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DECHLORINATION OF CHLORINATED HYDROCARBONS IN A MONOPOLAR PACKED BED ELECTROCHEMICAL REACTOR[1]

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Abstract

A monopolar packed bed electrochemical reactor was presented in which performance indicators were measured with pentachlorophenol (PCP) model compound. Dechlorination of PCP in this reactor showed similar results to those achieved by SCHMAL and coworkers in a multifibre cell. Dechlorination of an aliphatic model compound, chinester (CHE) (ethyl-[d,1-cis,trans-2,2-dimethyl-3-|2,2'dichlorvinyl|]-1-cyclopropane carboxylate) showed 80% dechlorination of CHE with 43% current efficiency at 0.6 A/dm^2 current density and 20 L/h flow rate.

Keywords: electroreductive dechlorination; organic chlorine removal by electroreduction.

Chemical process industry produces large quantities of waste waters containing toxic or non-biodegradable chlorinated hydrocarbons in low (10–1000 mg/L) concentration. The toxicity of these compounds is connected with the chlorine content and their biodegradability is strongly affected by chlorine substitution in the molecule [1].

Electrochemical reduction of chlorinated organics in diluted waste streams is a powerful method offering a low temperature alternative to incineration and a clean process releasing no other chemicals into the waste waters, moreover the cost-effectiveness of this method does not depend on a large throughput in order to achieve economics of scale [2].

The overall reaction of the cathodic dechlorination is:

$$R - Cl + 2e^- + H_2O \rightarrow RH + Cl^- + OH^-.$$

For industrially applicable reduction of chlorinated organics in waste waters, the following aspects must be considered:

- The potentials required for the reduction of chlorinated organics in aqueous solution can be very negative (more than -2V), therefore it will not always be possible to prevent hydrogen evolution as a competing reaction, which decreases current efficiency and, as a result, increases energy consumption. However, at low concentrations occurring in the practice (often less than

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100 ppm) energy consumption is not normally a factor of major importance [3].

- Owing to the low concentration of the compounds to be converted, only three-dimensional electrodes can be used, if the method is to be commercially viable.
- Among the electrode materials suitable for use in practice, carbon has a relatively high overpotential for the hydrogen evolution reaction, has a very large surface area and is relatively cheap.

Current methods of electrochemical reduction of chlorinated organic species are at their infancy and therefore some of the most promising research areas will be mentioned here.

SCHMAL et al. of TNO Delft (the Netherlands) have examined the electrochemical dechlorination of eight priority compounds from the EC-list [4] using a MP-Cell (Electro Cell Systems AB) and cathodes of bundles of carbon fibres and carbon felt [5], [6]. The compounds investigated were: 2-amino-4-chlorophenol, 4-chloronitrobenzene, dichlorvos (DDVP), hexachloroethane, pentachlorophenol (PCP), 2,4,5-T, tetrachloroethane and 1,2,4-trichlorobenzene [5].

The experiments were performed in a batch type recycle mode with 1 liter solution at a constant current. The electrolyte was usually aqueous $NaOH/NA_2SO_4$.

Experiments showed that after 20 minutes of electrolysis at a current of 10 A, the initial concentration of PCP (50 ppm) fell to about 1 ppm. The current efficiency was low (about 1%) but could be increased considerably by the addition of small quantities of certain surfactants [7], [8]. Despite the low current efficiency (0.2–3%), the energy consumption was relatively low (about 30 kWh/m^3). The decay of PCP as well as the rise and fall of the four intermediate chlorophenols confirmed that the organic skeleton remained intact during the cathodic treatment [5]. Toxicity decreased by a factor of 20, with the final product being phenol and some monochlorophenol. Similarly, *p*-chloronitrobenzene and dichlorvos (DDVP) were dehalogenated to 0.1 and 1 ppm, respectively. The cost of energy was not felt to be prohibitive when compared to alternative treatment costs of these waste waters.

ZIMMER et al. [9] dehalogenated chloroform, 5-chlorosalicyclic acid, 2-methoxy-5-chlorobenzoic acid and 4-chloroanilin (each in 1 g/L concentration) in aqueous sulfuric acid solution, using Cu, Pb and Ni cathodes in a Micro-Flow Cell (Electro Cell AB). Chloroform showed reactions on Cu and Pb cathodes already at low current densities of 2–5 mA/cm^3 and with high current yield, but cathodic degradation of aromatic compounds occurred only at high current densities of 50–75 mA/cm^2 at Pb cathodes in a 0.05 M NaOH electrolyte.

Dechlorination of polychlorinated biphenyl wastes [10] greatly reduces the toxicity and is less energy intensive than complete oxidation. A novel process [11]–[14] developed by Electrosynthesis Co. Inc. and PCB. Sandpiper (COLUMBUS, Ohio USA) and commercialized by Electro Cell System AB [15] was used to reduce large volumes of mineral and silicone oils containing about 1000 ppm polychlorinated biphenyls from transformer washing. 30–50% current efficiencies for the decrease in the polychlorinated biphenyl concentration from 700 to less than

1 ppm was possible. Mediated electrochemical reduction of PCB-s may offer a viable alternative to direct reduction [16]–[18].

CABOT et al. reported dechlorination of chlorinated fluorohydrocarbons by electrochemical reduction in NH_4Cl containing aqueous methanolic solution, using Pb cathode and a hydrogen diffusion anode consisting of Pd foil with electrodeposited Pd black [19].

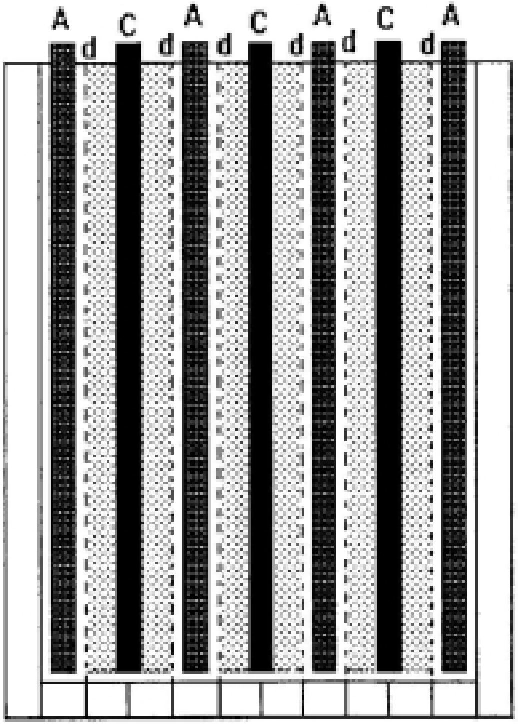

Fig. 1. Cross section of the monopolar packed bed electrochemical reactor. A – Anode; C – Cathode; d – diaphragm

Prompted by the research of the late eighties done by SCHMAL et al. [20], [21], a monopolar packed bed electrochemical reactor filled with porous granular graphite (electrographite) as cathode material was built in our laboratory, in which dechlorination of different process waste waters containing chlorinated hydrocarbons in low concentrations (produced by the Hungarian chemical industry) were investigated and the performance of the cell tested. The chlorine concentration of a selected process waste water changed from 672 to 82.9 ppm on a single cycle, with a current efficiency of 84.6% and an energy consumption of 1.76 kWh/kg chlorine removed [22].

This paper reports a study on the electrochemical reduction of one aromatic and one aliphatic chlorinated hydrocarbon model compound, using the formerly built electrochemical reactor to identify the optimum conditions for a useful reactor performance.

1. Experimental

Experiments were performed in a divided, monopolar, packed bed flow-through electrochemical reactor consisting of three cathode and four anode compartments. The body of the cell was made of polypropylene. The dimensions of the cathode and anode compartments were the same $7 \times 1.5 \times 47$ cm per compartment. The cathode feeders and the anodes were made of graphite sheets, while the cathode compartments were filled with porous, granular graphite (electrographite) particles of 1.5–2.5 mm diameter situated on both sides of the cathode feeders. Ionac MC 3470 cation exchange membranes were used as cell dividers. The cross section and dimensions of the cell can be seen in *Figs. 1* and *2*, respectively. *Fig. 3* shows the flow-circuit of the experimental reactor. Experiments were performed in a batch type mode with 50 liter solution, at constant current. The potential distribution was measured with a Ag/AgCl reference electrode connected with Luggin capillary. The conditions which were maintained at fairly constant level were:

Total volume of the cathode and anode compartments (empty): 3.4 dm^3
Superficial velocity: $0.24 - 1.1 \times 10^{-3}$ m/s
Temperature: 20–25 °C
Height and width (in dm) of the feeders and anodes: $0.08 \times 0.6 \times 5.5$
Diaphragm area: 0.21 m^2

The model compounds investigated were: pentachlorophenol (PCP) and chinester (CHE): (ethyl-[d,1-cis, trans-2,2-dimethyl-3-|2,2’ dichlorvinyl|]-1-cyclopropane carboxylate or DVCA-ethylester). PCP is a polar, non-biodegradable, very toxic compound, the chinesther is possibly the main component of a process waste water produced by the Hungarian chemical industry in large quantities. The initial concentration of the organochlorine compounds was in the range of 50–1000 mg per liter solution. The electrolyte was usually aqueous 0.1–1M NaOH/Na$_2$SO$_4$.

The dechlorination reaction was followed by Thin Layer Chromatography (TLC) method and by measuring the decrease in the Cl$^-$-ion yield potentiometrically, using argentometric titration.

2. Results and Discussion

The PCP model compound was used for the measurement of some performance indicators in the packed bed cell and for testing the feasibility of the dechlorination method.

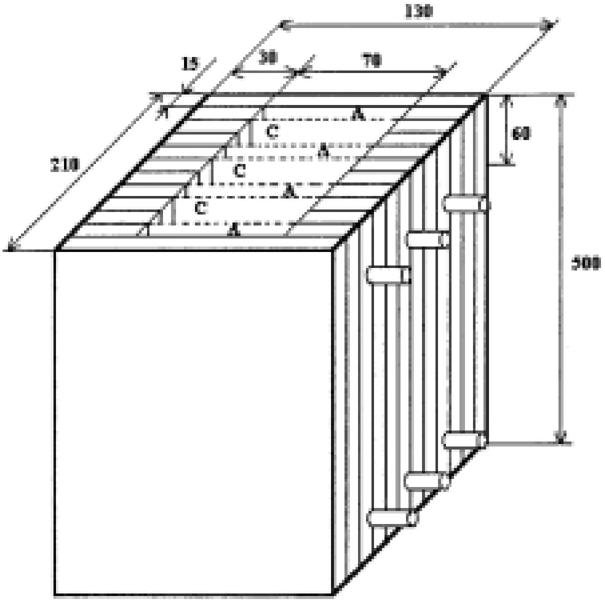

Fig. 2. Dimension of the monopolar packed bed electrochemical reactor (in mm). A–Anode area; C – Cathode area

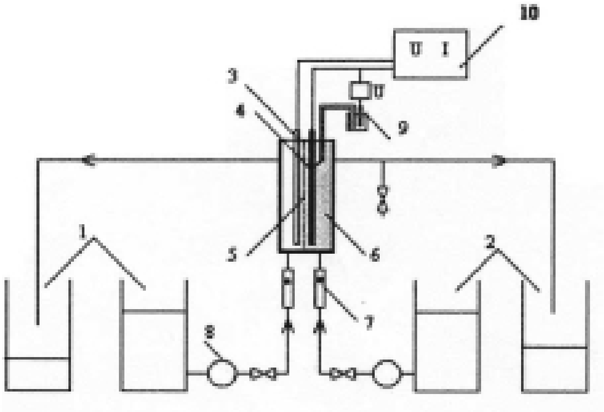

Fig. 3. Flow-circuit of the experimental equipment. 1 – Anolyte tank; 2 – Catholyte tank; 3 – Anode; 4 – Cathode feeder; 5 – Diaphragm; 6 – Cathode bed; 7 – Flow meters; 8 – Pumps; 9 – Reference electrode; 10 – Power supply

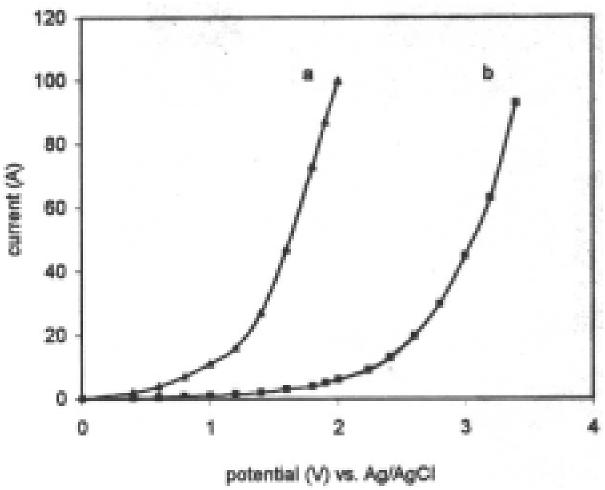

Fig. 4. Cathodic polarisation curves in aqueous solution of pentachlorophenol (c = 100 ppm). a – with electrographite particles; b – without electrographite particles

Table 1. Results of the electroreductive dechlorination of PCP (on a single pass)

Current (A)	Flow rate (L/h)	Cell voltage (V)	Potential vs. Ag/AgCl electrode (V)	CI concentration difference (ppm)	Current efficiency (%)	Energy consumption (kWh/m^3)	CI removal rate (g/m^{2}h)
20	1	4–5	1.35	10	0.05	90	0.05
40	1	4–6	1.45	98	0.24	200	0.49
60	1	6–8	1.60	276	0.46	420	1.38
80	1	8–10	1.80	468	0.59	720	2.34
100	1	9–11	2.25	452	0.57	1000	2.26
80	2	8–10	1.75	482	1.20	360	2.41
80	3	8–10	1.75	423	1.58	240	2.12
80	4	8–10	1.75	282	1.41	180	1.41
80	8	8–10	1.75	73	0.73	90	0.37
80	12	8–10	1.70	12	0.18	60	0.06

Time of electrolysis: 1 h
Electrolyte: 0.1 M NaOH/0.1 M Na_2SO_4

Initial concentration: 1000 ppm
Temperature: 25–30 °C

Fig. 4 shows the polarisation curves measured on the cathode in PCP containing aqueous solution (100 ppm) taken in the packed bed cell with and without the electrographite particles. The results showed that the presence of the filling resulted

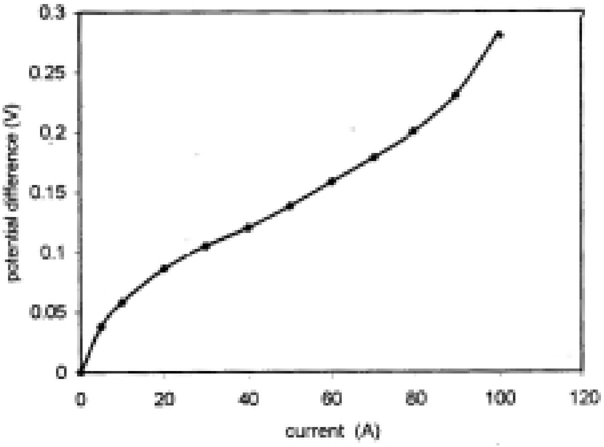

Fig. 5. Variation of cathodic potential difference with the cell current (between the measuring points of the diaphragm [M_D] and that of the cathode feeder [M_F])

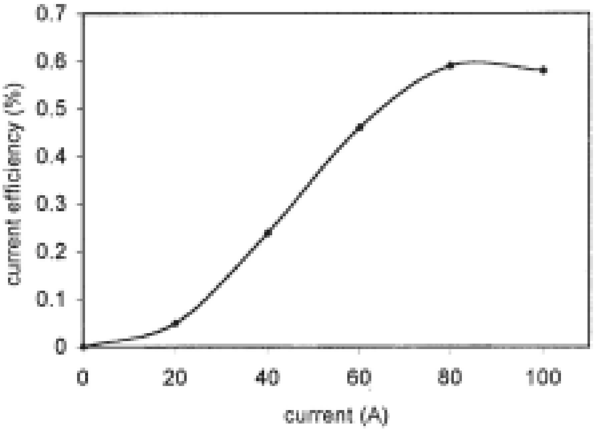

Fig. 6. Variation of current efficiency with the cell current at dechlorination of PCP (flow rate: 1 L/h)

in a 10–20-fold increase in the cell current, therefore the electrochemically active surface of the particles can be estimated as 2–4 m^2.

The cathode potential values measured vs. Ag/AgCl reference electrode (as far as 2 mm from the diaphragm as well as from the cathode feeder) were 1.96 V. (M_D) and 1.7V (M_F), respectively. In *Fig.* 5 the potential differences between the measuring points of the diaphragm and that of the cathode feeder ($M_D - M_F$) are

Table 2. Dechlorination data of chinester in the packed bed reactor (on a single pass)

Flow rate (L/h)	Current density (A/dm^2)	CI concentration difference (ppm)	Current efficiency (%)	Energy consumption (kWh/kg)	CI removal rate (g/m^{2}h)
5	0.1	180	34.0	6.7	4.3
	0.2	223	21.3	10.7	5.4
	0.4	249	11.8	19.2	5.9
	0.6	181	5.7	39.8	4.3
	0.8	106	2.5	90.9	2.5
	1.0	32	0.6	375	0.8
	1.2	6	0.1	2250	0.1
10	0.1	159	53.0	4.3	6.7
	0.2	244	41.6	5.5	10.5
	0.4	309	26.4	8.6	13.3
	0.6	308	17.5	13.0	13.2
	0.8	235	10.0	22.7	10.1
	1.0	132	4.5	50.8	5.7
	1.2	42	1.2	189	1.8
15	0.1	131	74.5	3.0	9.4
	0.2	227	64.6	3.5	16.2
	0.4	309	44.0	5.2	22.1
	0.6	317	30.0	7.6	22.6
	0.8	242	17.1	13.2	17.3
	1.0	162	9.2	24.6	11.6
	1.2	84	4.0	26.7	6.0
20	0.1	118	89.5	2.5	11.3
	0.2	209	79.0	2.9	19.9
	0.4	319	60.5	3.8	30.4
	0.6	341	43.0	5.3	32.4
	0.8	301	28.4	7.9	28.7
	1.0	194	14.7	15.4	18.5
	1.2	95	6.0	37.9	9.0

Initial concentration: 424 ppm
Cell voltage: 2–3 V
Temperature: 25–30 °C
Time of electrolysis: 0.25 hour

plotted against the current applied.

Dechlorination of PCP with an initial concentration of 1000 ppm, carried out in the packed-bed cell on a single cycle, showed that the best performance could

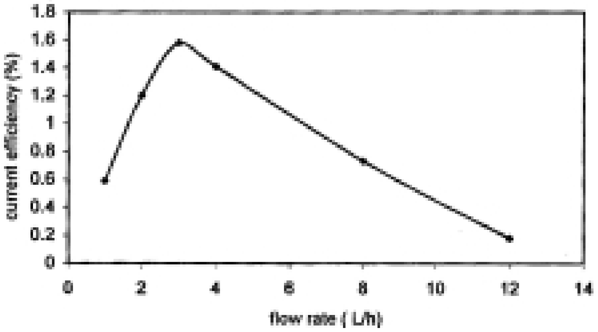

Fig. 7. Variation of current efficiency with the electrolyte flow rate at dechlorination of PCP (current: 80 A)

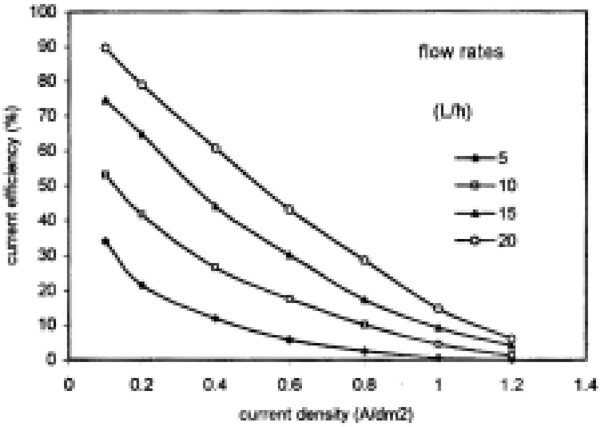

Fig. 8. Effect of current density on the current efficiency at different flow rates for dechlorination of chinester

be achieved with a fairly high current of 80 A and a slow flow rate of 2-4 L/h. (See *Figs*. 6 and 7 as well as *Table* 1) Under these circumstances the best current efficiency was 1.58% and the dechlorination rate 2.41 g/m^{2}h (48% dechlorination).

Data for the reductive dechlorination of chinester (CHE) measured over a range of experimental conditions are demonstrated in *Table* 2 and in *Figs*. 8 and 9. In the calculation of the current density the surface of the diaphragm, (20 dm^2) was used, but in the determination of the superficial velocity the useful area of the cross section of the cathode compartment ($7 \times 2.4 \times 3 = 50.4$ cm^2) was taken into consideration.

The results indicated that the dechlorination of CHE could be carried out

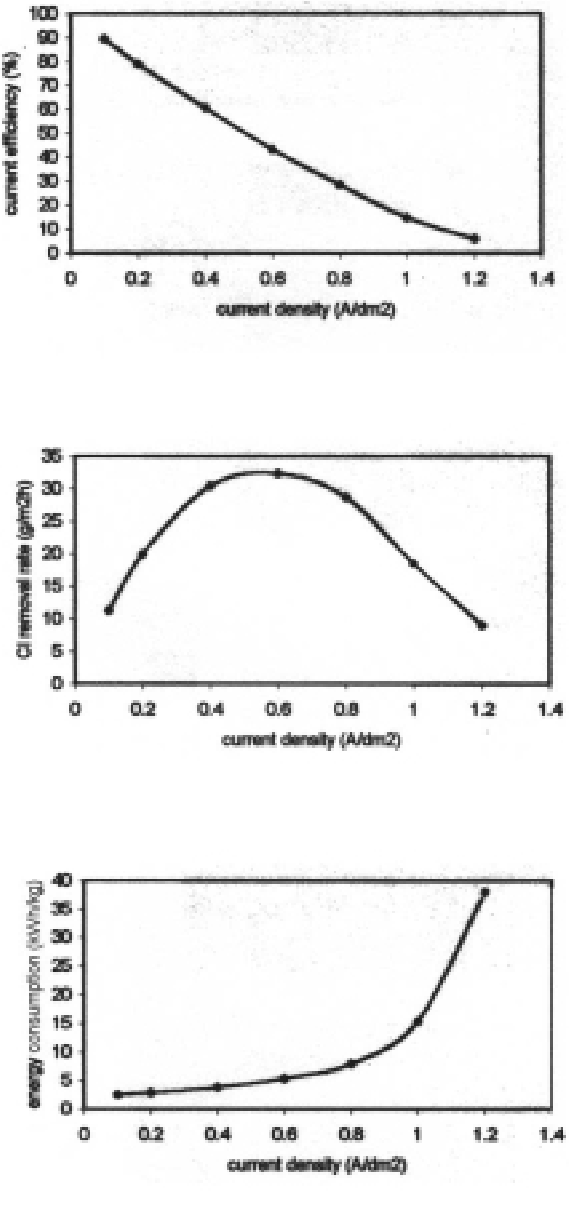

Fig. 9. Effect of current density on different performance indicators at the reduction of chinester (flow rate 20 L/h). – Superficial velocity: 1.1×10^{-3} m/s; – Initial Cl concentration: 424 ppm; Final Cl concentration: 83 ppm; – Cell voltage: 2–3 V

under milder experimental conditions than those applied for PCP. The best current efficiency as well as the maximum value of the total amount of chlorine reduced was found at a higher flow rate of 20 L/h. The decrease in the chlorine concentration seemed to be independent of the flow rate and showed a maximum at current densities of 0.4–0.6 A/dm^2. 80% dechlorination of CHE was achieved in 15 minutes with 43% current efficiency applying 0.6 A/dm^2 current density and 20 L/h flow rate on a single pass.

3. Conclusions

Dechlorination of PCP in a flow-through electrochemical cell filled with porous granular graphite (electrographite) showed comparable results to those given by SCHMAL and coworkers [8].

Experiments performed for the reductive elimination of chlorine atoms of CHE suggest that the method is feasible mainly for aliphatic hydrocarbons where effective dechlorination could be achieved at low current densities and higher flow rates. At low current density hydrogen evolution is at the minimum, the potential values are low and there is no need of cooling. A further advantage of the electrochemical dechlorination in the packed bed reactor is that the equipment and the electrographite particles are cheap therefore it holds promise as a practical method for dechlorination of process waste waters containing chlorine in low concentration.

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