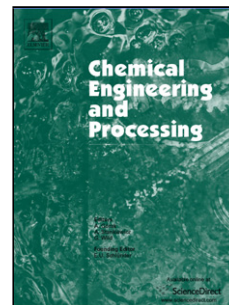


# Journal Pre-proof

Evaluation of a decaying swirling flow electrochemical reactor for the manufacture of colloidal sulphur by reduction of sulphur dioxide

C.C. Contigiani (Investigation) (Formal analysis), J.P. Fornés (Investigation) (Formal analysis), O. González Pérez (Validation), J.M. Bisang (Conceptualization) (Methodology) (Writing - review and editing)



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**Evaluation of a decaying swirling flow electrochemical reactor for the  
manufacture of colloidal sulphur by reduction of sulphur dioxide**

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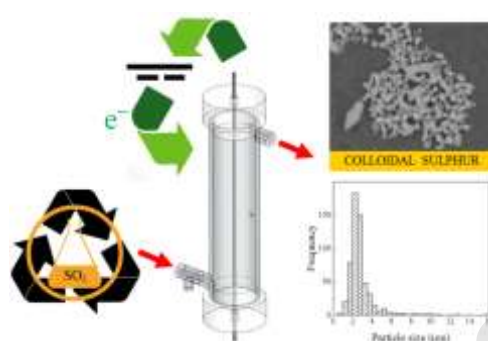
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## Graphical abstract

**Research highlights**

- A reactor with swirling flow is suitable for electrochemical production of colloidal sulphur
- Colloidal sulphur is the main product of sulphur dioxide reduction
- Swirling flow detaches the sulphur deposited at the cathode
- The solution was completely exhausted in sulphur dioxide

## Abstract

The behaviour of an electrochemical reactor with decaying swirling flow is analysed for the production of colloidal sulphur using sulphur dioxide from synthetic effluents as raw material. The experiments were done under potentiostatic control with single- and two-phase flow. The best results were obtained at a cathodic potential of  $-0.7$  V, against a saturated calomel electrode. Thus, in a single-phase experiment at a volumetric flow rate of  $8 \text{ dm}^3 \text{ min}^{-1}$  and  $1 \text{ g dm}^{-3} \text{ SO}_2$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  as a supporting electrolyte, the current efficiency was 64% with a specific energy consumption of  $22.7 \text{ kW h kg}^{-1}$  and a space time yield of  $5.6 \text{ kg m}^{-3} \text{ h}^{-1}$ , achieving a total removal of sulphur dioxide after 15 min of operation. For sulphur dioxide concentrations lower than  $2.5 \text{ g dm}^{-3}$  the cathode surface remained free of a sulphur layer due to the impingement action of the swirling flow. Similar results were obtained under a two-phase flow of 5%  $\text{SO}_2$  in nitrogen. In this case, the sulphur particles presented mainly spheroidal shape with an average size of  $2.8 \text{ }\mu\text{m}$  being of high purity. The comparison with other types of electrochemical reactors concludes that the equipment with swirling flow represents the best option.

Keywords: colloidal sulphur, electrochemical reactor, sulphur dioxide, swirling flow

## 1. Introduction

Sulphur particles of small size, in the order of a few  $\mu\text{m}$ , are used for the fertilizer production [1] and also in cosmetics [2], pharmaceutical [3], soap [4] and many other industries [5]. Additionally, its bioefficacy as miticidal and fungicidal agent was demonstrated [6-8]. Thus, the uses and price of this material, called colloidal sulphur, are

fully different from those of the conventional sulphur powders. The World Customs Organization assigns different HSN codes for both species: 28020030 is given for the former and the general code 250300 for the latter and other kinds of sulphur. Several physical, chemical and electrochemical procedures can be used for the manufacture of colloidal sulphur [9]. Likewise, numerous anthropogenic activities [10] generate sulphur dioxide that represents a deleterious agent for the environment requiring its treatment. Bakir Öğütveren [11] summarised the electrochemical processes for the removal of sulphur oxides, being electrochemistry a promising alternative for the abatement of the pollutant. Therefore, the production of colloidal sulphur by electrochemical reduction of sulphur dioxide is an attractive procedure that allows a contaminant to be used as raw material for the generation of a useful species with a high commercial value. The fundamental aspects of the process related to materials for the electrodes and kinetic control were previously reported [12], concluding that 316L stainless steel is a suitable cathode material. Moreover, the production of sulphur was analysed by using a parallel-plate electrochemical reactor with convergent flow [9] or a rotating cylinder electrode [12]. The main issue for sulphur production is the passivation of the cathode due to its surface is covered with an insulating layer of sulphur, which restricts the flow of current. This problem was minimised detaching the sulphur layer at the rotating cylinder electrode with the application of ultrasound [13] or more recently with the use of a modified hydrocyclone [14]. In the latter equipment the impingement action of the helical flow on the cathode surface allows the detachment of the sulphur powder and at the same time the particles are classified, being the largest ones separated through the spigot.

Accounting that the reduction of sulphur dioxide in an acidic solution is mass transfer controlled working under limiting current conditions in a narrow range of potentials [12], it is revealed that three-dimensional electrodes are not appropriate for this

task. Based on the above statement it is inferred that the electrochemical reactor must present the following three characteristics: (i) two-dimensional electrodes, (ii) good mass transfer conditions, and (iii) a hydrodynamics able to detach the sulphur deposited on the cathode. These requirements could be satisfied by a reactor with decaying swirling flow. This reactor was studied by Walsh and Wilson [15] to treat spent metal finishing process liquors using the “Metelec Concentric Cylindrical Cell” and by Wang [16, 17] for the electrowinning, electrorefining or recovery of metals according to the EMEW cell (EMEW Clean Technology, Vancouver, BC, Canada). Thus, the main objective of the present contribution is to assess the performance of a decaying swirling flow electrochemical reactor for the production of colloidal sulphur by the sulphur dioxide abatement, working under single- or two-phase systems, with the characterization of the reaction products.

## 2. Experimental

Fig. 1 depicts schematically the electrochemical reactor and the right-hand side summarises its internal dimensions. The reactor casing, a 316L stainless steel pipe with a thickness of 3.85 mm, was used as a cathode having a 52.8 mm internal diameter and 200 mm length. The anode was made of a 316 stainless steel tube, 3.25 mm external diameter, placed in the central axis of the equipment from the top to the bottom. This arrangement becomes uniform the primary potential distribution inside the reactor. To avoid the anodic dissolution of the stainless steel tube, the anode was electroplated with lead from a fluoborate bath [18] to give an external radius of 4.0 mm, being 13.2 the ratio between the cathode and anode surface areas. The anode was electrically connected at both ends in order to ensure isopotentiality of its metal phase. Under operating conditions lead was oxidised to  $\text{PbO}_2$ , evidenced by its colour change to dark-brown. The absence of lead ions

in the solution after an experiment was checked by an additional qualitative analysis using the spot test with sodium rhodizonate [19], which is a sensitive procedure with a  $0.1 \mu\text{g}$  per  $0.05 \text{ dm}^3$  drop as limit of identification. Thus, the stability of the anode under the working conditions was demonstrated. The cathodic potential was controlled against a saturated calomel electrode, SCE, connected to a Haber–Luggin capillary placed in the central part of the cathode. The interelectrode gap was  $24.4 \text{ mm}$  and the electrolyte volume inside the reactor was  $0.4354 \text{ dm}^3$ . The ports for the tangential inlet and outlet of the electrolyte at the bottom and at the top of the reactor, respectively, were  $6 \text{ mm}$  in diameter. The dimensions of the inlet port and the interelectrode gap were adopted in order to generate an expansion swirl flow, increasing the mass transfer coefficient [20]. The reactor was made part of a recirculation system consisting of a pump, a flow meter, a reservoir and connections to maintain the temperature at the preset value.

Two types of electrolyte were employed. In the single-phase experiments, a solution of  $1, 2.5$  or  $5 \text{ g dm}^{-3} \text{ SO}_2$  was used in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  as supporting electrolyte. The electrolyte was prepared by dissolving sodium sulphite into an aqueous solution of sulphuric acid to obtain the above concentrations. All chemicals, supplied by Cicarelli Laboratories (Santa Fe, Argentina), were of analytical grade and were employed without further purification. Deionised water was used in all trials. In the two-phase experiments, gas-liquid, a mixture of  $5\% \text{ SO}_2$  and  $95\% \text{ N}_2$ , provided by Indura Argentina S.A., was supplied at  $0.1 \text{ MPa}$  together with the electrolyte by means of a tee fitting at the reactor inlet.

The experiments were carried out potentiostatically using a home-made direct-current source ( $500 \text{ A}, 30 \text{ V}$ ). A manual control of the cathode potential was found to be adequate for these experiments at high currents and both cell potential difference,  $U \text{ (V)}$ , and current,  $I \text{ (A)}$ , were measured. At the end of the experiment the sulphur was allowed

to settle in the electrolyte. The solution was taken out and the amount of elemental sulphur in the precipitate,  $m$  (g or kg), was determined with the method described by Morris and co-workers [21]. Thus by boiling in a sodium sulphite solution, sulphur was oxidised to thiosulphate according to



the excess of sulphite was bound with formaldehyde and the thiosulphate was determined by iodometric titration. The initial sulphur dioxide concentration was theoretically evaluated according to the preparation method above cited. Likewise, at the end of each experiment, the final concentration of sulphur dioxide in the solution was determined by iodometric analysis. Hence, sulphur dioxide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulphate, using starch as an indicator [22].

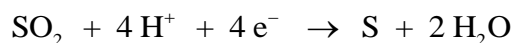
After an experiment, either in single- or two-phase flow, a sample of the colloidal sulphur was taken out from the settled suspension in the reservoir, for morphological characterisation. A drop of the suspension was placed on a glass slide and allowed to dry. Drops of deionised water were added and the solution was absorbed with a filter paper. This procedure was repeated four times in order to wash the sulphur particles and aims to avoid altering them. The residual sulphur powder was dried in a desiccator over silica gel and the size and morphology of the particles were characterised by scanning electron microscopy, SEM. A benchtop Scanning Electron Microscope PhenomWorld model PROX (The Netherlands) equipped with an energy dispersive X-ray spectrometer, EDS, was used both for the acquisition of SEM images and for the determination of colloidal sulphur composition.

### 3. Results and discussion



### 3.1. Reactions

The chemical and electrochemical environment of this system is quite complex, and in the following, only the main reactions are listed. The reduction of sulphur dioxide to sulphur is expected to occur at the cathode, according to



(2)

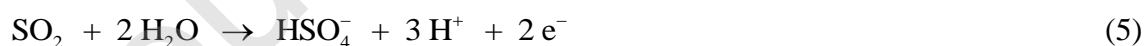
At potentials more negative than  $-0.5 \text{ V}$ , it is also likely to get hydrogen evolution as a side cathodic reaction [12]



diminishing the current efficiency for the production of colloidal sulphur. However, hydrogen evolution can also have some beneficial aspects such as the increase in the mass transfer of sulphur dioxide to the cathode surface due to bubble-induced convection and it can contribute to the removal of the sulphur layer. Likewise, oxygen evolution occurs at the anode



Also, the oxidation of sulphur dioxide to sulphuric acid can take place at the anode, in accordance with



However, the presence of colloidal sulphur inhibits the oxidation of sulphur dioxide [12]. Furthermore, other anodic reactions under mass-transfer control can be disregarded because of the high ratio between the cathode and anode surface areas.

### 3.2. Definition of the Figures of Merit

From the experimental data, the figures of merit for sulphur production that characterise the reactor performance given by the mean values of: current efficiency,  $\Phi_S^e$  (%), specific energy consumption,  $w_S^e$  (kW h kg<sup>-1</sup>), space time yield,  $\sigma_S$  (kg m<sup>-3</sup> h<sup>-1</sup>), for sulphur production, and conversion,  $x$  (%), were calculated with the following equations, respectively

$$\Phi_S^e = \frac{4Fm}{M \int_0^t I(t) dt} \quad (6)$$

$$w_S^e = \frac{\int_0^t I(t) U(t) dt}{m} \quad (7)$$

$$\sigma_S = \frac{m}{Vt} \quad (8)$$

and

$$x = \frac{c(0) - c(t)}{c(0)} 100 \quad (9)$$

where  $c$  (g dm<sup>-3</sup>) is the concentration of sulphur dioxide,  $F$  is the Faraday constant,  $M$  is the molar mass of sulphur,  $t$  (s or h) is the duration of the experiment, and  $V$  (m<sup>3</sup>) is the electrolyte volume in the reactor.

A relevant parameter that characterises the process is also the molar yield towards the sulphur production,  $Y_S$  (%), defined as [23]

$$Y_S = \frac{\text{moles of sulphur formed}}{\text{moles of sulphur dioxide reacted}} 100 \quad (10)$$

Considering the initial and final sulphur dioxide concentrations, the moles of reacted sulphur dioxide were evaluated for the single-phase system. For this calculation under two-phase flow the amount of sulphur dioxide entered by the gas phase was also considered in the mass balance.

### 3.3. Effect of temperature

Colloidal sulphur can be oxidised by sulphur dioxide in a similar manner than that given by Eq. (1) and the thiosulphate formed decomposes in several products due to its instability in an acid medium [24,25]. Thus, to elucidate the loss of sulphur by this reaction in the electrolyte volume, preliminary experiments were carried out using a solution of  $5 \text{ g dm}^{-3} \text{ SO}_2$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  with the addition of 0.2 g of a commercial sulphur powder with a mean particle size of  $18.3 \text{ }\mu\text{m}$  and  $11.4 \text{ }\mu\text{m}$  standard deviation. The experiments were done with a solution volume of  $0.6 \text{ dm}^3$  in a glass beaker continuously stirred, by means of a Teflon-coated bar, and heated using a magnetic stirrer-cum-heater. At the end of the experiment the remaining sulphur powder was allowed to settle and its amount was determined according to the analytical procedure above cited. Table 1 reports on the loss of sulphur by chemical reaction as a function of both temperature,  $T$  ( $^\circ\text{C}$ ), and time of the experiment. It can be observed that at  $30 \text{ }^\circ\text{C}$  the loss of sulphur is negligible, increases with both temperature and time and it becomes important at  $60 \text{ }^\circ\text{C}$ . For this reason, a temperature of  $30 \text{ }^\circ\text{C}$  was adopted in all electrochemical experiments reported here in order to avoid the spontaneous reaction given by Eq. (1).

### 3.4. Single-phase and two-phase experiments

Fig. 2 shows the temporal variation of the current and the current density,  $j$  ( $\text{A m}^{-2}$ ), for the reduction of sulphur dioxide in the single-phase system at different values of the cathodic potential,  $E_{\text{SCE}}$  (V), for a volumetric flow rate,  $q$ , of  $8 \text{ dm}^3 \text{ min}^{-1}$  and Fig. 3 reports on the corresponding figures of merit. The increase in current with the decreasing potential in Fig. 2 can be attributed to the improvement of hydrogen evolution as side reaction. Fig. 3 shows, as expected, that when the cathodic potential becomes more

negative the cell potential difference increases and the current efficiency for sulphur production decreases as a consequence of the enhancement in hydrogen evolution. Taking into account Eq. (7) the specific energy consumption is increased. From Fig. 3 it can be inferred that a potential of  $-0.7$  V, against saturated calomel electrode, represents a convenient value for the cathodic potential due to the highest current efficiency with acceptable values for the space time yield and specific energy consumption. The latter figure of merit presents a marked increase when the cathodic potential is more negative than  $-0.7$  V.

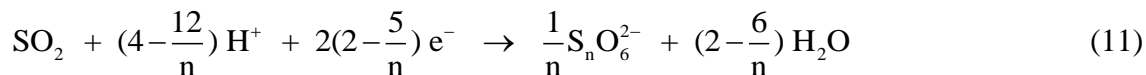
Sulphur dioxide reduction involves a large number of simultaneously occurring chemical and electrochemical reactions, which are highly coupled, making it difficult the mathematical treatment of the system in order to determine the best working conditions. Due to the chemical and electrochemical complexity of the system, a factorial  $3^2$ -design of experiments was carried out with two levels of sulphur dioxide concentration,  $1 \text{ g dm}^{-3}$  and  $5 \text{ g dm}^{-3}$ , volumetric flow rate,  $5 \text{ dm}^3 \text{ min}^{-1}$  and  $8 \text{ dm}^3 \text{ min}^{-1}$ , and duration of the experiments, 15 min or 30 min. The temporal variations of the current for these experiments are displayed in Fig. 4 and the related figures of merit are shown in Fig. 5. An additional experiment performed at a concentration of  $2.5 \text{ g dm}^{-3}$ ,  $8 \text{ dm}^3 \text{ min}^{-1}$  volumetric flow rate during 15 min is also reported. Fig. 4 reveals a good concordance in the current for the experiments with different duration maintaining constant the other working conditions. Thus, the quality of the experimental results is suitable enough for a performance discussion of the electrochemical reactor.

Fig. 5 shows that at a volumetric flow rate of  $8 \text{ dm}^3 \text{ min}^{-1}$  and for the lowest value of concentration, a time of 15 min is enough for an almost total abatement of sulphur dioxide. Likewise, for the highest concentration value the conversion decreases when the volumetric flow rate increases, as can be expected due to the shorter residence time in the

reactor. Additionally, it must be emphasised that the visual observation of the cathode after the experiments done with concentrations of sulphur dioxide of 1 and 2.5 g dm<sup>-3</sup> revealed that the electrode surface was completely free of deposited sulphur at both volumetric flow rates. However, at the highest value of concentration the cathode surface in the outlet region was covered with a thin layer of sulphur. Considering that the reduction of sulphur dioxide in both a rotating cylinder electrode [12] and a parallel-plate electrochemical reactor [9] was always passivated by a sulphur layer, it can be concluded that the impingement effect of the swirling flow on the cathode surface is suitable to avoid its passivation. However, at the highest concentration of sulphur dioxide, the impingement effect is not sufficient to completely detach the sulphur layer mainly in the region where the swirling flow is dampened. This finding defines working conditions where the cathode is not passivated, showing the reactor with swirling flow as a promising device for an efficient production of colloidal sulphur. Likewise, the space time yield is enhanced as the volumetric flow rate increases, with the exception of the experiments performed with a sulphur dioxide concentration of 5 g dm<sup>-3</sup> at 30 min where the cathode passivation restricts the reactor performance. From the above discussion the appropriate working conditions for the production of colloidal sulphur by reduction of sulphur dioxide are given by: 8 dm<sup>3</sup> min<sup>-1</sup> volumetric flow rate and concentrations lower than 2.5 g dm<sup>-3</sup>, where it can be expected an unpassivated cathode working in a single-phase system with current efficiencies of 64–77%, space time yield and specific energy consumption of approximately 6 kg m<sup>-3</sup> h<sup>-1</sup> and 20 kW h kg<sup>-1</sup>, respectively. The latter value is quite large but the process is still viable due to the high price of colloidal sulphur.

On the other hand, it was observed that the highest value of molar yield toward sulphur, nearly of 33%, was achieved at low concentration of sulphur dioxide. In order to explain the low value of molar yield, sulphur dioxide must also be reduced to other

sulphur compounds involving a lower charge per mole of reacted sulphur dioxide than that in Eq. (2). Between the possible side cathodic products, the formation of polythionates in accordance with



was detected in the solution with a test based in the addition of mercuric chloride [26, 27]. The mass balance for sulphur of the experiments reported in Figs. 4 and 5 is compatible with the formation of trithionate,  $n = 3$  in Eq. (11). For example, in the experiment performed at a concentration of  $1 \text{ g dm}^{-3}$  and  $5 \text{ dm}^3 \text{ min}^{-1}$  volumetric flow rate during 15 min the moles of reacted sulphur dioxide were 46 mmol giving 16 mmol of sulphur and the remaining 30 mmol of sulphur dioxide were reduced to yield 10 mmol of trithionate. However, Eqs. (2), (11) and (3) are highly coupled because they involve hydrogen ions as a reagent and the molar yield is strongly dependent on the working conditions, achieving a maximum of 33%. Likewise, in some experiments the final solution showed a very pale blue colour, which visible absorption spectra showed a peak at 585 nm attributable to the formation of the trisulphur radical ion [28]. Assuming a molar absorptivity of this ion of ca.  $4.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , in accordance with the paper cited previously, its concentration can be estimated lower than 1 ppm. Therefore, the formation of this species is irrelevant in the sulphur mass balance. The above results are similar to those previously reported related to the spontaneous reduction of sulphur dioxide by contact deposition with 304 stainless steel [27]. However, it must be remarked that this behaviour was not observed in analogous experiments with 316 stainless steel. Thus, the formation of colloidal sulphur appears to be the attractive cathodic product and polythionates are formed as the main side species having also useful applications. Hence, Falco et al. [29] proposed a similar acid solution of polythionates, produced in a biological reactor, for the recovery of manganese from spent batteries. An alternative way is the

oxidation of polythionates to sulphate by means of hydrogen peroxide [30], oxygen and  $\text{Fe}^{3+}$  ions [31], transforming the residual solution into a harmless substance.

Furthermore, experiments with a two-phase flow were done. Here, the supporting electrolyte was also  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  with an initial sulphur dioxide concentration of  $1.0$  or  $2.5 \text{ g dm}^{-3}$ , the latter value is close to the steady-state concentration under these two-phase working conditions [13]. The gas volumetric flow rate,  $q_g$ , was  $1.5$  or  $2 \text{ dm}^3 \text{ min}^{-1}$  under ambient conditions and the liquid volumetric flow rate was  $8 \text{ dm}^3 \text{ min}^{-1}$ . Under these examined working conditions, the mean value of: space time yield was  $3.1 \text{ kg m}^{-3} \text{ h}^{-1}$ , with a current efficiency and specific energy consumption of  $43.3\%$  and  $33 \text{ kW h kg}^{-1}$ , for sulphur production, respectively. The conversion was  $62\%$  for the experiment with a sulphur dioxide concentration of  $2.5 \text{ g dm}^{-3}$ . These values are of the same order of magnitude that those reported in Fig. 5 for the single-phase case showing a moderate influence of the gas phase on the behaviour of the system. Thus, the suitability of an electrochemical reactor with decaying swirling flow was validated for the management of two-phase flow.

#### 4. Morphological characterization of colloidal sulphur

Fig. 6, Part (a), shows a typical micrograph of the product from a single-phase experiment and Part (b) for the two-phase case. The volumetric flow rates of the liquid and gas phases were  $8$  and  $1.5 \text{ dm}^3 \text{ min}^{-1}$ , respectively, and  $-0.7 \text{ V}$  the cathodic potential. The morphology of the sulphur powder in the single-phase case is characterised by particles of different shapes, whereas those obtained under two-phase flow are predominantly spheroids with only some of them of parallelepipedal shape and crystalline morphology. Likewise, they are smaller than the previous ones. In the histograms presented in Fig. 7, corresponding to the cases reported in Fig. 6, the largest dimension

of the particles was used for the statistical analysis based on 408 and 573 independent size measurements for the single- and two-phase cases, respectively. The average value of the particles in Fig. 7, Part (a), is 7.4  $\mu\text{m}$  with a standard deviation of 3.8  $\mu\text{m}$  and 2.8  $\mu\text{m}$  with a standard deviation of 1.5  $\mu\text{m}$  for Part (b). The differences in morphology and particle size between both cases can be mainly attributed to the changes in concentration of sulphur dioxide during the experiment. For the single-phase flow a large variation in concentration takes place generating diverse morphologies and particles sizes. On the contrary in the two-phase flow, sulphur dioxide is continuously replenished in the solution phase from the gas stream giving a more uniform product. The insets in the upper-right corners of Fig. 7 displays spectra of EDS analysis of the samples, where only the characteristic peaks corresponding to sulphur are observed, without the presence of the metals forming the electrodes, verifying the high purity of the colloidal sulphur.

## 5. Comparison of electrochemical reactors for colloidal sulphur production

Fig. 8 compares the figures of merit of five types of electrochemical reactors for the production of colloidal sulphur by reduction of sulphur dioxide. The reactors considered are: rotating cylinder electrode [12], RCE, rotating cylinder electrode with ultrasound assistance [13], RCEUA, parallel-plate electrochemical reactor with a double convergent flow [9], PPER, modified hydrocyclone [14], MHC, and electrochemical reactor with swirling flow, SF. The last one was analysed here. One of the most relevant figures of merit is the space time yield showing the best value for the PPER. However, this reactor presents as a main issue that the cathode surface is covered with an insulating layer of sulphur. The rotating cylinder electrode shows a lower value of space time yield and the passivation can be avoided with application of ultrasound, improving the reactor performance. Reactors based on the modified hydrocyclone or swirling flow concepts



present similar values of space time yield and specific energy consumption without cathode passivation in both cases due to the impingement effect of the helical flow. However, it must be emphasised that this encouraging result of the impingement effect can be counteracted by flow-induced corrosion problems, requiring a control of the device during long-term operation. In the reactor with swirling flow of the present study was used a large interelectrode gap, 24.4 mm, which contrasts with that for the MHC, 7.25 mm. In the design of the reactor with swirling flow, it was privileged at the inlet an expansion swirl flow in order to improve the mass transfer conditions [20]. However, in counterpart the large interelectrode gap increases the reactor volume decreasing the space time yield and at the same time enlarges both the ohmic drop in the electrolyte and the cell potential difference, increasing the specific energy consumption. Thus, it must be emphasised that there is scope for considerable optimisation of the interelectrode gap for industrial applications in order to improve the performance of the electrochemical reactor with swirling flow, revealing this device as a promising one.

## 6. Conclusions

An electrochemical reactor with decaying swirling flow represents an appropriate device for the production of colloidal sulphur, allowing the removal of sulphur dioxide from effluents, due to:

- For sulphur dioxide concentrations lower than  $2.5 \text{ g dm}^{-3}$  the passivation of the cathode is avoided because the impingement effect of the swirling flow detaches the sulphur layer.
- It is possible to produce a useful species with commercial value, colloidal sulphur, transforming a risky pollutant, sulphur dioxide.
- The reactor can be operated either in single- or two-phase flow.

- The secondary products of the process, polythionates, also have practical applications or the residual solution can be transformed into an innocuous one.

Author statement

**C. C. Contigiani:** Investigation, Formal analysis. **J. P. Fornés:** Investigation, Formal analysis. **O. González Pérez:** Validation. **J. M. Bisang:** Conceptualization, Methodology, Writing - Review & Editing.

Declarations of interest: none

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## LEGENDS

Fig. 1. Schematic representation of the decaying swirling flow electrochemical reactor. (a) Cathode; (b) electrical connections to anode; (c) connection for Haber–Luggin capillary; (d) tangential electrolyte inlet; (e) tangential electrolyte outlet; (f) gas feeder for two-phase system. Right-hand side: thick full line: cathode; thick dotted line: anode. Internal dimensions of the reactor in mm.

Fig. 2. Current as a function of time at different cathodic potentials under single-phase flow.  $5 \text{ g dm}^{-3} \text{ SO}_2$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  as a supporting electrolyte.  $q = 8 \text{ dm}^3 \text{ min}^{-1}$ .  $T = 30 \text{ }^\circ\text{C}$ .

Fig. 3. Figures of merit for colloidal sulphur production for the experiments reported in Fig. 2.  $5 \text{ g dm}^{-3} \text{ SO}_2$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  as a supporting electrolyte.  $q = 8 \text{ dm}^3 \text{ min}^{-1}$ .  $t = 15 \text{ min}$ .  $T = 30 \text{ }^\circ\text{C}$ .

Fig. 4. Current as a function of time for the  $3^2$ -design of single-phase experiments reported in Fig. 5. Volumetric flow rate:  $q$  ( $\text{dm}^3 \text{ min}^{-1}$ ), initial sulphur dioxide concentration:  $c$  ( $\text{g dm}^{-3}$ ), duration of the experiment:  $t$  (min). Supporting electrolyte:  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ .  $E_{\text{SCE}} = -0.7 \text{ V}$ .  $T = 30 \text{ }^\circ\text{C}$ .

Fig. 5. Figures of merit for the  $3^2$ -design of single-phase experiments for sulphur dioxide reduction as a function of concentration, liquid volumetric flow rate and duration of the experiment. Current efficiency:  $\Phi_s^e$  (%), space time yield:  $\sigma_s$  ( $\text{kg m}^{-3} \text{ h}^{-1}$ ), specific energy consumption:  $w_s^e$  ( $\text{kW h kg}^{-1}$ ), conversion:  $x$  (%). Supporting electrolyte:  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ .  $E_{\text{SCE}} = -0.7 \text{ V}$ .  $T = 30 \text{ }^\circ\text{C}$ .

Fig. 6. Scanning electron micrographs of colloidal sulphur particles. Part (a): sample obtained under single-phase flow with magnification:  $\times 2900$ . Part (b): sample obtained under two-phase flow with magnification:  $\times 5400$  and  $q_g = 1.5 \text{ dm}^3 \text{ min}^{-1}$ .  $E_{\text{SCE}} = -0.7 \text{ V}$ .  $T = 30 \text{ }^\circ\text{C}$ .  $t = 15 \text{ min}$ .  $q = 8 \text{ dm}^3 \text{ min}^{-1}$ .

Fig. 7. Particle size distributions. Part (a): single-phase flow. Part (b): two-phase flow,  $q_g = 1.5 \text{ dm}^3 \text{ min}^{-1}$ .  $E_{\text{SCE}} = -0.7 \text{ V}$ .  $T = 30 \text{ }^\circ\text{C}$ .  $t = 1 \text{ h}$ .  $q = 8 \text{ dm}^3 \text{ min}^{-1}$ . Inset: EDS spectrum of the colloidal sulphur.

Fig. 8. Comparison of the figures of merit of different electrochemical reactors for the production of sulphur by reduction of sulphur dioxide. RCE: rotating cylinder electrode [12], RCEUA: rotating cylinder electrode with ultrasound assistance [13], PPER: parallel-plate electrochemical reactor with a double convergent flow [9], MHC: modified hydrocyclone [14], SF: electrochemical reactor with swirling flow, this work. Working conditions unless otherwise is stated in the graph: single-phase flow,  $5 \text{ g dm}^{-3} \text{ SO}_2$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  as a supporting electrolyte.  $E_{\text{SCE}} = -0.7 \text{ V}$ .  $T = 30 \text{ }^\circ\text{C}$ .



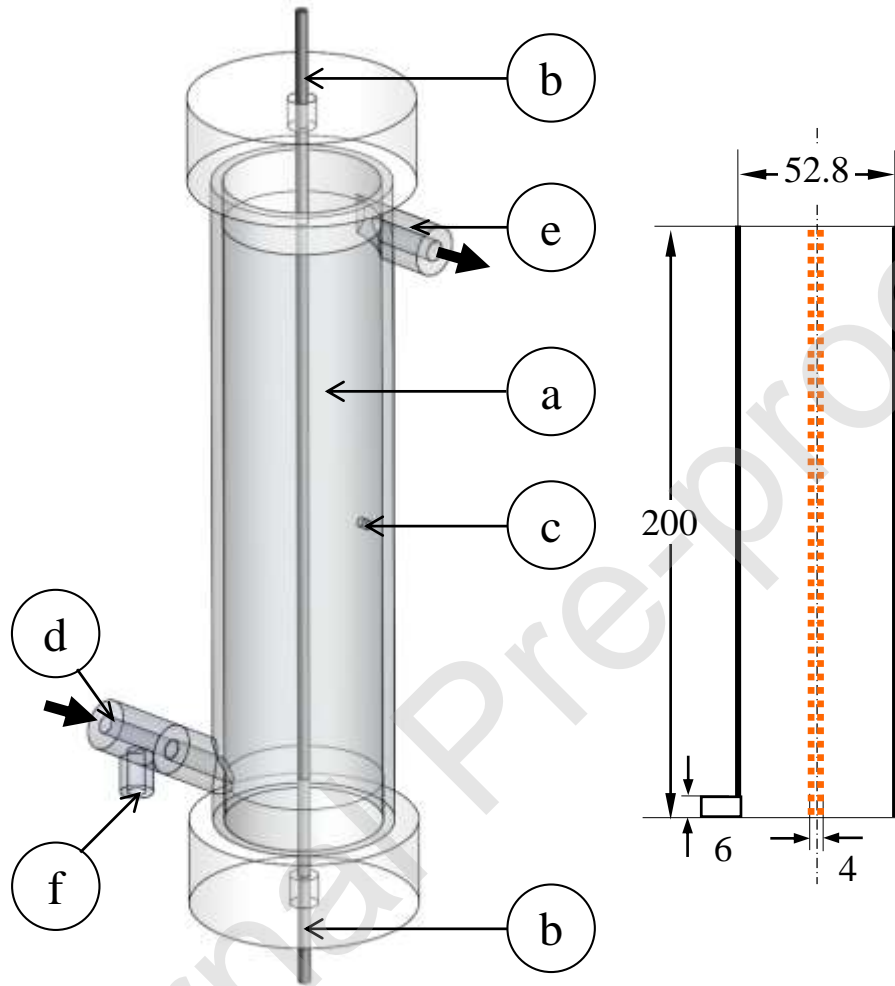


Fig. 1.

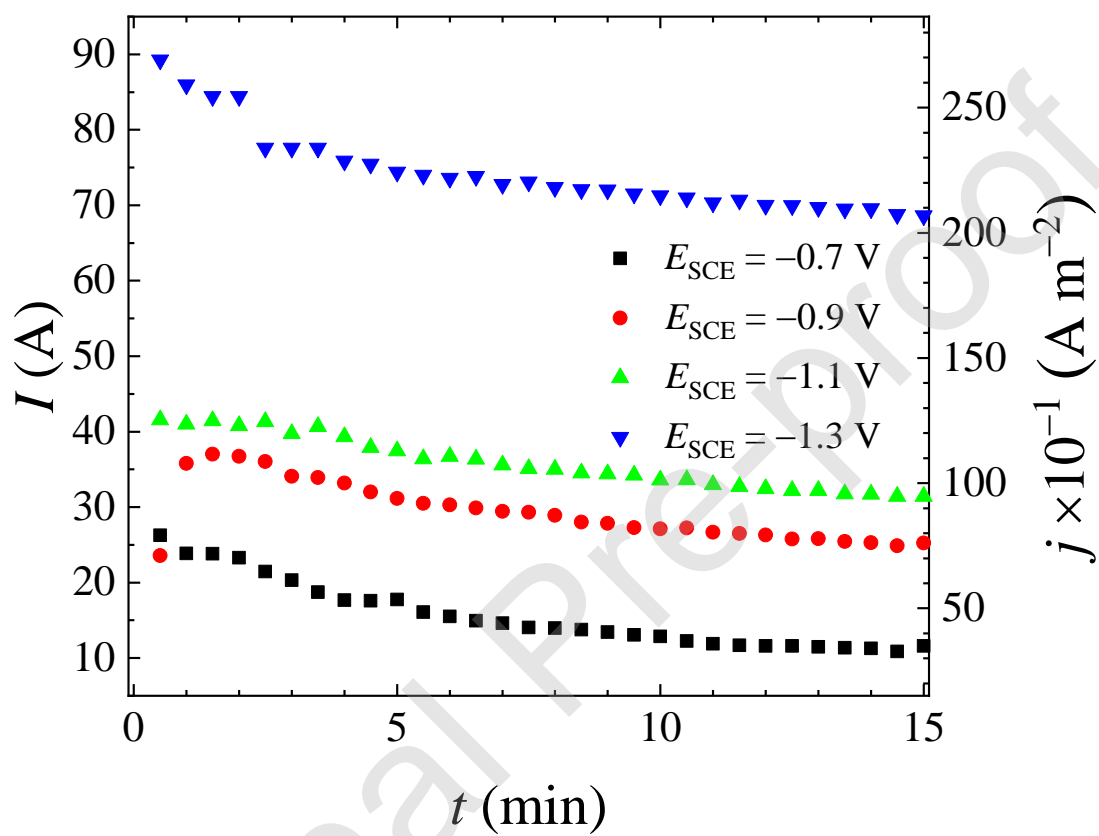


Fig. 2.

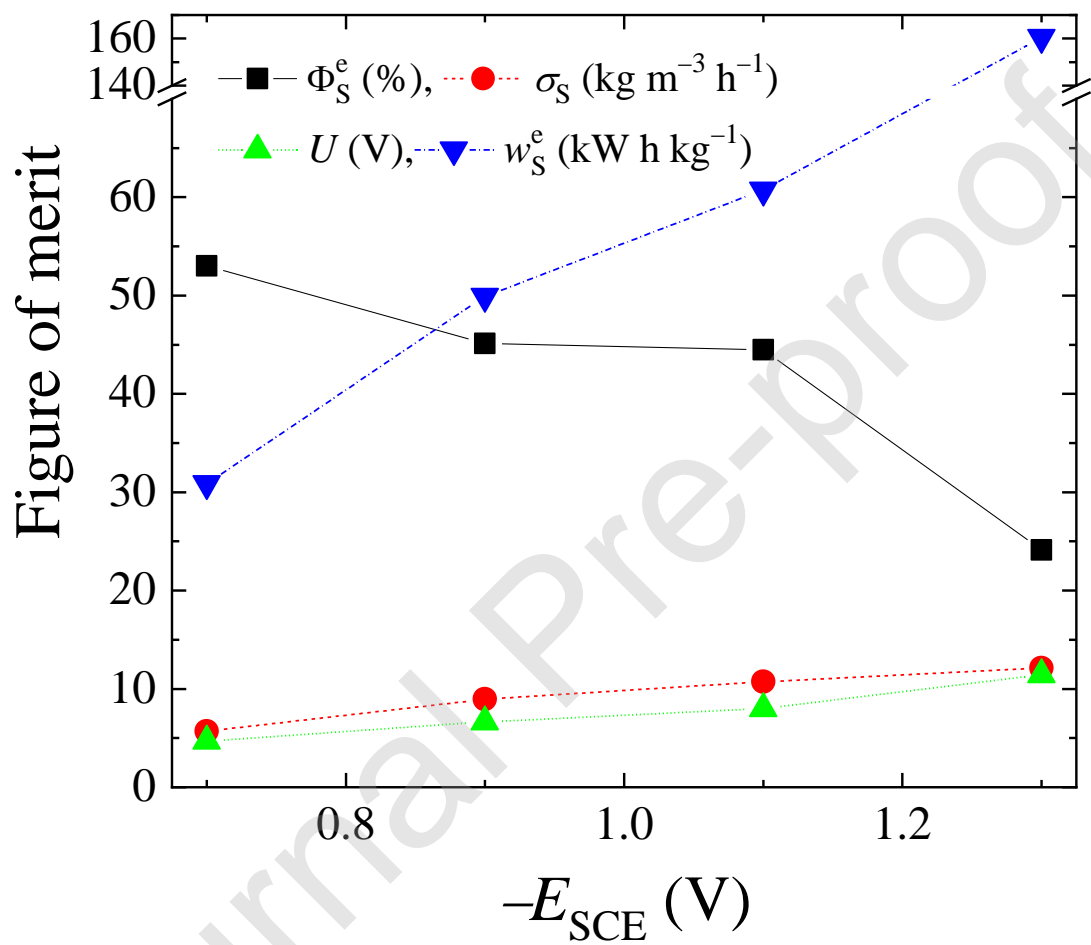


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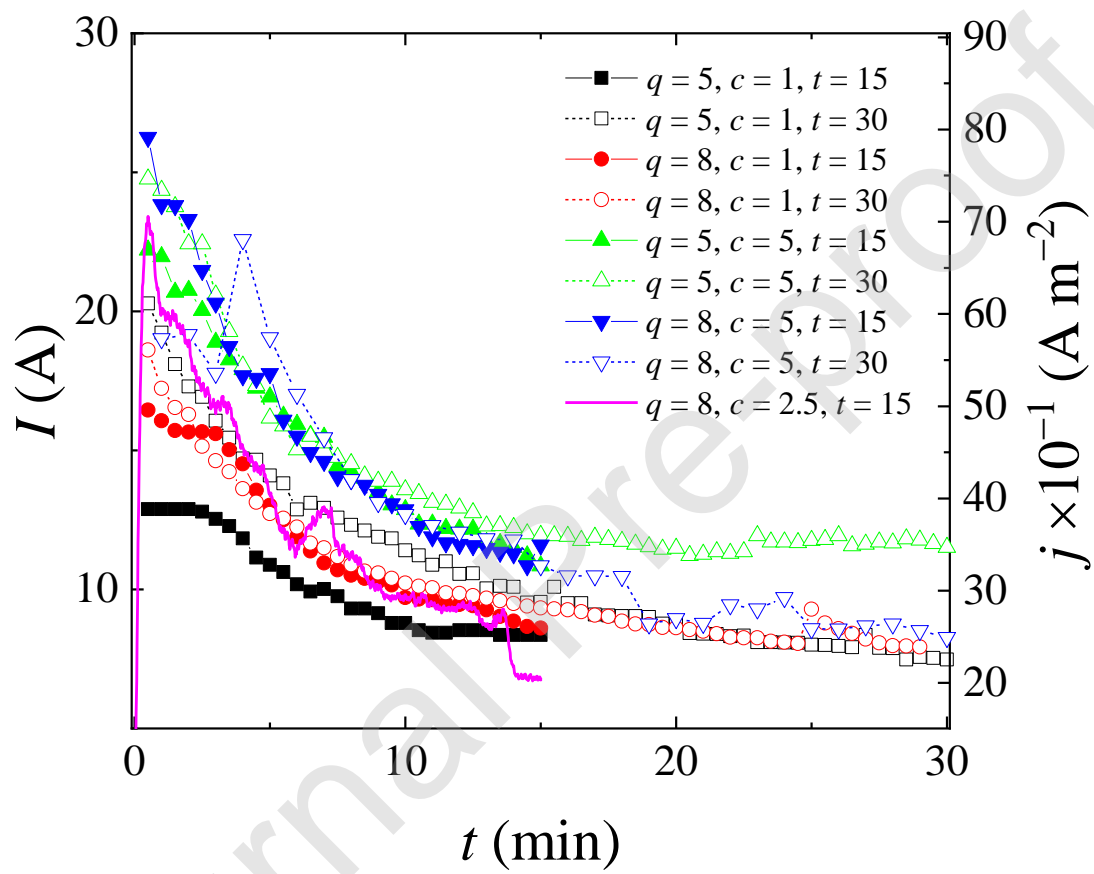


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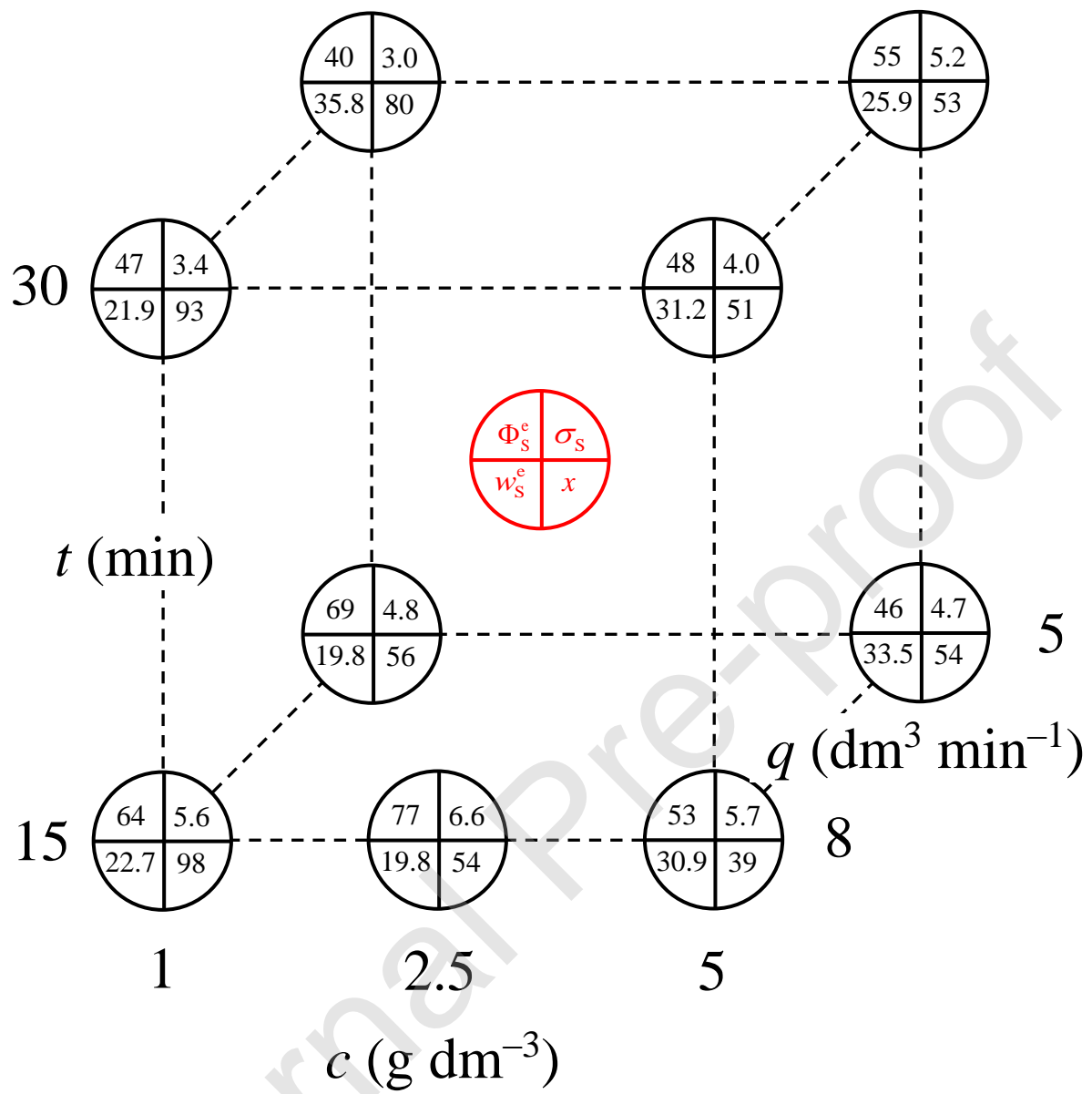


Fig. 5.

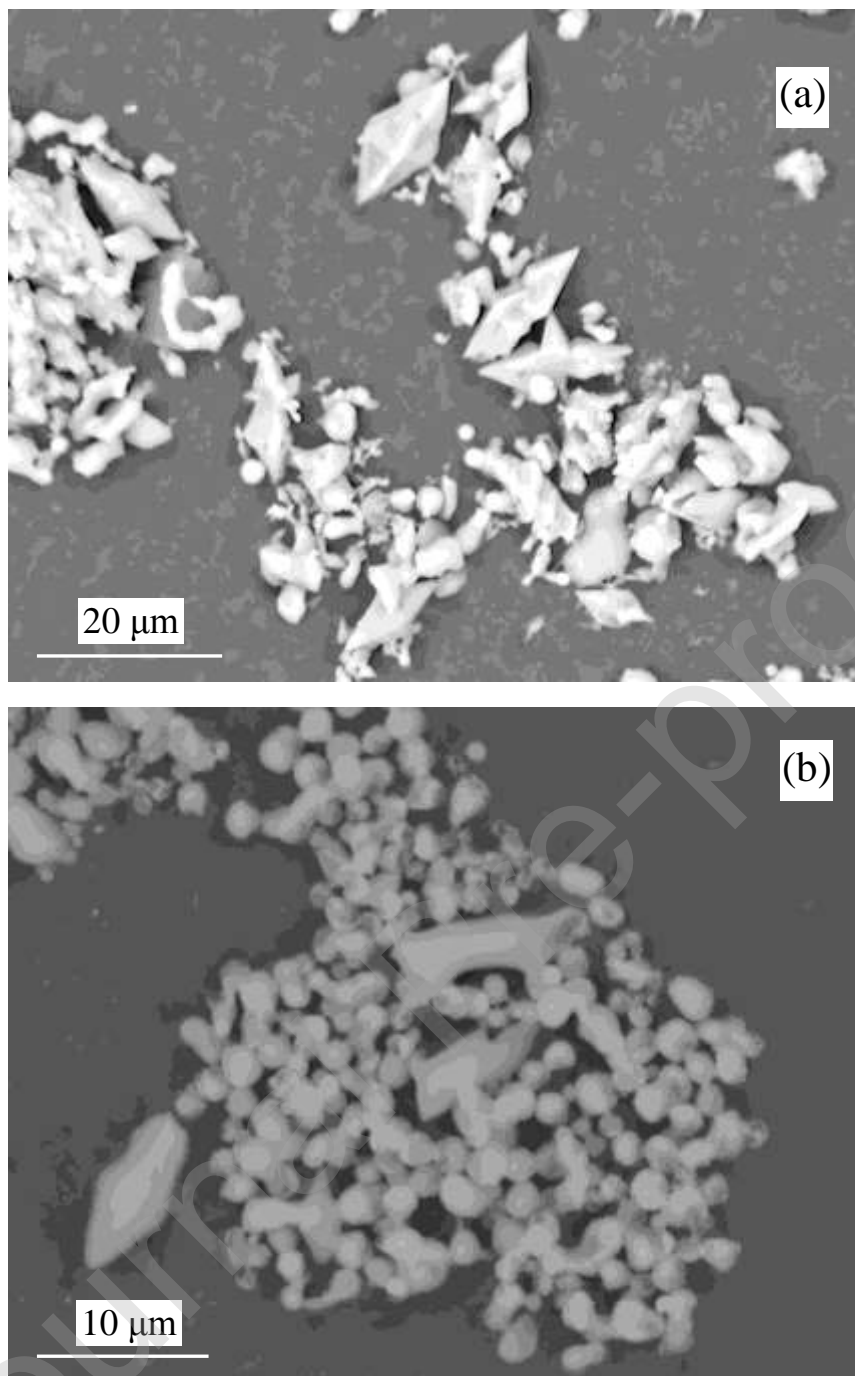


Fig. 6.

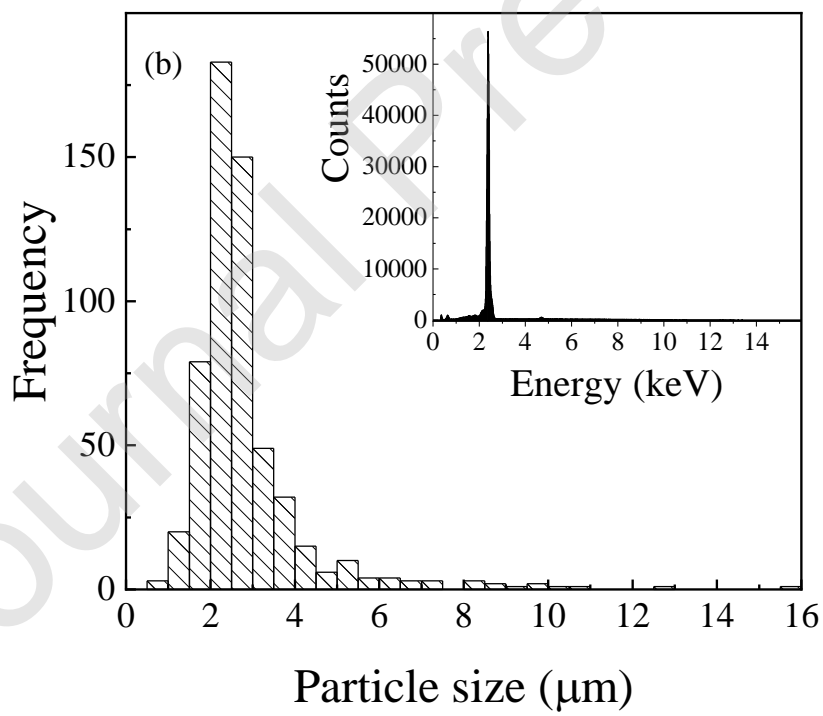
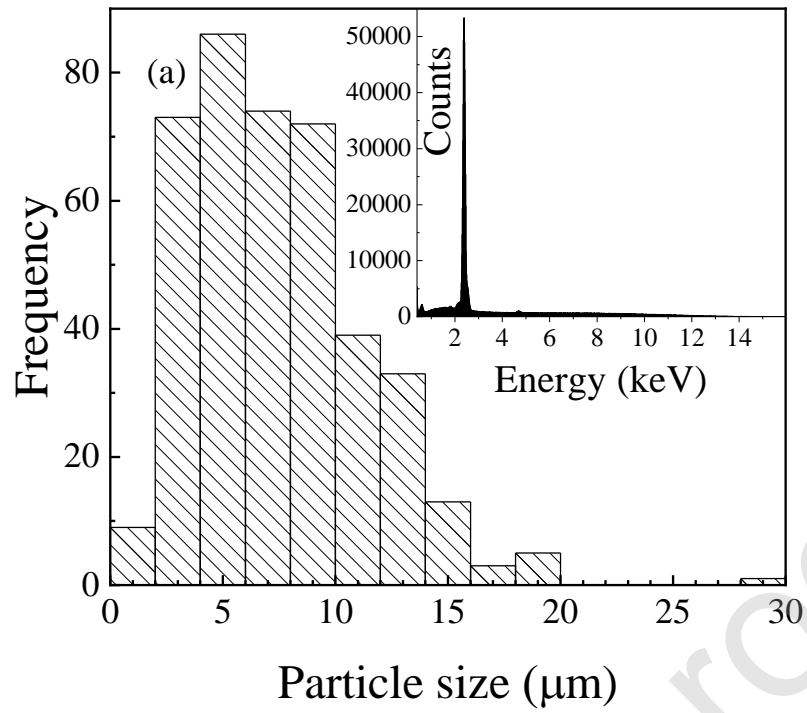


Fig. 7.

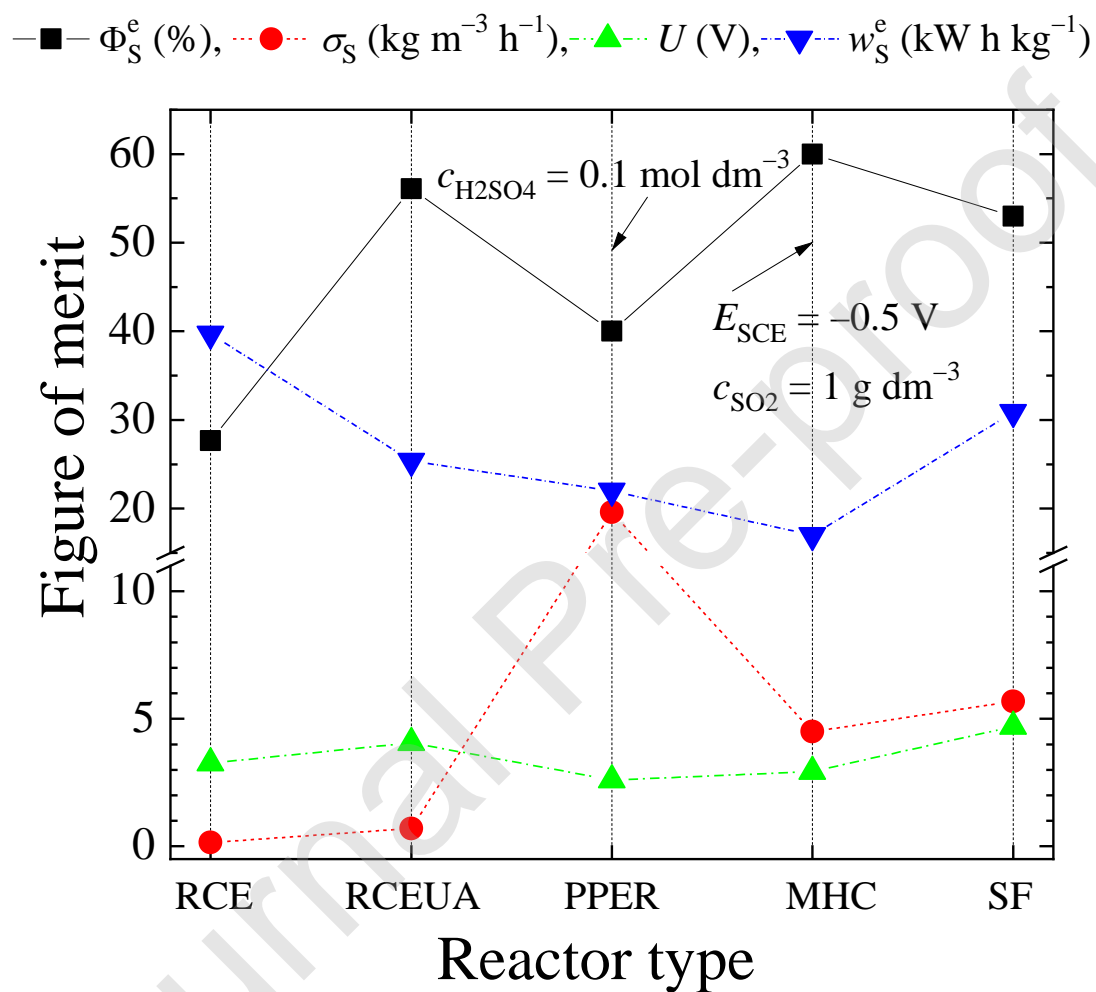


Fig. 8.



**Table 1.**

Loss of sulphur by chemical oxidation

Solution:  $c \cong 5 \text{ g dm}^{-3}$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  with the addition of sulphur powder.

Loss of sulphur (%)	
$T = 30 \text{ }^\circ\text{C}$ and $t = 1 \text{ h}$	0.4
$T = 45 \text{ }^\circ\text{C}$ and $t = 1 \text{ h}$	3
$T = 45 \text{ }^\circ\text{C}$ and $t = 3 \text{ h}$	4
$T = 60 \text{ }^\circ\text{C}$ and $t = 1 \text{ h}$	8

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