Abstract

To develop a circular economy, nutrients from waste streams need to be recovered and brought back to agricultural production as much as possible. Liquid waste streams pose a specific problem because high water content makes transport expensive. Treatment of wastewater and diluted waste streams to recover nutrients are briefly discussed, and two options that are not much used are discussed: sorption to increase the fraction of nutrients found in the solid phase and nitrification of liquid to reduce nitrogen losses. Then, availability of nutrients to plants and environmental effects are discussed. It is concluded that there is little information on how treatment options affect how bioavailable the nutrients are and that this should be taken into account when treatment option is chosen.

Keywords: biofertilizer, nutrients, liquid waste, bioavailability, environmental effects

1. Introduction

Many organic waste streams have high nutrient content, and can, if treated properly, become good fertilizers and soil improvers. There are many reasons to promote this use:

1. Resource efficiency: Nutrients in waste resource can replace mineral fertilizers and therefore reduce resource mining and energy use.

2. Organic agriculture cannot use mineral fertilizers and needs to use organic fertilizers to get nutrients for crop growth.
3. Organic fertilizers also contain organic matter as well as organically bound nutrients. Organic matter can improve soil fertility and reduce soil degradation in some cases, and organically bound nutrients are released slowly.

4. Carbon can be sequestered in the soil and reduce atmospheric build-up.

The benefits of organic matter additions to soil have been stated by many authors [1–4]; however, the evidence suggests that mineral fertilizers usually are better at supplying plants with nutrients and avoid leaching losses, at least in the short term. However, in the longer term, building organic matter in the soil can improve nutrient retention. Slow release of nutrients may be beneficial for some crops (with long-period nutrient uptake e.g. root crops) and under some conditions (humid conditions with leaching losses early in the season), but less beneficial for other crops and conditions [5].

Many organic waste streams contain a lot of water, making transport difficult and expensive in economic and environmental terms. Examples of diluted waste streams can be sewage, biogas digestate, animal manure, various industrial waste streams, animal manure and fish sludge from aquaculture.

An overview of wastewater treatment can be found in textbooks, for example, [6–8]. Choice of treatment has so far almost exclusively focused on cleaning the water sufficiently to be discharged to the recipient; the resource recovery perspective has not received much attention. However, this is now changing because of concern of resource mining, particularly for phosphorus [9, 10] and high-energy consumption in nitrogen fertilizer production [11].

Options for concentration (alone or in combination) can be:

- dewatering (by centrifuge or press)
- flocculation, settling
- precipitation
- drying, evaporation
- biological stabilization, wet composting

In most cases, liquid waste streams are left to let whatever can settle do so. There are also methods to increase settling and flocculation. Some form of stabilization is also common, either aerobic by use of oxygen or by anaerobic digestion for biogas production.

Dewatering leaves an organic rest with relatively low water content and a liquid residue with dissolved substances. As soluble nutrients are the most readily plant available, that means that a large fraction of the plant available nutrients will be found in the liquid phase. Often no good use of the liquid phase can be found, and it enters into sewage treatment systems. In many cases also some chemicals (polymers) are required to give proper separation [12]. This is costly, and chemicals can also have potentially negative environmental effects.

Dissolved nutrients can be precipitated out of solution. This is commonly done to get phosphorus out of wastewater before discharge to the recipient. Unfortunately, an almost
insoluble salt results, and plant availability is very low [13, 14], although different for different precipitation chemicals [15].

Drying or water reduction by evaporation can be good options if cheap or waste heat is available. However, most liquid waste streams contain most of the nitrogen on ammonium form, and some measures must be applied to prevent losses of nitrogen as ammonia [16]. This is commonly achieved by acidifying the solution first or collecting the ammonia in biofilter acid trap afterwards.

Fertilizer products developed from organic residues can be called organic fertilizers or biofertilizers. This chapter deals with biofertilizers developed from liquid waste streams and discusses how biofertilizer quality in agricultural and environmental terms depend on treatment.

2. New treatment option to increase fraction in the solid phase and make liquid waste stable

Some newer options to increase recycling are discussed before Sorption is a physical and chemical process by which one substance becomes attached to another. By adding cheap sorbents to a liquid waste stream prior to dewatering, the fraction of nutrients found in the solid phase after dewatering can be increased. Nitrification is a microbial process where ammonium is transferred to nitrate. This leaves a stable solution that can be applied and evaporated without losses of ammonia.

2.1. Sorption

Some sorbents can be used to remove nutrients from liquid waste streams and concentrate them in a solid phase that can be separated by dewatering. Sorption is a physical and chemical process by which one substance becomes attached to another. Sorbents are the solid substances they attach to, sorbate are the substances (dissolved or gaseous) that attach. Organic material is a weak sorbent, sorption properties can be greatly increased by charring [17]. The sorbents can be charred organic material (e.g. biochar, hydrochar, activated carbon) or some clay or other minerals (bentonite, zeolite, vermiculite). Cation exchange is the most common; there are reports on removal of ammonium ([18–24]). Some authors also report potassium removal [22, 23]. Sorption of anions appears to be more difficult, but there are some reports of phosphorous sorption [18, 20, 22–26]. Sorption of nitrate is difficult, but it appears that it can be achieved on some biochars produced at high temperature [27, 28]. There are also reports of sorption of hydrogen sulfide (reviewed by [29]) and also one report on ammonia removal from the gas phase [30].

2.2. Nitrification

It is possible to reduce or eliminate losses of ammonia from liquid waste by reducing pH, or nitrogen can be collected in biofilters or by stripping afterwards [31].

Losses of ammonia from liquid waste can also be eliminated by transforming ammonium to nitrate by a microbial process prior to storage and/or evaporation and application. The process
also lowers pH, and that will also reduce ammonia volatilization, so that a small free and stable product will be the result. There are reports on tests on this for digestate and urine [32–34]. This process happens naturally in soil, and it can also be made to happen in an aerated reactor, this is done in many sewage treatment plants [35, 36]. It is also similar to wet-composting where nitrogen transformations happen as well as carbon consumption and stabilization [37].

Nitrification has two steps; both are microbially mediated [35]. In the first step, ammonia is oxidized to nitrite (NO$_2^-$) by bacteria belonging to the genus *Nitrosomonas*. In the second step, nitrite is oxidized to nitrate (NO$_3^-$), mostly by *Nitrospiria* and *Nitrobacter* microorganisms [35, 38, 39]. However, high nitrite concentrations inhibit both processes, and it is therefore important to control the processes so that the intermediate products do not accumulate. This means process parameters must be controlled so that both steps can proceed at the same rate [40]. As ammonia oxidizing bacteria use ammonia as a substrate, not ammonium, this generally means controlling parameters of the concentration of free ammonia in solution is kept relatively low, for example, moderate pH and temperature [40].

3. What do we know about how treatment options affect plant availability?

It is known from numerous studies that not all nutrients in biofertilizers based on organic residues are available to crop plants, and sometimes also become available only after some time, and predicting the availability over time can be challenging [41, 42]. Plants take up dissolved nutrients, and nutrients that are dissolved or readily soluble will usually be 100% plant available. This is the case for mineral fertilizers. Most studies of plant availability of nutrient have assessed final products, for example, [43–47]. There are few studies assessing the same waste residue treated in different ways. This makes it difficult to disentangle the effect of feedstock from the effect of treatment option.

Dissolved nutrients in liquid organic waste will usually be bioavailable. Dewatering will therefore usually mean that most of the readily plant available nutrients are found in the liquid phase. How well plant nutrients are recycled will then depend on what happens to the liquid phase. Often it is not recycled optimally because transport costs are too high.

Precipitation can make nutrients less available, or even almost unavailable. This is well known for phosphorus removal from sewage treatment [15, 48]. The most common precipitation agents are aluminum and iron salts, leaving phosphorous almost unavailable to crop plants. Excess precipitation chemicals may even make soil phosphorus less available.

It is usually assumed that drying does not affect nutrient quality, so that plant availability remains unaltered. However, there is very little experimental evidence confirming that this is actually true. Knoop et al. [49] compared composting and drying as treatment options. They found that the content of plant available nitrogen decreased during drying although less than during composting, probably because the most plant available nitrogen is lost as ammonia. The fraction of phosphorus that was plant available also decreased during drying. There was no difference between air (20–30°C) and own dried (70°C). However, phosphorus availability
was measured chemically; it is not certain that this corresponded exactly to actual plant availability measured in plant growth experiments. We have some indications that drying at high temperature at least may make phosphorus more plant available. This requires further study.

Most biological stabilization options will make the nutrients more available as they are decomposition processes, which mineralize the nutrients. However, during aerobic treatment (composting), some of the nitrogen is lost, more the more open the process is [50–52]. Anaerobic treatment will also usually make nutrients more available [53], an exception is phosphorus during anaerobic digestion of precipitated sewage sludge [54], probably because excess precipitation chemicals are used, which precipitate mineralized phosphorus.

Adding sorbents before dewatering can be a way to increase the fraction of nutrients found in the liquid phase as discussed in Section 2. The authors usually state that solid product can be applied in agriculture as a fertilizer, but there are surprisingly few studies that investigate if sorbed nutrients are as bioavailable as nutrients added the conventional way. One study found that ammonia sorbed as gas was bioavailable, but the degree of availability was not compared to conventional fertilizer application [55]. Another study found that sorbed nutrients were slowly desorbed in soil [56]. Our own unpublished studies suggest that ammonium sorbed to zeolite is less plant available than conventionally added ammonium. A recent study [57] found that at least some nitrogen sorbed to zeolite from urine was plant available. They also suggest that nitrification could be an important driver of release of nitrogen from zeolite, as liming increased the recovery of mineral nitrogen. It is possible that zeolite and other sorbents provide surface area for biofilm development, and it could therefore stimulate nitrification. This requires further study.

Nitrification has also been discussed as a possible way to treat liquid waste. The question if nitrate or ammonium is the preferable fertilizer is a complicated one. Usually nitrate is preferred, because it can be taken up faster and only ammonium as a fertilizer can be harmful to some plants [58, 59]. However, nitrate is also more easily leached and can be lost from the soil profile before plants can take it up. As such, ammonium can be regarded as a slow release fertilizer, as it is usually quite quickly nitrified in agricultural soil.

4. How does treatment affect environmental performance of biofertilizers?

Most environmental problems related to fertilizer use, either mineral or organic, are related to losses to the environment, as leaching and runoff and as gas. Loss of nitrogen and phosphorus to waterways and coastal areas can result in eutrophication and algal blooms [60]. Losses of ammonia gas can also lead to over-fertilization and acidification [61]. In addition, a small fraction of the nitrogen lost as gas is lost as nitrous oxide, a powerful greenhouse gas and as NOx [62, 63]. The best way to avoid losses is therefore to time fertilizer application or availability with crop demand, so that the crop can take it up before it is lost, this will be a win-win situation. Losses can also be reduced by reducing application rates, but this will also reduce yield.
Biofertilizers usually induce larger losses per unit nutrients added than mineral fertilizers. This is partly because not all nutrients in organic fertilizers are immediately available and may become available later when plants cannot take them up. However, this depends on crop type as well, some crops take up nutrients throughout the growing season, and then slow-release fertilizers may be an advantage [5].

The environmental effect of acidification has not been much studied. Particularly the effect on losses of nitrogen a nitrous oxide would be an interesting field of study, as the effect of pH on emissions of this gas is particularly complicated [62–66]. Denitrification rate increases with pH up to above neutral, but the fraction that is nitrous oxide rather than dinitrogen gas is higher at acidic pH. The effect on emission of the greenhouse gas nitrous oxide is therefore difficult to predict.

Addition of sorbents to increase the fraction of nutrients found in the solid phase has been discussed in Section 2. There is also some evidence that sorbents could reduce gaseous losses from soils, including greenhouse gases. Vermiculite and bentonite have been shown to decrease emissions of ammonia and nitrous oxide when mixed with manure prior to [67, 68] and increase nutrient retention after application [69]. However, Dietrich [70] did not find any effect of bentonite additions to digestate on nitrous oxide emission, so this also requires further study.

Nitrification as treatment option was also discussed in Section 2. Most environmental effects are related to losses; as mentioned in the previous section, nitrate is more easily lost by leaching. However, it is also more easily taken up by plants, and if application is timed with demand, losses can be low. As greenhouse gases can be emitted by a number of processes [62, 63, 71], it is difficult to predict if nitrification prior to application will increase or decrease emissions. However, a review found lower emissions from nitrate-based fertilizers [62], suggesting that nitrification may be favorable.

5. Conclusion and outlook

Sorption can be a good way to get a larger fraction of available nutrients in the solid phase prior to dewatering. Nitrification prior to storage and application may be a good way to reduce losses of nitrogen. However, little is known about if these and other treatments affect how plant available the nutrients are. More effort should be directed at understanding how treatment options affect plant availability, to be able to choose the best options.

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Conflict of interest

The author declares no conflict of interest.

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