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Research Article

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Removal Organic Matter and of Phosphates Using Photochemical and Biological Methods for the Treatment of Municipal Wastewater in Peru

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Abstract

In this work, the percentage of removal of organic matter and phosphates from municipal wastewater of the Wastewater Treatment Plant (WWTP) Puca Puca, Ayacucho Region, Peru was determined by applying the combined method of photochemical water treatment and biological, which consists of coupling the photolysis process and the microalgae culture technique using Chlorella sp. The experience was carried out at the laboratory level using a photoreactor with an ultraviolet (UV) lamp for the photolysis process and a set of bioreactors that were illuminated with a light emitting diode (LED) lamp and continuously injected with CO2 from the air and a pure gas system during the biological process. Finally, with the application of the integrated photochemical and biological method, it was possible to reduce the organic matter of the municipal wastewater of the Puca Puca WWTP from 226 to 102.6 mg/L (54.60%) and from 93 to 55.17 mg/L (40.68%) for chemical and biochemical oxygen demand respectively; and phosphates from 6.8 to 4.1 mg/L (33.82%). A similar performance was observed in the cultivation of microalgae with wastewater without prior treatment with Photolysis. In this case, the decrease in chemical and biochemical oxygen demand was from 226 to 90.9 mg/L (59.78%) and from 93 to 48.78 mg/L (47.55%) respectively, and phosphates from 6.8 to 4 mg/L (41.18%).

Keywords: Biochemical oxygen demand, Chlorella sp, Chemical oxygen demand, Photolysis, Phosphates.

Introduction

Discharging municipal wastewater without proper treatment is a major challenge today. A large majority of traditional wastewater treatment plants (WWTP) discharge into natural water bodies without proper treatment because these systems have not been designed to effectively remove emerging pollutants [1]. Traditional pollutants in municipal wastewater are characterized by high levels of organic matter, nitrogen, chlorides, sulfides, volatile acids, fats and oils of animal or plant origin [2]. There are also organic microcontaminants called Emerging Pollutants (ECs) or Persistent Organic Pollutants (POPs), they are organic traces of synthetic organic substances that provide pharmaceutical residues, detergents, personal care products, pesticides, among others [3, 4].

Therefore, in domestic wastewater we can find various types of pollutants, but the most worrisome are POPs and nutrients such as phosphate due to their negative effects on ecosystems. Traces of POPs bioaccumulate in the tissues of living beings through the food chain and once in the body, they can cause cancer, damage to the nervous, reproductive, immune or liver systems of humans [5]. Likewise, phosphates derived from the use of causal fertilizers and detergents in rivers and lakes with eutrophication problems affect the life of various aquatic species [6]. Likewise, they can produce toxins through the proliferation of cyanobacteria and limit the transport of oxygen to the tissues [7].

Supreme Decree No. 004-2017-MINAM where the environmental quality parameters (EQPs) for water are approved, set the maximum allowable limits for Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) for vegetable irrigation water and animal drink are 15 and 40 mg/L respectively [8]. Also mentions that the effluents from the WWTP usually have BOD and COD levels between 100-400 mg/L and 200-500 mg/L respectively [2]. Like many municipal wastewater treatment plants, the Puca Puca plant (located in the Huanta district of Ayacucho Region, Peru) borders the maximum allowable limits for organic matter in municipal water discharges.

For example, an analysis of the water quality of the effluent from the Puca Puca plant shows that the COD level (192 mg/L) is close to the maximum allowed limit established by Supreme Decree No. 003-2010-MINAM for effluents of domestic or municipal wastewater treatment plants (COD = 200 mg/L) and accurately exceeds the Environmental Quality Standards (EQS) established by Supreme Decree No. 004-2017-MINAM for irrigation water for vegetables and animal beverages (COD = 40 mg/L) [8, 9]. The Puca Puca plant collects domestic and sewage water from the central areas of the city and discharges to the Chiwa river, in turn they are used for irrigation of agricultural areas of tall stem plants such as papaya and pacay and short stem such as vegetables, alfalfa and others [10].

In this context, it is proposed to couple the photochemical method (Photolysis) with a biological one (Chlorella sp. cultivation) to improve the physicochemical characteristics of municipal wastewater and generate biomass for the generation of other valuable. This integrated system can be applied in municipal wastewater treatment plants as an alternative option to traditional methods.

Materials and Methods

Photolysis Process

Photolysis belongs to the family of advanced oxidation processes and use of ultraviolet energy to degrade some
organic pollutants. Due to UV energy, pollutants reach an excited singlet state that can later produce triplet states and undergo haemolysis, heterolysis or photoionization. In many cases, homolytic cleavage can produce R* radicals (see equation 1). These radicals using chain reactions produced smaller but molecular end producers [11].

$$R - R + hv \rightarrow R - R^* \rightarrow 2R^* \quad (1)$$

Biological Process

Microalgae require nutrients such as light, carbon, nitrogen, and phosphorus for their growth; therefore, these photosynthetic organisms are used in municipal wastewater treatment systems due to treat wastewater and high levels of biomass growth. The most important biological reactions occur during cell growth and the degradation of organic matter [12]. Growth kinetics, which may be limited by a nutrient, are normally represented using the Monod equation (see equation 2) [13].

$$\mu = \mu_m \frac{S}{K_S + S} \quad (2)$$

Where

μ_m: maximum specific growth rate (d^{-1})
μ: specific growth rate (d^{-1})
S: growth limiting substrate concentration (g/L))
K_S: semi-saturation constant, substrate concentration such that the growth rate is half the maximum (g / L)

Sample

The sampling points of the municipal wastewater Puca de Huanta Ayacucho Region were selected at random. 15 liters of wastewater were collected in dark hermetic gallons and were transported in conditioned coolers to the Chemical Engineering Laboratory of the Faculty of Chemical and Textile Engineering of the National University of Engineering, where the corresponding treatment was carried out.

Obtaining the inoculum

A representative sample of Chlorella sp microalgae was provided by the Institute del Mar del Peru (IMARPE). Following the working proportions of the mentioned institute, 10 mL of the sample (see figure 1) supplied was added to 40 mL of municipal waste water sample. The culture was performed in a 250 ml Erlenmeyer flask for 5 days, and was illuminated with an LED lamp and injected CO_2 until the microalgae increased their population density after consuming the nutrients present in the wastewater. Once the culture reached a density of 0.0301 g/L, it was taken to continue with the experimental stage.

Figure 1: Inoculum

Experimental procedure

The research was carried out at the laboratory level and an attempt was made to relate the variables through a systematic and controlled process. For this, two residual water treatment methods were adapted: Photochemical (UV radiation) and Biological (Chlorella sp culture). A photocatalytic reactor (see figure 2) was used carry out the Photolysis and glass and plastic containers that functioned as bioreactors for the cultivation of Chlorella sp in municipal wastewater.

In Photolysis, 750 ml of municipal wastewater after characterization was exposed to ultraviolet radiation (190 y 280 nm) [11]. Dissolved oxygen was measured every 10 minutes by triplicate, and BOD, COD and phosphorus tests were performed before and after treatment.

Figure 2: Photoreactor used in photolysis

The biological method consisted of two experimental groups. The first group is conforming by 3 culture units of Chlorella sp microalgae in 250 mL capacity Erlenmeyer flasks, where the municipal wastewater used was previously exposed to UV radiation. The first flask was intermittently injected with 99.9% CO_2 in a flow range of 1 LPM for 3 seconds every half hour; the second was supplied with air continuously (0.03% of CO2) and the last with no gaseous fluid [14]. The second group had the same conditions as the first, but wastewater was used without being exposed to UV radiation previously. Both groups were performed in duplicate and the optical density was continuously measured to assess whether or not there is a significant difference between their microalgae growth averages. Then, in both groups (see figure 3), the unit with the highest microalgae growth was replicated in 2 L.

Figure 3: Schematic of the experimental procedure

In order to report numerical data and treat them statistically, aliquots will be taken sequentially to measure absorbance (688 nm) pH, temperature and phosphates [15].

Results and Discussion

Characterization of the wastewater from the Puca Puca WWTP

The characterization was made to the samples taken in the affluent and effluent of the Puca Puca WWTP.

Table 1: Characterization of the affluent and effluent of the Puca Puca WWTP

Characterization		WWTP Puca Puca	
Parameters	**Unit**	**Affluent**	**Effluent**
COD	mg/L	226	192
BOD	mg/L	93	69
Phosphate	mg/L	6.8	4.5
pH	-	7.72	7.98
Temperature	°C	20.1	20.3
Conductivity	m/S	640	660
color	-	200	275

The photolytic treatment gradually degrades the organic matter and this is evidenced by the increase in dissolved oxygen during the treatment (Dissolved oxygen = 2.150 + 0.08 time, r2=0 ,976). In 20 minutes, an acceptable level of dissolved oxygen was obtained (4 mg/L). The BOD and COD removal percentage after 50 minutes of UV radiation treatment were 67.20% and 76.55% respectively.

During the biological treatment in groups, it was observed that group 1 (see figure 5), biological treatment with residual water previously exposed to UV radiation, showed maximum microalgal growth on day 12. The control unit presented a long latency time that lasted until the ninth day immediately starting a fairly pronounced exponential growth, while the units cultivated with CO2 and air supply had a similar behavior among them. The latter presented a minimum latency period of 3 days and a prolonged exponential phase with not so steep inclination. The maximum optical densities reached by the crops with CO_2 and air supply were 62.65 and 70.5 respectively, while the control unit only reached a maximum density of 58.75.

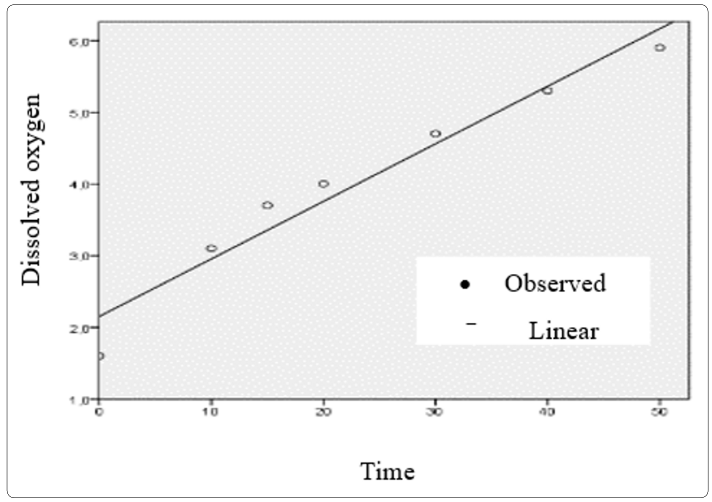

Figure 4: Dissolved oxygen vs Time

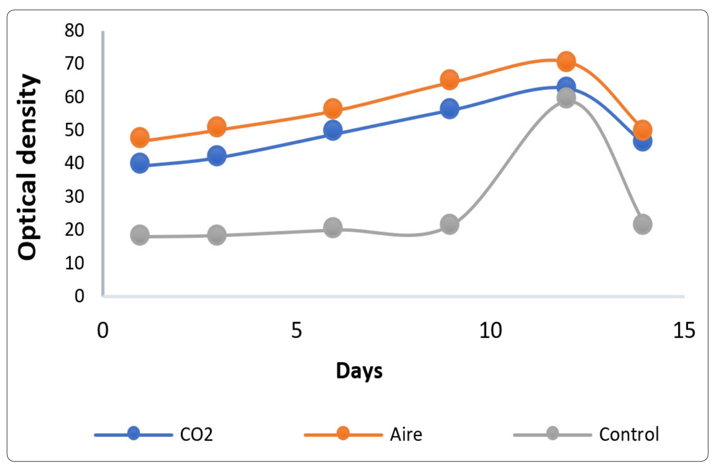

Figure 5: Optical density vs Days (group 1)

In group 2 (see figure 6), biological treatment with residual water without prior exposure to UV radiation, it was observed that the maximum densities reached by the control units, culture with CO2 supply and with air were 45.85, 70.2 and 75.75 respectively in 9 days of culture. The control unit did not present an adaptation phase, but a short exponential phase. Units with CO2 and air supply had a similar cell growth, they showed a smoothed exponential phase from day 3.

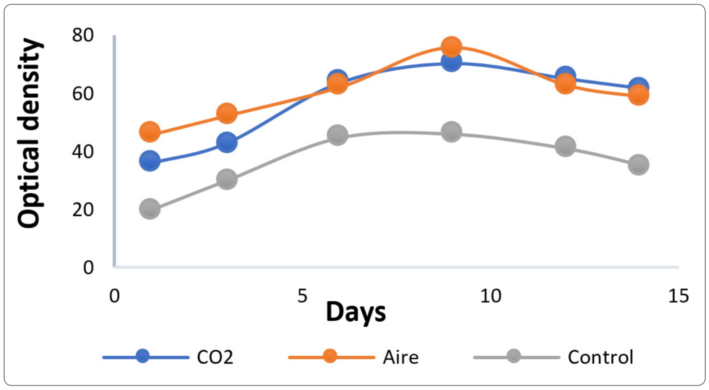

Figure 6: Optical density vs Days (group 2)

Replicated samples from groups 1 (with UV) and 2 (without UV) showed maximum density, productivity and specific growth rate of 69.65, 0.024 (g / L / day), 0.192 (day ^ -1) and 72.95, 0.024 (g / L / day), 0.30 (g / L / day) respectively. The maximum growth time reached by groups 1 and 2 was 12 and 9 days respectively without presenting the adaptation phase.

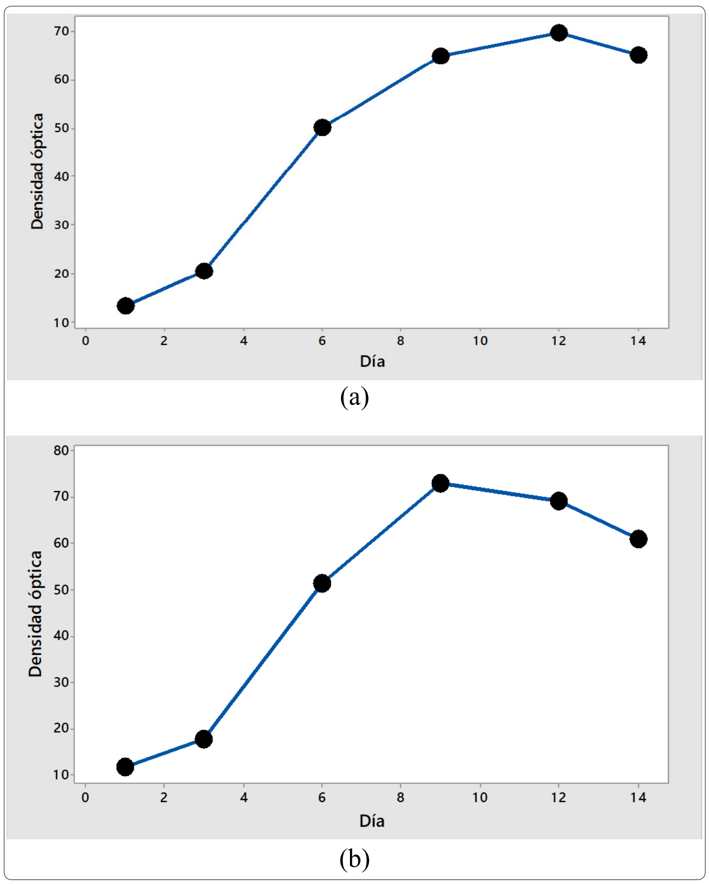

Figure 7: (a), Growth of Chlorella sp in culture with continuous air supply. (b) with UV

Phosphates were slowly reduced after the different treatments. It was observed that the photolytic process removes phosphates very little (from 6.8 mg/L to 5.9 mg/L) and the biological process with and without exposure to UV rays reduces the phosphate level to approximately 4 mg/L. The equation representing the reduction of phosphates for the Biological treatment with UV is as follows: Phosphorus (mg/L) = 3,838+, 075/Biomass (mg/L), r2 = 0.966).

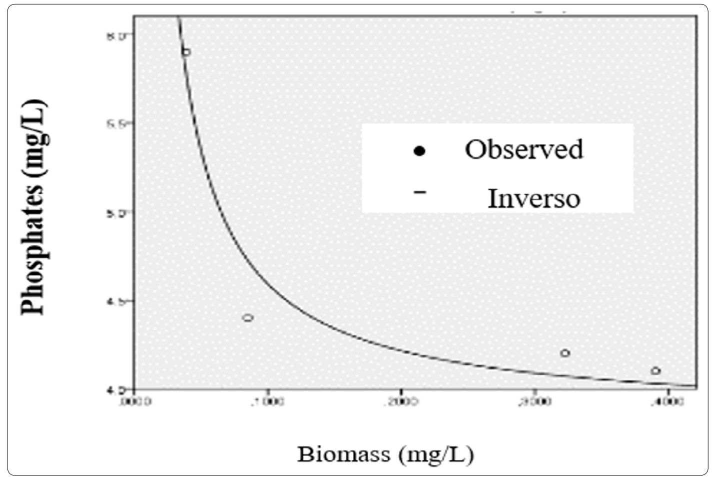

Figure 8: Phosphate reduction vs biomass growth

The characterization of municipal residual water after the treatments applied were:

Table 1: Characterization of wastewater after treatments

Parameters	Photolysis	Biological +UV	Biological Without UV
COD (mg/L)	53	102.6	90.9
BOD (mg/L)	30.5	55.17	48.78
Phosphate (mg/L)	5..9	4.1	4
pH	7.9	9.42	9.42
Temperature °C	21	23	22.9
Conductivity (m/S)	680	530	540
color	170	500	500

Regarding the results obtained from the chemical oxygen demand obtained through the photolytic process, it can be affirmed that the COD analysis in our experience showed a removal rate of 76.55%, which is significantly higher than the results obtained by 11.42% and 6% respectively [16, 17]. This difference is probably due to the characteristics of the wastewater used by the authors (high content of initial organic load) and therefore the photodegradation process turns out to be less efficient due to the difficulty in degrading.

On the other hand, regarding the removal of organic matter, it was observed that the study achieved a COD reduction percentage of 74.4% and our experiment 59.78% [18]. Both tests had a cultivation time between 7 and 10 days and similar experimental conditions such as the use of Chlorella as a microalgae base to treat municipal wastewater and CO_2 supply from various sources such as air and air enriched with CO_2.

Regarding productivity, in the study carried out by 0.3302g/L/day was obtained, which is higher than the value obtained in our experience (0.024g/L/day), possibly due to the difference in the assimilation capacity of each Chlorella microalgae strain, the low initial nutrient content of the wastewater collected by our study or perhaps the limited light exposure on the medium. Finally, the phosphate removal percentage values obtained by different authors such as were in the range of 75 to 88% showing to be almost double what was obtained in this experience (41.18%) [18,19].

Conclusions

After comparing the percentages of removal of BOD, COD and phosphates, it is concluded that photolysis treatment is more effective in reducing BOD and COD levels than for phosphates. Contrary to this, biological treatment with microalgae culture removes phosphates better than organic matter (BOD and COD). In some cases, the pH in microalgae cultures tended to grow continuously, but it can be controlled with a minimal injection of CO_2. Regarding temperature, this varied throughout the crop between 22 and 25°C. Finally, with the application of the photochemical and biological method, it was possible to reduce the organic matter of the municipal wastewater of the Puca WWTP from 226 to 102.6 mg/L (54.60%) and from 93 to 55.17 mg/L (40.68%) to the chemical and biochemical oxygen demand respectively; and phosphates from 6.8 to 4.1 mg/L (33.82%). However, a similar performance was observed in the cultivation of microalgae with wastewater without prior treatment with Photolysis. In this case, the decrease in chemical and biochemical oxygen demand was from 226 to 90.9 mg/L (59.78%) and from 93 to 48.78 mg/L (47.55%) respectively, and phosphates from 6.8 to 4 mg/L (41.18%) [20].

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