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Effect of pulsed flow on the performance of carbon felt electrode

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Abstract

The effect of pulsed flow on mass transfer in an electrolytic reactor was investigated using carbon felt electrode arranged in a way that the electrolyte and the current flows were parallel to each other. In these experiments, a solution of potassium ferri- and ferro-cyanide with inactive compound of sodium hydroxide was employed. The electrolyte superficial velocity was in the range 4.29×10^{-4}–$18.2 \times 10^{-4}\,\mathrm{m\,s^{-1}}$. The frequency and the normalised amplitude of the pulse in the flow rate were changed in the range 0.17–3.55 $\mathrm{s^{-1}}$ and 3.5×10^{-3}–1.0×10^{-2} m, respectively. The experiments showed that the pulsed flow increased significantly the transfer of reacting ions onto the electrode surface up to a frequency of 1.5 $\mathrm{s^{-1}}$ and over this frequency the current ratio was effected slightly with increasing frequency. The increasing amplitude also had a positive effect on transfer rate, but not as pronounced as the frequency. An increase in the mass transfer rate between approximately 6.8 and 33.5 times of those of the flow with no pulse was obtained, depending upon the experimental conditions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbon felt electrode; Electrolytic reactor; Facilitated transport; Periodic flows; Process intensification

1. Introduction

Process intensification (PI) [1–3] is a radical new approach to process design and operation in order to achieve: (1) at least 10-fold decrease in process equipment volume, and therefore corresponding increase in the relevant heat and/or mass transfer rates; (2) elimination of parasitic process steps and unwanted by-products, and (3) very fast continuous process. Most of the intensive processes are environmentally friendly, and they deliver substantial energy, capital and operating cost reduction, enhanced process safety, and novel/improved products. Attributes of PI can be summed as: smaller, safer and cheaper compared with the current technology. Therefore, PI is seen as an important element in achieving sustainable development [4].

PI can be achieved through several routes as summarised in [1], including the use of periodic flow (pulsed, or oscillatory flows), diffusion/conduction path reduction. Pulsed or oscillatory flow technology, which can also be called periodic flow, has been used within different fields of chemical engineering to enhance momentum, heat and mass transfer processes [5–9]. The enhancement of mass transfer can be further achieved by the superimposition of flow field with another process field such as electric field [10,11]. Further enhancement can be obtained in such processes by electrode design in order to reduce diffusion/conduction pathway. The three-dimensional electrodes such as porous materials, foams and felts have found a wide range of applications in purification of wastewater, in fuel cells and batteries and in the electro-synthesis of chemicals. Such structured electrodes [12] have high surface area and promote turbulence, resulting in higher mass transfer and chemical reaction rates. Furthermore, the high permeability of these materials due to their high void fraction allows an easy flow of the solution and a low effective electrolyte resistively. There are several studies in the literature using these types of electrodes. Here some of the studies using carbonaceous materials are reviewed. Oren and Soffer [13] removed traces of mercuric ions from aqueous solutions using graphite felt electrodes. Golub and Oren [14] and Abda et al. [15] studied the removal of chromium with the use of fibrous carbon electrodes. Vatistas et al. [16] studied mass transfer in a flow-through carbon felt electrode assuming plug flow conditions. The mass transfer process for a carbon felt electrode was studied by Carta et al. [17] for flow-by electrode operation and an empirical

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Nomenclature

a	surface area of the felt per volume ($m^2\,m^{-3}$)
A	modified pulse amplitude (m)
d_h	equivalent diameter of the filament (m)
I	current in pulsed flow (A)
I_0	current in pulse-free flow (A)
L	thickness of the cathode (m)
N	number of experimental data
$Re_{dh} = d_h U/\nu$	Reynolds number
$Re_\omega = d_h(\omega/\nu)^{1/2}$	frequency Reynolds number
U	superficial velocity ($m\,s^{-1}$)

Greek letters

β	dimensionless amplitude
ε	void fraction of the felt
ν	kinematic viscosity ($m^2\,s^{-1}$)
ω	frequency (s^{-1})

correlation between Sherwood and Reynolds numbers was developed.

Pulsed flow in electrochemical systems has been employed widely. Some of the works, especially those applied to three-dimensional electrodes, will be reviewed briefly. Guinon et al. [18] investigated the effect of pulsating flow on the mass transfer for a spherical electrode. They found that pulsation had negative effect in the absence of flow reversal. However, in the presence of flow reversal, mass transfer increased with both frequency and amplitude of the pulse and decreased with mean flow velocity. Cognet et al. [19,20] investigated mass transfer performance of metallic foams in an electrochemical pulsed flow reactor. They observed that the amplitude and frequency of the pulsation were the key hydrodynamic factors in their electrochemical synthesis. Perez-Herranz et al. [21,22] employed pulsed flow to improve mass transfer in an annular electro-dialysis cell, employing limiting diffusion current technique, and observed that with increasing frequency and amplitude, Belmant et al. [23] applied pulsed flow to improve mass transfer and phase contact between aqueous phase and organic phase, and to ensure hydraulic transport of emulsion into electro-organic synthesis for the reduction of acetophenone on a three-dimensional electrode.

Although there are some investigations on mass transfer to carbon felt electrodes, no study on the intensification of mass transfer for carbon felt electrodes was observed. Furthermore, most of the researchers used a system in which the current flow and electrolyte flow were orthogonal, and the parallel configuration was not considered. The aim of this study is to study the performance of a carbon felt electrode by applying a hydrodynamic pulse to the system in which current and electrolyte flows are superimposed in parallel.

2. Experimental

All the piping section of the experimental system was made of PVC in order to ensure chemical inertness and to avoid the effect of the light on potassium ferro/ferri-cyanide solution supported by NaOH. The mass transfer rates were measured using the electrochemical limiting current technique. The schematic view of the experimental setup is shown in Fig. 1(a). A pump was used to re-circulate the solution in the system, flow rate of the solution was measured with a rotameter. In order to avoid the effect of oxygen, the reservoir was kept under a blanket of nitrogen during the experiments. The temperature was kept constant at 25 ± 1°C with a cooling coil. The potential applied to the cell was supplied by a DC power supply. The cell current was recorded using a computer via a data acquisition card. Pulsation was applied by means of a PVC tube having a diameter of 0.021 m. The motor rotation motion was transformed into translational motion by a crankshaft system. An eccentric cam mechanism was used to convert the cyclic motion of a rotating disk to the oscillatory movement of the piston. The amplitude of pulsation was adjusted by changing the eccentricity of the cam while the pulsation frequency was varied by changing the rotational speed of the motor.

An electrochemical cell with dimensions of 0.06 m height, 0.06 m width and 0.04 m depth each was constructed in plastic. Carbon felt electrodes were kept in place by PVC screens as shown in Fig. 1(b). One layer of the carbon felt of 1 cm thickness as cathode was placed in the bottom section of the cell and the inlet section was filled with nylon fibre to provide a uniform electrolyte flow before the cathode electrode, while upper compartment was filled with three layers of carbon felt (total thickness: 3 cm) to work as anode. This provides some three times electrode area compared with cathode and thus ensures a cathodic controlled process. Platinum wires were used as current feeder. The current and electrolyte flow were parallel to each other. To avoid the contact of the carbon felt filaments of the cathode and anode, two PVC screens were used between the cathode and anode felts, leaving a space of 1 cm between the electrodes. Graphitised carbon felt used in the study as flow through electrode was provided from Donac. The cathode and anode volumes were $0.06 \times 0.04 \times 0.01$ and $0.06 \times 0.04 \times 0.03\,m^3$, respectively. The physical characteristics of the felt are summarised in Table 1.

The electrochemical limiting current technique was used. The electrolyte consisted of potassium ferricyanide ($5\,mol\,m^{-3}$) and ferrocyanide ($20\,mol\,m^{-3}$) with sodium hydroxide ($500\,mol\,m^{-3}$) as the supporting electrolyte. The physical properties of the solution are given in Table 2. While preparing the solution and before each run, the solution was de-oxygenated by bubbling nitrogen through the solution. During the experiments, the working solution remained under a nitrogen atmosphere. The electrolyte was freshly made and ferricyanide concentration was determined before and after each run by UV spectrophotometer.

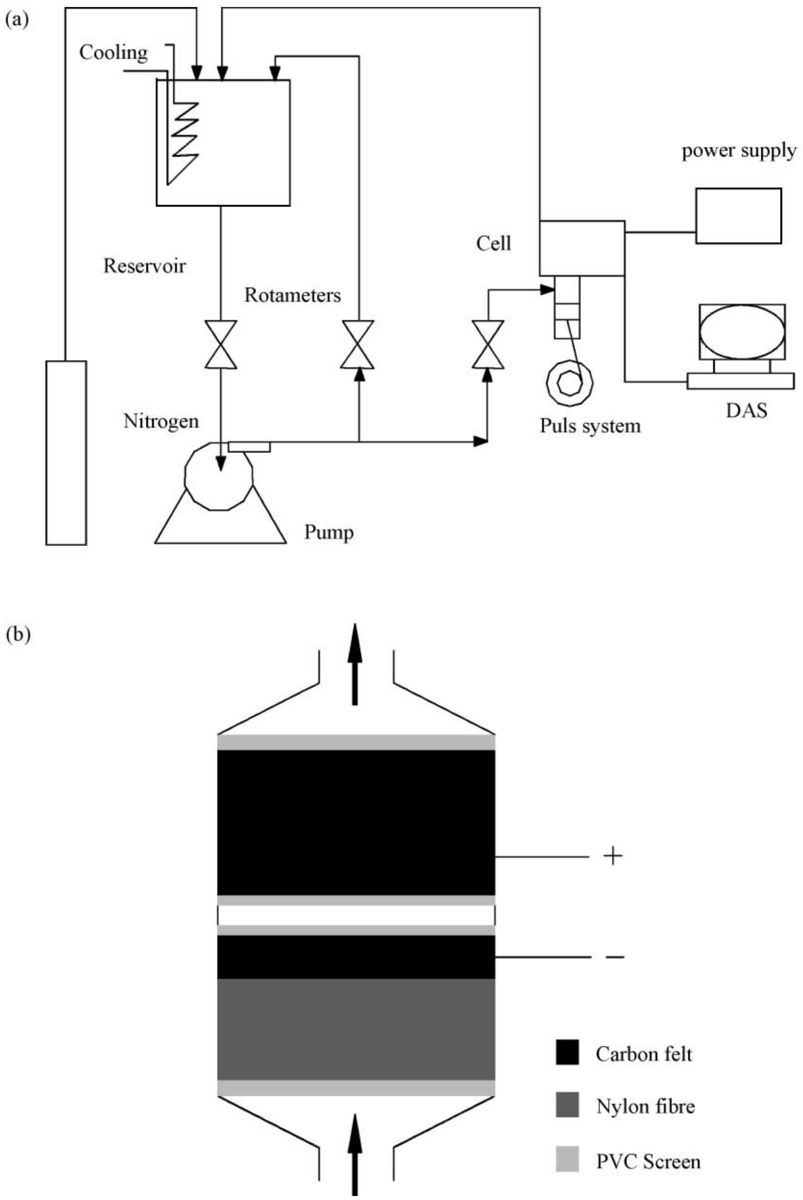

Fig. 1. Diagrammatic view of the experimental setup (a) and cross-section of cell (b).

During the experimental run, the reservoir concentration did not change because of the electrochemical reaction at the counter-electrode being the reverse of that at the working electrode.

Before each experimental run, the electrodes were cleaned using dilute (5%, w/w) sulphuric acid followed by CCl_4 wash. In order to remove any possible impurities and to

Table 1
Physical properties of carbon felt electrode

Product code	SG221
Thickness (m)	0.01
Surface weight (g/m^2)	500
Void volume (%)	97
Specific surface area ($m^2\,m^{-3}$)	9375
Filament diameter (μm)	13
Electric resistivity ($10^{-2}\,\Omega\,cm$)	0.3
Density (g/cm^3)	0.05
Carbon content (wt.%)	min. 99
Specific gravity	1.64

Table 2
Physical properties of electrolyte

Density ($kg\,m^{-3}$)	1030
Kinematic viscosity ($m^2\,s^{-1}$)	9.71×10^{-7}
Diffusion coefficient ($m^2\,s^{-1}$)	7.30×10^{-10}
Schmidt number	1330

activate the electrodes, an overvoltage was applied to the electrodes before using them in the experiments. The range of the experimental parameters were: (1) fluid velocity in the range 4.29×10^{-4}–18.2×10^{-4} m s^{-1}; (2) pulsation frequency was in the range 0.17–3.55 s^{-1}, and (3) pulse amplitude was in the range 0.0037–0.01 m. Here the pulse amplitude is defined as the amplitude of the volumetric flow rate divided by the cross-sectional area of the electrode perpendicular to the direction of flow and current. In our experiments, this area remained constant at $6 \times 4 = 24$ cm^2. The advantages of using low fluid velocity include low pressure drop and high conversion per pass, thus enabling the handling of low concentration electrolytes with reduced re-circulation. Low electrolyte velocities have been used previously by Carta et al. [17].

3. Results and discussion

Before the experiments with pulsed flow, the experiments were carried out without any pulse (steady flow) in order to determine the potential corresponding to the electrochemical limiting current. As seen from Fig. 2, the system has a good limiting current plateau, approaching to the critical flow rate at the electrolyte superficial velocity of 0.00182 m s^{-1}. Limiting current plateau could not be obtained when pulsed flow was applied. This behaviour can be attributed to the fact that the concentration is not zero at the electrode surface due to increasing transfer rate of the reacting ions to the surface and that the current distribution in the electrodes of extended surface area may not be uniform. Therefore, in order to investigate the electrode performance, the ratio of the current for pulsed flow and for steady (no pulse) flow is evaluated. All experiments were carried out with an applied potential difference of 1 V, which is approximately the midpoint value of limiting current plateau. Some examples of time-dependent current readings for pulsed flow are given in Fig. 3. Before the calculation of the current ratios, an average of readings over 1 min was taken for pulsed flow.

Fig. 4 shows the effect of pulsed flow on current at the amplitude of 5×10^{-3} m at various superficial electrolyte velocities. Increasing frequency substantially increases current flow up to a critical frequency of 1.5 s^{-1}. However, electrolyte superficial velocity appears to have no substantial effect on the current ratio. After reaching to the critical frequency of 1.5 s^{-1}, no pronounced effect of the frequency on current flow was observed, indicating that the diffusional flow rate of active ion through fluid film is fast enough for the system to be mainly reaction controlled at the electrode surface. However, as seen in Fig. 5, increasing amplitude of pulsed flow at the frequency of 2.5 s^{-1} also enhances the current ratio although it is not as effective as the frequency. This behaviour shows that the film resistance of the electrolyte still plays a role in controlling the reaction rate, although it is not so pronounced as that of the reaction at the cathode. Fig. 6 shows that the current ratio at a frequency of 2.5 s^{-1} and amplitude of 1×10^{-2} m increases with increasing applied potential. At an applied potential of 0.1 V, the current ratio is smaller compared with the potentials of 1.0 and 1.4 V. This is because of the fact that at 0.1 V, the process is mainly chemical reaction controlled, rather than diffusion. While increasing the potential from 0.1 to 1 V considerably increases the current ratio, between the overpotentials of 1.0 and 1.4 V, increasing potential enhances the current ratio slightly. This confirms that both the rate controlling factors (chemical reaction at the surface and electrolyte film) are important in the rate of the process.

Fig. 7 shows that the current ratio enhancement is much higher when the superficial velocity is low. The current ratio reaches to ca. 28 for the lowest electrolyte flow rate used in the present work. This indicates that the reduction in the mass transfer boundary layer thickness is more pronounced when the mean flow rate is low, during the flow rate surge, boundary layer thickness reduction is more effective

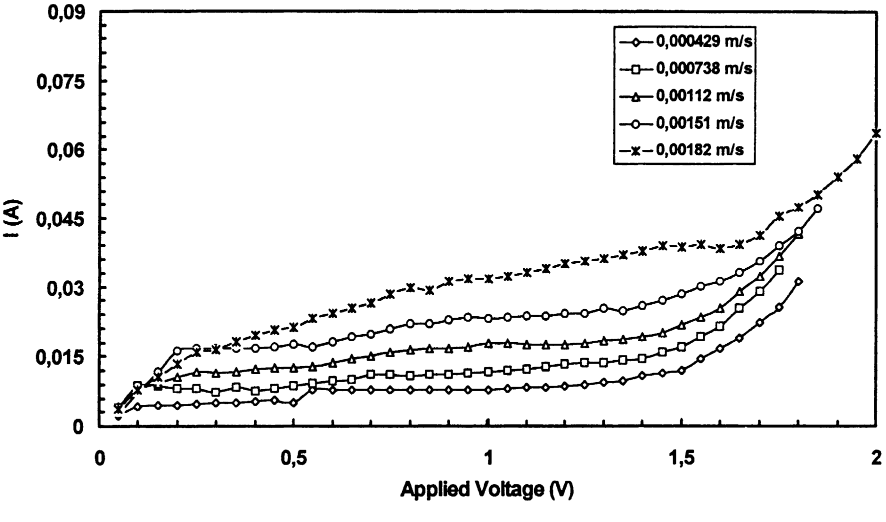

Fig. 2. Variation of limiting current with applied potential as a function of superficial velocity.

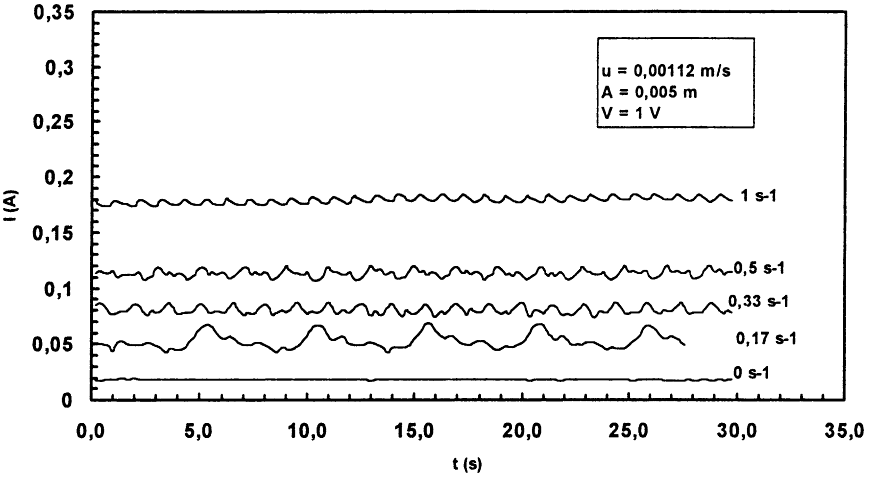

Fig. 3. Variation of limiting current with time.

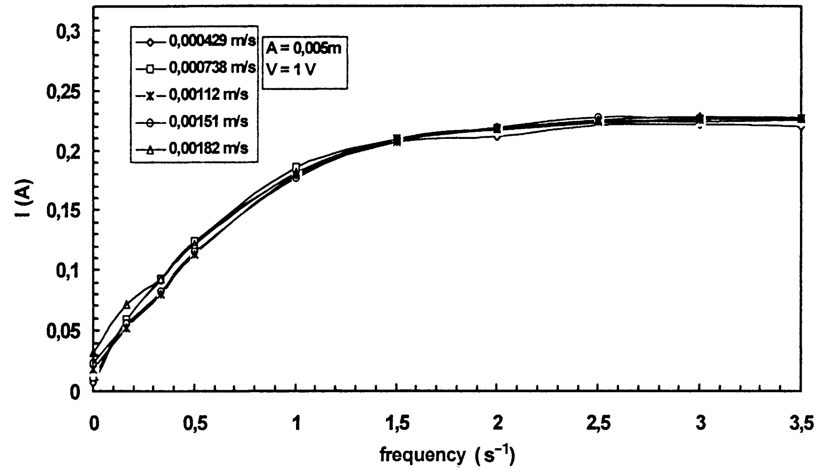

Fig. 4. Effect of pulse frequency on limiting current as a function of superficial velocity.

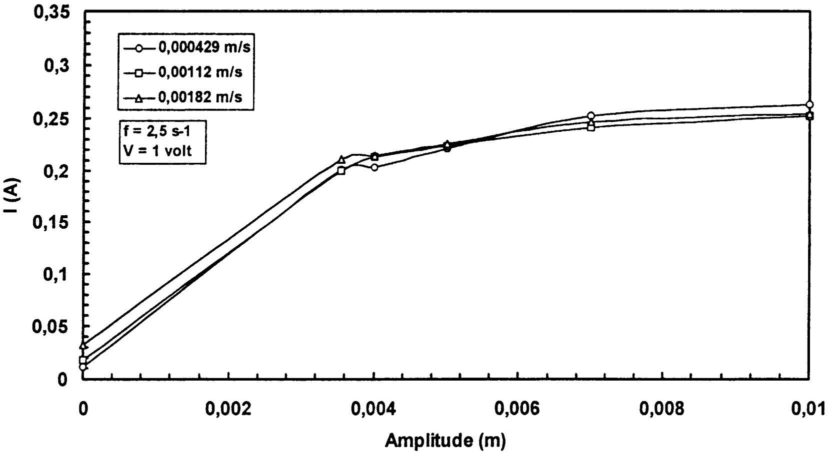

Fig. 5. Effect of pulse amplitude on limiting current as a function of superficial velocity.

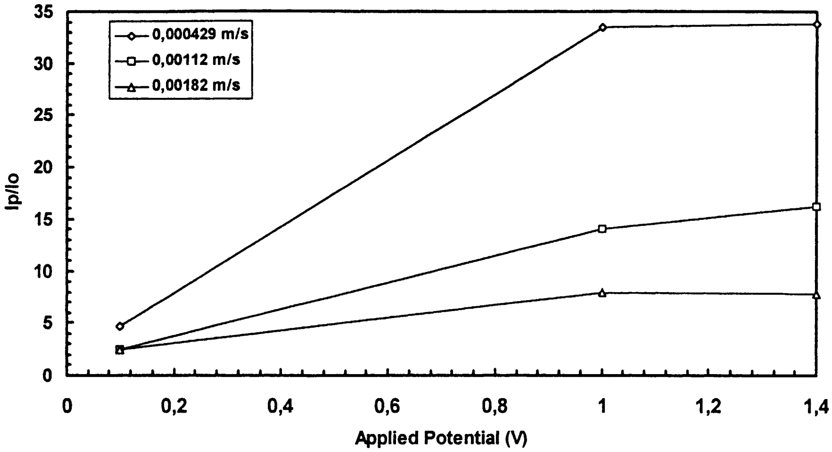

Fig. 6. Variation of current ratio with applied potential as a function of superficial velocity.

compared with the increased thickness in the flow rate decay period of the pulse. Irrespective of the superficial velocity, the current ratio increases with the frequency until the critical frequency of $1.5\,\mathrm{s}^{-1}$. However, as shown in Fig. 8, increasing amplitude further enhances mass transfer rate, reaching a current ratio of ca. 33.5. Therefore, the increase in current flow is between 6.8 and 33.5 times the current in the system with no pulsed flow at the same mass velocity, depending upon the experimental conditions. The positive effect of the frequency in increasing the performance of the system is much more pronounced than that of the amplitude.

The current ratio was correlated in terms of non-dimensional parameters and the following correlation equation by multiple regression was obtained:

$$\frac{I}{I_0} = 0.869 Re_{\mathrm{dh}}^{-0.94} Re_{\varpi}^{0.88} \beta^{0.20} \tag{1}$$

where

$$Re_{\mathrm{dh}} = \frac{d_{\mathrm{h}} U}{\nu} \tag{2}$$

$$Re_{\omega} = d_{\mathrm{h}} \left(\frac{\omega}{\nu}\right)^{1/2} \tag{3}$$

$$\beta = \frac{A}{L} \tag{4}$$

$$d_{\mathrm{h}} = 4\frac{\varepsilon}{a} \tag{5}$$

where A is the modified pulse amplitude ((volume of the electrolyte pulse per half cycle)/(electrode area for flow)), I the cell current in pulsed flow, I_0 the cell current in steady flow, L the thickness of the cathode, a the specific surface area of the electrode, d_{h} the equivalent diameter of the filament, ω the pulse frequency, ν the kinematic viscosity and U the superficial velocity.

The agreement between the predicted and the experimental results is shown in Fig. 9. The relative mean squares of errors were calculated from the following equation:

$$E\% = \left[\frac{1}{N}\sum_{J=1}^{N} \frac{((I/I_0)^{\mathrm{PR}} - (I/I_0)^{\mathrm{EX}})^2}{(I/I_0)^{\mathrm{PR}}}\right]^{1/2} \tag{6}$$

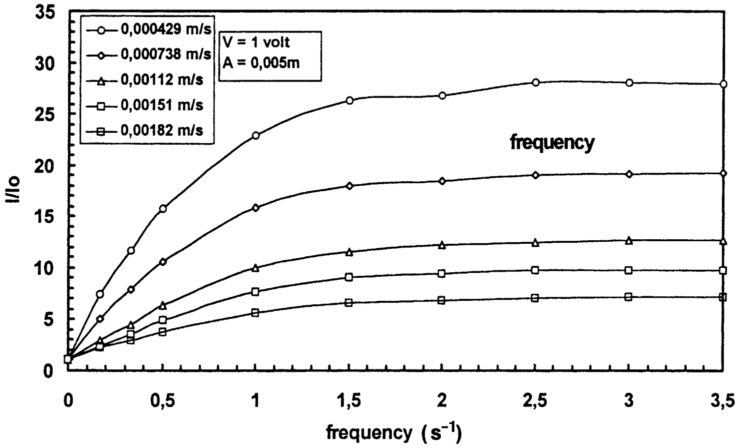

Fig. 7. Variation of current ratio with pulse frequency as a function of superficial velocity.

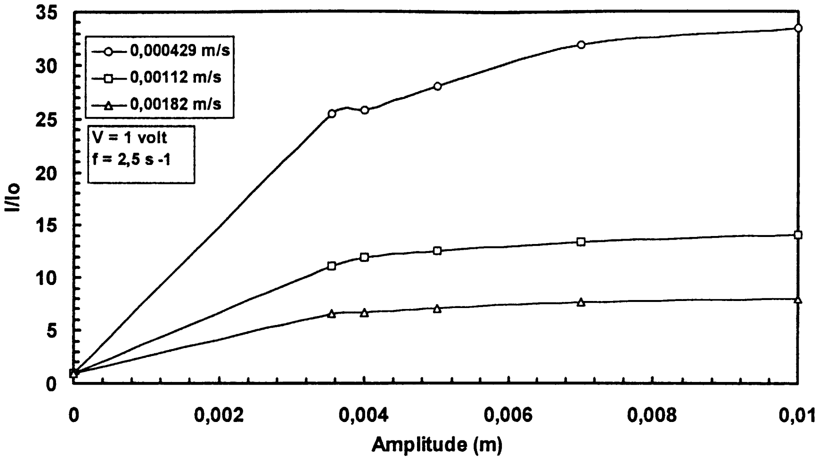

Fig. 8. Variation of current ratio with pulse amplitude as a function of superficial velocity.

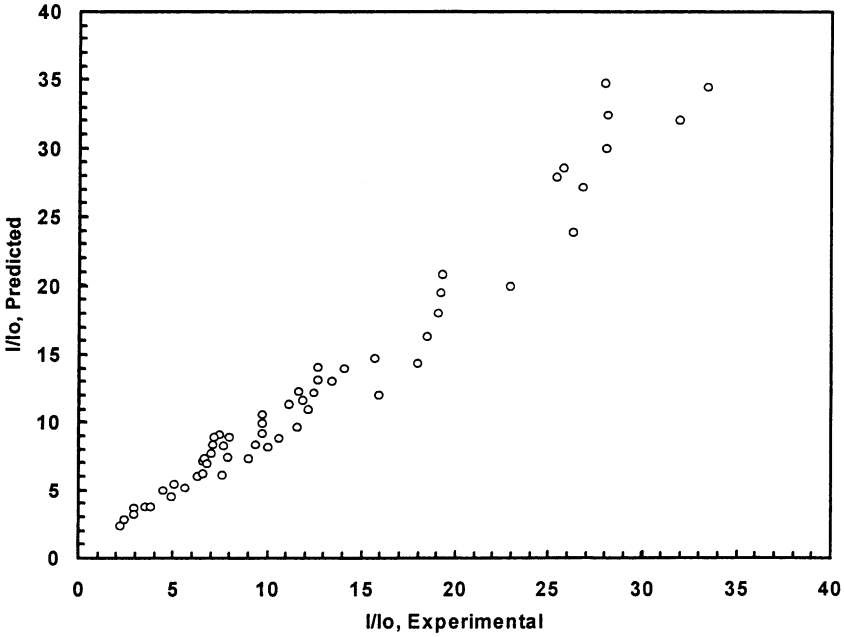

Fig. 9. Agreement between predicted and experimental results.

where N is the number of data, $(I/I_0)^{\mathrm{PR}}$ predicted results from Eq. (1) and $(I/I_0)^{\mathrm{EX}}$ the experimental data. The correlation represents the experimental data with a relative mean squares of 12.4%.

4. Conclusions

The present results indicate that the mass transfer rates as quantified by the current density during flow through porous electrodes can be intensified by as much as 33-fold by pulsating the flow. The pulsation frequency, particularly at low flow rates, is the most important factor for intensification while the pulse amplitude is secondary in the intensification process. However, the intensification is reduced when the mean flow is increased. A correlation is obtained between the ratio of current densities in the presence and absence of pulsation and the Reynolds numbers for superficial flow and frequency as well as dimensionless amplitude.

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