Tailoring Non-conventional Water Resources for Sustainable and Safe Reuse in Agriculture

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In water scarce areas, like the Mediterranean Region where the lack of irrigation water is already limiting agricultural production, the valorization of non-concventional water resources is utmost important. Accordingly, in this study, we aimed to provide safe and locally sustainable ways of water supply for the Mediterranean agricultural sector by exploiting non-conventional water resources for irrigation purpose. In this context, pilot scale anaerobic reactors treating urban wastewater were operated coupling upflow anaerobıc sludge blanket (UASB) reactor and ultrafiltration anaerobic membrane bioreactor (AnMBR). The resulting permeate is of high quality, accomplishing the EU quality standards for irrigation water reuse, also in terms of *E.coli* as the main microbial indicator. However, contaminants of emerging concern (CECs) can be a further limitation for safe reuse of the reclaimed water. Hence, molecularly imprinted polymers (MIPs) were further integrated as the final refining step for the selective removal of CECs. Diclofenac was used as the target compound with a removal efficiency up to 50% in the final effluent. In parallel, an intensive pilot system was operated for brine treatment through evaporation, chemical addition and precipitation, and forward osmosis, where up to 77% Mg^{2+} and 45% Ca^{2+} recovery rates were achieved. The recovered Mg-salts from the brine treatment were then used as an external source to enhance the struvite precipitation in the N- and P-rich effluent of AnMBR. The preliminary tests showed that only hydroxiapatite salts precipitated without any external P addition.

1. Introduction

Water stress occurs in many areas of the EU, particularly in the Mediterranean area. Since agriculture is the largest consumer of freshwater, non-conventional water resources have high potential to complement conventional water resources used in agricultural sector. In this context, the European Commission approved the regulation on minimum requirements for water reuse (EC, REGULATION (EU) 2020/741). These specific EU requirements vary according to the type of irrigated crops and according to the method of irrigation, taking into account the potential risk of contamination of the products. The strictest requirements are provided for class A, where reclaimed water can be in contact with the edible parts of irrigated food crops. Anaerobic processes can enable synergistic application of reclaimed water reuse and nutrient recovery (N, P) that can bring economic benefits to wastewater treatment operators and end-users of treated wastewater (Foglia et al., 2019). However, a further barrier in water reuse sector regards the CECs precence in wastewater. Indeed, conventional wastewater treatment processes do not remove CECs; this aspect contributes adverse effects on humans and the ecosystem through water discharges (Parlapiano et al., 2021). Accordingly, H2020 Prima Project FIT4REUSE (www.fit4reuse.org) aims to provide safe and locally sustainable ways of water supply for the Mediterranean agricultural sector by exploiting non-conventional water resources, such as treated wastewater and desalted water. In this scenario, the object was to evalutate the combination of two parallel treatment trains in order to enable water reuse for both irrigation and aquifer recharge and to promote P-recovery by mixing the two resulting effluents. Finally, for the selective removal of CECs in the final effluent, MIPs adsorption studies were conducted at lab scale as a further refining step, as a promising innovative application at pilot/full scale.

2. Materials and methods

The overall concept is depicted in Figure 1. The pilot-scale units were located in the wastewater treatment plant (WWTP) of Falconara Marittima (Italy). The treatment train aimed to enable water reuse for irrigation from municipal wastewater (PILOT SCALE 1 + LAB SCALE 1) and aquifer recharge from brine (PILOT SCALE 2), while LAB SCALE 2 aimed to achieve P-recovery from two resulting effluents.
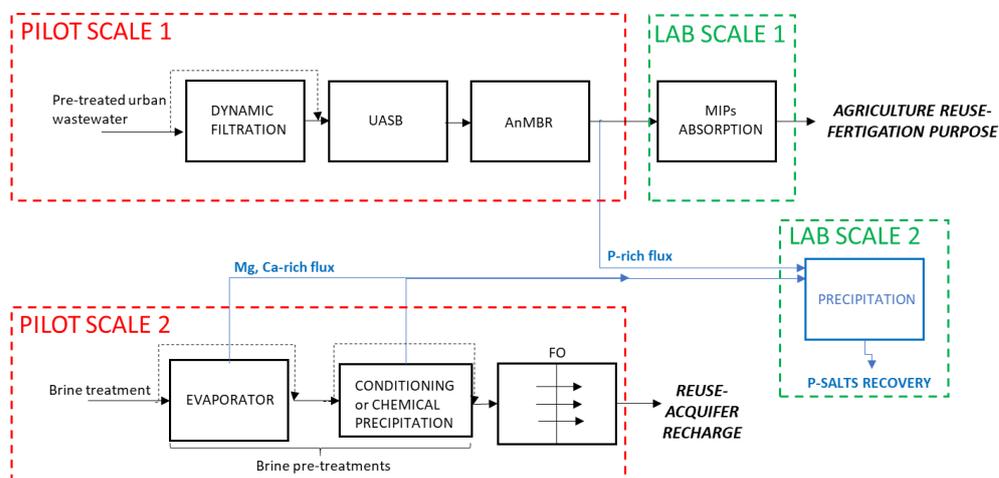

Figure 1: Overall concept for non-conventional water sources use and P-recovery

2.1. Pilot-scale anaerobic treatment system

In the wastewater treatment line, following the preliminary treatment units (screening, degritting and grease removal) of the full-scale WWTP of Falconara Marittima, the pretreated influent was fed to the pilot-scale system. The PILOT SCALE 1 is composed of a dynamic rotating belt filter (RBF) (Salsnes SF 1000 by Trojan Technologies), 16 L of UASB reactor and an ultrafiltration chamber with pore size of 0.03 μm and a filtration area of 0.5 m^2, in a sidestream submerged configuration. The UASB was operated at an influent flowrate of 3L/h at 37±3.7°C and at an influent organic loading rate of 0.54±0.15 kgCOD/m^3/d. Routine physical-chemical analyses were conducted once a week. All the samples were analyzed according to Standard Methods (APHA, 2005).

2.2. Lab-scale adsorption tests via MIPs

The enhanced removal of CECs via molecularly imprinted polymer (MIP) after the UASB+AnMBR configuration was investigated at the lab-scale (LAB SCALE 1). Preliminary adsorption tests were done in distilled water using diclofenac (DCF) as the target compound to optimise operating conditions. MIPs were synthesized via bulk polymerization adapting the procedure reported by Samah et al. (2018). DCF acidic form was obtained by dissolving diclofenac sodium salt (DCF-Na) in water (7 mg/L) and acidifying the solution with HCl 1M DCF-Na/water solution and stirred for 10 min; HCl 1M was then added in 1:1 molar ratio with the precipitation of DCF, which was filtered through 0.45 μm filter paper and washed with HCl 1M to remove the unreacted reagent. MIP synthesis was performed through sonication by dissolving 1 mmol DCF as the template and 4 mmol methacrylic acid (MAA) as the monomer in 30 mL of acetonitrile. 20 mmol of ethylene glycol dimethyl acrylate (EGDMA) and 0.12 mmol of 2.2 azobisisobutyronitrile (AIBN) were added to create and promote the polymer matrix around the template molecules. The solution was purged with nitrogen for 10 min to remove oxygen from the solution. The sealed solution was heated at 60°C for 24 h to obtain a monolith polymer which was crushed and washed several times through sonication with methanol/acetic acid (9/1, v/v) mixture until a complete removal of DCF. A final washing step with 50 mL of methanol for two cycles was performed and the polymer was centrifuged at 6000 rpm for 10 min. Afterwards, the polymer was dried at 40°C in oven for overnight, then grounded and sieved to have 20-100 μm particles. Similarly, Non-Imprinted Polymers (NIP) were synthesized in the same way without using the template molecule in the pre-polymerization step and used as a control to evaluate the efficacy of the obtained polymers. Morphologıcal characterization and adsorption capacity of the MIP and NIP was performed by Scanning Electron Microscopy (SEM) using a Philips XL20 with tungsten filament at a voltage of 10 KV and by UV-VIS spectroscopy using a Synergy HT (Biotek) multiplate reading, respectively. MIP and NIP adsorption behaviour was investigated in batch tests with different concentrations of DCF-sodium (DCF-Na)

aqueous solutions (25 mg/L-600 mg/L of DCF-Na solutions in distilled water at pH=7 at room temperature). The DCF concentration was determined by UV spectrophotometry at λ = 276 nm. Further lab-scale batch adsorption tests were then conducted using the permeate of the AnMBR reactor operated in the PILOT SCALE 1 configuration. The DCF-Na was spiked at different concentrations (25 mg/L-300 mg/L). The amount of DCF adsorbed per mass unit of polymer (q_e, mg/g) was calculated by the difference between the initial DCF concentration (C_i, mg/L) and the concentration at the equilibrium (C_e, mg/L) using the following equation (Eq 1), where "V" is the volume of solution and "m" is the mass of polymer used in the experiment.

$$q_e = (C_i - C_e)\frac{V}{m} \tag{1}$$

2.3. Pilot-scale brine treatment system

An intensive pilot system (PILOT SCALE 2) was operated to enable wider use of desalted water through forward osmosis (FO) process. The PILOT SCALE 2 has the purpose to minimize brine volume, to recover valuable resources and to improve water reuse. In order to remove possible scaling agents (mainly potential organic foulants and Mg and Ca-salts) before osmosis, the raw brine were pre-treated by thermal evaporation or/and chemical conditioning and precipitation. The evaporation unit (FORMECO DiQ 20 AX) is composed of an electrical resistance, an oil chamber, an evaporation tank (30 L capacity) equipped with a mixer and a cooling system for the collection of the distillate. For the chemical treatment unit, a precipitation tank is placed with a capacity of 100 L, equipped with a mixer, a peristaltic pump and manual valves to collect supernatant. The FO pilot unit is equipped with Aquaporin HFFO2 membranes with an effective filter area of 2.3 m^2 each. Following the optimization of Mg^{2+} and Ca^{2+} recovery and evaporation efficiency at the lab-scale by varying operating conditions such as temperature, pH and the concentration of external reagents (i.e. NaOH), pilot-scale tests were conducted separately in chemical conditioning and thermal treatment lines to recover Mg^{2+} and Ca^{2+}.

2.4. Lab-scale struvite precipitation

Preliminary tests were performed to assess the feasibility of P-salts recovery through precipitation (LAB SCALE 2) in the effluents of the anaerobic reactors (UASB effluent and AnMBR permeate). A laboratory ageing test was carried out in 3 L glass beakers at room temperature and lasted for 10 days. The tests were conducted without any external pH adjustment (pH=8.3). Main parameters such as pH, conductivity, alkalinity, anions (Cl^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) were monitored. At the end of the test, the precipitate was allowed to settle at the bottom and the liquid fraction was removed. Then, the residual wet fraction was dried at 105 °C and analysed through Scanning Electron Microscope (SEM) for qualitative and quantity analysis of precipitated compounds. Moreover, a modelling estimation was made using the Visual MINTEQ, a freeware chemical equilibrium model, to evaluate the possible P-salts precipitation from a thermodynamic point of view. In this context, Mg-precipitate recovered from the brine treatment was considered as an external source to enhance struvite ((NH_4)$MgPO_4 \cdot 6(H_2O)$) formation in the N-P rich permeate of the AnMBR. The maximum amount of precipitated struvite was estimated by using the molar concentration of PO_4^{3-}, which is the ion with the lowest concentration compared to the other struvite compounds ($NH4^+$ and Mg^{2+}).

3. Results and discussion

3.1 Performances of the overall wastewater treatment (PILOT SCALE 1)

The characteristics of the final effluent of the PILOT SCALE 1, that applies the AnMBR as tertiary treatment, is given in Table 1. The final effluent quality was found to be suitable for agricultural reuse according to new EU Regulation 2020/741, also from a microbiological point of view. Since the mainstream anaerobic treatments combining UASB and AnMBR are characterized by high rate of hydrolysis, the release of nutrients occur. The nutrient-rich flux permeate has high N and P contents equal to 20 mgN/L and 6 mgP/L, respectively (Foglia et al. 2020). This means that the combination of UASB + AnMBR enables water reuse and/or fertigation as well as alternarive nutrients recovery through final precipitation. Further advantages of the AnMBR unit is the pathogen reduction such as *E.coli* in the permeate, which provies a physical disinfection treatment without any chemical addition and any by-product formation, compared to the conventional disinfection methods (such as chlorination or ozonation) (Harb at al.,2017).

Table 1: Anaerobic effluent characteristics from PILOT SCALE 1 for safe reuse

	COD	TSS	TN	TP	*E. coli*
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(UFC/100mL)
Effluent PILOT SCALE 1	28±17	0	15±1	3±0.6	<10

Despite AnMBR garantuees a disinfection stage for wastewater, it shows a selective and often poor removal capacity for CECs, lower than 10 % for estriol, estrone, ibuprofen and carbamazepine. In particular considering DCF removal, this is less than 1 % (Monsalvo at al.,2014). Hence, further adsorption tests were conducted at lab-scale for the selective removal of DCF from the final effluent.

3.2 MIPs synthesis and performance of adsorption tests (LAB SCALE 1)

The MIP synthesis was successfully performed with a yield up to 90 %. As shown in Figure 2, MIP and NIP have different surface morphologies, since MIP particles show a very marked porosity with pores between 50 and 100 nm. This results in a much wider contact surface and thus in an increased permeability.
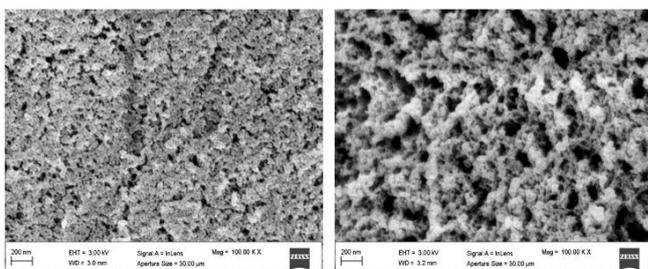

Figure 2: SEM images of NIPs (left side) and MIPs (right side) synthesized

The results of the preliminary batch tests are reported in Figure 3. The greater adsorption efficiency of MIP compered to NIP is clearly evident . The MIPs adsorption capacity, expressed as mgDCF/g polymer, was found to be from 49 to 60 % higher than that of NIPs.
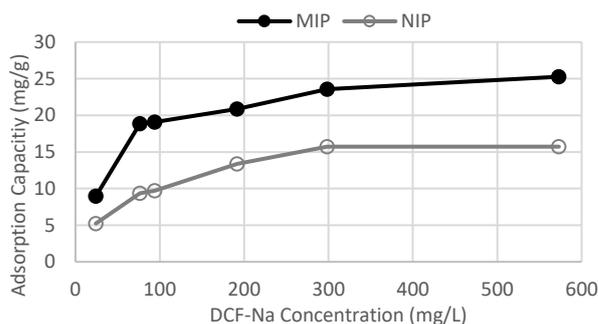

Figure 3: Batch test adsorption analysis performed on MIP (blue) and NIP (red) at different concentration of DCF-Na in distilled water

In order to investigate the binding mechanism of the polymers, isotherm models were used and in particular the experimental equilibrium data obtained with MIPs and NIPs were further studied with the Langmuir and Freundlich isotherm models (Table 2). The best fitting was achieved with Freundlich model for MIPs (r^2=0.94) and with Langmuir isotherm model for NIPs (r^2=0.97). The correlation obtained through isotherms analysis indicated a greater etherogeneity of the MIP binding sites. In fact, MIPs are characterized by the presence of both selective sites created around the template molecules and non-specific sites similar to NIP; whereas NIPs are made of homogeneus monolayer binding sites (Zheng et al., 2017). The maximum adsorption capacities of MIPs and NIPs were q_{MIP}=25.3 and q_{NIP}=15.7 mg/g, respectively, with an imprinting factor (IF) value of 1.61, indicating that the imprinting effect of the target molecule in the polymerization improves the efficiency of the polymer (Eq. 2).

Table 2: Adsorption data on the base of isotherm equation analysis

Polymers	Langmuir r2	Freundlich r2	KL	qmax, eq.	KF	qmax, exp	IF
MIP	0.7879	0.9378	0.1077	23.99	1.516	25.27	1.61
NIP	0.9651	0.9586	0.0196	17.73	2.008	15.72	

The batch tests on MIPs were further carried out also using the effluent of the AnMBR to evaluate the efficiency for a future pilot-scale implementation (Figure 4). The DCF removal efficiency was reduced by 50% for

concentrations below 100 mg/L of DCF-Na, while at higher concentrations between 200-300 mg/L, the adsorption capacity had a similar trend observed with distilled water. Further studies will be conducted to understand the effects of chemical factors (pH, ionic strength, organic matter) on the MIPs' performance.
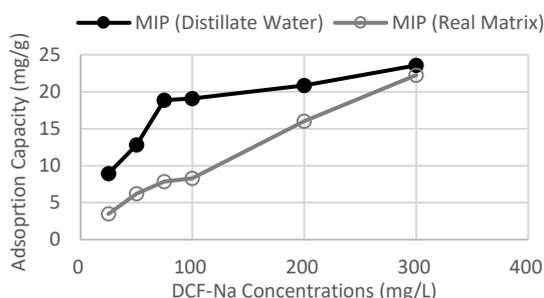

Figure 4: Adsorption tests performed on MIPs at different concentration of DCF-Na in AnMBR permeate

3.3 Performances of the brine pre-treatments (PILOT SCALE 2)

Raw brine fed to the PILOT SCALE 2 were initially characterized in terms of ionic forms, TDS, TSS and TS as reported in Table 3.

Table 3: Raw brine physical and chemical characteristics

	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	TDS	TSS	TS
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
RAW BRINE	3885	14800	730	3514	1854	58411	76	58487

So far, conditioning 30 L raw brine at pH 9.3 with the addition of 9.3 mL NaOH/L resulted up to 77% Mg^{2+} and 45% Ca^{2+} recovery rates. The volume of the residual precipitate was around 5 L with solids content of 6.4 %TS. The content of Mg in the residue was up to 27 gMg/100gTS, meanwhile the content of Ca was 9 gCa/ 100 gTS (Table 4). Although the chemical precipitation reduces hardness ions and is the most common pre-treatment process, this technique is challenging for managing the operation at optimal chemical dosage especially during temporal variation in brine characteristics (Semblante et al.,2018). On the other hand, after the thermal pre-treatment of 15 L of raw brine at 150°C and -0.4 bar for 4 h, the volume of the residual precipitate was 0.9 L with solids content of 95 %TS, while Mg and Ca contents were 7.2 gMg/100gTS and 1.5 gCa/100gTS, respectively (Table 4).

Table 4: Characteristics of the residual precipitates form brine-pretreatments

	Efficiency	Dry content	Mg content	Ca content
	Residual volume %	TS%	gMg/100gTS	gCa/100gTS
Residue from chemical conditioning	17	6.4	27	7.2
Residue from thermal evaporation	6	95	9	1.5

3.4 Preliminary results for P-recovery from anaerobic treated wastewater (LAB SCALE 2)

Phosphorus recovery, as struvite or phosphorous salts, can prevent the depletion of phosphate rocks, a critical raw material which supply security is at risk (Akyol et al.,2020). Based on the SEM results obtained from the preliminary ageing tests on the UASB effluent and on AnMBR permeate, given the high concentrations of Ca^{2+}, PO_4^{3-}, SO_4^{2-} in the samples, $CaSO_4$ and $Ca_3(PO_4)_2$ were the main precipitated salts in the UASB effluent (Figure 5a) and in the AnMBR permeate (Figure 5b), respectively. In addition, using the VISUAL MINTEQ tool, the precipitation of $CaSO_4$, as well as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) were further confirmed for the UASB effluent and AnMBR permeate, respectively. Up to 13 mg of struvite/L can be recovered from the AnMBR permeate at the natural pH of the matrix as 8.3. At this point, the precipitated Mg from the brine pre-treatment both via thermal and chemical conditioning can be easliy used as an external source to enhance the recovery of the different P-salts from anaerobic effluent at different pH values. Lab tests combining AnMBR permeate and brine precipitates will be evaluated in future activities.
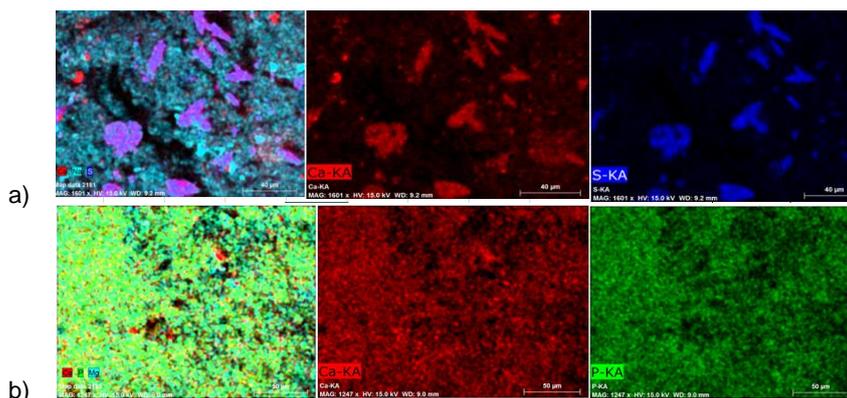
Figure 5: SEM elementary map of a) UASB effluent precipitates b) AnMBR permeate precipitates

4. Conclusions

Although anaerobic processes for wastewater treatment, in this case UASB coupled with AnMBR, accomplish the EU quality standards for reuse in agriculture, the CECs in the final effluent represent hazard for human health and the environment. Targeted CECs compounds can be removed and safe water reuse can be enabled by implementing an additional refinement step such as MIPs adsorption process. On the other side, recovered Mg-salts from brine pre-treament can be effectively used for struvite or other P-salts precipitation in the AnMBR permeate, that represents a NH_4^+ and PO_4^{3-} rich flux.

Acknowledgements

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