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Possible impacts of exogenous pollutants occurring in waste activated sludge during anaerobic digestion

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ABSTRACT: Anaerobic digestion is considered as a biological procedure as the metabolisms included in the digestion process of waste activated sludge are easily affected by distinct operating conditions. This study investgates the impact of regularly distinguishable pollutants with high concentrations in waste activated sludge such as nanoparticles, pharmaceutical products and heavy metals on the execution of waste activated sludge digestion. Different types of exogenous pollutants showed different effects on the sludge methanogenesis and acidification processes, hydrolysis and solubilization as well as the correlating concentrations. It was also observed that the majority of the pollutants observed in the waste activated sludge would normally react towards anaerobic digestion at low levels but exhibit obvious negative impacts at high dosages.

KEYWORDS: Activated sludge; anaerobic digestion; pharmaceutical products; persistent organic pollutants, heavy metals.

1. Introduction

One of the main international environmental challenges currently in the twenty-first century is the sustainable management of wastewater sludge as the government of countries worldwide have just implemented a newly stern regulation for sludge treatment and disposal [1]. As the rate of industrialization and urbanization increases drastically annually, the production of wastewater sludge as a by-product of treatment plants is also unavoidably increasing in huge amounts. The flow diagram of activated sludge wastewater treatment is shown in Fig. 1. The activated sludge process is considered by many the most energy-saving procedure for the extraction of pollutants but the drawback is the huge production of waste activated sludge [2]. In the United States, it is estimated that nearly 130.5 gallons of wastewater is treated per day and the reported waste activated sludge generation rate ranges from 0.1 to 0.3 kg/m^3 given the average rate of treated wastewater is around 0.24 kg/m^3 [3]. Some studies have also stated that the residual management cost of the wastewater sludge disposal at incinerators and landfills accounts for up to 50% of the total wastewater treatment cost [4]. Nonetheless, a substantial amount of biomass within the waste activated sludge such as carbohydrates and proteins can be recuperated and harnessed which can be used as an efficient resource reutilization of waste activated sludge to partly compensate for the operating costs and it maybe an optimistic management approach for the disposal of waste activated sludge [5].

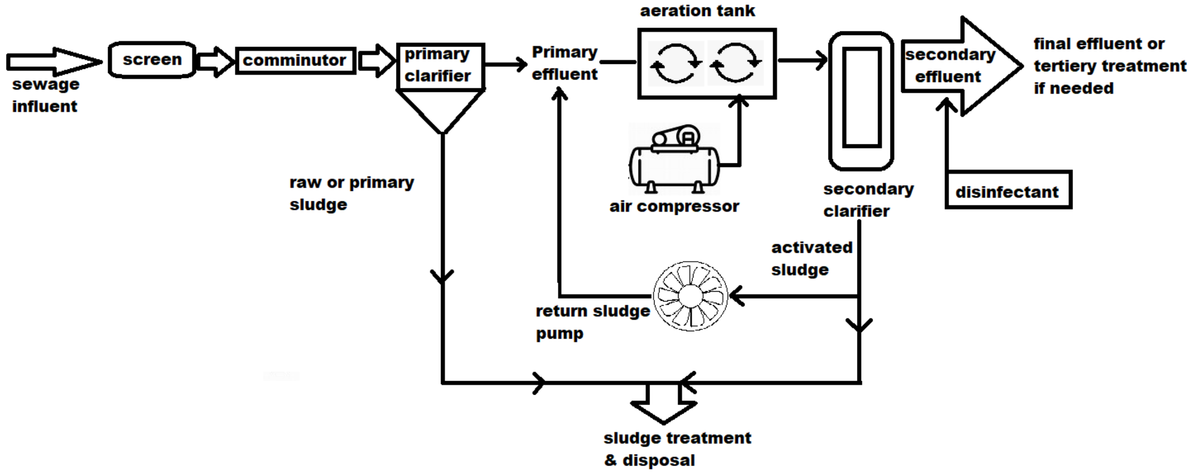

Figure 1. Flow diagram of activated sludge wastewater treatment

According to a study published, it has stated that one of the most optimal and eco-friendly bioprocesses to recycle chemicals and renewable fuels such as methane, hydrogen and short chained fatty acids from waste activated sludge in treatment plants is through anaerobic digestion [6]. The recuperation of short chained fatty acids from the unaltered waste activated sludge can be utilized as an external carbon sources to enhance the operation of wastewater biological nutrient extraction when the chemical oxygen demand is inadequate in the influents of the wastewater treatment plants [7]. In addition, energy produced by the methane and hydrogen can be stockpiled and this concurrent resource recuperation with waste activated sludge depletion and stabilization are able to reap significant economical and environmental advantages for wastewater treatment plants [8]. Anaerobic digestion is considered as a biological procedure as the metabolisms included in the digestion process of waste activated sludge are easily affected by distinct operating conditions. Hence, several earlier studies had been immensely concentrated on investigations with relation towards numureous pre-treatment methods such as microwave-, alkaline-, thermal-, and ultrasonic pre-treatment to enhance the hydrolysis and solubilization processes [9]. Studies with relation towards the coherent control of fundamental process parameters such as temperature, mixing additives and pH had also been focused on in order to improve the metabolic activities for adequate digestion execution [10]. The utilization of anaerobic digestion of waswater is shown in Fig. 2.

Nowadays, wastewater treatment plants mostly obtain both manufacturing and municipal wastewater which will result in many undesirable pollutants to be present in the wastewater such as persistent organic pollutants and heavy metals. These pollutants are relatively troublesome to be biodegraded effectively through conventional treatment procedures in wastewater treatment plants but are comparatively easier to adsorb and gather in waste activated sludge in concentrated levels by sedimentation taking place in the primary and secondary clarifiers [11]. Stern regulation controls are required to be implemented towards these exogenous pollutants as it is common for them to evince specific biotoxicity and ecotoxicity towards living organisms in the environment [12]. Hence, the active participation of functional pathogens in the process of anaerobic digestion is pivotal and it is also directly associated with the digestion efficiency. Previous studies have also identified the side effects of exogenous pollutant towards waste activated sludge digestion as it mostly depends on the concentrations and the specific species [13,14]. The objective of this study was to illustrate the impact of regularly distinguishable pollutants with high concentrations in waste activated sludge such as nanoparticles, pharmaceutical products and heavy metals on the execution of waste activated sludge digestion. The fundamental mechanism and plausible mitigation actions are deduced based on the current knowledge while the opinion for future investigation is also prospected.

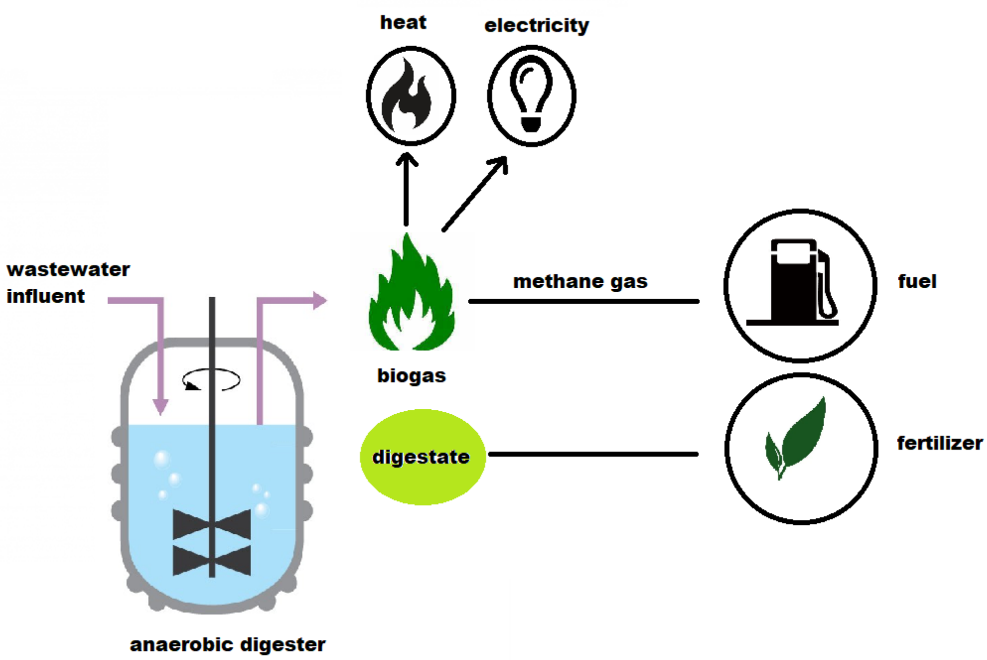

Figure 2. Utilization of anaerobic digestion of waswater

2. Impact of pollutants on activated slude anaerobic digestion

2.1 Heavy metals

The most constantly identified heavy metals with high concentration in waste activated sludge are mainly copper, iron, zinc, nickel, manganese, lead, aluminium and chromium [15]. In general, these heavy metals are capable of exhibiting inhibitory, stimulatory and even toxic in most anaerobic reactions based on the type of metal species, pH and redox potential of the process, concentration and ionic form of the solution. To ensure optimum functioning of the enzymes and coenzymes involved in the biochemical process of anaerobic digestion, certain metals are needed to act as the micro-nutrients [16]. For example, iron can be regarded as the cofactors of cytochrome and enzymes in methylotrophic methanogens to invigorate the electron transport of metabolism [17]. Another example is that molybdate which are commonly present in formaldehyde dehydrogenase is crucial towards the optimum functioning of enzymes in acetogenic Clostridia. Hence, only a small dosage of these heavy metals is required to enhance the functionality of pathogens and help the performance of the anaerobic digestion. A previous study has shown that by linearly increasing nickel and cobalt concentrations, the methane generation rates had accelerated and broke the micronutrient restraint [7].

With accordance to Table 1 below, it can be seen that the potential effects of heavy metals towards anaerobic digestion has great differences with subject to the various species. A previous study had discovered that during acidogenesis, the relative toxicity of heavy metals towards butyric and acetic acid generation was in the order of Copper > Zinc > Chromium > Cadmium > Lead >Nickel while for methanogenic activities, the relative toxicity towards the short chained fatty acids deteriorating organisms was subsequent to the order of Cadmium > Copper > Chromium > Zinc > Lead > Nickel [18]. However, another study published that the hindrance on methanogenic activity in anaerobic starch deteriorating organisms was in the order of Zinc > Chromium > Nickel ≈ Cadmium given the IC_{50} value of 7, 25, 34 and 36 mg/L [19]. In general, methanogens have higher sensitivity towards heavy metals when compared with acidogens. For instance, it was observed that the decrease in methane generation did not halt the huge amounts of short chained fatty acids from stockpiling in the anaerobic reactors with the input of heavy metals which designates methanogenic inhibition but not necessarily acidogenesis [20]. Lin has indicated that the IC_{50} values for copper and zinc during methanogenesis were 11.8 and 14.7 mg/L while for acidogenesis the IC_{50} values were 0.85 and 3.3 mg/L respectively which designates lower permissiveness of acidogens towards copper and zinc in contrast with that of methanogens [21]. In addition, the chance of synergistic effects on the anaerobic process may occur due to the mixture of various heavy metal [22].

Heavy metals are also capable of causing toxicity in the biological systems through various methods such as the impediment of the membrane transport processes and substitutive ligand binding. During the anaerobic digestion process, the enzymes and pathogens are anticipated to combine together with the heavy metals at high concentrations in order for cytotoxic reactions to occur causing the performance and biochemistry of processes to alter [23]. For instance, the toxicity exerted by the heavy metals was ascribed to distort enzymatic operation and structure through replacement or binding of metals naturally existing matters [5]. Hence, functional genes and microbial abundances of enzymes will be greatly affected during the anaerobic digestion of waste activated sludge. In order to solve these potential negative impacts of heavy metals on waste activated sludge digestion, the precipitation and complexation method can be implemented to nullify the toxicity exerted by the heavy metals. For example, ethylene diamine tetraacetic acid has the capability to alleviate heavy metals' inhibition on enzymes due to it being able to complex with various types of heavy metals [7]. Nevertheless, another study has stated that there could be competition from other substrates and ions as other heavy metals are also released during waste activated sludge digestion which will result in competition for the ethylene diamine tetraacetic acid [24]. Another method to neutralise the toxicity of heavy metals is through alkaline treatment as the alkaline has the potential to deteriorate sludge and fasten the solubilization and hydrolysis of waste activated sludge [25]. A previous study has also shown that precipitation with carbonates and phosphates with heavy metals are also potentially able to neutralise heavy metal toxicity [26].

2.2. Inorganic nanoparticle pollutants.

Many products utilized in our everyday life nowadays are produced with the help of nanotechnology such as pharmaceutical products, cosmetic products, powdered food, pills and sunscreen. This increase in nanoparticle containing products has played a major role in the sudden spike of numerous nanoparticles in wastewater treatment plants. These nanoparticles are also quite hard to be extracted and cause major harm to the environment [27]. Several researches have investigated the plausible characteristics of nanoparticles in waste activated sludge digestion and the results obtained varied based on the various kind of nanoparticles [28]. Small concentrations of iron and iron (III) oxide nanoparticles are capable of enhancing waste activated sludge digestion performances as they are a kind of semi-conductor which enable them to facilitate the methanogenesis process by enhancing the interspecies electron transfer as anaerobic digestion of waste activated sludge occurs [29]. A previous study has shown that the increase of direct interspecies electron transfer has assisted the acetate-consuming anaerobes to enhance the performances of anaerobic digestion as the methane production was discovered to have gained by 18.5% and 50.7% with 35 and 125 mg/L of graphene respectively [30]. These nanoparticles which have the capability of the direct interspecies electron transfer in the process are alike to enzymes in catalytic reactions. The existence of iron nanoparticles in the anaerobic digestion have helped the processes of waste activated sludge hydrolysis and solubilization through the formation of micro-electrolysis accompanied by sludge to distort the matrix of the cemented sludge while unleashing a significant amount of soluble substrates for further biodeterioration [31]. Furthermore, the iron ions are able to precipitate with sulphur ions to mitigate the side effects of sulphur towards the microbe populations as iron is a major component for Fe-S clusters formation in enzymes and is responsible for the transportation of electrons for cellular redox activity [16]. Nonetheless, a previous study has identified that iron nanoparticles is only advantageous towards the solubilization and acidogenesis processes during anaerobic digestion while impeding the activity of methanogenesis as the study conducted an experiment which found that the production of methane was considerable reduced by at least 25% when iron nanoparticles exists during the anaerobic digestion [32].

In general, only certain nanoparticle types are able to enhance the performance of anaerobic digestions while the other nanoparticle types such as aluminium (III) oxide, gold, silicon oxide and titanium oxide had no relative impacts towards the waste activated sludge digestion. For example, titanium oxide was observed to have exhibited no impacts towards waste activated sludge digestion in mesophilic conditions but resulted in an enhancement of biogas production under thermophilic conditions [33]. However, with reference to another study, it has stated that titanium oxide was an important factor in aiding the hydrolysis of microbe substrates such as polysaccharides during the anaerobic digestion which invigorated the growth activity of photosynthetic bacteria [34]. Table 1 illustrates the various types of nanoparticles and the impacts they have towards the waste activated sludge digestion from various studies previously.

As for the negative effects of nanoparticles, a study has presumed that nanoparticles have the potential to infiltrate the cell membranes and enter the cell, resulting in the generation of reactive oxygen species [7]. Uncontrolled reactive oxygen species generation may lead to the membrane being oxidatively stressed and the membrane becoming homeostatically imbalanced which will cause the cell membrane to be injured by the nanoparticles as a result of the unleashed lactate dehydrogenase within the nanoparticle reactors [6]. Hence, the cellular metabolism in charge of the anaerobic digestion will malfunction and harm the cell instead. For instance, enzyme reactions of protease and amylase within cells were discovered to have been impaired due to the presence of zinc oxide nanoparticle [36]. In addition, several types of nanoparticles have the potential to exhibit toxicity during anaerobic digestion. A previous study had conducted an experiment with relation to the silver nanoparticle and have observed that the gene duplicates of the entire methanogens had significantly decreased as the silver nanoparticles were exposed to the microaerobic environment, resulting in a conflict between the acetoclastic methanogens and the hydrogenotrophic methanogens [32]. Therefore, the natural physiochemical characteristics such as chemical properties and particles size matter and the environmental conditions play key roles in whether toxic substances will be released from the nanoparticles. Another key factor influencing nanoparticle from exhibiting toxicity is the physiochemical parameters [7]. Various studies previously have stated that the wrapping effect of granular substrates was directed with the help of electrostatic association between fermentation substrate and nanoparticles which would result in the powerful sorption of organic substrates in waste activated sludge digestion system, thus reducing the amount of dissolved organic substrates present in the system, resulting in a big hindrance in the generation of methane [37,38]. To solve the issue, thermal treatment of graphene oxide mixed with waste activated sludge can be done or limiting the graphene oxide to only its zero valent form graphene so that the carboxyl groups of graphene oxide can be eliminated through the release of soluble chemical oxygen demand from graphene oxide [37].

Table 1. Various types of nanoparticles and their effects on waste activated sludge digestion.

Type of nanoparticles	Concentration	Impacts on waste activated sludge digestion	References
Iron	0.015 g/kg TSS	15 – 20 % increase in methane production	[6]
Iron	0.9 g/L	More than 300 % increase in methane production	[35]
Iron	5.6 g/L	More then 500% increase in short chained fatty acid production	[31]
Iron	15 – 20 mM	25 % decrease in methane production	[32]
Iron (III) Oxide	0.1 g/kg TSS	15 – 20% increase in methane production	[6]
Silver	0.5 g/kg TSS	25 – 30% decrease in methane production	[6]
Silver	0.04 g/kg TSS	No effect towards methane production	[32]
Titanium Oxide	0.15 g/kg TSS	No effect towards methane production	[36]
Titanium Oxide	0.45 g/L	10 - 20 % increase in biogas production during thermophilic conditions	[33]
Aluminium (III) Oxide	0.75 g/L	No effect towards methane production	[36]
Silicon oxide	0.15 mg/kg TSS	No effect towards methane production	[36]
Graphene	35 mg/L	18.5% increase in methane production	[30]
Graphene	125 mg/L	50.7 % increase in methane production	[30]
Copper	15 mg/g TSS	45 % decrease in short chained fatty acid production	[28]
Cerium Oxide	0.65 mg/L	90% decrease in methane production	[33]
Gold	50 mg/L	No significant effect	[33]

2.3 Persistent organic pollutants

Xenobiotics are more commonly referred to as fabricated organic pollutants which does not come naturally in the environment such as pharmaceuticals, facial products, antibiotics, pesticides, and persistent organic pollutants [39]. Most of these products release harmful chemicals which greatly pollute and harm the environment and if they are chemically bonded together with air pollutants, it may endanger human health as well [40]. In general, certain pollutants, especially those with hydrophobic properties are removed by adsorption to waste activated sludge during the treatment processes. It is expected that the production of xenobiotics will only keep increasing and the contents of it in various products are expected to increase to a higher level in the future [13]. Persistent organic pollutants are no strangers in waste activated sludge as studies have reported numerous types of persistent organic pollutant of relatively high concentration regularly present in waste activated sludge [14,41]. Persistent organic pollutants have great chronic effects towards anaerobic digestion as most products contain di-ethylhexyl phthalate which is one of the recalcitrant phthalic acid esters that impedes the methanogenic effect [14]. A study has published that the generation rate of methane was reduced by 20 – 40% during a two-month exposure period due to the progressive increase of di-ethylhexyl phthalate concentrations [42]. The accumulation of di-ethylhexyl phthalate within the anaerobic digester for long periods will result in 2-ethly hexanol to be released during the hydrolysis and solubilization of di-ethlyhexyl phthalate which is the key reason for the reduction in methane rate [43].

However, several persistent organic pollutants such as nonyphenol and polycyclic aromatic hydrocarbon in waste activated sludge were discovered to have enhanced the generation of short chained fatty acids when exposed towards alkaline for long periods of time [44]. For instance, it was found that the relationship between the concentration of polycyclic aromatic hydrocarbon and the average concentration of short chained fatty acids was directly proportional to each other as when the polycyclic aromatic hydrocarbon concentration increased from 0 to 90 mg/kg TSS, the average short chained fatty acids also raised from 2200 to 3300 mg COD/L [14]. This was mostly down to the generation of acetic acid as the polycyclic aromatic hydrocarbon and nonyphenol have the ability to enhance microbial activity in harsh alkaline conditions which contributed towards the improved generation of acetic acid. Another study made a presumption that the persistent organic pollutants had activated its self-defensive mechanism of acidogenic bacterium to generate more extracellular polymeric substances such as producing a thicker cell wall to shield themselves against the harsh alkaline environment and toxic substrates [7]. For example, a typical fermentative bacterium had its extracellular polymeric substances content improved by 30% in the polycyclic aromatic hydrocarbon reactors in contrast with that of no polycyclic aromatic hydrocarbon additions [14].

2.4. Pharmaceuticals and personal care products

Many wastewater treatment plants nowadays have observed high concentration levels of pharmaceuticals and personal care products in wastewater and these products may still be active in waste activated sludge which have the ability to impact the biological metabolism processes [45]. One of the pharmaceuticals and personal care products which have recently garnered a lot of attention recently is antibiotics due to many people abusing it. A previous study has conducted an experiment regarding fluoroquinolone antibiotics during anaerobic digestion of waste activated sludge and observed that there was a small increase in methane generation from the thermally hydrolysed sludge when low level of fluoroquinolone was present within while a decrease in methane was observed when high dosages of fluoroquinolone were added [46]. As for sulphonamide antibiotics, a previous study has observed that they encouraged the generation of short chained fatty acids predominantly acetic acid by stimulating the hydrolysis, acidification and solubilization of waste activated sludge [47]. The enzyme reactions of acetate kinase and protease were relatively enhanced under the presence of the sulphonamide while the methanogenic production was hindered [13]. Hence, it can be deduced that methanogenic activity can be influenced by antibiotics. Another study has also proposed that the methanogens adsorbing capability towards the cellular membrane was connected with the pharmaceuticals' hindrance on the methanogens [7]. For instance, it was identified that acetoclastic methanogens were less impervious to the pharmaceuticals suppression influences when compared with hydrogenotrophic methanogens [41]. The various types of xenobiotics and their respective impacts towards anaerobic digestion in waste activated sludge was shown in Table 2.

Table 2. Impacts of various types of xenobiotic organic pollutants towards the waste activated sludge anaerobic digestion.

Name of Xenobiotics	Type classification	Dosage	Impacts towards anaerobic digestion in waste activated sludge	References
Di-ethylhexyl phthalate	Persistent organic pollutant	80 – 100 mg/L	35 – 45% reduction in methane generation after long periods of exposure	[43]
Di-ethylhexyl phthalate	Persistent organic pollutant	50 – 175 mg C/L	20 – 40% reduction in methane generation over a two month period	[42]
Sulfadiazine	Antibiotics	40 – 60 mg/kg TSS	32 % increase in short chained fatty acid generation	[13]
Sulfamethazine	Antibiotics	20 – 30 mg/kg VSS	More than 150% increase in short chained fatty acid generation	[47]
Benzalkonium chloride	Biocides	0.1 – 100 mg/L	From no visible impact gradually to complete inhibition	[48]
Chlorhexidine	Biocides	50 – 70 mg/kg TSS	74 % increase in short chained fatty acid generation	[7]
Phenanthrene	Persistent organic pollutants	100 mg/kg TSS	More than 70% of acetic acid generation at pH 10 over long periods of exposure	[14]
Surfactin	Surfactant	0.01 – 0.05 g/g TSS	Enhance short chained fatty acid generation by 4 times	[51]
APG	Surfactant	0.05 – 0.2 g/g TSS	Enhance short chained fatty acid generation by 81%	[2]
Triclocarban	Antibacterial agent	100 – 550 mg/kg TSS	Enhance short chained fatty acid generation by 86%	[49]
Ciprofloxacin	Antibiotics	0.03 – 55 mg/L	No impact at low dose but reduce methane production by 42 % at high dosage	[52]
Dichlofenac	Anti-inflammatory drug	3- 20 mg/kg TSS	Enhance short chained fatty acid generation by 46 %	[47]

The other group of xenobiotics which are also widely perceived in waste activated sludge are antimicrobial and biocidal agents which are largely implemented within personal care products such as sunscreen, toner and etc. Numerous antimicrobial and biocidal agents have shown side effects during anaerobic digestion such as benzalkonium chloride which steadily reduces the generation of methane from no visible influence at low concentration to practically complete suppression at high concentrations. Benzalkonium chloride is also able to synergise with other homogenous pollutants to result in a larger inhibitory influence [48]. In general, our daily products which contain antimicrobial and biocidal agents has evident surfactant-like properties which has either hydrophobic or hydrophilic ends that results in methanogens being more at risk to the pollutants [7]. From a different perspective, these surfactant-like characteristics of the microbial and biocidal agents can help in the extracellular polymeric substance distortion in the anaerobic digestion systems of waste activated sludge which would play a key role in the increase of bioavailable substrates for acetogenic bacteria, thus resulting in the enhanced production of short chained fatty acids [49]. For example, it was observed that if low concentrations of chlorhexidine and hexadecyltrimethylammonium bromide were present during anaerobic digestion of waste activated sludge, the accumulation of short chained fatty acids was raised from 570 mg COD/L to 2150 mg COD/L due to the increase in acceleration of both acidification and hydrolysis procedures [7]. Furthermore, the hindrance of methanogenic reactions also plays a part in the enhancement of short chained fatty acid due to the significant decrease of acetoclastic methanogens. It can be deduced that the dosage of biocides is directly proportional to the immensity of biocides toxicity unleashed [50].

3. Conclusions

Different types of exogenous pollutants would display different effects on the sludge methanogenesis and acidification processes, hydrolysis and solubilization as well as the correlating concentrations. It was also observed that the majority of the pollutants observed in the waste activated sludge would normally react towards anaerobic digestion at low levels but exhibit obvious negative impacts at high dosages. In general, methanogens are considered be more easily impacted by the toxic substrates and thus methanogenesis is more vulnerable when compared with acidification and hydrolysis. The result of these synergetic impacts might result in high levels of toxicity exhibited during the reaction which may harm the ecological system but information with relation towards the synergetic impacts are still limited.

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Competing Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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