

Sulfur dioxide removal from flue gases by electrochemical absorption

Ümran Tezcan Ün^{a,*}, A. Savas Koparal^b, Ülker Bakır Öğütveren^b

^a Department of Environmental Engineering, Anadolu University, 26470 Eskişehir, Turkey

^b Applied Research Center for Environmental Problems, Anadolu University, 26470 Eskişehir, Turkey

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Abstract

Electrochemical absorption and oxidation of SO₂ in aqueous solutions of sulfuric acid on Pt expanded mesh anode with the electrolyte recycle in a unique reactor design and electrode configuration has been investigated. Numerous experimental runs have been carried out in order to observe the performance of the reactor as a function of the operating conditions: the current density, temperature, volume flow rate of the electrolyte, the sulfuric acid concentration, volume flow rate of the gas, the components of gas mixture, and initial SO₂ concentration. The removal efficiency of >93%, which meets the regulations requirement in Turkey, was obtained with an energy consumption of 2.22×10^{-2} kWh m⁻³ and current efficiency of 47%.

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1. Introduction

Sulfur dioxide in flue gas generated as a result of combustion of fossil fuel in, e.g., thermal power plants, etc., is the main cause of global environmental problems such as air pollution and acid rain. Sulfur dioxide has also been reported to support the reactions that create ozone depletion in the stratosphere. Many countries have therefore adopted strict regulations regarding SO₂ emissions from coal- and oil-fired boilers in power plants, which are one of the primary sources of SO₂ emissions.

The removal of pollutants such as sulfur dioxide or nitrogen oxides from industrial waste gas represents a large domain of investigations. Electrochemical processes, which do not require the continuous use of chemical reagents, can bring a helpful contribution in the proposal or development of depollution processes, as demonstrated by the various investigations published [1]. With respect to process engineering there are different alternatives for carrying out an electrochemical gas purification process. In principle the waste gas component which has to be removed can be absorbed by an aqueous electrolyte and is

then converted electrochemically either by oxidation to produce species such as sulfate and dithionite or by reduction to produce sulfur [2,3]. The electrochemical oxidation of sulfur dioxide can be achieved either through a direct process at an anode surface or using a redox mediator through a chemical process, which has to be regenerated at the electrode [1]. In the electrolysis of the sulfur dioxide absorbed in aqueous sulfuric acid solution, SO₂ is oxidized at the anode while hydrogen is produced at the cathode [2,4]. It is also possible that the process involves a chemical oxidation of SO₂ by adsorbed oxygen species [5]. Oxidation of SO₂ can also be used for production of hydrogen gas [6]. Furthermore, the removal of SO₂ from the copper ions containing wastes provides electrowinning of copper simultaneously [7].

The mechanism of SO₂ oxidation in aqueous sulfate solutions is complex and depends significantly on anode material and the pH of the solution. In this respect a range of anode materials for the anodic oxidation of sulfur dioxide in sulfuric acid have been investigated. Electrode materials such as Pt, Pd, Au, Ru, Re, Ir, Rh were investigated by Lu and Ammon [8] and palladium, palladium coated graphite and palladium coated Ebonex, platinumised titanium, stainless steel, lead dioxide, glass carbon and impregnated and non-impregnated graphite were investigated by Scott and Taama [9] in concentrated acid media. The electrochemical oxidation of SO₂ has also been studied on polycrystalline gold electrodes by Quijada et al. [10]. In this study Pt has been selected as electrode material because of its catalytic activity

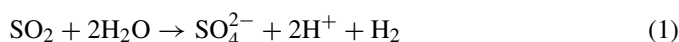
* Corresponding author at: Anadolu Üniversitesi, Çevre Mühendisliği Bölümü, 26470 Eskişehir, Turkey. Tel.: +90 222 321 35 50x6412; fax: +90 222 323 95 01.

E-mail address: utezcan@anadolu.edu.tr (Ü.T. Ün).

Nomenclature

C_0	initial concentration of SO_2 (ppm)
CE	current efficiency (%)
EC	energy consumption (kWh m^{-3})
G	gas flow rate (L min^{-1})
i	current density (A m^{-2})
L	liquid flow rate (L min^{-1})
RE	removal efficiency (%)
T	temperature ($^{\circ}\text{C}$)

for the anodic oxidation of SO_2 . The overall reaction for the oxidation of SO_2 can be written as



where hydrogen is formed at the cathode.

A general problem in removal of gases is the more or less low solubility of the gas in the aqueous electrolyte. This difficulty can be overcome shifting the gas–liquid equilibrium towards the liquid phase by permanent electrochemical conversion of the primarily dissolved species in the aqueous phase [2]. When making use of an absorption column with conducting material operating as a packed bed electrode, a definite improvement of absorptivity can be expected even at relatively short residence times of the gas phase.

Electrochemical oxidation of SO_2 has been studied in the fluidized bed electrodes [11], in dished electrode membrane (DEM) cell [12], in divided and undivided batch cells [13], in small pilot scale sieve-plate electrochemical reactor (SPER) [3,14].

The objective of this research was to investigate the performance of a reactor, which has unique design and electrode configuration for gas–liquid reaction systems for the direct electrooxidation of sulfur dioxide to sulfuric acid. This application is to enable for recovery of SO_2 from waste gases, and its recycling in the form of sulfuric acid.

2. Experimental details

2.1. Reagents and analytical

All chemicals were reagent grade and used without further purification. Stock solutions were prepared with deionized water. The electrolyte used in this work, which has a volume of 3 L, was sulfuric acid of 5% unless otherwise stated, and was prepared by dilution of concentrated H_2SO_4 . Prepurified nitrogen and CO_2 was used for dilution of sulfur dioxide.

2.2. The setup

The reactor used in this study was a cylindrical electrochemical reactor having a height of 50 cm and an internal diameter of 7.5 cm as shown in Fig. 1. The reactor combines the function of gas absorption and electrochemical reaction in one unit. The design provides good inter-phase and intra-phase mass transport. Dissolved sulfur dioxide is oxidized at a platinum expanded

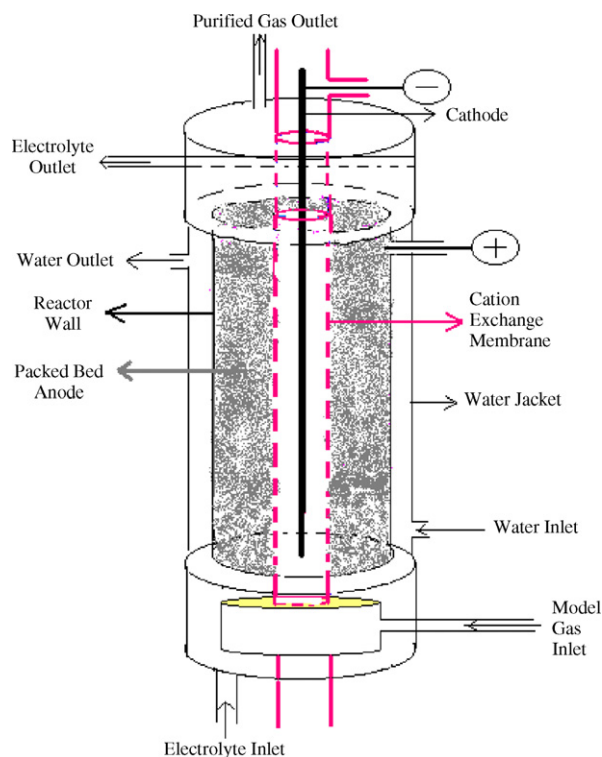


Fig. 1. Electrochemical reactor.

mesh anode (coated with 20 g Pt/m^2). The platinum expanded mesh sheet supplied from Magneto Chemie and having a height of 50 cm and a length of 170 cm was so wrapped as cylindrically that the packed bed anode was formed. The anode matrix has uniform porosity of 0.57. The counter electrode was a titanium rod supplied by Bağ. San. Tic. San. A.Ş. and located in the center of the reactor, and was separated from the anodic compartment by a cationic membrane to avoid SO_2 reduction. The electrodes were not pretreated or anodically polarized prior to an experimental run. After each run they were cleaned and rinsed with distilled water. Cell voltage was supplied by a power supply (Statron, Type 2257).

The electrochemical reactor was placed in a gas and electrolyte flow circuit as shown in Fig. 2. A gas mixture containing SO_2 is fed at the bottom of the column via stainless steel distributor having $100 \mu\text{m}$ pores (Mott Industrial) for distributing the gas uniformly throughout the electrolyte at a volumetric flow rate G . Efficient mixing of the gas is ensured by continuous flow in packed-bed column. The gas comes into contact with the electrolyte introducing from the bottom of the reactor at a flow rate of L .

Model gas mixture was prepared using SO_2 , CO_2 , air and N_2 by means of multi channel flow controller (MKS Inst. 647B Multi Channel Flow/Pressure Controller and Mass Flow Meter Type 1179A). In the measuring the gas flow rate mass flow meters were used. Gas flow rates were converted to normalized volumetric flow rate. SO_2 was mixed with nitrogen (except experiments investigated influence of gas composition) prior to introduction into the reactor. Composition of the gaseous phase at the inlet and outlet of the reactor was continuously determined using a gas analyzer (Teledyne Analytical Inst., Type IR

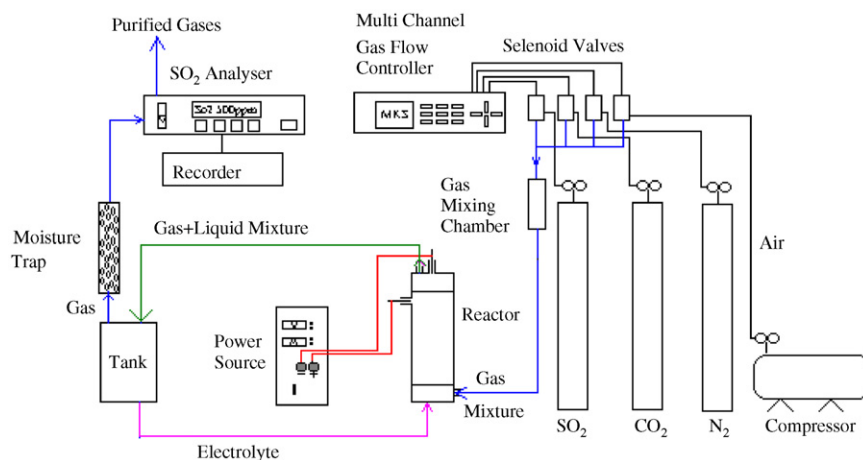


Fig. 2. Experimental setup.

7000) and recorded by an X–Y recorder (Linseis LY 16100-II). The analyzer was calibrated at SO₂ concentration of 0 ppm with nitrogen and at SO₂ concentration of 2000 ppm with standard calibration gas before each experiment. Graphical point of each concentration reported in this paper was an average value of at least two separate readings assuring reproducibility.

2.3. Procedures

Prior to electrolysis the system was operated for a couple of hours to achieve saturation of electrolyte with SO₂. After saturation of the electrolyte with SO₂ up to feed gas concentration a series of current was applied. During electrolysis the system was operated with a continuous supply of feed gas and diluted sulfuric acid solution was continuously recycled throughout the reactor.

The SO₂ removal efficiency was defined as the SO₂ concentration difference at the outlet and inlet of the reactor. All current efficiency data quoted in this work were computed from the loss of SO₂ in the exit gas.

3. Results and discussion

A number of experiments with different gas compositions were conducted to observe the effects of current density, i (A m⁻²); gas flow rate, G (L min⁻¹); liquid flow rate, L (L min⁻¹); temperature, T (°C), initial concentration of pollutant gas, C_0 (ppm, vol.); temperature, T (°C), scrubbing liquid concentration, %H₂SO₄ (w) and gas compositions on process performance represented with removal efficiency, RE (%), current efficiency CE (%) and energy consumption, EC (kWh m⁻³). Calculation of efficiencies was made by determination of SO₂ concentrations continuously in the inlet and outlet of the gas composition using online SO₂ analyzer.

3.1. Influence of the process parameters

3.1.1. Current density

The outlet concentration profile of SO₂ up to saturation of the electrolyte (curve I) and the curve after the current was

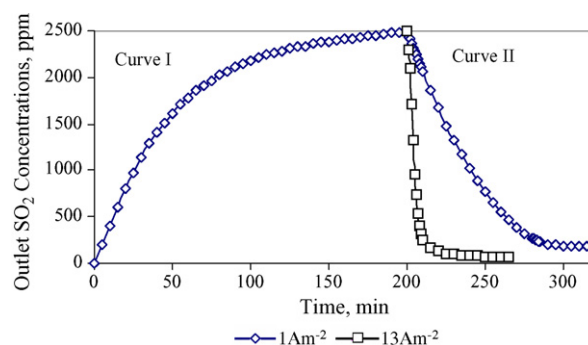


Fig. 3. Gas outlet concentration during electrochemical absorption of SO₂ as a function of current density ($C_0 = 2500$ ppm, $G = 1.5$ L min⁻¹, $L = 1.7$ L min⁻¹, $T = 20$ °C).

switched on (curve II) were shown in Fig. 3. After saturation of the electrolyte two different current densities (1 and 13 A m⁻²) were applied for a certain time interval. The outlet concentrations of SO₂ decreased from 2500 ppm to constant values of 180 and 71 ppm for 1 and 13 A m⁻² in 5 and 4 h, respectively. Table 1 shows removal efficiency, current efficiency and energy consumption of the reactor at two different current densities. Removal efficiencies of 97% at 13 A m⁻² and 93% at 1 A m⁻² were achieved with current efficiencies of 4 and 47%, respectively, with same saturation concentration and flow rates. In all experiments performed for this purpose, the current efficiency

Table 1
Percent removal rate, current efficiency and energy consumption as a function of current density, gas flow rate and initial SO₂ concentration

	i^a (A m ⁻²)		G^b (L min ⁻¹)		C_0^c (ppm)	
	1	13	1.5	10	2500	5000
RE (%)	92.8	97.2	97.4	89.3	97.2	92.2
CE (%)	46.6	3.8	3.76	23.0	48.8	92.6
EC (×10 ⁻² kWh m ⁻³)	2.2	57.7	57.7	8.5	2.5	2.0

^a $C_0 = 2500$ ppm, $G = 1.5$ L min⁻¹, $L = 1.7$ L min⁻¹, $T = 20$ °C.

^b $C_0 = 2500$ ppm, $i = 13$ A m⁻², $L = 0.3$ L min⁻¹, $T = 50$ °C.

^c $i = 1$ A m⁻², $G = 1.5$ L min⁻¹, $L = 0.3$ L min⁻¹, $T = 50$ °C.

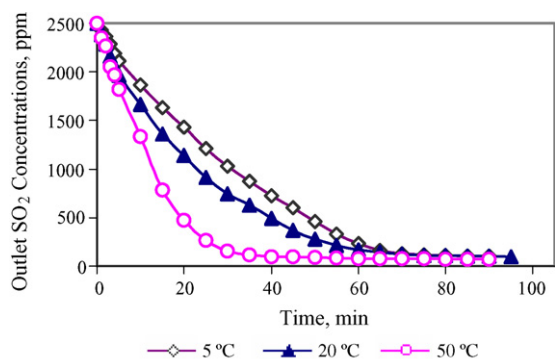


Fig. 4. SO_2 outlet concentration as a function of temperature ($C_0 = 2500$ ppm, $i = 1 \text{ A m}^{-2}$, $G = 1.5 \text{ L min}^{-1}$, $L = 0.3 \text{ L min}^{-1}$).

was relatively low and the removal efficiency was relatively high due to high current density.

Lower current efficiencies in higher current densities are due to the oxygen evolution at the anode as a by-product causing a loss in current efficiency. This result was a good agreement with the results observed by Kreysa and Külp [4]. The cell voltages were 2 and 4 V at current densities of 1 and 13 A m^{-2} , respectively. These correspond to the energy consumptions in the range of $0.022\text{--}0.577 \text{ kWh m}^{-3}$. The major contributing factor to the increase in energy consumption in this system is the effective electrolyte resistivity. Although the electrical conductivity of the sulfuric acid solutions are relatively high, the gas sparging operation, plus the generation of hydrogen gas in situ, produces a relatively large gas fraction which significantly reduces the electrolyte conductivity.

3.1.2. Temperature

A series of runs was performed at different temperatures, say 5, 20 and $50 \text{ }^\circ\text{C}$, provided by gas and liquid conditions were held constant: SO_2 concentration was set at 2500 ppm, while current density was 1 A m^{-2} , gas flow rate was 1.5 L min^{-1} and electrolyte flow rate was 0.3 L min^{-1} .

Fig. 4 shows outlet SO_2 concentrations and Fig. 5 shows the variation of removal efficiency, current efficiency and energy consumption for the oxidation of sulfur dioxide on platinum electrode in the temperature range of $5\text{--}50 \text{ }^\circ\text{C}$ of the aqueous

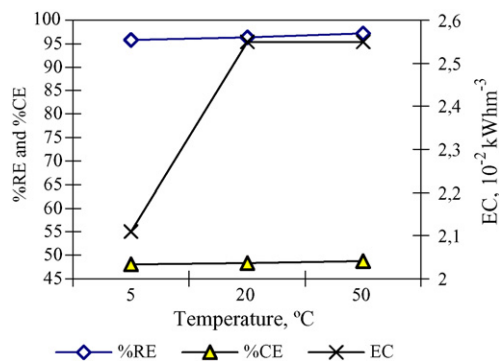


Fig. 5. Percent removal efficiency, current efficiency and energy consumption as a function of temperature ($C_0 = 2500$ ppm, $i = 1 \text{ A m}^{-2}$, $G = 1.5 \text{ L min}^{-1}$, $L = 0.3 \text{ L min}^{-1}$).

solution. It can be seen an increase in the removal efficiency, from 95.8 to 97.2%, with an increase in temperature from 5 to $50 \text{ }^\circ\text{C}$ at a given current density because of the variation of solution activity with temperature. Energy consumption increased because of the voltage rise with temperature. Current efficiency was also increased as seen in Fig. 5. It is suggested from these results that the electrochemical SO_2 oxidation is effected even if slightly by temperature increase. As the temperature increase the electrode kinetics and diffusion-convection phenomena are to be accelerated, however the solubility of SO_2 is reduced. On the overall process, acceleration of kinetics and mass transfer phenomena have dominant effect on the performance than the solubility of SO_2 .

3.1.3. Electrolyte flow rate

The gas and the electrolyte were passed through the reactor with cocurrent up-flows. The variation of gas outlet concentration with electrolyte flow rate for initial SO_2 concentration of 2500 ppm, gas flow rate of 1.5 L min^{-1} and current density of 1 A m^{-2} was shown in Fig. 6. Inlet SO_2 concentration of 2500 ppm decreased to 90 ppm at 0.3 L min^{-1} and to 180 ppm at 1.7 L min^{-1} in 120 min. It was observed that the SO_2 outlet concentration increased with increasing electrolyte flow rate probably due to the decrease in residence time and therefore the decrease in the liquid-to-electrode mass transfer rate.

Decrease in the removal efficiency with increase in electrolyte flow rate as shown in Fig. 7, is in the contrast of the results of conventional absorption of SO_2 into sulfuric acid solutions obtained by Colle et al. [15], in which the efficiency improved with increasing load of washing liquid due to the increase of the gas–liquid interfacial area. Energy consumption and current efficiency decreased with increasing electrolyte flow rate.

3.1.4. Electrolyte concentration

In anodic electrochemical absorption of SO_2 , diluted sulfuric acid was used as an electrolyte. The redox reaction produces only H_2SO_4 and hydrogen, as seen from Eq. (1). Therefore, the acid becomes more concentrated as the process proceeds. Sulfuric acid solutions of 1, 5 and 10% by weight were used to observe the

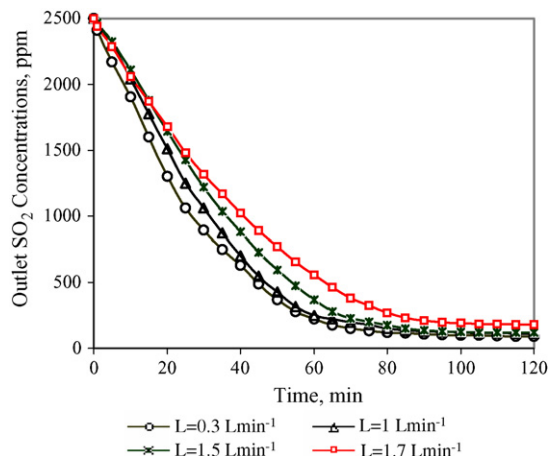


Fig. 6. SO_2 outlet concentration as a function of electrolyte flow rate ($C_0 = 2500$ ppm, $i = 1 \text{ A m}^{-2}$, $G = 1.5 \text{ L min}^{-1}$, $T = 50 \text{ }^\circ\text{C}$).

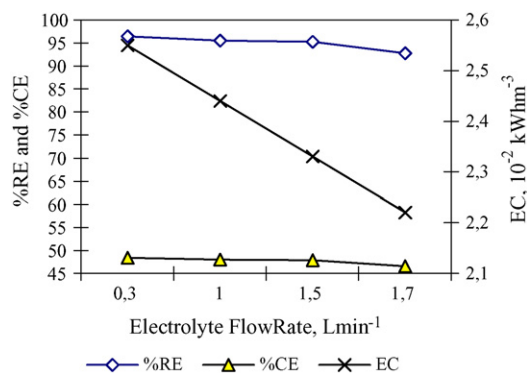


Fig. 7. Percent removal efficiency, current efficiency and energy consumption as a function of electrolyte flow rate ($C_0 = 2500 \text{ ppm}$, $i = 1 \text{ A m}^{-2}$, $G = 1.5 \text{ L min}^{-1}$, $T = 50 \text{ }^\circ\text{C}$).

effect of electrolyte concentration on the process efficiency. The variation of outlet concentration of SO_2 for different electrolyte concentrations was shown in Fig. 8 for initial SO_2 concentration of 2500 ppm, gas flow rate of 1.5 L min^{-1} and current density of 1 A m^{-2} .

The oxidation rate apparently decreased in higher acid concentrations as shown in Fig. 8. This result was well suited with observation on Pd electrode by Scott and Taama [9]. The effect of sulfuric acid concentration on the oxidation of SO_2 is explained as partly associated with the change in the activity of H^+ ions and relative concentrations of sulphony species (SO_2 , SO_2^-) and related effects on the electrode materials by Scott and Taama [9]. Increase in percentage of H_2SO_4 affected the removal efficiency, current efficiency and energy consumption adversely as shown in Fig. 9. Thus, there is no significant advantage to increase acid concentration for improving removal efficiency and energy consumption.

3.1.5. Gas flow rate

The gas flow rate related to the volume of the reactor (space velocity) is a very important economic viability parameter for absorption process. The abatement of sulfur dioxide is enhanced at lower gas flow rates because of higher residence time in the

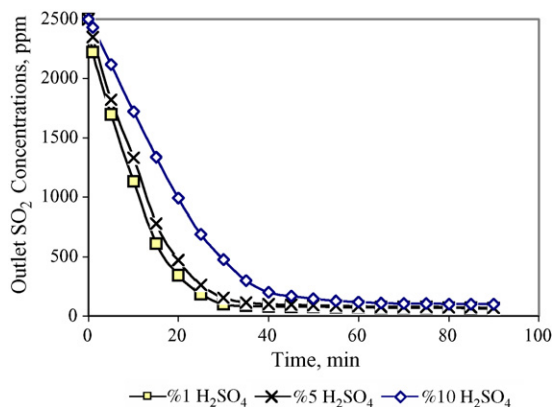


Fig. 8. Outlet concentration profile of SO_2 as a function of sulfuric acid concentration ($C_0 = 2500 \text{ ppm}$, $i = 1 \text{ A m}^{-2}$, $L = 0.3 \text{ L min}^{-1}$, $G = 1.5 \text{ L min}^{-1}$, $T = 50 \text{ }^\circ\text{C}$).

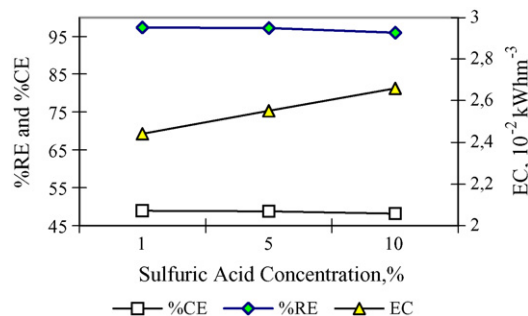


Fig. 9. Percent removal efficiency, current efficiency, and energy consumption as a function of sulfuric acid concentration ($C_0 = 2500 \text{ ppm}$, $i = 1 \text{ A m}^{-2}$, $L = 0.3 \text{ L min}^{-1}$, $G = 1.5 \text{ L min}^{-1}$, $T = 50 \text{ }^\circ\text{C}$).

reactor. Fig. 10 represents the SO_2 outlet concentration profiles as a function of gas flow rate. After 70 min electrolysis the outlet concentration of SO_2 decreased from 2500 to 268 ppm at 10 L min^{-1} and to 82 ppm at 1.5 L min^{-1} . Removal efficiency, energy consumption and current efficiency were also shown as a function of gas flow rate in Table 1. For SO_2 concentration of 2500 ppm and current density of 13 A m^{-2} the removal efficiency decreased from 97.4% at 1.5 L min^{-1} to 89.3% at 10 L min^{-1} .

It can be seen from Table 1 that the removal efficiency of SO_2 in the reactor is very high, due to the continuous bursting, reformation and regeneration of bubbles along the vertical height of the column. But the removal efficiency decreased with the increase in the gas flow rate, for constant liquid flow rates. This is good agreement with the results of Kreysa and Külps [4] with 5% potassium sulfate electrolyte. Especially the decrease in removal efficiency of SO_2 , with the increase in gas flow rate was more significant at lower current densities and resulted from overload of SO_2 per unit time. Therefore, higher current density should be applied at higher gas flow rate. Current efficiency increased with increasing gas flow rate as shown in Table 1. This can be explained by the increase in gas-to-liquid mass transfer rate through the increase in gas flow rate and the decrease in gas residence time. Higher gas flow rate resulted in lower energy consumption due to the decrease in voltage.

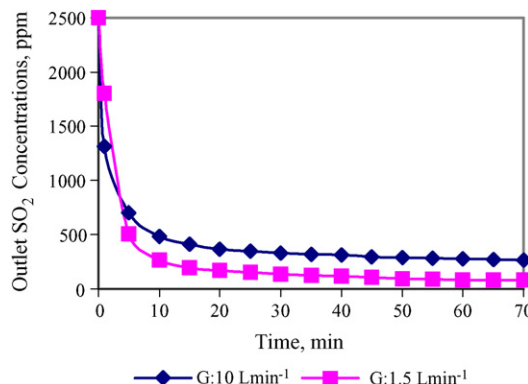


Fig. 10. SO_2 outlet concentration as a function of gas flow rate ($C_0 = 2500 \text{ ppm}$, $i = 13 \text{ A m}^{-2}$, $L = 0.3 \text{ L min}^{-1}$, $T = 50 \text{ }^\circ\text{C}$).

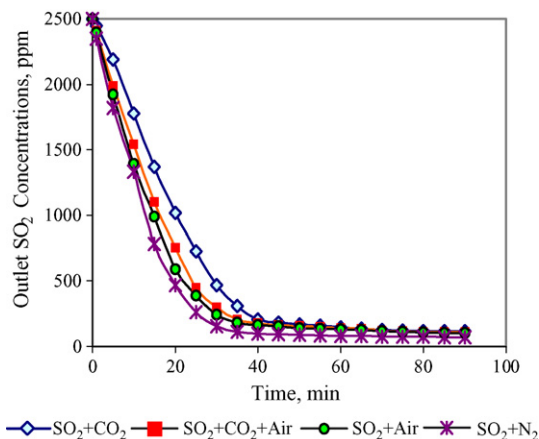


Fig. 11. Variation of outlet SO_2 concentration with components of gas mixture ($C_0 = 2500$ ppm, $i = 1 \text{ A m}^{-2}$, $L = 0.3 \text{ L min}^{-1}$, $G = 1.5 \text{ L min}^{-1}$, $T = 50^\circ \text{C}$).

3.1.6. Gas composition

Flue gases contain carbon dioxide and air and this should be taken into account in the development of the equipment for desulphurization of waste gases. In order to determine the effects of these gases on electrochemical SO_2 absorption, gas mixtures containing $\text{SO}_2 + \text{air}$, $\text{SO}_2 + \text{CO}_2$, $\text{SO}_2 + \text{N}_2$, $\text{SO}_2 + \text{CO}_2 + \text{air}$ were fed to the electrochemical absorption column. Variation of outlet SO_2 concentration for different gas compositions was shown in Fig. 11 for current density of 1 A m^{-2} , initial SO_2 concentration of 2500 ppm and gas flow rate of 1.5 L min^{-1} , electrolyte flow rate of 0.3 L min^{-1} . After 1.5 h of electrolysis, outlet SO_2 concentration was 70 ppm for $\text{SO}_2 + \text{N}_2$, 103 ppm for $\text{SO}_2 + \text{air}$, 112 ppm for $\text{SO}_2 + \text{CO}_2 + \text{air}$ and 116 ppm for $\text{SO}_2 + \text{CO}_2$.

It can be seen from the Fig. 12 that the presence of CO_2 actually led to decrease in the SO_2 removal efficiency. This can be due to the CO_2 adsorption by some of the active centers and partially blocking the surface area of the electrode causing the activity of the electrode to decrease. This should be taken into account in the design of electrochemical process for desulphurization of gases containing CO_2 . Oxygen in the air and produced as a byproduct from the anodic oxidation of water led to increase in removal efficiency whereas the current efficiency was decreased. Dilution of sulfur dioxide with air instead of

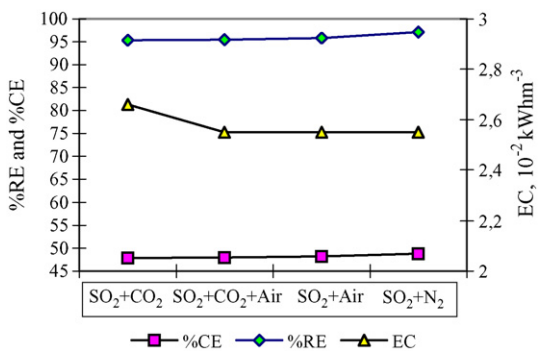


Fig. 12. Percent removal efficiency, current efficiency and energy consumption as a function of components of gas mixture ($C_0 = 2500$ ppm, $i = 1 \text{ A m}^{-2}$, $L = 0.3 \text{ L min}^{-1}$, $G = 1.5 \text{ L min}^{-1}$, $T = 50^\circ \text{C}$).

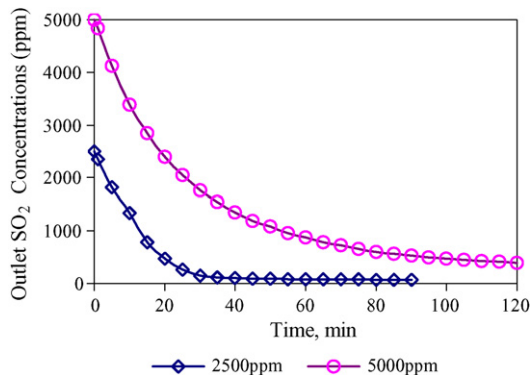


Fig. 13. SO_2 outlet concentration profiles as a function of initial SO_2 concentration ($i = 1 \text{ A m}^{-2}$, $G = 1.5 \text{ L min}^{-1}$, $L = 0.3 \text{ L min}^{-1}$, $T = 50^\circ \text{C}$).

nitrogen reduced the cell voltage. Therefore the lowest value of energy consumption was obtained for the mixture of $\text{SO}_2 + \text{air}$.

3.1.7. Initial SO_2 concentration

Gas pollutant concentrations have been selected from usual values in several types of industrial flue gas compositions, so two different sulfur dioxide concentrations were investigated. The concentration profiles for these two initial SO_2 concentrations during electrochemical absorption were shown in Fig. 13.

Increasing the concentration of SO_2 in the flue gas from 2500 to 5000 ppm, the removal efficiency at 1 A m^{-2} decreased from 97.2 to 92.2% as shown in Table 1. On the other hand the amount of gas removed per unit time increased with increasing initial SO_2 concentration. This result was approved with a lower energy consumption value. However current efficiency increased from 49 to 93% and then decreased with time as the concentration of SO_2 falls. Energy consumption values were 2.55×10^{-2} and 2.00×10^{-2} for the SO_2 concentrations of 2500 and 5000 ppm, respectively. Overall the variation of SO_2 concentration with time follows an exponential decay as can be seen from the Fig. 13. This variation indicates that the oxidation of SO_2 is under mass transfer control.

4. Conclusion

Although the principle of electrochemical treatment of waste gas had been used by several authors, this paper establishes that gas–liquid absorption can be simply coupled to electrochemical reaction. Direct oxidation of SO_2 in sulfuric acid has been demonstrated on expanded mesh Pt anode. High removal efficiency of >93 which meets the regulations requirement, and current efficiency of 47% during the experiments were achieved.

Regarding the energy requirement for electrochemical conversion, electrochemical gas purification from power stations is probably not competitive economically with traditional processes. However, there are many applications in industry and in flue gas purification from smaller heating units where energy consumption is not a decisive factor. There is no need for a desorption step and the investment and energy costs can be kept lower in electrochemical absorption. Furthermore, no chemicals are required instead a re-usable solution such as sulfuric acid is produced for which an equivalent credit is obtained.

It may be additionally of interest to find a profitable use for the produced hydrogen. Finally, electrochemical oxidation of SO₂ can be considered as a process in which no waste is produced.

In many of these cases electrochemical gas purification processes may, in the future, contribute towards providing reliable and automatically running process units, which may help to protect the environment.

Acknowledgement

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