APPLICATION OF THE COLD PLASMA OF GLIDARC TYPE TO THE TREATMENT OF WASTEWATERS FROM SLAUGHTERHOUSES: ABATEMENT OF PHOSPHATES AND NITRATES

Jourdin Gongwala
Department of Chemistry, Higher Teachers' Training College, University of Maroua, Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, Cameroon
Daniel Fotio
Department of Chemistry, Higher Teachers' Training College, University of Maroua, Cameroon
Paltahe Abba
Department of Chemistry, Higher Teachers' Training College, University of Maroua, Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, Cameroon
Gaston Payom
Samuel Laminsi
Daniel Njopwouo
Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, Cameroon

Abstract

Acidified and non acidified samples of wastewaters from the Etoudi's slaughterhouse (Yaounde, Cameroon) were analyzed before and after having been exposed to an electric discharge in a cold plasma reactor at different exposure times. Analyses reveal that untreated and non acidified wastewaters (pH = 7.8) contain 230.4 mgL^{-1} of phosphate (PO_4^{3-}) and 479.6 mgL^{-1} of nitrate (NO_3^-) ions. Exposure of these wastewaters to the gliding discharge ("glidarc") operated in humid air induces PO_4^{3-} and NO_3^- concentrations abatement by 41.55% for phosphates and 86.24% for nitrates within 20 min of exposure for a gas flow rate of 800 Lh^{-1}, which confirms the efficiency of the glidarc treatment in humid air in case of waste treatments. On the other hand, exposure of acidified wastewaters (pH = 2.2) to the glidarc in the same conditions showed that PO_4^{3-} and NO_3^- concentrations increase with exposure time; this result is in conformity with oxidation phenomena induced by the glidarc and previously presented by several authors. From these results the efficiency of the “glidarc” technique in degrading phosphates and nitrates in basic medium was proven.

Keywords: Cold plasma, Nitrates, Phosphates, Slaughterhouse, Wastewaters

Introduction

The phosphates and the nitrates are the pollutants having generally an agricultural origin via the use of the chemical manures. The nutrition and the physiological dismissals of the animals slaughtered in the slaughterhouses are at the origin of their presence in wastewaters of these structures. These pollutants have ominous and varied effects on the environment: water illnesses, eutrophication of the water bodies etc. In the closed surroundings, as the lakes, the ponds, the phosphates provoke with the nitrates, a deadly dystrophication for fauna and flora as well as for men (Rodier, 2009). Thus, the need for the prevention or the reduction or the eradication of this phenomenon is necessary. The notions of these parameters should be integrated into any purification and wastewater treatment systems, before its discharge into the receiving environment. The technique of treatment by plasma offers more convenience and advantage nowadays for the treatment of wastewaters from slaughterhouses (Gnokam-Zumgang et al., 2010, Gongwala et al., 2012, Labioui et al., 2007). Plasma is defined itself as a globally neutral sparkling mixture of the point of electric view containing loaded particles (ions and electrons) and neutral particles (molecules, atoms and radical), most often in excited states (Doubla, 2002, Fridman, 2008; Held, 1994). Plasma is a peak technique adapted to the cleanup of wastewaters with numerous advantages: absence of catalysts, reduced cost, efficiency of reduction in a short time, etc (Brisset, 2009). The aim of this work is to attempt the degradation of phosphates and nitrates contained in the wastewaters sampled from the “Etoudi’s Slaughterhouse” (Yaounde, Cameroon) by using the gliding arc plasma (“glidarc”). The plasma gas used is humid air which generates reactive species as HO° and NO° radicals with their derivatives H_2O_2, HNO_3 and ONOOH. These species induce acid and oxidizing effects while reacting with species contained in aqueous solutions as shown by Brisset et al. (2011).

Material and methods

The following observations on the sampling site oriented the operations: the activities are continuous every day, all year round with the same productions; the discharge of the wastewaters is continuous irrespective of the season; the flow of the discharged wastewaters is rather and continuous through only one channel into the receiving river.

Therefore, the sampling was done at a time in only one point. All arrangements were taken to have representative and homogeneous samples (Rodier, 2009).

The analyses were done by spectrophotometric titrations achieved with the help of a Hach DR/2010 "Portable Spectrophotometer datalogging" device.

The measures of pH and temperature were done by a “HANNA HI 9811-5 pH/°C/EC/TDS” numeric display multimeter. Before any measure of pH, the pH-meter was calibrated previously with the help of buffer solutions (Na_2HPO_4/H_2NaPO_4, pH = 6.85 and/or $KHC_8H_4O_4$, pH = 4.01).

The concentration of the phosphates was determined by the method of "molybdovanadate". 1 mL of the reactive molybdovanadate was added to every sample of wastewaters as well as a witness (distilled water). If the molecules of orthophosphates are present, they are going to react with the molybdate in an acidic environment to form the phosphomolybdate complex (Rodier, 2009). In presence of vanadium, the vanadomolybdophosphoric acid has a yellow color. The intensity of the coloration is proportional to the concentration of the present phosphates in the middle (Rodier, 2009). The results were read by a “Hach DR/3900 spectrophotometer” device and expressed in mgL^{-1} of PO_4^{3-}.

The concentration of ammonium ions was determined by a colorimetric method using the Nessler reagent with the help of a “Hach DR/3900 spectrophotometer” device. After distillation in the presence of 40% sodium hydroxide using the Buchi K-350 distiller of the samples previously filtered, 25 mL of distillate was collected in a boric acid buffer and placed in a spectrophotometric cell. 3 drops of mineral stabilizer and polyvinylic alcohol were added successively followed by 1 mL of Nessler reagent. The coloration of the complex due to the presence of the NH_4^+ ions was explored to carry out the analysis on a “Hach DR/3900 spectrophotometer” device at 425 nm wave length (Rodier, 2009). The concentration of the ammonium ions was read on the display screen of the digital device with reference to a witness constituted of distilled water. The results are expressed in mgL^{-1} of NH_4^+.

The concentration of the nitrate ions was determined by the method of reduction to cadmium with the help of a “Hach DR/2010 spectrophotometer” device. After introduction of 10 mL of sample in a spectrophotometric cell, a sachet of Nitraver 5 was added. The mixture was homogenized and allowed for 5 minutes (time of reaction). The coloration developed in presence of the NO_3^- was explored to determine the concentration of nitrate ions with the spectrophotometer at 500 nm wave length (Rodier, 2009). The concentration of the nitrate ions was read on the display screen of the digital device with reference to a witness constituted of 25 mL of the sample. The results are expressed in mgL^{-1}.

Levels of nitrite ions were determined by the method of Ferrosulfate. After introduction of 25 mL of sample into a spectrophotometric cell, a small bag of reagent (Nitriver 2 nitrite) was added. The mixture was then homogenized and then allowed to stand for 20 minutes (reaction time). The determination of the concentration was read by a spectrophotometer at 373 nm with respect to a witness solution, and the results are expressed in mgL^{-1}.

For the treatment, the cold plasma gotten by gliding electric discharge named glidarc was used. Its principle is based on the formation of an electric discharge between two divergent electrodes raised to an appropriate potential difference; the discharge is blown by a sparkling throw directed according to the axis of the reactor and it explodes in non-thermal plasma that licks a target and its species react to target-plasma interface (Doubla, 2002). The glidarc reactor used in batch conditions is sketched in Fig. 1. This reactor is a cylindrical vessel of 2.3 cm long and 10 cm inner diameter. Compressed air passes through a distilled water-filled bubbling flask, becoming water-saturated before injection into the reactor through a nozzle along the axis of two divergent electrodes at the flow rate of 800 Lh^{-1}. The two aluminum electrodes were connected to an Aupem-Sefli HV transformer (10 kV; 50 Hz in open conditions; maximum intensity delivered 100 mA). When the circuit is connected, an electric arc forms between the electrodes at the minimum gap (closed to 3 mm). The arc is pushed away by the feeding gas flow, sweeps along the increasing electrodes gap and breaks in a large plasma plume. A new arc then appears and develops according to the same procedure. The arc glides along the electrodes and licks the liquid surface 30 to 35 mm far from the tips and allows chemical reactions to take place at the interface liquid-plasma plume. The contact surface was increased by means of magnetic stirring of target solution.

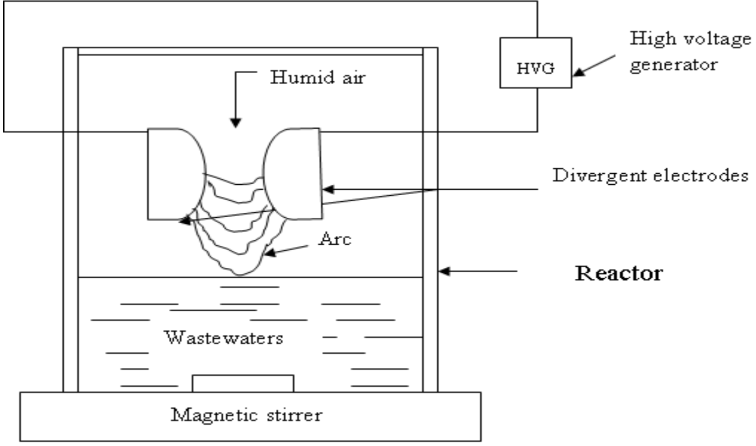

Fig. 1: Experimental set-up of the glidarc

The samples were analyzed before and after having been exposed to an electric discharge in a cold plasma reactor at different exposure times. The results of all these operations are presented in the next section.

Results and discussions

pH and temperature variation

The results were obtained by varying the time of exposure, at the plasma gas flow rate of 800 Lh^{-1}. As the pH of the collected wastewaters was that of a basic medium (pH = 7.8), sulfuric acid was added to have an acidic medium (pH = 2.2). The aim of acidifying the sample is to study the evolution of phosphates and nitrates concentration with respect to the exposure time in two different media i.e. basic and acidic.

Fig. 2 shows the evolution of the pH as a function of the exposure time t*. For both the acidified and the non acidified samples the pH decreases according to previous results obtained by Moussa et al. (2005). Acid effects are ascribed to NO° via nitrous and nitric acids (Brisset and Hnatiuc, 2012).

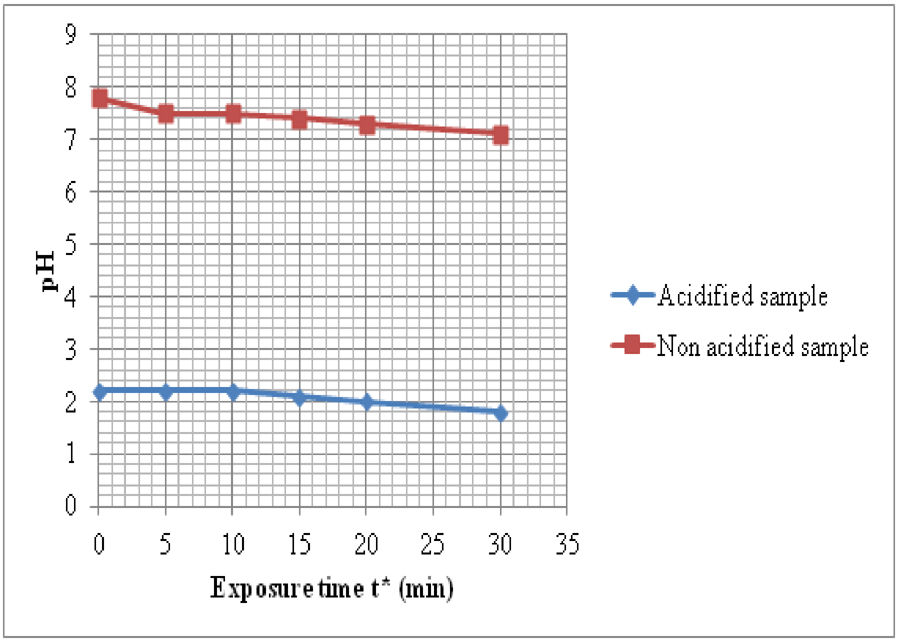

Fig. 2: Evolution of the pH as a function of the exposure time t*

The addition of sulfuric acid in the wastewaters increases the temperature of the sample throughout the treatment time as shown on Fig. 3. It is known that the dissolution of an acid in water is an exothermic reaction. The evolution of the temperature is related to acidic properties of the "glidarc" as confirmed by the pH decrease.

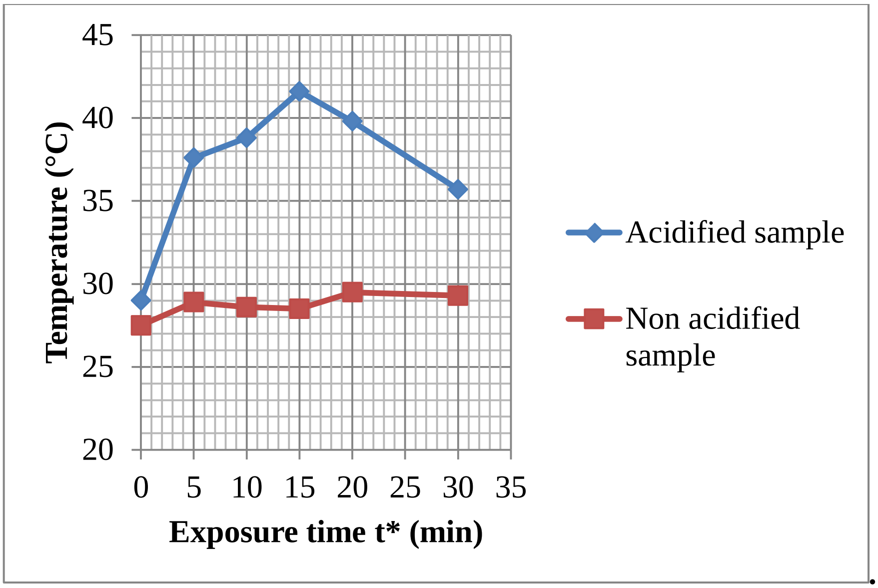

Fig. 3: Evolution of the temperature as a function of the exposure time t*

Nitrates abatement

The analyzed samples are polluted because the Ghanaian norm indicates that the concentration of nitrates must be less than 50 mgL^{-1} in any wastewaters before its discharge (Rodier, 2009). Fig. 4 shows that the concentration of nitrates decreases significantly until 20 min of exposure time t* in a basic medium (non acidified sample). About 86.24% abatement of nitrates in the sample is then observed. This result is a proof that glidarc plasma is an efficient technique to reduce pollution due to nitrates in slaughterhouse wastewaters.

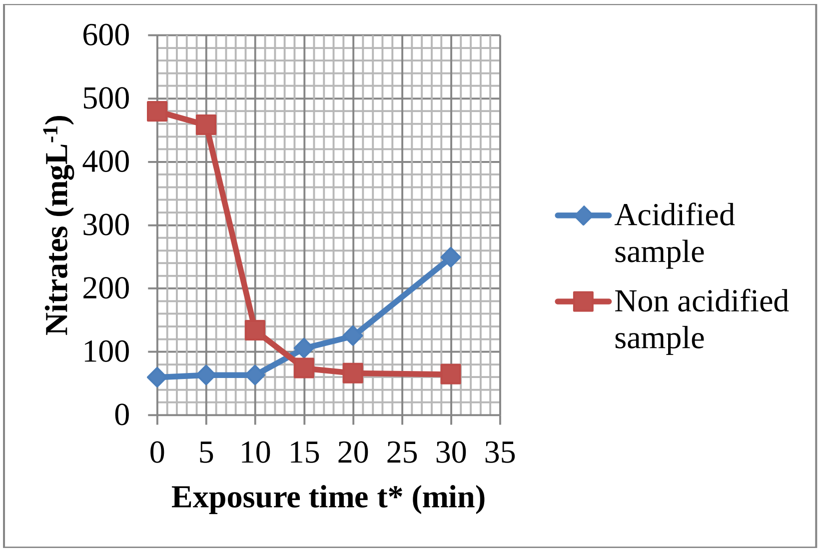

Fig. 4: Evolution of the nitrates as a function of the exposure time t*

In an acid medium, the concentration of nitrates increases with exposure time t*. This increasing evolution of nitrates is probably due to the strong oxidation properties of HO° radicals and its derivatives (Brisset et al., 2011). It means that species as nitrites and ammonium ions present in these wastewaters may be oxidized into nitrates by the above reactive humid air induced species (See Fig. 5 and Fig. 6).

It is important to note that the above result is obtained in a basic medium and the evolution of nitrates is linked to the evolutions of ammoniums and nitrites.

Ammonium transformation

The ammonium concentration decreases in basic medium as well as in acidic medium (Fig. 5). This evolution is explained by the fact that ammonium ions are oxidized into nitrites and nitrates quite quickly as stated by Rodier (2009).

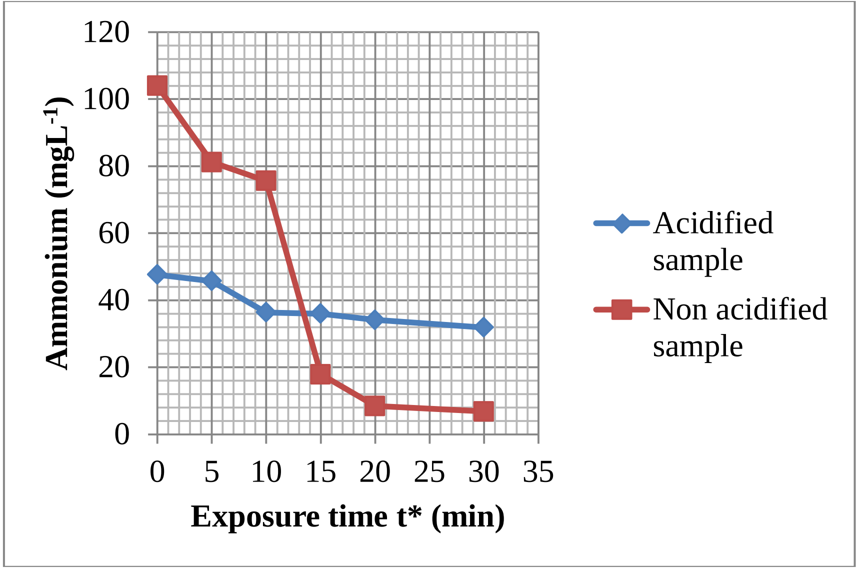

Fig. 5: Evolution of the ammonium as a function of the exposure time t*

Regarding the ammonia toxicity for fish freshwater fauna, it is recognized that it is not the ionized ammonia form (NH_4^+) which is toxic but the unionized form ammonia (NH_3). The sensitivity threshold long-term regardless of the fish life would be 0.3 mgL^{-1} of NH_3 (Rodier, 2009).

Nitrites variation

Fig. 6 shows an increase in the evolution of nitrites concentration before it decreases after 5 and 15 min in acidified and non acidified media respectively. The increasing part of the curves corresponds to the additional transformation of ammonium into nitrites (Eq. 1) and the decreasing one may be explained by the oxidation of nitrites into nitrates (Eq. 2).

$NH_4^+ + 2H_2O \rightleftarrows NO_2^- + 8H^+ + 6e^-$ Eq. 1

$NO_2^- + H_2O \rightleftarrows NO_3^- + 2H^+ + 2e^-$ Eq. 2

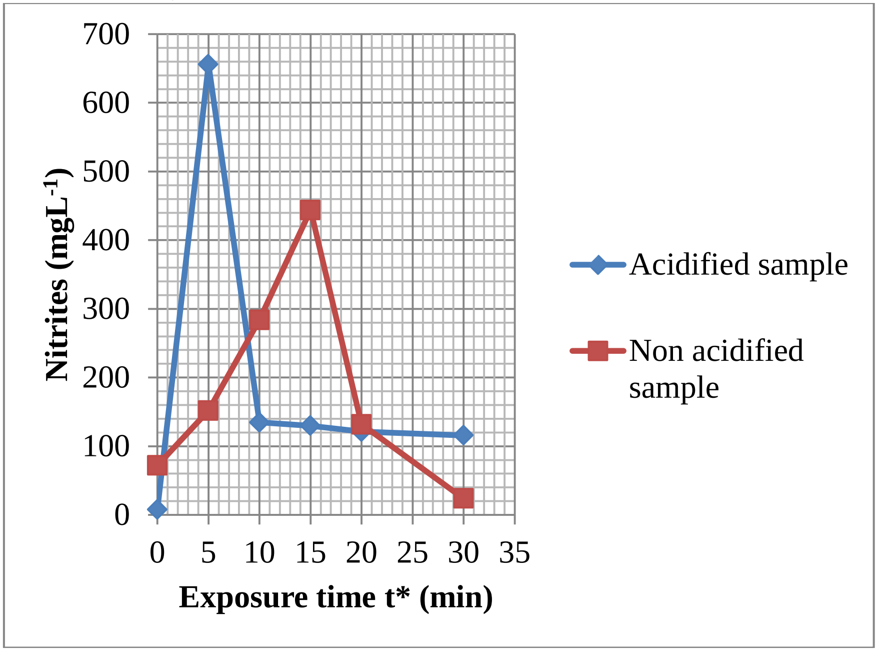

Fig. 6: Evolution of the nitrites as a function of the exposure time t*

Phosphates abatement

The extremely elevated content of phosphates in relation to the Italian norm (0.5 mgL^{-1}) shows a higher pollution according to Rodier (2009). The evolution of phosphate ions concentration with respect to exposure time is similar to that of nitrate ions as shown in Fig. 7. The treatment of the non acidified sample leads to a weaker abatement percentage i.e. 41.55% in 20 min of exposure.

Acidification of the sample lowers the rate of phosphate confirming the acidifying effect of plasma (Moussa, 2005, Hnatiuc, 2002). This phenomenon can be justified by the reaction between the H^+ ions and phosphate ions to give phosphoric acid according to Eq. 3. On the other hand, the slight increase of phosphates observed during acid treatment may be due to the oxidation of phosphorus, which has the same source, into phosphate ions (Eq. 4).

$3H^+ + PO_4^{3-} \longrightarrow H_3PO_4$ Eq. 3

$P + 4H_2O \rightleftarrows PO_4^{3-} + 8H^+ + 5e^-$ Eq. 4

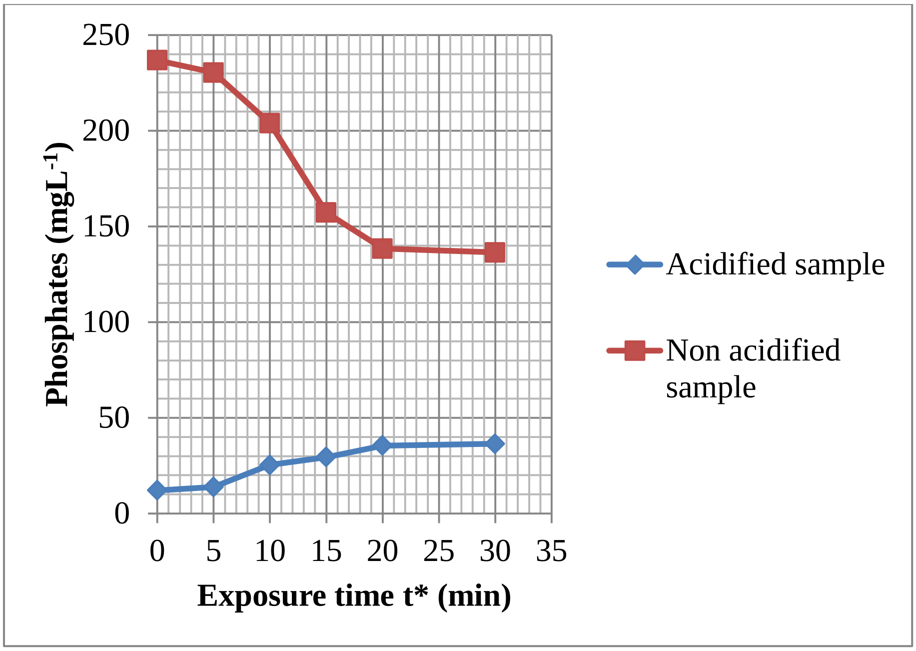

Fig. 7: Evolution of the phosphates as a function of the exposure time t*

Conclusion

The wastewaters of the "Etoudi's Slaughterhouse" are basic (pH = 7.8) and polluted by phosphates and nitrates. After 20 min exposure time to gliding discharge ("glidarc") process, the pollutants mentioned above are abated by 41.55% for phosphates and 86.24% for nitrates. By acidifying the sample, the results of analyses show the concentration of phosphates and nitrates increasing with exposure time to cold plasma, what is in conformity to previous studies. Hence, the present work has the merit of revealing the possibility to degrade phosphates and nitrates in basic medium by non thermal plasma of glidarc type.

Acknowledgments

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