Experimental study on municipal and industrial reclaimed wastewater refinement for agricultural reuse

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ABSTRACT

The present study is aimed at verifying the possibility of reusing municipal and industrial reclaimed wastewaters for the irrigation of container-grown ornamental shrubs, paying attention to the refinery treatment. The research has been carried out in the district of Pistoia (Central Italy), which represents one of the main nursery areas in Europe. Two experimental sites, each consisting of a refinery treatment pilot plant (filtration and disinfection) and an agronomic area, were set-up. In this paper the attention is focused on the selection of the refinery treatment. The combined process of peracetic acid (PAA) and ultraviolet irradiation (UV) chosen for the disinfection treatment proved to be very effective for the inactivation of microorganisms for both municipal and industrial wastewaters. The high efficiency is recognised as being brought about by the formation of free radicals due to the photolysis of the PAA when in the presence of the UV rays. A preliminary cost analysis has been carried out in order to highlight the most economically advantageous solution which guarantees the compliance to the Italian limits for wastewater reuse in agriculture (Escherichia Coli 10 CFU/100 mL).

Key words | disinfection, irrigation, peracetic acid, reuse, ultraviolet irradiation, wastewater

INTRODUCTION

The district of Pistoia (Central Italy) represents one of the main plant nursery area in Europe. Currently, the surface intended for plant nurseries in the whole province of Pistoia is 5,000 ha for both field-grown and container-grown plants.

According to the results of field investigation carried out in this area (Benvenuti et al. 2000), the estimated average daily water contribution for the areas assigned to container-grown plants is 16 mm. Considering the surface occupied by container-grown plants and the duration of the well watered season (from May to October), the yearly water consumption, relevant to the plain of Pistoia and only for the container-grown plants, is approximately 12 Mm³. Since nursery container production of woody plants is likely to be one of the agriculture practices with the highest water demand, most of the nursery producers are facing increasing pressures to avoid using high-quality water supplies for irrigation (Gordon 1994; Bailey et al. 1996).

Therefore, it is important to evaluate alternative water sources for irrigation (so called non-conventional water resources) in order to maintain a high qualitative and quantitative production standard. Among the non-conventional water resources, reclaimed wastewater (RWW) can be considered the most important for irrigation. Reclaimed wastewater reuse for the production of ornamental plants has some peculiarities compared to the same practice in other agricultural fields. The ornamental plant production is a high added-value activity and for this reason higher economic margins are possible in order to refine reclaimed wastewater; at the same time the high value of the plants requires that the effect of reclaimed wastewater irrigation has to be carefully evaluated.

In the Pistoia nursery area, the irrigation water demand is mainly met by the use of groundwater whose exploitation takes place in competition with potable
water uses. In this context, a verification of the possibility of reusing treated wastewater for irrigation, making groundwater resources available for other purposes, becomes extremely interesting.

The amounts of RWW available in the nursery area (3 Mm³/y), coming from the Pistoia municipal wastewater treatment plant (WWTP), can only partially cover the water demand for the irrigation of container-grown plants (12 Mm³/y). As a consequence, the possibility of reusing the effluents coming from WWTPs located in Prato (Tuscany, Italy), which is a few kilometres far from the nursery area and represents one of the biggest Italian textile district, was considered.

Dealing with the RWW reuse project, both the following aspects were considered:

- identifying a suitable refinery treatment facility in order to make the effluents in compliance with the national regulations (D.M. 185/2003) for RWW to be reused for irrigation;
- assessing the effect of RWW on some ornamental plant species representative of the local nursery production (Lubello et al. 2004; Gori et al. 2008).

In this paper the attention is focused on the first aspect. As regards the agronomic aspects, the following conclusions can be drawn. Experimental results indicate no major limitations for the use of the tertiary effluent as an irrigation source in plant nursery (Gori et al. 2004; Lubello et al. 2004). Concerning industrial wastewaters, the treated effluent was suitable for the irrigation of ornamental plants but the use of drip irrigation should be suggested in order to avoid a decrease in the quality of the plants produced due to tip and edge burn of leaves. Moreover, because of the salt-sensibility of numerous plants, the use of a tertiary effluent with such water quality can always be recommended for short periods (Gori et al. 2008).

As far as refinery treatments are concerned, municipal wastewater effluents are commonly disinfected by chlorination. Due to its well known phytotoxic effect (Whipker 1999), attempts are under way worldwide to find safer alternative disinfection agents able to meet the stringent microbial requirements usually required for wastewater reuse. The Italian law in force for agricultural reuse (D.M. 185/2003) sets the limit for Escherichia Coli (E. coli) of 10 CFU/100 mL (80% of the samples) and 100 CFU/100 mL (maximum admissible value).

Various schemes of tertiary treatment have been proposed for agricultural wastewater reuse: secondary effluent further submitted to coagulation–flocculation, sand filtration and final disinfection, ultraviolet irradiation and membrane filtration (Lazarova et al. 1999; Liberti et al. 2002; Petala et al. 2002; Pollice et al. 2004; Gómez et al. 2006, 2007).

In this research, for the refinement of textile RWW, sand filtration and disinfection with a combined treatment of peracetic acid (PAA) and UV was experimented. Since the disinfection process of PAA seems to take place according to radical type reactions, we have attempted to research if and how the UV could accelerate such reactions (Caretti & Lubello 2003).

Contrary to other AOPs (UV/H₂O₂, O₃/H₂O₂, O₃/UV, TiO₂/UV), numerous bibliographic references for the combined treatment between PAA and UV do not exist (Rajala-Mustonen et al. 1997; Liberti et al. 2002; Caretti & Lubello 2003). It is possible to revert back to the peroxide acids theory to show how the action of UV produces a homolytic rupture on the O-O bond of the peracetic acid molecule, with the subsequent formation of the hydroxyl radical:

\[ CH_3CO_3H \rightarrow hv \rightarrow CH_3CO_2H + \cdot OH \]

The CH₃CO₂⁻ molecule rapidly declines forming CH₃ and CO₂, while the molecule of peracetic acid can subsequently react with the ‘OH radicals produced, according to the following reactions of addition and subtraction of a labile hydrogen:

\[ CH_3CO_3H + \cdot OH \rightarrow CH_3CO_4H_2 \rightarrow CH_3CO_2H + \cdot OOH \]

\[ CH_3CO_2H + \cdot OH \rightarrow CH_3CO^- + O_2 + H_2O \]

The presence of hydrogen peroxide within the commercial product of the PAA contributes not only to the formation of new peracetic acid as soon as it is consumed, but also to the formation of new hydroxyl radicals.

In previous studies, the possibility of using the combined treatment of PAA and UV to disinfect secondary wastewater effluents has been evaluated. The analyses carried out showed
the effective synergy between the two treatments and the considerable increase of the effectiveness of the combined treatment as compared to the single treatments considered separately (Lubello et al. 2002). Moreover, the combined treatment of PAA and UV proved to be more effective than the combined treatment of hydrogen peroxide (H₂O₂) and UV (Lubello et al. 2002). This result has been confirmed by spectroscopic analysis, which showed a remarkable increase in the production of free radicals when moving from the combined treatment of H₂O₂ and UV to the combined treatment of PAA and UV (Bianchini et al. 2002).

The objective of this study was to investigate the suitability of the PAA/UV treatment for both municipal and industrial wastewater disinfection in order to assess operation conditions required to meet the Italian microbiological limits for agricultural reuse and to determine the cost required to meet such values.

METHODS

Tertiary treatment pilot plants

Experimental trials have been carried out within the Pistoia and the Calice WWTPs.

Pistoia WWTP treats approximately 8,000 m³/d of municipal wastewaters. It is a conventional activated sludge plant consisting of pretreatment (fine bar screen, sand removal and degrease), primary sedimentation, denitrification, oxidation-nitrification and secondary settling.

Calice WWTP is located in Prato and treats around 25,000 m³/d of sewage wastewater originating from textile (70%) and domestic (30%) activities. The WWTP is based on preliminary and primary treatment (screening, grit and oil removal, chemically enhanced primary sedimentation) and a conventional nitrification–denitrification activated-sludge process. Due to the poor settling capacity of the activated sludge, secondary effluent is further treated with coagulation–floculation and chemical decolourisation before it is discharged in the receiving water body.

The experimental sites set up within the Pistoia and the Calice WWTPs consist of a refinery treatment pilot plant and an agronomic experimental area. Figure 1 shows the layout of the experimental sites.

During the experiment, the effects of different solutions were evaluated, namely: disinfection with PAA, disinfection with UV, addition of PAA downstream the UV device (UV + PAA) and addition of PAA upstream the UV device (PAA + UV). In the third case, the contact time of PAA is negligible and equal to the residence time in the UV reactor, varying between 3 and 12 seconds according to the entrance capacity. On the contrary, when the PAA is introduced downstream of the treatment with UV rays, a contact time was allowed which, based on what was observed in the preliminary laboratory tests (Caretti & Lubello 2003), was calculated at 50 minutes.

The pre-treatment of the secondary effluent before disinfection consists of two rapid filters (OFSY 30-Culligan). PAA was added through a commercial solution.
containing, by weight, hydrogen peroxide (28%), acetic acid (8%), water and stabilisers (59%) and PAA (5%). PAA dosages ranged from 1 to 16 mg/L.

UV irradiation was provided by a cylindrical closed system (diameter 163 mm, length 792 mm, 13.6 L volume, contact time of 7 seconds at a flow rate of 8 m³/h) equipped with 8 low pressure lamps (electric power 0.8 kW) (M8S, Montagna s.r.l.). According to the information provided by the manufacturer, different UV doses were provided changing the flow rate (from 2 to 16 m³/h) and the dose was calculated taking into account the absorbance of water at 254 nm.

Inside the storage tank, before being sent to the irrigators or to the backwashing filters, the water which, after disinfection, presents a bacterial content respecting the limits for wastewater reuse for irrigation, risks being subject to bacterial regrowth.

In order to avoid this phenomenon, 2 mg/L of PAA with a bacteriostatic function is dosed within the tank.

### WASTEWATER CHARACTERISATION

The pilot plants were fed by WWTP effluents, whose main chemical–physical and microbiological characteristics are summarised in Table 1.

In order to enhance the efficiency of the disinfection, a filtration step was used before the treatment. The effects of the filtration are shown in Table 2.

### RESULTS AND DISCUSSION

The E. coli content in the Pistoia filtered samples before the disinfection treatment varied between 9,600 and 108,000 CFU/100 mL with a mean value of approximately 36,500 CFU/100 mL. Given the extreme variability of the microorganisms concentration in the effluent, a disinfection system must be perfected which is capable of guaranteeing inactivation up to 5 log in order to ensure the compliance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Method</th>
<th>Calice effluent</th>
<th>Pistoia effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH unit</td>
<td>Specific probe</td>
<td>8.09 ± 0.35</td>
<td>7.70 ± 0.25</td>
</tr>
<tr>
<td>Conductivity</td>
<td>µS/cm</td>
<td>Specific probe</td>
<td>1.97 ± 0.17</td>
<td>7.09 ± 0.63</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>mg/L</td>
<td>IRSA-CNR 2090 method</td>
<td>4.6 ± 2.6</td>
<td>7.4 ± 2.4</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>–</td>
<td>n.a.</td>
<td>2.8 ± 1.2</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>Rapid kit (Merck Spectroquant)</td>
<td>68.2 ± 14.9</td>
<td>37 ± 9.3</td>
</tr>
<tr>
<td>Ammonium</td>
<td>mg N/L</td>
<td>Rapid kit (Merck Spectroquant)</td>
<td>0.74 ± 1.12</td>
<td>0.50 ± 0.85</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg N/L</td>
<td>Rapid kit (Merck Spectroquant)</td>
<td>15.3 ± 14.9</td>
<td>9.6 ± 4.3</td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>mg P/L</td>
<td>Rapid kit (Merck Spectroquant)</td>
<td>0.1 ± 0.01</td>
<td>2.1 ± 0.25</td>
</tr>
<tr>
<td>Potassium</td>
<td>mg/L</td>
<td>IRSA-CNR 3240 method</td>
<td>22.2 ± 9.1</td>
<td>15.0 ± 2.10</td>
</tr>
<tr>
<td>Surfactants</td>
<td>mg/L</td>
<td>IRSA-CNR 5170 + 5180 methods</td>
<td>0.79 ± 0.3</td>
<td>n.a.</td>
</tr>
<tr>
<td>Absorbance at 254 nm</td>
<td>cm⁻¹</td>
<td>Spectrophotometric measure</td>
<td>0.60 ± 0.13</td>
<td>n.a.</td>
</tr>
<tr>
<td>Absorbance at 420 nm</td>
<td>cm⁻¹</td>
<td>Spectrophotometric measure</td>
<td>0.13 ± 0.04</td>
<td>n.a.</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/L</td>
<td>IRSA-CNR 4090 method</td>
<td>390 ± 127</td>
<td>84 ± 19</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg/L</td>
<td>IRSA-CNR 3270 method</td>
<td>318 ± 120</td>
<td>100 ± 12</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/L</td>
<td>IRSA-CNR 3130 method</td>
<td>70.8 ± 14</td>
<td>80 ± 17</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/L</td>
<td>IRSA-CNR 3180 method</td>
<td>22.9 ± 4.2</td>
<td>20 ± 5.5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mgCaCO₃/L</td>
<td>IRSA-CNR 2010 method</td>
<td>316.5 ± 105.2</td>
<td>142 ± 37</td>
</tr>
<tr>
<td>E. coli</td>
<td>CFU/100 mL</td>
<td>Membrane filtration Technique</td>
<td>1,900 ± 620</td>
<td>36,500 ± 7,500</td>
</tr>
<tr>
<td>Total coliforms</td>
<td>CFU/100 mL</td>
<td>Membrane filtration Technique</td>
<td>2,900 ± 1,310</td>
<td>307,000 ± 85,000</td>
</tr>
</tbody>
</table>

n.a.: not analysed.
with Italian legislation for wastewater reuse for irrigation (E. coli 10 CFU/100 mL). In the experimental conditions considered (2–8 ppm PAA with 10–30 minutes contact time; 100–220 mJ/cm² UV) it has been impossible to meet the microbiological limits by the exclusive use of UV irradiation or PAA.

Moreover, the introduction of PAA before UV guarantees, in equal dosages, significantly better results as compared to the case in which the disinfectant is introduced after the physical treatment. In fact, regarding this last case, the effectiveness of the combination of the two treatments simply results from the summation of the effects of the single disinfectants by direct action. However, when the PAA is introduced before the UV, the resulting effect goes beyond simple summation, which confirms a real synergy between the two treatments (Caretti & Lubello 2003).

Based on these results, the configuration which provides for the addition of PAA before UV guarantees, in equal dosages, significantly better results as compared to the case in which the disinfectant is introduced after the physical treatment. In fact, regarding this last case, the effectiveness of the combination of the two treatments simply results from the summation of the effects of the single disinfectants by direct action. However, when the PAA is introduced before the UV, the resulting effect goes beyond simple summation, which confirms a real synergy between the two treatments (Caretti & Lubello 2003).

Table 2 | Chemical–physical characteristics of the filtered effluents (mean ± st.dev)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Calice filtered effluent</th>
<th>Pistoia filtered effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total suspended solids</td>
<td>mg/L</td>
<td>2.6 ± 1.3</td>
<td>0.8 ± 1.2</td>
</tr>
<tr>
<td>Absorbance at 254 nm</td>
<td>cm⁻¹</td>
<td>0.59 ± 0.07</td>
<td>0.027 ± 0.011</td>
</tr>
<tr>
<td>Absorbance at 420 nm</td>
<td>cm⁻¹</td>
<td>0.056 ± 0.014</td>
<td>n.a.</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>n.a.</td>
<td>0.9 ± 0.3</td>
</tr>
</tbody>
</table>

n.a: not analysed.

As far as E. coli are concerned, the results obtained by the final pilot plant configuration, ranging the dosages of PAA and UV, are shown in Table 3.

The E. coli content in the Calice filtered samples before the disinfection treatment varied between 980 and 2,800 CFU/100 mL with a mean value of approximately 1,900 CFU/100 mL. Such values are significantly lower than the Pistoia’s ones because Calice WWTP treats not only municipal but also industrial wastewaters.

Nevertheless, because of the highest value of the UV₂₅₄ₙₘ absorbance, in order to reach similar disinfection efficiency, higher UV dosages are expected for treating mixed industrial and municipal Calice wastewaters than for treating the municipal Pistoia wastewaters.

The mean log inactivation, in the case of total inactivation, corresponds to the log of the maximum E. coli content measured in our experiments (5.03 for Pistoia and 3.45 for Calice).

The addition of the PAA upstream to the UV proved to be very effective for the inactivation of E. coli in the filtered effluent of both WWTPs. Within the experimented dose ranges, for both PAA and UV, the higher the dose, the higher the E. coli inactivation.

The effluent characteristics greatly influence the disinfection efficiency. As a matter of fact, the Calice WWTP effluent, which presents lower microbiological content but higher values of the UV₂₅₄ₙₘ absorbance, was significantly more difficult to disinfect by means of the combined treatment PAA/UV as compared to the Pistoia WWTP effluent.

Table 3 | Average values of log inactivation and E. coli content for different combinations of PAA and UV doses (values are average of 20 samples)

<table>
<thead>
<tr>
<th>PISTOIA</th>
<th>Mean log inactivation</th>
<th>Mean E. Coli content</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV (mJ/cm²)</td>
<td>PAA (mg/L)</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>3.62</td>
<td>3.99</td>
</tr>
<tr>
<td>4</td>
<td>3.95</td>
<td>4.13</td>
</tr>
<tr>
<td>8</td>
<td>4.25</td>
<td>4.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CALICE</th>
<th>Mean log inactivation</th>
<th>Mean E. Coli content</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV (mJ/cm²)</td>
<td>PAA (mg/L)</td>
<td>129</td>
</tr>
<tr>
<td>2</td>
<td>1.85</td>
<td>2.37</td>
</tr>
<tr>
<td>4</td>
<td>1.92</td>
<td>2.84</td>
</tr>
<tr>
<td>8</td>
<td>2.55</td>
<td>3.17</td>
</tr>
<tr>
<td>16</td>
<td>3.24</td>
<td>3.45</td>
</tr>
</tbody>
</table>

Table 4 shows, among all the experimented combinations of PAA and UV doses, the ones that guarantee the total inactivation or the compliance with the law limits for all the analysed samples.

In order to determine the best combination of PAA and UV doses between the different solutions that guarantee compliance to the Italian legislation, an economic analysis was performed considering a continuous (24h a day) running of the plant, no longer on a pilot scale but on a...
real scale (capacity of 300 m³/h). Costs include the sand filtration and the disinfection system with PAA and UV (equipment, chemicals, energy) and the addition of 2 ppm of PAA as a bacteriostatic agent in the storage tank.

Figures 2 and 3 show the isocost curves superimposed to the inactivation graphs for both Pistoia and Calice pilot plants.

As far as the Pistoia WWTP is concerned, the costs of UV and PAA combinations that are able to assure the compliance with the law value for all samples are in the range of 0.035–0.067 €/m³. The combination of 2 mg PAA/L and 192 mJ/cm² of UV was the cheapest solution.

As far as the Calice WWTP is concerned, the costs of UV and PAA combinations that are able to assure the compliance with the law value for all samples are in the range of 0.033–0.067 €/m³. The combination of 2 mg PAA/L and 170 mJ/cm² of UV was the cheapest solution.

Comparing Figures 2 and 3, we can observe that the UV dosage beyond which E. coli is totally inactivated regardless of the PAA dosage is lower for the Calice WWTP than for the Pistoia ones (170 and 220 mJ/cm², respectively).

In addition, the Calice WWTP effluent, in spite of its high absorbance at 420 nm, can be refined with a combination of PAA/UV, which has a cost similar to that required for the refinement of the Pistoia WWTP effluent. This can be attributed to the lower E. coli content of the mixed industrial and domestic wastewater.

**CONCLUSIONS**

The objective of this study was to investigate the suitability of the PAA/UV treatment for agricultural reuse of both the effluent of a municipal WWTP (Pistoia) and of a mixed municipal and industrial WWTP (Calice). According to the experimental results the following conclusions can be drawn.

- There are no major limitations for the use of the tertiary effluent as an irrigation source in plant nurseries. As far
as industrial wastewaters are concerned, the use of drip irrigation should be suggested and the use of the tertiary effluent is recommended for short periods.

- In the experimental conditions investigated, neither the treatment with only PAA nor the treatment with only UV are capable of guaranteeing the disinfection level required by Italian legislation for wastewater reuse in agriculture.

- Considering the combined treatment of the two disinfectant agents, the effectiveness increases and when PAA is added upstream the UV process synergic effect was evident. As a consequence, this configuration has been chosen in the final refinery treatment scheme for both the Pistoia and Calice pilot plants.

- In the final scheme of the pilot plants (Filtration and PAA/UV treatment), the most economically competitive solution which guarantees compliance to the limits of Italian legislation for agricultural wastewater reuse, is by the disinfection with a combination PAA-UV of 2 mg/L and 220 mJ/cm² for the municipal reclaimed wastewater and 2 mg/L and 170 mJ/cm² for the mixed municipal and industrial reclaimed wastewaters.

- In spite of the different characteristics of the Pistoia and Calice WWTP effluents in terms of absorbance and E. coli content, the costs for their refinement are very similar (0.035 and 0.033 €/m³ respectively).

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