Effects of Cathode Materials and Electrode Separation on Electrochemical On- Site Production of Sodium Hypochlorite Using Single Batch Reactor

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Abstract—This work has been devoted to investigate the effects of using available and inexpensive cathodic materials, such as steel, Al, and Zn, beside the change of spacing between electrodes on the efficiency of the on-site electrochemical production of sodium hypochlorite using a single batch electrolysis cell. The rate of NaOCl production generally increases in the order : Zn > Al > steel at all separations except at 14 cm, where the production rate with steel cathode is found remarkably higher than that with Al cathode. While at ambient electrode separation, it is clearly evident that the electrochemical activation increases in the order: Zn > Al > steel. This may be attributed to the lowering in the electronic resistivity in the order: Zn < Al < steel. Generally, the best on- site generation of sodium hypochlorite was observed for Zn electrode having the surface area of 66.3 cm^2, and separated from the graphite anode by 8 cm within the electrolysis time of 120 min, by applying DC voltage 9.5 V with measured current density of 176.5 $mA.cm^{2-}$ at 25 °C as an ambient temperature. The best effective concentration value of sodium hypochlorite at the previous conditions was 0.054%.

Index Terms—Sodium hypochlorite, Steal, Zn, Al, Electrochemical on- site production.

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1 INTRODUCTION

SODIUM hypochlorite (NaOCl) is most often encountered as a pale greenish yellow dilute solution commonly known as liquid bleach or simply bleach, a household chemical widely used (since the 18th century) as a disinfectant or a bleaching agent. The compound in solution is unstable and easily decomposes, liberating chlorine, which is the active principle of such products. Indeed, sodium hypochlorite is the oldest and still most important chlorine-based bleach [1,2].

Anhydrous sodium hypochlorite can be prepared; however, like many hypochlorites, it is highly unstable and decomposes explosively on heating or friction [3]. The decomposition is accelerated by carbon dioxide at atmospheric levels [4,5]. It is a white solid with the orthorombic crystal structure [6].

Near the end of the nineteenth century, E. S. Smith patented the chloralkali process: a method of producing sodium hypochlorite involving the electrolysis of brine to produce sodium hydroxide and chlorine gas, which then mixed to form sodium hypochlorite [7-9]. The key reactions are:

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \text{ (at the anode)} \qquad (1)$$

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,HO^- \text{ (at the cathode)} \qquad (2)$$

On-site generation (OSG) of sodium hypochlorite is an important technique based on scientific principles which has been practiced for decades. It uses sodium chloride (NaCl) dissolved on water and apply electricity current with low DC voltage to produce sodium hypochlorite and other oxidant species. The on-site generated chlorine has different uses in the commercial and industrial world, such as disinfection of swimming pools and cooling towers and etc. The biggest application of OSGs technology is municipal drinking water purifying. The benefits of using OSGs have been transformed into several water municipalities to replace traditional chlorine delivery systems such as chlorine gas, sodium hypochlorite concentrate, and bulk calcium hypochlorite for using of OSG systems [10,11]. Rengarajan, *et al.*, studied the effect of current density, temperature and the concentration of sodium chloride in the efficiency of producing sodium hypochlorite. The results indicated that the maximum current efficiency for the production of sodium hypochlorite is achieved at current density of 5-10 $A.dm^2$, 313K, between 5-10 $A.dm^2$ and keeping the NaCl concentration between 40-50 gm L^{-1}[12]. In other hand Hooper discussed the technical advances that have been made in the equipment used for generating 0.8% sodium hypochlorite on-site. It was concluded that generating sodium hypochlorite on-site is a viable, cost effective and safe alternative to 12.5% commercial grade sodium hypochlorite and chorine tablets [13]. Abdul-Wahab and Al-Weshahi studied the problems associated with brine or wastewater generated from desalination production process. It has been shedding light on the business opportunities associated with brine wastes by using the brine for on-site generation (OSG) of sodium hypochlorite, it has been found that the amount of hypochlorite generated depends on the time of the reaction and the DC voltage supplied[14]. More recently, Chakrabarti, *et al.* have

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investigated the on-site electrochemical production of sodium hypochlorite for a power plant utilizing seawater. They studied the effects of different type of electrodes, current density, surface area ratio between anode to cathode and the spacing between the anode and cathode. The results showed that coated titanium electrode shows excellent stability as compared to other tested electrode materials and production of NaOCl reached to an optimum value of about 6315 mg L^{-1} [15].

However, the titanium as electrode materials is expensive and not available in Yemen. Therefore the present research work aims to investigate the effects of using available and inexpensive cathodic materials, such as steel, aluminum (Al), and zinc (Zn), beside the change of spacing between electrodes on the efficiency of the on-site electrochemical production of sodium hypochlorite using a single batch electrolysis cell.

2 MATERIALS & METHODS

2.1 Materials & chemicals

The following materials, chemicals and equipment (Table 1) were used in the electrolysis process to produce sodium hypochlorite from brine water.

TABLE 1
MATERIALS AND CHEMICALS USED IN THE PRESENT STUDY.

Material/Chemical	Assay %	Source
Potassium iodide (KI)	99.0-100	BDH
Sodium thiosulfate ($Na_2S_2O_3$)	99	LABTECH Chemicals
Sodium hydroxide (NaOH)	96.5	ADWIC
Distilled water	-	Our Lab.
Tap water	-	Our Lab.
Salt (NaCl)	Commercial grade	Local market
Starch indicator	Analytical grade	BDH
Stainless steal	Commercial grade	Local market
Aluminum (Al)	Commercial grade	Local market
Zinc (Zn)	Commercial grade	Local market
Graphite rods	Commercial grade	Local market
DC electrical source (9.5 V)	-	Local market

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2.2 On-site electrochemical production of sodium hypochlorite

A 2.0- L tap water was placed in a single batch reactor made of polypropylene. Accurately weighed amounts of NaCl and NaOH were then dissolved to obtain 12 w/v % NaCl and 0.01 N NaOH (the electrolyte used). Two connected graphite rods with a total surface area of 24.5 cm^{-2} as anode were immersed in the electrolyte and in each run a thin plate of steel, Al, and Zn with the total surface area of 116.6, 66, and 69.3 cm^2, respectively, as cathode was placed at different separation from the anode; 5, 8, 11, and 14 cm. After connecting anode and cathode to DC power supply of 9.5 V, A 5- mL reaction mixture at different time intervals (10, 20, 30, upto 120 min) was transferred into a flask containing excess amount of KI solution. The resultant solution was then titrated with a standard $Na_2S_2O_3$ solution (0.01N) using drops of starch solution as an indicator.

3 RESULTS & DISCUSSION

The kinetic profiles of electrochemical production of NaOCl using steel cathode located at different separations from the anode made of two graphite rods are presented in Figure 1. The calculated total surface areas of electrodes were equal to 24.5, and 116.6 cm^2 for graphite (anode) and steel (cathode) , respectively .The red lines shown in the figure represent the linear regression fitting to the experimental data. The rates of NaOCl production (*v*) obtained from the slopes of fitted lines are summarized in Table 2 along with corresponding statistical parameters ; standard deviation (SD), squared correlation coefficient (R^2), and error probability (*p*). Generally, the production rate gradually increases as the electrode separation between steel electrode and anode increases upto 8 cm and it thereafter suddenly increases at 14 cm as depicted in Figure 2.

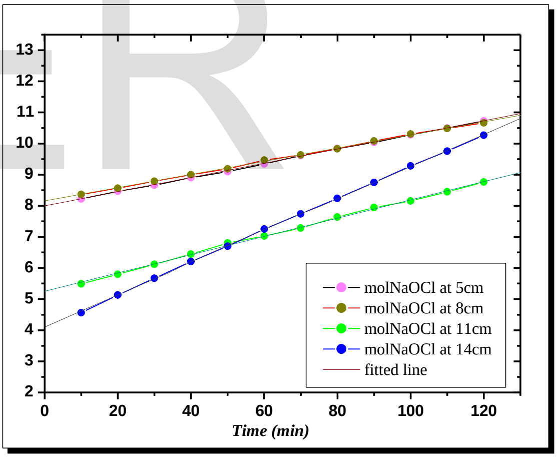

Figure 1. Kinetic profile of NaOCl electrochemical production using steal cathode separated at 5,8,11 and 14 cm from the anode.

TABLE 2
ESTIMATED RATE OF NAOCL ELECTROCHEMICAL PRODUCTION USING STEEL CATHODE AT DIFFERENT SEPARATIONS FROM GRAPHITE ANODE.

Electrode separation (cm)	*v* *Mol NaOCl L^{-1} min^{-1}*	*R^2*	*SD*
5	1.14×10^{-7}	0.94	1.67×10^{-5}
8	1.06×10^{-7}	0.95	2.07×10^{-5}
11	1.47×10^{-7}	0.96	1.08×10^{-5}
14	2.58×10^{-7}	0.96	1.61×10^{-5}

Area of steel electrode = 116.6 cm^2

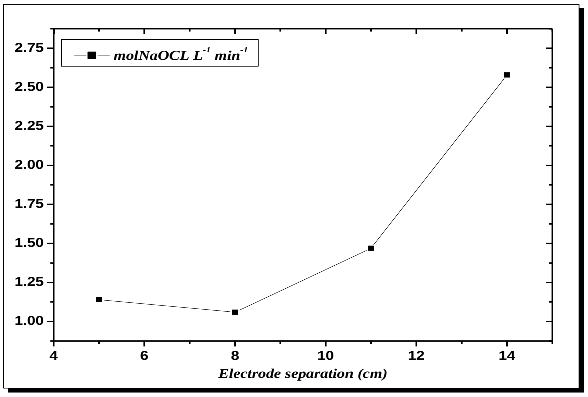

Figure 2. Production rate of NaOCl as a function of electrode separation using steel cathode.

At the same electrode separation using Al as cathode with a total surface area of 66 cm^2, the kinetic profiles are shown in Figure 3 and the estimated values of NaOCl production rate are listed in Table 3. As clearly seen from Figure 4, it is important to note that the variation of production rate with Al cathode separation shows a maximum at 8 cm and beyond it gradually decreases with increasing electrode separation.

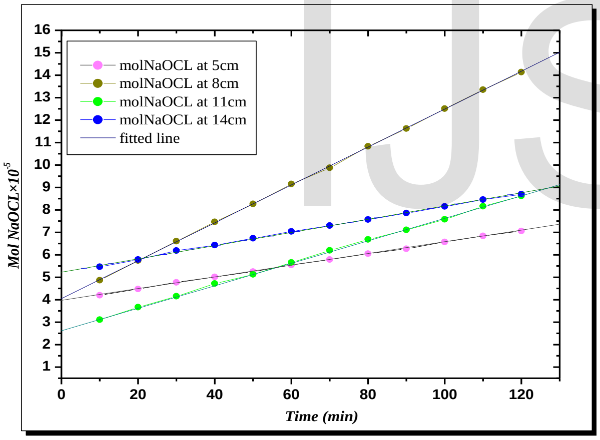

Figure 3. Kinetic profile of NaOCl electrochemical production using Al cathode separated at 5,8,11 and 14 cm from the anode.

TABLE 3
ESTIMATED RATE OF NAOCL ELECTROCHEMICAL PRODUCTION USING AL CATHODE AT DIFFERENT SEPARATIONS FROM GRAPHITE ANODE.

Electrode separation (cm)	v Mol NaOCl L^{-1} min^{-1}	R^2	*SD*
5	1.31×10^{-7}	0.93	1.19×10^{-5}
8	4.22×10^{-7}	0.95	1.90×10^{-5}
11	2.51×10^{-7}	0.95	1.08×10^{-5}
14	1.48×10^{-7}	0.96	1.89×10^{-5}

Area of Al electrode = 66 cm²

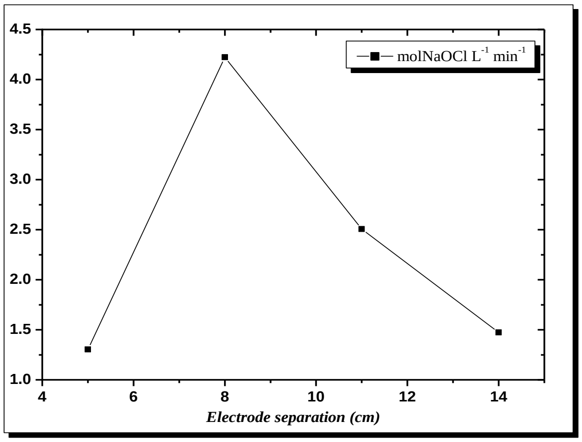

Figure 4. Production rate of NaOCl as a function of electrode separation using Al cathode.

For Zn cathode with a total surface area of 69.3 cm², the kinetic profiles are shown in Figure 5 and values of production rate are listed in Table 4. Similar to what has been observed in the case of Al, a maximum production rate is also seen at 8 cm for Zn cathode in the variation of the NaOCl production rate as a function of electrode separation. The variation in both two cases are generally similar except for Zn at electrode separation of 14 cm, where the production rate again increases after dropping beyond the maximum point as clearly presented in Figure 6.

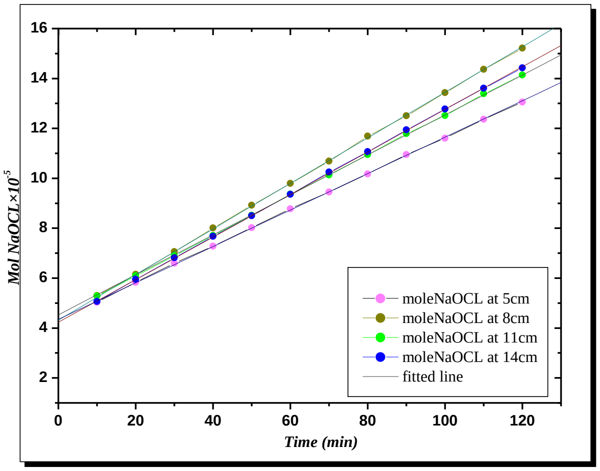

Figure 5. Kinetic profile of NaOCl electrochemical production using Zn cathode separated at 5,8,11 and 14 cm from the anode.

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TABLE 4
ESTIMATED RATE OF NAOCL ELECTROCHEMICAL PRODUCTION USING ZN CATHODE AT DIFFERENT SEPARATIONS FROM GRAPHITE ANODE.

Electrode separation (cm)	*v* *Mol NaOC L^{-1} min^{-1}*	*R^2*	*SD*
5	3.65×10^{-7}	0.95	1.16×10^{-5}
8	4.57×10^{-7}	0.98	1.30×10^{-5}
11	4.01×10^{-7}	0.97	2.12×10^{-5}
14	4.27×10^{-7}	0.94	1.89×10^{-5}

Area of Zn electrode = 69.3 cm^2

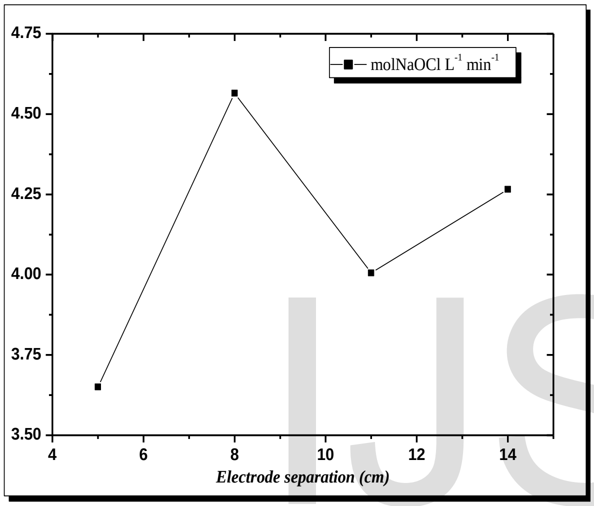

Figure 6. Production rate of NaOCl as a function of electrode separation using Zn cathode.

TABLE 5
VALUES OF NAOCL PRODUCTION RATE OF DIFFERENT CATHODE MATERIALS AT DIFFERENT ELECTRODE SEPARATIONS.

Electrode	***v*** **Mol NaOCl L^{-1} min^{-1}**			
	@ 5 cm	**@ 8 cm**	**@ 11 cm**	**@ 14 cm**
Steel	1.14×10^{-7}	1.06×10^{-7}	1.47×10^{-7}	2.58×10^{-7}
Al	1.31×10^{-7}	4.22×10^{-7}	2.51×10^{-7}	1.48×10^{-7}
Zn	3.65×10^{-7}	4.57×10^{-7}	4.01×10^{-7}	4.27×10^{-7}

Table 5 and Figure 7 illustrate the variation of NaOCl production rates with type of cathode material used at ambient electrode separations. The interesting point to be emphasized here is that the rate of NaOCl production generally increases in the order : Zn > Al > steel at all separations except at 14 cm, where the production rate with steel cathode is found remarkably higher than that with Al cathode as illustrated in Figure 7(d).

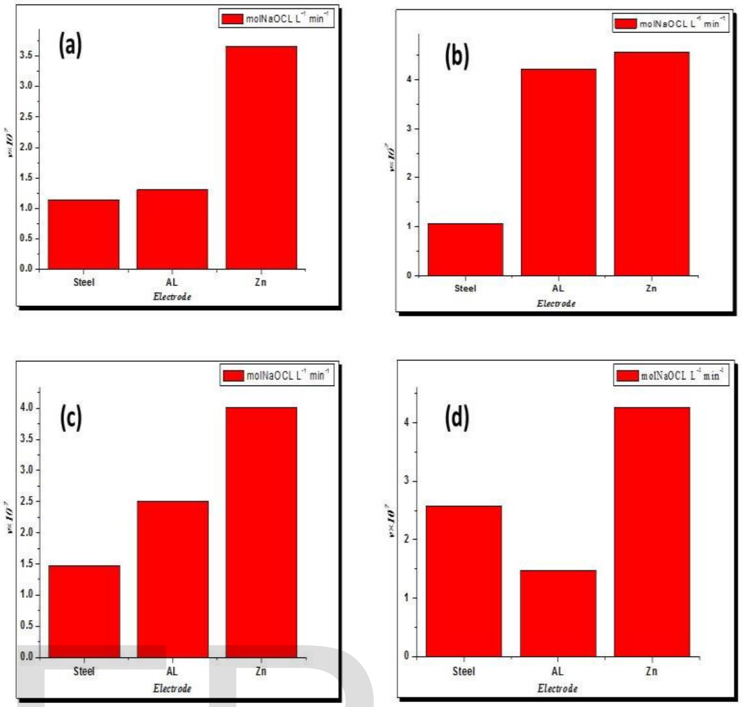

Figure 7. Variation of electrochemical production rates of NaOCl with cathode materials at electrode separation of (a) 5, (b) 8, (c) 11, and (d) 14 cm.

At constant initial concentration of reactants, since the cathode surface area is sufficiently greater than anode one, the rates of electrolytic reactions remain dependent of the material of which the cathode is made [16] and of the electrode separation [17]. In this research work, the total surface areas of steel, Al, and Zn cathode were made sufficiently greater than graphite electrode. At ambient electrode separation, it is clearly evident that the electrochemical activation increases in the order: Zn > Al > steel. This may be attributed to the lowering in the electronic resistivity in the order: Zn < Al < steel [18].

However, at applied over-potential (~ 5 V), which is greater than the equilibrium potential of the redox reaction (~ 2.1863V in the case of electrolysis of NaCl aqueous solution), the rate of production is greatly influenced by the electrode separation [17]. In the case of Zn, and Al, it seems that the electrochemical production of NaOCl proceeds slowly with further decreasing electrode separation due to the capacitive polarization[19] and with further increasing separation due to the auto-decomposition of NaOCl or fast evolution of Cl_2 gas at the anode [20,21]. While in the case of steel, the production of NaOCl goes on increasing with the increase of electrode separation. This can be attributed to the greater resistivity of steel, and hence the maximum electrolytic reaction rate may

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be observed behind the range of separation applied in this study *i.e.,* behind 14 cm as evidenced by the sudden increase in the production rate at this point of electrode separation (Figure 2).

4 CONCLUSION

The main objective of this research work was to study the effects of using available and inexpensive cathodic materials, such as stainless steel, Al, and Zn on the efficiency of the on-site electrochemical production of sodium hypochlorite using a single batch electrolysis cell and to determine the appropriate spacing between electrodes. The concentration of sodium hypochlorite produced using stainless steel, aluminum, and zinc were 0.030%, 0.042%, and 0.054%, respectively. It was found that zinc electrode was the best material in under operating conditions. So it is practically possible to use brine water for the on-site electrochemical production of sodium hypochlorite with useful concentration using available and inexpensive cathodic materials other than titanium. Comparing the different analysis aspects, taking the safety considerations, the environmental, healthy, economic and political issues, it is clear the sodium hypochlorite generated on-site was the best cost-effectiveness scenario that maintains sufficient safety and health concerns and overcomes the political and operational challenges.

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