Application of nanosilver in swimming pool water treatment technology†

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Abstract: The paper presents the possibility of applying a colloidal solution of nanosilver in a closed circuit of pool water treatment. The applied nanosilver solution is characterized as having a very high biocidal effect, with no negative impact on the human and animal body, or the environment. Samples of pool water for the control were taken from 5 points of pool circuit. The safety of water was appraised by comparing bacteriological and physicochemical tests results with admissible values specified in hygienic requirements. Results shows that nanosilver solution can be successfully applied for precoating the filter bed and supporting the disinfection system. A special attention was paid to the bacteriological purity and the stability of the disinfectant concentration.

Keywords: nanosilver; the quality of pool water; pool water treatment technology

1. Introduction

Due to high demand for water recreation activities and rehabilitation in water, swimming pool facilities must function correctly and the basis for proper operation are safe and reliable swimming pool installations.

Strict requirements regarding swimming pool water [1-5] caused traditional and one-stage filtration systems to be insufficient [6-9]. Because of that some of the existing facilities are being modernized and fitted with additional devices and processes that boost the efficiency of water treatment [10-12].

Swimming pool water treatment systems that guarantee healthy water include prefiltration, surface coagulation run in various filter beds, ultrafiltration, disinfection with sodium hypochlorite or calcium hypochlorite aided by ozonization or UV irradiation, and pH correction [6-12].

Pool water treatment processes may also incorporate nanosilver products. Nanosilver is increasingly used in consumer products from washing machines and refrigerators to other devices. Silver nanoparticles are known as excellent antimicrobial agents, and therefore they could be used as alternative disinfectant agents for the disinfection of drinking water or recreational water [13-16].

This paper presents the research on the use of colloidal solution of nanosilver in the technology of swimming pool water.

The main objective of the research was the analysis of the quality of swimming pool water treated with a system that incorporates: colloidal solution of nanosilver aiding the final disinfection of water with sodium hypochlorite, vacuum filter with multilayered bed and low pressure UV lamp.
2. Materials and Methods

In the tested swimming pool, during morning hours, there are physiotherapy sessions for patients suffering from various injuries. In the afternoon, there are swimming lessons for infants and their parents. The swimming pool is equipped with a vertical water flow system with a capacity of 30m³/h and 4 stations with massage jets. The swimming pool dimensions (3.2×5.4×1.2) allow for a comfortable rehabilitation of 6 to 8 persons. The swimming pool draws water from the municipal water supply system. Water deficits that are the result of evaporation, splashing and the need to wash filter beds are replenished by drawing water into the retention tank. The basic requirement for a correct circulation of swimming pool water is a closed circulation system with an active overflow. The treated water is introduced to the pool through 14 jets located at the bottom of the pool basin. The water is drained through the top overflow troughs to the retention tank. Then, the water is sucked by the circulation pump. Before the pump, there is a mesh filter whose aim is to capture large solid contaminants. The pump moves the water to the filter where, after the application of a disinfectant and a pH correction solution, it is directed to the swimming pool through heat exchangers. Before the filters, a coagulant solution is applied (2.5÷10% solution of aluminium hydroxide chloride). To impregnate the filter, it was precoated with 11L colloidal solution of nanosilver (hygienic certificate) on the first day of research. The swimming pool water treatment system uses a multilayered vacuum filter with sand and hydroanthracite bed with an area of 1 m² and height of 1.2 m. The filtrate pipe was supplemented with a low pressure UV lamp. The treatment system is an automatic system controlled by an analyzer monitoring the quality indicators values of the water that is drained from the swimming pool basin.

The samples for physicochemical and bacteriological tests were taken from five points in the pool water circuit: swimming pool basin (SP), retention tank (RT), before filter (BF), after filter and before UV lamp (AF) and water supply (WS).

The tests results, collected over a 2 month period, were analyzed. The water samples were subjected to bacteriological (once a week) and physicochemical (twice a week) analyses that measured basic control parameters of pool water quality [1-5].

The samples were collected and marked in accordance with applicable standards and methods [17,18].

The physicochemical parameters that best described the water quality in the tested pool were: pH (colorimetric method - photometer DSC 400, Dinotec and potentiometric method - HQ11D Digital pH meter kit, Hach), redox (potentiometric method - ORP electrode; HQ11D Digital, Hach), free and combined chlorine (DPD colorimetric method, photometer DSC 400, Dinotec and POCKET Colorimeter II, Hach), silver ion, oxidisability (COD), chlorides and nitrates (spectrophotometer DR5000 UV/VIS, Hach).

The bacteriological parameters that best described the water quality in the tested pool were: *Escherichia coli* (method compliant with: PN-EN ISO 9308-1:2004), total plate count in 36°C after 48 hours (method compliant with: PN-EN ISO 622:2004), *Legionella sp.* (method compliant with: PN-ISO 11731-2:2006) and coagulase positive staphylococci (method compliant with procedure: KJ-I-5.4-44M ver. 01 of 11.06.2007).

During the tests, the values of water pH, redox potential and the concentration of free chlorine and combined chlorine were read every day, directly from the screen of control and measurement device SCL DINOTEC. The obtained tests results were compared against the recommendations of DIN 19643 [1,3], WHO [2], ZHK NIZP-PZH [4] and the permissible values specified in the decree [5], (Table 1).
### 3. Results and Discussion

The physicochemical and bacteriological tests of the samples of swimming pool water taken from 5 points in the pool water circuit allowed to determine that the quality of water met the requirements in this regard. Table 2 presents the results of the bacteriological analyses demonstrating if the water is suitable for bathing and being the result of the used treatment method.

In all samples subjected to microbiological analysis no CFU (colony-forming unit) of *Pseudomonas aeruginosa* and coagulase positive staphylococci was found. CFU of *Escherichia coli* and fecal coliforms were found in water samples collected during the first day of the research, < 5 CFU of *E. coli* and < 5 CFU of fecal coliforms. CFU of *Legionella sp.* was detected three times in water supplementing the circuit (WS). Despite the presence of *Legionella sp.* in the water supplementing the circuit, the remaining samples: SP, RT, BF and AF did not contain CFU of *Legionella sp.*, proving the high efficiency of the treatment and disinfection system. In all water samples after the filter and before UV lamp (AF) the total plate count was also high and significantly exceeded the recommended values for pool basin water, i.e. 20 CFU/1ml. Such a high number of CFU of bacteria in the filtrate proved that they were being washed out from the bed. Despite the use of nanosilver for precoating the filter bed, the conditions in the filter were favorable for bacterial growth. Nevertheless, CFU of bacteria in other points demonstrated the effectiveness of the disinfection system.

#### Table 1. Recommendations and permissible values of swimming pool water quality

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Total plate count in 36°C after 48 hours (CFU/1mL)</td>
<td>&lt;200</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Coliform bacteria of the fecal type (CFU/100mL)</td>
<td>&lt;1</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td><em>Escherichia coli</em> (CFU/100mL)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><em>Legionella sp.</em> (CFU/100mL)</td>
<td>&lt;1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em> (CFU/100mL)</td>
<td>&lt;1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Coagulase-positive staphylococci (CFU/100mL)</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>pH (-)</td>
<td>7.2±7.8</td>
<td>6.5±7.6</td>
<td>6.5±7.6</td>
<td>6.5±7.6</td>
</tr>
<tr>
<td>Redox (mV)</td>
<td>720</td>
<td>750</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>Free chlorine (mgCl₂/L)</td>
<td>0.5±1.2</td>
<td>0.3±0.6</td>
<td>0.1±0.3</td>
<td>0.3±0.6</td>
</tr>
<tr>
<td>Combined chlorine (mgCl₂/L)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Silver (mgAg/L)</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COD (mgO₂/L)</td>
<td>-</td>
<td>4.0³</td>
<td>5.0³</td>
<td>4.0³</td>
</tr>
<tr>
<td>Chlorides (mgCl⁻/L)</td>
<td>-</td>
<td>-</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Nitrates (mgNO₃/L)</td>
<td>-</td>
<td>20</td>
<td>30</td>
<td>20</td>
</tr>
</tbody>
</table>

1 Depending on the method of water disinfection
2 WHO [23].
3 Difference in COD values in swimming pool water and COD in water supplementing circulation system.

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Table 2. Bacteriological parameters of water quality in tested pool circuit

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SP</th>
<th>RT</th>
<th>BF</th>
<th>AF</th>
<th>WS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total plate count in 36°C after 48 hours (CFU/1mL)</td>
<td>1 1 0 10 18</td>
<td>5 0 0 42</td>
<td>1 12 2</td>
<td>2.5·10³</td>
<td>5.7·10³</td>
</tr>
<tr>
<td>Coliform bacteria of the fecal type (CFU/100mL)</td>
<td>≤5</td>
<td>≤5</td>
<td>≤5</td>
<td>≤5</td>
<td>≤5</td>
</tr>
<tr>
<td><em>Escherichia coli</em> (CFU/100mL)</td>
<td>≤5</td>
<td>≤5</td>
<td>≤5</td>
<td>≤5</td>
<td>≤5</td>
</tr>
<tr>
<td><em>Legionella</em> sp. (CFU/100mL)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em> (CFU/100mL)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Coagulase-positive staphylococci (CFU/100mL)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1 shows the average values of physicochemical parameters that supplement the bacteriological ones and co-determine if the pool is fit for use.

Water pH in every collection point was within the required range, i.e. 6.5-7.6 (Figure 1a).

Values of redox potential are especially important for pool basin water. The values obtained during in situ tests were within the range of: 725-765 mV (on average: 758 mV) what proved that the bathers were sufficiently protected against contamination (Figure 1b).

The concentrations of free chlorine in the pool water (Figure 1c), due to the automatic dosage of NaOCl solution, were stable and within the range of: 0.38-0.43 mgCl₂/L (on average: 0.41 mgCl₂/L). A systematic decrease of free chlorine was observed in the subsequent parts of the pool circuit. Filtering the water through a filtration bed with an anthracite layer resulted in a decrease in the concentration of free chlorine, on average, by 88.68%.

Due to the adverse effects on the bathers [19-22], the permissible content of combined chlorine in pool water according to [1-4] is 0.2 mgCl₂/L, and according to [5] is 0.3 mgCl₂/L. There were no complaints from the bathers when the concentrations of bounded chlorine in water samples taken from the pool basin exceeded the concentrations stipulated in DIN19643, on average, by 0.11 mgCl₂/L (Figure 1d).

Because the circuit water was supplemented with 11L of colloidal solution of nanosilver, the presence of silver was determined as an additional parameter. It should maintain microbiological stability in the pool basin and be neutral to the bathers. According to the recommendations of WHO [23] the content of silver in drinking water should not exceed 0.01 mg/L. The concentrations of silver in the pool circuit water were, on average: 0.002-0.008 mg/L (Figure 1e).

During the tests, in the majority of samples, oxidisability index (COD) was below 1.0 mgO₂/L (Figure 1f) and the permissible value is 5 mgO₂/L. Oxidisability above the permissible value (9.46 mgO₂/L) was detected in only one water sample from SP. In the same water sample the value of total organic carbon (TOC) also exceeded the permissible value and amounted to 14.5 mgC/L. High contamination level of water in the analysed sample was also confirmed by high concentration of chlorides, 282 mgCl⁻/L.

The content of chlorides and nitrates in the tested water was satisfactory (Figure 1g and 1h). However, during the filtration cycle they were concentrating in the pool basin. As the water supply was low in concentrations of chlorides (12 mgCl⁻/L) it was determined that the intake of “fresh”
water for the pool circuit was not sufficient. This fact was also confirmed by the concentration of nitrates which increased with the filtration time.

Figure 1. Physical and chemical parameters of water quality in tested pool circuit: (a) pH; (b) Redox; (c) Free chlorine; (d) Combined chlorine; (e) Silver; (f) COD; (g) Chlorides; (h) Nitrates in swimming pool (SP), retention tank (RT), before filter (BF), after filter (AF) and in water from supply system (WS)
4. Conclusions

The performed tests indicate the effectiveness of the proposed pool water treatment system incorporating dosing of nanosilver colloidal solution, vacuum filter with multilayered bed and irradiating the circuit water with UV light. The parameters of water quality in the pool basin were compliant with the requirements in this regard.

- The low levels of silver in pool water samples about 0.008 mg/L did not cause a risk to the health of bathers. Silver concentrations up to 0.1 mg/L may be tolerated in the case of silver salts to maintain the bacteriological quality of drinking water [24].
- Despite the use of the colloidal solution of nanosilver, as bacteriostats product, it was found that favorable conditions for the development of bacterial colonies were present in the bed. The anthracite and sand filtration bed facilitated the growth of bacteria which then were washed out to the filtrate.
- Although CFU of bacteria in the filtrate samples was high, water from the pool basin contained only 1 CFU/1mL (permissible number: 100 CFU/1mL). Thus, the two-step disinfection (UV + NaOCl) was sufficient to ensure safe bath.
- The redox values further confirmed the effectiveness of protecting the pool water against bacteriological contamination.
- Additionally, a systematic decrease in free chlorine concentration was observed in water samples taken from the subsequent parts of the pool circuit (filtering the water through a filtration bed with an anthracite layer decreased it by 88.6%) and the systematic increase of chlorides and nitrates during the filtration cycle indicated that an insufficient amount of water was taken into the pool circuit.

Institute of Water and Wastewater Engineering research team continues to study the use of silver salt-based products to support swimming pool disinfection process.

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Author Contributions: J. Wyczarska-Kokot. and F. Piechurski conceived and designed the experiments and performed the experiments and analyzed the data; J. Wyczarska-Kokot wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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4. ZHK NIZP-PZH. Recommendations on sanitary and hygienic requirements for swimming pools and water quality in pools for babies and children from 6 months to 3 years old, 2012 (in Polish).


