Electrolytic treatment of latex wastewater

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Abstract

A novel method of latex wastewater treatment was developed based on in-situ hypochlorous acid generation. The hypochlorous acid was generated in an undivided electrolytic cell consisting of two sets of graphite as anode and stainless sheets as cathode. The generated hypochlorous acid served as an oxidizing agent to destroy the organic present in the latex wastewater. For an influent COD concentration of 3,820 mg/L at an initial pH 4.5; current density of 74.5 mA/cm²; sodium chloride content 3% and electrolysis period of 90 min, resulted in the following residual concentration pH 7.3; COD 78 mg/L; BOD₅ 55 mg/L; TOC 45 mg/L; residual total chlorine 136 mg/L; turbidity 17 NTU and temperature 54°C, respectively. In the case of 2% sodium chloride content for the above, said operating condition resulted in a residual concentration of pH 7; COD 162 mg/L; BOD₅ 105 mg/L; TOC 90 mg/L; residual total chlorine 122 mg/L; turbidity 26 NTU and temperature 60°C respectively. The energy requirements were found to be 35 and 50 Wh/L while treating 24 L of latex wastewater at 3 and 2% sodium chloride concentration at a current density 74.5 mA/cm². The observed energy difference was due to the improved conductivity at high sodium chloride content.

Keywords: Electrolytic treatment; Latex wastewater; Hypochlorous acid; Chlorine, Rubber wastewater, Electrochemical treatment

1. Introduction

Until the 1980s the agro-based industrial sector played a very significant role in Malaysia’s economy. However, in the mid-80s, large tracts of rubber land were converted for industrial, commercial and residential uses. The above changing scenario in the last two decades was responsible for a gradual decline in raw natural rubber production, and Malaysia lost its position as the world’s largest natural rubber producer which it held for the past many decades. Presently, Malaysia is the fourth largest rubber producer in the world — after Thailand,
Indonesia and India. The wastewater generated from the latex processing unit had the following characteristics: pH 4.2–4.8; COD 2,000–6,000 mg/L; BOD$_5$ 1,000–3,500 mg/L; suspended solids 250–400 mg/L and TKN 250–700 mg/L. The conventional method of rubber wastewater treatment are based on the following treatment scheme, namely: an anaerobic-cum-facultative lagoon system; anaerobic-cum-aerated lagoon system; aerated lagoon system (with extended aeration); and oxidation ditch system [1,2]. The effectiveness of treatment units like coagulation [3], stabilization ponds [4], ponding and activated sludge system [5], rock bed filtration [6] and ultrafiltration [7,8] were also investigated using rubber wastewater.

As the conventional latex wastewater treatments were based on biological methods, it leads to longer hydraulic retention time and subjected to failures if shock loaded. In the case of electrochemical treatment, they were neither subjected to failure due to variation in wastewater flow nor strength. The most promising way to carry out electrolytic treatment in a convenient and cost effective method is to generate chlorine or hypochlorous acid as and when required using sea water or brine liquor.

The electrochemical method of waste treatment came into existence when it was first employed to treat sewage [9]. The applicability of electrochemical treatment were also tested using industrial effluents from textiles [10–14], olive mills [15,16], swine manure [17], tanneries [18], beer [19] and distilleries [20]. The electrochemical oxidation of organic matter was investigated using electrodes like graphite rods [18], porous carbon felt [21], boron-doped diamonds [22], ruthenium mixed oxides [23], DSA and graphite felt [24], Ti/TiO$_2$–RuO$_2$–IrO$_2$ [25], Ti/Pt, Ti/PbO$_2$ and Ti/MnO$_2$ [26] and Ti/Pt–Ir, Ti/PbO$_2$, Ti/PdO–Co$_3$O$_4$ and Ti/RhO$_x$–TiO$_2$ [27].

In this present investigation the electrochemical oxidation of latex wastewater was carried out based on in-situ hypochlorous acid generation. The hypochlorous acid was generated using a graphite rod as the anode and stainless sheet as the cathode in an undivided electrolytic reactor.

2. Material and methods
2.1. Latex wastewater characteristics

The raw latex wastewater was collected from Titi Latex Sdn Bhd., Malaysia, whose characteristic are presented in Table 1. The latex wastewater was preserved at a temperature less than 4°C, but was above the freezing point in order to prevent the wastewater from undergoing biodegradation due to microbial action [28].

2.2. Electrolytic reactor set-up

The electrolytic reactor had a circular shape with the following dimensions viz: 300 mm inner diameter and 450 mm height with a liquid volume of 24 L as shown in Fig. 1. The graphite rod (270 mm L and 60 mm Ø) served as the anode, while the perforated stainless steel sheet (270 mm L, 50 mm W and thickness of 0.8 mm) served as the cathode. Two sets of anodes and cathodes were employed during the electrolysis, while each set of anodes was surrounded by two cathode sheets. The distance between anode and cathode was 20 mm. A rectifier had an input of 230 V and variable output of 0–20 V, and a maximum current of 100 A was used as a direct current source. The reactor content was kept under mixed conditions using a recirculation pump having a capacity of 3 L/min. The electrolytic reactor had a provision for removing floating and settled sludge, while the quantum and nature of sludge formation depends on the characteristics of the wastewater under investigation.

2.3. Analytical method

The organic strength of the wastewater was determined by COD and TOC methods [29],
while its biodegradability was measured based on BOD₅. The total chlorine concentration in the sample was determined by the iodometric method. The clarity of the wastewater was determined with by nephelometric method. The suspended solid was determined by drying the filtered residue at 105°C, whereas the total solid was determined by drying the sample at 105°C. In the case of total dissolved solids the filtrate was dried at 180°C. The ammoniacal nitrogen was determined by the titrimetric method. The total microbial count was determined using the membrane filter method [28].

2.4. Experimental method

During electrolysis, chlorine was produced at the anode and hydrogen gas at the cathode. As the anode and cathode were kept in an undivided electrolytic reactor, the generated chlorine undergoes a disproportionation reaction resulting in hypochlorous acid (Cl₂ + H₂O → HOCl + HCl). Further disproportion of OCℓ⁻ to ClO₃⁻ was favoured at high temperature (approximately 75°C) and under alkaline conditions (3OCℓ⁻ → ClO₃⁻ + 2Cl⁻). At 20°C the hypochlorous acid dissociates to the extent of 3% at pH 6; 30% at pH 7 and 80% at pH 8 [30]. The samples of effluent were drawn periodically and were analyzed to assess the performance of the electrolytic system. The experimental variables such as current densities (37.2 and 74.5 mA/cm²); pH (4.5–7.5) and sodium chloride concentration (1, 2 and 3%) were evaluated systematically. The initial experiments were carried out using potable water at 3% sodium chloride concentration for a pH range 4.5 to 7.5 insteps of 0.5, in order to determine the amount of total chlorine generated.

3. Results and discussion

The variation on total chlorine production in potable water was investigated for an initial sodium chloride concentration of 3% at a fixed current density of 50 mA/cm² by varying the
initial pH from 4.5 to 7.5. The results showed that irrespective of the initial pH the total chlorine production was more or less the same for a given electrolysis period. For example during 15 min of electrolysis period at a fixed current density of 50 mA/cm² for an initial pH value of 4.5; 5.5; 6.5 and 7.5, the total residual chlorine concentration was found to be 568; 572; 580 and 592 mg/L respectively. For the above said operating conditions the corresponding residual pH was found to be 5.8, 6.7, 7.3 and 8.1 respectively. As the pH value increased higher than 7.5, the generated hypochlorous acid will be converted into hypochlorite ion which is a weak oxidizing agent. Hence the reactor pH determines the efficiency of generated chlorine towards oxidizing the organic matter present in the wastewater. As the raw latex wastewater had an initial pH value of 5.2, it was subjected to pH adjustment using sulfuric acid in order to attain a value of 4.5±0.1. Prior to electrochemical oxidation, the latex wastewater was subjected to screening, which had a clear opening of 2 mm.

The initial experiments on the latex wastewater treatment were carried out at varying sodium chloride content namely 1, 2 and 3% for a fixed pH value of 4.5 and at an initial COD concentration of 3,820 mg/L. The results showed that the end of 50 min of electrolysis period for the above said condition resulted in a residual COD value of 3,278, 2,956 and 2,650 mg/L respectively. As the COD removal efficiency was lower at 1% sodium chloride concentration, the further treatment of latex wastewater was carried out at an electrolyte concentration of 2% and 3% respectively.

Fig. 2 shows the residual COD concentration during the electrolysis period for an initial COD concentration of 3,820 mg/L at current densities of 37.2 and 74.5 mA/cm². For example, at 37.2 mA/cm² of current density with an electrolyte concentration of 2% and 3% and 30 min of electrolysis period resulted in a residual COD value of 2,956 and 2,650 mg/L respectively. In the case of electrolysis at a current density 74.5 mA/cm² for the above said electrolyte concentration and electrolysis period resulted in a residual COD value of 2,247 and 1,912 mg/L respectively. Further increase in the electrolysis period showed a decrease in residual COD concentration irrespective of the current densities. In the case of 3% sodium chloride as electrolyte at a current densities of 37.2 and 74.5 mA/cm², for an electrolysis period of 90 min resulted in a residual COD concentration of 435 and 78 mg/L respectively. The results showed that at a higher current density more hypochlorous acid was generated, leading to the oxidation of organic matter present in the wastewater in a shorter period.

The residual BOD₅ concentration versus the electrolysis period is shown in Fig. 3, at 2% and 3% electrolyte for current densities 37.2 and 74.5 mA/cm². As shown in Fig. 3, with the increase in electrolysis period for a given current density resulted in a lower BOD₅ value. For example, in the case of 90 min of electrolysis at current densities 37.2 and 74.5 mA/cm² with 3% electrolyte concentration resulted in a residual BOD₅ value of 240 and 55 mg/L respectively.

The total organic carbon (TOC) removal during the electrolysis period is shown in Fig. 4 for current densities of 37.2 and 74.5 mA/cm² at
As the electrolysis period and current density increased, the residual total organic carbon concentration decreased. For example at the end of 90 min of electrolysis with 3% sodium chloride as electrolyte for a current density 37.2 and 74.5 mA/cm², the residual TOC value was found to be 220 and 45 mg/L respectively. The results showed that in the case of current density of 74.5 mA/cm² the COD/TOC ratio decreased from 3.4 to 1.7 respectively. The decrease in COD/TOC ratio shows that the organic carbon was destroyed due to the oxidizing action of the generated hypochlorous acid. In the case of phenol-formaldehyde resin wastewater treatment based on hypochlorous oxidation resulted in a decrease in COD/TOC ratio from 4.3 to 1.3 [25], while the flavor manufacturing facility wastewater showed a decrease in COD/TOC ratio from 3.3 to 1.7 [31].

The total residual chlorine concentration during the electrolysis period is shown in Fig. 5 for an initial COD concentration of 3820 mg/L at varying sodium chloride content (2 and 3%) and current densities of 37.2 and 74.5 mA/cm² respectively. The results showed that the residual chlorine level was low during initial period of electrolysis (15 min.), but a further increase in the electrolysis period showed a gradual rise in residual chlorine concentration. For example at a current density of 37.2 mA/cm² for an electrolyte content of 2% and 3% at the end of 30 min of electrolysis, the total residual chlorine concentration was found to be 13 and 28 mg/L respectively, whereas at a current density of 74.5 mA/cm² for the above condition resulted in a total residual chlorine concentration of 45 and.
58 mg/L respectively. In the case of 3% sodium chloride as electrolyte for the current densities of 37.2 and 74.5 mA/cm² and an electrolysis period of 90 min resulted in a total residual chlorine concentration of 96 and 136 mg/L respectively. The reason for the rise in total residual chlorine concentration during the electrolysis at current density 74.5 mA/cm² when compared to 37.2 mA/cm² was due to greater chlorine generation at a higher current density. Moreover, the accumulation of hypochorous acid was relatively low as it was utilized to destroy the organic content of the latex wastewater, as shown in Fig. 2. During electrolysis, the chlorine was converted into chlorine gas at the graphite anode. The generated chlorine gas undergoes disproportionation reaction leading to the formation of hypochlorous acid. The hypochlorous acid oxidizes the organic matter and is reduced to chlorine. In the absence of organic substance the accumulation of residual chlorine was remarkable as the same was illustrated when electrolysis was conducted using potable water.

Fig. 6 shows the residual turbidity level during the electrolysis period at varying sodium chloride content 2% and 3% and current densities 37.2 and 74.5 mA/cm² for an influent COD concentration 3,820 mg/L. At the end of 30 min of electrolysis period for a current density 37.2 mA/cm² with 2% and 3% electrolyte concentration resulted in a residual turbidity value of 280 and 260 NTU respectively. In the case of a current density of 74.5 mA/cm², for the above electrolyte concentration and electrolysis period, the residual turbidity was found to be 250 and 205 NTU respectively. In the case of a current density of 74.5 mA/cm², for the above electrolyte concentration and electrolysis period, the residual turbidity was found to be 250 and 205 NTU respectively. Further increase in the electrolysis period showed a gradual decrease in turbidity. As shown in Fig. 6, the residual turbidity showed a minimum value at 3% sodium chloride content for a given current density. For example at a current densities 37.2 and 74.5 mA/cm² with 3% electrolyte and an electrolysis period of 90 min resulted in a residual turbidity value of 65 and 17 NTU respectively. The initial latex wastewater had an appearance of pale milky white liquid with a turbidity of 530 NTU, but during the electrolysis it turned into transparent potable water in appearance with fine suspended solids. The 17 NTU which was obtained at 3% sodium chloride at 74.5 mA/cm² was due to fine suspended solids of the rubber particles. The sample, when subjected to clarification for 30 min settling time, yielded a turbidity value of 10 NTU with a residual COD concentration of 60 mg/L.

The electrolyte temperature during the electrolysis of latex wastewater is shown in Fig. 7 for 2% and 3% electrolyte concentration and at current densities 37.2 and 74.5 mA/cm². For example, a current density of 37.2 mA/cm² and 30 min of electrolysis period with electrolyte concentration of 2% and 3% resulted in an electrolyte temperature of 28°C and 26°C respectively. For the above condition, the case of current density at 74.5 mA/cm² resulted in an electrolyte temperature of 38°C and 32°C respectively. The reason for the low electrolyte temperature for a given current density at 3% electrolyte when compared to 2% electrolyte was due to the improved conductance. The results showed that with the increase in electrolysis period a gradual increase in electrolyte temperature occurred. In the case of 3% sodium chloride as electrolyte, a current density of 37.2 and
74.5 mA/cm² for an electrolysis period of 90 min resulted in an electrolyte temperature of 40°C and 54°C respectively.

The electrolyte pH versus the electrolysis period is shown in Fig. 8 for varying current densities (37.2 and 74.5 mA/cm²) and electrolyte concentration (2% and 3% NaCl). For example, at a current density of 37.2 mA/cm² for a sodium chloride content of 2 and 3% at the end of 30 min of electrolysis, the electrolyte pH was found to be 4.7 and 4.7 respectively. For the above said condition in the case of a current density 74.5 mA/cm², the electrolyte pH was found to be 4.9 and 5.3 respectively. A further increase in the electrolysis period showed a gradual increase in electrolyte pH. In the case of 3% sodium chloride as the electrolyte, current densities of 37.2 and 74.5 mA/cm² for an electrolysis period of 90 min resulted in an electrolyte pH value of 6.5 and 7.3 respectively. The rise in pH during the electrolysis was due to loss of hydrogen gas at the cathode, resulting in hydroxide ion accumulation. As the electrolyte pH and temperature were below 7.5 and 75°C, the formation of ClO₃⁻ was negligible in the present investigation [32].

The influent latex wastewater had an ammoniacal nitrogen content of mg/L. The results showed that during 15 min of electrolysis for varying current densities (37.2 and 74.5 mA/cm²) and electrolyte concentration (2% and 3% NaCl) the ammoniacal nitrogen value reached below the detectable limit. The supernatant of raw latex wastewater had an initial microbial count of 180 CFU/mL. The results showed that an electrolysis period of 90 min at a current density 74.5 mA/cm² and 3% electrolyte concentration resulted in an undetectable level of microbial count. Hence it can be concluded that disinfection also occurred during the treatment process.

The energy requirement for treating latex wastewater was investigated at varying sodium chloride concentrations (2% and 3%) and fixed current densities of 37.2 and 74.5 mA/cm². The results showed that for an electrolyte concentration of 2% and 3% at a current density 37.2 mA/cm², the energy requirements were found to be 23, 19 and 15 Wh/L respectively. In the case of electrolytic treatment, a current density of 74.5 mA/cm² for the above condition resulted in energy requirements of 50 and 35 Wh/L respectively. The observed low energy requirement at 3% electrolyte was due to the improved conductivity in comparison to the 2% electrolyte addition.

### 4. Conclusion

The present investigation revealed that in-situ generation of hypochlorous acid was effective
towards the treatment of latex wastewater. The optimum operating conditions were found to be at an initial pH 4.5, sodium chloride content 3% and current density 74.5 mA/cm². The results showed that at the end of a 90-min electrolysis period for the above operating condition, the treated wastewater had the following characteristics: pH 7.3, COD 78 mg/L, BOD₅ 55 mg/L, TOC 45 mg/L, residual total chlorine 136 mg/L, turbidity 17 NTU and temperature 54°C.

During the electrochemical oxidation process, the latex wastewater undergoes in-situ disinfection due to the generated hypochlorous acid. Moreover, the excess chlorine concentration can be reduced either by storing the treated wastewater in a holding tank or by the addition of bisulfite.

References