Adding value to wastewater by resource recovery and reformulation as growth media: current prospects and potential

M.-P. Zacharof and R. W. Lovitt

ABSTRACT

Wastewater, despite being a serious environmental constraint, has been identified as a source of valuable commodities including phosphate, ammonia, metal ions and volatile fatty acids. Using low-cost physical pre-treatments, filtration technology gives the opportunity of recovering materials in purified concentrated liquid form and purified water. Filtration also allows manipulation of the nutrient content in the effluents enabling the formulation of a series of streams enriched with important chemical components, enabling their reformulation into balanced nutrient media for microbial growth and the production of biofuels, acids and other chemicals such as lipids and enzymes. This approach benefits industry through the use of a relatively abundant inexpensive feedstock able to be recycled to produce high value chemicals while reducing the carbon footprint of the fermentation and reducing waste disposal. Examples of potential schemes of nutrient formulation and their application are presented.

Key words | membranes, microbial growth, platform chemicals, sustainability, wastewater

M.-P. Zacharof (corresponding author)
R. W. Lovitt
Centre for Complex Fluid Processing (CCFP),
College of Engineering, Swansea University,
SA2 8PP Swansea,
UK;
Centre for Water Advanced Technologies and Environmental Research (CWATER),
College of Engineering, Swansea University,
SA2 8PP Swansea,
UK; and
Systems and Process Engineering Centre (SPEC),
College of Engineering, Swansea University,
SA2 8PP Swansea,
UK
E-mail: *myrtozacharof1981@yahoo.com*

INTRODUCTION

Wastewater – domestic, municipal, or industrial – is a serious environmental problem that needs to be treated effectively in order to be safely discharged in the environment. Wastewater is often found to contain hazardous chemicals including metals (e.g. As, Pb, Cr, Cd and Zn), toxic compounds such as endocrine disruptors, dyes and a strong, pungent odour due to the high content of organic matter. However, waste streams have also been identified as a source of valuable commodities including phosphate, ammonia, metal ions and volatile fatty acids (VFA) (Jung & Lovitt 2011).

Various methods have been proposed for treating wastewater to make it safe for discharge in the environment that require costly plant processes using energy, bioremediation and additional physical and chemical treatments (Tchobanoglous *et al.* 2004). These treatments generally do not allow either the recovery or the reuse of chemicals leading to the loss and dilution of important resources (Zacharof & Lovitt 2013).

This review will investigate membrane processes and their potential for valorising wastewater by recovering valuable nutrients that could also be precisely reformulated as media for microbial production of platform chemicals. It will be argued that such an approach will improve waste treatment by reducing its costs by producing clean water and valuable chemical streams. This strategy could have a significant impact enhancing environmental sustainability of biofuels and chemicals production.

RESOURCE RECOVERY: COSTS AND OUTLOOK

Currently living in a low carbon economy, with growing awareness over environmental protection and strengthening of water resource-related legislation, the need to recover chemicals from wastes becomes apparent (Angelis-Dimakis *et al.* 2011). The continuously rising human population

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results in rising demand for food, energy and water. Food production has become heavily industrialised and therefore regulated generating millions of tonnes of waste per annum. For example, the demand and supply of cheese in the EU has reached 6,385,000 tonnes per annum, producing 40,420,800 tonnes of whey, a watery by-product of cheese processing rich in lactose, proteins and salts but with an exceptionally high organic content. Of this, the vast majority is being recycled, incorporated in animal feed and food supplements; however, a surplus of about 13,462,000 tonnes remains, and processing and treatment is expensive especially for small and medium cheese producing industries (Koller *et al.* 2008). Food additives and flavour enhancers such as monosodium glutamate, an enhancer used in canned vegetables, soups, processed meat and Chinese food, generate thousands of tonnes of highly acidic organic (pH 2) waste with a chemical oxygen demand ranging between 10,000 and 40,000 mg/L (Xue *et al.* 2008).

Moreover, the food industry is shifting towards the intensive production of ready to eat foods that are consumed in venues with fewer conventional methods of stabilising food, therefore resulting in even larger amounts of waste (Jones *et al.* 2005). In addition to the directly occurring waste due to food processing (slaughterhouse, dairy, wheat and corn milling, sugar and starch processing, vegetative processing, fish and poultry processing, alcoholic and non-alcoholic beverages and soft drinks manufacturing and processing), the food industry is associated with agricultural waste (organic waste and agricultural residues) produced by intensive animal and crop farming to satisfy the demand for food, reaching 264,854 tonnes per annum (GOV.UK 2014) in the United Kingdom alone. Agricultural waste comes third in terms of waste industry size, comparable only with municipal solid waste (Li & Yu 2011). Such waste imposes environmental constraints, since conventional treatments such as landfilling or landspreading may cause eutrophication and land and water toxicity due to the freely available nutrients and metals spread in the water and soil. There are also human health concerns due to land-related pathogenicity contained in the raw materials (Zacharof & Lovitt 2014a).

However, these effluents do contain various valuable chemicals, including VFA, nitrogen as ammonia, phosphate and metals. For example, phosphate rock, a non-renewable natural resource, is of critical importance due to its numerous uses in various products such as fertilisers, food additives and drinking water treatment. Although its production is carbon neutral, the mining of phosphate is becoming more expensive and there are supply risks related to environmental and socio-political issues. By 2035 it is calculated that the demand for phosphorus will outpace the supply as the finite resource becomes increasingly expensive (800% rise between 2006 (US$50) and 2008 (US$400), current value over US$500/tonne). At the same time phosphorus removal from wastewater has to improve as water discharge standards become more stringent, making water treatment more expensive. VFA such as acetic acid have a market size of 3,500,000 tonnes/year with a market value of $800/t while butyric acid reaches US$2000/t and a market size of 30,000 t/year (Zacharof & Lovitt 2013).

Ammonia has a market value of US$800/t with a global consumption of over 150 million tonnes. As well as being used heavily in fertilisers it is also an important component of various commercial and industrial products. It has a large production carbon footprint (best practice being 4 tonnes of CO_2 per tonne of ammonia) as during its synthesis methane is reformed to produce H_2 and CO_2. In addition, the disposal and return of ammonia to the atmosphere through nitrification and denitrification adds additional costs to wastewater treatment.

Consequently, reclaiming these valuable chemicals such as phosphorus, ammonia, metals and organic acids are important steps to improve sustainability and reduce the environmental impact of these potentially hazardous materials. This approach has multiple benefits including: recycled materials that will substitute for newly synthesised or mined materials; the reduction in the volume and concentration of waste will reduce demand and costs in waste treatment plants; creation of valuable streams such as formulation of nutrient streams for application in agriculture and bioprocessing (Zacharof & Lovitt 2013).

MEMBRANE TECHNOLOGY AND RESOURCE RECOVERY

Recovery and separation of wastewater, with its diverse composition and complex physicochemical nature, calls for innovative, cost-effective engineering methods and strategies for recovery of materials. Within this context, low energy physical treatments such as dilution, sedimentation and filtration/diafiltration using pressure driven membrane technology can offer a viable solution.

Particle separation can be achieved over a wide range of membrane technologies covering microfiltration (MF), ultrafiltration, nanofiltration (NF) and reverse osmosis (RO); the substances of interest can be clarified, fractionated, and concentrated to produce high value streams at low cost. Membrane technology is still a rapidly developing technology, it is easily scalable with numerous arrangements and alternatives, often easy to incorporate and integrate into waste treatment processes. They offer high productivity and low operational cost compared with other competing technologies, since there is no phase change of water and minimal or no use of chemical additives (Zacharof & Lovitt 2014b).

The use of membranes in industry as a downstream and upstream processing option has been proven as an attractive, cost-effective option, applicable in numerous well-defined waste systems. Examples from the food industry include processing waste of alcoholic (beer) and non-alcoholic beverages (orange juice), edible oils (olive, vegetable) and dairy (whey, milk), while examples from the chemical industry include processing of tanning wastewater, electroplating effluents and effluents rich in hazardous chemicals (Al-Amoudi & Lovitt 2007).

Nevertheless, membrane technology in these systems has been applied within the scope of removal of chemicals such as arsenic, so the effluents can be safely disposed in the environment rather than with the aim of recovery.

The utilisation of membranes though is accompanied by numerous engineering challenges, of which the most prominent is membrane fouling. Fouling is a complex multifactorial phenomenon, which is rather difficult to describe precisely and is largely dependent on the feed water composition. However, the general definition is deposition on the membrane surface of dissolved and undissolved substances forming an undesirable layer causing flux decline. Fouling can be classified into three major categories: (a) inorganic fouling due to the deposition on the membrane surface of colloidal matter, minerals, and hardness scales; (b) biofouling, namely microbial attachment on the membrane surface followed by growth and multiplication under the presence of sufficient amounts of organic nutrients either deposited on the membrane or existing in the feed; and (c) organic fouling caused by humic acid and other derivatives of natural organic matter (Van der Bruggen *et al.* 2002).

When fouling occurs it leads to an increase in production cost, as there is an increase in energy demand, additional labour for cleaning and maintenance, use of chemical agents for cleaning and reduction in membrane life expectancy, as fouling reduces the performance of the membranes, regardless of its type. Judicious usage of membranes systems operating conditions, including temperature and pH, and development of pre-treatment processes such as sedimentation, coagulation, precipitation, dilution, membrane modification and mixing to homogenisation, wherever this is possible, can constitute fouling a reversible process and extend the membranes' shelf life.

Processing complex waste effluent through membranes imposes the hurdle of fouling, which if irreversible can be detrimental to the process. Addressing this phenomenon effectively would require pre-treatment with methods capable of separating large particulates and heavy solids from the liquid mass. Pre-treatment is sought out, depending on the treatment objectives, since it is known that if the desired flux cannot be achieved with the existing nature of the feed, the recovery of the substances is influenced by flux maintenance and clean-in-place frequency, creating a less-than-targeted value because of the many undesirable elements in the feed.

A major role in the selection of a pre-treatment scheme is played by the overall lifetime economics of the designed system. For the economic evaluation several parameters are taken into account such as the system's capital cost, membrane replacement costs after a certain amount of time, chemical costs, disposal of non-chemical and chemical waste, labour and chemicals cost.

Low-cost, non-chemical pre-treatment, such as dilution, sedimentation, sieving and air flotation are preferable. However, chemical conditioning as a pre-treatment scheme can also be a viable option for systems that require a different method of pre-treatment to meet filtration goals. Examples include chemical disinfection, biofouling control, coagulation, oxidation, pH adjustment and scale inhibition. However, when using chemical disinfectants such as oxidants, the membrane material should be taken into consideration especially in the case of organic polymeric membranes where extreme pH of the feed water might cause chemical deterioration of the membrane surface.

Using this technology, wastewater itself can be valorised as clean water (Figure 1) by removing coarse particles, indigenous microbial/viral load, toxic substances and colorants. These materials, once separated and concentrated into streams, can act as sources of nutrients, organics and salts that when precisely formulated, can serve as growth media for microbial production of platform chemicals and biofuels.

These effluents, if used as nutrient media, are potentially highly profitable, especially when compared with the traditional synthetic media or that derived from food sources such as crops.

Filtration allows manipulation of the nutrient content, since it can be combined with leaching and acidification using MF or selective separation and concentration using subsequent NF and RO processes. This approach has several advantages such as: recycled materials that will substitute for newly synthesised or mined materials; and reduction in the volume and concentration of waste which will reduce demand and costs in waste treatment plants.

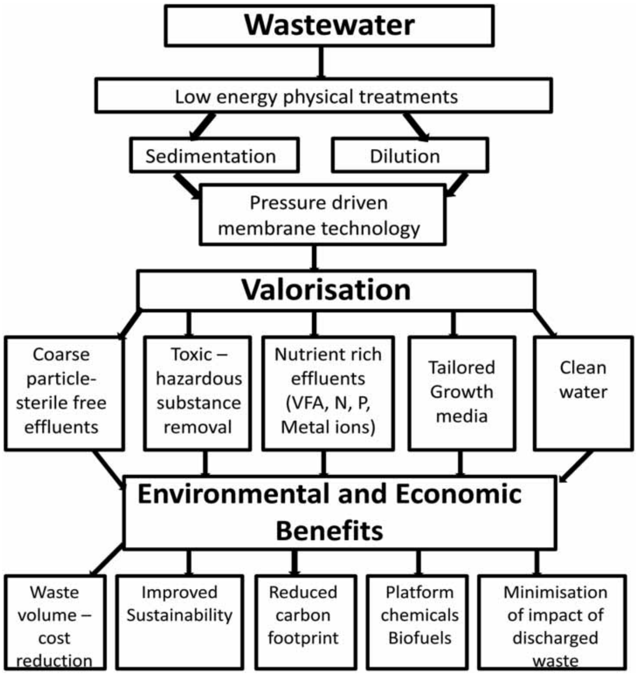

Figure 1 | Valorisation and benefits of filtration treatment of wastewater.

GROWTH MEDIA FOR MICROBIAL PRODUCTION SYSTEMS

Industrial wastewaters from food processing industries, breweries and agricultural wastewater from animal confinements are ideal candidates for biotechnological production of high value and platform chemicals (Angenent *et al.* 2004); however, their effective formulation remains a necessity. These effluents, if used as nutrient media, are potentially highly profitable, especially when compared with the traditional synthetic media or that derived from food sources such as crops. For example, the cost of Man de Rogosa broth, a well-known nutrient medium used in research and development of starter cultures in the dairy industry, can reach US$1311 per kilo, while a formulated waste-derived nutritive effluent can cost as little as US$2.4 per kilo of nutrients (VFA, ammonia, phosphate) recovered (Zacharof & Lovitt 2014a).

Previous research has shown the strong potential of discharged waste effluents to be used as nutrient media for production of various biobased chemicals (Table 1).

However, these studies have been conducted into relatively dilute effluents or leachates, with relatively low solids content, such as whey or municipal wastewater percolate. These effluents have not been formulated in order to address the precise nutritional needs of the microorganisms used, consequently the productivity of chemicals is feasible but remains in most cases lower than conventional methods, such as fermentations on defined or semi-defined media (Zacharof & Lovitt 2013). On the other hand, filtration allows manipulation of the nutrient content, since it can be combined with leaching and acidification using MF or selective separation and concentration using subsequent NF and RO processes (Figure 2).

Furthermore, if filtration is used with diafiltration or dewatering depending on the amount of nutrients needed to be recovered, the wastewater effluents are gradually depleted, becoming safe for disposal in the environment. If the depleted wastes do have a small amount of phosphate

Table 1 | High value chemicals bioproduction from waste sources

Waste stream	Microbial strain	End product	End product concentration	References
Whey	*Pseudomonas hydrogenovora*	Polyhydroxyalkanoates (PHA)	2.0 g/L	Koller *et al.* (2008)
Sugar molasses	Mixed culture	Polyhydroxyalkanoates (PHA)	0.2–0.6 g/L	Albuquerque *et al.* (2010)
Agro-industrial oily waste	*Pseudomonas aeruginosa* NCIMB 40045	Polyhydroxyalkanoates (PHA)	2.3 g/L	Fernandez *et al.* (2005)
Monosodium glutamate	*Rhodolotura glutinis*	Biodiesel	11.56% w/w	Xue *et al.* (2006)
Dairy manure	*Rhizopus oryzae*	L-(+) lactic acid	1.14–1.57 g/L	Sun *et al.* (2012)
Grains	*Lactobacillus* spp. *Bacillus* spp.	Lactic acid	0.38–4.20 g/L	Gao *et al.* (2011)
Municipal	*Bacillus thuringiensis*	Biopesticides	3,300 IU/μL	Montiel *et al.* (2001)
Olive mill	*Candida cylindracea* NRRL Y-17506	Lipase	9.23 IU/mL	D'Annibale *et al.* (2006)
Starch	*Rhodolotura glutinis*	Biodiesel	30% w/w	Xue *et al.* (2010)
Spent fermentation broth	*Trichosporon dermatis*	Microbial oil	13.50% w/w	Peng *et al.* (2013)
Sugarcane	*Aspergillus terreus*	Single cell protein	25% w/w	El-Nawwi & El-Kader (1996)

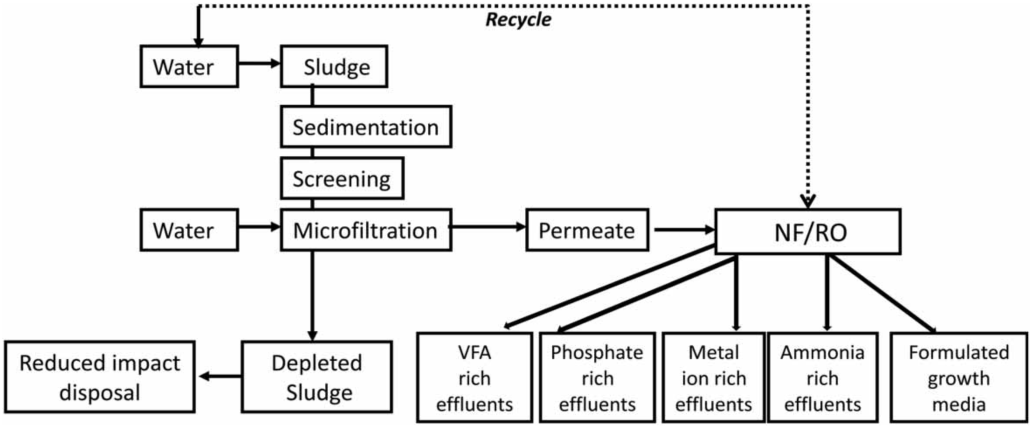

Figure 2 | Processing and recovery scheme for VFA, nutrients and formulated growth media.

and ammonia this can be recycled by being placed back in the processing system (Zacharof & Lovitt 2014a).

Other benefits of this approach include a minimisation in costs due to the reduction in steam sterilisation, extensive pre-treatment using chemicals or enzymes and recovery costs since filtration successfully removes the high solids content, the indigenous flora and the majority of impurities.

These streams can then be blended enabling the formulation of different concentrations of appropriate proportions (Gerardo *et al.* 2013; Zacharof & Lovitt 2014a) suitable for supplying the nutritional needs of microbial fermentations for intensive production of biofuels, acids and other chemicals such as lipids and enzymes (Li & Yu 2011). For example, for the production of ethanol by *Saccharomyces* spp., the commonly used synthetic medium has a high (30 g/L) nitrogen content due to the presence of ammonium salts, yeast extract and peptone. If waste effluents were used instead, the nitrogen sources could be supplemented via organic matter in the form of ammonia and the other components such as phosphorus and metals.

CASE STUDIES

Our work on MF systems has indicated that the energy cost per cubic metre is US$1.55 for anaerobically digested effluents of agricultural waste origin consisting of 11.9 g/L dry solids containing 56.31 mmol/L N, 1.31 mmol/L of P, 22.11 mmol/L acetic acid and 16.71 butyric acid mmol/L VFA. The resulting permeate was found to contain 2.65 g/L VFA, 0.96 g/L ammonia and 1.91 g/L phosphate at a pH of 7.83. This medium has been used successfully to grow industrially important microbes, *Lactobacillus plantarum* NCIMB 7014, *Clostridium butyricum* NCIMB 7432, *Escherichia coli* NCIMB 8277, *Schizochitrium limacinum S21* NCIMB MYAB81 and *Saccharomyces cerevisiae* NCYC 1681, giving equivalent results to those of synthetic media (Zacharof *et al.* 2014).

All the microorganisms, apart from *L. plantarum*, grew successfully on the treated effluents, reaching 1.5 g/L of biomass. Interestingly decolorisation was observed when *E. coli* was grown on the treated effluents, resulting in an optical density of 0.02, a reduction of 80%, suggesting that this microorganism might serve as a bioremediation agent (Zacharof *et al.* 2014).

CONCLUSIONS

The main challenge remains to recover high value substances cost effectively, while demonstrating successfully the applicability of this strategy on a large scale. Certainly, this approach can greatly benefit industry through the use of a relatively abundant inexpensive feedstock able to be recycled to produce high value chemicals while reducing the carbon footprint using fermentation and reducing waste disposal.

Such a system, namely development of a complete membrane processing strategy within the scope of nutrient recovery, can be effectively integrated in existing waste treatment systems, for example in wastewater treatment plants and anaerobic digesters, practically closing the ecological loops related to human activity. The produced waste containing carbon, nitrogen, phosphate and water can be successfully converted to combined heat and energy via anaerobic digestion, while the surplus digestates, processed through membranes, and the generated energy can be used in fermentations to produce energy, liquid fuels and important chemicals (Figure 3).

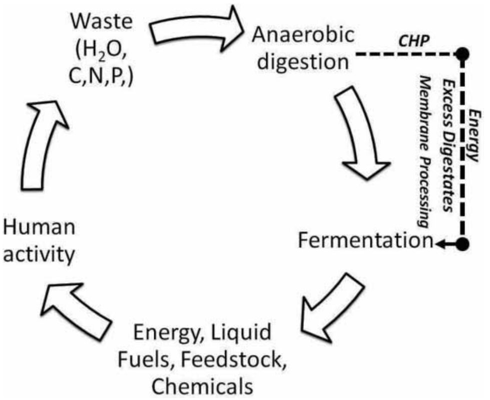

Figure 3 | Process integration with current systems of waste treatment.

The benefits of such an approach will be further assessed by an analysis and comparison of the carbon footprint and the costs of synthetic and waste-derived growth media, in order to fully estimate the applicability at large scale of such an approach.

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