Chapter 6

Treatment of Textile Wastewater Using a Novel Electrocoagulation Reactor Design

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Abstract

This study explored the best operating conditions for a novel electrocoagulation (EC) reactor with the rotating anode for textile wastewater treatment. The influence of operating parameters like interelectrode distance (IED), current density (CD), temperature, pH, operating time (RT) and rotation speed on the removal efficiency of the contaminant was studied. A comparative study was done using conventional model with static electrodes in two phases under same textile wastewater. The findings revealed that the optimal conditions for textile wastewater treatment were attained at RT = 10 min, CD = 4 mA/cm^2, rotation speed = 150 rpm, temperature = 25°C, IED = 1 cm and pH = 4.57. The removal efficiencies of color, biological oxygen demand (BOD), turbidity, chemical oxygen demand (COD) and total suspended solid (TSS) were 98.50, 95.55, 96, 98 and 97.10%, respectively, within the first 10 min of the reaction. The results of the experiment reveal that the newly designed reactor incorporated with cathode rings and rotated anode impellers provide a superior treatment efficiency within a short reaction time. The novel EC reactor with a rotating anode significantly enhanced textile wastewater treatment compared to the conventional model. The values of adsorption and passivation resistance validated the pollutants removal rate.

Keywords: rotated anode reactor, textile wastewater, electrode consumption, electrocoagulation

1. Introduction

Electrocoagulation (EC) process involves in situ coagulant formation with sacrificial anode dissolution. Generally, the anode is prepared using iron or aluminum (Al) [1, 2]. The metal ions

interact to generate insoluble OH^- ions. The generated insoluble hydroxides adsorb the contaminants from the solution either by electrostatic attraction or complexation before the coagulation [3, 4]. Lessening of the electrodes' internal resistance drop (IR-drop) is one of the most essentials toward reducing the total cost of EC operation to enhance the current performance by enhancing the state of turbulence. Both oxygen and hydrogen gas emerged near the cathode and anode as soon as each gas bubble nucleates. The bubbles are like insulating spherical figures, generating a film that fouls oxide over the electrode surface (passivation effects). This issue increases the total electrical resistance of the cell, thereby needing a superior quantity of electrical energy to attain the optimal removal [5]. To moderate the bubble accumulation, the electrolyte flow around the electrodes must be augmented for the bubbles to be pushed out [6].

To proffer solution to these, the current EC reactor with rotating anode was conducted to enhance the reactors' overall efficiency [7]. Additionally, the leading objective of the present work is to study the treatment of textile wastewater using a novel EC reactor under optimum operating conditions and to compare the performance with that of conventional EC reactor.

2. Materials and methods

2.1. Wastewater characteristics

The wastewater used for the present study was obtained from one of the foremost textile industries in Babylon (Iraq). For dyeing of fabrics, the industry employs Imperon Violet KB (CAS #: 6358-46-9). **Table 1** presents the major characteristics of the textile wastewater, while **Table 2** shows the properties of the employed Imperon Violet KB.

2.2. EC rotating anode reactor

Figure 1 illustrates the new EC reactor employed in the current study. The reactor (10 L working volume) was made from Perspex and has a cylindrical form stirred tank setting (total length = 500 mm; inner diameter = 174 mm; external diameter = 180 mm). To keep the impeller structure and sustain the rotation of the electrode, a 32-mm-diameter rotating shaft was attached to a regulating speed motor. The motor is a DC electrical type and offers a number of steady-state speeds in the range of 0–1000 rpm. The electrodes were produced from the aluminum substance; the rotating anode comprises ten impellers. All the impellers have four rods (diameter = 12 mm, length = 30 mm) each and ten rings, which were employed as the cathode. Every one of the ring (thickness = 12 mm, internal diameter = 134 mm, diameter = 172 mm) was serially organized, maintaining 30 mm distance of apart. The entire active surface area is 500 cm^2; the reactor comprises three equally spaced baffles to establish the cathode rings by terminating the rotation and tangential flow arrangements of the mass fluid. The endorsed surface area-to-volume ratio ranges from 5 to 45 m^2/m^3 [8]. In the current model, the ratio was minimized (to 5 m^2/m^3) with the aid of a small area of the electrode for treatment of a great wastewater volume. The patent novelty filing was performed with application number PI 2015702202.

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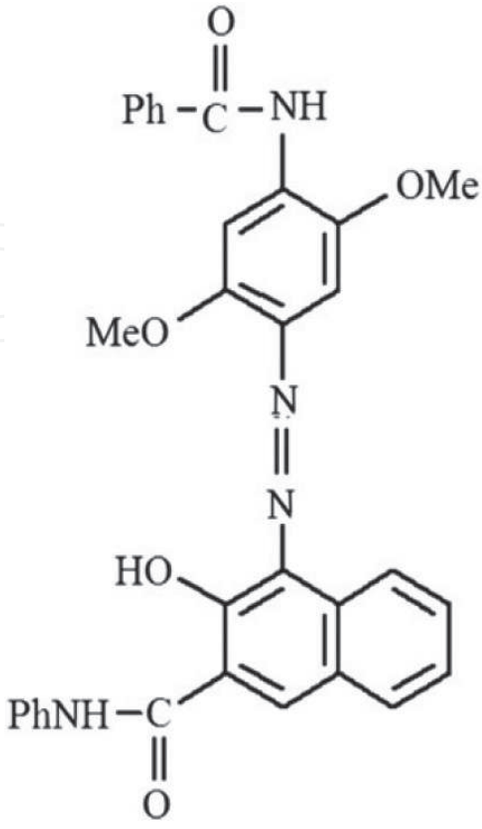
Parameters	Values
Electrical conductivity (μS/cm)	1455
Turbidity (NTU)	396
Total suspension solid, TSS (mg/L)	3270
Total dissolved solid, TDS (mg/L)	1250
Dissolved oxygen, DO (mg/L)	0.72
pH	4.50
Chlorides, Cl^- (mg/L)	35
Sulfate (mg/L)	678
Phosphate (mg/L)	7.2
Nitrates (mg/L)	11
Phenols (mg/L)	335
Oil and grease (mg/L)	3.2
BOD (mg/L)	112
COD (mg/L)	990

Table 1. Characteristics of textile wastewater.

2.3. Experimental procedure

The performance of EC process was determined based on color removal, TSS and COD. The experiment was initially performed by investigating the influence of CD and the anode rotation speed. The overall competence of the reactor was investigated using three major variables: overall rotation speed of the anode, CD and processing time. The value of RT of 10–30 min was maintained. Three values of CD (4, 6 and 8 mA/cm^2) with different steady-state anode rotation speed (75, 150 and 250 rpm) were observed at room temperature (25–27°C). The selection of the current densities was based on some initial studies, which show an insignificant change in the total removal efficiency when the value of CD exceeds 8 mA/cm^2. For all the runs, a 10 L sample was used for the EC process, and nine different batches of EC runs were performed. Upon concluding each run, a primary sample was removed, and the cells were washed with a 5% HCl solution for 10 min and subsequently washed using a sponge. The anode and cathode were linked to the positive and negative parts of DC power supply (YIZHAN, 0–6 A; 0-40 V, China). 30 V was used as the main voltage was for each experiment. For voltage measurement, a voltmeter was attached to the cell in parallel. For each run, the current was kept constant by using a variable resistance and monitored using an ammeter. For each iteration, the samples were left to settle for 30 min and subsequently filtered. About 100 ml of supernatant sample was collected for examination and analysis in replicates. The same parameters were examined for the entire replicated sample.

Color	Imperon Violet KB
Chemical structure	
Chemical formula	$C_{32}H_{26}N_4O_5$
The molecular weight (g/mol)	546.57
λ_{max} (nm)*	533

*Absorbance of 0.34 at 533.

Table 2. Properties of Imperon violet KB.

The experiment was performed using four different sets of operating conditions to obtain best parameters. The influence of pH on the EC system was investigated at varying pH values (5–10 by addition of 0.5 M NaOH). Some secondary electrolytes like Na_2SO_4 and NaCl (0.0, 0.02, 0.05 and 0.10 kg/m^3) were added to the wastewater toward investigating the effect of electrolyte support on the removal efficiency. The influence of temperature was studied, ranging from 25 to 45°C using water circulation to sustain the temperature as the EC process proceeds. The IED between the cathode rings and anode impellers were attained for various distance (1, 1.5 and 2 cm). At the end of experimentation, the best operating condition was determined again in triplicate to confirm the accuracy of the EC operation and repeatability for treatment of textile wastewater pollutants. For comparison study using same textile wastewater, the results of the conventional model with parallel electrodes in two phases have been observed by our previous works using EC alone by aluminum plates [9] and on enhancing of EC process by combining with electro-oxidation (EO) using titanium plates [10].

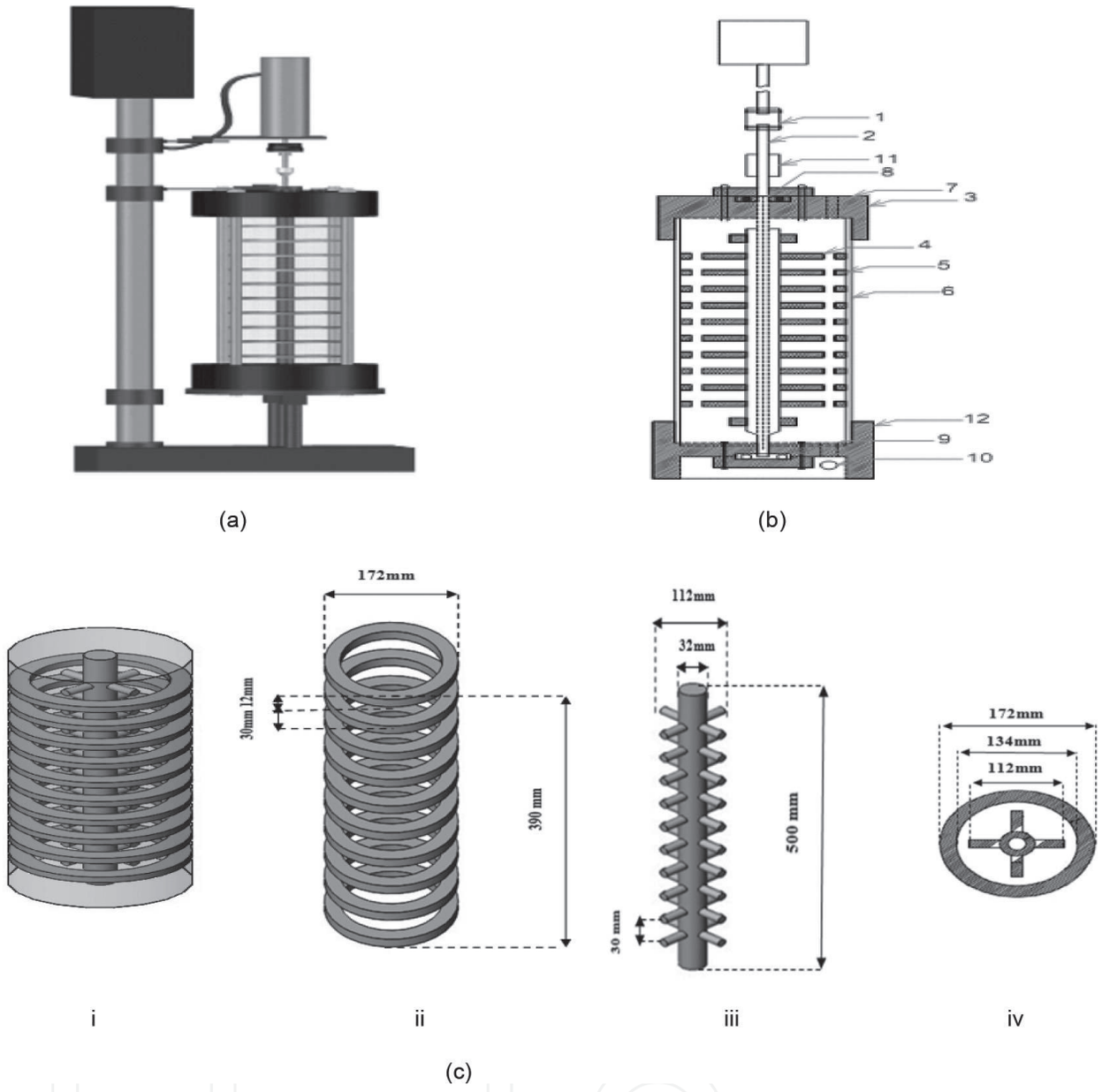


Figure 1. (a) Illustration of EC rotating anode setup. (b) Representation of the EC rotating anode system: (1) motor variable speed, (2) stainless steel shaft (D = 32 mm), (3) Teflon flange cover (upper) (H = 100 mm, D = 280 mm), (4) impeller anode aluminum rod (D = 12 mm, L = 30 mm, no = 4), (5) aluminum ring cathode (T = 12 mm, d.In = 132 mm, D.Out =1 72 mm, no = 10), (6) Perspex reactor (L = 500 mm, d.In = 174 cm, D.Out = 180 mm), (7) upper ports (D = 10 mm, no = 3), (8) ball bearing, (9) thrust bearing, (10) lower port (D = 10 mm), (11) zoom couping and (12) Teflon flange cover (lower) (D = 280 mm, H = 100 mm). (c) Electrode configurations: (i) cathode and anode, (ii) anode impellers, (iii) cathode rings and (iv) top view of cathode rings and impeller anode.

The passivation and adsorption phenomenon was also investigated using the electrochemical impedance spectroscopy. The experiment was performed using AC signal potential amplitude maintained at 10 mV, and the observed frequency range was 0.01–10^5 Hz. A potentiostat was employed to carry out the electrochemical impedance assays. The impedance experiments were performed in a single-partition, three-electrode system, consisting of an Al electrode

(1:25 of the original size) as the working electrode, a platinum wire as a counter electrode and Ag/AgCl (3 M KCl) electrode as a reference electrode.

2.4. Chemical analysis

The efficiency of the new EC reactor for the entire treatment was analyzed based on color removal performances, TSS and COD. For every iteration, the electrical potential was kept constant at 30 V. The COD was determined using a Closed Reflux-Titrimetric technique. The determination of TDS and TSS was performed using gravimetric technique. The phenol content was determined using HPLC. ODS Hypersil C18 column (4.6 mm×150 mm×5 μm) at 25 was employed for separation of aromatic and phenolic compounds with the aid of water/acetonitrile (40/60, v/v) being the mobile phase. The flow rate of the mobile phase and the injection volumes was 1 mL/min and 5 μL. 254 nm detection wavelength was used. The samples were subjected to filtration by using a 0.25 μm membrane filter. The amount of grease and oil (G&O) was determined using solvent extraction technique. The amount of dissolved oxygen (DO) and BOD was determined using DO meter. The turbidity, conductivity and pH were also determined in the present study. The color was analyzed through absorbance using a UV–Vis spectrophotometer with a wavelength corresponding to the peak absorbance value for the textile effluence (533 nm). The sample filtration was carried out with the aid of Whatman 934 AH filter. The rotating anode speed was monitored using a microprocessor digital meter. The ion was analyzed using ionic chromatography ICS-2000. The whole analytical works were performed based on the prescribed procedures in the standard techniques [11]. The determination of color removal, TSS and COD was done using formulas stated by [12–15] among others.

2.5. Sludge compaction analysis

The sludge of the textile wastewater was allowed to sit for 1 h to boost the alliance of the sediments. The two concentrations of cationic polymer (LPM 3135 polymer, 10 and 40 mg/L) were examined to enhance the settling process. The volume of the space engaged by the solid (mL) was measured at fixed time intervals. The weight of the wet residue (the solid portion) was determined, after which the samples were dried for approximately 24 h at 100°C to obtain the whole residual solids. The specific resistance to filtration (SRF) and the cake-dry solid was estimated to properly depict the dewater capability of the sludge using Buchner funnel filtration with pressure (0.015 mPas). The SRF formula (in m/kg) is defined as [16].

$$RF(SRF) = (2KbPA^2)/\mu a_w \quad (1)$$

where P is the pressure during sludge filtration (mPas), A is the filtered area, μ is the viscosity of the filtrate (N.s/m^2), a_w is the weight of the solid per unit volume of filtrate (kg/m^3) and Kb is the slope of the *V* vs. t/*V* plot. Whatman glass fiber filter (Grade 934-AH) was used. Measuring and estimating dryness of the general cake were performed by the following equation:

$$\text{Sludge dryness (\%)} = 100 \times \left[(m_3 - m_1)/(m_2 - m_1)\right] \quad (2)$$

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where m_1 and m_2 are the mass of the cup (with the membrane) after and before the filtration process and m_3 is the mass of the same cup after the drying for 24 h at 100°C.

A sludge volume index (SVI) was implemented to decide the settling properties of the sludge suspensions. The SVI (mL/g) is the volume (in mm) used by 1 g of a suspension subject to 30 min of settling [11]. The SVI is defined as.

$$SVI = VD_{30}/TSS \tag{3}$$

where TSS is the concentration of suspended solids (g/L) and VD_{30} is the volume of settled sludge after 30 min (mL/L).

2.6. Economic analysis

The total operating costs for treatment of wastewater process include electricity, equipment, chemical usage, labor, maintenance and sludge disposal. For EC process, the major costs of operation include the cost of electricity and electrode material. In this study, the cost of chemical supplements and sludge disposal was added as well. The total cost of operation (TCO) was computed using [3].

$$TCO = a\,C_{energy} + b\,C_{electrode} + d\,C_{sludge} + e\,C_{chemicals} \tag{4}$$

$$C_{energy} = UIRT/V \tag{5}$$

$$C_{electrode} = M_w\,I\,RT/ZFV \tag{6}$$

where C_{energy} = denotes intake of energy per cubic meter of wastewater (kWh/m^3); $C_{electrode}$ = intake of electrode for treatment of 1 m^3 of wastewater (kg/m^3); C_{sludge} = quantity of sludge per m^3 of wastewater (kg/m^3); $C_{chemical}$ = amount of chemicals (kg/m^3).; a = total cost of electricity (about 0.075US$/kWh); b = cost of iron or aluminum (2.5US$/kg); d = sludge disposal cost excluding the drying and including transportation (0.06US$/kg); e = cost of chemicals that can be added: LPM 3135 polymer (3.0US$/kg), NaOH (0.5US$/kg), Na_2SO_4 (0.25US$/kg) and NaCl (0.06US$/kg); U = voltage; I = intensity of the current; RT = EC electrolysis time; V = textile wastewater working volume; M_w = molar mass of the iron (55.84 g/mol) or aluminum (26.98 g/mol); Z = quantity of electrons moved (3); F = Faraday constant (96,500 C/mol).

The operating expense was computed according to the Iraqi market prices for the year 2017. For EC rotating anode, the total consumption of electrical energy was estimated as follows:

$$C_{energy}\,(kWh/m^3) = \left(C_{energy}\right)_S + \left(C_{energy}\right)_M \tag{7}$$

where $(C_{energy})_M$ signifies the rate at which the DC motor anode rotation consumed electrical energy and $(C_{energy})_S$ signifies the amount of electrical energy consumed by the reacting system

(electricity received by the cathode and the anode because of DC power supply). The values of $(C_{energy})_M$ and $(C_{energy})_S$ were determined from Eq. (5).

3. Results and discussion

3.1. Efficiency and reproducibility of the novel EC reactor

The investigations of the best parameters have been discussed in our previous research [17]. The major EC operation in the textile wastewater was executed in triplicate to confirm the efficiency and reproducibility of the application when the best operating conditions (CD = 4 mA/cm^2, temperature = 25°C, RT = 10 min, pH = 4. 57, rotation speed = 150 rpm and d_e = 1 cm) are used. The performance of the novel EC system was investigated based on the levels of BOD, Al, color, phenols, turbidity, COD, G&O, TDS, DO, nitrates, sulfate, phosphate and TSS. The summary of the results of the parameters is shown in **Figure 2** and **Table 3**. The EC operation exhibited 97.1% total removal efficiency of COD. After the EC treatment process, the G&O and BOD_5 in the wastewater had values of 0.1 and 5 mg/L, respectively. The hydrophobic capacity of G&O resulted in a higher affinity combining with the H_2 bubbles created at the cathode. The (G&O)-H_2 complex gathered on the surface of the liquid, which could be skimmed with ease [18].

The proposed EC design enables superior efficiencies and simultaneously reduces energy consumption in comparison with other reports. Un and Aytac [12] studied textile wastewater treatment by EC process in a packed-bed electrochemical reactor. They reported 96.88% removal efficiency for COD and observed that the color was almost completely removed after 1 h of EC

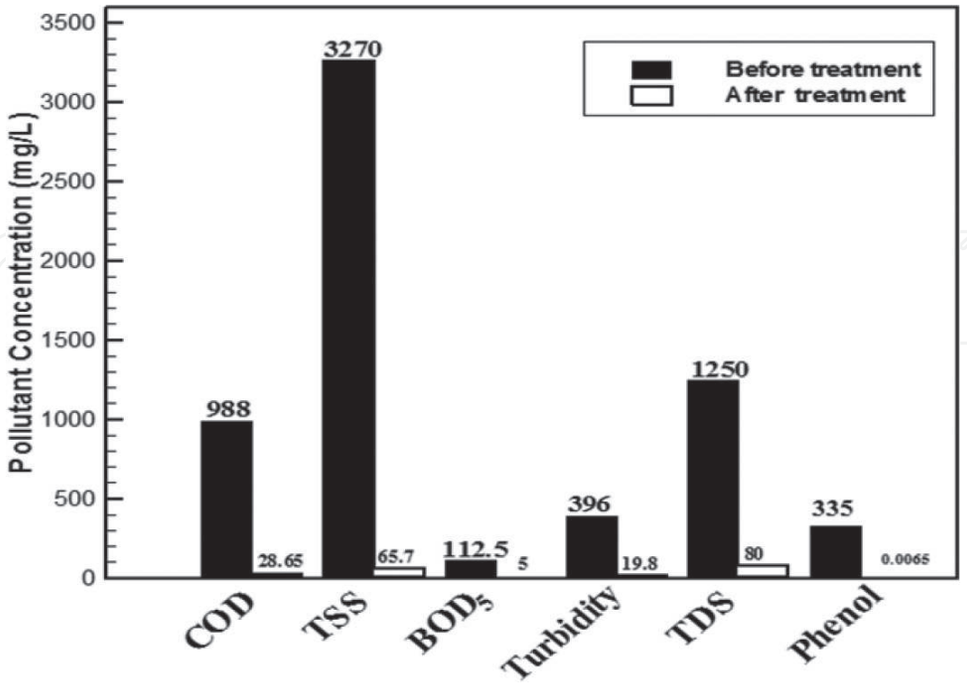

Figure 2. The removal efficacy of several parameters of the textile wastewater using the best operating condition.

Parameters	Raw effluent	Treated effluent	Allowable limit (EPA) 1996	Removal (%)
Electrical conductivity (μS/cm)	1455	2000	ID	—
Initial pH	4.57	4.57	—	—
Final pH	—	6.92	6–8	—
Energy consumption (kwh/m^3)	—	0.966	—	—
Electrode consumption (kg/m^3)	—	0.038		—
Sludge production (kg/m^3)		1.44		
Polymer consumption (kg/m^3)		0.01		
O&G (mg/L)	3	0.1	5–40	96.66
BOD_5 (mg/L)	112.5	5.00	5–45.5	95.55
COD (mg/L)	988	28.65	20–500	97.10
TSS (mg/L)	3270	65.70	60–300	98.00
Color observance at 533 NM	0.3400	0.0051	ID	98.50
TDS (mg/L)	1250	80.00	5–180	93.60
Turbidity (NTU)	396	19.80	15–50	96.00
DO (mg/L)	0.7	14.5	4.5–15	
Sulfate (mg/L)	678	17.00	ID	97.50
Phosphate (mg/L)	7.2	0.23	ID	96.80
Nitrates (mg/L)	11	0.2	ID	98.18
Phenols (mg/L)	335	0.0065	10	99.99
Chlorides Cl^- (mg/L)	33	0.4	ID	—
Aluminum (mg/L)	1.50	6.00	—	—
Electrical energy cost (US$/$m^3$)	—	0.072	—	—
Electrode consumption cost (US$/$m^3$)	—	0.095	—	—
Sludge disposition cost (US$/$m^3$)	—	0.086	—	—
Polymer cost (US$/$m^3$)	—	0.030	—	—
Total operating cost (US$/$m^3$)	—	0.283	—	—

Table 3. Efficiency and reproducibility of EC rotating anode in textile wastewater treatment using the best operating conditions (CD = 4 mA/cm^2, temperature = 25°C, rotation speed = 150 rpm, RT = 10 min, pH = 4.57, d_e = 1 cm).

operation. However, in this work, the 97% COD removal efficiency was obtained after 10 min reaction. Merzouk et al. [15] also studied the textile wastewater treatment using electro-flotation and EC using a batch reactor (electrode gap = 1 cm, conductivity = 2.1 μS/cm, pH = 7.6 and density = 11.55 mA/cm^2). With the best operating conditions, the obtained results are as follow: TSS = 85.5%, color = 93%, COD = 79.7%, BOD_5 = 88.9% and turbidity = 76.2%. Comparing with

the above results, this study utilizes only EC under the best operating conditions and exhibits superior removal efficiencies: TSS 98%, color >98%, BOD_5 = 95.55%, COD 97% and turbidity = 96%. In recent time, El-Ashtoukhy et al. [19] examined phenol removal from wastewater generated from oil refinery using a fixed-bed anode electrochemical reactor consisting random Al raschig rings. At pH = 7, CD = 8.59 mA/cm^2 and concentration of NaCl = 1 g/L, around 80% phenol reduction was observed after 2 h using 40 mg/L as the primary phenol concentration.

In this study, the concentration of primary phenol is 350.0 mg/L, and after 10 min, about 99.99% was extracted, while 0.009 mg/L of phenol remains with the cured wastewater. Furthermore, Martinez-Delgadillo et al. (2012) investigated Cr (VI) reduction to Cr (III) with the aid of Fe (II) in a rotating ring iron electrode. Their report shows up to 99.9% removal of Cr (VI) between 22 and 42 min contact time at an angular velocity ranging from 0 to 230 rpm (at 5 A). In the current study, the optimal reaction time and current were 10 min and 2 A, to confirm the reduction in power consumption and low cost of operation. Moreover, this work also reports high TDS removal efficiency (93.6%) when the best set of operating parameters were used, and the phosphate concentration was decreased to 0.23 from 7.2 mg/L. The Al electrode suspension displayed a rise in the whole dissolved concentration to 6.00 from 1.5 mg/L during the operation. In comparison with the quality standards of global textile wastewater [20, 21], the findings support the analysis of the efficacy of the EC system for treatment of textile wastewater for various usages. The outcomes show that the COD, turbidity, TDS, BOD and DO are all lower than the acceptable limit. Conversely, the generally pH level of the treated effluence was basic (6.9 ± 0.04) to some extent, which is under the acceptable limit. Similarly, the oil and grease, as well as the total phenols, fall under the acceptable limit. Under optimal conditions, the real electrode consumption was 0.038 kg/m^3, while the energy consumption was 0.966 kWh/m^3, 0.9 kWh/m^3 for DC power supply consumption and 0.066 kWh/m^3 for DC motor of rotating anode. For settling metallic sludge study after adding 0.01 kg/m^3 LPM3135 polymers, a 5% sludge dryness and 63 mL/g SVI were noted in the course of the analysis. The sludge production was 1.44 kg/m^3. Furthermore, the SRF utilized in these investigations was (4.6×10^{12}m/kg). The results revealed that the main cost of the treatment operation per m^3 [Eq. (4)] of wastewater, using the best set of operating parameters, is roughly 0.283 US$.

3.2. Comparison performance of the EC rotating anode with the conventional model

Table 4 shows a comparative study between EC rotating anode and the conventional static electrodes in two-phase EC process alone and EC-EO process depending on the results of each model at the optimal conditions. Each model has the same optimal applied current to volume ratio (0.2 A/L). Although the EC model with rotating anode has the lowest surface area to volume ratio (5 m^2/m^3), it can be seen that this reactor model obtained the best removal efficiency of contaminant textile wastewater (COD, TSS and the color). The minimum reaction time (10 min) was achieved by EC model with rotating anode compared with a conventional model in two phases (90 min) which demonstrated the activity of electrodes for the treatment and reduced significantly the energy consumption to 0.966 kwh/m^3. Furthermore, the rotation speed of anode affects the energy consumption by reducing the main voltage and passivation films. The EC process with rotating anode showed excellent treatment without setting the initial pH or using supporting electrolyte. The electrode consumption and sludge production were less than the conventional model with static electrodes. As for the operating costs, the

EC model with rotating anode was lower than the conventional model with static electrodes (EC rotating anode = 0.283US$/m^3, while conventional static electrode including EC = 1.76 US$/m^3 and EC-EO =1.69 US$/m^3).

3.3. Passivation and adsorption phenomenon

Electrochemical impedance spectroscopy is one of the most effective methods for investigation of electrochemical constraints of the electrolyte/electrode interface [22–24]. The impedance method was employed to study the effect of color adsorption on the Al anode and rotation speed (rpm) of the electrode on electrode passivity. The electrolyte was real textile effluence, and the potential of 0 V vs. Ag/AgCl, and frequency ranging from 0.01 to 10^5 Hz, was used for performance evaluation of the electrolyte/anode interface. **Figure 3(a)** presents the Nyquist plot for the anode at varying speed of rotation (0, 75, 100 and 150 rpm). Two semicircles were detected at low frequencies and high frequencies. **Figure 3(b)** presents the best fits for the Al electrode impedance spectra. The fitting parameters comprise the solution resistance (R_s) in parallel with a combination of the double-layer capacitance (C_{dl}) and impedance of the faradic reaction. On the other hand, the faradic reaction impedance comprises passivation resistance (R_{ct}), accompanied by adsorption capacitance (C_{ads}) and adsorption resistance (R_{ads}) [25–28]. **Table 5** summarizes the impedance parameters. Temporarily, the first semicircle diameter signifies the values of R_{ct}, and the diameter of the second semicircle signifies the values of R_{ads}.

Parameters	EC rotating anode	EC static electrode	EC-EO static electrode
Materials	Al-Al	Mp Al-Bp Al	Mp Ti-Bp Al
COD removal (%)	97.10	92.60	93.50
TSS removal (%)	98.00	96.40	97.00
Color removal (%)	98.50	96.50	97.50
Initial pH	Natural	6.00	6.00
Conductivity (μS/cm)	2000	1980	1910
Current/volume ratio (A/L)	0.2	0.2	0.2
Surface area/volume ratio (m^2/m^3)	5	12	12
RT (min)	10	90	90
Electrode consumption (kg/m^3)	0.038	0.1	0.087
Energy consumption (kwh/m^3)	0.966	8.49	9.00
Sludge production (kg/m^3)	1.44	3.50	2.88
NaOH (kg/m^3)	No add	1.26	1.20
NaCl (kg/m^3)	No add	0.1	No add
Operation cost (US$/m^3)	0.283	1.76	1.69

Table 4. Comparison of the EC rotating anode with the conventional model static electrode (EC alone and EC-EO) at optimal conditions.

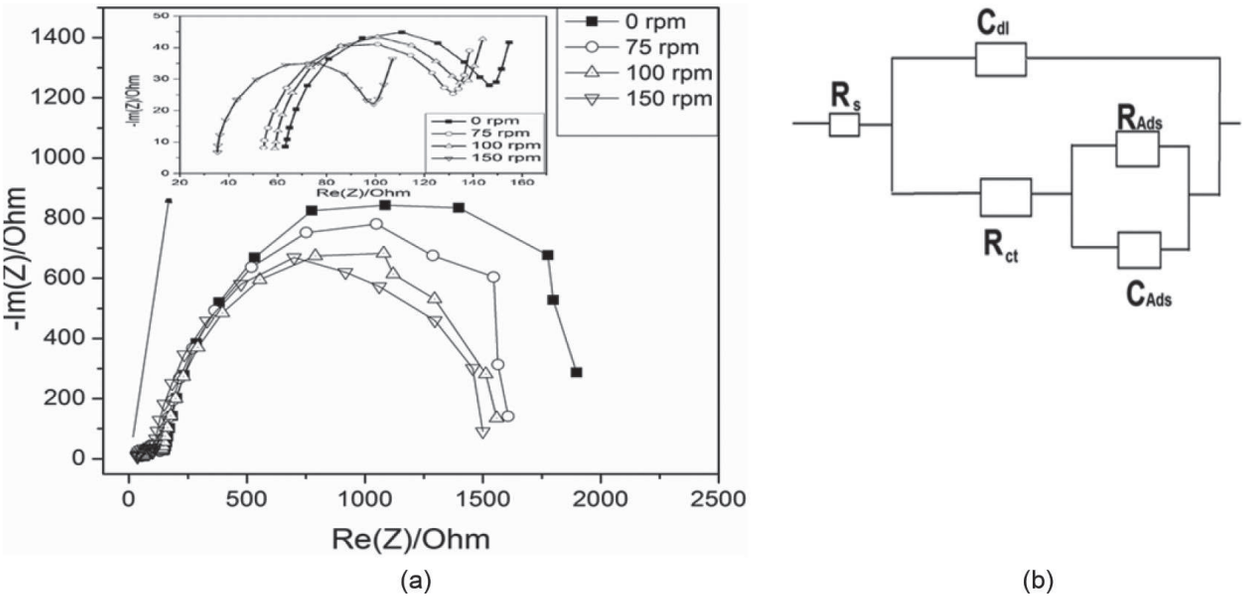

Figure 3. (a) Nyquist plots of the Al anode in an aqueous textile wastewater solution at 25°C temperature and varying electrode speed of rotation. (b) Equivalent circuits utilized to fit the Nyquist plots.

Rotation speed (rpm)	R_s(Ω)	R_{ct}(Ω)	C_{dl}(μF)	R_{ads} (Ω)	C_{ads}(μF)
0	63.30	96.98	0.128	1774	7.18
75	56.90	88.89	0.129	1531	7.36
100	59. 08	90.00	0.145	1369	7.13
150	40.54	41.65	0.412	1151	8.31

Table 5. Electrochemical impedance data extracted from the Nyquist plots at varying speed of rotation (rpm).

From **Table 5** and **Figure 3(a)**, it is clear that the values of R_{ct} and R_{ads} significantly declined with a rise in the rotation speed of the Al anode from 0 attaining the lowest value at 150 rpm. Therefore, the fouling rate of the anode was lessened, and the rate of adsorption of color to the interface of the anode increased at 150 rpm. Conversely, the highest values of the adsorption capacitance and double-layer capacitance were observed at 150 rpm. This elucidates the improvement in the rate of removal upon rotating the anode at 150 rpm as the EC experiment proceeds. It also confirms that the designed model can be a panacea to the limitation of the previous model.

4. Conclusions

The use of novel EC reactor in textile wastewater treatment exhibits a higher removal efficiency than the erstwhile models. The efficiency of the textile effluence pollutant removal with high values was achieved using a lower CD, precisely 4 mA/cm^2, at initial reaction period (10 min) at 1 cm interelectrode distance (IED) and 150 rpm anode rotation speed. A rise in the value of CD enhanced the efficiency of EC process in the treatment of textile wastewater. The setting of the

solution pH to increase the solution temperature and the addition of any chemicals (Na_2SO_4 or NaCl) is not required. The economic viability of the operation of the reactor is influenced by the parameters. The energy and electrode consumption of the EC increases as the CD increases. The optimal energy and electrode consumptions were 0.038 kg/m^3 and 0.966 kWh/m^3, which led to the lower cost of operation (0.283US$/m^3). The novel EC reactor with rotating anode significantly enhanced the textile wastewater treatment by improving the pollutant removal rate, reducing reaction time of treatment, without any additional chemicals during the process, and reducing the operation cost compared to conventional model (EC and EC-EO). It was found that the passivation phenomenon reduced with the increased rotation speed of anode, which enhanced the EC process performance and validated the novel reactor design.

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Conflict of interest

The authors whose names are listed in the beginning of this chapter certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership or other equity interest; and expert testimony or patent-licensing arrangements) or nonfinancial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) on the subject matter or materials discussed in this manuscript.

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Chapter 7

Innovation of Coagulation-Flocculation Processes Using Biopolyelectrolytes and Zeta Potential for Water Reuse

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Additional information is available at the end of the chapter

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Abstract

The coagulation-flocculation process is one of the conventional technologies used for the treatment of different types of industrial wastewater. The zeta potential is a key parameter that allows to determine the effective pH, the type and the correct biopolyelectrolyte dose to return the water quality using coagulation-flocculation. In this chapter, we present the application of a natural cationic biopolyelectrolyte (chitosan) to make the separation and recovery of cellulose fiber more efficient and to increase the reuse of treated water from the pulp and paper industry. The result of the coagulation-flocculation test at pH 5.4 and a chitosan dose = 10 mg/L shows that the treated water has the following values: biochemical oxygen demand = 150 mg O_2/L, turbidity = 5 FAU, total suspended solids = 2 mg/L, chemical oxygen demand = 200 mg/L and hardness = 250 mg $CaCO_3$/L. The quality of water obtained allows its discharge to a natural water body, in which it is possible to continue with a biological treatment stage, or to reuse the treated water for the manufacture of paper. Additionally, this coagulation-flocculation process can be coupled to an advanced oxidation process to increase the quality of the water and mineralize the content of organic material.

Keywords: zeta potential, wastewater treatment, biopolyelectrolytes, coagulation-flocculation

1. Introduction

The issue regarding the quality and use of water has several aspects: the first option is the most common and of greater importance, than a simple view, which becomes the vital liquid

to survive and perform daily activities. Its quality directly affects the health and well-being of society [1]. The second corresponds to the use of water as the main raw material for the manufacture of some products and the operation of production processes. The interaction of water with the environment is influenced by the water quality that both society and the industrial sector confer on water.

Each type of industry has a particular interest in the care of water quality and its reuse, which is why day by day, they require new strategies to treat and recycle the wastewater they generate in the different production processes [1]. Water quality is affected by various chemical substances that dissolve in water used in each stage of the manufacturing process.

In general, the main pollutants that are identified in the industrial wastewater are suspended particles, organic matter, heavy metals, the hardness of the water and fats and oils [2]. One of the pollutants frequently present in the industrial wastewater is suspended particles or solids. According to the nature of the production processes, the particles in suspension can be organic and inorganic and can be present in different particle sizes. The content of organic matter in industrial wastewater is attributed to the organic compounds (colorants, additives, nutrients, carbohydrates, etc.) that can be biodegradable or difficult to be degraded, and that are incorporated into the water at the time of use [3]. The levels of concentration in which these contaminants or undesirable substances are present in the wastewater are directly related to the operating conditions of the productive processes. The presence of these pollutants in the water causes an impact on the efficiency of the production processes, limits the reuse of water, increases the consumption of clean water, the discharge of the wastewater generated contaminates the water bodies, and this implies sanctions to the industry for exceeding the maximum permissible limits at the effluent discharge point [3].

There is an urgent need of environmentally friendly and cheaper technologies to eliminate the chemical toxicants from wastewater to improve the water quality.

Several methods that have been developed to eliminate these present pollutants from wastewater are as follows: reverse osmosis, solvent extraction, coagulation-flocculation, membrane separation, chemical precipitation, advanced oxidation processes, ion exchange, evaporation, electrolysis [4–6], photochemical [7], activated sludge [8], anaerobic and aerobic treatment [9, 10], electrodialysis [11], ultrasonic treatment [12], magnetic separation [13] and adsorption [14–16].

As part of the integral management of water in the industry, the development of environmentally friendly technologies is involved. In this chapter, we propose one of the strategies to restore the water quality (decontaminate, purify, remove undesirable substances for a specific use), which consists of the application of natural functional polymeric materials in physicochemical/electrochemical systems for the elimination of contaminants [17]. One of the simple and efficient methods for the separation of various types of contaminants is coagulation-flocculation, in which chemical substances are used as synthetic coagulant-flocculating agents (polyelectrolytes) [18]. However, in order to employ the different renewable sources, which are rich in polymeric materials and available in the region, as shrimp waste from the fishing industry will be used as a raw material for the production of functional polyelectrolytes and give it an added value. Due to the type of interactions that occur at a molecular level between the contaminants and the polyelectrolytes in the coagulation-flocculation processes, the zeta

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potential measurements are key to determine the best operating conditions and understand the mechanisms of interface (contaminant-biopolyelectrolyte). In this chapter, the physicochemical characterization of six types of industrial wastewater is presented. Due to the complexity and variety of the contaminants present in these types of wastewater, only the wastewater treatability results of the pulp and paper industry are presented.

2. Experimental

2.1. Wastewater sampling

In this chapter, the physicochemical characterization of six types of industrial wastewater and how to develop a treatment strategy for water recovery and how to add value to the byproducts formed are presented. The wastewater sampling protocol was followed as recommended by Mexican sampling standard (NMX-AA-003-1980). Residual water samples were taken from the nixtamalization industry (nejayote) that is dedicated to the manufacture of corn products and their derivatives. Another sample was collected from a candy factory that generates wastewater with a high content of dyes and suspended particles. The third case corresponds to a company dedicated to the recycling of cellulose and paper, which uses well water for its paper and cardboard manufacturing process. Another type of water sample was collected from the industry that is dedicated to the collection of hazardous waste that contains a greater proportion of oil and water. Finally, there is the sector dedicated to the metalworking industry and the semiconductor industry. Tested parameters were: total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), turbidity, color, particle size, electrical conductivity (EC), zeta potential (ζ), total phosphorous (TP), biological oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC) and total nitrogen (TN). Tests were carried out following the current Mexican standard procedures that are equivalent to those published by EPA (AWWA standard methods, respectively).

2.2. Extraction of chitosan biopolyelectrolyte

Chitosan (Ch) was obtained from waste shrimp shells using the adapted method proposed by the authors Goycoolea et al. [19].

2.3. Zeta potential = f (pH) profiles of the industrial wastewater and chitosan

Zeta Potential from wastewater and biopolyelectrolyte data was recorded on a Stabino Particle Charge Mapping (Microtrac). The measurements were done at ambient temperature in Teflon cuvettes. Influence of pH on the zeta potential behavior of each biopolyelectrolytes was studied within a pH range of 2–11 with 0.1 M NaOH and 0.1 M HCl [20].

2.4. Wastewater coagulation-flocculation tests using chitosan

The performance of cationic chitosan biopolyelectrolyte in the coagulation-flocculation of wastewater from the cellulose and paper recycling industry was carried out using 20 mL of residual water at pH 5.4 and in different doses of chitosan extracted from the shrimp shells.

After each addition of chitosan, the mixture of residual water with chitosan was stirred at 200 rpm for 2 min and subsequently at 50 rpm for 20 min. For the evaluation of the quality of the treated water, a sample of the supernatant was extracted [21].

3. Results and discussion

Tables 1 and **2** show the physicochemical characterization of the six types of industrial wastewater. The values of the main residual water quality parameters such as BOD_5, COD, alkalinity, hardness, pH, electrical conductivity, content of dissolved and suspended solids, settleable solids, temperature, turbidity, nitrogen and total phosphorus, heavy metals are shown. Of these normative parameters, the environmental legislation dictates which ones must comply, considering the type of industry and body of discharge of residual water. Additionally, other non-regulated parameters, which are fundamental to understand and operate the coagulation-flocculation process, such as particle size, turbidity, total organic carbon, biodegradability and zeta potential [21]. The measurement of these parameters is key to implement the design and sequence of an industrial wastewater treatment train to achieve the best quality of treated water.

In all types of wastewater, the regulated parameters exceed the maximum permissible limits, both for their discharge to the water receiving bodies and for their reuse. One of the main pollutants present in industrial wastewater is the content of dissolved and suspended solids, where these can be organic and inorganic depending on the source of the wastewater. Generally, the first stage of a wastewater treatment train consists of the elimination of the suspended particles; this is where the coagulation-flocculation processes are applied. Considering the main interactions that occur between the suspended particles and the coagulant-flocculant agents, the zeta potential is a key parameter to determine the surface charge density of the suspended particles and the polyelectrolytes, as well as the optimum dose to perform the solid-liquid separation of the suspended particles.

Figure 1 shows the $\zeta = f(pH)$ profiles of each type of industrial wastewater, metalworking, candy factory, nejayote, recycled oils, recycled cellulose and paper. These profiles show that all the wastewater has negative zeta potential values at $pH > 5$, while at $pH < 5$, zeta potential values are close to neutrality or positive. With exception, the wastewater from the electroplating processes shows positive zeta potential values at $pH < 6.0$, and at $pH > 7.0$ presents negative zeta potential values. As expected, in order to carry out a coagulation-flocculation process in an efficient way, it is necessary to add a polyelectrolyte with a positive charge to neutralize the negative charge of the wastewater from the pulp and paper industry. The monitoring of the zeta potential value with respect to the polyelectrolyte dose in the wastewater allows to construct the coagulation-flocculation operation curves, and this ensures that the operators of the wastewater treatment plants avoid the problem of overdosing of coagulant-flocculant agents and save on the consumption of chemical substances [22]. In this chapter, the capacity of a biopolyelectrolyte extracted from the shrimp waste for the clarification of wastewater from the cellulose and paper recycling industry was evaluated. This was done with the aim of increasing the reuse potential of the treated water and improving the efficiency of solid-liquid separation processes for the recovery of cellulose fiber present in industrial wastewater.

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Parameter	Nixtamalization wastewater	Parameter	Candy Industry wastewater
Temperature (°C)	38	Temperature (°C)	26
Sedimentable solids, SS (mL/L)	850	SS (mL/L)	25
Total Dissolved Solids, TDS (mg/L)	47,200	TDS (mg/L)	12,743
Total Suspended Solids, TSS (mg/L)	2000	TSS (mg/L)	2342
Turbidity (FAU)	1500	Turbidity (FAU)	1676
Alkalinity (mg/L $CaCO_3$)	1025	Alkalinity (mg/L $CaCO_3$)	500
Electric conductivity, EC (mS/cm)	5.42	EC (mS/cm)	1.30
ζ (mV)	−10.5	ζ (mV)	−25.7
Particle size of dissolved part (nm)	100–600	Particle size of dissolved part (nm)	300–800
Color (Pt-Co)	8580	Color (Pt-Co)	6572
pH	10.0–12.0	pH	6.7
Chemical Oxygen Demand, COD (mg O_2/L)	28,450	COD (mg O_2/L)	786
Total Organic Carbon, TOC (mg C/L)	9836	TOC (mg C/L)	250
Biochemical Oxygen Demand, BOD_5 (mg O_2/L)	2700	BOD_5 (mg O_2/L)	653
Total Phosphorus, TP (mg P/L)	1321	TP (mg P/L)	142
Total Nitrogen, TN (mg N/L)	418	TN (mg N/L)	120
Biodegradability (BOD_5/COD)	0.27	Biodegradability (BOD_5/COD)	0.83

Parameter	Recycled cellulose and paper wastewater	Parameter	Recycled oils wastewater
Temperature (°C)	35	Temperature (°C)	28
Chlorides (mg/L)	900	Zn (mg/L)	10.2
Total hardness (mg/L)	3800	Cu (mg/L)	12.2
Alkalinity (mg/L $CaCO_3$)	850	Alkalinity (mg/L $CaCO_3$)	100
Fats and oils (mg/L)	11	Fats and oils (mg/L)	6732
TSS (mg/L)	500	TSS (mg/L)	15,000
TDS (mg/L)	3500	TDS (mg/L)	3500
SS (mL/L)	438	SS (mL/L)	438
Turbidity (FAU)	560	Turbidity (FAU)	350
EC (mS/cm)	1.00	EC (mS/cm)	2.00
ζ (mV)	−25.8	ζ (mV)	−2.1

Parameter	Recycled cellulose and paper wastewater	Parameter	Recycled oils wastewater
Particle size (nm)	500	Particle size (nm)	750
Color (Pt-Co)	3000	Color (Pt-Co)	2340
pH	5.4	pH	7.63
COD (mg O_2/L)	8000	COD (mg O_2/L)	43,650
TOC (mg C/L)	1890	TOC (mg C/L)	5200
BOD_5 (mg O_2/L)	4000	BOD_5 (mg O_2/L)	17,500
Total Nitrogen, TN (mg N/L)	88	Biodegradability (BOD_5/COD)	0.4
Total Phosphorus, TP (mg P/L)	16		
Biodegradability (BOD_5/COD)	0.5		

Table 1. Physicochemical characterization of industrial wastewater: Nixtamalization, recycled cellulose and paper and recycled oils wastewater.

Parameter	Electroplating wastewater	Parameter	Metalworking wastewater
Temperature (°C)	25	Temperature (°C)	32
Sn (mg/L)	4854	Zn (mg/L)	7.78
Pb (mg/L)	1044	Ni (mg/L)	41.57
Fe (mg/L)	683	Cr (mg/L)	7.44
TSS (mg/L)	4510	Cd (mg/L)	0.47
Turbidity (FAU)	2990	SS (mg/L)	9
EC (mS/cm)	74	Fats and oils (mg/L)	465.66
ζ (mV)	26	TSS (mg/L)	3352.63
Particle size (nm)	346	Turbidity (FAU)	2990
Color (Pt-Co)	6742	EC (mS/cm)	327
pH	0.8	ζ (mV)	−10.0
COD (mg O_2/L)	1432	Particle size (nm)	678
TOC (mg C/L)	125	Color (Pt-Co)	2500
BOD_5 (mg O_2/L)	30	pH	7.36
TN (mg N/L)	50.6	COD (mg O_2/L)	64,800
Biodegradability (BOD_5/COD)	0.02	TOC (mg C/L)	3858
		BOD_5 (mg O_2/L)	2857
		TN (mg N/L)	316.8
		Biodegradability (BOD_5/COD)	0.04

Table 2. Physicochemical characterization of industrial wastewater: Electroplating and metalworking wastewater.

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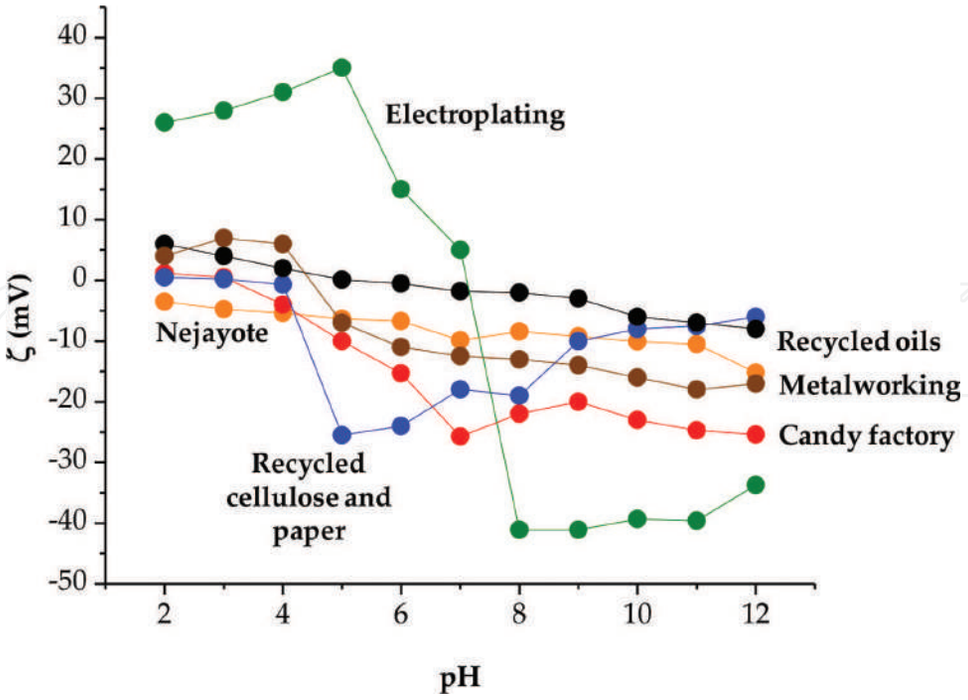

Figure 1. ζ = f (pH) profiles from industrial wastewater: Candy factory, metalworking, recycled oils, nejayote, electroplating and recycled cellulose and paper.

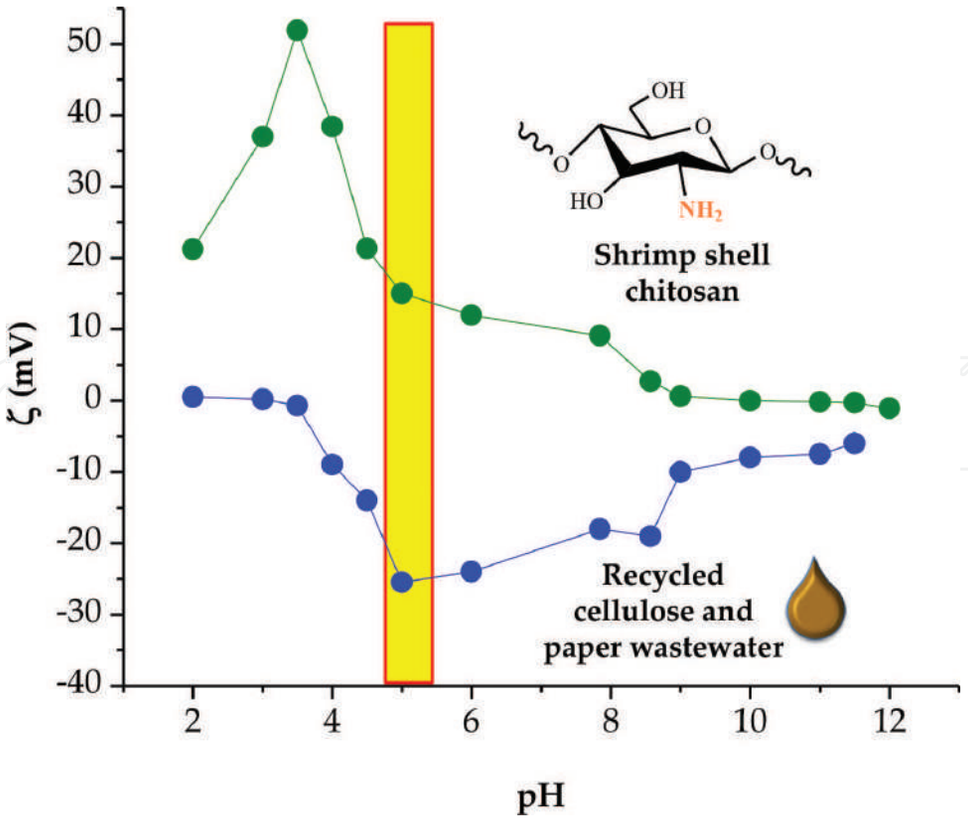

Figure 2. ζ = f (pH) profiles of recycled cellulose and paper wastewater and chitosan.

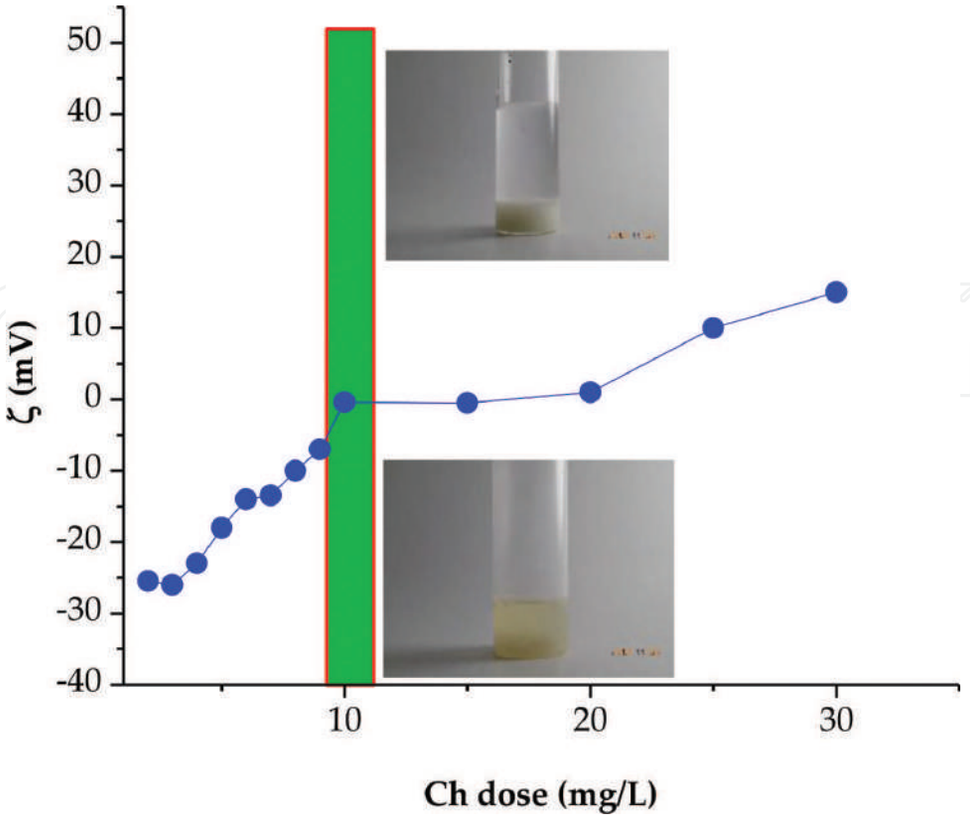

Figure 3. ζ = f (chitosan dose) in coagulation-flocculation tests from recycled cellulose and paper wastewater.

Figure 2 shows the variation of zeta potential with respect to the pH of the wastewater and chitosan. The zeta potential value of the wastewater shows that the suspended particles have a negative surface charge density at pH 5–9. The ζ = f (pH) profile shows that at pH = 4.0 and pH > 10.0, the wastewater has two isoelectric points (ζ = 0). The stability of the particles to remain suspended is due to the value of the negative zeta potential (ζ = −25.5 mV). In order to destabilize the dispersion of cellulose fiber particles, the addition of a cationic coagulant-flocculant agent that allows the neutralization of the negative surface charge is necessary. The wastewater at pH 5.4 has a ζ = −25.5 mV and the chitosan ζ = 15.0 mV, the dosage of chitosan at this pH by pure electrostatic interaction ensures its reaction.

In **Figure 3**, it is shown that the zeta potential value of the wastewater from cellulose and paper industry increases linearly as the dose of chitosan increases (ζ = −25.5 mV to ζ = −5.1 mV), reaching the isoelectric point at a dose of 10 mg/L chitosan. The water treated at pH 5.4 with chitosan has a value of BOD_5 = 150 mg O_2/L, turbidity = 5 FAU, TSS = 2 mg/L, COD = 200 mg/L and hardness = 250 mg $CaCO_3$/L, and the treated water with these physicochemical characteristics can be discharged into the municipal sewer system or reused as process water.

4. Conclusions

The wastewater generated by industries is becoming more complex and difficult to treat to restore its quality and reuse it. The coagulation-flocculation process has become one of the

most used technologies to remove suspended particles, dyes and heavy metals; however, one of the trends consists of the substitution of synthetic coagulant-flocculant agents with biopolyelectrolytes. This leads to the development of environmentally friendly technologies, and take advantage of the waste that contains biodegradable polymeric materials and with high potential for its application in the elimination of toxic pollutants from industrial wastewater. In this chapter, the wastewater treatment of the cellulose and paper industry was carried out through a coagulation-flocculation process using a dose of 10 mg/L chitosan at pH 5.4. Through the zeta potential measurements, the pH = 5.4 at which the chitosan and the wastewater have an opposite electric charge was determined, and the best dose of chitosan to maximize the recovery of cellulose fiber and obtain the best quality of treated water.

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Conflict of interest

The authors state that there is no conflict of interest.

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Chapter 8

The Role of Bacteria on the Breakdown of Recalcitrant Polychlorinated Biphenyls (PCBs) Compounds in Wastewater

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Additional information is available at the end of the chapter

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Abstract

Pseudomonas aeruginosa was used to assess their potentials to degrade PCBs at concentrations of 1.0 μg/mL. An aliquot of 1.0 μL of the bacterial suspension with an optical density of 1.0 at 600 nm was used as an inoculum of the assay. Isolates were analysed for their ability to degrade PCB (Aroclor 1260) by measuring a shift in the wavemax using Cary 300 UV-visible spectrophotometer for a period of 96 hours. The presence /absence of the compounds was checked using high performance liquid chromatography (HPLC) UFLC Shimadzu using florescence detector pump RF-20A and system gold column C18 (CTO-20A) after 96 h. PCBs were extracted from wastewater samples from both Gaborone and Mafikeng using the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) extraction kit, and analysis was performed using the gas chromatography mass spectrometer (GC-MS). The bacteria were able to degrade these compounds under different pH values of 5.0, 7.0, 8.0, and 9.0 and temperatures of 20, 27, 30, and 35°C. Degradation occurred at the most at 35°C and the least at 20°C for PCB samples that were used in the study. The bacteria strain was able to completely degrade Aroclor 1260 that was incoperated into the wastewater samples within 96 h. This was shown by a shift in the wavelength from 224 to 270 nm, which indicated that Aroclor 1260 was degraded and therefore forming a chlorobenzoate derivative. From this finding, it can be concluded that the sewage water samples did not possess PCB (Aroclor 1260) after treatment with bacteria and can be safely recycled.

Keywords: *Pseudomonas aeruginosa*, sewage water, PCBs, recycled, breakdown

1. Background

One of the key areas in sustainable development entails the promotion of environmental management and introduction of new technologies to treat large quantities of waste. This includes treatment of wastewater for recycling purposes [1]. The adverse effects of global warming have mostly been experienced by countries in Africa, resulting in scarcity of water as a natural resource. This has prompted a great global concern to recycle and conserve water, especially in sub-Saharan Africa where the problem of water scarcity has affected most countries [2]. South Africa is faced with freshwater scarcity, which is exacerbated by its increasing demand, pollution, unsustainable use, and climate change [3].

The presence of chemicals in the environment calls for quantification of such so as to come up with a risk analysis posed by these chemicals [4, 5]. According to Guillen et al., substances such as pharmaceuticals, perfluorinated acids, perfluorosulfonates, PAHs, PCBs, pesticides, and surfactants are mostly found in wastewater [4]. Ying et al. also noted that the presence of pharmaceutically active compounds in wastewater is a major concern [6]. Several methods may be used to determine quantitatively, these substances from wastewater, which is mainly from sewage treatment plants [6]. According to Ying et al., although much research has been done regarding the removal of these substances, it was mainly on activated sludge and no work has been done on wastewater [6].

Some strains of organism *Acinetobacter* have the ability to degrade pollutants such as biphenyls from wastewater [7]. *Enterobacter cloacae* secretes an emulsifier that increases the hydrophobicity of the bacterial cell surface and also neutralizes the surface charge of cells [8]. This as a result increases the ability of the bacteria to degrade PCBs [8, 9]. Biosurfactants are also effective at extremes of temperature, pH, and salinity [9, 10], a property that is essential in the biodegradation of PCBs as they are hydrophobic organic compounds [11]. This property causes these recalcitrant compounds to be removed through physico-chemical means or treatments, limited bioavailability to microorganisms, and limited availability to oxidative and reductive chemicals when applied in treatments [8].

This study is very important in contributing toward addressing sustainable development goal 6. With the global emphasis of conservation of natural resources and the three Rs, that is, reduce, reuse, and recycle, this research is very important. The research is my original proposal which was stimulated by quite a number of issues, such as the scarcity of water although there is a lot of water that is being let to waste. Also the high prevalence of cancer cases with no direct link to water but with a view to eliminate the possibility of such cancer causing chemicals with direct attention on PCBs, from sewage which in most cases the effluent is released into the environment.

2. Brief literature

2.1. Physio-chemical properties of polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) consist of two benzene rings with a carbon-to-carbon bond between carbon 1 on one ring and carbon 1 on the other ring [12]. PCBs have varying number of chlorines in their structure [12–14], as shown in **Figure 1**.

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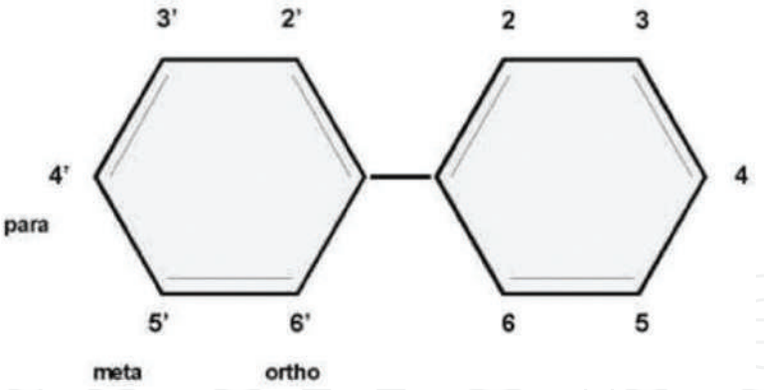

Figure 1. Structure of PCBs (*source*: [14]).

Toxicity of PCBs is dependent upon the number of chlorines present on the biphenyl structure and their position, that is, the co-planar congeners [13, 14]. The PCB congeners that have been deemed to be highly toxic were those that had chlorine atoms attached to the 3,4-ortho positions, followed by those with 5–10 chlorine atoms in the para and meta positions [13].

PCBs toxicity has been largely associated with their structure. This has resulted in PCBs being placed into categories, namely coplanar or non-*ortho*-substituted "*arene*" substitution patterns or noncoplanar or *ortho*-substituted congeners [15]. The coplanar group members are characterized by a fairly rigid structure, with the biphenyl rings in the same plane giving them a molecule structure similar to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans. Based on this structure, this group of PCBs act in the same way as these molecules as an agonist of the aryl hydrocarbon receptor (AhR) in organisms [16]. This group of PCBs is considered contributors to overall dioxin toxicity [16].

On the other hand, the other group of PCBs, noncoplanar PCBs, has chlorine atoms at the *ortho* positions. According to Ross [17], they have not been found to activate the AhR and are not considered part of the dioxin group; however, they have been implicated in having some neurotoxic and immunotoxic effects, although at levels much higher than normally associated with dioxins, and thus of much less concern to regulatory bodies [18, 19].

According to Rudel et al. PCBs are very stable compounds and do not decompose readily [18]. Their chemical inability to oxidize and reduce in the natural environment gives them this characteristic; they have a long half-life (8–15 years) and are insoluble in water, thus the recalcitrant property [18]. The biodegradability (and solubility in water) of PCBs is also dependent upon the number of chlorine molecules it has [12, 13]. The more chlorine molecules contained in a compound renders that compound less biodegradable [12]. PCBs are mostly hydrophobic; some are less hydrophilic [20, 21]. These properties result in bioaccumulation of these compounds as they do no dissolve in water, and thus, they render them difficult to be biodegraded [12, 14, 20, 22].

2.2. Elimination of PCBs

Although the Stockholm Convention on Persistent Organic Pollutants (POPs) (of which PCBs are part of) signed in 2001 was aimed at eliminating and/or restricting the production and use of POPs [23], more of these ubiquitous substances are still being introduced into the

environment through various human activities [24]. Water has become a widely used environmental matrix for monitoring POPs [20, 25, 26], although most studies on PCBs have been carried out on contaminated soils than water [27].

The destruction of PCBs by chemical, thermal, and biochemical processes is extremely difficult and presents the risk of generating extremely toxic dibenzodioxins and dibenzofurans through partial oxidation [12, 16, 27].

2.3. Effects of polychlorinated biphenyls (PCBs) on human health

PCB mixtures have been associated with cancer incidents in animals from long time back [17, 28, 29]. PCBs were found to induce liver tumors, thyroid adenomas, intestinal metaplasia, and adenocarcinomas in rats and mice [29]. Exposure to some environmental chemicals such as DDT and PCBs has been associated with a drop in sperm count, breast cancer, testicular cancer, and hypospadias, which are all associated with endocrine disruption caused by these chemicals [30]. This comes as a result of some PCB congeners being able to occupy thyroid receptors, thus interrupting their action [17, 30].

PCBs accumulate in the fats of organisms and get passed on from one organism to the other in food chains [31, 32], thus causing bioaccumulation. They get entry into the human body and animals through the skin, lungs, and gastrointestinal tract [13]. PCBs then get distributed to various parts of the body via blood and accumulate in different tissues [31, 33]. The effects of PCBs on humans depend on age, sex, and part of the body affected by chemicals [13]. The liver, as the major organ for removal of toxins in the body, is usually highly affected by PCBs [13, 29]. Humans become exposed to PCBs through consumption of contaminated fish, meat, and dairy products [28] and also through grains grown in PCB contaminated soils [13, 28]. PCBs have been isolated from human milk and serum [31, 34] and have been found to have effects on breastfed children leading to low IQ and endocrine-related ailments [28, 31, 34]. Some studies have shown an increase in cancer mortality in workers exposed to PCBs [13].

2.4. Biodegradation

Biodegradation is the metabolic ability of microorganisms to transform or mineralize organic contaminants into less harmful, non-hazardous substances, which are integrated into natural biochemical cycles [27, 35]. Specific bacteria having bio-degradative potential for various chemical substances in wastewater as well as raw water may be used to treat water [35] for purposes of safe recycling. Bacteria, unlike other organisms, have the ability to interact better with man-made and naturally occurring compounds, which result in such compounds being changed structurally and eventually degraded [35]. This is in a way a better cleanup strategy that can be used in the cleanup of wastewater as it is environment friendly [35]. Use of mixed population of microbes is usually recommended as it has been seen to yield faster results as the two different microbes attack different parts through different mechanisms resulting in effective breakdown of the toxic compound [21, 33]. This activity also creates a condition of co-metabolism [33].

PCBs may not be readily biodegradable, but studies have shown that some bacteria species such as *Vibrio cholera*, *Acinetobacter 1woffnii*, *Aeromonas hydrophila*, *Pseudomonas aeruginosa*, *Pseudomonas putida*, *Rhodococcus* sp., *Bacillus* sp., and *Burkholderia* sp. have the ability to breakdown these compounds, although it is through a very long route [11, 13, 21, 36, 37, 51]. This may be achieved through co-metabolism and mineralization [8, 35]. They use of a metabolic pathway similar in all these bacteria, which comprise four steps catalyzed by enzymes BphA, BphB, BphC, and BphD [37]. The pathway, according to Petric et al., is initiated by insertion of two oxygen atoms at the carbon positions 2, 3 of one aromatic ring [37]. This is followed by dehydrogenation meta-cleavage and hydrolysis forming a 5-carbon compound [37]. The process follows a biphenyl catabolic pathway [37].

2.5. Biodegradation of xenobiotic compounds

According to Heider and Rabus, xenobiotic compound due to its recalcitrant nature is hard to break down [38]. The recalcitrant nature of these compounds is a result of the complexity of its chemical composition [8]. Breakdown of these compounds occurs when enzymes act on certain groups present in the compound [38]. The halocarbons, for example, the halogen group, are targeted, with enzymes such as oxygenases playing a major role in their breakdown [8]. The enzymes target the bonds such as ester-, amide-, or ether bonds present in the compounds leading to break down of these compounds [39, 40]. The enzymes may target the aliphatic chains and in aromatic compounds, the aromatic components may be targeted [40]. The mode of attack as well as the site depends primarily on the action of enzyme, its concentration, and favorable conditions [40]. According to Abor-Amer [40], the xenobiotics do not act as a source of energy to microbes and as a result, they are not degraded while the presence of a suitable substrate induces its breakdown [39]. These substrates are known as co-metabolites, and the process of degradation is known asco-metabolism [39]. Gratuitous metabolism is another process in which xenobiotics serve as substrates and are acted upon to release energy [8].

The processes described cannot be achieved through the use of *Moringa oleifera* in treating wastewater to remove PCBs. It is evident from literature that the removal of these compounds using plant protein has not been fully studied [52]. Plant protein has been found to be slightly efficient with the reduction of fecal coliforms and other bacteria [41, 42], which has made Moringa treatment to be applicable. The use of *Moringa oleifera* seed powder in water treatment plants has been found to target mainly microorganisms, thus reducing turbidity [43]. Although this mode of water treatment has been used, especially in rural areas of the developing countries, synthetic polymers, aluminum sulfate, ferric chloride, and poly aluminum chlorides used together with this powder have been reported to be unsafe [41, 43, 44]. The action of *Moringa oleifera* seed powder has been reported to be based on the ability of the protein contained in the seeds to be able to form coagulants, which reduce water turbidity by acting on coliforms [45]. The bacteria found to be mainly involved in biodegradation of POPs and PCBs have been found mostly not to be coliforms [11, 13]. After treating water with Moringa seed powder, 10^1–10^5 of bacteria is left [45]. Taking into cognizance that Moringa is a tree, sustainability of tree growth and productivity, which relies on environmental conditions, may not be viable. This will therefore affect production and maintenance of the Moringa tree

species, given the global warming and related environmental problems. Growing of bacteria indoors is quite sustainable, when compared to growth of plants although Lea argues that propagation is affordable [44].

3. Materials and method

3.1. Sample collection

Water released from the wastewater treatment plant (effluent) was obtained from Notwane Sewage Treatment Plant situated in Gaborone, Botswana. It was collected from the sampling site in sterile 250 ml Duran bottles and immediately placed on ice in a cooler box with ice. The samples were taken to the Department of Biological Sciences, North-West University, Mafikeng for analysis. Samples were analyzed within 24 h of sampling. The treatment plant treats 40,000 m^3 per day of sewage.

3.2. Biodegradation of PCBs in wastewater by isolate *Pseudomonas aeruginosa*

In the study carried out by the author, out of the many bacteria stated in literature, only *Pseudomonas aeruginosa* isolated from the wastewater sampled during the study was used. The water samples were divided into two parts, one part was sterilized by autoclaving at 121°C for 15 min and the other half was left unsterilized. The wastewater samples were treated with Aroclors of polychlorinated biphenyls (PCBs) obtained from SUPELCO Solutions Within™, USA, through Lehlabile Scientific, South Africa. The PCBs were supplied as Aroclors. Aroclor 1242 (Lot No. LB8851), 1248 (Lot No. LB88969), and 1260 (Lot No. LB92109) in 1 ml ampoules at concentration 1000 μg/ml dissolved in isooctane were used in this study. The purity for each Aroclor was not stated.

To each 100 ml wastewater sample in a 250 ml flask, 10 μl of polychlorinated biphenyls Aroclors mixture, herein referred to as PCBs, was added. The sterilized wastewater samples were inoculated with a colony of the 18 h old culture of the test organism, which was identified as *Pseudomonas aeruginosa* (with accession number from the gene bank of CP 006832 in a study carried out in 2014). Non-sterilized wastewater without bacterial inoculation (Control 1) and sterilized wastewater without inoculation (Control 2) were both treated with PCBs and were the controls. The flasks were wrapped with aluminum foil to exclude light and were incubated at 30°C in the dark in a rotary shaker at 150 rpm [46]. A 5 ml was aseptically taken at 24 h intervals from each setup/flask for detection of PCBs using HPLC and spectral changes were checked at 200–800 nm using Cary 300 UV-visible spectrophotometer, for a period of 96 h.

Analysis for PCB using HPLC was carried out as described by Roy et al. with some modifications [46]. A 1 ml was sampled from each setup to check for residual PCB at 24 h interval. The compounds were extracted by adding 10 ml each of dichloromethane and acetone. The mixture was incubated in a rotary shaker for 24 h at 30°C. After incubation, the mixture was centrifuged for 10 min at 12,000 rpm at 4°C using a Hermle Z326k high speed microcentrifuge, Labortechnik GmbH (LASEC, South Africa). The extra water was pipetted and 4 g

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of anhydrous sodium sulfate mixed with a PCB-containing solvent to remove residual water. The extract was concentrated to 1.5 ml using a rotary evaporator Stuart RE300DB, LASEC, South Africa and filtered with 0.45 μm PTFE syringe filters. Extracts were analyzed by high performance liquid chromatography (HPLC) UFLC Shimadzu using a florescence detector pump RF-20A and system gold column C18 (CTO-20A). The excitation level was set at 254 nm, emission level at 390 nm. The mobile phase used was a mixture of acetonitrile and water (80:20) as described by Roy et al. [46]. Data analysis was computed using real-time analysis. All chemicals used were of HPLC grade supplied by Sigma Aldrich through Lehlabile Scientific, South Africa.

4. Results

4.1. Degradation of PCBs by *Pseudomonas aeruginosa*

Samples of wastewater from the Notwane Sewage Treatment Plant were used in this study to find out the degree of biodegradation of PCBs in wastewater un-inoculated and inoculated with the test organism. Spectral changes (a shift in wavelength (λ_{max}) in nm), detected using the UV-visible spectrophotometer, were used as an indication that the compounds were broken down into new products. The results of the wavemax (λ_{max}) nm obtained are presented in **Figure 2**.

The results shown by chromatogram indicated that there was a shift in λ_{max} from 224 to 270 nm in 0 h of incubation to 96 h of incubation at 30°C on a rotary shaker in the dark. These results were obtained using a Cary 300 UV-visible spectrophotometer at a wavelength range of 200–800 nm. The results were an indication that isolates *Pseudomonas aeruginosa* was able to degrade Aroclor 1260 into chlorobenzoates and derivatives, which have wavelength ranging from 244 to 270 nm, hence the shift in wavelength.

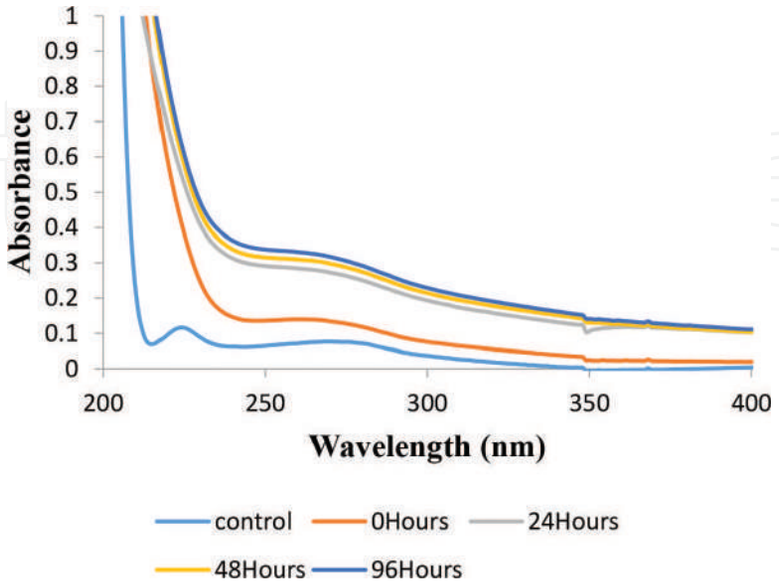

Figure 2. Spectral changes of PCB degradation in water inoculated with isolate *Pseudomonas aeruginosa*.

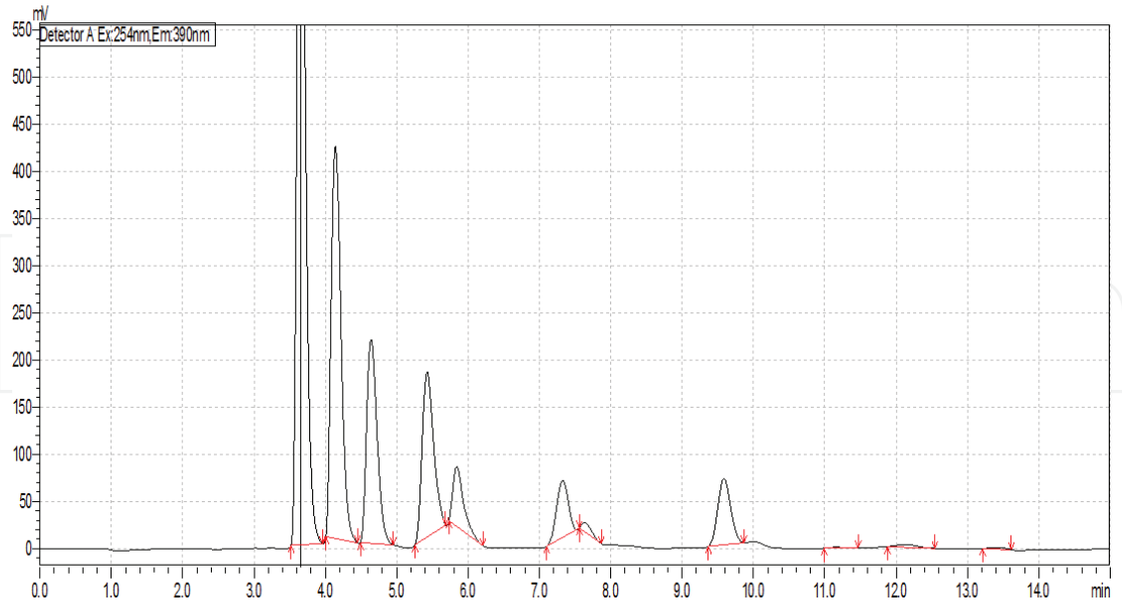

Figure 3. HPLC chromatogram for PCBs standard using a florescence detector method at 10 µl injection volume.

4.2. Results from high performance liquid chromatography (HPLC)

HPLC chromatogram depicted differences in picks obtained for the experiments, the controls, and the standards. Although concentrations were not determined, no PCBs were detected by HPLC after 96 h of incubation. This was an indication that the bacteria degraded the compounds, hence the chromatogram shown in **Figure 4**. The chromatogram obtained for the experiments was compared with the chromatogram for the PCB standard using the retention times for the compounds in the standard, which was represented in **Figure 3**. The results for

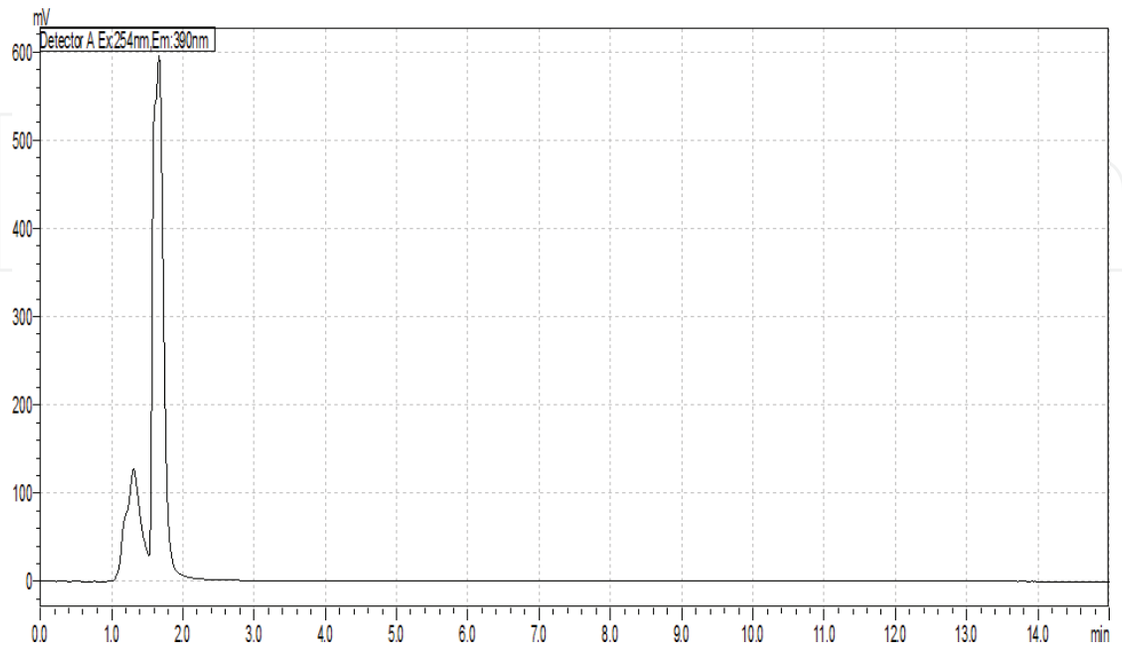

Figure 4. Chromatogram for PCB biodegradation experiment after 96 h of incubation.

PCB standard presented in **Figure 3** showed that there were several compounds in the Aroclor; thus, the many picks, which are not found when the same treatment was extended to the experiment, resulted in **Figure 4**.

The chromatogram shows that the components of the standard had retention times ranging from 3.647 to 13.119 min. The components picked by the instrument are indicated by the red line marking the beginning and ending of the peak. The instrument could not detect the actual names of the compounds though.

The wastewater was sterilized and thereafter inoculated with the test organism and PCBs mixture added. **Figure 4** shows that no peaks were picked by the HPLC. This is an indication that the polychlorinated biphenyls added to the wastewater were completely broken down by isolate *Pseudomonas aeruginosa* resulting in complete elimination.

Representation of **Figure 4** is a clear indication that there were no detectable amounts of compounds after Aroclor was subjected to bacterial treatment. The compounds were broken down in 5 days. There are no peaks shown as compared to the chromatogram shown in **Figure 3**.

5. Discussion

The wavelength maximum (λ_{max}) observed after 96 h ranged from 264 to 269 nm on average for PCBs (**Figure 2**). These results indicated that the PCBs were broken down forming new products with different wavelength and thus the change. This implies that the bacteria were able to use them as their sole source of carbon; thus, the biodegradation of the PCBs added to wastewater. The shifts are an indication of the presence of initial ring oxidation metabolites and ring fission metabolites [19, 47]. PCBs first get degraded into chlorobenzoates [47] that have been found to have λ_{max} ranging from 210 to 214 nm in the B-band and 244 to 270 nm in the C-band when dissolved in water [48], a range that was observed in the results obtained after 24 h of culturing the organism used in this study in PCBs Aroclor mixture, results of which are shown in **Figure 2**. The results depicted that the bacteria was able to breakdown the PCBs, which were similar to results in a similar studies by Vrchotova et al. and Seeger et al. [47, 49]. In their studies [47, 49], the product chlorobenzoate was biodegraded into benzoate and eventually pyruvate and acetyladehyde, which are essential in the tricarboxylic cycle (TCA) [47, 49].

The HPLC run confirmed that the compound was biodegraded by the bacteria isolate *Pseudomonas aeruginosa* as presented in **Figures 3** and **4**, which was also proved by Heider and Rabus, Roy et al. and Raja et al. [38, 46, 50] in their studies. No PCB compound was detected after 96 h of exposure to the bacteria in wastewater.

6. Conclusion

Pseudomonas aeruginosa, isolated from wastewater in the Notwane Sewage Treatment Plant was successfully used in biodegradation of recalcitrant polychlorinated biphenyls (PCBs). This having been successfully employed at the micro level, and further tests can be carried out to

validate the results obtained in this study. With this recommendation in place, it is ideal to say that employing bacteria in the biodegradation processes of recalcitrant PCBs will be highly cost effective as it is a biotechnological process. The process will enable developing countries to employ effective but easy to maintain at a cost effective mode means of wastewater treatment. This wholly will also enable these countries to address the problem of water shortage at the same time practicing water conservation strategies. This is in a way contributing toward addressing the sustainable development goals (SDGs). With the findings from this study, a recommendation for further experimentation on a larger scale is made so as to safely recycle the sewage water for purposes of redirecting to Gaborone dam. This in a way will aid in curbing the problem of water shortage, of course, taking into consideration other factors, such as total coliforms, *Escherichia coli,* and other pathogenic organisms and chemicals. These have to be within the expected standards according to Botswana Bureau of Standards (BOBS) limits as well as international World Health Organization (WHO) standards.

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Conflict of interest

The author declares that there is no conflict of interests regarding the publication of this paper.

Other declarations

This chapter was extracted from the thesis (unpublished) of my research for PhD, which was undertaken in 2014 with University of North West, Mafikeng Campus in South Africa.

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