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Review

Urban Wastewater Mining for Circular Resource Recovery: Approaches and Technology Analysis

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Abstract: Urban areas comprise less than 1% of the Earth's land surface, yet they host more than half the global population and are responsible for the majority of global energy use and related CO_2 emissions. Urbanization is increasing the speed and local intensity of water cycle exploitation, with a large number of cities suffering from water shortage problems globally. Wastewater (used water) contains considerable amounts of embedded energy and recoverable materials. Studies and applications have demonstrated that recovering or re-capturing water, energy, and materials from wastewater is a viable endeavor, with several notable examples worldwide. Reclaiming all these resources through more widespread application of effective technological approaches could be feasible and potentially profitable, although challenging from several points of view. This paper reviews the possibilities and technical opportunities applicable to the mining of resources within the urban water cycle and discusses emerging technologies and issues pertaining to resource recovery and reuse applications. The present and future sustainability of approaches is also discussed. Since sewage management issues are not "one size fits all", local conditions must be carefully considered when designing optimal local resource recovery solutions, which are influenced not just by technology but also by multiple economic, geographical, and social factors.

Keywords: urban wastewater; water reuse; energy; nutrients; secondary raw materials; circular economy

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1. Introduction

Urban areas comprise less than 1% of the Earth's land surface yet host more than half the global population. There are already 43 megacities (i.e., those with >10^7 inhabitants) worldwide, and their number is constantly growing [1]. Cities are responsible for the majority (≈75%) of global energy use and related CO_2 emissions, requiring a constant influx of natural resources, raw materials, food, and energy to sustain the activities of their inhabitants and generate equivalent outgoing fluxes of waste materials. It has been estimated that continuing urbanization under unchanged paradigms could increase the global annual consumption of raw materials by 125% within the next 40 years [2].

Cities contain huge amounts of unexploited materials such as household solid waste, construction rubble, and electronic waste, which represent generally untapped values. Under old paradigms, i.e., linear consumption, these are released after use, accumulating within the city or in its close proximity, and exerting significant pressures on the natural environment and human health, well beyond the immediate urban surroundings. Urban resource mining, which refers to all activities and processes involved in reclaiming valuable resource compounds, energy, and elements generated from urban catabolism, is, therefore, becoming increasingly popular. Cities and their consumption cycles should, therefore, be re-engineered according to this principle [3].

Urban mining has many advantages over primary mining (i.e., the transfer of materials from below-ground resources to above-ground stock), as materials are already in a place where they are most likely to be needed again and could thus be more easily reused. With fossil fuels becoming more expensive and environmentally unacceptable, secondary raw material recycling could become competitive compared to conventional mining, eliminating the need for long-range transportation and reducing the associated land degradation and water pollution. Urban mining in its various forms is fully adherent to the concept of the Circular Economy (CE), supported by current EU policy [4], with roots in the "3R" (Reduce, Reuse, and Recycle) framework.

Among the most critical natural resources, water is a key element of the global water–energy–food (WEF) nexus and is essential for life, environment, health, and the sustainability of society. Water is the universal solvent, carrying both harmful and valuable resources, including energy, nutrients, minerals, chemical products, etc. Its global use has grown exponentially with the human population and economic development since the industrial era. Estimates of aggregate water use show a 15-fold increase between 1800 and 1980 (13-fold for irrigation-related irretrievable water losses), compared to a global population increase by a factor of just 4 [5]. Global water withdrawals are small compared to continental areas' runoff (for example, in 2000, the former amounted to 4000–5000 km^3 against the latter's 40,000 km^3), but hydrologic analysis shows that only about one-third of global runoff is actually accessible for anthropic use [5]. Furthermore, even if a country has overall "statistically" sufficient resources, water stress may still occur in its drier regions or around large cities. Urbanization, in fact, increases the speed and intensity of local water exploitation.

Figure 1 illustrates the water stress estimates for Europe in 2030 [6]. It can be seen that contrary to common belief, water stress is not exclusive to Mediterranean regions. Serious challenges to the sustainability of the urban water cycle (UWC) may derive from climatic variability, which is expected to affect water availability due to increasing temperatures, shifting precipitation patterns and snow cover, rising sea levels, the modified frequency and intensity of flood/drought patterns, and pollution. Evidence is already pointing to such adverse impacts on water utilities, with studies suggesting that extreme weather events contribute to poor water quality, floods, and damage to infrastructure [7].

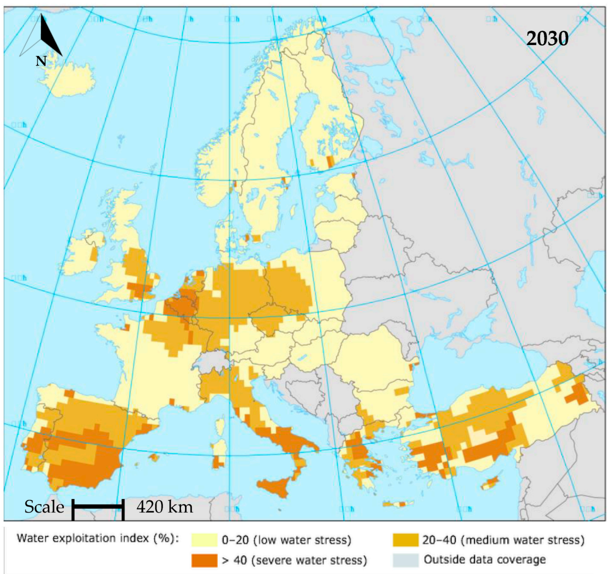

Figure 1. Water stress 2030 forecast for Europe [6].

Urbanization carries, as an additional, inevitable consequence, some degree of downstream water quality degradation. More pollutants are produced per capita in urban settings than in sparsely populated areas. Despite years of efforts and a global aim to reduce untreated discharges by 50% by 2030, only a small proportion of total wastewater discharges (about 20%) is collected and treated at present, ranging from over 70% in developed countries to less than 10% in low-income ones [8].

Urban wastewaters (UWW) often contain emerging pollutants such as pharmaceuticals (antibiotics, analgesics, narcotics, etc.), pesticides, heavy metals, pathogens, organics, PCBs, PFASs, etc., which are not always removed through conventional pollution-abatement technology [9]. Furthermore, urban watersheds lose the ability to retain water due to their increased imperviousness; thus, pollutants are easily mobilized from urban surfaces by high runoff [10]. Surface water quality may be negatively affected by as little as 5% imperviousness [11,12], affecting possible resource use and requiring long-range freshwater harvesting and transfer.

Water abstractions exceeding local availability may put socio-economic growth and urban sustainability at risk. Typically, water stress may be assumed when water availability drops below 1700 m^3/person/year; a level of 1000 m^3/person/year defines water scarcity conditions, whereas below 500 m^3/person/year, absolute scarcity ensues [13].

Water reuse is gaining momentum within the framework of the implementation of CE concepts [14]. The mining of used water from urban areas could significantly improve its sustainable supply and the recirculation of embedded resources, and it could substantially accelerate the transition of urban areas' use–consume–discharge patterns to circular ones. For this to occur, it is essential to pay close attention to unconventional water sources, such as urban runoff [15], municipal wastewater [16], and various industrial waste streams [17]. Studies and applications have demonstrated that recovering water, energy, and materials, including value-added minerals, rare elements, precious metals, and industrially valuable chemical products from wastewater and its by-products, such as biological sludge, is possible [18–21]. For this reason, wastewater treatment plants (WWTPs) are undergoing a paradigmatic change that foresees their transformation into water and resource recovery facilities (WRRFs) [22].

This paper reviews, using a holistic approach, the possibilities and technical opportunities applicable to UWW mining, and discusses emerging technologies and issues pertaining to resource recovery and reuse applications.

2. Wastewater or "Usedwater"?

Globally, approximately 380 billion m^3/year of municipal wastewater is generated, a figure expected to increase by 50% by 2050 [23]. In addition to the primary motivation of sanitation and the safe disposal of waste-rich streams, a second purpose has recently emerged in wastewater collection and treatment practices: to increase resource recovery and reuse in response to the aforementioned scarcity and circularity issues. The key to future UWC sustainability was summarized in the "one water" paradigm, implying that water should be available for multiple reuses, up to direct potable reuse. It is not unintentional that the United Nations [13] defined wastewater as an "untapped available water source"; hence, "usedwater" seems to be a more appropriate definition of sewage in WEF nexus-coherent terminology. Improved "usedwater" treatment and reuse, as called for in Sustainable Development Goal (SDG) Target 6.3 (Clean Water and Sanitation), would help the global transition to a Circular Economy. Figure 2 summarizes the current global situation of used-water reuse by application sectors [8].

2.1. Usedwater Generation and Composition

Wastewater/used water generated using current sewerage technology consists of over 99% water, the rest being solids, dissolved and particulate matter, microorganisms, nutrients, heavy metals, and micropollutants, with composition differing widely between locations. The current sanitation paradigm, in fact, has made little substantial progress regarding waste collection and transport modes since early history, with large amounts of water used as the universal carrier for small amounts of unwanted residuals and gravity as the main driving force. Conventional gravity sewers are mainstream practice, often exclusively associated with urban sanitation; however, as pointed out by Beder [24] over 30 years ago, the current technical paradigm is based on a consensus dating to early 20th century knowledge and technology, thereby constraining engineering education and practice and hindering the consideration of possible alternatives that could be better suited to present conditions and challenges.

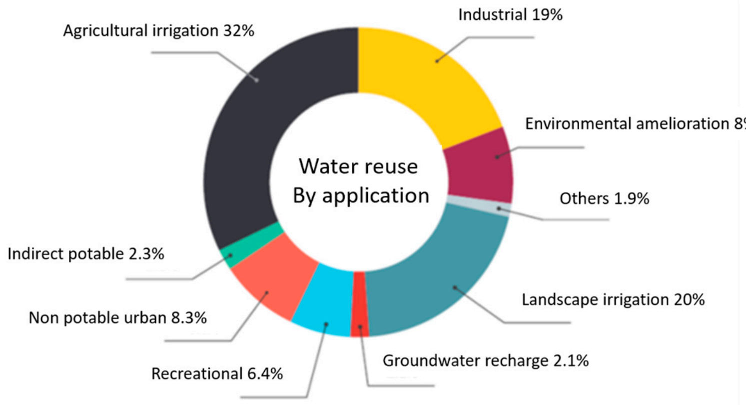

Figure 2. Global used-water reuse by application sector (from [8]). Direct potable reuse is included under the "Others" category.

The result is an extremely inefficient, water- and energy-thirsty sewerage infrastructure, with significant impacts on the environment and economy, both locally and globally. Overall, the UWC accounts for approximately 2% of total energy use in the US, generating over 45 million t/year of GHG emissions. At the municipal level, these systems are typically among the largest energy consumers, often accounting for 30–40% of local energy bills [25]. Arguments in favor of decentralized water and used-water management systems abound since they facilitate local water, energy, and nutrient recovery [26,27].

2.1.1. Centralized vs. Decentralized Used-Water Generation and Management

Decentralized UWW management consists of a variety of approaches for the collection, treatment, and disposal/reuse of used water from individual dwellings or clusters, entire communities, or industrial/institutional settings, where wastewater is managed as close as possible to its generation source. Decentralized systems can be managed either as autonomous, stand-alone facilities or integrated into existing centralized systems [26]. In either case, decentralization can be a sustainable alternative for communities considering the implementation of new sewerage systems or revamping existing ones. Among the competitive advantages of decentralization are the more efficient distribution of infrastructural investment costs by reducing pipe diameters and extensions and operational pumping requirements; the possibility to extend UWW treatment coverage on a need-to basis, leading to a more efficient reduction of related environmental impacts and risks to public health; the possibility for staged planning (lower WWTP design flow), better hydraulic operating conditions, more concentrated flows, and lower high-quality water demand [28].

A comparative study in India showed that decentralized systems, configured in large cluster subsystems, are cheaper to operate compared to centralized ones. They may, however, require higher initial capital costs and total footprint, even though they are distributed among several small sites rather than being located in a single large area [29]. Other studies have indicated that centralized, far-reaching sewer systems require higher initial investments, often constituting over 80% of the entire cost of the urban sewerage infrastructure [30].

The outcome of the ongoing debate about the costs/benefits of centralized versus decentralized systems largely depends on the adopted technologies, as an actual cost comparison between possible sewerage alternatives is strongly affected by specific technical solutions and local conditions. It has, however, been established beyond doubt that decentralized approaches are closer to the Circular Economy concept compared to centralized ones, locally bridging the gap between waste and reuse [26]. Process technology for water reuse should be chosen carefully and appropriately, considering that progress in monitoring [31] and information control, as well as the automation (ICA) of treatment facilities [32], have reached reliability levels that substantially improve the robustness, performance, and economy of decentralized solutions and can significantly contribute to a reduction in their initial investment and operating costs.

Source segregation (separation) at the household level has been defined as a "new sanitation" paradigm to re-establish the balance of carbon, nutrient, and water cycles and promote resource recovery [33]. By separating sources, specific used-water components (i.e., "black water" (BW) from toilets and kitchen sinks; "grey water" (GW) from showers, washbasins, and laundries; and "yellow water" (YW) separately collected urine) could be optimally directed to enhance resource and water recovery according to their specific composition [34]. Compared to GW, BW volumes are much smaller (up to approximately one-third of total household discharged volumes using current technology), but they are much higher in pollutant concentrations, as illustrated in Table 1.

Table 1. Characteristics of streams from domestic source separation.

	Black Water (BW)	Grey Water (GW)	Yellow Water (YW)
COD (mg/L)	5000–93,000	200–500	4000–11,000
N (mg/L)	1500–16,000	6–25	4000–11,000
P (mg/L)	500–3000	0.4–8	200–4000
Solids	High	Low	N/A
Pathogens	High	Low	High
Micropollutants	High	High	Low *

Note: * with the possible exception of pharmaceutical residues and their metabolites.

The fractions and characteristics of these streams, as well as those of "conventional" wastewater, vary significantly depending on the location and installed fixtures; therefore, the values indicated above are purely indicative.

Source separation could help overcome current, inefficient used-water management paradigms, under which large volumes of valuable drinking quality water are employed for the dilution and transport of waste materials, making it difficult to efficiently recover embedded resources due to present technological limitations. Studies comparing the feasibility of different types of source-separation approaches, considering different levels of decentralization, over conventional centralized approaches have been conducted using common economic assessment methodologies, factoring in the estimated recovery of resources. Simulations have proven that most source-separated alternatives can be competitive alternatives to conventional ones, despite some possible drawbacks [35].

Source-separation approaches are not exempt from operational drawbacks if inappropriate technologies are used. BW segregation, combined with the use of ultra-low-flush toilets, may induce the deposition of solids and the clogging of sub-horizontal domestic pipes and sewers designed under conventional paradigms, since approximately one-third of household water usage originates from toilet flushing. Furthermore, low-flush toilets could actually increase water consumption and BW dilution due to inefficient flushing and its repetition [36]. Segregated BW could be more efficiently collected by systems that are less infrastructure- and energy-intensive, such as vacuum sewers, as these only require about 0.5 L/flush [37] and would provide more concentrated WWTP influents, suitable for anaerobic treatment. With substantial immediate energy savings through aeration avoidance and improved resources, such as N and P, recovery possibilities would thus ensue [38–40]. Vacuum sewer systems, an alternative to conventional (gravity) sewerage systems, may offer other substantial advantages for decentralized, source-separated applications. In addition to lower-cost materials (typically polyvinyl chloride, PVC), smaller-diameter pipes, and shallower installation depths, they require less energy (by about 30%) for operation [37].

An alternative to fully decentralized solutions is so-called "sewer mining", a lesser-known option for introducing decentralized reuse possibilities into existing centralized systems. Sewer mining was originally pioneered in Australia to provide non-potable water for urban, industrial, and domestic uses [41]. It consists of tapping into existing centralized mains to divert raw sewage aliquots and treating them on the spot for specific local purposes. This avoids long-distance pumping to a centralized WWTP and pumps the effluents back to users. Despite many success stories, there are challenges in the adoption of this solution in Europe, including, but not limited to, public perception, regulatory frameworks, and financial constraints. A prototype sewer-mining system was tested in Athens (Greece) to assess the performance of available state-of-the-art solutions in view of its possible implementation in a European context [42].

2.2. Residual Energy and Materials in Used Water

Used water contains considerable amounts of embedded energy and recoverable materials. According to theoretical calculations, its chemical energy content is 3.86 kWh/kg of mineralized COD [43]. Shizas and Bagley [44] compared the actual energy consumption of the North Toronto WWTP (6.8 MWh/day) to the energy content estimate of its influent flow (62.8 MWh/day), highlighting a ratio greater than 9. The chemical energy content of used water could exceed 550 TWh/year globally (>2% of global electric energy consumption); in practice, however, this cannot be fully exploited with current technologies.

Although usually neglected in favor of the former, used water also contains large amounts of low-grade thermal energy (1.17 kWh/m^3 °C) as residuals from household (bathing, laundry, and cooking) or industrial (cooling and process) activities. The sewage temperature at discharge is usually around 30 °C; by the time it reaches a WWTP, it decreases by 10–15 °C, depending on the local climate, season, and distance traveled. With sewage flow rates in large cities more or less constant all year, this makes potentially exploitable thermal energy even more abundant than chemicals, especially near discharge points. Heat recovery by water-source heat pumps (WSHP) is already a feasible option for heating/cooling buildings, greenhouses, and other local uses [45].

Used water is a carrier of nutrients, particularly nitrogen (N) and phosphorus (P), which are key elements of the WEF nexus and essential for food and feed production. The EU's Agriculture Directorate has recently underlined the strategic role of fertilizer supply in food security following a 70% decline in ammonia production, linked to international political developments since 2022. At the same time, it recognized the role of nutrient recycling from waste streams to improve the sector's resilience. In March 2022, the European Parliament adopted a resolution recommending that alternative sources of nutrients be utilized to the fullest extent, particularly by increasing the use of organic fertilizer products obtained from sewage sludge [46].

An Inefficient Nutrient Management Paradigm

N is the second major nutrient element in fertilizers, normally fixed as ammonia by the conversion of natural gas (CH_4) through C-N substitution via the energy-intensive Haber–Bosch process [47], which requires 37–45 MJ/kg of atmospheric N fixed and consumes up to 2% of global annual energy production [48]. Domestic used water carries about 2×10^7 t NH_4/year, about 19% of the pre-2020 global industrial production [49]. Recovery of nitrogen in (N-NH_4^+) form, suitable for crop uptake, could substitute the current inefficient mainstream wastewater treatment paradigm, where ammonium is removed through sequential nitrification/denitrification and converted into gaseous N_2. In addition, nitrous oxide (N_2O), a known obligatory intermediate in heterotrophic denitrification and autotrophic nitrification (with a greenhouse effect 300 times greater than CO_2), is generated at an estimated 3.2% fraction of its global anthropogenic emissions [50].

Nitrification alone requires around 50% (between 42–45 MJ/kg N removed) of the energy demand of a conventionally designed treatment facility, whereas the more efficient Anammox process requires about half of that [51]. Therefore, the full cycle to first remove and then regenerate ammonium requires up to 90 MJ/kg N. The Haber–Bosch process also causes additional CO_2 emissions of about 1.6 t/t anhydrous NH_3 fertilizer produced since H_2 to fix ammonia from atmospheric N_2 is usually obtained from methane conversion.

Phosphorous is an irreplaceable component of fertilizers, derived from finite global mineral deposits (phosphate rock, PR). Human excreta carried by used water contain about 16% of the mineral phosphorus consumed worldwide. Currently, P is usually removed from wastewater for environmental protection, often in non-reusable form; recovering and recycling it could contribute to reducing humankind's dependence on mined PR and extending the lifespan of ascertained mineral reserves [52].

As discussed in the following sections, the recovery of ammonia [53,54] and phosphorus [55] is possible at different stages of the used-water processing cycle.

3. UWW Mining: Approaches and Technologies

Additional resources are generated within the UWW processing cycle itself: microbiological activity transforms the original organic compounds into biomass and fuels (e.g., biogas) and generates secondary recoverable resources embedded in biomass such as lipids, polyhydroxyalkanoates (PHAs), proteins, and other products [56]. Economic and sustainability considerations suggest that resources embedded in sludge (energy, nutrients, raw materials, and process by-products) should also be properly exploited to consolidate a virtuous wastewater-based Circular Economy cycle [57]. These options are discussed in the following sections.

The mining of water resources can start immediately after their first use, even before they are discharged into the sewer system. Stream segregation has been proposed as an approach to improving wastewater resource management by separating domestic wastewater streams at their origin to allow for effective source control and better exploitation of waste material cycles [33]. Past studies have shown that by combining wastewater streams of different qualities, the likelihood of achieving higher-quality water reuse decreases [58].

Domestic stream separation generates a low-dilution, organic-rich stream (BW), which can be further separated in BW proper, yellow water (YW), and a diluted GW stream. The typical ranges of these streams' characteristics were summarized in Table 1. BW (without urine) contains more than 50% of domestic wastes' organic matter and the highest number of pathogens. GW is the least polluted domestic water fraction and, after proper treatment, can be returned to almost any point in the water cycle [59]. Onsite GW treatment [60,61] could recover a resource suitable for local urban uses such as toilet flushing, building or industrial cooling and cleaning, street washing, and landscape irrigation, among others. Applicable approaches vary widely [62], ranging from nature-based (e.g., constructed wetlands) [63] to advanced systems such as compact biological processes, membrane bioreactors, and bioelectrochemical systems [64,65].

Low-quality water use typically accounts for approximately two-thirds of household consumption, for which nature-based technologies may be appropriate due to their low cost, low energy use, and limited technical and operational requirements. However, they are land-intensive and cannot be easily implemented in urbanized areas. To overcome this drawback, "vertical" solutions (i.e., green walls, living walls, and green facades) that can be applied with similar functions in high-density urban areas have recently been developed [66].

YW is the richest stream in terms of nutrient content; therefore, it can be exploited for the facile recovery of fertilizers [67,68]. On average, a person excretes about 550 L urine/year, containing approximately 0.4 kg P, 4 kg N, and 0.9 kg K. Throughout history, the direct application of urine as a fertilizer has been common practice [69], with the potential risk of contamination from pathogens. Nowadays, concerns also include emerging pollutants (pharmaceuticals, hormone residue, and micropollutants) [70]. Methods for the safe recovery of nutrients from separated YW have also been developed [68].

Wastewater segregation enables water reuse according to the desired quality and better resource recovery in industrial settings. Often, industries discharge partially treated effluents to municipal sewers rather than recovering resources onsite due to specific contaminant issues. Streams contaminated with poorly treatable or resilient substances may prevent water internal reuse or energy recovery, but their segregation and ad hoc treatment could enhance process water management, [71].

The following sections address specific approaches and technologies for water reuse and resource recovery.

3.1. Water Reuse Opportunities

Historically, the most prevalent application of treated effluent reuse has been in irrigation [72]. It has been estimated that today, 12% of global freshwater withdrawals for agricultural irrigation could be readily and safely replaced with WWTPs' effluents that might, in many circumstances, actually be among the best sources for this purpose [13]. Effluents could also represent a free source of nutrients in combined irrigation and fertilization (fertigation) of urban green or agricultural crops. It has been determined that lawns and turfgrass account for the large water demands in some US urban areas, up to 70% of public water consumption. Fertigation with treated effluents could avoid excessive nutrient leaching from chemical fertilizers' application, supplying N and P in a form suitable for rapid uptake by root systems, thereby reducing groundwater contamination [73]. Tailoring effluents to the desired nutrient composition for the receiving crops could enhance the economic sustainability of fertigation reuse [18].

The reuse of water resources requires more intense processing compared to raw water sources, as natural attenuation barriers are removed. In water-stressed areas, the implementation of fit-for-purpose (FfP) used-water treatment could provide a local supply for almost any required reuse, from processes to drinking water, as proven by long-running schemes implemented in Windhoek (Namibia), Singapore, and several other locations worldwide [74]. FfP is implemented through multiple barrier-treatment (MBT) schemes, which treat raw or used water to specific quality standards through subsequent increasingly selective contaminant-removing steps.

In areas of high water stress, dual distribution systems for "drinking water substitution" have been designed to separate high-quality water for drinking from lower-quality reclaimed water targeted for other purposes. Centralized reclaimed water distribution maintains the supply of potable water from scarce sources through existing networks, offering an alternative, controlled supply of treated used water aimed at less demanding uses. Dual systems, known as "purple networks" in the US, allocate additional water resources under supply stress conditions. While not reducing the delivery cost of potable water, they may reduce the overall burden of water supply at the community level: even compounding the investment needed for infrastructure replication, economies may occur when raw water sources have insufficient capacity, poor initial quality, or are remotely located, making delivery of locally reclaimed water more efficient [75].

Although technically feasible in most circumstances, the economics of water reuse strongly depend on local conditions. On average, the cost of supply from traditional water sources is increasing, and at the same time, the differential cost of providing reusable sources is narrowing. The average cost of conventional WWTP effluents is between 0.15 and 0.30 US$/m^3, and the production of reclaimed water to satisfy most non-potable reuses costs 0.25–0.50 USD/m^3 [76]. Long-term (48 years) operation of the Windhoek facility in Namibia required an average cost of sewage reclaimed for direct potable reuse of 0.72 EUR/m^3 [77].

The cost of reclaimed resources must be compared with the price of local freshwater supplies. In the western US, for example, this ranges from 0.02 to 1.18 US$/m^3, with an average value of 0.64 US$/m^3 [78]. Given the indispensable and highly strategic nature of water, the pressures of increasing scarcity and growing demand will make the additional cost of producing reusable quality water less relevant compared to other factors. Figure 3 summarizes the possible options for urban used-water mining.

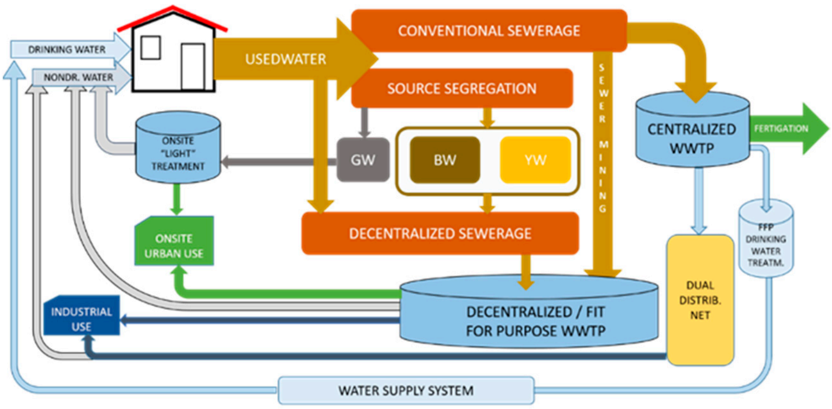

Figure 3. Possible options for urban used-water mining.

Local measures aimed at the reuse of relatively clean rainwater from urban impervious areas (roofs, parking areas) can result in significant environmental and financial advantages to property owners and communities at large, as well as increased resilience to stressed supplies and disposal networks. In segregated collection systems, stormwater could be collected separately from other flows and sent to temporary storage for reuse, with or without partial treatment, or sent for infiltration [79,80]. Low-Impact Development (LID), as well as "Sponge City" approaches, provide cost-effective and resilient solutions that integrate land development, stormwater management, and water quality sustainability in urban water bodies. Managed aquifer recharge (MAR), designed to infiltrate urban runoff and treated municipal effluents into aquifers, is also considered an appropriate water reuse technique for potable supply augmentation and for countering saline intrusion in coastal areas. MAR is becoming popular due to its low implementation costs, low evaporation losses, and the possibility of infiltration of large flows from different sources [79].

Table 2 summarizes the pros and cons of the possible reuses for treated water. The greatest challenges in the water reuse domain concern public acceptance, criteria establishment, and economic and energy management aspects rather than pure technological ones. An appropriate techno-economical approach cannot ignore essential public communication and stakeholder involvement.

3.2. UWW Energy-Mining Technologies

3.2.1. Thermal Energy

A great deal of thermal energy is contained in used water. Upon discharge, it may even induce detrimental ecological effects by modifying receiving streams' thermal profiles. Harvesting this energy through heat pump technology is an established and widely used practice. It has been estimated that heat recovery from large sewage collectors could meet between 7 and 18% of the domestic heat demand in an urban catchment of 80,000 P.E. [81]. A detailed example of urban mains' heat exploitation for the heating and cooling of a new commercial building was reported by Cecconet et al. [19]. WWTP's effluent-recovered heat could be a renewable heat source for low-intensity uses such as nearby produce or solar sludge-drying greenhouses [82,83] and anaerobic digester heating [84]. High-grade heat from biogas combustion could then be directed to other uses beyond a treatment facility's premises. However, technical limitations exist, including corrosion and circuit fouling in sewage heat exchanger applications, as well as the feasible distance, limited to a few (3–5) km, for district heating [85].

Alternative heat-recovery possibilities consist of direct harvesting at the point of discharge of large-scale users, such as schools, military barracks, hospitals, sports facilities, and swimming pools, upstream of sewer connections, where segregated, relatively "clean" GW streams (e.g., showers and sinks) can be exploited [86]. The efficient utilization of thermal energy in UWW depends on the appropriate design, selection, and maintenance of heat exchangers since they operate with dirty water, fouling, blocking, and corrosion problems may arise [87].

Table 2. Summary of the pros and cons of possible treated water reuses.

Type of Reuse	Pros	Cons	Comments	Ref.
Irrigation	Treated water reused for irrigation can reduce freshwater consumption. Irrigation with treated effluents can contribute N and P, necessary for crops.	Possibility of crop contamination by various contaminants, including emerging substances and pathogens.	Fertigation contributes water and nutrients to crops. Soil and crop types should be compatible with effluent characteristics. Stakeholders' (farmers, consumers) perception and acceptance of this practice are essential.	[13,18,72,73]
Urban and industrial uses	Treated effluents are suitable for several types of non-potable reuse, allowing the use of high-quality freshwater for potable use.	Infrastructure is usually absent for dual water distribution.	Dual-distribution networks present in water-scarce areas. Fit-for-purpose treatment can provide reused water at competitive costs. Industrial, non-contact uses are usually well accepted.	[8,14,17,27,74–76,80]
Domestic uses	Onsite treated used water could provide about 2/3 of current domestic uses that do not require drinking water quality.	Dual piping in households required.	Acceptance of domestic reuse practices depends on water availability situations (scarcity conditions and cost of drinking water). Proper public communication is highly important.	[34,59–61,63,65,66]
Aquifer recharge and Indirect potable reuse	Replenishment of aquifers increases future availability of water and supply resilience. Low-cost practice. Impurities are naturally filtered by subsoil formations.	Hydrogeological conditions should be verified to avoid preferential contaminant transport. Excessive recharge may affect underground infrastructure.	Urbanization reduces aquifer recharge. MAR and similar approaches can restore hydrological groundwater balance. Aquifer recharge is part of many indirect potable reuse schemes. IPR schemes are often accepted as they "blend" with the natural water cycle.	[8,13–16,74,79,80]
Direct Potable reuse	Can provide drinking water to areas with critical water scarcity. This practice is a consolidated technology with many application examples globally.	Treatment can be energy-intensive. Citizens' acceptance may initially be low.	Treatment technology can provide drinking water directly from WWTP effluents. DPR acceptance increases with water shortage and can be boosted by proper communication strategies.	[13,14,74,77,78]

Importantly, it should also be remembered that biochemical reactions are temperature-dependent. Excessive heat extraction from sewage prior to biological treatment may decrease process rates and treatment efficiency [88].

Current technology does not allow direct electricity generation from low-grade heat; however, thermoelectric generators (TEGs) could soon be applied in this field. By virtue of the Seebeck Effect, TEGs can directly transform thermal energy into electricity in the presence of hot sources and cold sinks [89]. This technology has been successfully applied for the exploitation of large heat gradients, but in wastewater applications, it is constrained by the low temperature of the hot source (T normally $\leq$ 30 °C) and the low ΔT between the heat source and sink (usually, ambient air). Large inflows (e.g., 1000s of m^3/day) in big facilities could, however, compensate for these limitations. Lab-scale tests showed an energy recovery of 4.5×10^{-4} kWh/m^3 under limited (2.8 °C) temperature gradients. With the introduction of new materials, TEG generation from used-water heat could soon become efficiently exploitable [90].

3.2.2. Chemical Energy

Traditionally, used water's embedded chemical energy, i.e., the energy contained in organic matter, is recovered through anaerobic fermentation (digestion) of biological sludge. Anaerobic sludge digestion (ASD) is perhaps the most common processing method for WWTPs' organic residuals since it stabilizes and converts volatile compounds into biogas (60–70% methane) at a yield of $\approx$1 m^3 biogas/kg of degraded organics. Biogas is an important aspect of European and global renewable energy strategies, together with liquid biofuels, since it provides storable energy [91]. Using prevalent technologies, however, only up to 30% of sludge's organic matter is mineralized, and as much as 70% remains unexploited after treatment [92]. Several optimization strategies can increase specific ASD methane yields. These include cell disruption for hydrolysis enhancement, methanation efficiency improvements through direct interspecies electron transfer (DIET) augmentation, and a combination of ASD and bioelectrochemical systems [93,94].

Paradigmatic changes in used-water management could improve the sector's sustainability and the recovery of residual resources [95]. Due to the high dilution inherent in mainstream sewerage design, aerobic processes have established themselves as an efficient way to process these flows; however, aeration alone can absorb up to 50–70% of the overall energy requirements of conventional WWTPs [51]. Processes operating with electron acceptors other than oxygen (i.e., anaerobic) could dispose of aeration requirements altogether, with substantial immediate energy savings, in addition to energy recovery. Initial limitations related to low sewage concentrations and slower anaerobic kinetics that hindered the generalized adoption of fermentation for sewage treatment were removed by the breakthrough development of upflow anaerobic sludge blanket (UASB) reactor technology.

UASB reactors are based on anaerobic biomass developed in granular form, kept in dynamic suspension within a thick sludge blanket [96]. Since the operating temperature has a primary impact on process kinetics, UASBs were initially applied mostly in tropical countries; however, due to low construction and operating costs, UASB-based sanitation has been adapted to cold and moderate climatic settings upon the proper modification of the operating parameters. At an operating temperature of 25 °C, well below the optimal anaerobic mesophilic range, COD conversion to CH_4 can reach 25–30% [97,98]. The combination of UASB and ASD can further improve process performance at low temperatures [99].

Improvements in UASB technology include high-rate expanded granular sludge beds (EGSBs), static granular bed reactors (SGBRs), internal circulation (IC) and internal circulation experience (ICX) reactors [100]. These optimize the capacity, operational stability, and methane recovery. Compared to traditional UASBs, high-rate reactors increase the organic loading capacity by three times or more. In addition, UASB technology is applicable in decentralized settings due to its low initial costs and operational simplicity. Source-segregated BW would be an ideal UASB influent due to its high organic and solid content [101].

In the renewable fuel realm, H_2 is a clean, carbon-free fossil fuel substitute, which is expected to play a main role in future energy scenarios since it contains more energy (122 kJ/g) on a mass basis than CH_4. Anaerobic fermentation generates hydrogen as an intermediate product of acidogenesis via acetate, butyrate, and caproate metabolic pathways [102]. However, such "biohydrogen" (bio-H_2) production occurs at low rates [103]. Operating conditions play a major role in bio-H_2 yield: at pH 5.0–5.5, fermentation intermediates approach optimal ratios, stimulating the microbial metabolism responsible for its synthesis. Several studies on bio-H_2 generation from food industry wastewater exist; however, few concern domestic wastewater. Fernandes et al. [104] reported H_2 yields of 200 mL/g COD from domestic sewage. Paudel et al. [105] observed yields of 1.014 mol H_2/mol of glucose using synthetic domestic wastewater at a loading rate of 3 g COD/L-d. Mu and Yu [106] demonstrated continuous bio-H_2 generation from sucrose-rich synthetic wastewater at substrate concentrations in the range of 5.33–28.07 g COD/L and HRTs of 3–30 hrs. Food industry wastewater is a suitable substrate for bio-H_2 production since it usually contains easily hydrolyzable carbohydrates and sufficient nutrients and requires mild pretreatment. Economic analysis of UASB reactors fed with biscuit wastewater showed that amounts of 414 mL H_2/g COD were removed, with a calculated payback period of 5.7 years [107]. According to recent research, bio-H_2 generation from industry wastewater can be economically and environmentally sustainable and efficiently applicable in multiple contexts [108].

Hydrogen can also be produced from wastewater through electrohydrogenesis in microbial electrolytic cells (MECs) [109]. MECs and microbial fuel cells (MFCs) are variants of bioelectrochemical (BE) technology, which is based on the potential of electro-active bacteria (EABs) catalysis to directly convert chemical energy within organic substrates into electrical energy [110]. In MFCs, EABs catalyze oxidation and reduction reactions, each occurring in a separate compartment (anode and cathode), externally connected by electric circuitry [111]. MFCs can produce energy from complex domestic and industrial wastewater. Although they show a high capacity in terms of pollutant removal, they are still characterized by several drawbacks, including limited electric production, which effectively hinders their practical appeal [110]. On the other hand, MECs can trigger otherwise unspontaneous chemical reactions through the application of external potential, making it possible to conveniently generate hydrogen from used water through the hydrogen–evolution reaction (HER):

$$2H^+ + 2e^- \rightarrow H_2 \quad (1)$$

Since EABs produce a voltage of approximately −0.3 V from organics' degradation, an additional 0.11 V would theoretically be required to induce the reaction. In practice, inputs of 0.25–0.8 V are required to trigger the HER due to MECs' internal losses [112]. This equates to an energy advantage of up to 86% compared to pure water electrolysis, which requires 1.8 V to split H_2O molecules.

Therefore, used-water bio-electrolysis could be implemented with significantly lower energy to produce bio-H_2 while serving a needed purpose, i.e., used-water treatment. This technology is still hindered by internal efficiency issues common to all bioelectrochemical systems, which generally still show low technology readiness (TRL $\leq$ 4) [113].

A part of the chemical energy component in used water, NH_3, represents roughly 43% of the embedded energy carried by human excreta [114] and could play an important role in future "usedwater-to-energy" strategies. In the energy sector, NH_3 is viewed as a next-generation carbon-free fuel. It contains 22.5 kJ/g (11.5 MJ/L), about half of the typical hydrocarbon fuels, and about 20% of H_2 by weight; however, its volumetric energy density is higher than the latter (8.49 MJ/L in liquid and 4.5 MJ/L in compressed form) [115]. The energy associated with used-water NH_3 equals about 0.1 TWh/year in a typical sewage flow of 10^6 m^3/day, approximately 10 TWh/year for the total sewage discharges in the EU [116].

As a fuel in thermal engines, NH_3 does not release CO_2 but generates NO_x, which can be abated with postprocessing. While H_2 remains the cleanest energy vector, its storage remains a big challenge. NH_3 is more economical to produce, store, and deliver compared to compressed and/or cryogenic hydrogen. The industrial infrastructure for NH_3 distribution already exists, whereas that of H_2 still needs widespread implementation. The economic and carbon emission aspects of ammonia recovery and its use as an energy source were recently discussed by Davey et al. [117]. Technologies allowing mainstream ammonium recovery from wastewater are available, and an 'ammonia-to-energy' approach could create a triple carbon benefit for the water sector's transition toward energy neutrality and "net zero" goals.

3.2.3. Potential Energy

Flowing water carries kinetic and potential energy. Small-jump, micro-hydropower installations, with minimal construction, diversion, and storage requirements, have gained popularity in irrigation and drainage canals, allowing electricity supplies in remote locations. Recent studies have indicated that the specific power generation costs of these small-scale hydrosystems are comparable to those of large-scale facilities [118]. Tapping sewer flows for power generation could also offer an efficient energy-harvesting solution. Hydropower generation from sewage is affected by several issues since used water contains solids (toilet paper, tissues, hair, Q-tips, organics, food/vegetable waste, etc.) which may clog microturbines. "Pico-hydraulic" turbines with improved performance for the passage of foreign matter have been studied and developed for this specific purpose [119]. Additionally, grey water discharges could be a potentially ideal source for hydropower generation in high-rise buildings (HRB), with internal source segregation, due to their low solid load. In cities with large numbers of HRBs (i.e., >13 floors), distributed power generation could be substantial. It has been estimated that in Hong Kong (≈8000 HRBs), about 220 MWh/day (80 GWh/year) could be generated from GW hydropower (≈2% of the city's overall consumption). In Mumbai (≈2300 HRBs), generation could amount to 64 MWh or 9% of the city's total power consumption. It was estimated that in a 20-story, 2000-resident HRB fitted with a dual BW/GW segregated system, the investment for GW hydropower generation would have a break-even period of about 7.7 years [120], similar to the one required by modern solar photovoltaic systems. Figure 4 summarizes the possible options for energy mining from UWW.

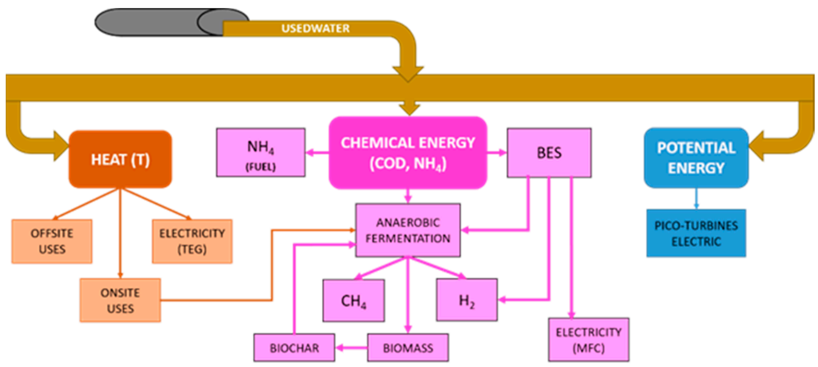

Figure 4. Components and options for used-water energy mining.

Table 3 summarizes the pros and cons of possible used-water energy-mining approaches. Their actual applicability should be considered after a detailed case-by-case evaluation of all the contributing factors based on LCA or techno-economic analysis, as well as environmental and social considerations.

3.3. UWW Nutrient Mining

Used water contains large amounts of nutrients. Human metabolism generates 10–12 g N/person per day and 2–4 g P/person per day, resulting in concentrations of 20–85 mg N/L and 4–15 mg P/L in "traditional" urban used water. As seen in Table 1, source segregation could dramatically increase these concentrations to up to 11,000–16,000 mg/L N and 3000–4000 mg/L P in separated yellow- and black-water streams. According to current WWTP design paradigms, nutrient removal, achievable through conventional aerobic processes, ranges from 6 to 20 mg N/L and 1 to 4 mg P/L due to biomass stoichiometry (metabolic uptake). Most often, this is not sufficient to fulfill applicable discharge limits, and additional removal is needed. This adds a significant energy and economic burden to treatment operations. The traditional removal of N and P is not targeted at their recovery [121], which, if implemented, could make UWW treatment more sustainable, reduce its costs, provide supplementary fertilizers to the WEF nexus, and generate value-added by-products for a used water-based CE. Recovery can be achieved from the liquid (anaerobic digestion supernatant, reject water, and sludge dewatering filtrate) or sludge phase (excess biosolids) [122,123].

3.3.1. Ammonia Recovery

Due to the usually low concentration of ammonia in sewage, the inherent challenge consists of retrieving ammonium in economically sustainable ways. Three main recovery processes are applied today: stripping (coupled with adsorption); membrane concentration (sometimes coupled with hydrothermal liquefaction); and struvite precipitation. The latter, however, contains only 6% of ammonium, and in practice, it is mainly effective in recovering phosphates. Recovery efficiency is higher for streams with a high (>2 g/L) NH_4-N concentration (digestate, source-separated urine, and industrial wastewater) [124].

Gas stripping, based on its conversion to a volatile form at a high temperature and/or pH, is widely used for ammonia recovery. The stripping mechanism can be described as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{2}$$

where the reaction's equilibrium is shifted toward the right side by raising the process's pH with alkaline reagents ("Alkali Stripping") and increasing its temperature. A turbulent air stream is insufflated in the reaction vessel, and the stripped ammonia is subsequently recovered in the form of ammonium salts ($(NH_4)_2SO_4$, (NH_4NO_3), or (NH_4Cl)) or as condensate. Highly acidic solutions require significant pH buffering, while an increased temperature and air supply imply energy consumption, making highly performant alkali stripping costly.

Vacuum thermal stripping (VTS) has emerged as an alternative to the former. With a vacuum maintained inside the reactor, stripping is achieved by boiling the solution at a lower temperature [125]. Improved stripping with a low energy input can also occur by exploiting molecular kinetic energy. Low-intensity electric fields (≈15 V/cm at 50 MHz) will cause polar ammonia and water molecules to align and increase their rotational and translational motion, accelerating stripping at a low temperature and airflow. This process saves both chemicals and energy, showing enhanced removal efficiency up to 94.3% at 22 °C, compared to 90.6% for conventional stripping at 36.8 °C [126].

Membrane concentration through forward osmosis (FO), reverse osmosis (RO), membrane distillation (MD), and electrodialysis (ED) can generate ammonia-enriched retentates, by separating undesired substances (e.g., heavy metals and pathogens). In FO, the osmotic pressure forces water to move from the feed to the draw side, with ammonium concentrating upstream [127]; however, the draw solute is gradually diluted, decreasing the osmotic pressure gradient, which negatively affects the concentration on the feed side. RO, on the other hand, works against the osmotic pressure between the feed and draw solutions and requires more energy than FO [128]. In MD, ammonium is volatilized in the heated feed solution and transferred across a microporous hydrophobic membrane as an effect of the temperature gradient [129].

Several studies have investigated ammonium removal through electrodialysis. In this case, ions driven by the electrical current move across selectively permeable membranes. Ammonium is retained in a cathodic chamber by a cation-exchange membrane (CEM). The higher the current, the higher the retained ammonium concentration and the energy consumption [130]. Ammonia recovery through electrodialysis was shown to be 50% more energy-efficient compared to other technologies, including stripping [131]. Selective electrodialysis (selectrodialysis, SED) combines ED with monovalent anion-exchange membranes (MVAs) and concentrates both phosphorus and ammonium by separating mono- and di-valent ions. MVA and CEM membranes recover phosphate and ammonia at the same concentrations [132,133]. Multi-compartment SED can concentrate phosphorus and ammonia separately, generating two separate, high-purity recovered streams free of heavy metals and pathogens, with a larger market potential [134]. In order to upgrade SED technology for large-scale applications, however, further investigations into the long-term performance and development of cost-effective membranes are needed [132].

In BESs, N recovery is mainly in the form of ammonia. MFCs can achieve 100% ammonia recovery with a positive energy balance and efficiency improvement over stripping. The high pH of catholytes driving ammonium conversion to ammonia gas can affect MFC ammonia [131]. Integrated BES/photobioreactor technology can recover nitrogen by concentrating it in algal biomass, which can be further converted into biochar [134] or processed by a biorefinery into various fuels and products [135].

Zeolite adsorption has been demonstrated as a simple technology to achieve excellent ammonium removal and recovery (>98%), even at initial concentrations below 1 mg NH_4-N/L. In full-scale applications, however, it suffers from fouling and a high chemical (NaCl) demand for regeneration. New polymer-based engineered adsorbents exhibit improved mechanisms and cost-effective regeneration without heavy chemical dosing [136]. Traditional zeolites show an adsorption capacity in the range of 11–54 mg NH_4-N/g, whereas new C-based adsorbents (e.g., Carboxymethyl chitosan-gpoly(acrylic acid)/palygorskite) can reach over four times that capacity [114].

3.3.2. Phosphorous Recovery

Globally, P recovery is a critical emerging issue since PR reserves are limited and concentrated in a few countries far away from the main users [52]. It has been estimated that 15–20% of global PR demand could be substituted with P recovered from municipal wastewater close to its utilization sites [137].

Struvite ($MgNH_4PO_4{\cdot}6H_2O$ or MAP, magnesium ammonium phosphate hexahydrate) is a slow-release source of P, NH_4^+, and Mg_2^+ that is suitable for agricultural fertilization. Spontaneous struvite precipitation represents a known, serious scaling problem in WWTPs since wastewater can spontaneously generate approximately 10 g of struvite/m^3 treated [138]. In a medium-sized WWTP (≈100,000 m^3/day capacity), struvite scaling remediation costs can exceed 100,000 USD/year [139]. Controlled struvite crystallization, in addition to solving this issue, can be a profitable alternative to chemical P removal due to savings in chemical additives and subsequent chemical sludge disposal.

MAP production from sewage varies from 0.89 to 13.7 kg/kg of influent P. Some of the currently adopted technologies are associated with shortcomings such as high operational costs (energy and chemicals) and large footprints [140]. Magnesium addition is usually required and could contribute to up to 75% of struvite's production costs. Other useful Mg-less P forms can be efficiently precipitated, including hydroxyapatite ($Ca_5(PO_4)_3OH$, or HAP), calcium phosphate ($Ca_3(PO_4)_2$, or CaP), and others [141]. The cost of recovery is influenced by the orthophosphate concentration in the solution. Estimates indicate that the cost of struvite production would drop from ≈2800 to 520 EUR/t of MAP if influent PO_4^{3-} concentrations were increased from 50 to 800 mg/L [142]. Incidentally, this could be another strong argument in favor of the implementation of used-water source segregation and low-dilution collection strategies, as discussed in Section 2.1.1.

ASD supernatant is a highly suitable stream for struvite recovery due to its concentrated P and NH_3 contents. P recovery can also occur from the aerobic liquid phase operated during the Enhanced Biological Phosphorus Removal (EBPR) process, which can temporarily concentrate phosphates into biological solids [143]. Struvite recovery technologies are commercially used in various proprietary processes such as OSTARA, PHOSPAQ, ANPHOS, MULTIFORM, PHOSNIX, PHOSTRIP, etc. They can accomplish 80% or more of P-recovery efficiencies, with variable normalized production rates (kg struvite/kg of P influent), and specific costs ranging between 3 and 10 USD/kg of P recovered [140,141]. Struvite precipitation could be improved by combining SED with a precipitation reactor. In one such study, phosphorus and ammonia were recovered in ranges of 86–94% and 96–100%, respectively [129].

Table 3. Summary of the pros and cons of possible used-water energy-mining approaches.

Technology	Pros	Cons	Comments	Ref.
Heat pumps	Mature technology. High, steady sewage flows allow consistent recovery. Can be applied in many situations, including segregated GW streams.	Issues with exchangers' corrosion and fouling can develop in raw sewage applications. Low-grade heat transfer is most efficient in proximity uses.	Applicable both in large sewer networks and WWTPs. Excessive heat extraction may impair biological treatment efficiency. High potential in densely populated areas.	[19,81–88]
Thermoelectric generators (TEGs)	Direct electricity generation from fluid-embedded heat possible through the Seebeck effect.	Most efficient at high thermal gradients (low in UWW applications). Expensive technology.	Not mature in the water sector. Efforts to exploit low-gradient, high-flow conditions are ongoing. Present potential is low.	[89,90]
Anaerobic Digestion (fermentation)	Mature, most common technology for energy recovery from organic wastes. UASB version applicable to diluted UWW. Energy recovered as biogas or, with process modification, hydrogen.	Lower efficiency at low temperatures. Biogas contains up to 40% CO_2 and must be upgraded for general use as a natural gas substitute.	Can be used as the first step in complex sludge biorefinery schemes, with sequential materials recovery. Could completely replace aerobic biodegradation processes in the presence of high concentrations of sewage. Very high potential for improvement.	[51,91–108]
Bioelectrochemical systems	Direct electricity generation from UWW organics. Possible to achieve hydrogen production at lower costs than pure water electrolysis.	Expensive technology, not yet applied on a large scale. Limited electrical recovery compared to theoretical potential.	TRL still low. More research is needed for successful full-scale applications. Presently, it has low potential.	[109–113,137]
Ammonia-fuel recovery	NH_4 can be used as C-free fuel, with modification of existing engine technology. More economical to produce than H_2, at a higher volumetric energy density.	High combustion temperature needed. Could generate NOx emissions if not properly controlled.	Ammonia-to-energy approach possible on a large scale and in heavy transport vehicles/ships. Good medium-term potential.	[114–117,124–132]
Picoturbine hydropower	Electricity generation from liquid streams' potential energy in high-rise buildings.	Picoturbines can be affected by solids and impurities in the flow. Needs buildings' internal plumbing adaptation.	New picoturbine types developed to allow use with BW. Application to less contaminated GW could be an efficient solution. Good potential in highly dense, vertically developed urban areas.	[119,120]

Membrane processes are used to recover P by pre-concentration via RO, FO, microfiltration (MF), or nanofiltration (NF), and subsequent precipitation as MAP or HAP. The integration of FO and biological processes is referred to as an osmotic membrane bioreactor (OMBR), where P is predominantly precipitated as amorphous CAP, with recovery higher than 95% [144]. The process, however, is adversely impacted by salinity that can foul membrane media and deteriorate permeate quality [145]. Combined hybrid FO-MD (membrane distillation) systems were shown to be effective in concentrating P from high-load sidestreams, achieving 90% phosphate recovery [146]. NF membranes that can effectively reject a variety of heavy metal ions are considered promising for P recycling. Newly developed NF media were shown to be effective in recovering up to 90% of influent P and the integration of FO-NF achieved up to 99% phosphate recovery [147].

Finally, P recovery is also possible from incinerated excess sewage sludge ashes (ISSA) via chemical extraction. In this case, care must be taken to avoid the possibility of heavy metal leaching (Zn, Cu, Pb, As), which can limit recovered P use in fertilizer production [123].

3.3.3. Other Nutrient Recovery Approaches

Algal-based sewage treatment has become popular in recent times due to its single-step removal of carbon and nutrients. Microalgae, including eukaryotic algae and cyanobacteria, have emerged as an environmentally friendly and sustainable alternative to energy-intensive and conventional biological treatment processes in use today. When incorporated into biological used-water treatment, they generate O_2 through photosynthesis, helping heterotrophic bacteria aerobically degrade organic matter and perform CO_2 bio-fixation [148]. As a renewable biomass source, excess microalgae can be fermented for biogas production after harvesting [149], and the embedded nutrients can be recovered through subsequent downstream processing. Various reactor types can be used for microalgal wastewater treatment [150] Harvesting via solid–liquid separation steps and subsequent drying should be carried out [151]. The latter step may be energy-intensive. Figure 5 summarizes the possible options for nutrient mining from used water.

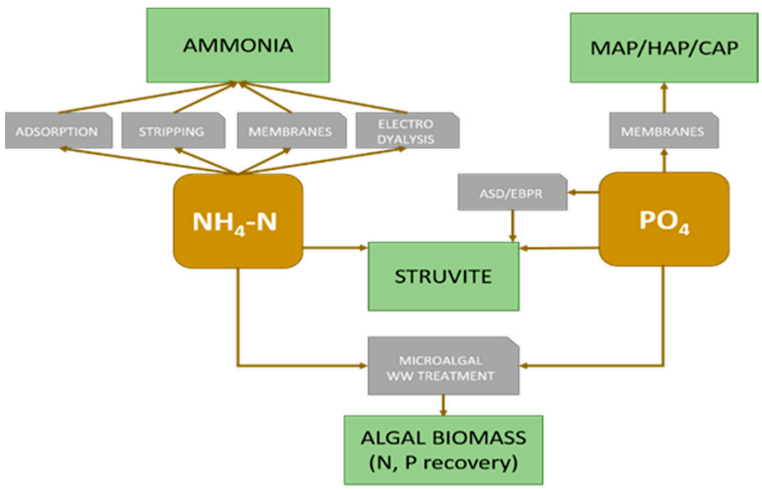

Figure 5. Pathways for used-water nutrient mining.

Table 4 summarizes the available opportunities for nutrient recovery from used water.

3.4. UWW Chemicals and Materials Mining

In addition to energy and nutrients, wastewater contains many other valuable components. Several technologies developed to pursue resource recovery challenges must account for the diluted nature of waste streams. Biological processes concentrate solute and suspended chemicals into biomass through uptake or adsorption, but the preliminary recovery of suspended materials could be attempted.

3.4.1. Cellulose, a Used Water-Embedded Resource

As a common industrial raw material, cellulose is a valuable resource present in used water, which originates mostly from toilet paper, although small amounts could also derive from kitchen waste, especially where sink comminutors are used, or street runoff in areas where combined sewers are present. In North America and Western Europe, the cellulose content in used water has been estimated to be about 157–178 mg SS/L, or 40–50% of total suspended solids (TSS). In Latin America, Africa, and Asia, the concentrations are generally lower [152]. Cellulose is one of the most abundant polysaccharides on Earth; however, notwithstanding its organic origin, it is poorly biodegradable. In typical AS systems, only about 30% of cellulose COD is degraded, and the rest accumulates in the excess sludge. Preliminary recovery would significantly reduce the organic load and aeration demand [153]. The aerobic degradation efficiency of cellulose increases significantly with the process temperature (values of 6.7% below 13 °C and 87% at 23 °C have been reported) and SRT (increasing from 13% at 5 days to 83% at 40 days) [154]. Sludge-accumulated cellulose represents 50–60% of its residual COD load, undergoing further degradation in ASD [154].

Table 4. Summary of possible nutrient recovery options from used water.

Element/ Technology	Pros	Cons	Comments	Ref.
Ammonia/ stripping	Easy implementation. Various process forms exist with different recovery yields.	pH buffering and high temperatures may be required.	Vacuum thermal stripping reduces the required process temperature.	[124–126]
Ammonia/ adsorption	Zeolite adsorption easy to implement. High recovery (>98%) even at low initial concentrations.	High chemical demand for regeneration. Filter suffers from fouling problems.	New polymer-based adsorbents may enhance recovery and cost-effectiveness.	[114,136]
Ammonia/ concentration	Membrane-based processes can recover pure ammonia (no metal, pathogen contamination).	Relatively energy intensive.	Forward and reverse osmosis, membrane distillation, and electrodialysis, alone or in combination, available at intermediate TRLs.	[127–134]
Ammonia/ others	Bioelectrochemical systems can achieve 100% ammonia recovery with a positive energy balance.	Technology more complex and costly than stripping/ adsorption. Low TRL (pilot scale only).	Material issues hinder BESs' industrial development. Promising technology for the future.	[131,133]
Phosphorous/ precipitation	P precipitation occurs naturally in WWTPs. Controlled precipitation can avoid serious scaling problems. High TRL.	Efficient precipitation requires costly chemical addition and controlled conditions. A P-concentrated solution is needed.	Can be implemented from the liquid or solids line. Struvite or other fertilizer-value minerals can be obtained. Many proprietary commercial processes are available. Can be combined with P pre-concentration by membranes or electrochemical technologies.	[129,137,139–147]
Phosphorous/ leaching	Incinerated sludge waste is an available P source. Chemical extraction technologies available.	Chemical extraction may cause heavy metal leaching, in addition to P. This could create subsequent reuse problems.	Pre-treatment agents (e.g., EDTA) can achieve high-purity P leaching from ISSA.	[123]

Toilet paper in sewers disintegrates into cellulose fibers of about 1 mm in size, which can be removed in WWTPs by grit chambers (≈20% efficiency) or primary clarifiers (up to 80% efficiency). Physical separation is highly effective; therefore, the mainstream technical solution currently adopted for cellulose recovery consists of replacing or supplementing primary clarifiers with rotating belt filters (RBFs). An RBF with a mesh size of 350 µm can retain 40% of influent SS or more. The benefits extend beyond mere cellulose recovery. In fact, by removing most solids, considerable energy savings (ranging from 22 to 28%) could be obtained by operating biological processes at reduced aeration. Pre-recovery of cellulose could also mitigate membrane fouling in membrane bioreactor (MBR) processes. Cellulose post-recovery with RBFs installed in secondary clarifiers' sludge extraction lines requires smaller equipment (with lower costs) due to lower flows, achieving lower cellulose recovery as a consequence of its degradation in biological units. Furthermore, in this case, no aeration requirement savings are achieved.

Unlike conventional clarification units, RBFs can efficiently handle wide flow transients and solids peaks [155,156]. Recently, an ionic liquid method was proposed to recover cellulose from a paper mill's sludge [157]. However, this requires substantial energy and chemical inputs and may not be applicable to municipal facilities. At present, RBFs are a consolidated technology for cellulose recovery, and more than 700 such large-scale installations exist in Europe and North America [158].

Recovered cellulose can be directly valorized as raw polymeric material in the construction and paper industries as a substrate for ASD (for biogas or volatile fatty acid production), producing higher yields compared to primary sludge, or in the production of chemicals, such as bioethanol and bioplastics [159]. Nanocellulose (an emerging material with exponentially growing industrial applications) recovered from used water is cheaper than the one derived from wood or agricultural residuals and can be combined with extracellular polymeric substances (EPSs) extracted from excess sludge to form entirely used water-derived biological nanocomposites. An extended analysis of cellulose recovery and valorization was recently presented by Liu et al. [152].

3.4.2. Protein Recovery

Animal proteins play a crucial role in the human diet and the WEF nexus since they are responsible for a considerable fraction of water consumption both in direct animal farming and the production of animal feed. Globally, the per capita consumption of animal products has more than doubled in the past 50 years, increasing pressure on both the environment and water resources.

Microbial protein (MP) consists of protein-rich (10–80% d.w.) biomass with an amino acid profile comparable to standard animal protein, and it has attracted strong interest as a possible substitute for conventional, highly impacting animal feeds, such as corn and soybean meals. Methane-oxidizing bacteria are MP-rich microorganisms that use methane as carbon and energy sources to assimilate N into proteins.

Ammonium nitrogen from N-rich effluents, such as anaerobic digestate or segregated urine, can, therefore, be exploited for further valorization by integrating wastewater treatment with MP production. A study at the Avedøre (Denmark) WWTP showed that integrated WWTP/MP systems can produce protein sources with a lower environmental impact compared to traditional soybean meal. The codigestion of used water, urban biowaste, and an organic fraction of municipal solid waste could enhance biogas production and the nutrient content of digestates, allowing for efficient MP cultivation and the substitution of chemical additives used in commercial MP fermentation [160].

3.4.3. UWW-Based Biorefineries

WWTP biomass ends up including most soluble and suspended molecules present in influent UWW through metabolic uptake into cells or adsorption/incorporation into flocs. The role of biosolids is highly relevant in the general economy and the sustainability of UWW processing. They are a non-negligible passive cost factor in its processing cycle and can considerably influence the effectiveness of a successful mining strategy. Exploitation of the full recovery potential of used water-embedded compounds can be achieved through sludge biorefineries. Biosolid biorefinery chains consist of preliminary separation (e.g., harvesting and drying), pre-treatment, and the processing of biomass (bacteria and/or microalgae) through a multitude of technological processes for subsequent conversion into value-added products. Figure 6 summarizes the possible biorefinery process applications and some of the resulting products.

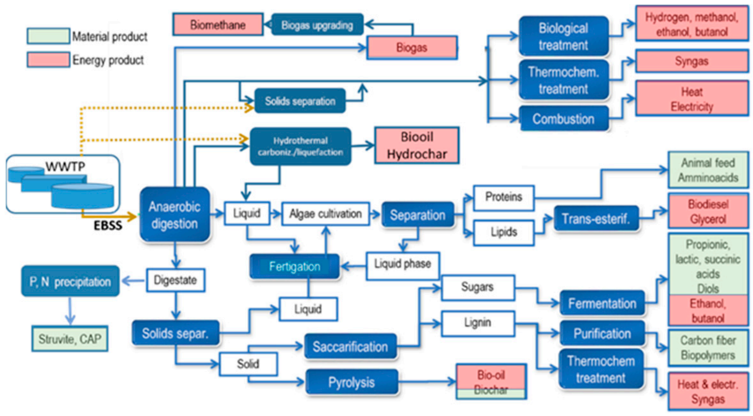

Figure 6. Possible biorefinery processes applicable to excess biological sewage sludge (EBSS) and resulting value-added products.

Some of the traditional processes in WWTPs (e.g., ASD) can already be considered part of a biorefinery scheme according to its definition. Recent approaches in sludge biorefineries have aimed at the direct recovery of specific biomass components, such as organic acids and/or alcohols, as well as other industrially relevant molecules (such as polyhydroxyalcanoates (PHAs), EPSs, VFAs, proteins, biopesticides, enzymes, and solvents) and biofuels considered more industrially valuable than biogas normally obtained from ASD. A state-of-the-art review of biorefinery possibilities was recently presented by Cecconet and Capodaglio [56]. Appropriately sequenced biorefinery processes can maximize the recovery of value-added products and facilitate the subsequent processing steps. For example, EPS and protein extraction may require the destruction of microbial cells, resulting in increased sludge dewaterability; this would improve its final disposal by thermochemical methods, with possible further product recovery opportunities [123,161,162].

3.4.4. Recovery of Metals from UWW

A considerable fraction of the anthropogenic discharges of metals ends up in wastewater. Apart from industrial discharges, UWW can be affected by heavy metal sources such as runoff from roofs, roads, or open-air deposits; wear from car tires and brakes; commercial and small industrial activities; car washes; etc. [163]. Heavy metal concentrations in wastewater are usually in the μg (less than one) to mg/L range [164]. Biological wastewater treatment processes are designed for the removal of organic matter by microorganisms, and the removal of heavy metals occurs as a side benefit, mostly through concentration (adsorption) onto excess biological sludge, where metal concentrations can reach μg/g levels (about 3 orders of magnitude higher than in wastewater) [164]. Metal pre-concentration from the liquid phase is essential for their recovery. Abiotic methods such as nanofiltration, electrodialysis, or reverse osmosis are efficient but costly for high flows and practically ineffective for low flows.

The presence of trace elements, including antimony, bismuth, and rare earth elements (REEs), has also been reported in wastewater (and biological sludges) at very low concentrations [165]. In such cases, adsorbent nanomaterials offer a promising recovery technology because of their potential high adsorption efficiency. However, the rather low REE concentrations suggest that recovery should be focused on the development of zero-waste processes. Factors such as the cost and reusability of nanomaterials influence the future potential of REE recovery [166].

Recovery technologies for metals are primarily aimed at biosolids as a concentrated repository. Several process alternatives exist, exploiting the thermal processes and chemical leaching of metals [162]. Two main obstacles hinder this practice: first, the relatively low concentrations that reduce the quantities of recoverable materials (and thus the processes' economic sustainability); and second, the fact that some methods, like acid leaching, may generate hazardous waste that will increase treatment and disposal costs and issues [162]. Westerhoff et al. determined that metals contained in excess biosolids could be valued at more than USD 13 per person per year in an urban area of 1 million people and that the most valuable elements (Ag, Cu, Au, P, Fe, Pd, Mn, Zn, Ir, Al, Cd, Ti, Ga, and Cr) in sewage sludge could yield a potential economic value of more than 280 USD/t of sludge [167]. The appropriate integration of metal recovery into the sludge processing end of the UWW cycle could contribute to reducing specific process costs while improving its CE footprint [168].

Table 5 summarizes the available approaches for chemical and material mining from used water. The evolution of the respective TRLs and the variability of international commodities markets are factors that strongly affect the sustainability of recovery.

Table 5. Summary of possible chemical and material mining opportunities from used water.

Material/ Chemical	Pros	Cons	Comments	Ref.
Cellulose	Valuable raw industrial material. Easily recovered through physical means. Removal of cellulose from WWTP influent could decrease aeration requirements by up to 30%.	Requires additional equipment. Some recovery processes may require substantial energy and chemical input.	Cellulose can be valorized as raw polymeric material in industrial applications or as substrate for AD, the production of chemicals, etc.	[152–159]
Protein	Protein-rich biomass has an amino acid profile comparable to standard animal protein and could be a substitute for soybean meal. Has less of an environmental impact than conventional animal protein sources.	Requires dedicated processes.	Methane-oxidizing bacteria are MP-rich microorganisms that use methane as carbon and energy sources to assimilate nitrogen into proteins. Integrated WWTP/microbial protein systems have been demonstrated.	[160]
Biorefinery-derived Products (PHAs, EPSs, VFAs, biopesticides, enzymes, etc.)	Molecules, more industrially valuable than biogas, are produced through microbial metabolism and immobilized in biomass during wastewater treatment.	Bioferinery processes are generally complex, and TRL is generally too low for commercial adoption.	Appropriate sequencing of biorefinery processes could maximize recovery of value-added products and facilitate subsequent biosolid processing steps	[56,57,135,160,161]
Metals, REEs	WWTPs concentrate metals and REEs from wastewater into biosolids. Metal content in wastewater could be highly valuable.	Low concentrations limit the quantities of recoverable materials from the liquid phase. Some recovery methods from the sludge phase may generate hazardous residues, increasing waste treatment and disposal costs.	Integration of metal recovery into the sludge processing end of wastewater treatment could contribute to improving its CE footprint.	[21,162–168]

4. Discussion

The (re)engineering of urban water systems will play an important role in providing water and WEF-related resources to growing urban populations globally, and in achieving sustainability and resilience in the face of predicted increasing demand and erratic climate patterns [169]. Organically implementing the short-cycled reuse of secondary water resources, such as used water, is an important aspect of UWC development planning, as it can permanently expand the original pool of resources essential to their continued performance and improve their response to temporary shocks.

In order for this to occur, a paradigmatic shift in UWW management seems necessary. The centralized management of water systems has been a common standard practice since the mid-1800s. However, it is increasingly evident that such an approach may not be optimal in view of renewed needs and technology. Both decentralized (independent water systems serving limited conurbation areas) and satellite (distributed throughout metropolitan areas but with functional connections with the main system) solutions can be considered efficient alternatives to centralized ones. It should be noted that there is no consensus on the definition of the size of a decentralized system. Some researchers define decentralized systems as those serving up to 5000 people. At the regulatory level, the US EPA extends this threshold to up to 10,000 people, and others (e.g., the Institute of Hydrology, Meteorology, and Environmental Studies, IDEAM) extend it to up to 30,000 people [28]. The definition should be instead related to the engineering context and environmental perspectives of planned interventions, remembering that water supply and sewage management are not "one size fits all". Local conditions must be carefully considered when designing local solutions, which are influenced by multiple economic, geographical, and social factors.

Many successful examples of used-water reuse exist worldwide. Over 3000 ascertained projects in Japan (>1800), the USA (>800), Australia (>450), Europe (>200), the Mediterranean and Middle East (>100), Latin America (>50), and sub-Saharan Africa (>20), including direct potable reuse (DPR), have been identified in previous surveys [170]. Nowadays, the number is most likely significantly higher, given the rapid development of such practices in rapidly developing countries such as China and India [171,172]. In Europe, about 10^9 m^3/year of treated UWW is reused, i.e., approximately 2.4% of WWTP effluents, but comprises less than 0.5% of annual freshwater withdrawals; however, the immediate reuse potential has been estimated to be at least six times the current volume. Most reuse in the EU is for irrigation purposes and, as of today, there are no known instances of DPR there, although cases of indirect potable reuse (IPR) via groundwater recharge and surface water body augmentation have been reported [163]. An essential prerequisite for the greater diffusion of water reuse is the development of guidelines addressing potential uses. Such regulations are gradually being introduced in the EU, the USA, and other countries [173,174].

The implementation of used-water mining will strongly impact the design and operation of water supplies and collection in the future. Over 60 countries around the world are already using centralized, recycled used-water systems for non-potable purposes. In some cases, these uses have extended to drinking water in the form of IPR or DPR [175,176]. When considering the introduction of water reuse schemes, it is important to examine and compare all possible benefits and drawbacks in the decision-making process. Assessments of NPR diffusion indicate that this practice is expanding, although the scale of individual projects will likely become smaller, with increasing popularity at the neighborhood scale. Decentralized reuse systems have, in fact, been proven to be economically advantageous in small, densely populated areas or new development projects, while centralized dual-distribution systems often turn out to be less cost-effective compared to the former through retrospective analyses, although they are technically successful [177]. DPR systems are usually implemented at a larger scale due to strict quality control and monitoring requirements and the pre-existence of distribution networks [176].

The WEF nexus approach is becoming more central to water sector sustainability in view of global efforts to implement the SDGs. The recovery of nutrients, renewable fuels, and materials is not only considered a paramount objective but will also add sustainability and resilience to UWW systems, relieving some of their operational costs. Examples of reuse/recovery technologies addressed in this review include several biological and non-biological routes. Possible combinations of these technologies are practically endless, but several non-technical issues may hinder the successful implementation of such schemes.

Different categories of hindrances include, in order of perceived relevance, economics and value-chain issues, policies, and societal factors. Among the former are process costs and the market value of recovered resources, as well as their quantity, quality, and final distribution. In particular, coherent regulations concerning standardization and quality assurance in recycled materials markets (including the "end-of-waste" concept) are needed. Process competitiveness can be initially boosted through direct economic or fiscal incentives to reduce the inherent economic advantage of traditionally established production cycles. These considerations also overlap with the policy realm; urban planning, building regulations, and regulatory loopholes can affect the implementation of reuse solutions, especially at the municipal scale.

Users' acceptance of UWW-recovered resources should not be taken for granted due to fear, psychological barriers, or misconceptions about the related risks and quality. Both water reuse and resource recovery and reuse projects cannot be successfully implemented without ample social acceptance or in the absence of clear legislation and shared political will. Social acceptance is usually higher when the public has a clear perception of the benefits and ineluctability of the adopted options, as seen, for example, in Windhoek and Singapore. Economic incentives and legislative updates could help speed up circular approaches to UWC management, as well as actions aimed at enabling the transfer of recovered resources to markets, thereby reducing legal barriers, and improving stakeholders' attitudes toward their acceptance [178].

A focus on optimizing the interactions of system components must be pursued in order to maximize the beneficial impacts of resource recovery. Thus, original site-specific solutions should be properly developed, considering the retrofitting of existing facilities and integration with new technologies. Given the number and complexities of the possible options, comparative LCA, TEA, and CE cycle analyses of alternative solutions should be desirable approaches to address all these issues [179].

5. Conclusions

Water availability constitutes one of the single, most significant factors that limit human development and is an impending threat to the continuing viability of many large cities. Reuse is recommended as a necessary solution to widen the pool of available water resources for urban populations and agriculture, and embedded resource recovery is seen as an opportunity to obtain essential materials deriving from unsustainable primary mining.

Many practical challenges related to policy and economics, as well as inertial thinking upholding a long tradition of linear consumption patterns, however, hinder the development of a UWC-based CE. Over time, intensive infrastructures and a prevalent mindset focused on a linear approach to UWW management have become established and persist to this day. Existing infrastructure is generally not adequate to support the full exploitation of water and embedded resources and will need to be optimized with new conceptual approaches and technological refurbishments based on a renewed understanding of resource flows through cities and the relationships between water, waste cycles, and the WEF nexus. In order to address the sustainability and circularity of water and embedded resource management, fundamental changes are needed in the way UWW is managed.

This review focused on approaches and technologies that could enable resource recovery from UWW by incorporating them into a UWC Circular Economy. Available and developing technologies, as well as opportunities for value-added UWW extractable products, have been discussed in this paper. The utilization of a systemic approach that takes into account local conditions and properly recovered product outlets is essential and will better enable the identification of opportunities and evaluation of the impacts and benefits of implementing UWW mining.

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