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Electro-oxidation of fish meal industry wastewater in a stirred batch reactor using a Ti/RuO$_2$ anode

Raju Meganathan IWA iD* and Rajagopalan Varadarajan

Department of Civil Engineering, University College of Engineering (BIT Campus) Anna University, Tiruchirappalli 620024, India
*Corresponding author. E-mail: sabariraju95@gmail.com

iD RM, 0000-0002-0449-0321

ABSTRACT

Fish meal is used as feed for fish, dogs and cats, and in the pharmaceutical industry. Direct electro-oxidation has been used to treat fish meal industry effluent and organic pollutant removal, and was studied in this project. The anode used was titanium coated with ruthenium oxide and the cathode was stainless steel. In addition to organic pollutants, color removal was also studied. The varying parameter was current density, and those used were 10, 20, 27, and 34 mA/cm^2. The effects of mechanical agitation and the inter-electrode distance on pollutant removal were also studied. The highest TOC and color removal (both 82%) were achieved at 34 mA/cm^2, using mechanical agitation with 1.5 cm electrode spacing. Without agitation, TOC removal efficiency was 72%. The results show that electro-oxidation can be an effective secondary treatment for fish meal industry effluent.

Key words: electro-oxidation, mechanical agitator, organic pollutants, Ti/RuO$_2$ anode, total organic carbon

HIGHLIGHTS

- The electro-oxidation process to treat fish meal industry wastewater has been discussed.
- The significance of using a mechanical agitator during the electro-oxidation process has been studied.
- The efficiency of Ti/RuO$_2$ anode in removing organic pollutants has been observed using a laboratory-scale batch reactor.
- Different parameters such as current densities, inter-electrode spacing, and pH have been discussed in this paper.

GRAPHICAL ABSTRACT
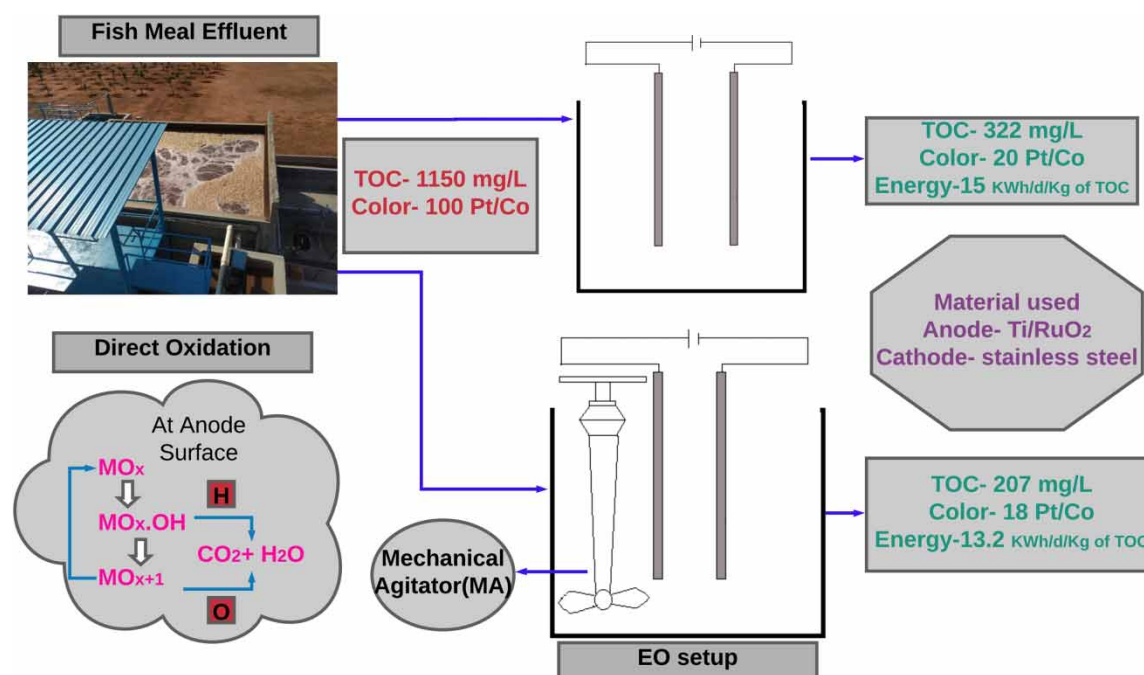
INTRODUCTION

Fish are eaten by people all round the world. Fish and fish products are some of the most widely traded things in international markets, and many industries are involved. Such industries can create environmental problems because of the large quantity of wastewater produced during processing, which can contain, for instance, pesticides, medications, and/or waste feed (Arvanitoyannis & Kassaveti 2008). Many methods are being adopted to treat the wastewater, including biological (Ching & Ghufran 2017), and combined chemical and biological (Cristovao et al. 2012). Riano et al. (2011) used biological methods to help photobioreactors treat fish processing wastewater. Although the use of biological methods reduces pollution considerably, it has disadvantages such as taking a long time, requiring management of the microorganisms used in the process, generation of biological sludge, and so on (Crini & Lichtfouse 2019).

In recent years, electrochemical technologies like electro-oxidation, electro-flotation, and electrocoagulation have received significant attention (Chen 2004). Electro-oxidation is the reaction that takes place on an electrode surface, usually a semiconductor or solid metal, or ionic conductor, due to the passage of current between electrodes. This happens inside a reactor containing the electrodes and electrolyte. Electro-oxidation has been used widely in wastewater treatment to oxidize organic pollutants (Holt et al. 2005), and there are two methods – direct and indirect oxidation. In direct oxidation, the pollutants are destroyed on the anode's surface, whereas in indirect oxidation, they are destroyed in solution. The advantage of direct over indirect oxidation is that it requires no chemicals and produces fewer secondary pollutants. Biological and electrochemical methods do not use harmful reagents, and have minimal impact on the environment (Chakchouk et al. 2017).

The efficiency of electrochemical methods depends mainly on the chemical nature of the anodes (Garcia-Gomez et al. 2014). Several types of anode material have been used to treat wastewater by electro-oxidation, including boron-doped diamond (Montilla et al. 2002; Rodrigo et al. 2010; Chen & Guohua 2011), lead and lead oxides (El-Ashtoukhy et al. 2009), and graphite (Wang et al. 2007). Doped electrodes have also been used in electrochemical treatment – for example, Fe-doped PbO_2 electrodes by Jiang et al. (2014). Several titanium-based anodes have been investigated for removing organic contaminants from olive oil mill wastewater (Gotsi et al. 2005). Titanium doped anodes such as Ti/RuO_2 and Ti/IrO_2 have longer lifetimes and greater electrochemically active area than other electrodes (Costa et al. 2008), and possess higher catalytic activity for oxygen evolution (Li et al. 2016).

Fish industry wastewater treatment using electro-oxidation has not been studied previously to the best of the authors' knowledge. The subject of this project was the efficiency of electro-oxidation in treating fish meal industry wastewater. Total organic carbon (TOC) and color removal were investigated, along with the related energy consumption.

MATERIALS AND METHODS

Materials

Electro-oxidation was carried out in the laboratory in a 5 L, cylindrical, borosilicate glass, batch reactor of 160 mm diameter and 350 mm depth. The cathodes and anodes were molybdenum-bearing grade stainless steel and ruthenium coated titanium (Ti/RuO_2) rods, respectively. Ti/RuO_2 is a type of active anode with good oxygen evolution characteristics, and titanium-based anodes produce relatively small amounts of sludge (Barrera-Díaz et al. 2012), non-active anodes like SnO_2 and PbO_2 are less resistant to corrosion (Chen 2004; Anglada et al. 2009). The other active anode types, like boron-doped diamond (BDD) are costly compared to Ti/RuO_2. The cathodes and anodes comprised high-quality rods. For the anodes, titanium rods were purchased in the market and coated in the laboratory using RuO_2 synthesized by thermal decomposition. Six anodes and six cathodes were used, and each was 6.35 mm in diameter and 300 mm tall. The cathodes and anodes were connected in series using copper wire. A rectifier was used to convert the AC supply to DC, and the electrodes received constant power.

Study sample

The effluent sample was collected from the wastewater treatment plant's primary settling tank at a fish meal factory in Periyapalayam, near Chennai, which processes around 20 tonnes of raw fish every day and generates about 7 m^3 of wastewater. The effluent sample was characterized in the laboratory – see Table 1.

Table 1 | Raw effluent characteristics

Parameter	Unit	Value
pH	n/a	7.23
TOC	mg/L	1,150
Color	Pt/Co	100

Experimental procedure

A trial run was conducted with distilled water to check the working condition of the electrodes. After that the original sample was put into the reactor for the experiments. In the first experiments the current density was varied – the densities applied were 10, 20, 27, and 34 mA/cm^2. The electrode surface area was about 60 cm^2, and the current densities and voltage were monitored using a multimeter (Unit, model number 5223) The first run was performed without using the mechanical agitator but the sample was stirred with a wooden stick for 2 minutes at hourly intervals. 200 ml aliquots were withdrawn from the reactor, also at hourly intervals, for testing.

In the second run, the sample was stirred continuously with a mechanical agitator, which gave good results and was used in subsequent runs (it was also noted that color removal occurred more quickly while using it). Different cathode-anode spacings – 1.5, 2.0 and 2.5 cm – were used in another set of runs. The optimum spacing was found to be 1.5 cm and was used subsequently – for example, when sample pH was altered to determine its effect on pollutant removal. Each experimental run was repeated thrice and the average value was taken for consideration.

A carbon analyzer was used to determine TOC. The sample was dried at 400 °C in an oven, then ground and homogenized, before being dried at 1,050 °C, prior to TOC determination. The sample's pH was measured in the laboratory using a pH meter calibrated using pH tablets.

The sample's color was measured using a spectrophotometer. The standard solution was prepared using chloroplatinate solution and distilled water.

CALCULATIONS

Removal efficiency

Pollutant removal efficiency was calculated using Equation (1):

$$\frac{TOC_I - TOC_t}{TOC_I} \times 100 \tag{1}$$

where TOC_I and TOC_t are the TOC concentrations in the sample initially and at time t, respectively.

Energy consumption

The energy source was the electric current and power consumption was calculated using Equations (2) and (3).

To determine the power in watts –

$$\text{Power} = \text{Voltage (V)} \times \text{Current (A)} \tag{2}$$

The power consumed is determined using

$$\text{Power (KWh/day/Kg-TOC)} = \frac{\text{Power (watts)} \times \text{time} \left(\frac{\text{hrs}}{\text{day}}\right)}{1000 \times \text{TOC removed (Kg)}} \tag{3}$$

RESULTS AND DISCUSSION

Current density

Current density is an important factor for organic pollutant removal using the electrochemical process (Silveira *et al.* 2015). At lower current densities there is a chance of a polymer layer forming on the anode surface and a

minimum of 5 mA/cm^2 is required for organic pollutant oxidation (Cossu *et al.* 1998). Many studies have shown that increasing current density increases proportional removal of the pollutant (Moraes & Bertazzoli 2005; Del *et al.* 2016; Fernandes *et al.* 2016). Increasing the current density also reduces energy efficiency because of side reactions (Quand-Meme *et al.* 2015; Ouarda *et al.* 2020). Moderate current densities – see above – were used in this study.

To determine the effect of current density on pollutant removal, it was increased from 10 to 34 mA/cm^2 in the reactor and the corresponding changes in TOC removal studied. Run time was fixed at 4 hours as TOC removal did not increase much after that (the sample was stirred manually at regular intervals).

As current density was increased, TOC removal also increased with respect to time. For 10 mA/cm^2 current density, TOC removal efficiency was 26% after four hours, while for 20, 27 and 34 mA/cm^2, the TOC removal efficiencies were 46, 55 and 72%, respectively. During the first hour, there was considerable bubble formation because of oxidation at the anode, but, as time increased, bubble formation decreased and after four hours there was no bubble formation. TOC removal efficiency is summarized in Table 2, and illustrated in Figures 1 and 2.

Table 2 | TOC removal efficiency (%) with and without mechanical agitation

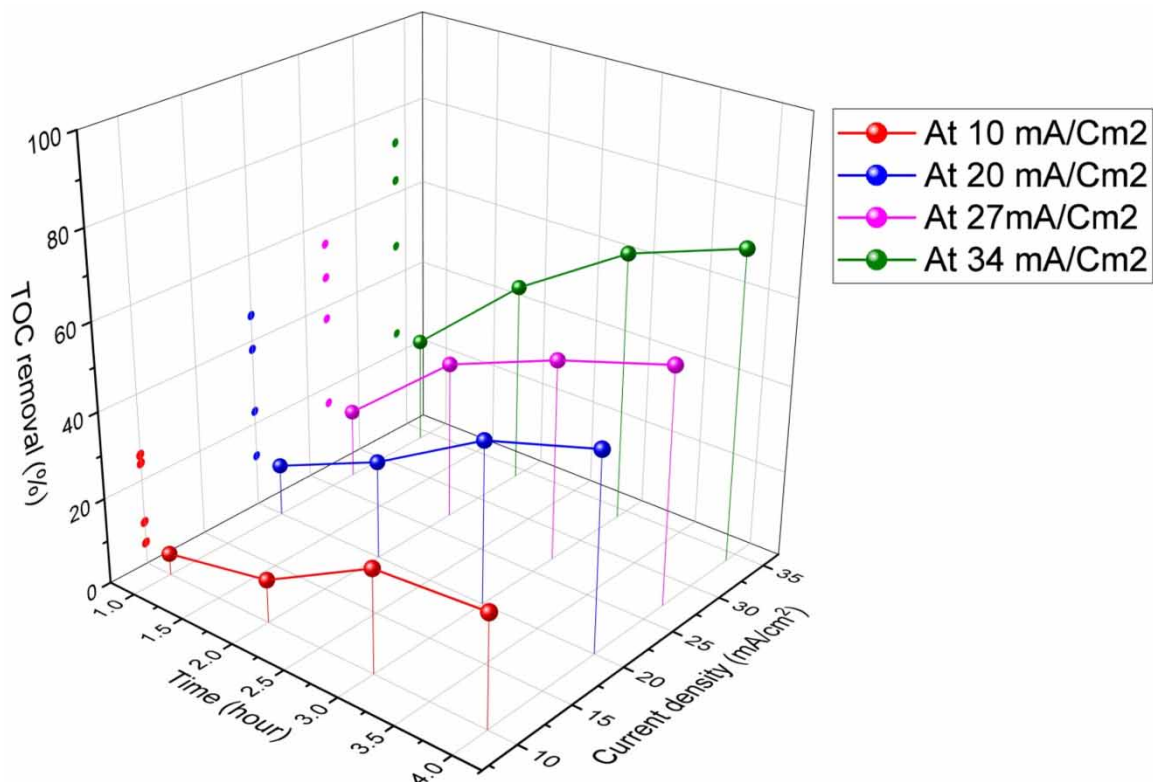| Current density (mA/cm^2)	Without mechanical agitator				With mechanical agitator			
	1 hour	2 hours	3 hours	4 hours	1 hour	2 hours	3 hours	4 hours
10	5	10	24	26	6	21	28	31
20	12	23	38	46	17	32	43	56
27	16	37	47	55	25	40	55	59
34	25	47	63	72	34	56	70	82

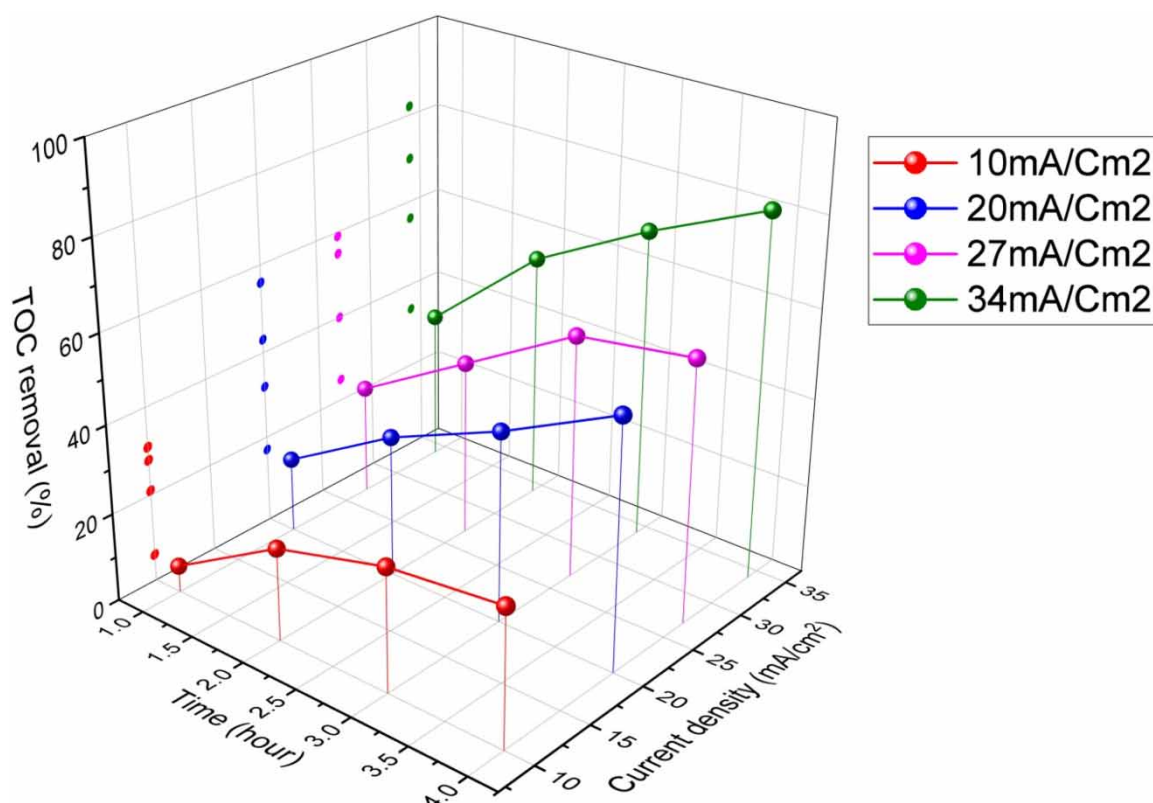**Figure 1** | TOC removal without the mechanical agitator.

Figure 2 | TOC removal with the mechanical agitator.

Current density and mechanical agitator

When an impeller or agitator is used in the electrochemical process, the rate of transfer of reactants to the anode surface increases (Nassar *et al.* 1983; El-Ashtoukhy *et al.* 2009). In the next run, a portable mechanical agitator was used in the reactor to study its effect on electro-oxidation efficiency and TOC removal (the agitator's speed had been optimized at 200 rpm previously). The use of mechanical agitators increased TOC removal. At 34 mA/ cm^2 current density, TOC removal was 82% after four hours, some 10% higher than the previous run (without an agitator). Even at lower current densities, TOC removal efficiency increased when a mechanical agitator (MA) was used. TOC removal efficiencies at 10, 20 and 27 mA/cm^2 were 31, 56 and 59%, respectively. Can (2015) has got the highest TOC removal (82.1%) using a magnetic stirrer, which is similar to this study's results. TOC removal efficiency with a mechanical agitator in use is shown in Figure 2, and TOC removal efficiency with mechanical agitation in Table 2.

Electrode spacing

Closer electrode spacing reduces energy consumption because the electrical resistance between cathode and anode is reduced (Quan *et al.* 2013). Zhang *et al.* (2011) found that the narrower inter-electrode gap increases pollution removal efficiency. Cathodes and anodes are important in electrooxidation because electron transfer occurs between them. The literature review for this study, however, yielded no clear explanation on the electrode spacing that should be used. Because of this, three different spacings – 1.5, 2.0 and 2.5 cm – were tested, based on the knowledge that 1 cm was too close. At 1.5 cm spacing the highest TOC removal was 82%, which fell to 76 and 75% at 2.0 and 2.5 cm, respectively – see Figure 3. On this basis, 1.5 cm spacing was used in all subsequent runs.

pH

Views on the operational pH range of wastewater during electro-oxidation are mixed. According to some reports acid pH during the process helps in pollutant removal (Lissens *et al.* 2003; Chu *et al.* 2010; Murugananthan *et al.* 2010). Others reports state that higher pH levels are more effective (Flox *et al.* 2005; Valero *et al.* 2014). Elaoud *et al.* (2011) reported that pollutant removal is unaffected by pH.
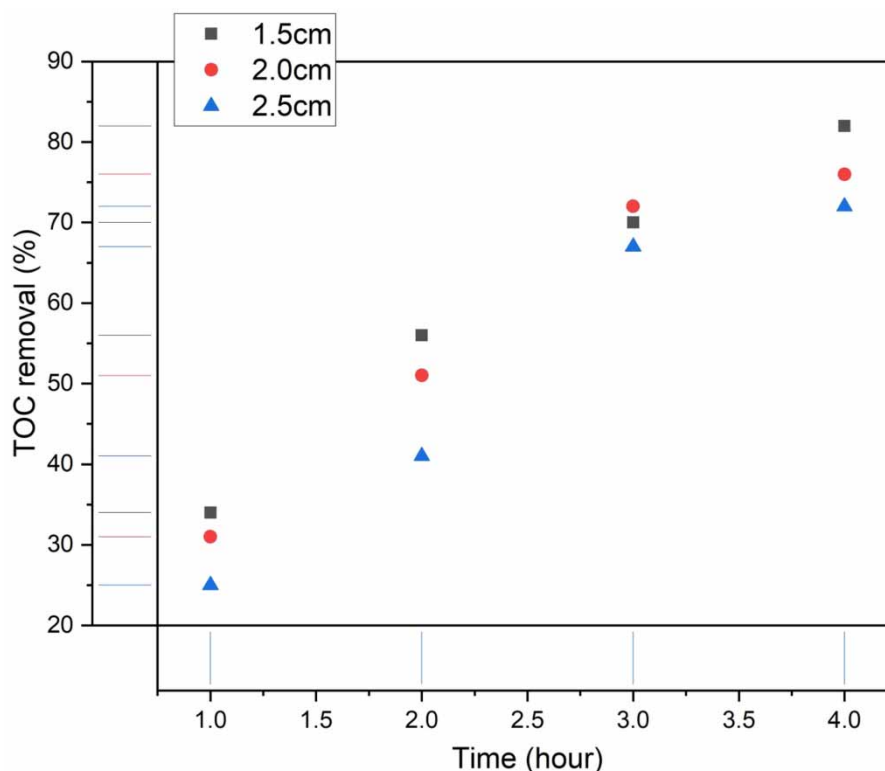
Figure 3 | TOC removal versus electrode spacing.

In this study, the sample's initial pH was 7.23 – that is, in the neutral range. To determine the effect of pH, it was adjusted to acidic (pH 4 and 2) and alkaline (pH 8 and 11) ranges. The best removal results came from the original sample (at neutral pH) after four hours' treatment – Figure 4. The graph shows clearly that, as the pH reaches the neutral range, TOC removal improves. However, the variation in removal efficiency was not very great, although the sample at pH 11 showed the lowest efficiency. So, in this study, pH adjustment was not required and the effluent could be treated with the original pH.

Color removal

The effluent's color change was seen clearly in the reactor during the experiment. The wastewater was dark gray initially, but almost colorless at the end. Color removal increased with increases in both current density and time. Color removal efficiency was 80% at 34 mA/cm^2 after four hours without using the mechanical agitator. Use of the agitator increased color removal considerably early in the trial but the proportional effect was much less after four hours, when efficiency was 2% higher at 82%. It is clear, however, that electro-oxidation can remove color from this effluent. Proportional color removal with and without mechanical agitator use is shown in Figure 5.

Energy consumption

Power consumption in electro-oxidation was calculated at the end of each run. Obviously, energy consumption increases with increasing current density. Energy consumption is shown in Figure 6.

Since electro-oxidation depends on electron transfer between anode and cathode, energy consumption is affected strongly by the spacing between them. The significance of the electrode gap on energy consumption was investigated at pH 7.23, and current density 34 mA/cm^2. It was found that when we increase the electrode gap the energy consumption also increases. The energy consumption at 1.5, 2.0, 2.5 cm were 13.26, 14.32, 14.44 kWh/day/kg-TOC respectively after four hours of treatment. The calculated energy consumptions at different electrode spacings are shown in Figure 7.

CONCLUSION

In this study, electro-oxidation using a Ti/RuO$_2$ electrode was shown to be effective in treating fish meal industry wastewater. TOC and color removal efficiencies of 82% were achieved for a retention time of four hours at
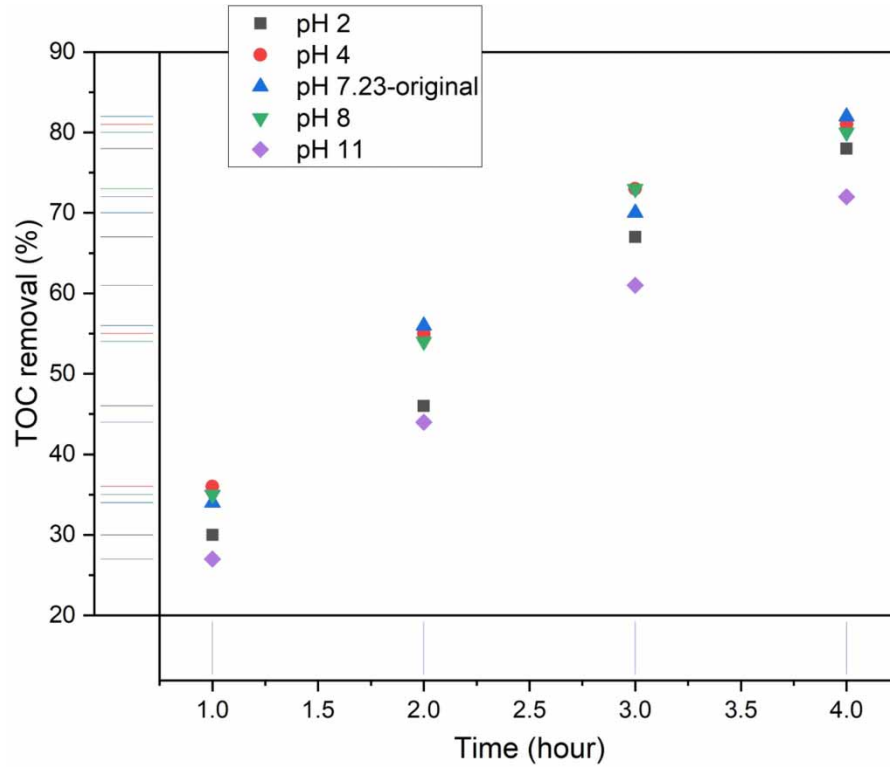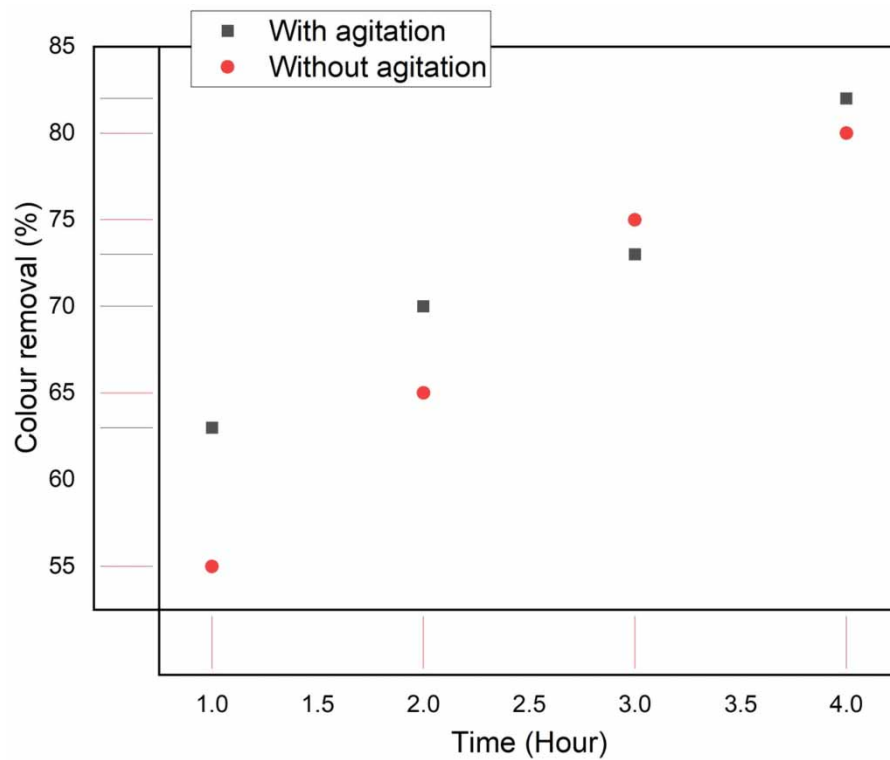
Figure 4 | TOC removal versus pH.

Figure 5 | Color removal with and without mechanical agitation at 34 mA/cm^2.

34 mA/cm^2 current density. Mechanical agitation proved valuable in removing both TOC and color, and reduced total energy consumption.
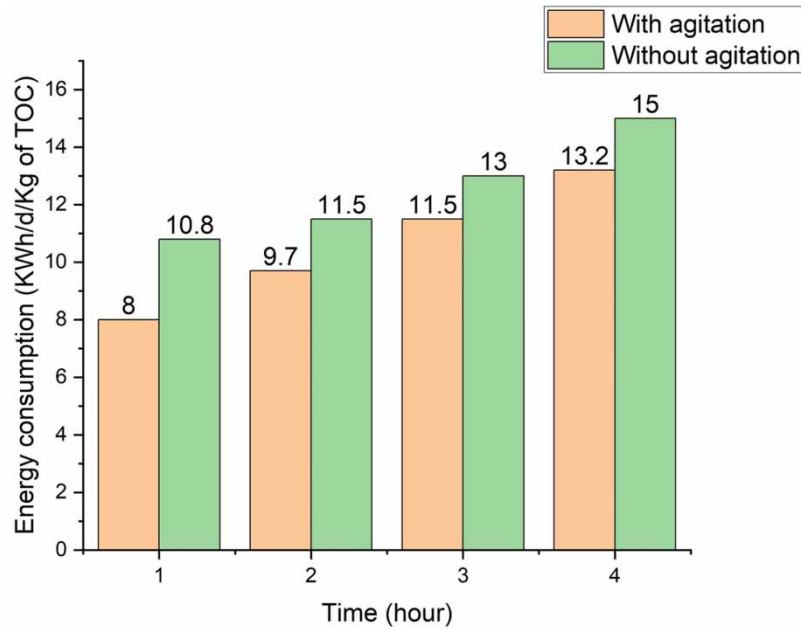
Figure 6 | Total energy consumption with and without mechanical agitation. As can be seen in Figure 6, energy consumption decreased when the mechanical agitator was used. In other words, power consumption can be reduced by using mechanical agitation. In the cases illustrated in the figure, the current density was 34 mA/cm^2.
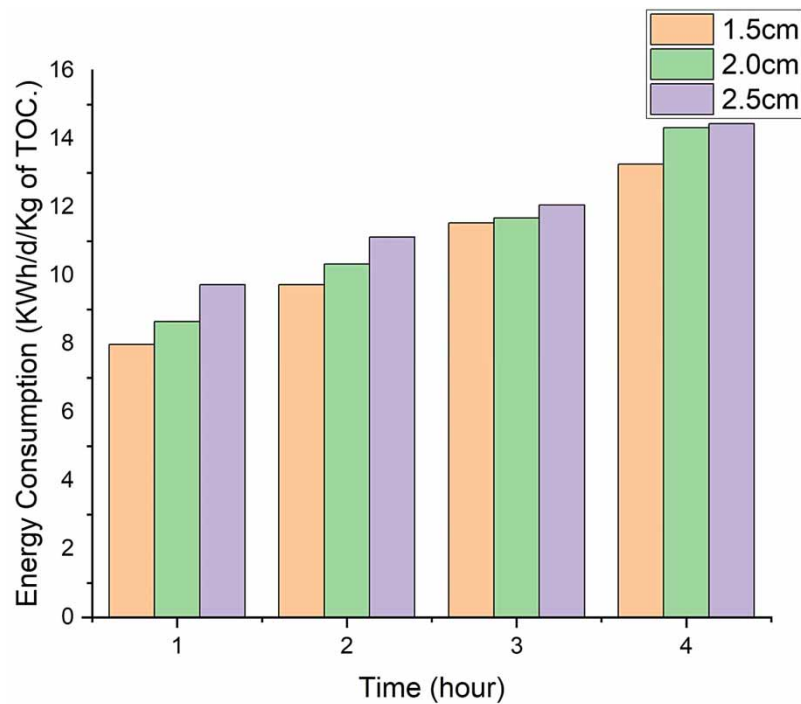

Figure 7 | Energy consumption versus electrode spacing.

While the inter-electrode spacing should be as small as possible in oxidation, there is no need to alter the waste-water's pH. No hazardous by-products were formed as no chemicals were used.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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