

APPLICATION OF SOLAR ENERGY IN WATER TREATMENT

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Abstract

In addition to the already well-known application in metal production, electroplating, electrochemical energy sources, electrochemistry is also applied in other branches of industry. Today, electrochemical technologies for the treatment of wastewater and drinking water are increasingly present. In recent years, new advanced oxidation processes based on electrochemical technology - Electrochemical advanced oxidation processes (EAOPs), have been developed for the treatment of persistent pollutants, which cannot be removed by conventional water treatments. EAOPs are based on "in situ" electrolytic formation of strong oxidants in an electrochemical reactor, able to degrade almost all organic pollutants. Despite their effectiveness in degrading different types of pollutants, the biggest challenge for EAOPs is high electricity demand to power these systems, which can have serious consequences from both an ecological and an economic point of view. The use of electricity from the distribution network to power electrochemical reactors is the biggest barrier to achieving commercial success of this technology. A possible solution to this challenge is the application of direct solar UV radiation to produce electric energy by use of a solar photovoltaic (PV) arrays for power supply of EAOPs. The aim of the research was to demonstrate the feasibility of using EAOPs directly powered by PV systems, as a sustainable system for efficient water treatment.

Key words: green energy, EAOPs, water pollution

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1. Introduction

There is an increasing demand for sustainable wastewater treatment (WWT) systems. When choosing WWT technologies, the impact of factors such as efficiency, sustainability, compliance with environmental regulatory standards and technology costs, should be considered (Gallego Schmid & Tarpani, 2019).

In the conventional WWT (coagulation, biological and chemical oxidation, etc.) many pollutants are only partially removed or even "pass" unchanged through WWT plants. Some of these pollutants can have serious consequences for human health and the environment. On the other hand, with advanced technologies it is possible to obtain high quality water.

Advanced oxidation processes (AOPs) are one of the most efficient methods for treatment of wastewater containing organic pollutants. AOPs are based on the *in situ* production of strong oxidants, mainly hydroxyl radicals ($\text{OH}\cdot$), which are one of the most powerful oxidizing species, capable of unselective oxidizing any organic pollutant to complete degradation or their transformation into less toxic by-products (Khan et al., 2020). AOPs in which the initiator of the $\text{OH}\cdot$ formation is electricity are named electrochemical advanced oxidation processes (EAOPs). These processes are based on the electrolytic *in situ* generation of $\text{OH}\cdot$ in an electrochemical reactor (ECR) and include processes such as electrochemical oxidation, electro-Fenton, photoelectrochemical and sono-electrochemical technologies, and capacitive deionization (Malinović et al., 2021). Generally, these processes do not require the addition of reagents, and pollutants are degraded by direct oxidation on the anode surface or indirectly oxidized by $\text{OH}\cdot$, or other active species such as chlorine compounds, O_3 , persulfates and H_2O_2 , air (Poyatos et al., 2010; Moreira et al., 2017). The advantages of EAOPs include high energy efficiency, possibility of automation, easy handling, simplicity of equipment and safety work. Disadvantages of the process are related to the low conductivity of many wastewaters, which requires the addition of supporting electrolytes (salts), costs of electricity supply, loss of activity and shortening life of the electrodes due to the deposition of organic matter on its surface (Sires et al., 2014).

Costs analysis of the electrochemical WWT shows that the main costs are investment and electricity costs for electrolysis. Investment costs include costs of designing and manufacturing of ECR, the addition of supporting electrolyte if the wastewaters conductivity is low, and the purchase of electrode materials. However, the biggest costs and at the same time the main disadvantage of the EAOPs are the costs of electricity for water electrolysis (Muddemann et al., 2021).

The use of renewable energy, such as solar photovoltaic cells, as an energy source for powering EAOPs is developing in recent years and is currently a interesting topic in which direct powering and the use of intermediate components for energy storage (batteries) are being investigated for obtaining efficient integrated technology. It is important to note that PV produce direct current (DC), which can be directly used by the EAOPs system. The direct use of electricity from the PV array to the ECR could provide energy autonomy for solar EAOPs as it does not require any connection to the grid (GilPavas et al., 2018; Valero et al., 2010).

Although it is still under development for optimization and further improvements, numerous results on independent, so-called "off-grid" PV modules that drive the electrochemical degradation of various organic pollutants at the laboratory/pilot level are literary available. In several studies, the electrodialysis process powered by PV cells was used for the treatment of groundwater (AlMadani, 2003), brackish water and reverse osmosis concentrate (Uche et al., 2013; Herrero-Gonzalez et al., 2018). In the largest number of studies, the electrooxidation (EO), as the most popular EAOPs, powered by PV cells (PV-EO) was used for the treatment of various wastewaters and pollutants. The PV-EO system proved to be effective in the treatment of river water (Ochiai et al., 2010), domestic wastewater (Cho et al., 2014), wastewater contaminated with phenol (Park et al., 2008), Remazol RB 133 dye (Valero et al., 2010), Methyl Red dye (Nie, et al., 2020), 2,4-dichlorophenoxyacetic acid (Souza et al., 2015), 2-nitrophenol (Nie et al., 2016). Also, the electro-Fenton process powered by PV cells has proven to be efficient for the treatment of textile industry wastewater (GilPavas et al., 2018) and the removal of Brilliant Blue FCF dye (Ganiyu et al., 2019).

1.1 Materials and methods

The experimental part of the research presents the application of EO process powered by PV array (PV-EO) for the removal of textile azo dye from synthetic wastewater (SWW) prepared in laboratory. The batch ECR was 500 cm³ capacity, in which electrodes of the same dimensions (60x50x2 mm) are placed. ECR was powered by electricity obtained from the monocrystalline silicon PV solar panel nominal power of 170W, a maximum current of 8.33 A and a maximum voltage of 20.41 V (SolarFAM, Netherland). The panel is placed on the roof of the Faculty of Technology University of Banja Luka (angle 45°, south oriented). Solar charge controller (MPPT) (SolarFAM, Netherland) was connect between PV and the 12 V batterie (MK Powered, 12 V/74 Ah) to ensure maximum electric energy available was always drawn from solar cells. The batterie was connected directly to output DC voltage regulator to regulate the current supply to the ECR. The experimental setup for PV-EO process is shown in Figure 1.

All experiments were performed at an ambient temperature ($\approx 20^{\circ}\text{C}$) with initial SWW volume of 400 cm³. For the preparation of SWW, *Bemacid Red E-TL* (BR) dye (CHT GmbH, Germany) was used and sodium chloride, 99.5% NaCl (Lachner, Czech Republic) was added as supporting electrolyte to increase electrical conductivity of SWW. The initial dye concentration was approximately 100 mg/L. Exact concentration before and after treatments was determined spectrophotometrically (PerkinElmer, LAMBDA 25).

Stainless steel, EN 1.4301 (SS) and graphite felt (GF) were used as cathodes and mixed metal oxides (MMO) were used as anodes: Ru mixed oxide (Ti substrate coated with 6g Ru/m²) and Ir-Ru mixed oxide (Ti substrate coated with 6g Ru-Ir/m²), (Metakem, Germany). Different combinations of anode : cathode pairs were placed in the ECR, connected to the output DC regulator and the current density was adjusted to 5 mA/cm² value (which in this case corresponded to a current intensity of 0.3 A).

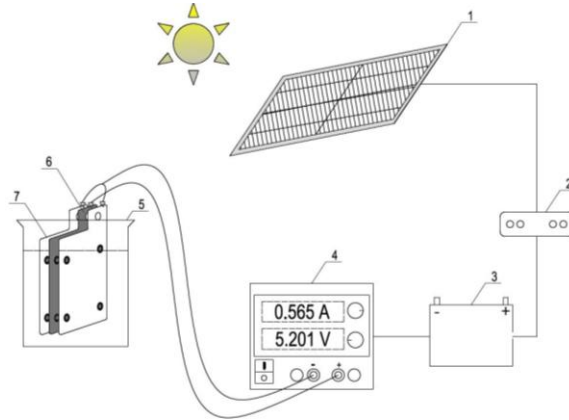


Figure 1. Scheme of PV-EO experimental setup (1- solar panel, 2- MPPT; 3- battery, 4- voltage and current regulator, 5- electrochemical cell, 6- anode, 7-cathodes)

2. Results

The results of BR removal from SWW by the PV-EO processes are expressed through the removal efficiency (E , %) and calculated according to the equation (1), where c_i and c_f are the initial and final concentration of BR expressed in mg/L.

$$E = \frac{c_i - c_f}{c_i} \cdot 100\% \quad (1)$$

The electrical energy used to remove a unit of pollutant or to treat unit of wastewater volume represents one of the most important technological indicators of the ECR operation, because it affects the overall cost of treatment. Specific energy consumption (W_{sp}) is calculated according to the equation (2), where I - is current [A], U - voltage on the electrochemical reactor [V], t - time [h], m - mass of the removed pollutant [kg], V - volume of wastewater [m^3].

$$W_{sp} = \frac{U \cdot I \cdot t}{m_{pollutanta}} \left[\frac{kWh}{kg_{pollutanta}} \right] \text{ or } W_{sp} = \frac{U \cdot I \cdot t}{V_{wastewater}} \left[\frac{kWh}{m^3} \right] \quad (2)$$

In this research, the impact of electrode material, electrolysis time and supporting electrolyte concentration on dye removal efficiency were examined and the energy consumption was also calculated. The results of the PV-EO process are shown in the following graphs (Figure 2, Figure 3 and Figure 4).

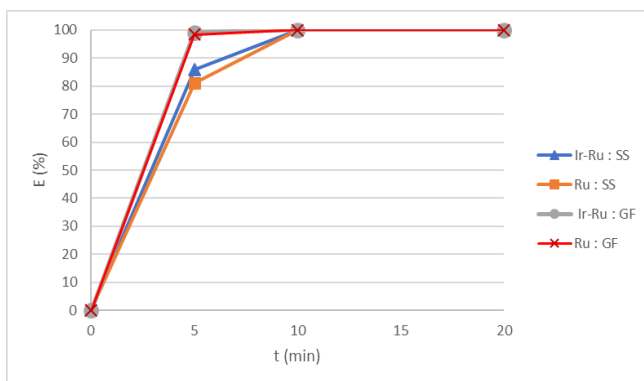


Figure 2. The impact of electrode material on BR dye removal efficiency at different treatment time ($j = 5 \text{ mA/cm}^2$; $C_{\text{NaCl}} = 2 \text{ g/L}$)

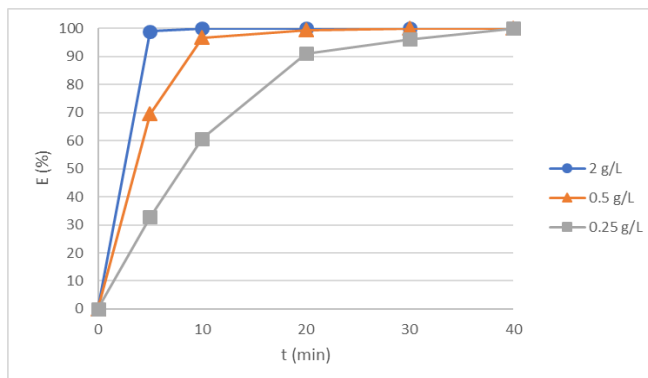


Figure 3. The impact of supporting electrolyte concentration on BR dye removal efficiency at different treatment time ($j = 5 \text{ mA/cm}^2$; Ir-Ru : GF electrode pair)

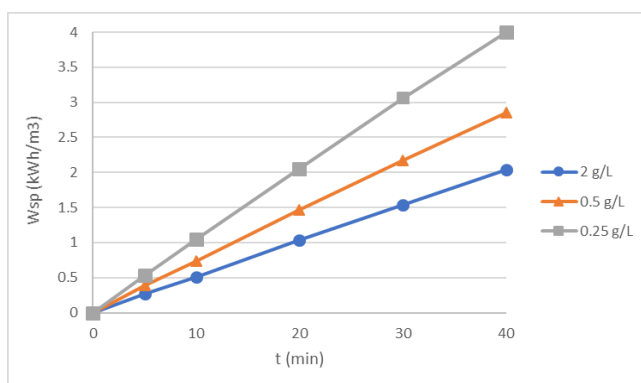


Figure 4. Energy consumption at different supporting electrolyte concentration and different treatment time ($j = 5 \text{ mA/cm}^2$; $C_{\text{NaCl}} = 2 \text{ g/L}$)

3. Discussion

The anodes are divided into “active” and “inactive” electrodes. “Active anodes” (low oxygen evolution overpotential) are good electrocatalysts for oxygen evolution (e.g., IrO_2 , Pt, RuO_2), and “inactive anodes” (high oxygen evolution overpotential) are poor electrocatalysts for the oxygen evolution overpotential (Malinović et al., 2021). The anodes used in this research are “active” and known for their electrocatalytic activity for chlorine evolution. These anodes have good electrocatalytic properties, but also long-term mechanical and chemical stability. Thanks to these properties, chlorine evolution activity can be effectively utilized for disposal of organics through the generation of active chlorine via indirect oxidation (Jiang et al., 2021; Feng et al., 2016). Based on the obtained results shown in Figure 2, it can be observed that treatment is highly efficient and almost complete BR dye removal is achieved in 10 minutes of treatment with all tested electrode pairs. Both MMO anodes are very efficient, but Ir-Ru MMO shows a slightly higher efficiency with a shorter treatment time. As a cathode material, GF proved to be efficient than SS. Since GF is a significantly cheaper material compared to SS, only electrode pair Ir-Ru: GF was used in the further research.

As the treatment proved to be effective in a very short time and it was shown that cheap cathode materials can be used, further research focus on reducing the concentration of the supporting electrolyte. Supporting electrolyte is necessary where conductivity of the wastewater is low. Electrical conductivity is directly related to the voltage on the ECR. When the water conductivity is higher, the voltage on the ECR is lower and consequently the lower W_{sp} , in accordance with equation (2). In all performed experiments NaCl was chosen, as one of the commonly used supporting electrolytes (Jiang et al., 2021). In addition to increasing the conductivity of water, chlorides present in water can be easily oxidized to chlorine and other reactive chlorine species (hypochlorite, hypochlorous acid) (Sires et al., 2014). In this way, in addition to the OH^\cdot formed *in situ* in ECR by the electrolysis of water, these reactive chlorine species increase the rate of oxidation and decomposition of

organic pollutants in water. From Figure 3 it can be seen that by reducing the NaCl concentration, removal efficiency decreases and a longer time is needed for complete dye removal. Also, as the NaCl concentration decreases, energy consumption increases (Figure 4).

In the EAOPs supplied with electricity from the distribution network, extending the treatment time is not desirable, because more energy is consumed, which makes the process more expensive. In that case, supporting electrolyte concentration is increased in order to reduce the voltage on the reactor and reduce the treatment time - and thus the treatment cost. But, since in these experiments the ECR was supplied with electricity from a solar panel, it provided the possibility to use lower NaCl concentrations and longer treatment times. In this way, the cost related to the addition of supporting chemicals is reduced.

In order to use energy more efficient and further simplify the process, direct connection of PV array to the ECR can be performed and use of storage battery systems can be avoided. This clearly contributes to the efficient use of energy (no energy losses in battery charge-discharge cycles) and reduces investment and maintenance costs of the storage system. But, changes in the intensity of solar radiation during the day lead to significant energy fluctuations, so the ECR is powered by a non-constant energy source. This power profile can affect the performance and efficiency of WWT (Souza et al., 2015). For the stated reason, the experiments were performed only by using the current stored in the battery.

The price of electricity varies from country to country. For example, currently the electricity price for industrial use in Europe is between 0.023 - 0.262 € per kWh/m³. Treatment of 1 m³ of wastewater containing BR dye as a pollutant, under experimentally determined treatment conditions ($C_{NaCl} = 0.25$ g/L, $j = 5$ mA/cm²) costs between 0.092 - 1.048 € for 40 minutes of treatment. Under these conditions, the electrochemical process enables the maximum BR removal (100%) to be achieved. This is one example of a very cheap treatment. However, in accordance with equation (2), energy consumption can be calculated per 1 kg of removed pollutant. In this case, the energy consumption for removing 1 kg of BR dye under the specified conditions amounts to 0.39 - 4.53 €. This can still be considered as cheap treatment, but one must keep in mind that some of the treatments would be significantly more expensive. This means for more polluted wastewater, the treatment would take longer, and therefore energy consumption would be higher.

4. Conclusions

Electrochemical technologies in WWT have great potential. From an environmental point of view, they have an advantage over conventional WWT, due to their high efficiency in the removal of pollutants and the fact there is no use of additional chemicals, or it is used in smaller quantities. The main lack in their mass application is economic profitability. It is necessary to invest additional research efforts in order to reduce the price of electrode material, extend electrodes lifetime, reduce energy consumption and use renewable energy sources. This research has shown that electrooxidation processes powered by renewable energy from solar

panel can be efficient, sustainable and cost-effective treatment for dyes removal from textile industry wastewaters. Finally, it can be concluded that EAOPs in combination with green renewable energy sources have great potential for their implementation and adapting the process on a commercial scale.

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