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The experimental optimization of the electrosynthesis of manganese(III) acetate in a bipolar packed-bed reactor

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Abstract

The electrochemical oxidation of Mn(II) acetate to Mn(III) acetate, which is an industrial oxidizing agent and catalyst, in acetic acid medium was investigated in a bipolar packed-bed electrode cell with mesh spacers. The simplex method was used for optimization. The experiments were carried out in two groups as batch and continuous processes. The chemical conversion ratio, chosen as the objective function was found to be 94.0% in batch process and 92.4% in continuous process under optimum conditions by considering the performance factors such as the current efficiency, the space–time yield and the energy consumption. These results showed the effectiveness of the simplex method.

Keywords: Electrochemical oxidation; Manganese(III) acetate; Bipolar electrodes; Optimization

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1. Introduction

The use of metal ion catalysts for the oxidation of aromatic hydrocarbons is well established and the industrial possibilities of the technique have been surveyed by Sheldon and Kochi [1]. Manganese(III) ion, which is one of the metal ion catalysts, has a special significance because of its use as oxidizing agent for the synthesis of organic compounds [2–4].

Manganese compound is generally used in the form of its acetates and the manganic ion can be regenerated from the manganous ion by common oxidizing agents such as potassium permanganate [5], peracid [6] and lead(IV) oxide [7]. More attractively, however, it can be generated electrolytically [8–13], thereby, obviating the use of additional chemicals.

The regenerative oxidation occurs at the anode according to the reaction:

$$\mathrm{Mn(II)} \rightarrow \mathrm{Mn(III)} + \mathrm{e}^-, \quad E_\mathrm{a} = -1.510\ \mathrm{V} \tag{1}$$

as a competing reaction oxygen is evolved [14]:

$$2\mathrm{OH}^- \rightarrow \tfrac{1}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + 2\mathrm{e}^-, \quad E_\mathrm{a} = -0.401\ \mathrm{V} \tag{2}$$

The reaction occurring at the cathode is

$$\mathrm{H}^+ + \mathrm{e}^- \rightarrow \tfrac{1}{2}\mathrm{H}_2, \quad E_\mathrm{c} = 0.000\ \mathrm{V} \tag{3}$$

Although, electrochemical methods have been widely used for the synthesis of Mn(III) acetate, there is no standard technique for choosing optimal experimental conditions. It can be both time consuming and difficult to obtain optimal experimental conditions unless the electrochemical system is well characterized. In today's world of intense financial competition, chemical processes must be optimized quickly if they are to become successful. From this point of view, the optimization of process conditions seems to be inevitable.

In this study, we have chosen bipolar packed-bed electrode cell since, we have long-standing interest in this type of reactor. The common feature in all of the reactors of this type is the use of an extended surface electrode as pseudo three-dimensional ones (i.e. Raschig rings) or true three-dimensional electrodes (i.e. meshes, foams and particulate beds). These electrode designs are characterized by high specific surface areas and space–time yields. Many design variations are possible for three-dimensional electrodes depending upon the nature of the electrical connections (monopolar and bipolar) and the flow conditions (flooded or trickle) [15–24]. The bipolar electrode cell, in addition to simplicity of electrical connection, has the advantage that

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it produces the equivalent amount of product to monopolar electrode cells using a lower current and a higher voltage and this can be more economic way of using power [25].

In our previous study, the effect of flow modes for both flooded and trickle flow using a bipolar packed-bed electrode cell was investigated for the electrosynthesis of manganese(III) acetate. Our results indicated that the flooded-flow mode represents a significant improvement in performance compared to the trickle one [26].

The purpose of this research is to increase the yield of Mn(III) acetate in a bench scale bipolar packed-bed electrochemical reactor operating in both batch and continuous manners, using the simplex algorithm method which is an efficient optimization technique applied in many fields of chemistry and engineering [27–29].

1.1. Simplex optimization

The method of simplex optimization was selected because it is ideally suited for a system whose efficiency depends upon several interdependent variables. Since, this method has been described in detail [30,31], only a general description will be given here.

The interactive simplex program used here allows the experimenter to set an initial value and allowed range for each of (n) variables to be tested. The value of aim function is introduced into the computer program that provides the experimental conditions. The program then selects n additional sets of parameters based on these initial conditions. Experiments are carried out under each of the ($n+1$) sets of conditions or "vertices". The response for each vertex is entered into the program. This generates the first point on a contour map in ($n+1$)-dimensional space, the experimental response being a function of the n variables. The program rejects the vertex that generated the worst response and uses it along with the remaining vertices to select a new vertex, or set of conditions predicted to give a better response. The process continues until an optimal or best response is obtained [32].

2. Experimental

2.1. Chemicals and analysis

All chemicals used were reagent grade and were used as received. Electrolysis solutions were prepared in glacial acetic acid. Since, each vertex requires an electrolysis solution in a specific concentration to that vertex, a series of acetic acid solutions in different concentrations were prepared. Mn(III) was routinely determined either by UV-Vis spectrophotometry at 456 nm, a wavelength where only Mn(III) absorbed, or by treating with measured excess of ferrous solution and backtitration with standard dichromate solution. The results obtained by both methods coincided well.

2.2. Experimental equipment

The experiments were carried out using a bipolar packed-bed reactor operating in batch and continuous modes. The reactor consisted of two concentric glass tubes, the inner of which (Ø = 17 mm) has 32 rows of Raschig rings made of graphite. Each Raschig ring was 5.4 mm long and 8 mm in outer diameter and 4 mm in inner diameter and porosity ε was 0.137. Three rings were placed vertically in each row and between them a thin disc type of polyester net with 1 mm thickness was inserted for electrochemical insulation. The fiber diameter of the net was ≅0.3 mm and the openings were ≅0.9 mm^2 (Korteks Inc., Turkey). The temperature of the column was kept at ambient temperature (298 K) by cooling with water passing through the outer jacket. Power to operate the cell was obtained from a 500 V/5 A dc unit and withdrawn from cells by graphite rods served as feeder electrodes which made contact with the top and the bottom rows of graphite Raschig rings. These feeders were located in vertical position to the reactor and distance between them was 18 cm. The reactor volume was 25 ml between the feeder electrodes. Fleischmann et al. [17] studied the effect of contacting patterns on the overall specificity of electrosynthetic reactions in an undivided, flooded, bipolar cell. They found that high space–time yields and current efficiencies could be obtained with a suitable choice of contacting pattern. From this point of view, we have chosen this type of polarity as seen in Fig. 1. Hewlett-Packard multimeters were used to monitor the applied voltage and the corresponding cell current. Flowmeter used was calibrated at 16 °C for 0.00017–1.2 cm^3 s^{-1}. The experimental

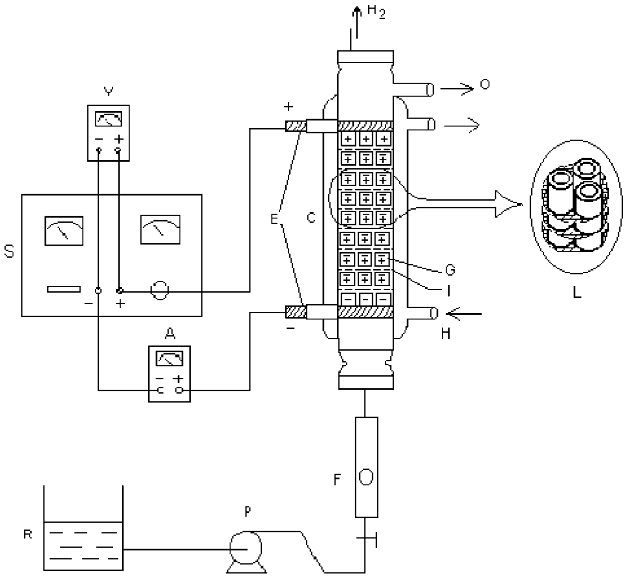

Fig. 1. Schematic of flow circuit and associated equipment for the continuous process: C: cell; E: feeder electrodes; I: insulator; G: graphite Raschig ring; H: cooling water; O: product outlet; F: flowmeter; P: peristaltic pump; R: glass storage tank; V: voltmeter; A: ampermeter; S: power supply, L: top view of the layers.

system used in this study was illustrated in Fig. 1. The same system was used for batch process, furthermore, a technique Model 254 electronic integrator was added to the system to measure the charge. Quantity of the Mn(III) acetate electrosynthesized was measured using a Jenway UV-Vis-6105 spectrophotometer. A computer program was written in gwbasic and run on IBM computer for the simplex optimization of reaction variables.

2.3. Experimental procedure

In batch process, the reactor was filled with electrolyte from the top and then current was supplied to the cell and when the charge per mole of reactant reached the predetermined value, electrolysis was terminated. Electrolyzed solution was discharged using a glass stopcock at the bottom of the reactor. These procedures were repeated in different conditions proposed for each new vertex.

In continuous process, electrolyte was introduced into the reactor from the bottom and it was operated in flooded-flow mode. Then, the required flow rate was adjusted and the current was supplied to the cell. The optimization experiments were carried out at two different flow rates of $0.02\,\mathrm{cm^3\,s^{-1}}$ (corresponding linear velocity: $1.76 \times 10^{-4}\,\mathrm{m\,s^{-1}}$) and $0.04\,\mathrm{cm^3\,s^{-1}}$ (corresponding linear velocity: $3.54 \times 10^{-4}\,\mathrm{m\,s^{-1}}$). The experiments were also performed with a flow rate of $0.08\,\mathrm{cm^3\,s^{-1}}$ (corresponding linear velocity: $7.08 \times 10^{-4}\,\mathrm{m\,s^{-1}}$) in addition to 0.02 and $0.04\,\mathrm{cm^3\,s^{-1}}$ flow rates in order to show clearly the relationships between the charge transfer control, the mass transfer control and the flow rate. Since, the success of optimization is due to the repetition of the experiments, the conditions of each electrolysis (vertex) were repeated at least three times and the results were found to be in accordance with each other. Thus, it was considered to be sufficient for optimization. Furthermore, the purity of electrogenerated Mn(III) acetate was controlled by UV and IR spectra as explained elsewhere [26].

3. Results and discussion

In industrial electrochemical processes one should obviously give a great importance to economic consideration. For this, the interest is to increase the space–time yield and current efficiency at the lowest possible energy consumption.

The concentration of the electroactive species is the major parameter that determines the maximum feasible current density and hence, the optimum space–time yield. Energy consumption does not depend directly on current density (because the passage of current is essential to the conversion of starting material to product) but really only on the cell voltage and the current efficiency. Hence, the energy consumption can be minimized only by selecting the electrolysis conditions so that the current is used solely for the reaction of interest and making the cell voltage as low as practicable [25]. In a bipolar packed-bed reactor, the shape of potential distribution (which affects the active area and hence the space–time yield of the reactor) depends upon electrode material, packing conditions, the volumetric flow rate, the electrode and electrolyte conductivity and the reactant level [15].

Under the light of above mentioned considerations, the process variables were chosen in continuous process as follows: (a) cell voltage; (b) concentration of manganous acetate; (c) concentration of sodium acetate (supporting electrolyte); (d) the water content of solution. Besides these variables the amount of electrical charge to be passed per mole of reactant (and hence the electrolysis time) was also chosen in batch process.

The lower and upper limits of all variables were selected with some discussion and pre-experiments. For instance, the upper levels of Mn(II) acetate and sodium acetate concentrations were determined by considering their solubilities in acetic acid (maximum solubilities were 0.125 and 1.8 M, respectively). The space–time yield and solution conductivity were taken into account to select the lower levels of the above two variables. To reduce the interval of optimization, the lower and upper limits of sodium acetate concentration were selected as 200 and 600 mM, respectively [33]. The use of tetrahydrate salt of manganese(II) acetate naturally limited the lower level of the water content of the system; the upper level of this variable was limited to 12% in view of probable disproportionation of Mn(III) acetate in aqueous solution [34]. The energy yield and possible side reactions were considered in determining the range for the charge per mole of reactant. The choice of the upper and lower levels of the cell voltage requires further considerations as the Kolbe reaction of the acetate ions competes with Mn(II) oxidation especially at high voltages. Kolbe reaction of acetate ions may occur at lower cell voltage (60 V) for the concentrated solutions of sodium acetate whereas a higher cell voltage (180 V) is required for the dilute solutions. This fact can be seen in the literature for solutions of varying sodium acetate concentrations [33]. Fig. 2 shows that the current density, which is calculated by dividing the total current to the area of three Raschig rings, varies with the cell voltage. From this figure, it is also seen that the Mn(II) oxidation becomes appreciable at cell voltages higher than 70 V, while the Kolbe reaction is not significant at this low concentration of sodium acetate (100 mM). As a result, five selected variables together with their lower and upper limits are given in Table 1 in batch process.

Table 1
Ranges for the levels of selected variables

Variable	Lower limit	Upper limit
Concentration of Mn(II) acetate (mM)	50	125
Concentration of sodium acetate (mM)	200	600
Water content (%)	5	12
Cell voltage (V)	70	200
Number of charge per mole of Mn(II) (F)	0.3	2.0

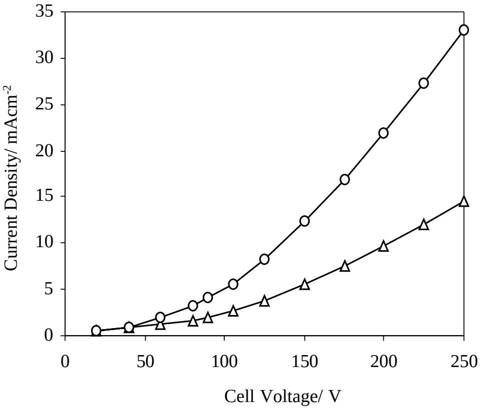

Fig. 2. Variation of current density with cell voltage for a range of Mn(II) acetate concentration (mM): (△) 50; (○) 125 and comprised of the 95% acetic acid/water mixture (by volume) with 100 mM sodium acetate.

The simplex algorithm requires six initial electrolyses, the conditions of each electrolysis constitute a vertex. In continuous process, four variables (excluding number of charge per mole of Mn(II) acetate) were selected. Thus, the simplex algorithm required five initial electrolyses. The remaining vertices of initial simplex were calculated by the algorithm using a user-specified step size. In present study, a step size was adopted as 20%.

Since, electrosynthesis is a heterogeneous process, the fractional conversion of the reactant depends on the ratio of the active electrode area to the cell volume and the flow rate of electrolyte. A high conversion per pass is desirable. This is obtainable with most cell designs, particularly with bipolar packed-bed electrode cell, when a slow flow rate is used which leads to a long residence time [25]. In this study, flow rates of 0.02 and 0.04 $cm^3\,s^{-1}$ were chosen as lower and upper ones, respectively, to show how the increase in the flow rate of the electrolyte can affect the conversion ratio.

The experimental conditions for the vertices of the initial simplex and variations of these variables throughout the optimization for batch process are given in Table 2 and continuous processes with two different flow rates are given in Tables 3 and 4. The conversion ratio of the Mn(II) acetate to Mn(III) acetate was selected as the objective function to be maximized. The variations of the objective function values are also presented in Tables 2–4 during the optimization in batch and continuous processes. In batch process, as seen in Table 2, the lowest cell voltage was 135 V in the first vertex. Increasing the cell voltage up to 170 V increased the rate of oxidation of Mn(II)–Mn(III). A further increase in the cell voltage such as up to 185 V cause a drop in the conversion ratio due to the competing Kolbe reaction [33].

Dependence of the conversion ratio on the manganese(II) acetate concentration is perhaps the only interesting outcome regarding the optimum conditions. As shown in Table 2, the minimum value of the Mn(II) acetate concentration was 88 mM and its maximum value was 102 mM during the optimization. These results showed that the Mn(II) concentration chosen in the range of 50–125 mM was more suitable. The maximum conversion ratio of 99.6% was obtained with the Mn(II) concentration of 98 mM. This Mn(II) concentration was in the range of 88–102 mM, therefore, it was concluded that the mass transfer limitations were efficient on the oxidation of Mn(II) ions.

Sodium acetate concentration is likely to have two mutually opposing effects on the conversion ratio of manganese(II) acetate. The first is the obvious positive effect due to the nature of the reaction:

$$\mathrm{Mn(OAc)_2 + OAc- \rightarrow Mn(OAc)_3 + e^-} \quad (4)$$

The second effect operates to reduce the conversion ratio, because the Kolbe reaction is facilitated by increased concentration of the acetate [26]. Although, the range of NaOAc concentration was chosen as 200–600 mM, the results exhibited that the range of 400–465 mM was efficient on the oxidation of Mn(II) ions.

The water content of the solution is important for the degree of ionization of sodium acetate and hence for the conductivity of the solution. The ionization of the solvent (acetic acid) is also increased by higher water content. This facilitates the use of lower cell voltages by increasing the concentration of hydronium ions to be reduced at the cathodes. Therefore, higher water contents bring about lower energy consumption [26]. However, the only unfavorable effect of high water content is increased disproportionation rate of

Table 2
Levels of variables of the initial simplex and the variation of these variables during the optimization for batch process

Vertex no.	Cell voltage (V)	Mn(II) concentration (mM)	NaOAc concentration (mM)	Water (%)	Charge per mole (F)	Conversion ratio (%)
1	135	88	400	8.5	1.15	90.0
2	161	88	400	8.5	1.15	93.7
3	150	100	400	8.5	1.15	91.5
4	150	92	465	8.5	1.15	94.1
5	150	92	416	9.5	1.15	90.7
6	150	92	416	8.5	1.41	89.7
7	150	92	416	9.0	0.89	98.6
8	145	92	417	9.0	0.62	94.0
9	170	98	439	9.0	1.04	99.6
10	185	102	458	9.5	0.99	95.5
11	160	96	432	8.0	1.00	98.0

Table 3
Levels of variables of the initial simplex and the variation of these variables during the optimization for continuous process with the flow rate of 0.02 $cm^3\,s^{-1}$

Vertex no.	Cell voltage (V)	Mn(II) concentration (mM)	NaOAc concentration (mM)	Water (%)	Conversion ratio (%)
1	135	88	400	8.5	83.8
2	160	88	400	8.5	89.2
3	150	100	400	8.5	87.9
4	150	92	465	8.5	89.3
5	150	92	416	9.5	86.4
6	170	98	440	9.0	92.4
7	190	103	461	9.0	89.6
8	165	97	437	7.5	90.4
9	170	88	471	8.5	93.6
10	185	81	507	8.0	91.6
11	170	100	507	8.5	93.2

the product. In this study, the stability of Mn(III) ions were kept by both increasing the acidity and the Mn(II) concentrations. Similar results can be encountered in the related literature [34,35]. The water content values of the solution provided by the simplex algorithm ranged from 8 to 9.5% are seen in Table 2.

The changes in the level of charge per mole of reactant exhibited no particular pattern. If the charge per mole of reactant is too high, side reactions could be more operative due to the prolonged electrolysis times. As shown in Table 2, the level of charge per mole of reactant was obtained as 1.04 F where the conversion ratio was maximum. This means that secondary reaction had no considerable effect on the yield of Mn(III) acetate.

In the cell used in this study, as in all bipolar cells, the voltage drop across one element is composed of many parts: the cathodic overvoltage, the difference in the reversible potentials of the cathodic and anodic reactions, the anodic overvoltage, the IR drop across the material of the electrode and the IR drop in the liquid phase [15,17]. In the case of poorly conductive electrolytes it is advantageous to reduce the inter-electrode gap (typically 0.1–1 mm) to lower the potential drop in the electrolyte in order to decrease the cell voltage and electrolyte power costs [15]. This situation was achieved by the use of bipolar packed-bed electrode cell with gaps in the order of 1 mm, which is particularly appropriate in the present case because the high resistivity of the electrolyte favors a low level of by-pass current [36,37]. As stated in literature, by-pass current can also be minimized by controlling the electrolyte flow, electrolyte composition and packing conditions [25]. In this study, regular packing mode, which was found to be the most efficient one by Kusakabe et al. [38] was also used instead of random one. According to the results given in Tables 3–5 it can be said that by-pass current was not in considerable extent.

Table 4
Levels of variables of the initial simplex and the variation of these variables during the optimization for continuous process with the flow rate of 0.04 $cm^3\,s^{-1}$

Vertex no.	Cell voltage (V)	Mn(II) conc. (mM)	NaOAc conc. (mM)	Water (%)	Conversion ratio (%)
1	135	88	400	8.5	70.0
2	160	88	400	8.5	79.0
3	150	100	400	8.5	76.0
4	150	92	465	8.5	80.0
5	150	92	416	9.5	77.0
6	170	98	440	9.0	85.0
7	190	103	461	9.0	80.2
8	165	85	461	9.5	83.6
9	170	89	467	8.5	84.3
10	170	94	517	9.5	85.6
11	170	97	575	9.5	82.2
12	190	91	478	10.0	81.6

In batch process, it can be seen from Table 2 that the maximum conversion ratio of 99.6% was obtained at the third step of vertex numbered 9 with Mn(II) concentration of 98 mM, NaOAc concentration of 439 mM, water content of 9% and charge per mole of reactant of 1.04 F at cell voltage of 170 V.

In continuous processes, the highest conversion ratios were obtained at a level of cell voltage of 170 V for two flow rates in Tables 3 and 4. The maximum conversion ratio was found as 93.6% at the fourth step of vertex with the flow rate of 0.02 $cm^3\,s^{-1}$, Mn(II) concentration of 88 mM, NaOAc concentration of 471 mM and water content of 8.5%.

Although, the optimization was aimed for the maximum conversion ratio both in batch and continuous processes with two different flow rates, other efficiency parameters such as the current yield, the energy consumption and the space–time yield must also be regarded [15]. According to Table 5, in batch process, considering the current efficiency of 151%, the space–time yield of 69.8 $kg\,m^{-3}\,h^{-1}$ and energy consumption of 11 $kWh\,kg^{-1}$, the optimum conversion ratio of Mn(II) acetate could be selected as 94% at vertex 8. Similarly, in continuous process, using the flow rate of 0.02 $cm^3\,s^{-1}$, the current efficiency of 94.4%, the space–time yield of 57.7 $kg\,m^{-3}\,h^{-1}$ and the energy consumption of 20.8 $kWh\,kg^{-1}$, the optimum conversion ratio could be chosen as 92.4% at vertex 6 and using the flow rate of 0.04 $cm^3\,s^{-1}$, the current efficiency of 183%, the space–time yield of 107.9 $kg\,m^{-3}\,h^{-1}$ and the energy

Table 5
Performance factors for batch and continuous processes

Vertex no.	Batch process			Continuous process (flow rate: 0.02 $cm^3\,s^{-1}$)			Continuous process (flow rate: 0.04 $cm^3\,s^{-1}$)		
	Current efficiency (%)	Space–time yield ($kg\,m^{-3}\,h^{-1}$)	Energy consumption ($kWh\,kg^{-1}$)	Current efficiency (%)	Space–time yield ($kg\,m^{-3}\,h^{-1}$)	Energy consumption ($kWh\,kg^{-1}$)	Current efficiency (%)	Space–time yield ($kg\,m^{-3}\,h^{-1}$)	Energy consumption ($kWh\,kg^{-1}$)
1	78.2	29.8	19.9	142.0	47.4	10.9	279	78.6	5.5
2	81.4	51.4	22.7	94.6	50.1	19.5	206	88.7	8.9
3	79.5	35.4	21.7	130.4	56.1	13.2	244	96.9	7.1
4	81.8	51.6	21.2	88.0	52.5	19.6	183	93.7	9.4
5	78.8	43.1	21.9	90.2	50.8	19.2	188	90.1	9.2
6	63.6	33.7	27.2	94.4	57.7	20.8	183	107.9	10.7
7	110.0	52.8	15.7	64.7	58.9	33.9	115	104.5	19.0
8	151.0	69.8	11.0	102.5	56.0	18.5	137	90.5	13.9
9	95.7	61.8	20.5	75.7	52.7	25.9	134	95.2	14.6
10	96.4	86.2	22.1	53.0	47.4	40.3	135	102.5	14.5
11	98.0	60.0	18.8	74.9	59.6	26.2	107	100.7	18.3
12	–	–	–	–	–	–	97	94.5	22.6

consumption of 10.7 $kWh\,kg^{-1}$, the optimum conversion ratio could be selected as 85% at vertex 6.

The conversion ratio of Mn(II) acetate versus cell voltage was investigated for three different flow rates in order to relate the results to the reaction environment in the reactor. As can be seen in Fig. 3, the conversion ratio is very sensitive to the applied cell voltage up to 100 V for 0.02 and 0.04 $cm^3\,s^{-1}$ flow rates, and this sensitivity decreases due to the influence of diffusion above 100 V and the process becomes completely mass transfer controlled at around 160 V cell voltage for both flow rates. For 0.08 $cm^3\,s^{-1}$ flow rate, the conversion ratio sensitivity to the applied voltage is lower as compared to the other flow rates (0.02 and 0.04 $cm^3\,s^{-1}$) and the process becomes completely mass transfer controlled again at about 160 V cell voltage. These results show that, the conversion ratio decreases as the flow rate increases. This can be explained by the fact that the mean residence time decreases as the flow rate increases [15]. However, the kinetics of the reactions may be investigated in a simple batch reactor as the subject of another study.

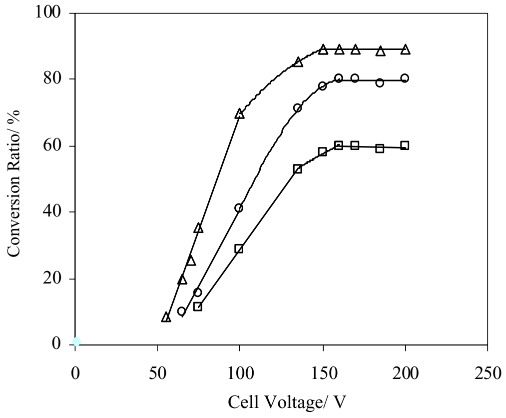

Fig. 3. Variation of conversion ratio with cell voltage for a range of volumetric flow rate ($cm^3\,s^{-1}$): (△) 0.02; (○) 0.04; (□) 0.08. The concentration of the solution: 400 mM sodium acetate in a 91.5% acetic acid/water mixture by volume, with 88 mM Mn(II).

As shown in Table 5, the current efficiency based on the current supplied to the cell exceeds 100%. This means that the electrochemical reaction takes place on each Raschig ring surface as well as at the feeder electrodes. If the graphite Raschig rings were not polarized, electrolysis would occurred only at the feeder electrodes [39]. Whereas, in the case of polarization, the bipolar packed-bed electrodes behave as if many feeder electrodes were arranged in series. Similar results can be seen in [38].

When a suitable steep potential drop is applied across the bipolar particle electrode cell, the opposite faces of each electrode have different polarities as the anodic and cathodic zones. This property leads to a higher value of the electrode area per unit cell volume, and thus higher reactant conversion values and space–time yields [15]. Furthermore, preliminary cyclic voltammetry studies [40] had shown that the Mn(III) produced at the anodic surfaces is not reduced back at the cathodic surfaces as shown in Fig. 4. Due to

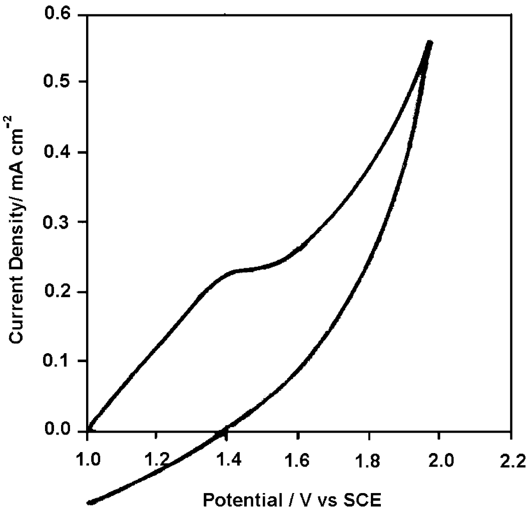

Fig. 4. The cyclic voltammogram of Mn(II) acetate (80 mM) on graphite working electrode at a scanning rate of 30 $mV\,s^{-1}$.

this irreversible nature of the reaction, the effectiveness of individual electrode polarities on the reactor performance can be seen clearly from the results both in batch and continuous processes.

4. Conclusions

We can conclude from this study that by careful control of process variables, the bipolar packed-bed electrode cell design presented in this work is potentially suitable for the production of Mn(III) acetate in both batch and continuous processes.

The experimental simplex optimization has been achieved with the minimum number of experiments. So, five variables were successfully optimized by performing only 11 experiments in batch processes with the optimum conversion ratio of 94% and in continuous processes, four variables were also successfully optimized by performing only 11 or 12 experiments using the flow rates of 0.02 and $0.04\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ with the optimum conversion ratios of 92.4 and 85%, respectively. In addition to the high conversion obtained in this study compared to the other electrochemical methods without doing any experimental optimization, the concentrated Mn(III) acetate solution can be used directly in organic syntheses without requiring any separation. This will provide a significant saving in energy consumption without causing any environmental problem. These facts show the importance of the study with respect to environmental considerations. However, some pilot plant experiments have to be done to determine the economy of the process.

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