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Application of Waste Derived Activated Carbon Felt Electrodes in Minimizing NaCl Use for Electrochemical Disinfection of Water

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In this study, disinfection of raw water using a low-cost activated carbon felt (ACF) electrode was carried out in a tubular electrochemical reactor. The potential of high surface area, appreciable pore network and possible application in disinfection without generating by-products of ACF informed its choice. The precursor utilized for the ACF production was an indigenous recycled palm shell waste from Malaysia. Chemical activation using phosphoric acid (H_3PO_4) was adopted and the physical characterisation of the final ACF presented a surface area of 1500 m^2/g. The water parameters of interest measured were turbidity, total dissolved solids (TDS), pH and total coliforms. The comparative disinfection study investigated the effect of the process performance with and without addition of minute concentrations of NaCl. The efficiency of electrochemical disinfection was assessed by means of disinfection rate, survival ratio, removal efficiency, coliforms count and electrical conductivity as a function of current density. It was found that disinfection was better in the presence of NaCl at concentration of 3 mg/l in comparison to values of 150 mg/l reported in the open literature. The water was completely disinfected at a low current density of 0.42 mA/cm^2 and the high efficiency of pathogen removal observed was attributed to the generation of hypochlorite ions. The low current used coupled with use of low-cost agricultural waste made the process cost effective and attractive.

Keywords: Disinfection, ACF, waste palm shells, survival ratio, NaCl

1. INTRODUCTION

Numerous physical and chemical disinfection methods have been widely studied for improving the quality of drinking water [1, 2]. In physical operations, pathogens are killed by UV radiation, ultrasound or by membrane filtration [2], but these don't produce any residual effects [2, 3]. In chemical disinfection pathogens are destroyed by chlorine dioxide/chloramines [2], ozone [4], hydrogen peroxide [5] and chlorination [2]. These processes are efficient and give residual effects, but they may produce some by products that may adversely affect human health [3]. Chlorine is the most common disinfectant used in the industry. However, direct use of chlorine may result in by products that can be carcinogenic [6]. The aim to reduce chlorination by-products as well as by-products of ozonation leads to the search of new alternative methods and technologies of water disinfection, such as electrochemical processes [7].

Electrochemical disinfection is found to be the most effective way to eradicate most pathogens [8, 9]. Electrochemical disinfection devices can be separated into two categories, direct electrolyzers and mixed oxidant generators [10]. Direct electrolyzers have direct contact with the contaminated water, whereas mixed oxidant generators produce a mixture of strong oxidizing species (such as free chlorine, ozone, short lived radicals and others) from a concentrated brine solution. Usually, the passage of electric current through water containing high sodium chloride salt generates hypochlorous acid or hypochlorite salts, which are very effective disinfecting agents [11].

Bergmann et al. [12, 13] found that the electrochemical disinfection of water involving the presence of chlorine components was better than conventional chlorinated systems due to its higher residual disinfection ability. In addition, Nakajima et al. [14] conducted electrolysis on tap water at 50 A using reactivated free chlorine for up to 30 min. They found that the major agent in the electrolysis of pathogens was free chlorine and the possible bactericidal mechanism was postulated to be via the destruction of bacterial membranes.

Martinez–Huitle [15] reviewed the role of conductive diamond electrodes for water purification. They concluded that the electrochemical disinfection using diamond electrodes generated sufficient chlorine based species for almost complete destruction of pathogens in comparison to disinfection via chlorination or direct application of hypochlorite (NaOCl) [16]. Despite its high disinfection efficiency and high chemical stability, diamond was found to be expensive, with low electrical conductivity and less surface area in comparison to carbon based materials such as felt, fibre or cloth.

Electrochemical disinfection using basal plane graphite electrodes was not found to be very effective as it had a small surface area and consequently could not disinfect large quantities of pathogens [17]. Literature is replete with studies reporting use of carbon in various forms for wastewater/water remediation [18], such as in screen-printed carbon electrode [19] or as carbon paste electrode [20], to name a few. However, efficiency of activated carbon for disinfection is yet to be proven due to possible limitation of adsorption and shielding of pathogens on the carbon surface [21]. Despite that, activated carbon felt (ACF) was found to possess a very high surface area along with a porous network formed with deep micro pores in a narrow range of sizes [22]. Moreover ACF was found to have important advantages with respect to the conventional granular activated carbons, such as, uniform distribution of micro pores, faster adsorption-desorption rate and high fluid permeability [22]. Hence, a better result was expected with ACF than the use of the classical activated carbon for electrochemical disinfection [18].

The aim of this study is to compare disinfection efficiency in the presence/absence of very dilute sodium chloride salt in water at very low applied current densities (i). A tubular electrochemical reactor is used to study the effect of current density on electrical conductivity (EC), total coliforms count (TCC), removal efficiency (η), disinfection rate (R_d) and survival ratio (R_s). Moreover, in this study, ACF is used as electrode material which has been made from recycled waste palm shells thus making it cheaper than commercial activated carbon.

2. METHODS AND MATERIALS

2.1. Chemicals

Lactose broth, phosphoric acid and pure NaCl salt were purchased from Merck, and other standard solutions for the measurement of EC, turbidity and pH were obtained from Hach.

2.2. Preparation and characterization of ACF

A solution of phosphoric acid (40–85 wt.%) was used to impregnate the precursors (waste palm shells). Based on literature reports [23, 24], a ratio of 3:1 was maintained for the phosphoric acid to recycled palm shell waste. Prior to heating the mixture and to ensure homogeneity, a 2 min stirring was observed after which the mixture was calcined for 30 min at 500 °C. The final product was washed with hot distilled water (100 °C) repeatedly until the filtrate was neutral. Oven drying the product at 120 °C for 12 h was then done and subsequently characterized.

2.3. Characterization

The textural characterization analysis of the samples was performed by the nitrogen adsorption/desorption measurements. A Micromeritics ASAP 2010 sorption apparatus using an Autosorb-1 (ASIMP Quantchrome, USA) was employed, and the sorption studies carried out at 77 K in the relative pressure range of 10^{-6}–1 atm. Prior to the sorption measurements, samples were degassed at 250 °C to 3 μm Hg under vacuum for 15 h. Surface area was calculated from experimental adsorption data over a relative pressure (P/P_0) range of 0.05–0.2 using the Brunauer, Emmett, and Teller (BET) method.

2.4. Experimental apparatus and procedure

The schematic diagram the electrochemical tubular reactor used in this research is as shown in Figure 1. The system configuration consisted of a glass tube (diameter 35 mm, length 35 cm) with inlet, outlet and overflow provisions. Two sheets of ACF and two ion-exchange membranes (DuPont) were interwoven, rolled and inserted into the reactor. One end of the glass tube was closed with a rubber cork stopper. To establish the input and output terminals, copper wire current collectors were attached to each sheet of ACF to serve as working and counter electrodes. The electrochemical cell was powered by a DC power supply (Thurlby Thandar Instruments Ltd. TTi EX354D) and all potentials were measured against the saturated calomel electrode (SCE). Raw water was fed to the system through the top of the cell, and the treated water left the reactor by the outlet provision at the bottom of the cell at a constant flow rate of 500 cm^3/h. Once treated, the water was collected in sterilized bottles and analyzed.

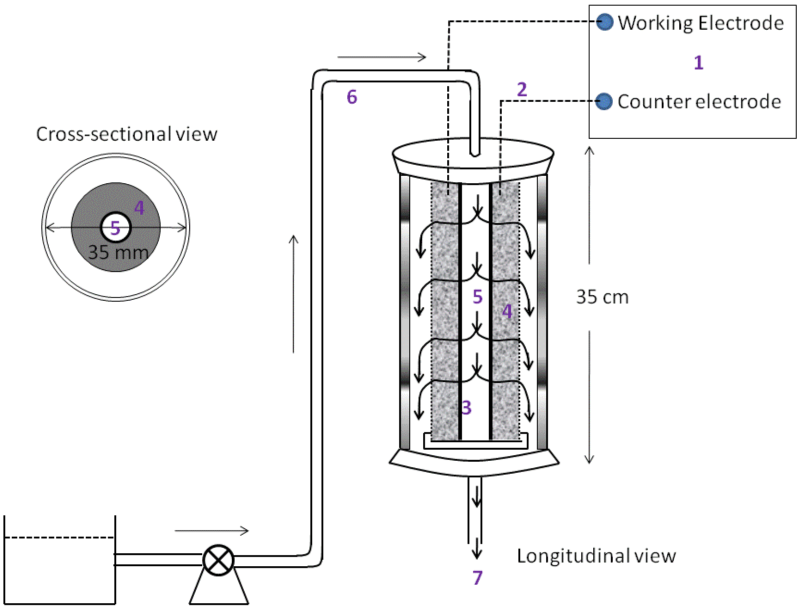

Figure 1. Schematic diagram of the electrochemical disinfection tubular reactor. Purple numbers represent the following: 1- DC power supply, 2- copper wires, 3- ion exchange membrane, 4- ACF electrodes, 5- glass bar, 6 – water inlet, 7- treated water outlet.

Prior to the commencement of disinfection, total coliforms tests were performed using the multiple fermentation tube method [25]. The pH of the water was continuously monitored (both upon inlet as well as from the effluent of the electrochemical cell).

In addition, other water characteristics such as pH, total dissolved solids (TDS), turbidity and EC were also recorded using a pH Meter (Martini MI 151), a turbidity meter (Hach 2100P-46500-0) and an EC meter (Hach Sension5), respectively. Each disinfection experimental run was conducted at a constant current for 15 min. Subsequent experiments were done by increasing the current by 0.02 A at intervals of 15 min until maximum disinfection was achieved. The same experimental procedure was then repeated on tap water samples dosed with 3 mg/l of NaCl.

R_s and R_d were calculated for both disinfected water samples using the expressions given in equation (1) and equation (2), respectively.

$$R_s = \frac{N_a}{N_b} \times 100 \qquad (1)$$

where, N_a is the microbial cell number after treatment and N_b is the microbial cell number before treatment.

$$R_d = \frac{\left[Q\left(C_b - C_a\right)\right]}{V_r} \tag{2}$$

where, C_a is the microbial cell concentration after treatment (cells per cm^3), C_b is the microbial cell concentration before treatment (cells per cm^3), V_r is the reactor volume (cm^3) and Q is the flow rate (cm^3/h). Further, each electrochemical disinfection test is conducted using fresh ACF with exactly the same characteristic to its predecessor. All experimental runs have been repeated at least three times in order to minimize any experimental uncertainty associated with the results.

3. RESULTS AND DISCUSSION

3.1. Characterization of ACF

Results from the characterization of ACF are shown in Table 1. A very high surface area of the ACF of 1500 m^2/g was found to be comparable to commercially reported values.

Table 1. Specifications of ACF prepared from waste palm shells

Parameter	**Value**
Specific surface area (m^2/g)	1500
Dimensions (mm^3)	160 × 150 × 4
Weight (g)	8.04
Thickness (mm)	4

3.2. Water Quality Parameters

The pH of tap water was determined to be about 7.8 as shown in Table 2. This was well within the drinking water pH range of 6.5 and 9.5 [26] or 6.5 and 8.5 [27]. As the literature reported that dissolved chlorine could only be present in water at a pH of 4 or under [26], the free chlorine test was not conducted in this experiment. In addition, the literature reported that the effect of pH variation in open circuit potential in the case of solutions without chlorides was more pronounced when metal electrodes were employed [28]. In these experiments, non-metallic electrodes were employed due to which pH variation was expected to be negligible and thus further measurements were not taken.

Table 2. Characteristics of untreated raw water and maximum contaminant limit (MCL) for each parameter specified by WHO

Parameter	**Value**	**MCL (WHO)**
Total Coliforms Count (MPN/100 ml)	900	0
TDS (mg/l)	232	1000
Turbidity (NTU)	1.97	5
pH	7.8	6.5 – 8.5
Electrical Conductivity (µS/cm)	479	250

Table 2 shows the basic quality parameters of tap water along with its respective maximum contaminant level as specified by the World Health Organization (WHO) [27]. The TDS and turbidity were in the safe range but EC and TCC values were beyond the limits specified by WHO. Hence, EC and TCC required monitoring during electrochemical water disinfection. The TCC analysis showed that the tap water contained 900 total coliforms per 100 ml, a clear indication of significant presence of pathogens, which meant that the water posed a serious risk to human health. Hence, this tap water was not fit for drinking purposes and needed further purification. As a consequence, electrochemical disinfection experiments were performed on two samples of raw tap water: 1) in the absence of sodium chloride salt and 2) in the presence of extremely dilute concentrations of sodium chloride salt (3 mg/l).

3.3. Electrochemical Disinfection

Figure 2 shows that TCC decreases with the increase of i from 0.0 to 0.67 mA/cm^2 in both environments, i.e., with and without sodium chloride salt. This is because at the higher i, more electrons are transferred to the microbial cells attached to the anode leading to decreased respiration and consequent cell death [17]. In the case of water without sodium chloride salt addition, the results show that *c.a.* 90% of pathogen removal takes place at i = 0.25 mA/cm^2 and the maximum disinfection is observed at i = 0.58 mA/cm^2.

However, with the addition of 3 mg/l NaCl in water, *c.a.* 90% disinfection is achieved at a lower current density of 0.167 mA/cm^2 in comparison to the water sample without addition of sodium chloride salt. Moreover, 100% disinfection is achieved at i = 0.33 mA/cm^2. The results thus seem to indicate that the presence of minute quantities of sodium chloride salt benefits the disinfection process.

EC of untreated water is 479 µS/cm, which is above the WHO limit thus warranting reduction. Figure 3 shows the trend in EC as the current density is increased for both solutions (i.e. with and without sodium chloride salt addition). The trend of EC in absence of sodium chloride salt is decreasing with the increase of current density from 0 to 0.67 mA/cm^2 and the lowest EC value of *c.a.* 355 µS/cm is obtained at i = 0.67 mA/cm^2.

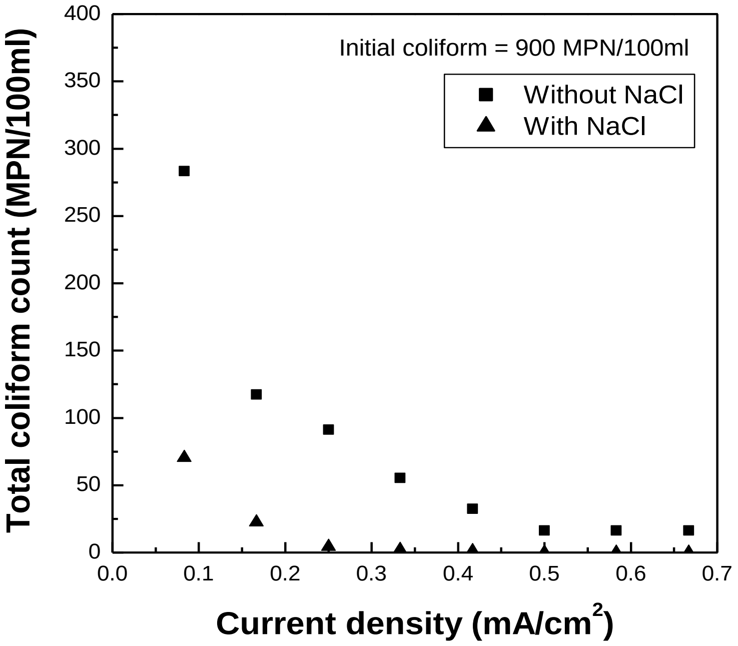

Figure 2. Effect of current density on TCC in both presence/absence of 3 mg/l sodium chloride salt in raw water disinfected using ACF electrodes.

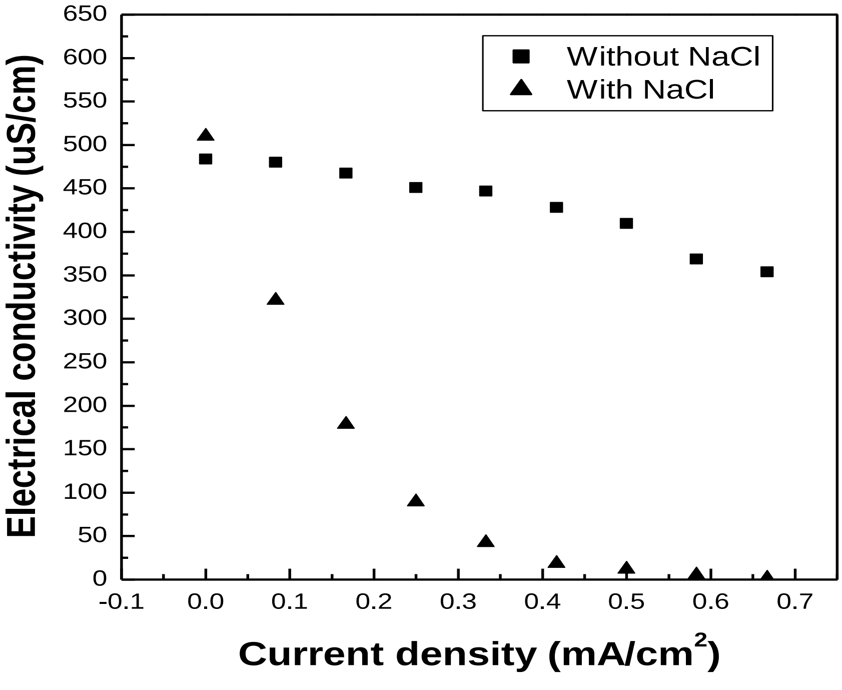

Figure 3 Effect of current density on EC in both presence/absence of 3 mg/l sodium chloride salt in raw water disinfected using ACF electrodes.

However, with the addition of 3 mg/l NaCl, EC decreases towards zero at the highest current density of 0.67 mA/cm^2 (Figure 3). One possible reason for this complete reduction in EC after the addition of sodium chloride salt may be due to the oxidation of other dissolved ions in solution by hypochlorite during the course of electrochemical disinfection [11].

Figure 4 shows the R_d and R_s values with the increase of *i* on ACF in both the absence and the presence of sodium chloride salt in solution. In both cases, the R_d increases linearly up to a certain value and then both rates level off to a value of *c.a.* 15.8 cells/cm^3-h at a current density of 0.5 mA/cm^2. This is because the higher the current density, the lesser is the pathogen cell concentration after treatment and consequently R_d increases [17]. Moreover, this increase is much higher at smaller applied current densities in the presence of sodium chloride than in its absence.

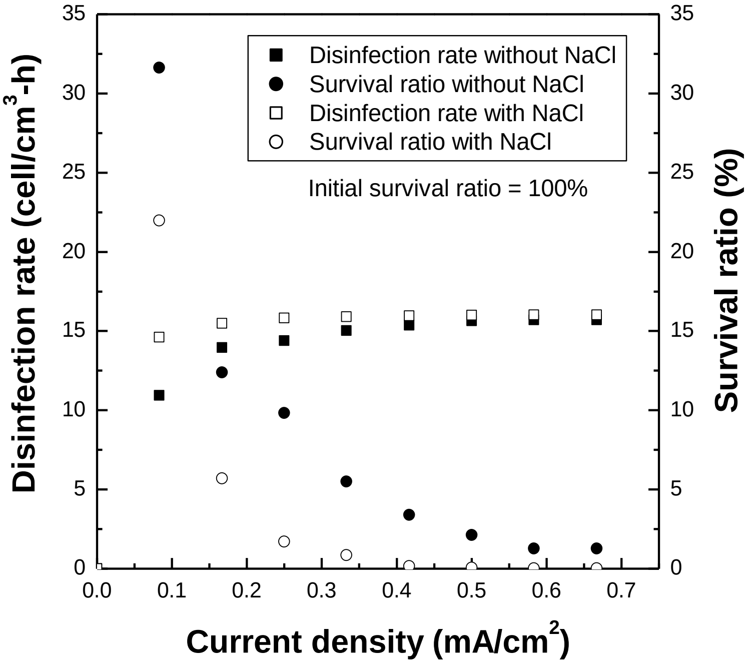

Figure 4 Effect of current density on R_d and R_s in both presence/absence of 3 mg/l sodium chloride salt in raw water disinfected using ACF electrodes.

However, it is observed that with further increase of *i* both disinfection curves are led to almost the same point indicating that the higher current densities have similar effect on pathogen removal whether sodium chloride is present in solution or not (Figure 4). For instance, it can be clearly seen from the results that in the absence of sodium chloride salt, at initial current density of 0.083 mA/cm^2, R_d = 11 cells/cm^3-h, while in the presence of sodium chloride salt , at the same *i* the R_d = 15 cells/cm^3-h.

Figure 4 also shows the decreasing trend of R_s for both environments. Similar differences are obtained in this case as for results with R_d (although the trend is reversed), i.e., survival ratio of microorganisms is minimized in the presence of sodium chloride salt than in its absence. It can be clearly seen from Figure 4 that in the absence of sodium chloride salt, at *i* = 0.083 mA/cm^2, R_s = 32%, while in the presence of sodium chloride, at the same current density, R_s = 22%. Moreover, this difference becomes much less with further increase of current density in a similar manner to results obtained with R_d. These differential values of 4 cells/cm^3-h in R_d and about 10% in R_s (with and without sodium chloride salt, respectively) at initial current densities is due to the production of hypochlorite ions (as discussed below) during the disinfection reaction (especially in the presence of sodium chloride salt). However, these produced hypochlorite ions are consumed with the passage of time and their concentration in solution becomes diluted thus leading both the disinfection rates to the same level (for the cases of NaCl present in solution in comparison to a salt free solution). These results show that in the presence of sodium chloride salt, electrochemical disinfection using ACF achieves almost complete eradication of pathogens from the water sample.

Figure 5 shows that the removal efficiency of pathogens increases with increase of i. Hence more cell concentration can be destroyed at higher i. It is evident from the results that 90% efficiency is achieved at i = 0.25 mA/cm^2 when the water sample doesn't contain sodium chloride salt. The efficiency approaches to 99% when i = 0.583 mA/cm^2. However, with the addition of 3 mg/l NaCl, results show that at i = 0.25 mA/cm^2, 98% removal efficiency is achieved. Further, it reaches to 100% when i is raised to a value of 0.42 mA/cm^2. This current density is much lower than the value applied in the absence of sodium chloride salt, i.e., the maximum removal efficiency is achieved at a lower i value when sodium chloride salt is present in the water sample.

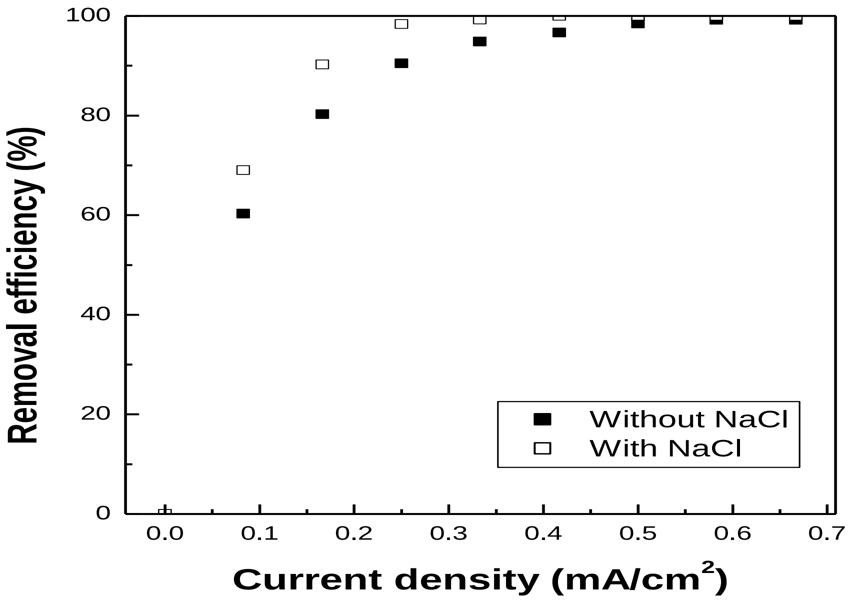

Figure 5 Effect of current density on η in both presence/absence of 3 mg/l sodium chloride salt in raw water disinfected using ACF electrodes.

Overall, better results in the presence of NaCl may be due to the formation of hypochlorite ions in the water sample. This can be understood in detail by the mechanism proposed by Kraft et al. [11]. According to them, two steps are involved in the production of hypochlorite. First step involves the primary oxidation of chloride to chlorine at the anode surface:

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$$

This is followed by the secondary solution phase reaction to hypochlorous acid:

$$Cl_{2(aq)} + 2\,H_2O \rightarrow HClO + Cl^- + H^+$$

Hypochlorous acid can dissociate to form hypochlorite and H^+ ions, the relative proportions of which depend upon the pH of the water [29].

$$HOCl \rightarrow ClO^- + H^+$$

In the pH range 6-9 (the pH of water used in this research lies within this range), the active chlorine is almost entirely constituted by hypochlorite ions (ClO^-) [29]. Hence, these produced hypochlorite ions may destroy the pathogens present in the case of direct electrolysis and as a result give higher R_d than the case where NaCl was not added to the water sample. It is anticipated that better results could be obtained if the activated carbon felt were pre-treated in a manner to reduce its hydrophobic nature. It was suggested by Chakrabarti and co-workers [30-32] that if carbon felt was heated at 500 °C for 1 h in a muffle furnace, then it could become more hydrophilic. As a result, future experiments are suggested using this pre-treatment and applying lower concentrations of NaCl (1 or 2 mg/l) for electrochemical disinfection of water.

4. CONCLUSION

Disinfection process of tap water in the presence and absence of sodium chloride salt was successfully carried out using activated carbon felt (ACF) electrodes in an electrochemical tubular reactor. The ACF was produced from indigenous waste palm shells available in abundance in Malaysia. The ACF was efficiently utilized for electrochemical disinfection of water when 3 mg/l of NaCl was added as supporting electrolyte due to higher conductivity of solution. Turbidity and total dissolved solids (TDS) were also checked and comparisons were made with the WHO limit. The results were found to be satisfactory. The total coliforms count (TCC), electrical conductivity (EC) and survival ratio (R_s) values decreased with increase of current density (i) both in the presence and absence of sodium chloride salt. However, an opposite increasing trend was observed in case of disinfection rate (R_d) and overall removal efficiency of pathogens with the increase in i. This indicated that the presence of sodium chloride salt did not affect the mechanism of reaction, i.e., the general trend in both cases were the same. However, their presence did minimize the EC, TCC and R_s values to almost nil and maximized the R_d and removal efficiency values, respectively at lower i values than in the absence of NaCl. This high efficiency of pathogens removal may be due to the generation of hypochlorite ions in the presence of NaCl. Further improvement can be achieved if the ACF is thermally treated to reduce its hydrophobic nature as documented in the literature.

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