.

Ag NPs are able to physically interact with the cell surface of various bacteria. This is particularly important in the case of gram-negative bacteria where numerous studies have observed the adhesion and accumulation of Ag NPs to the bacterial surface. Many studies have reported that Ag NPs can damage cell membranes leading to structural changes, which render bacteria more permeable (Lazar, 2011). This effect is highly influenced by the nanoparticles' size, shape and concentration (Lu et. al., 2010) and a study using *Escherichia coli* (Lazar, 2011) confirmed that Ag NPs accumulation on the membrane cell creates gaps in the integrity of the bilayer which predisposes it to a permeability increase and finally bacterial cell death (Rai et. al., 2014)

Metal oxide nanoparticles, such as titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), silicon dioxide (SiO_2) and zinc oxide (ZnO), have received increasing interests due to their widespread industrial, medical and military applications and their intentionally or unintentionally release into the environment affecting human health, soil and aquatic organisms. Although the exact mechanism of toxicity for each nanoparticle is not fully understood, there are various characteristics that may result in damage to exposed organisms. Nanoparticles generate reactive oxygen species (ROS) such as free radicals (OH^-), singlet oxygen ($_1O^2$) and super oxides (O_2^-) which exerts several adverse effects on microorganisms including disruption of cell wall, damage of DNA/RNA (Pelletier *et al*., 2010). Adverse effects included membrane leakage of sugars and proteins, enzyme inhibition, cell disruption, and scattered vesicles which slowly dissolve thus inhibiting cellular respiration and cell growth (Wen-Ru *et al*., 2010). Nano-Al_2O_3, nano-SiO_2 and nano-ZnO were observed to be harmful to *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas fluorescens* (Mu, *et al* 2011). The antibacterial effects of nanoparticles on *B. subtilis* and *E. coli* increased from SiO_2 to TiO_2 to ZnO. Nano-ZnO was observed to cause significant toxicity to the viability of gram negative bacterial cells (Mu, *et al* 2011).

Chen, *et al* (2014) reviewed the toxic effect of nanomaterials on biomass and found Ag NPs, nano-Al_2O_3, nano-SiO_2 and nano-TiO_2 are chemically stable NPs that have no adverse effects on microbes under anaerobic conditions while nano-Au presented no or low toxicity to anaerobic biomass and nano-CeO_2 was the most toxic to both mesophilic and thermophilic biomass. The release of metal ions caused by corrosion and dissolution of the NPs resulted toxicity in the anaerobic digestion process. These toxic compounds principally obstruct the activities methane formation, a decrease in the methane content of biogas, or can even cause complete failure of methanogenesis.

3.3.2 Mechanism inhibition seed/plant growth

The sludge dewaterability depends on various factors. Extracellular polymeric substance (EPS), which is secreted by microorganisms are the major components of sludge flocs, is important factor that influences the dewaterability of sludge. High amount of EPS will increase the viscosity of the waste sludge and therefore make it difficult to dewater. Finally, the accumulation of NPs (e. g., CeO_2, ZnO) on sludge made the digested sludge become unsuitable to be used as a biosolid, since the contaminated digested sludge caused great inhibition on root growth and seed germination of plants.

3.3.3 Effect and impact of nanomaterials on biomass

Theivasanthi and Alagar (2011) found that nanoparticles synthesized in electrolysis method are showing antibacterial activities against both gram (-) and gram (+) bacteria. Changes in Surface Area to Volume Ratio of copper are enhancing its antibacterial activities. Copper nanoparticles synthesized in electrolysis method are showing more antibacterial activities (for *E.Coli* bacteria) than copper nanoparticles synthesized in chemical reduction method. Using electrical power while on synthesizing of copper nanoparticles is increasing its antibacterial activities. The chemicals involved in the synthesis of nanoparticles are commonly available, cheap, and non-toxic. The technology can be implemented with minimum infrastructure. The experiments suggest the possibility to use this material in water purification, air filtration, air quality management, antibacterial packaging, etc. Microorganisms play the key role for biochemical conversion of biomass. Therefore, the inhibition of their activity reduces the energy yield capacity of biomass. The various effects of different nanomaterials are shown in table 3.1.

Table 3.1: Effect of nanomaterials on biomass

NMs	**Effects**	**Remarks**	**References**
CeO_2	Inhibit biogas and CH_4 in AD	High conc. 1,000 mg/l	Nguyen, 2013
	Increase biogas volume	Low conc.10 mg/l	
	Digested sludge inhibit root growth and germination		
ZnO	Inhibit biogas and CH_4 in AD	High conc. 1,000 mg/l	Nguyen, 2013
	Overcome inhibition effect	Tolerable exposure conc.	
	Digested sludge inhibit root growth and germination		
CuO	Reduction of 30% of the biogas production from the total biogas	Low concentration 15 mg/ l	Luna del Risco, M. *et al*, 2011
	Biogas production less inhibited	microparticles of CuO	
AgO - 5 nm	Complete inhibition of growth and viability	At E.coli bacteria	Wen-Ru *et al*, 2010
AgO-TiO_2 at 100 nm	Photoactivated inhibition of growth and viability	At E.coli bacteria	Pan *et al.*, 2010
.5 mg/L AgO at 9-12 nm	Toxic to the respiration of bacteria	Nitrifying bacteria	Choi *et al.*, 2008
10, 50 μgL^{-1} AgO	inhibiting the growth of E. coli by 70 and 100% respectively	E. coli	Sondi, 2004
Fe_3O_4 NPs	Enhanced AD, and higher CH_4 and organic matter processing	drug delivery systems	Víctor and Ferrer, 2011

Ganzoury and Allam, (2015) reviewed the impact of three types of nano additives on the biogas production. The categories are: (1) metal oxides, (2) zero-valent metals, and (3) nano-ash and carbon-based materials. Table 3.2 summarized the reviewed results.

Table 3.2: Impact of nanomaterials on biogas production

Catagories	**Nanomaterials**	**Impact**
Metal oxides	ZnO, CuO, MnO_2, Al_2O_3	Reduce Biogas production rate
Metal oxides/zero valent metals	TiO_2,CeO_2,Nano zero valance iron (NZVI)	Mixed effect depending on the conc. of nano materials and digestion time
Zero-valent metals	Nano Iron	Enhanced methane production
Metal oxides	Metal NPS encapsulated in porous SiO_2	Significant increase methane production
Nano-ash and carbon-based materials	Silver/Gold nanoparticle	Decrease or no change on biogas production depending on the conc. in the reactor
	Micro/Nano fly ash or Micro/ Nano bottom ash	Increase biogas production
	Fullerene (C60) and SiO_2 NPs, single-walled C-nanotubes	No change in Biogas production

Conclusion

The performance of AD can be affected by various nanomaterials. It is very important to better understand the complex mechanisms by which these particles interact with the biomass and the process of conversion and potentially overcome adverse effects and optimise the positive effects. Particle size can influence the rate of anaerobic digestion as it affects the surface area for biodegradation of biomass. All nanoparticles regardless of their chemical constituents have surface area to volume ratios that are extremely high. This causes nanoparticles' physical properties to be dominated by the effect of the surface atoms and capping agents on the nanoparticles surface. High surface area to volume ratio is important for applications such as catalysis. Reactions take place at the surface of a chemical or material; the greater the surface for the same volume, the greater is the reactivity. Therefore, the response and interaction of different nanoparticles are different with microorganisms. Although only a few studies have reported the antibacterial properties of copper nanoparticles which have a significant potential as bactericidal agent however, other nanoparticles, such as platinum, gold, iron oxide, silica and its oxides have not shown bactericidal effects in studies with *Escherichia coli*. The addition of magnetite NPs (Fe_3O_4 NPs) can enhance the methane production due to the presence of the non-toxic Fe^{3+} and Fe^{3+} ions through the stimulating of bacterial growth.

Nanoparticles have been popular in recent years and they have been applied widely in many fields. These nanoparticles have been used as fuel catalyst to reduce harmful emission from engine combustion. But researchers found that NPs cause inhibition effects on biodegradation, nitrification and anaerobic digestion process (Liu *et al*., 2011; García *et al*., 2012). The adverse effect, inhibition or enhancement of energy conversion depends upon the particle size, concentration and time. There is a potential scope to find out the effect of nanomaterials with other biomasses: e. g., agricultural, MSW. To identify a best possible use of nanoparticles in bioenergy systems is very important. The present review could be an important tool for a further research on "nanotechnology in bioenergy".

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